Acidification in Finland

Edited by

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Finnish Acidification
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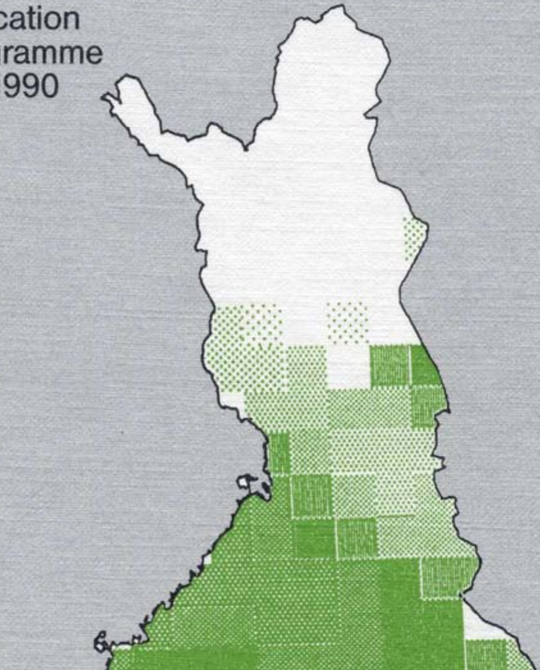
HAPRO 1985-1990



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Preface

"Acidification in Finland" has been the theme of HAPRO, the Finnish Acidification Research Programme, in 1985–1990. HAPRO has been a multidisciplinary programme funded by the Finnish government. Seven universities, eight governmental research institutes and numerous expert consultants have taken part in this work. The objective of the programme has been to contribute to air pollution abatement and the management of natural resources by obtaining and processing facts, information and understanding on the so-called acidic precipitation issue. In practise, the programme has organized surveys of emissions, compiled measurements of concentrations and deposition, documented the existing state of Finnish ecosystems, carried out investigations on cause-and-effect relationships, developed, tested and applied different kinds of models including integrated assessment models and supported international exchange of information.

After a short planning phase of the programme, the General Plan for HAPRO was adopted at the end of 1984. The years 1985 and 1986 can be considered as the period of establishing the research. Most of the research measurements and analyses were done in 1987 to 1988 supporting the documentation period in 1989. HAPRO will come to completion in 1990 with emphasis on assessment and the exchange of information.

Chapters of this book were first drafted in the spring of 1989. An international reviewing panel chaired by Dr. Leen Hordijk from the Netherlands met in Helsinki in June 1989 to examine the manuscripts. In this way the manuscripts passed an intensive peer review in a relatively short period of time. The manuscripts were corrected and updated in July–September 1989 and were sent to the publisher.

This book is the summary of the primary results and findings of HAPRO. It mainly contains original material that has not been published before. The aim has been that the material and methods are sufficiently documented in each chapter in order to allow the reader to take a critical look at the results. It is fair to say that the majority of Finnish research on the acidic precipitation issue in the second half of the 1980s is included in the chapters of this book. We sincerely thank all institutes, organizations and people who have taken part in the preparation of this book. In particular, we would like to acknowledge the scientists – people who have done the job.

Helsinki, Spring 1990
PEKKA KAUPPI, PIA ANTTILA and KAARLE KENTTÄMIES

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Introduction to This Book

Finnish ecosystems are sensitive to pollution damage because of the harsh climate and the scarcity of species. Pollution damage would have a large impact on Finland, because the character of the Finnish landscape and the national economy are heavily based on natural and seminatural ecosystems, in particular, forests and lakes and streams.

Finland like all countries would prefer to act in favour of environmental protection rather than to let damage occur and try to repair it thereafter. The country cannot afford losing the production capacity of forests even if the forests could later be revitalized. Trees are grown at rotations between 70 to 160 years. Productivity has to be maintained all the time. An interruption, that is a massive forest decline, would involve enormous costs.

Protection approach has guided HAPRO research. The programme has aimed at assessing future scenarios and trends. Monitoring the past has been a necessary element of research but only in the sense that it sets the footings for assessments of the future. Surveys and inventories have described the base-line conditions. Experiments have clarified cause-and-effect relationships. Results have been incorporated into assessment models.

The reports of this book have been organized in five main sections. Section 1 describes emissions, atmospheric processes and deposition. Section 2 deals with terrestrial environments and includes reports on soil chemistry, soil microbiology, vegetation and insects, trees and materials effects. Section 3 is the water part including reports on water chemistry and on biota in lakes and streams. Sections 4 and 5 are devoted to liming, and to secondary effects and assessment, respectively.

Sections 1 to 3 are organized in a similar way so that they begin with monitoring and survey reports. Then they continue with reports on models and experimental results. Sections 4 and 5 deal with the scientific background of ecosystem revitalization and pollution abatement. They include reports on secondary effects such as the waste production of flue gas desulphurization and the potential economic reflections of forest damage abroad through the international trade of forest products.

Emissions into the atmosphere are described first. In the 1950's and 1960's sulphur emissions grew substantially, as a matter of fact faster in Finland than in many other countries. Then the emissions peaked in the mid-1970's and have declined since. This decline will continue at a rate that depends on abatement strategies. NO_x emissions have not peaked yet but the Finnish government has made commitments so that they will begin to decline [I. SAVOLAINEN, M. TÄHTINEN (1) and J. ANHAVA et al. (21)].[1] The next report is on ammonia emissions [R. NISKANEN et al. (31)]. Manure is the main source of ammonia in Finland and emissions are concentrated in western Finland.

The study of air quality together with meteorological data provides a climatological picture of the atmospheric environment in Finland [S.M. JOFFRE et al. (43)]. This report describes air concentration levels of SO_2, NO_2, aerosol sulphate and nitrate, ozone and includes some results on volatile biogenic organic compounds, too. The precipitation chemistry measurements include sulphate, nitrate, ammonium, strong acids, calcium, magnesium, potassium, sodium and chloride. The study shows that meteorological conditions and the origin of air masses were the primary modulators of the observed concentrations. The southwestern and southeastern sectors make the greatest contribution to the pollutant load in southern and central Finland.

The next report is a simulation study on the formation processes of acid aerosols with a special emphasis on Finnish weather conditions and concentration levels [M. KULMALA (95)]. The anthropogenic emissions of alkaline aerosols in Finland are investigated in report [P. ANTTILA (111)]. The research topic of this study is the origin of the specific neutralizing deposition occurring in southern Finland, a phenomenon reported in [S.M. JOFFRE et al. (43), O. JÄRVINEN, T. VÄNNI (151) and A. HYVÄRINEN (199)]. The performance characteristics of five commercial sulphur dioxide monitors were compared in [J. WALDEN et al. (135)].

The deposition characteristics in Finland are described next [O. JÄRVINEN, T. VÄNNI (151) to (199)]. Continuous bulk deposition monitoring has been carried out at almost 40 stations between 1971 to 1988 [O. JÄRVINEN, T. VÄNNI (151)]. According to these measurements sulphur, nitrogen, strong acid and Ca deposition have a south-north gradient, the deposition being higher in the south. Sulphur deposition has not changed over time during the measurement period, while nitrate deposition has increased.

Model calculations indicate two regions of high sulphur deposition [J.-P. TUOVINEN et al. (167)]. One is in southern Finland and is connected with the general south-north gradient. The other one is in northeastern Finland due to the high sulphur emissions in the Kola Peninsula in the USSR. For both nitrate nitrogen and ammonia nitrogen the highest deposition fluxes occur in southeastern Finland.

Tree canopies reduce the ammonium and nitrate contents of precipitation and increase the fluxes of sulphate, magnesium, potassium and calcium ions onto forest soils [A. HYVÄRINEN (199)]. Especially in spruce-dominated stands the fluxes of strong acids and sulphate are estimated higher when sampled below the canopy rather than on open land.

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[1] The numbers in round brackets show the first page of the report in this book.

A chemistry survey of Finnish agricultural soils was carried out in 1974 and in 1986 [R. ERVIÖ et al. (217)]. The soil chemistry is mainly affected by cultivation measures. However, a slight increase of cadmium levels and a decrease of lead levels may partly be due to changes in atmospheric deposition.

Mineral soils account for two-thirds of all forest land. Moraine soils dominate. Granite is the common parent material whereas calcareous soils are nearly missing. Podsolic profiles form strong vertical gradients for most soil characteristics. Quantitative estimates are given for characteristics such as cation exchange capacity and base saturation of the upper layers of forest soils [P. TAMMINEN, M. STARR (237) to A. NISSINEN, H. ILVESNIEMI (287)]. Organic (peat) soils are dealt with in a similar way in [A. PÄTILÄ (305)]. Finnish forest ecosystems, at least those chosen for fertilization experiments, have not yet reached the state of nitrogen saturation because nitrogen fertilization substantially increases tree growth [E. MÄLKÖNEN et al. (325)]. Indications of a decrease in the microbiological activity of forest soils have been detected in polluted urban areas [K. PALMGREN et al. (351) and R. OHTONEN et al. (373)].

A quite dramatic change in the composition of epiphytic lichens is documented over a large fraction of Finnish forests [M. KUUSINEN et al. (397)]. This report documents declining trends from the 1960's to 1980's of the lichen species that are sensitive to air pollution. Several chemical compounds show spatial patterns with high and low concentration regions as measured from samples of *Hypogymnia physodes*, a common epiphytic lichen [E. KUBIN (421)]. The impact of a local air pollution gradient on insect fauna is reported in [K. HELIÖVAARA, R. VÄISÄNEN (447)]. Experiments using simulated acid rain have been carried out although using relatively small dosages and short treatment durations at this stage [M. VUORINEN (469) to M. LODENIUS, J. MALM (495)].

Forest growth in Finland on the average has not declined, on the contrary it has considerably increased [P. NÖJD (507)]. Early warnings of possible future declines are investigated using defoliation assessments [E.-L. JUKOLA-SULONEN (523)]. Defoliation is often associated with agents of abiotic and biotic damage [S. NEVALAINEN, H. YLI-KOJOLA (561)]. Analytical principles of the research linking air pollutants to forest characteristics are presented in [P. HARI (583)]. Coincidence of air pollution and severe climate is the topic of the experimental research reported in [S. HUTTUNEN et al. (607)].

Case studies near fur animal farms illustrate the pathways of forest effects of high ammonia loading [A. FERM et al. (635)]. Another case study in an industrial environment deals with a mix of pollutant species with sulphur, nitrogen and fluoride as the damaging agents [A. WULFF et al. (669)]. A new method is reported in [R. JALKANEN, T. KURKELA (691)] which would allow constructing needle retention histories of Scots pine trees. The relationships between soil characteristics and tree performance are described in [H. RAITIO (699) and H. AROVAARA, H. ILVESNIEMI (715)].

The study on the effects of air pollutants on construction materials showed obvious damage to lime-washed and plastered surfaces in polluted urban areas

[T.K. Kaunisto et al. (737)]. Also the corrosion rate of steel was found to be high in these areas. However, quantitative conclusions cannot be made yet about the importance of air pollution on the deterioration of materials in Finland.

The acidity of Finnish small lakes reflects the interaction of atmospheric sulphur loading, the catchment sensitivity and the amounts of organic anions originating from peatlands. The survey of statistically selected small lakes ($n = 987$) quantified the chemical characteristics of Finnish lakes. The share of acidic lakes was 12% (4900 lakes) but naturally acidic humic lakes dominate (75–85%) this group [M. Forsius et al. (759)]. Organic anion, median 89 $\mu Eq\,l^{-1}$, is the main anion in the whole lake population, but in southern Finland, in highest sulphur deposition areas, strong acids exceed organic acidity in most lakes [P. Kortelainen, J. Mannio (849)]. Applications of two process-oriented models (MAGIC and RLM) showed that acidification of sensitive surface waters will continue unless significant emission reductions can be realized [J. Kämäri et al. (781)].

Mass balance studies of forested basins indicated that the deposition and dissolution of sulphur dioxide produces more hydrogen ions than direct (wet) deposition of H^+. A significant retention of sulphate was observed in all basins [K. Kallio, L. Kauppi (811)]. In fairly well buffered catchments, even during peak flows in spring time the fraction of fresh meltwater was only 30–40% of the runoff. No trends were found in the acidity of runoff water in this type of catchment during the 25 years of monitoring. However, an increase of nitrate concentrations in the runoff water was detected in some catchments. It has probably been affected by the growing nitrogen deposition [A. Lepistö, Seuna (825)].

Studies from the groundwater monitoring network showed increasing trends in sulphate, calcium and nitrate concentrations in the southern part of Finland. Decreasing values and increasing aluminium concentrations were found only in areas of high local sulphur deposition [J. Soveri, T. Ahlberg (865)].

Atmospheric trace metal concentrations in the water and sediments of headwater lakes were higher in southern Finland than in northern Finland. In southern parts of the country the share of anthropogenic atmospheric load was 60–95% for Cd, Hg and Pb. Acid conditions favoured high concentrations of Al, Mn, Zn, Pb and Cd in water and a much higher concentration of Pb in fish liver and bones than in neutral lakes [M. Verta et al. (883)].

In the historical, palaeolimnological research of 30 acid-sensitive lakes, 43% of the lakes were acidified in the near past, 27% had no trends and 20% were naturally acidic. The recent acidification was restricted to southern Finland, where almost all acidic lakes have acidified since 1900. In central and northern Finland, on the other hand, the proportion of naturally acidic lakes was higher [P. Huttunen et al. (1071)].

The effects of acidity (pH) on the present status of biota in small lakes and brooks were studied in the joint research of 140 lakes [L. Heitto (963) to J.J. Meriläinen, J. Hynynen (1029)]. Effects of acidity could be detected at all ecological levels. Macrozoobenthos and diatom communities were perhaps the most promising objects for monitoring purposes. The invasion *Sphagnum* mosses and absence of most elodeids were found in some acidified lakes [L. Heitto, (963)]. The occurrence of some dinoflagellate phytoplankton species was regulated largely by water pH, whereas water colour, phsphorus and nitrogen concentrations had stronger influence in other groups [P. Kippo-Edlund, A. Heitto (973)]. Periphytic diatoms of the littoral zone seemed to possess a pH-indicator potential [P. Eloranta (985)]. The composition of surface sediment diatoms correlated closely with the pH of autumn lake water. Planktonic diatom species proved to be very sensitive to acidification. Canonical correspondence analysis predicted rather precisely the actual pH value [P. Huttunen, J. Turkia (995)]. The species diversity of crustacean zooplankton was significantly reduced in lakes with a low pH value. However, in polyhumic lakes the impoverishment of fauna at low pH was less pronounced [J. Sarvala, S. Halsinaho (1009)]. The biomass and number of animals of benthic invertebrates showed no correlation with lake acidity although the number of species decreased with increasing pH. The presence of certain acid-sensitive species among snails, mayflies and mussels was closely related to the yearly minimum pH and so they are valuable indicators [J.J. Meriläinen, J. Hynynen (1029)]. In the invertebrate survey of lake outlet brooks, two indicator methods were compared. As a practical result, the monitoring of lake outlet invertebrates has been recommended for lake monitoring purposes [H. Hämäläinen, P. Huttunen (1051)].

The fish survey of 80 small lakes in southern and central Finland showed that roach and perch populations usually changed in response to acidification. In some extreme cases offspring were nonexistent during the 1980's. In some acid lakes roach populations disappeared already 40 years ago [M. Rask, P. Tuunainen (911)]. In the physiological studies, synergistic effects of hypoxia and acid water was found on blood respiratory properties and ion concentrations [M. Nikinmaa et al. (929)]. The delayed ovulation of whitefish females was detected when fishes were exposed to acidic, aluminium-enriched water [P.J. Vuorinen et al. (941)].

The response of forest soils to liming can be detected for several decades after soil treatment. In spite of the seemingly positive changes in soil characteristics, tree growth tends to decrease after liming for the reasons discussed in [J. Derome, A. Pätilä (1093)].

The effects on biota of experimental liming of small lakes were clearly detected [K. Salonen et al. (1145)]. However, the duration of effects was short especially in humic waters. The amount of lime needed to neutralize humic lakes (colour 200–350 Pt mg l^{-1}) is over twofold as compared with that needed in clear water lakes [E. Alasaarela et al. (1117) to K. Salonen et al. (1145)].

An integrated assessment model has been developed for HAPRO with contributions from several research disciplines [M. Johansson et al. (1171)]. Additional studies to assist strategy evaluations include economic comparisons for sulphur emission reductions [M. Hongisto, M. Wallin (1195)], an assessment of the

FGD-waste problems [J. RANTA (1209)] and an evaluation of the economic impact of forest damage through the international market of timber and forest products [H. SEPPÄLÄ et al. (1217)].

This book was compiled with an *analytical perspective* in mind. It illustrates the wide range of methods, materials, inventory techniques, experimental approaches and primary results of Finnish acidic precipitation research. A number of purely methodological reports were included in this book. These are the bits and pieces, which were subjected to peer review. Critical evaluation of these basic elements will continue while the *synthesis* of all this material is being prepared at the same time. These two phases – analysis and synthesis – will bring the HAPRO programme to a completion toward the end of 1990.

PART 1 AIR

1.1 Emissions

Sulphur Dioxide and Nitrogen Oxide Emission Scenarios for Finland

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Summary

A model is presented for the estimation of the future SO_2 and NO_x emissions in Finland on the basis of energy use and traffic scenarios and emission reduction strategies. The model is part of the Finnish Integrated Acidification Assessment Model system (HAKOMA).

The energy use is given in the model for five sectors and nine fuels. Process emissions from the industry have been included also. The plant register of the model includes the 190 biggest power and industrial plants (about 500 boilers) in Finland.

The model is applied in this chapter to three energy use scenarios which consist of (1) a long-term scenario published by the Finnish Ministry of Trade and Industry, and of scenarios of (2) maximal use of natural gas and of (3) strong energy conservation. Sulphur emissions are estimated for three reduction strategies: no reductions as a theoretical reference; reductions mandated by the Finnish government; and maximum reductions to estimate the potential of strict measures. The NO_x emissions are estimated for two reduction strategies: no reductions; and assumed reductions in energy production and transportation.

Introduction

The emission estimates of SO_2 and NO_x for Finland have been calculated for the years 1950–2040 with the emission submodels of the Finnish Integrated Acidification Assessment Model (HAKOMA) (Johansson et al. 1989; Savolainen and Tähtinen 1988, 1989). The emission calculations have been made on the basis of energy use and traffic scenarios, and on the basis of alternative assumptions on emission control strategies.

The current aim of Finland is to reduce the sulphur emissions by 50% from the level in the year 1980 by the year 1993. Nitrogen oxide emissions will be limited to the level of the year 1987 by 1995. It has been planned to go further and reduce the NO_x emissions by 30% from the level of 1980 by 1998. This study is based to a large extent on information obtained from the Finnish ministries and statistics; however, the results present only views of the authors.

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The HAKOMA model system consists of modules covering energy use, emissions, emission abatement; dispersion, transformation and deposition of sulphur, and impacts on forest soils and lakes. The HAKOMA model is being completed soon with an ammonia (NH_3) emission module and with deposition modules for NO_x and NH_3 emissions. The model system is developed by the Technical Research Centre of Finland in co-operation with other national institutes and the International Institute of Applied Systems Analysis (IIASA) (Alcamo et al. 1987).

The main purpose of the emission modules is to make SO_2 and NO_x emission estimates to be used as a source term for the atmospheric dispersion calculations and further in soil and lake impact studies. The emission modules can also be used to study the effectiveness of different abatement measures. It is possible to give plant type-, size- and location-dependent emission factors, which represent typical values for certain abatement measures. The emissions have been calculated for a rather long time span mainly in order to study the slow acidification processes in soils in various alternative scenarios (Johansson et al. this volume).

Emission Model

General

The emissions are estimated on the basis of energy use and traffic performance scenarios. Alternative emission control strategies can be considered in the calculation. The model includes a comprehensive list of power and industrial plants in Finland.

The energy use and emission calculations have been made for the time period 1950–2040. There are a total of 14 calculation years with a time interval of 5 years from 1970 to 2010, otherwise the time interval is 10 years. The energy use is given in the model for five sectors and nine fuels. The sectors considered are: industry, electricity production, district heating, domestic heating and transportation. The electricity production sector in the model consists only of ordinary condensation power. About 25% of the total electricity production is produced as back pressure power in the industrial and district heating plants, and they are considered in the respective sectors in the model. The domestic heating sector also considers energy use of agriculture, forestry and households. The fuels considered in the model are: heavy fuel oil, light fuel oil, diesel oil, gasoline, natural gas, hard coal, peat, waste liquors from pulp industry and others (mainly wood). The sulphur emission model uses 44 geographical emission areas. In the NO_x model the emissions are calculated separately for all municipalities (461). Both emission models use three height categories of the emissions. The effective release heights have been estimated on the basis of the stack heights of the plants. The height classes used are 0–50 m, 50–100 m and over 100 m.

Calculation of the SO_2 Emissions

Sulphur emissions from energy use are calculated on the basis of fuel consumption, sulphur contents of fuels and factors describing the amount of sulphur retained in the ash. Process emissions from the industry are calculated on the basis of production. Different release abatement measures (fuel- and plant-specific measures) are taken into account in the calculations.

The emission model has a data file of 190 plants (about 500 boilers) based on the register of the Ministry of Environment. The plant file consists of main plant characteristics in the reference year (1986). Important data for the model are power production, height of the stack, real fuel use in the reference year and calculated or measured emission data of each plant in the reference year. With the employment of this plant file, the energy use and the emissions of the plant sectors (industry, electricity production and district heating) can be distributed geographically for the reference year. The stack data and information on flue gas temperature and volume flow have been used to estimate effective heights of the emissions. In addition to the existing plants, also a list of future planned plants is given. The possible plans to build new plants are not known for a period longer than 10 years. Therefore the existing plants are assumed to operate for the whole time period. The geographical and the height distribution of the emissions for history and future are estimated using the plant stock of the reference year, the list of new plants and fuel use indices in each sector for the considered time period.

The sulphur process emissions from the industry are estimated on the basis of industrial production. The energy use scenarios include assumptions on the development of production in the main groups of industry. Process industry releases have been divided into pulp, basic metal, chemical and oil refining industries.

The energy use data by municipalities for the domestic heating sector have been taken from the statistics provided by the Central Statistical Office of Finland and data for the traffic sector from the statistics of the sold motor fuels by municipalities. The emissions of these two sectors always belong to the lowest height class.

The energy use given in a scenario is allocated to the plants, so that the new plants are assumed to operate with full load. The rest of the energy use is divided between old plants in proportion to the energy use of the considered fuel and sector in the reference year. There was a minor fraction of fuel use in the reference year, that was burned in small, mostly industrial plants, which are not included in the list of the plants in the emission module. This fuel use is divided between the emission areas according to the population.

The following main types of the sulphur emission restrictions can be presently considered in the emission model:

- sulphur contents of fuels as a function of time and location;
- maximum sulphur dioxide output per consumed fuel [mg (SO_2) MJ^{-1}] depending on the main fuel of the plant, plant size and location;

- maximum sulphur dioxide output per industrial production [kg (SO_2) t^{-1}] depending on industrial subsector.

Calculation of the NO_x Emissions

A survey of nitrogen oxide emissions from various types of boilers in Finland (Hupa et al. 1987) classifies boilers according to their main fuel, combustion technique and size. A specific emission factor [mg (NO_2) MJ^{-1}] has been determined for each class. They correspond to the situation of no control measures to limit NO_x emissions. The emission factors are shown in Table 1. The factors are for maximum capacity utilization of the boilers. The factors are approximately 10–30% lower if plants operate at half load. The dependence of the emission factors on load is considered in the model in big coal-fired boilers.

The use of energy in domestic heating by municipalities is from statistics. The used emission factors [mg (NO_2) MJ^{-1}] for domestic heating are (Jaanu 1987): heavy fuel oil 180, light fuel oil 50, coal 375 and firewood 60.

Because the transportation causes about half of the total NO_x emissions in Finland, this sector has been described more accurately than other sectors in the NO_x emission model. It consists of road traffic and other mobile sources, which include train, ship, and air traffic and mobile machinery such as tractors etc. The vehicles in the road traffic have been divided into passenger cars, vans, trucks and

Table 1. NO_x emission factors for main boiler types (Hupa et al. 1987)

Main fuel	Combustion technique	Size (MW)	Emission factor [mg (NO_2) MJ^{-1}]
Oil	Burner firing	5–50	200
	Burner firing	>50	240
	Gas turbine	>5	360
Coal	Hor. firing	>5	420[a]
	Tang. firing	>5	250[a]
	Grate firing	>5	170
Natural gas	Burner firing	>5	100
	Burner firing	50–150	150
	Burner firing	>150	250
Peat	Grate firing	5–50	240
	Grate firing	>50	220
	Dust combustion	5–50	260
	Dust combustion	>50	300
	Combined grate/dust	5–50	260
	Combined grate/dust	>50	300
	Fluidized bed	>5	160
Wood and bark	Grate firing	5–50	80
	Grate firing	>50	100
Black liquor		>5	50
Sulphite liquor		>5	120

[a] Load dependence considered.

buses. The passenger cars and vans are further divided into gasoline- and diesel-powered cars. Because of the lack of mileage and emission data, the vehicles have not been divided into weight classes. The model uses estimates for the mileage in cities and countryside for different vehicle types. For the reference year (1985) the model uses detailed data of transport performances by municipalities (461) for road traffic. The mileage estimates for the future can be given by provinces (12) to the model. They are distributed into municipalities as in the reference year. The exhaust restrictions usually concern only new vehicles, therefore also forecasts for numbers of new vehicles registered in the future are needed. Forecasts up to the year 2010 for the transport performances and for the registration of new vehicles have been issued by the State Road and Waterways Authority.

In the calculation of NO_x emissions from road traffic, emission factors [g (NO_2) km^{-1}] for different cars and engine types are used. The emission factors are speed-dependent and the transport performance has therefore been divided into highway and urban driving. The emission factors are easier to estimate for highway driving with relatively constant speed. In urban driving the travel distances are often short and the engines remain cool. There are also more accelerations and decelerations in urban driving than in highway driving, which makes the emission factors more inaccurate. Table 2 shows the emission factors used corresponding to the present car fleet with no measures to reduce NO_x emissions. The values are based on unpublished information obtained from the Ministry of Environment and from the measurements of emission factors at the Technical Research Centre of Finland.

In the computation of future emissions, new values of emission factors can be given both for the stationary and the mobile sources. In the case of the mobile sources, the model calculates effective emission factors for vehicle types on the basis of the changing car fleet. In the calculation of the renewal of the car fleet, the number of new cars is estimated on the basis of the increase in the number of cars and on the basis of the number of new cars replacing old ones.

Table 2. NO_x emission factors [g (NO_2) km^{-1}] for road traffic

Car type	Highway driving	Urban driving
Passenger cars		
gasoline	3.2	1.0
diesel	0.6	0.7
Vans		
gasoline	3.2	1.0
diesel	0.6	0.7
Trucks	14.0	14.0
Buses	16.0	26.0

Input Data for the Emission Scenarios

Energy Use

The main energy use scenario of this study is based on the reference (Ministry of Trade and Industry 1988). This scenario (abbr. KTM, from the Finnish name of the ministry) assumes that the GDP will increase by 100% by the year 2030. Most of the growth actually takes place before the year 2010 and the GDP is assumed to be thereafter almost constant. After the year 2030 the scenario values are assumed to be constant to 2040. Two other scenarios have been developed using this scenario as a basis. The first one assumes a maximum use of natural gas and the other a strong energy conservation. The purpose of these scenarios is to consider the potential that they give to the emission reductions. In the KTM scenario the total primary energy consumption is assumed to increase by 31% by 2010, which corresponds approximately to an annual growth rate of 1.3%. In 1986–1988 the primary energy consumption grew on an average of 2.5% yr^{-1} in Finland. In the OECD countries the average growth rate was 1.8% yr^{-1}. The electricity consumption is assumed to increase by 2.4% per year in the KTM scenario before the year 2010. In 1986–1988 the growth rate was on an average 4.3%. In the short term the actual growth rates have exceeded the assumed growth rates of the long-term scenario. In the KTM scenario the growth of the energy demand is covered to a large extent by increasing the use of hard coal. The share of natural gas and peat are slowly increasing while the share of oil is decreasing. The total energy use in the scenario is almost constant after the year 2010. The KTM energy use scenario is shown by fuels in Fig. 1 and by sectors in Fig. 2.

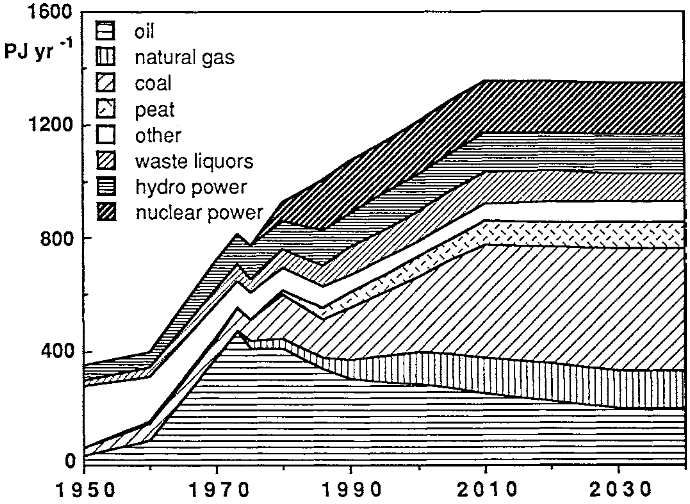

Fig. 1. Total primary energy consumption (PJ yr^{-1}) by energy source, the reference (KTM) energy use scenario (imports of electricity not included)

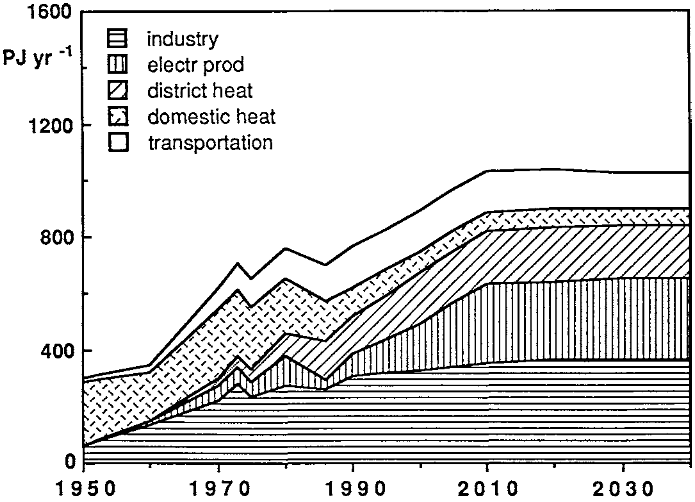

Fig. 2. Use of fuels by sectors, the reference (KTM) energy use scenario (nuclear fuels not included)

In the natural gas scenario the total primary energy use is the same as in the KTM scenario. The main purpose is the substitution of coal with natural gas to a large extent. The coal consumption is limited to the level of 1990 and the remaining energy demand is covered with natural gas. After the year 2000 the use of coal is assumed to decrease slowly.

In the energy conservation scenario the efficiency of the energy consumption is assumed to increase strongly in industry and space heating. In industry the need of heat is assumed to decrease to 50% and the need of electricity to 75% per unit production before the year 2030. In space heating the heat demand is assumed to decrease to 50% per unit building volume. The total energy consumption would decrease from the values of the KTM scenario by 8% to the year 2000 and by 20% to the year 2030 (Tamminen 1988).

New Plants

In addition to the list of existing plants included in the code, a list of new plants can be given for the computations. An official plan for electricity supply for 10 years in advance has been made every year in Finland. This consists of the best available electricity use scenario, of the capacity of electricity supply at the moment and of the need of new capacity. The report has a list of planned new power plants. These plants have been taken into consideration in the HAKOMA model. Because the list of the new plants covers the next 10 years only, the existing plants are assumed to operate for the whole time period. It can be assumed that the old plants are, with time, renewed to correspond the emission regulations of the time considered, and the geographical distribution of the plants is not changed.

Transport Performance

Scenarios for transport performances and for registration of new vehicles to the year 2010 have been issued by the State Road and Waterways Authority. The scenarios are based on the estimated growth of population. According to the scenario, the car population is increasing the whole time, but more slowly than in the 1980's. The growth of the transport performance in the 1980's was 3.0–3.5% yr^{-1}. In the 1990's, the growth is assumed to be 2.7% and in the beginning of the next century only 0.7% per year. For simplicity, after 2010, the values are assumed to be constant to the year 2040.

Sulphur Contents of Fuels

It is very difficult to predict the development of sulphur contents in fuels. It depends among others on the sulphur contents of the imported coals and crude oils. The HAKOMA model therefore uses present values of sulphur contents for the whole time period. Some restrictions have been made by the state and these have naturally been taken into consideration. Table 3 shows the assumed sulphur contents of fuels in different control strategies. For peat the sulphur content is assumed to be the whole time period 0.2% (weight). Natural gas and wood are not assumed to contain significant amounts of sulphur.

SO_2 Reduction Measures

The sulphur emissions have been calculated for three control strategies:
0. no reductions (theoretical case) as a reference for comparison;
1. reductions mandated by the Finnish government; and
2. maximum reductions to test the effect of the best available emission abatement measures.

In 1987 the Finnish government issued restrictions on the sulphur content of fuels and also emission limits for plants. When drawing up the restrictions, attention was paid to the need to reduce the emissions in the industrialized Southern Finland. Further, that the measures should concern all sectors responsible for the emissions and the costs for the measures should be reasonable. In the case of the maximum emission abatement measures the restrictions were made stricter for all oil boilers and for large coal-fired plants. The sulphur emission restrictions for both the mandated case and the maximum control case are presented in Table 4.

NO_x Reduction Measures

The NO_x emissions have been calculated for two cases:
0. no reductions; and
1. planned (all not yet confirmed) restrictions.

Table 3. Sulphur contents of fuels (weight %) in the considered emission reduction strategies

0. No reductions

	HOIL[a]	HOIL[b]	LOIL	DIESEL	GASO	COAL
1986	2.40	2.40	0.19	0.15	0.04	0.79
1990	2.40	2.40	0.19	0.19	0.01	0.80
1995	2.70	2.70	0.19	0.19	0.01	0.90
2000	2.70	2.70	0.20	0.19	0.01	0.95
2005	2.70	2.70	0.20	0.19	0.01	0.95
2010	2.70	2.70	0.20	0.19	0.01	0.95
2020	2.70	2.70	0.20	0.19	0.01	0.95
2030	2.70	2.70	0.20	0.19	0.01	0.95
2040	2.70	2.70	0.20	0.19	0.01	0.95

1. Mandated reductions

	HOIL[a]	HOIL[b]	LOIL	DIESEL	GASO	COAL
1986	2.40	2.40	0.19	0.15	0.04	0.79
1990	2.40	2.40	0.19	0.19	0.01	0.80
1995	1.00	2.70	0.19	0.19	0.01	0.90
2000	1.00	2.70	0.20	0.19	0.01	0.95
2005	1.00	2.70	0.20	0.19	0.01	0.95
2010	1.00	2.70	0.20	0.19	0.01	0.95
2020	1.00	2.70	0.20	0.19	0.01	0.95
2030	1.00	2.70	0.20	0.19	0.01	0.95
2040	1.00	2.70	0.20	0.19	0.01	0.95

2. Maximum reductions

	HOIL[a]	HOIL[b]	LOIL	DIESEL	GASO	COAL
1986	2.40	2.40	0.19	0.15	0.04	0.79
1990	2.40	2.40	0.19	0.19	0.01	0.80
1995	1.00	1.00	0.19	0.19	0.01	0.90
2000	1.00	1.00	0.15	0.15	0.01	0.80
2005	1.00	1.00	0.15	0.15	0.01	0.80
2010	1.00	1.00	0.15	0.15	0.01	0.80
2020	1.00	1.00	0.15	0.15	0.01	0.80
2030	1.00	1.00	0.15	0.15	0.01	0.80
2040	1.00	1.00	0.15	0.15	0.01	0.80

[a] Southern Finland
[b] Northern Finland
HOIL heavy fuel oil; LOIL light fuel oil; DIESEL diesel oil; GASO gasoline; COAL hard coal.

A state committee has considered proposals for the boiler NO_x emission restrictions, but they have not yet been confirmed by the state. Table 5 gives the criteria which have been used in the emission calculations in this study. Different values have been given for existing and new boilers. The limits are based on the work of the committee mentioned and they can mainly be met with primary methods. Only large new coal-fired units would need catalytic control. In the calculations it has

Table 4. Sulphur dioxide emission reduction measures used in the emission calculation for mandated and maximum reduction strategies

Restriction (the year of coming into force in parenthesis)	Reduction strategies	
	Mandated	Maximum
1. Maximum sulphur content (weight %) in light fuel and diesel oil	0.2 (1991)	0.2 (1991)
2. Maximum sulphur content (weight %) in coal used plants without desulphurization	1.2 (1988) 1.0 (1994)	1.2 (1988) 1.0 (1994)
3.1 Maximum sulphur dioxide emission (mg MJ^{-1}) for new coal combustion plants		
a) 50–150 MW(th)	230 (1987)	230 (1987)
b) > 150 MW	140 (1987)	140 (1987) 60 (2000)
3.2 Maximum sulphur dioxide emission (mg MJ^{-1}) for existing coal combustion plants		
a) 5–50 MW(th)		265 (2000)
b) 50–150 MW		140 (2000)
c) 150–200 MW		60 (2000)
d) >200 MW	230 (1994)	230 (1994) 60 (2000)
4. Maximum sulphur dioxide emission (mg MJ^{-1}) for oil-burning plants over 5 MW in urban areas in		
a) Southern Finland	500 (1991)	500 (1991) 230 (2000)
b) Other parts of Finland	1350 (1991)	230 (2000)
5. Maximum sulphur dioxide emission [kg (manufactured ton)$^{-1}$] for		
a) new sulphate pulp plants	4 (1987)	4 (1987)
b) old sulphate pulp plants	6 (1998)	6 (1998) 4 (2000)
c) new sulphuric acid plants	4–5 (1987)	4–5 (1987)
d) old sulphuric acid plants	7 (1993)	7 (1993) 5 (1995)
e) old iron and steel plants	3 (1990)	3 (1990) 2 (2000)
f) oil refineries		2 (2000)

been assumed that practically all of the existing plants will be renewed by the year 2005 to correspond to the emission restrictions of new plants.

In 1988 a new standard was given for maximum NO_x emission for passenger cars in Finland. It is independent of car size and fuel, and is 0.62 g (NO_2) km^{-1}. It is valid for new passenger car models from the year 1990 and for all new passenger cars from the year 1992. The limit value requires catalytic converters in gasoline-fuelled passenger cars. The catalytic converters will decrease the emission factor

Table 5. Assumed restrictions for boilers in NO_x emission calculations

Main fuel	Size (MW)	Emission limit [mg (NO_2) MJ^{-1}]
New boilers (from the year 1989 onwards)		
Coal	50–300	150
	>300	70
Oil	50–150	120
	>150	80
Natural gas		
Boiler	>50	50
Gas turbine	>50	100
Domestic fuel	>50	150
Existing boilers (from the year 1995 onwards)		
Coal		
Hor. firing	>100	230
Tang. firing	>100	180
Oil		
Boiler	>100	120
Gas turbine	>100	150
Natural gas		
Boiler	>100	80
Gas turbine	>100	100
Peat	>100	180

for highway driving to approximately 0.3 g km^{-1} and for urban driving to 0.5 g km^{-1}. The fact that the catalytic converters are not so effective at low temperatures causes the higher emission factor for urban driving. Diesel-powered passenger cars are assumed to decrease the emissions to the new standard by adjustments of engines. There are also plans to force emission limits for trucks and buses. They are not yet confirmed, but they are assumed to be used from the year 1995 for new vehicles, and the value is assumed to be 7.0 g km^{-1}. The emission estimates of mobile sources other than road traffic are based on fuel consumptions and emission factors (Jaakko Pöyry Oy 1986). No abatement measures are assumed to reduce the nitrogen oxide emissions from this subsector, although measures can be expected in the long term.

Results

SO_2 Emissions

Figure 3 gives the annual emissions by sectors for the KTM scenario with mandated reductions. The emissions of sulphur dioxide in Finland have been about 590 kt in 1980, but have declined to about 320 kt in 1986. The decline was mainly due to the strong decrease of the use of heavy fuel oil. Nuclear power production has also increased since 1980. The most important sector concerning

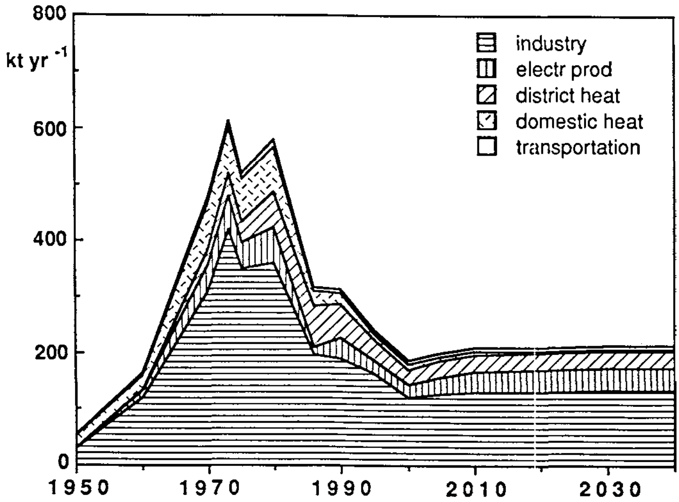

Fig. 3. Sulphur emissions [kt (SO_2) yr^{-1}] by sectors for the reference (KTM) energy use scenario with the mandated restrictions

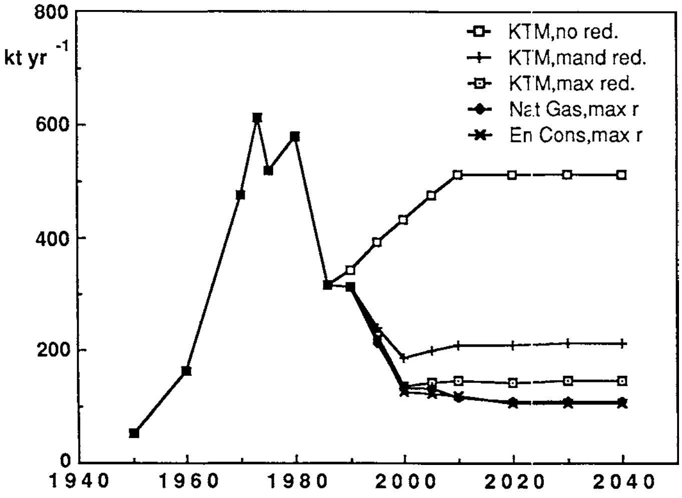

Fig. 4. Sulphur emissions [kt (SO_2) yr^{-1}] for the considered emission reduction measures and energy use scenarios

sulphur emissions is industry. About 61% of the total sulphur emissions in 1986 was due to the industry. In 1986 about 62% of the releases from industry originated in fuels and the remaining 38% were process emissions. The mandated reduction measures will decrease the total sulphur emissions in the future to about 210 kt yr^{-1}.

The effectiveness of sulphur emission reductions measures for the reference (KTM) energy use scenario is presented in Fig. 4. In the case where no restrictions have been assumed, the emissions increase from 320 kt in 1986 to about 510 kt in 2010. In the case with the emission restrictions confirmed by the state, the releases decrease to a level of 210 kt. The case with use of the best available emission control technology results in sulphur dioxide emissions of about 150 kt. In Fig. 4 the two other energy use scenarios with the maximum reduction strategy are presented. The curves for maximum natural gas scenario and energy conservation scenario run very close to each other and reach a level of 120 kt (SO_2) in 2010. The emissions from the natural gas scenario with mandated reductions would be about 150 kt in 2010, and from the conservation scenario with the mandated reductions about 170 kt.

NO_x Emissions

Figure 5 gives the development of nitrogen oxide emissions for mobile sources in the case of the confirmed emission restrictions for passenger cars and the assumed emission restrictions for heavy traffic. The NO_x emissions from transportation were 135 kt in 1986. The emissions are declining to about 120 kt in 2000. In the year 2010, when all cars are supposed to fulfil the restrictions, the NO_x emissions reach the level of 80 kt yr^{-1}. Without any emission restrictions the emissions would be about 170 kt in the year 2010.

A considerable amount of the nitrogen oxide emissions in Fig. 5 originates from the subsector "other", which includes train, ship and air traffic and mobile machinery.

Figure 6 shows the calculation results of the total nitrogen oxide emissions with the KTM energy use scenario and the expected restrictions. The emissions

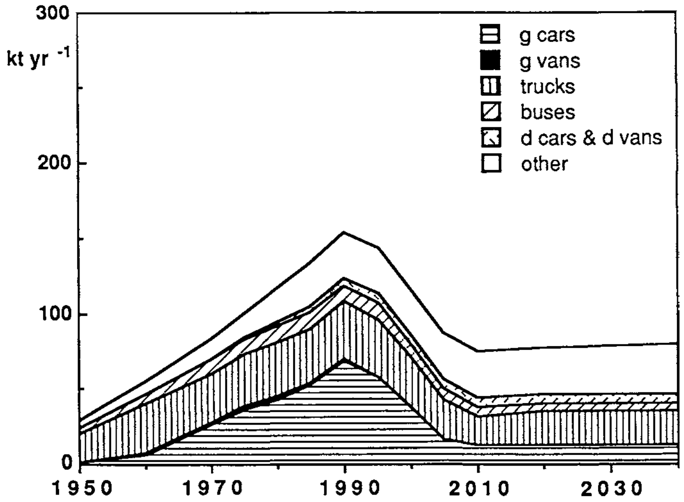

Fig. 5. Nitrogen oxide emissions [kt (NO_2) yr^{-1}] for transportation sector with restrictions: *g* gasoline; *d* diesel

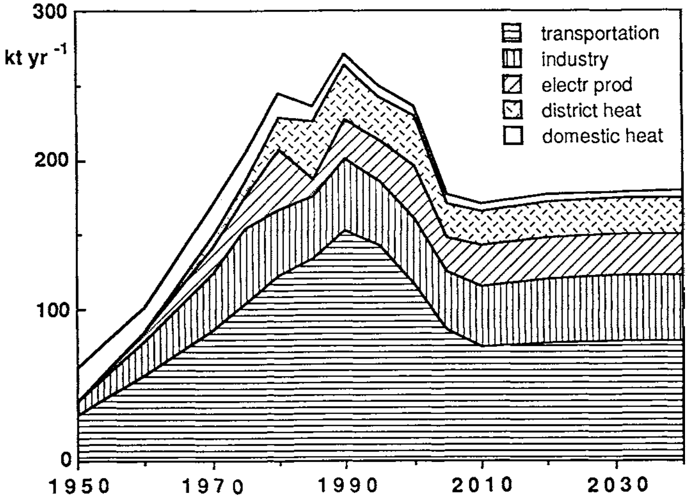

Fig. 6. Nitrogen oxide emissions [kt (NO_2) yr^{-1}] by sectors for the reference (KTM) energy use scenario and the assumed emission restrictions

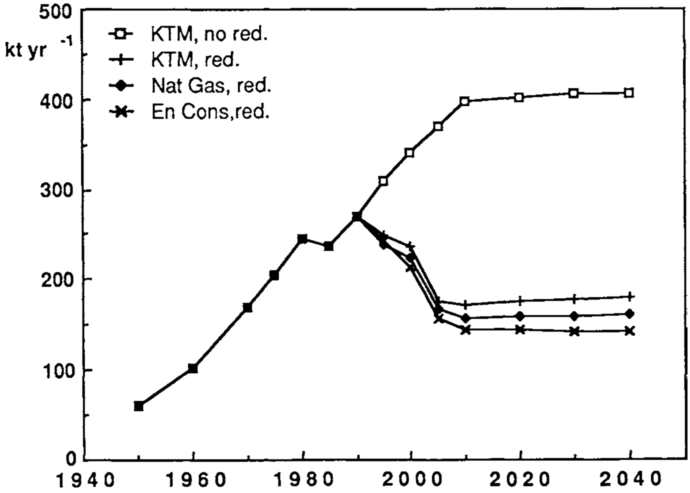

Fig. 7. Nitrogen oxide emissions [kt (NO_2) yr^{-1}] for the considered energy use scenarios

have been about 240 kt NO_2 in 1986. The calculations give a decline to 170 kt in 2010. The decrease of the emissions from the year 1990 to 1995 is due to the assumed emission restriction measures. The strong decrease of the emissions before the year 2005 is partly due to the renewal of the boiler stock.

In Fig. 7 the effectiveness of the reduction measures is shown. In the calculation case without restrictions the nitrogen oxide emissions would be 400 kt NO_2 in the year 2010. A reduction of about 57% is obtained with the restrictions. Figure 7 shows also the development of the nitrogen oxide emissions for the two other energy use scenarios: maximum natural gas use scenario and strong energy conservation scenario, both with the assumed emission reduction measures.

Discussion and Conclusions

The aim of the HAKOMA emission submodel is to make emission estimates that can be used as source terms for the atmospheric dispersion calculations and further in the impact studies. The model calculates on the basis of energy use and transportation scenarios the effects of different abatement measures and gives the emissions by fuels, by sectors, by height classes and by geographical areas. In this study, fixed energy use scenarios have been employed for long time spans, mainly to obtain long-term emission scenarios for the estimation of slow soil acidification in various deposition scenarios.

The calculated emission scenarios include inaccuracy, due, for example, to the uncertainty in the descriptions of the emission abatement measures, sulphur contents of fuels and nitrogen oxide emission factors. Especially, the grouping of boilers into classes with certain nitrogen oxide emission factors causes uncertainty. Also the NO_x emission factors in the transportation sector for vehicles in different conditions and for mobile sources other than road traffic might include considerable inaccuracy. Eggleston (1988) estimated with the employment of probabilistic methods that the uncertainty described with a band of two standard deviations ($\pm 2\sigma$) is about 7% for the present SO_2 emission inventory and 17% for the NO_x emission inventory in the U.K. The uncertainty estimates of the present annual emissions in the U.S.A. are 12% for SO_2 and 24% for NO_x (NAPAP 1988). However, the uncertainty in the case of Finland might be smaller due to the more detailed description of stationary emission sources in Finland.

The estimates of future energy use and traffic volume are likely to cause the greatest uncertainty in the results. The energy use in Finland is closely connected to the economic growth in Finland and further to the economy of the world. The increase rate of traffic performance and number of new cars are also closely connected to the economic welfare. The long-term scenarios in this study base on the assumptions of relatively favourable economic growth, although in the recent years the growth rate has even exceeded the assumptions of the scenarios considered. The HAKOMA emission model has also been used to study energy use scenarios based on different assumptions on economic growth and energy conservation (Savolainen and Tähtinen 1988). In that application, the scenarios of slow economic growth gave very different emissions compared to the scenarios of moderate economic growth. The sulphur emissions of a slow growth scenario with mandated sulphur controls were even more than 30% lower in 2010 than the emissions of a moderate growth scenario with the same assumptions on control measures and energy conservation.

The energy use scenarios in this study assume also that the amount of electricity produced with nuclear power remains constant throughout the time period considered. A new nuclear power plant of 1000 MW_e would reduce the sulphur emissions of about 10 kt yr^{-1} and nitrogen oxide emissions of about 5 kt yr^{-1}, depending on the fuel and plant type it replaces and on the assumed emission abatement measures.

In the future, several natural gas fuelled district heating power plants will be built, which use the so-called combined cycle technique (gas turbine + steam turbine). These plants produce about twice as much electricity as the conventional district heating plants. When this extra electricity production replaces condensation power (coal plants), there is a potential to reduce acidifying emissions further. However, there will be a maximum limit in the use of natural gas imposed by the structure of the distribution network and the security aspects of the entire energy system (Energy committee 1989).

The energy use scenarios considered are for the whole country. The local development of energy use can be quite different from the average development. The long-term scenarios do not take into consideration short-term fluctuations of energy use caused by market conditions and, for example, by the availability of hydro and nuclear power.

According to the model calculations of this study, the mandated and planned emission reduction measures will limit the total SO_2 and NO_x emissions in Finland considerably. Energy conservation and increased use of natural gas have also great potential to lower the emissions of SO_2 and NO_x. In the long term, considerable changes are possible in the use of fuels, energy conservation and emission abatement measures. Also new techniques and the renewal of the plant stock (e.g. power plants and industrial plants) will give potential to great emission reductions.

For a decision-maker of the pollution control it is also important to consider the costs of emission reductions. An abatement cost module for cost-effectiveness studies is planned to be put into operation later. Additionally a study has been started considering the whole energy system and its costs with various emission constraints and energy demands.

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NO_x Emissions at the Beginning of the 1980s in Finland

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Summary

Nitrogen oxide emissions in Finland are estimated for the years 1980 and 1983. Emission sources included in this study are traffic and mobile machinery, energy generation, industry and other anthropogenic sources. The emissions from natural biological and chemical processes are not estimated. NO_x emissions in Finland in 1980 were 283,600 t NO_2 a^{-1} and in 1983 247,700 t NO_2 a^{-1}. The share of traffic of the total anthropogenic emission was 50 and 60%, respectively.

Introduction

In order to determine the total emissions of nitrogen oxides in Finland the sources were divided into four groups:

- traffic and mobile machinery
- power and heat generation
- industrial processes
- other anthropogenic sources

The emissions from natural biological and chemical processes were not covered by the study.

All nitrogen oxide emissions are expressed in this study as nitrogen dioxide (NO_2) in accordance with international practice. All calculations were carried out on an annual basis for 1980 and 1983.

This study with complete references has been published in Finnish (Jaakko Pöyry Oy 1986). This article describes the calculation principles, basic assumptions and the main results of the study.

Traffic

Road Traffic

Road traffic consists of cars, vans, lorries, buses and motor-cycles. Special vehicles like fire engines, ambulances etc. are not included but they are classified in the

Kauppi et al. (Eds).
Acidification in Finland

Table 1. NO_x emission from Finnish road traffic in 1983

	Number of vehicles	Average mileage km a^{-1}	Specific emission g NO_2 km^{-1}	Annual emission t NO_2 a^{-1}
Cars				
petrol	1,277,603	16,300	2.55	53,100
diesel	103,644	32,300	0.65	2,200
Vans				
petrol	50,201	16,500	5.2	4,300
diesel	61,529	16,500	0.7	700
Lorries[a]	53,026	45,100	21	50,200
Buses	9,083	73,800	18	12,100
Motorcycles	46,520	5,000	0.3	70
Mopeds	165,970	3,900	0.05	30
Total				122,700
Breakdown in				
petrol vehicles				57,500
diesel vehicles				65,200

[a] All lorries and buses are assumed to be diesel-driven.

group miscellaneous mobile sources. Based on investigations in Sweden, Holland and the United States, the specific emissions were estimated corresponding to the actual distribution of vehicle and engine types, city/highway mileage and so forth in Finland. (Olsson 1983; Ministry of Housing 1983; EPA 1975). NO_x emissions from traffic and mobile machinery for the years 1980 and 1983 have been calculated with the aid of unit emission factors based on the transport performance (g km^{-1}) or fuel consumption (g l^{-1}, g kg^{-1}). In road traffic NO_x emissions (g km^{-1}) typically increase with an increase in speed (Roads and Waterways Administration, 1984). The transport performance has generally been divided into town traffic and road traffic, with separate emission factors for each type of traffic (g km^{-1}). The average unit emission factor has been estimated in proportion to the relative shares of town and road traffic, to the extent that information on relative shares has been available (Roads and Waterways Administration, 1984). The results and average specific emissions by vehicle group are presented in Table 1 for the year 1983. The results for the year 1980 were practically the same, with total emissions of 120,200 t NO_2 a^{-1}.

Mobile Machinery

The group of mobile machines is composed of tractors and harvesting machines used in agriculture and forestry, excavating machines, compressors, front-end loaders and other machines currently used in civil works. Their emissions are estimated based on statistics of their fuel consumption (Ministry of Trade and Industry 1984a). The fuel consumptions, emission factors and emissions were of similar amounts in 1980 and 1983.

Table 2. Fuel consumption and NO_x emissions from mobile machinery 1983

	Fuel consumption $m^3\ a^{-1}$	Emission factor kg $NO_x\ m^{-3}$	Annual emission t $NO_2\ a^{-1}$
Agricultural machinery	225,000	40	9000
Forestry machinery	47,000	40	1900
Civil works machinery	138,000	50	6900
Total	410,000	–	17,800

Emission factors for light fuel oil were based on U.S. estimates. The values for 1983 are shown in Table 2.

Other Traffic Sources

The emissions from railway traffic and domestic ships were estimated according to the Energy Statistics in Finland (Ministry of Trade and Industry 1984a.)

The foreign ships' emissions were estimated with the following statistical data (National Board of Navigation 1983):

- 22,000 ships visited Finnish harbours in 1983
- all foreign ships and 95% of the Finnish merchant marine are motor ships and only 5% steamships
- average fuel oil consumption in harbours of 1200 l during about 12 h stay;
- fuel consumption during voyage 70 l km^{-1}
- emissions calculated within Finnish borders with an average cruising length of 50 km
- emission factor 32 kg $NO_2\ m^{-3}$

The emissions from small pleasure craft and fishing boats were estimated as follows:

	Petrol	Diesel	Total
Number of boats	250,000	20,000	270,000
Annual usage, h per boat	25	100	–
Fuel consumption, $m^3\ a^{-1}$	31,300	10,000	41,300
Emission factor, kg $NO_2\ m^{-3}$	0.8	41	–
NO_x emission, t a^{-1}	25	410	435

A summary of emissions from railway and waterway traffic is shown in Table 3.

Air traffic emissions originate from commercial aviation, pleasure flights and military aviation. Most of the emissions are related to take-off and landing, and specific coefficients from reliable sources.

The National Board of Civil Aviation keeps statistics on the number of landings to all Finnish airports (National Board of Civil Aviation 1984). The estimated nitrogen oxide emissions from aviation are shown in Table 4.

Table 3. NO_x emissions from trains, ships and boats in 1983

	Fuel consumption $m^3 a^{-1}$	Emission factor kg NO_2 m^{-3}	Annual emissions t NO_2 a^{-1}
Railway traffic	94,000	44	4100
Domestic ship traffic	38,000	37	1200
Foreign ship traffic	103,000	32	3300
Boat traffic	41,000	10	400
Total	276,000	–	9000

Table 4. NO_x emissions from aviation in 1983

	Commercial aviation	Military aviation	Recreational flying	Total
Landings	64,260	63,160	118,140	245,560
Specific emission, kg per landing	12	1	0.3	–
NO_x emission, t a^{-1}	770	60	40	870

Miscellaneous mobile sources like special vans (ambulances, fire engines) tractors outside agriculture and forestry, etc. were estimated to give rise to about 3000 t a^{-1} annual nitrogen oxide emissions. The estimate was based on statistics on their fuel consumptions.

Total Emissions of Traffic and Mobile Machinery

A summary of the above-mentioned sources of NO_x emissions is presented in Fig. 1. The emissions were similar in amount in 1980 and 1983.

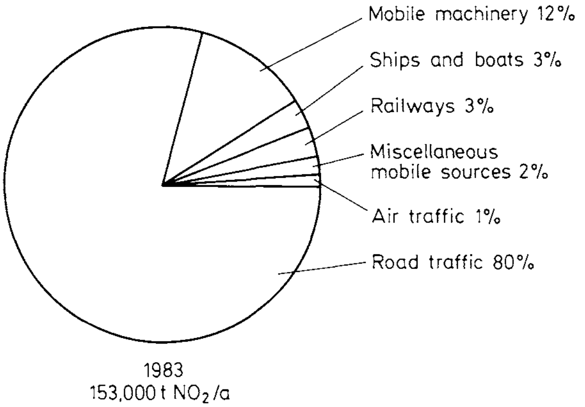

Fig. 1. The NO_x emissions from traffic and mobile machinery in 1983

Power and Heat Generation

Introduction

The emissions from power and heat generation were estimated by fuel, by energy sector based on fuel consumptions (Ministry of Trade and Industry 1984a) and emission factors. The NO_x emission factors are generally expressed in mg NO_2 MJ^{-1} and calculated on the net heat value of the fuel. Since NO_x emissions can originate from the combustion air as well as from the nitrogen content of the fuel, both sources are included in the emission factors. The nitrogen content of coal is typically 1.0–2.2% elemental nitrogen by dry weight, whereas the corresponding value for heavy fuel oil is 0.3% and for light fuel oil about 0.2%. The nitrogen content of bark varies typically between 0.1–0.5% by weight and for wood waste is less than 0.1%. The content of elemental nitrogen in peat is higher and values 1.5–2% are common.

Emission factors from Finnish, Swedish and U.S. investigations were compared and the calculations were based on Scandinavian emission factors. (Pohjola et al. 1983; Ministry of Trade and Industry 1984b). The values from EPA represent new boilers with bigger unit sizes than is common in Scandinavia, as well as the application of low NO_x technology. This was not common in Finland at the beginning of the 1980s. The emission factor for coal was based on available measurements in Finnish power plants (Pohjola et al. 1983). This value depends on boiler size and type and burning conditions, and the use of a single factor introduces some uncertainty. Later, somewhat lower emission factors (170–420 mg MJ^{-1}) were used (Hupa et al. 1987). The net heat values of fuels and emission factors used in the calculations are shown in Table 5.

The nitrogen oxide emissions by fuel types are shown in Table 6.

The main reasons for the rapid decrease in NO_x emissions in 1983 were the very favourable conditions for production of hydroelectric power and the increased utilisation of nuclear energy. Since 1983, no new nuclear power plants have been

Table 5. Average NO_x emission factors and net heat values of various fuels

	Emission factor	Net heat value	
	mg NO_2 MJ^{-1}	MJ kg^{-1}	MJ m^{-3}n
Coal	470	25	
Heavy fuel oil	156	40.6	
Light fuel oil	156	42.7	
Natural gas			
Industrial boilers and gas	156	–	38.4
District heating	38	–	38.4
Peat			
Industrial boilers and district heating	220	9.6	
Separate small-scale units	100	9.6	
Wood waste, bark and other solid fuels	100	6–10	

Table 6. NO_x emissions by fuel types

	1980 $tNO_2\,a^{-1}$	1983 $tNO_2\,a^{-1}$
Coal	63,000	34,000
Heavy fuel oil	21,000	13,000
Light fuel oil	6,200	4,300
Natural gas	4,100	2,800
Peat	4,300	7,400
Wood waste and bark	7,700	7,200
Total	106,300	68,700

built in Finland, and therefore the increased demand has been covered mainly with increased burning of fossil fuels.

The same emissions can also be calculated by sector, and these are presented in Fig. 2.

The reasons for the considerable decrease in power generation emissions were discussed in connection with Table 5. The replacement of separate small heating units with district heating is also reflected in the emissions of these categories.

The emissions of nitrogen oxides from power generation are heavily concentrated in the southern part of the country. About 60% of the NO_x emissions from heating and about 50% of the industrial heat and power generation emissions also originate from southern Finland.

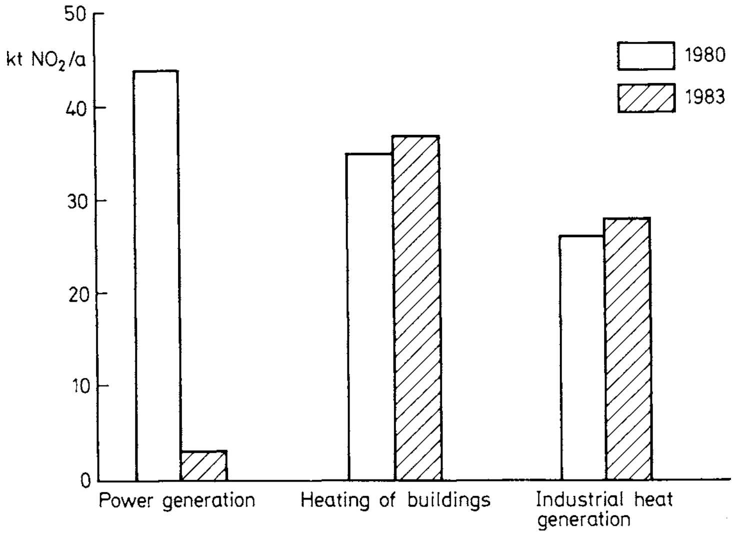

Fig. 2. Emissions from power and heat generation by sector

Industrial Processes

Production in Main Sectors

The production figures for industrial plants contributing to NO_x emissions are presented in Table 7. It should be emphasised that, for example, within the production of inorganic chemicals, there is substantial production of phosphate fertilisers, chlorine, caustic soda, sulphuric acid and so forth which are not significant for NO_x emissions.

NO_x Emissions

The emissions have been estimated based on specific emissions from each branch of industry. Each branch has its own typical sources, as the following examples illustrate.

	Origin of typical emissions
Iron and steel	Converters, sinter plants, coke ovens, nitric acid pickling, lime burning, etc.
Pulp	Recovery boilers, lime kilns
Nitric acid	Burning of ammonia, heat recovery, cooling and absorption of tail gases

Specific emission factors were used for the cement industry, pulp industry, iron and steel industry and glass industry, and they were checked by comparing Finnish measurements with foreign studies. Emissions from the chemical industry were based on measurements and estimates which were made by the companies. The emissions from inorganic and organic chemical manufacturing come from a few large integrated plants and it would have been extremely difficult to relate them to the production figures of all main products and by-products.

The results of the estimates are presented in Table 8 and Fig. 3.

Table 7. Production level of relevant industrial branches

	Unit × 1000	Production 1980	1983
Oil refineries and plastics	tons of crude oil a^{-1}	700	700
Nitric acid	t HNO^3 a^{-1}	400	490
Kraft pulp	ADt a^{-1}[a]	3800	3800
Sulphite pulp	ADt a^{-1}[a]	800	600
NSSC pulp	ADt a^{-1}[a]	260	280
Raw iron	t a^{-1}	2000	1900
Raw steel	t a^{-1}	2500	2400
Cement	t a^{-1}	1800	1900
Glass	t a^{-1}	60	50

([a] ADT = air dry metric ton).

Table 8. NO_x Emissions from Finnish industry

	1980 $tNO_2\ a^{-1}$	1983 $tNO_2\ a^{-1}$
Oil refining and organic chemicals	4630	4630
Kraft pulping	4490	4480
Inorganic chemicals	3400	2900
Building materials	3300	3370
Iron and steel manufacturing	3000	3000
Sulphite and NSSC pulping	1020	700
Other metals manufacturing	450	450
Plate glass manufacturing	180	170
Total	20,470	19,700

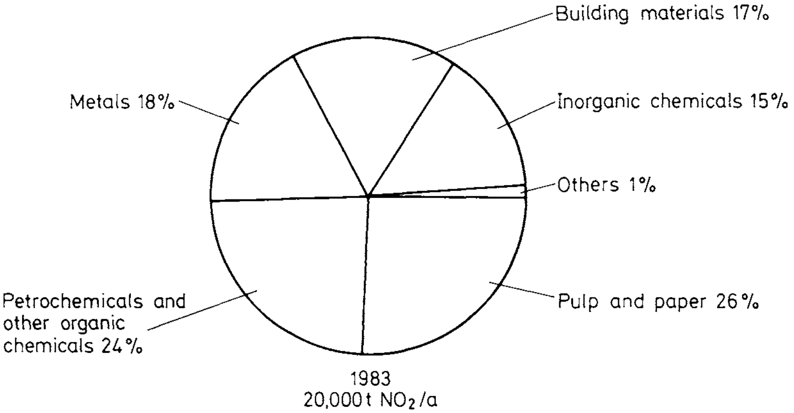

Fig. 3. Industrial NO_x emissions

Other Anthropogenic Sources

The most important other emissions of NO_x come from waste water treatment plants, waste disposal areas for municipal waste and garbage, and fertilising of fields. They were estimated based on available statistics on waste water treatment and fertilising of agricultural lands. The information on solid wastes were based on the best available official estimates. The order of magnitude of these emissions was estimated to be:

	$tNO_2\ a^{-1}$ in 1983
Waste water treatment	2600
Waste disposal areas	400
Fertilising fields	2900

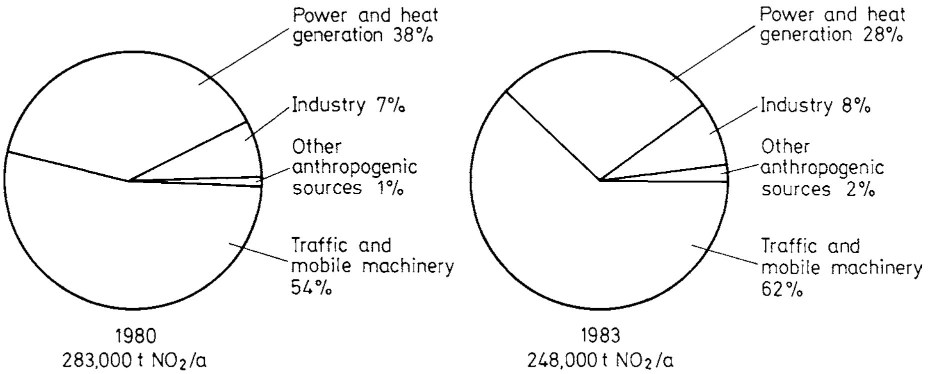

Fig. 4. Nitrogen oxide emissions in Finland at the beginning of the Finnish Acidification Research Programme

There were about 4.5 million inhabitants in Finland in 1980–1983 and the area of cultivated land was approximately 2.5 million hectares.

Conclusions and Discussion

NO_x emissions in Finland in 1980 and 1983 are shown by source in the following:

Source of emission	NO_x emission	
	1980 $tNO_2\,a^{-1}$	1983 $tNO_2\,a^{-1}$
Traffic and mobile machinery	151,600	153,400
Energy production	106,300	68,700
Industry	20,500	19,700
Other anthropogenic sources	5,200	5,900
Total	283,600	247,700

The same information is presented in Fig. 4. It shows that the share of traffic of the total anthropogenic emissions in 1980 was over 50% and in 1983 over 60%, although the absolute emissions of traffic remained practically unchanged. The strong increase in the relative share was due to a decrease in the production of condensing power using coal as the main fuel. The main reason for this was the favourable conditions for hydroelectric power and increased utilisation of nuclear power. As a result, the share of energy generation of total emissions dropped from 38% in 1980 to 28% in 1983.

Industry's share of the total emissions in 1980 and 1983 was 7–8% and the share of other anthropogenic sources about 2%.

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Ammonia Emissions in the 1980s

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Summary

The emission of ammonia from manure accounts for a major part of the nitrogen emission in agriculture. The annual ammonia emission from livestock manure is estimated at 30,000 tons of nitrogen. Nitrogen emissions from fur animal farms are estimated to be about 4000 tons a year. Nitrogen evaporation from artificial fertilizers in the field is estimated to be about 7500 tons a year. Industrial ammonia emissions are much less, amounting to about 1000 tons of nitrogen a year. The annual emission of ammonia nitrogen from all domestic sources is estimated to be 43,000 tons. Of this amount, manure is the source of roughly 80%. Nitrogen emissions arising from ammonia vary regionally from 0.01 to 0.4 g m^{-2}. Ammonia emissions throughout Europe contribute to the deposition in Finland. The total deposition is about 45,000 tons of nitrogen. If the ammonia deposition were distributed evenly over the whole area of Finland, the nitrogen would amount to 0.13 g m^{-2}.

Introduction

In addition to emission of nitrogen oxides, the release of ammonia also has an effect on the total load of nitrogen. The main source of ammonia emissions is agriculture, primarily livestock manure. Other sources of ammonia deposition in Finland are industry and long-range transport.

Ammonia is a base which produces 1 mol of ammonium ions and 1 mol of hydroxyl ions when dissolved in water. The ammonium fallout as such does not increase soil acidity. Acidity may be increased if ammonium is nitrified in soil. In nitrification, the ammonium ion is oxidized biologically to nitrite. Then 2 mol of hydrogen ions are released per 1 mol of nitrogen (White 1979). Because 1 mol of hydroxyl ions is released when 1 mol of ammonia is dissolved in water, the net effect is the production of 1 mol of hydrogen ions. In reality, not all the ammonium nitrogen is nitrified. Nitrification proceeds most rapidly in soils with a pH near neutrality. In acidic mineral soils, e.g. forest soils, nitrification is weak; then ammonium does not have an acidifying effect. In bare soils, ammonium fallout may be an important source of nitrogen for plants. Excessive ammonium, however, can disturb the uptake of other nutrient cations, thereby causing deficiencies.

Kauppi et al. (Eds).
Acidification in Finland

Agricultural Emissions

Emission from Livestock Manure

Livestock can only partially utilize the nitrogen in feeds; the rest is passed into manure. The annual amount of nitrogen contained in the manure of different domestic animals is presented in Table 1. The annual output of livestock manure is estimated to contain about 63,000 tons of nitrogen (Table 2), i.e. 2.6 g m^{-2} of arable area (Keränen and Niskanen 1987). In calculation of N output in livestock manure, the number of animals was expressed as animal units according to Steineck (1974) and Buijsman et al. (1984). One dairy cow corresponded to 1.25 bulls over 2 years old, 2 calves over 1 year old and 4 calves under 1 year old; one sow with piglets to 2 fatting pigs and one hen to 3.3 chickens under 6 months old. As far as cows and horses are concerned, only the winter-time (245 days per year), when animals are fed in the stable, is involved in the output estimate.

Ammonia Emission During the Storage of Manure

Losses of nitrogen during the storage of manure are caused mainly by the volatilization of ammonia. The amounts of loss depend on the method and duration of manure storage and management. In Finland, about 80% of cow

Table 1. Annual amount of nitrogen contained in the manure of domestic animals. (Steineck 1974; Buijsman et al. 1984)

Animal	Amount of manure kg per animal		Annual amount of N, kg per animal
	Daily	Annually	
Cow			
Dung	23–30	8500–11,000	36
Urine	9–14	3500–5000	39
Total			75
Sow			
Dung	5.5	2000	8.8
Urine	6.9	2500	11.2
Total			20.0
Pig (20–90 kg)			
Dung	2	700	3.3
Urine	3	1100	6.7
Total			10.0
Poultry	0.12	40–50	0.54
Horse			
Dung	20		47
Urine	6		
Fur animals			
Fox	0.12	45	1.5
Mink	0.05	19	0.9

manure and 42% of swine manure are stored with litter (Kemppainen 1985), the rest being stored as slurry.

When manure is stored with litter, the least loss of nitrogen occurs in tight heaps under anaerobic conditions. Then the loss of nitrogen is 5–20% for 3–7 months (Kirchmann 1985). Under conditions corresponding to the Finnish climate, the loss of nitrogen from straw-manure compost is 14–33% for 5–7 months (Kirchmann 1985). Draining of urine into a well with a tight cover reduces the loss of ammonia. Then less than 10% of the nitrogen is lost during an 8-month period (Iversen 1924). In Finland, about half the farms using litter in the storage of manure have a urine well, nearly all of which (94%) are covered (Kemppainen 1985).

In the litter method, the amount of nitrogen lost during the storage of manure is estimated to be 25%, the amount of nitrogen being lost from urine in a tight well to be 10% (Keränen and Niskanen 1987). About 50% of the nitrogen in cow and swine droppings is contained in urine; litter binds about one-third of this amount. As half of the farms have a urine well, about one-sixth of the nitrogen is stored in wells. Under these circumstances, the loss of nitrogen in the litter method is 5/6 × 25% + 1/6 × 10% = 22.5%.

In the slurry method, more ammonia is evaporated from the surface of slurry than from deeper layers. The loss of nitrogen from the surface layer (15 cm) is about 50%, but it is only 10% from the deeper layers (Kofoed et al. 1969). In Finland, about 37% of the slurry basins are uncovered (Kemppainen 1985), which increases the volatilization of ammonia. Under these circumstances, the loss of nitrogen from slurry can be estimated to be 15% (Keränen and Niskanen 1987).

Considering the storage method, the mean loss of nitrogen can be estimated as follows (Keränen and Niskanen 1987):

Cattle manure	Litter method	0.8 × 22.5%	= 18%
	Slurry method	0.2 × 15%	= 3%
			21%
Swine manure	Litter method	0.42 × 22.5%	= 9.5%
	Slurry method	0.58 × 15%	= 8.7%
			18.2%

Using the same loss percent for manure of hens and horses as for cow manure, the total annual loss of nitrogen during the storage of manure is estimated to be 13,000 tons (Table 2).

Ammonia Emission During the Application of Manure and During the Grazing Period

Ammonia nitrogen in manure is liable to volatilize after spreading. About 26% of the nitrogen in litter manure, 56–70% of that in slurry and over 85% of that in urine is soluble and evaporates easily (Kemppainen 1984). Half of the ammonia-derived nitrogen in litter manure (Lauer et al. 1976) and in slurry (Beauchamp et al.

Table 2. The annual output of nitrogen in manure and its losses (tons a^{-1}). (Keränen and Niskanen 1987)

Animal (no. of animal units June 1986)	Amount of N output in manure	Loss of N during storage	Amount of N spread in fields	Loss of N in fields	Loss of N during the grazing period	Total loss of N
Cattle (942,300)						
Litter manure	31,630	7,910	23,720	4,740		
Slurry	9,490	1,420	8,060	1,800		
Urine	6,330	630	5,690	1,710		
Total	47,450	9,960	37,470	8,250	5,630	23,840
Sows and Pigs (1,030,700)						
Litter manure	3,610	900	2,700	540		
Slurry	5,970	900	5,080	1,420		
Urine	720	70	650	200		
Total	10,300	1,870	8,430	2,160		4,030
Poultry (7,053,600)						
	3,810	800	3,010	660		1,460
Horses (38,700)	1,220	260	970	210		470
Fur animals	8,000					4,000
Total	70,780	12,890	49,880	11,280		33,800

1978) can evaporate in 1–4 days if the manure is not ploughed in. In Finland. ploughing is usually done 1 day after spreading, but urine is partially (22%) spread to vegetation (Kemppainen 1985).

In the field, the loss of nitrogen from litter manure is estimated to be 20%, that from urine 30% (Keränen and Niskanen 1987). Volatilization from slurry is estimated to be 40% of the soluble nitrogen, i.e. 22.4% of total nitrogen in cow slurry and 28% of that in swine slurry (Keränen and Niskanen 1987). It is thought that during the grazing period (120 days), 40% of the nitrogen in urine and 5% of that in dung evaporate (Buijsman et al. 1984). It is estimated that in fields and pastures, the total annual loss of nitrogen from manure is about 17,000 tons (Table 2) (Keränen and Niskanen 1987).

Emission from the Manure of Fur Animals

There are over 5700 fur farms in Finland, most of which are situated on the Ostrobothnian coast (Ferm et al., this Vol.). The number of fur animals is comparable to the number of furs produced, which came to about 6.5 million in 1988.

The fur animals are mostly minks and foxes, the dung of which is very rich in nitrogen. The estimated (Helin 1982) amount of nitrogen produced per fur is 1.5 kg for fox and 0.9 kg for mink (Table 1).

The dung of fur animals drops to the ground beneath the cages and remains there for some time. According to the instructions given by the Finnish health authorities, the dung should be removed at least seven times a year. The dung can be removed to a refuse tip, stored at the grounds of the fur farm for an unspecified period of time, or it can be used as manure and spread in the fields. During storage the manure can be treated with peat or litter, which reduce the ammonia emissions.

The total amount of nitrogen in the dung is estimated to be 8000 tons per year. Ammonia emissions from the dung are estimated to be 40–50% of the total nitrogen content. This means that the ammonia emission from fur farms comes to 3200 to 4000 tons of nitrogen per year (Table 2). The emission factors for fur animals have not been studied over a long period, and many issues are yet to be solved.

Ammonia emissions from fur farms have caused local disturbances in the growth of forests (Ferm et al. this Vol.).

Emission from Artificial Fertilizers

In Finland, about 200,000 tons of nitrogen are sold annually, contained in artificial fertilizers, more than 80% being in mixed fertilizers. The amount of nitrogen corresponds to about 9 g m^{-2} of arable area. In artificial fertilizers, nitrogen is in the form of ammonium nitrate, ammonium sulphate or urea. In mixed fertilizers, two-thirds of the nitrogen is in the form of ammonium nitrogen. Because Finnish

Table 3. Annual emission of ammonia from artificial fertilizers. (Keränen and Niskanen 1987)

Fertilizer	Sale[a] of N, tons	Emission of ammonia nitrogen	
		% of N	N tons
Ammonium nitrate (salt-peter)	24,610	5	1230
Ammonium sulphate	200	5	10
Urea	4,320	20	860
Ammonium N in mixed fertilizers	108,690	5	5400
Total	137,820		7500

[a] Fertilization year 1984–1985.

soils are acidic, evaporation of ammonia from artificial fertilizers after spreading is not very high; in addition, placement fertilization is a common practice.

Because Finnish experimental results are lacking, estimation of the volatilization of ammonia from artificial fertilizers is based on results obtained in other countries. In acid soil, the volatilization of ammonia from ammonium nitrate and sulphate can be estimated to be 0–5% of the nitrogen (Martin and Chapman 1951; Wahhab et al. 1957; Kresge and Satchell 1960; Carter and Allison 1961). Evaporation of ammonia from urea depends on the activity of urease enzymes in soil. In the climate of Finland, the volatilization of ammonia may amount to 3–20% of the nitrogen in urea (Overrein 1968; Nömmik 1973). The total annual emission of ammonia nitrogen from artificial fertilizers can be estimated to be 7500 tons (Table 3) (Keränen and Niskanen 1987).

Total Agricultural Emissions

The total annual emission from the manure of livestock and fur animals is estimated to be about 34,000 tons of nitrogen (Table 2), or 41,000 tons of ammonia. Of this, cattle manure accounts for about 70% of the total emission. More than half of the nitrogen in manure can evaporate; the losses during storage and after the application of manure are about equal (Table 2). It is important to plough the manure into the soil as soon as possible, because the volatilization of ammonia occurring after the spreading of manure can cause the concentration of ammonia in the air to rise to a detrimental level (Beauchamp 1983).

It is estimated that the annual emission of ammonia nitrogen from the manure of livestock and fur animals and from artificial fertilizers is about 41,000 tons, i.e. 1.8 g m^{-2} of arable area (Keränen and Niskanen 1987). Of this, about 80% originates from livestock manure. The annual ammonia emission is 2.2 g m^{-2} of arable area. The annual ammonia emissions are much higher on the European Continent, where animal husbandry is very intense: Holland 6.4, Belgium 5.2, France 4.4 and Denmark 3.8 g m^{-2} (Buijsman et al. 1984).

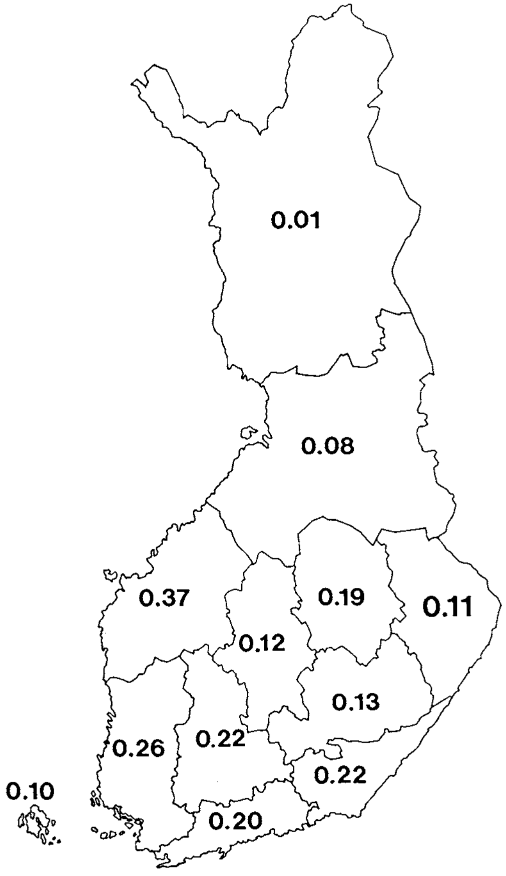

Fig. 1. Emissions of ammonia nitrogen (g m^{-2}) from livestock manure and artificial fertilizers in the different provinces of Finland. (Keränen and Niskanen 1987)

There are regional variations in emissions. The estimated emissions in the different provinces of Finland are presented in Fig. 1. The emissions are the greatest, about 0.4 g m^{-2}, in Vaasa province, and about 0.3 g m^{-2} in Turku and Pori province. The lowest emissions, 0.01 g m^{-2}, occur in Lapland province.

Finnish experimental results are very limited, and estimates of emission are based mainly on results obtained in other countries. It is possible that the actual emissions are lower than have been estimated. In Finland, the management of manure is somewhat different than in other countries located farther south. Manure is spread mostly in the spring and autumn, and is ploughed in soon after application. The number of livestock is also fairly small in relation to the arable area, and manure can be used sensibly. In other countries, the number of livestock may be high in relation to the arable area; then the amounts of manure spread can be very high. The application of manure may also be continued throughout the year.

Industrial Emissions

Fertilizer and ammonia production plants are the main sources of industrial emissions of ammonia (Buijsman et al. 1986). Industry emits much less ammonia than does agriculture. The industrial emissions of ammonia in Finland are estimated to be about 1000 tons of nitrogen per year.

According to the Ministry of the Environment, the largest local sources of industrial ammonia emission are in Uusikaupunki (about 400 tons nitrogen per year) and Kokkola and Oulu (each about 200 tons of nitrogen per year).

Total Deposition of Ammonia

Ammonia emissions in Europe contribute to the Finnish ammonia deposition. According to the latest estimates (Eliassen et al. 1988), the total ammonia deposition in Finland is 45,400 tons of nitrogen per year. Of this amount only about 30% (13,300 tons of nitrogen) originates from domestic sources. The rest is transported to Finland from foreign sources, mainly from the Soviet Union (which accounts for approximately 40% of the deposition).

If the annual deposition of ammonia nitrogen (45,400 tons) were distributed evenly throughout the whole area of Finland (338,145 km^2), the average deposition of ammonia nitrogen would amount to 0.13 $g\ m^{-2}$.

The atmospheric chemistry and the transportation models for ammonia contain many uncertain questions which should be borne in mind when these figures are used.

Conclusions

Total Finnish ammonia emissions in the 1980's are estimated to be 43,000 tons of nitrogen a year. Yearly variations throughout the decade have been small. In the future, ammonia emissions are expected to decrease by 10–25% due to the predicted decrease in the number of dairy cows.

Ammonia emission from livestock manure is a complex process, depending on agricultural practices and meteorological conditions. The Finnish ammonia emissions have been calculated using foreign data on emission factors. In Finland the amount of manure produced per arable land is small compared to most European countries and can be used sensibly as a fertilizer. The actual Finnish ammonia emissions could therefore be somewhat lower than estimated.

Ammonia deposition in Finland is estimated to be about 45,000 tons of nitrogen a year. The Finnish ammonia emissions cannot account for all the deposition. More than half of the deposition is estimated to originate from other countries, mainly from the Soviet Union. The current ammonia models cannot express the transportation and deposition accurately, so these figures should be viewed with caution.

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1.2 Atmospheric Processes

On the Effects of Meteorological Factors on Air Pollution Concentrations and Deposition in Finland

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Summary

This chapter reports on pollutant concentrations in air and precipitation as well as deposition observed in the 1980's in Finland, with special emphasis on the meteorological variability. A theoretical description of the main physical processes is also given.

Our results show that air and precipitation concentrations follow specific patterns principally determined by the air mass origin, the season and the local conditions (the stability of the atmospheric layer and the type of surface). The southwestern and southeastern sectors make the greatest contribution to the pollutant load in Finland. Late winter and early spring have the highest concentrations due to a combination of maximum emissions, specific wind patterns and air chemistry. Although concentrations observed in Southern Finland are higher, they are more readily neutralized by basic constituents. In forested Central Finland, rain or snow acidity is more episodic. Nitrate seems to be more closely related to acidity than sulphate. Ozone concentrations above the potential damage threshold of 60 $\mu g\, m^{-3}$ are often observed, especially when air masses come from the European industrialized zones. Shipborne observations show that the Baltic Sea Basin cannot be considered as a pristine region, and from time to time high deposition values can be observed.

1 Introduction

The first serious concern about the adverse effects of acidification processes on the environment in Europe was already raised in the 1960's. Swedish and Norwegian scientists stressed the likely connection between observed damage and the long-range transport of air pollution (Odén 1968; Munn and Bolin 1971; Rodhe 1972; Rodhe et al. 1972). Thus, from the start it was clear that meteorology was the key factor modulating the transport, diffusion and deposition of air pollution. The first concrete agreements for the monitoring of air pollution compounds and the assessment of their paths over Europe were reached in the mid-1970's (OECD 1979). After a preliminary agreement on the reduction of sulphur emissions, alternative theories for forest decline, together with the increase of nitrogen oxides

Kauppi et al. (Eds).
Acidification in Finland

and volatile hydrocarbon emissions, especially in connection with increasing traffic, put the spotlight on oxidants in the 1980's.

The first comprehensive review of air quality in Finland was carried out by Kulmala et al. (1982). In 1985, the Finnish Research Project on Acidification (HAPRO) was initiated to determine the extent and future development of damage to water and forest ecosystems, and to estimate how such damage could be efficiently reduced and prevented. Thus, in the framework of this project, it was clear that the assessment of prevailing pollutant concentrations in air and precipitation, their relationship with deposition distribution, and their dependence on local and large-scale climatological, meteorological and chemical factors would be of great interest for ecological, forestry and lake research.

This article will report on several air chemistry projects financed by HAPRO and carried out at the Finnish Meteorological Institute (FMI). It includes the following projects: (1) acidification episodes climatology, (2) occurrence of ozone in Finland, and (3) transformation and deposition of gaseous and particulate pollutants over the Baltic Sea. Additionally, it includes a fourth project on the role of forest hydrocarbon emissions in ozone formation, carried out in cooperation with the University of Kuopio. The pollutants of interest here will be sulphur dioxide (SO_2), ozone (O_3), nitrogen dioxide (NO_2) and aerosol sulphate (aer$SO_4^=$), as well as the main ions in precipitation and the pH. Although initially these different projects were independently planned and had quite a different focus, we will try here to reconcile them under a common framework, aiming at a unified description of the atmospheric composition in Finland and its close surroundings.

We will concentrate on the seasonal and diurnal variability of the concentration levels and on the distinction between the different wind direction sectors. Results presented here are not exhaustive but rather will give an overall survey of air chemistry activities performed in Finland, and give a general insight into Northern European regional conditions of acidifying and photo-oxidant processes. We shall particularly concentrate on air pollution aspects that could best serve scientists from other disciplines, especially those involved in HAPRO. Additional results can be found in other reports quoted in the References, and in forthcoming papers. At the beginning of this chapter we will present, for readers not familiar with atmospheric sciences, a general review on the interactions between meteorology and air chemistry and the way they can be treated in atmospheric models. Furthermore, the meteorological variability of the parameterized processes included in these models will also be introduced.

2 Air Chemistry and Meteorology

2.1 The Unities of the Study: Space, Time and Action

As in classical drama, we must define the three unities which characterize our area of research. First of all, the spatial unity will stipulate a frame within which variability is observed. The routine measurements presented in this article are sampled at three ground stations forming a triangle of about 400 km on one side (Fig. 1). The additional marine measurements encompass an area adjacent to the previous one and extending to about 700 km. Thus, taken together, these measurements resolve features on or larger than the meso-α scale (≈200–2000 km, according to the classification of Orlanski 1975). Depending on the stability, sampled data will more or less vertically integrate the conditions prevailing in the so-called atmospheric boundary layer (ABL), extending from the surface up to several hundred metres. More specifically, the ABL height depends on the season, the type of underlying surface and the meteorological situation. The ABL can also be defined as that part of the atmosphere which contains fluid which has recently been close to the surface but has been spread upwards by turbulent diffusion (Stewart 1979). Since the basic oscillation period that is applied to the atmosphere is the inertial oscillation, and since the day itself is the period of the heating-cooling cycle at the lower boundary, the term "recently" means approximately "within 1 day". Data sampled over 24 h will thus have integrated the ABL content over a mesoscale length, and features like fronts can be statistically differentiated from the data. Further, day-by-day differences will also reflect the exchange between the ABL and the free atmosphere aloft.

Some of the reported measurements (Sect. 5) are sampled over 1 h, so that they will also resolve local phenomena on the meso-γ (≈2–20 km, such as urban effects, ground inversions or cloud and fog patterns) and meso-β scale (20–200 km; orographic effects, cloud clusters, squall lines and nocturnal low-level jets). It is also clear that due to the plethora of different phenomena modulating the concentrations, we need as many "realizations" of a given random experiment as possible, in order to obtain statistically significant results for average properties (means, medians, standard deviations etc.).

The underlying line of action in this article is the contribution of meteorological fluctuations to the observed variability of the chemical compound concentrations. In effect, each different meteorological situation will bring its own air sample, corresponding to specific chemical laboratory conditions. The wind direction will correspond to different initial reactant concentrations through emissions, the wind speed will set different mixing conditions, the temperature will modulate some reaction rates, while the vertical temperature gradient will set the stability conditions; the solar radiation will initiate photochemistry and allow the formation and/or destruction of certain radicals, while the humidity will catalyze certain reactions and link the gas phase to liquid and solid phase chemistry.

Usually, routine chemical measurements, such as those reported in this article, are carried out near the earth's surface. Ground-level observations inside the ABL represent the results of a complex mixture of local and larger-scale meteorological and chemical influences. This is illustrated in Fig. 2 with a time series of 5 days of ozone measurements at Ähtäri (Central Finland) in May 1988, which shows the modulation of chemical concentrations by the prevailing meteorology. The ozone concentration remained rather constant for the first 2 days during which the air

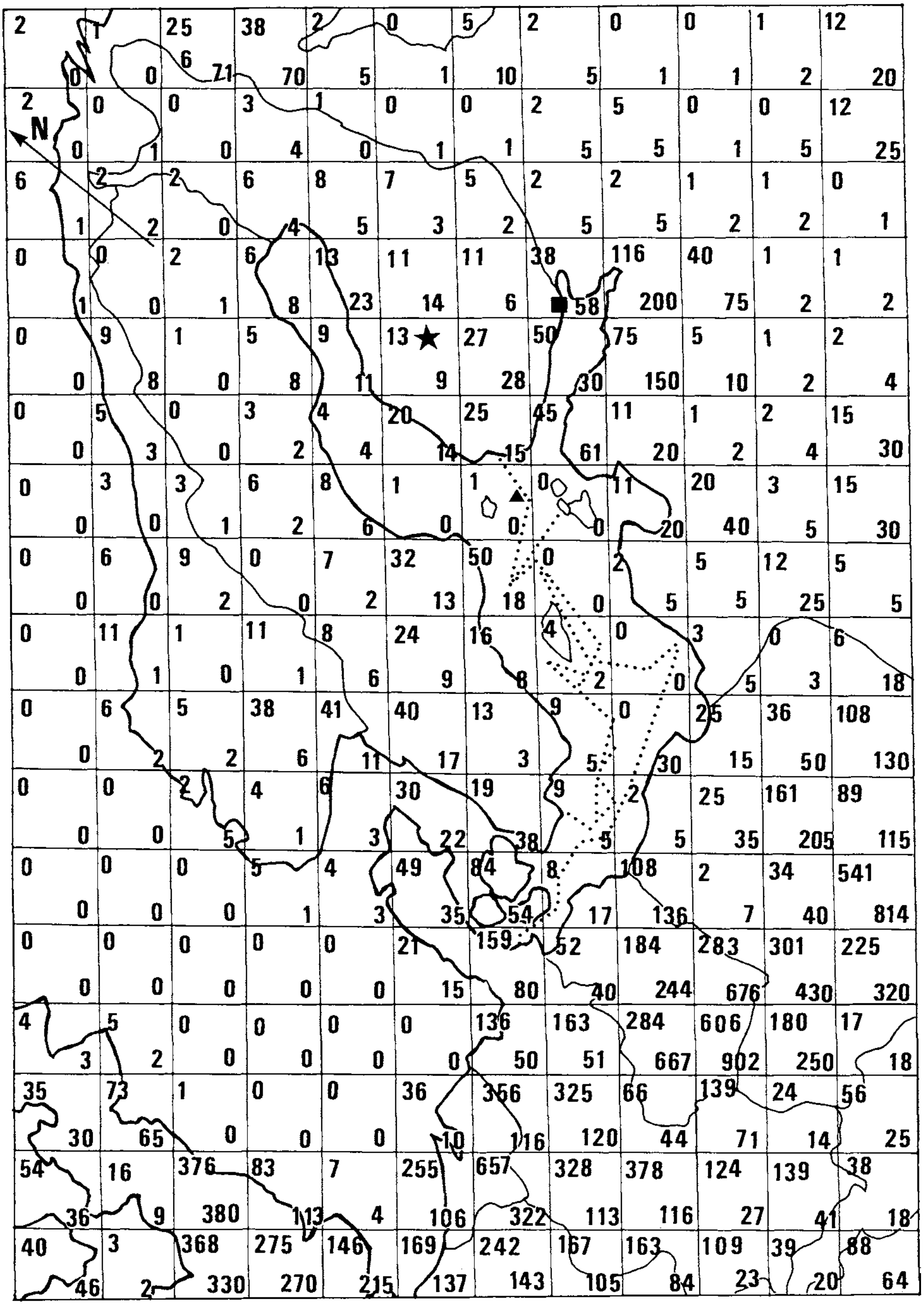

Fig. 1. Map of northern Europe with the Finnish EMEP stations Utö *triangle*; Virolahti *square*; Ähtäri *star*) overlaying the sulphur dioxide and nitrogen oxides 1985 emission grid. The *upper left value* is for NO_x (in kT of NO_2), while the *lower right value* is for SO_2 (in kT of S). Tuovinen et al. (this Vol.) present new s-emission data from the Soviet Union. The route of R/V Akademik Shuleykin in the Baltic Sea (April–June 1985) is also shown with *black dots*

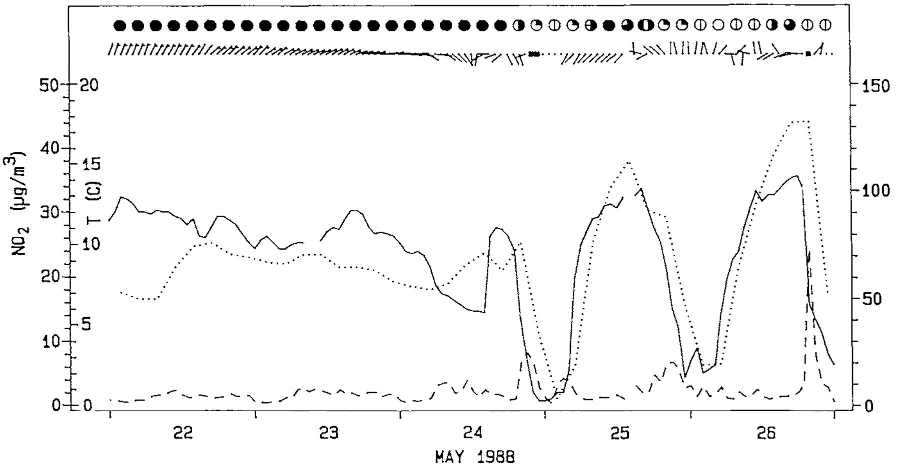

Fig. 2. A 5-day time series of ozone (*continuous line*) and nitrogen dioxide (*dashed line*) concentrations together with meteorological variables. The wind vector and the cloudiness are depicted at the *top* of the figure; the *dotted line* represents the air temperature

came from the northeast at a moderate speed (high mixing); the temperature was also rather constant due to full cloudiness. From the evening of May 23, the ozone concentration steadily decreased as the wind direction shifted to the east and the wind velocity decreased, while the temperature and the cloudiness remained about the same. As the wind turned to the south, the ozone reached a local minimum. On the evening of May 24 the ozone rose suddenly as the wind direction shifted to the southwest, although the wind speed decreased to very low values. During the subsequent night, the ozone decreased strongly to near-zero values along with a decrease in the wind and the temperature. The cloudiness had then practically disappeared, enabling the formation of a surface inversion with an uptake of ozone by vegetation and no replacement of it from aloft. The next 2 days displayed typical diurnal cycles for the ozone, the temperature and the wind speed, while the wind direction fluctuated strongly. At the same time, nitrogen dioxide started to display its own cycle, with a morning peak due to the photodissociation of nitrogen trioxide and the HONO radical together with the breakup of the nocturnal inversion. In summary, this 5 days' sequence showed that O_3 concentrations varied during the first part in response to the origin of the air masses together with weak chemical interactions, while during the second phase photochemistry modulated by local meteorology dominated.

2.2 The Basic Components of Air Chemistry

The earth's atmosphere should not be considered separately from its environment, the biosphere and the geosphere: all three form a whole with a rich chemistry and multiple interactions. Although the main concern is with the abatement of anthropogenic emissions, the occurrence of biogenic emissions should not be neglected, since natural compounds can become important reactants in the presence of increased levels of certain species. For instance, natural hydrocarbons can lead either to the production or the destruction of ozone, depending on the nitrogen oxide level (high or low, respectively). In Fig. 3 we present a schematic diagram illustrating the air chemistry of odd nitrogen, sulphur dioxide, and ammonia in the troposphere (typically, 0–10 km), and their coupling with the lower stratosphere. It can be seen that all the components are interrelated and that aerosols, mainly through heterogeneous chemistry, play an important role in the coupling between sulphur, reduced nitrogen and oxidized nitrogen compounds.

We will not dwell here on the details of the chemistry of the species of interest, but rather refer the reader to, for instance, Finlayson-Pitts and Pitts (1986), Seinfeld (1986), or Cox (1988). It should be noted that the primary products such as sulphur dioxide (SO_2), ammonia (NH_3) and nitrogen monoxide (NO) have both anthropogenic and biogenic sources. For the sulphur budget the total natural (sea spray, biogenic decay and volcanoes) and man-made emissions are about equal in the northern hemisphere (Cullis and Hirschler, 1979). However, these are not homogeneously distributed; for example, Georgii (1982) reported that 38% (probably closer to 25% at the present time) of the global anthropogenic S-emissions take place in Europe, on 2% of the global area. For NO_x ($= NO + NO_2$), the situation is more complicated, but natural sources (mainly soil releases and lightning) are about half that of man-made sources (fossil fuel burning, biomass burning). For NH_3, natural releases have been very approximately estimated to 25% of the total emission (Van Ham, 1989). On the other hand, natural emissions of non-methane hydrocarbons (mainly isoprene and terpenes) represent roughly 90% of total carbon emissions, but including the contribution of carbon monoxide (mainly anthropogenic) and methane (60% anthropogenic) changes the natural contribution to approximately 40% of the global emissions (from a compilation of various sources by Van Ham 1989). Carbon dioxide is not considered in these estimates due to its low reactivity.

We also notice from the diagram in Fig. 3 that the hydroxyl radical (OH), water vapour (H_2O), oxidants such as ozone or hydrogen peroxide (H_2O_2), as well as organic radicals, are important species with multiple contributions to the cycles of the main elements.

2.3 Requirements of Atmospheric Models

2.3.1 Models and Parameterization Schemes

It is obvious that in order to untangle, understand and especially to predict such a complex dynamical and chemical system as the atmosphere, we need numerical models. Depending on the aims and possibilities, several types of models with varying degrees of complexity and applicability are available. Models require

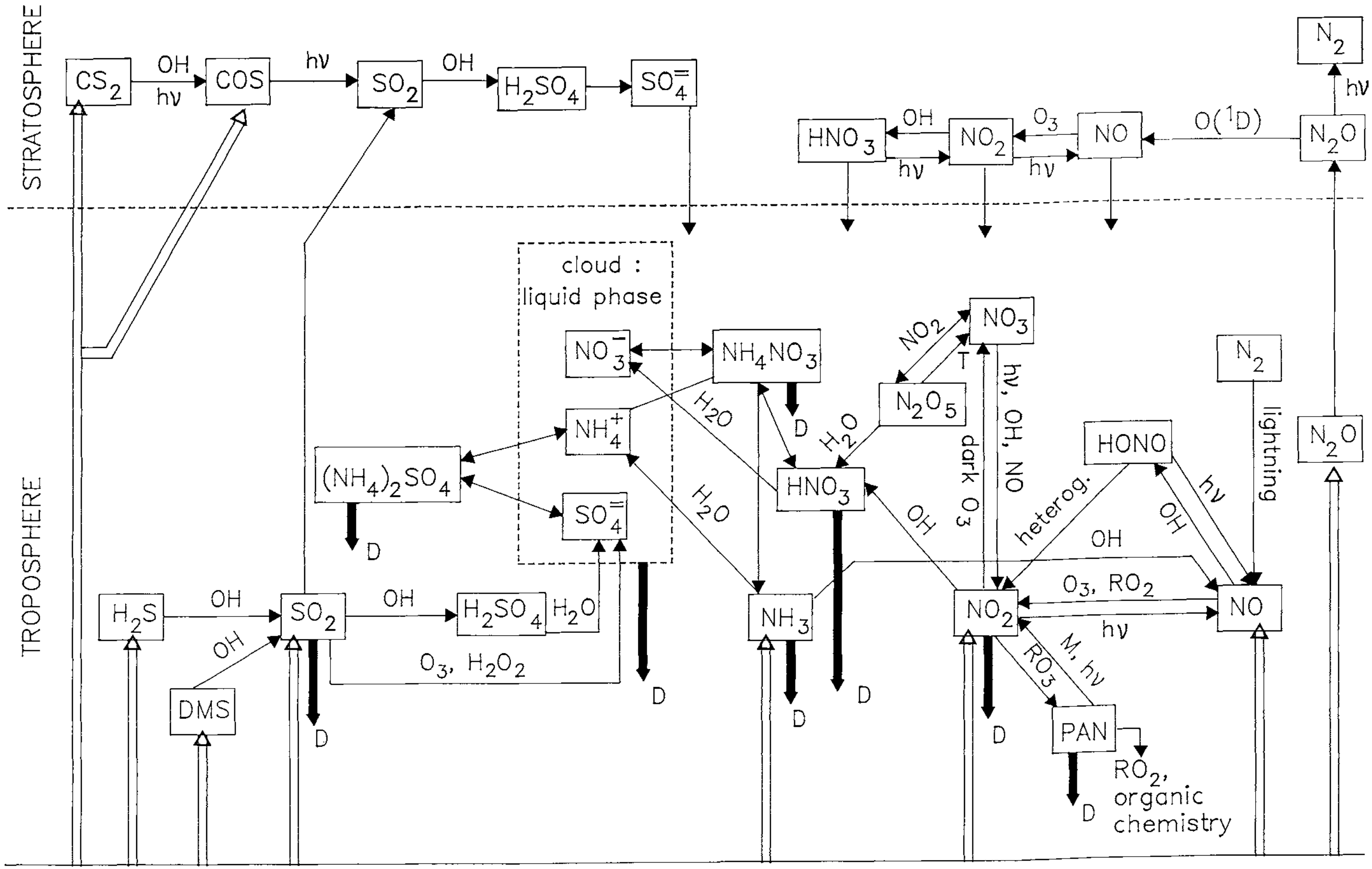

Fig. 3. Schematic diagram of air chemistry reactions for sulphur and nitrogen compounds. The *thick black arrows* with a *D* illustrate deposition routes (wet and/or dry), while the *open thick arrows* represent emissions (biogenic and/or anthropogenic)

observational data as input, as well as for their validation and for tuning parameterization schemes used to simulate the physical and chemical processes. Some specific applications of numerical models are described by Tuovinen et al. (this Vol.).

The simplest are the Lagrangian-type models, where a mixed column of air is advected along air trajectories over an emission field. Material is deposited from the air column and chemical transformations occur within it. The concentration changes are assessed by moving with an air parcel along its trajectory. One such model is the EMEP model (Eliassen and Saltbones 1983). The height of the air column generally corresponds to the ABL height h, but this is a very elusive quantity, difficult to assess from routine data or even to model. The basic evolution equation for the concentration q_i of a given compound i in this type of model can be written as:

$$\frac{Dq_i}{Dt} = (1 - \alpha_i)\frac{Q_i}{h} - \left(\frac{v_{di}}{h} + k_{ti} + k_{wi}\right) q_i, \tag{1}$$

where D/Dt is the overall time derivative, Q is the emission rate in the underlying grid, v_d is the dry deposition velocity, k_t the chemical conversion rate and k_w the wet scavenging rate (deposition by precipitation). The factor α appearing in the emission term represents the portion of the species i that is immediately deposited or directly emitted as a secondary product. The pathway of the air masses, or more specifically of the air column in question, can be computed using meteorological wind fields within the accuracy limitations of meteorological measurements and the spatial coverage of the measuring networks. Usually these air trajectories are calculated 2 to 4 days backwards from a receptor (measuring station) point, or forward from an emitter (source) point. Tracking for longer than 3 to 4 days is not practicable, as observational and smoothing errors that have accumulated all along the path yield too uncertain a trajectory. The second term of the right-hand side in Eq. (1) expresses the basic atmospheric processes (v_d, k_w, k_t and h) that will be described more accurately below. We will use this type of model later, under Variability over the Baltic Sea.

An alternative approach (the so-called Eulerian approach) is to solve the mass conservation equation on a fixed grid, i.e.

$$\frac{dq_i}{dt} + \mathbf{V}\cdot\nabla q_i = \frac{d}{dy}\left(K_y \frac{dq_i}{dz} + \frac{d}{dz}(K_z \frac{dq_i}{dz}\right) + Q - L. \tag{2}$$

In this type of model, concentration changes are studied at fixed grid points with the air masses sweeping over them. Here we need knowledge of the turbulent diffusivity coefficients K_y and K_z which scale on the ABL height h, of the parameters k_t and k_w included in the loss terms L, and of the dry deposition velocity included as the lower boundary condition. Thus, it appears that both modelling approaches require knowledge of the same parameters. Lagrangian models [as in Eq. (1)] are simpler but cannot include very many details, while the Eulerian type of models [Eq. (2)] can cope with complex types of flow and complicated parameterization schemes (non-linear chemistry, vertical gradients of properties etc.) but are more sensitive to the numerical integration scheme and to the input data. On the other hand, models do not generally take into account the complicated structure of the ABL within and above forest canopies (e.g. Hutchison and Hicks 1985).

It is important to recognize that the parameters v_d, k_w and k_t are bulk parameterization terms, simulating the overall effects of the physico-chemical processes. They do not reproduce explicitly all the mechanisms that work sequentially or in parallel, and contribute to the intricate mechanisms of dry and wet scavenging or the chemical conversion processes. Consequently, these parameterization schemes will be based on field or laboratory data relating non-measured or theoretical concepts to observable quantities. The lowest level of parameterization will be to use a constant value averaged over a broad or, better, a specific range of external conditions. Complexity will be increased by expressing them as a function of one, two or several other computable or observable quantities. The possibilities of using our data for such applications will be pointed out in this chapter.

Another use of the data is for testing model performance in a wide range of different situations or for studying the sensitivity of model results to the type or quality of observational inputs that are used.

2.3.2 Description of the Key Physico-Chemical Parameters

a) Dry Deposition

As a contaminated air mass flows over a surface, turbulent and molecular diffusion exchange gases and particles with the underlying surface. As this process goes on for a long period of time, a significant amount of material can be deposited to the surface. Dry deposition is parameterized using the deposition velocity v_d such that the flux of compound i at some reference height z_r is $F_{Di} = v_{di} \cdot q_i$ where q_i is the concentration at z_r (≈ 1 m). Sometimes it is referred to through the dry deposition rate $k_d = v_d \, h^{-1}$. One can show that v_d is the reverse of a resistance R(z) to the transfer of mass. The total resistance R can be decomposed into

$$R_i\,(z_r) = R_a + R_{mi} + R_{si} = 1/v_{di}(z_r), \tag{3}$$

where R_a is the aerodynamic resistance, R_m the molecular resistance and R_s the surface resistance to uptake. This latter is a complex function of the chemical, physical and biological properties of the surface, themselves depending on the time of year, the time of day and the state of the surface (depending on meteorological conditions, e.g. wet or dry). For perfect surface sinks (e.g. a water surface for soluble gases, SO_2 and NH_3) R_s goes to zero.

The aerodynamic resistance R_a depends on the turbulent structure of the lowest layers (a few tens of metres) of the atmosphere, which in turn depends on the wind velocity and the hydrostatic stability conditions determined by the air-surface temperature difference (e.g. Hicks et al. 1987; Businger 1986):

$$R_a = (k\ u_*)^{-1}\ [\ln(z_r/z_o) - \Psi_{qi}], \tag{4}$$

where u_* is the friction velocity, k the Karman constant (≈ 0.4), z_o the surface roughness length and Ψ_q the correction due to stability to the vertical profile of q_i.

The molecular resistance through the viscous sublayer (the lowest millimetre or so of the atmosphere close to the earth's surface) is given by

$$R_{mi} = (k\ u_*)^{-1}\ \ln(z_o/z_{oci}), \tag{5}$$

where z_{oci} is the roughness length for the species under consideration and depends on dynamical parameters like u_* and z_o, as well as on molecular properties like the viscosity and the diffusivity coefficients (e.g. Joffre 1988a).

The surface resistance for a vegetation cover depends on many factors and can be parameterized following the method of Hicks et al. (1987) shown schematically in Fig. 4. We review in Table 1 the range of typical values reported in the literature for v_d above various types of surface. It must be kept in mind that, due to the number of different physical, chemical and biological effects influencing dry deposition, the reported values are just indicators of the relative intensity of this process for the given compounds (Mac Mahon and Denison 1979; Hosker and Lindberg 1982).

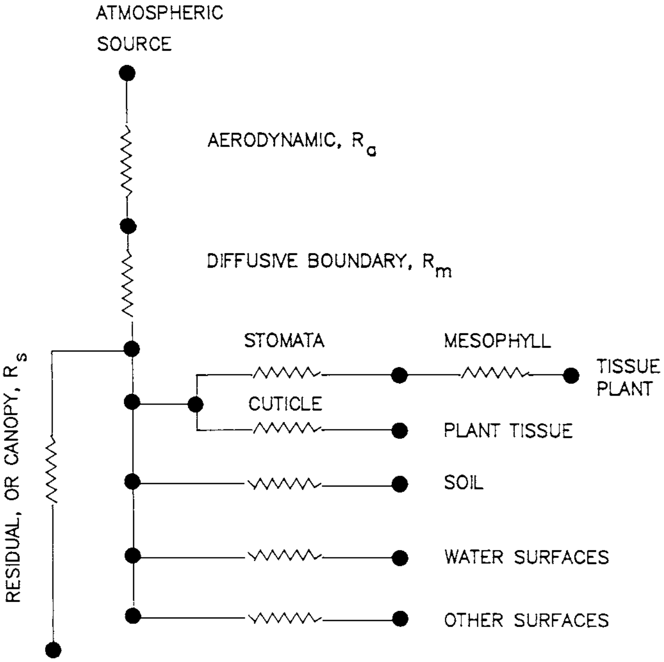

Fig. 4. Schematic illustration of a resistance model for the computation of dry deposition to vegetation. (Hicks et al 1987)

Table 1. Typical values of the dry deposition velocity (in cm s^{-1}) for different compounds and surfaces (negative velocity denotes upward emission)

	Water	Snow	Soil	Grass	Crop	Forest
Gases						
O_3 day	0.01–0.05	0.06	0.25–0.6	0.6	0.4–1.3	0.2–1
night				0.3	0.1–0.3	0.05–0.1
SO_2	0.8–1.5	0.1–0.2	0.8–1.2	0.8–1.3	0.4–1.3	0.2–1
HNO_3				1.0–4.7	5–26	3.5
NO_2				0.5	0.25	
Particles						
$D<0.06$ µm[a]	0.01–0.2		<0	0.03–0.06	0.1	>0.6
$0.06<D<2$ µm[b]	0.001–0.03			0.01		0.7
$D>2$ µm[c]	1.25–3.5			5	<1	>0.1

[a] Nuclei mode, [b] accumulation mode, [c] coarse mode, according to particle diameter D.

b) Wet Deposition

The wet scavenging rate k_{wi} for species i is generally expressed through a washout ratio W_{Ri}, which is the ratio of the concentration of material in surface-level precipitation q_{wi} to the concentration of material in surface-level air q_i, i.e.

$$k_{wi} = W_{Ri} P h_p^{-1} \tag{6}$$

Here P is the precipitation intensity (e.g. in mm h^{-1}) and h_p the depth of the homogeneous layer of precipitation, not necessarily equal to h but in practice generally taken as such. In analogy with the treatment of dry deposition, we can see that $k_w = v_w \cdot h_p^{-1}$, where v_w is a wet deposition velocity, typically 10 to 100 times larger than v_d. The scavenging rate k_w is generally assumed proportional to the square root of the rainfall rate (e.g. Smith and Hunt 1978). The wet deposition flux at the surface (in kg m^{-2} s^{-1}) is given by

$$F_{Wi} = W_{Ri} P q_i . \tag{7}$$

Note that in theory W_R, P, q_w and q depend on the vertical coordinate z if the precipitation layer is not vertically homogeneous, or if the actual vertical profiles have not been integrated over h_p. At this stage, it is important to differentiate between precipitation scavenging of particles and of gases.

Particle scavenging by precipitation can proceed in several ways. The most efficient process is when small particles act as condensation nuclei during cloud formation. Theoretically, the scavenging coefficient k_w for particles, besides being a function of the particle size, depends basically on the diameter and fall velocity of the falling droplets (themselves dependent on the type and development stage of the cloud, i.e. on its dynamics), on the collision efficiency between droplets and particles, on the collecting droplet size distribution, and on relative humidity (see Slinn 1983). A major problem is to understand how particles become associated with precipitation and this complexity is generally hidden in "quasi-constant" coefficients. The intermittency of precipitation fields is sometimes taken into account through some probability coefficient (e.g. Eliassen and Saltbones 1983; Smith 1981). In the case of gas scavenging by droplets, difficulties arise when the scavenged gas has an appreciable vapour pressure over the surface of the droplet, meaning that the composition of the droplet must be known in order to predict the net rate of transfer of material to the droplet.

The resulting washout ratios for gases of low molecular weight are substantially smaller than for aerosols (Peters 1983; Slinn et al. 1978). Consequently, it seems generally acceptable to ignore the wet removal of most reactive gases and, instead, to assume that reactive pollutant gases are converted to their products before they are scavenged. It seems that W_R is smaller for remote sites than for polluted areas (Duce 1986). Typically, W_R values expressed as mass ratios vary between a few hundreds and a few thousands for aerosols (e.g. Mac Mahon and Denison 1979; Duce 1986), being one order of magnitude smaller for low molecular weight gases.

c) The Conversion Rate

The conversion rate, k_t, between a precursor and its secondary product also depends on meteorological conditions. Transformation can proceed through gas phase reactions or through oxidation in the liquid phase (Calvert and Stockwell 1984). Photochemical processes, for instance, depend on the air temperature or solar radiation (itself depending on the season, hour, cloudiness and turbidity) and on the history of the air mass (origin and transport time). This is illustrated in Fig. 5, in which is shown the dependence of the ratio $SO_2/SO_4^=$ on the wind direction and the season at the station of Virolahti in Southern Finland. We notice that the ratio is much lower in summer, indicating both older air masses and quicker oxidation of SO_2 into sulphate. The winter curve with much higher values of the ratio displays a strong dependence on wind direction, indicating close

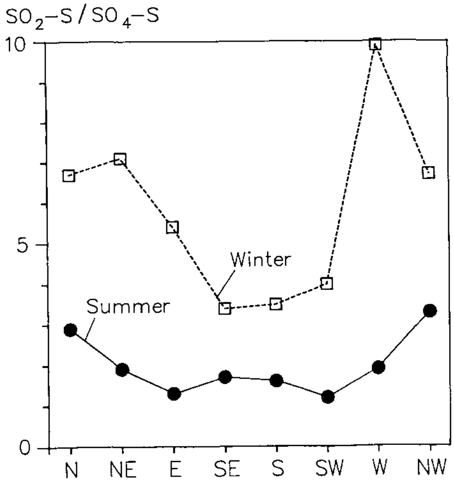

Fig. 5. Dependence of the ratio $SO_2-S/SO_4^= - S$ at Virolahti (1980–85) on wind direction for winter (*open squares*) and summer (*black dots*)

sources in the W and NW-N-NE sectors and a large contribution from long-range transport in the SE-S-SW sectors.

Heterogeneous reactions imply the absorption of gaseous species onto aerosol particles or by droplets. Furthermore, other species, like ammonia, hydrogen peroxide, ozone and water vapour, can enhance sulphur oxidation (Penkett et al. 1979). For instance, Joffre and Lindfors (1989) found from observations over the Baltic Sea that the sulphur dioxide to sulphate ratio decreases, i.e. oxidation is activated, with increasing humidity and increasing ammonia concentration.

d) The Mixing Height

The ABL height describing the vertical extent of the volume allowed for pollutant dispersion should be either determined empirically from radiosonde observations, or assessed parametrically. It varies strongly with the internal structure of the ABL (especially thermal stability) and external conditions (large-scale dynamics). Several diagnostic and prognostic relationships for h have been proposed in the literature (e.g. Stull 1988). Above the ABL is the free atmosphere or troposphere.

Hydrostatic stability is probably the primary parameter describing dispersion and the dry deposition capability of the atmosphere. It can best be estimated using an easily measurable bulk Richardson number $\mathrm{Ri_B}$ defined as

$$\mathrm{Ri_B} = (g/T_1)\ \Delta z\ \Delta T/V_2^2, \tag{8}$$

where g is the acceleration due to gravity ($= 9.81\ \mathrm{m/s^2}$), $\Delta T = T_1 - T_2$, the air temperature difference (in K) between two levels, z_1 and z_2, within the surface layer (0–20 m, $\Delta z = z_2 - z_1$) and V is the wind speed at z_2. It is recommended to have z_1 close to the surface (≈ 1 m) and z_2 between 10 and 20 m. Positive values of $\mathrm{Ri_B}$ will correspond to stable conditions (weak mixing, low ABL), negative $\mathrm{Ri_B}$-values will imply unstable thermal stability (enhanced thermal mixing, rising ABL), while $\mathrm{Ri_B} = 0$ means neutral or adiabatic conditions with wind mixing only ($\Delta T \approx 0$). The ABL height h varies typically between a few metres (surface-based inversions with no wind and large ΔT) and 500 m (high wind, small ΔT) under stable conditions (generally at night or during lightless winter). Under unstable conditions h can vary rapidly in time, rising from a few hundred meters at sunrise to 1–2 km at the end of the afternoon under sunny summer conditions (large negative ΔT values). Note also that such unstable conditions can be produced by a cold air mass advected above a much warmer surface, as in the case of polar air outbreaks over the warm Baltic Sea in autumn or early winter.

3 Measurements of Atmospheric Properties

3.1 Stations and Data

Most of the data presented in this article have been obtained from Finnish EMEP (co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe) stations run by the Finnish Meteorological

Institute (FMI). This means that the sampling and the analytical methods for pollutant measurements (gaseous, particulate and in precipitation) are standardized with other European countries (CCC 1977), and quality control is assured by intercalibration tests. The location of the three Finnish EMEP stations (Utö, Virolahti and Ähtäri) is shown in Fig. 1 together with the EMEP emission grid for sulphur dioxide (as sulphur) and nitrogen oxides (as NO_2).

These stations represent different environmental conditions. Utö (lat. 59°47′N, long. 21°23′E; elevation 6 m) is a small rocky island on the outskirts of the Finnish archipelago, Virolahti (60°31′N, 27°41′E; 8 m) is situated in a rural area near the coast in eastern Finland, and Ähtäri (62°33′N, 24°13′E; 160 m) in central forested Finland. Virolahti is only a little over 100 km northwest of the industrial area of Leningrad. Although the island of Utö is isolated, the presence of a diesel generator close to the samplers may from time to time yield higher concentrations for winds from the northern sector.

EMEP measurements were already started in 1973 but our results on SO_2, aerosol sulphate, and the main precipitation ions (sulphate, nitrate, ammonium, magnesium and strong acid) cover the period 1980–85, which is homogeneous and of higher quality for these stations. Additionally, some preliminary results on precipitation concentration of chloride and calcium, started in 1986, as well as for sodium and potassium, started in 1988, will be reported. Ozone measurements were started in 1985 on Utö and in 1986 at Ähtäri, while nitrogen dioxide measurements were started in 1986 at both stations. The reported ozone and NO_2 results extend up to December 1988.

In the last section of this article we report on some airborne pollutant measurements carried out on board a research vessel in the Baltic Sea area in April–June 1985. The route of the ship is also indicated in Fig. 1. The measurements were performed following EMEP standards and are thus comparable to other measurements. Great care was taken to prevent contamination from the ship by an automatic cut-off of the samplers when the wind direction was from the stack of the ship.

3.2 Techniques

3.2.1 Chemical Data

The sampling was performed on a daily basis for all components except ozone and nitrogen dioxide, which were sampled every minute but integrated over 1 h. Twenty-four-hour samples were collected every morning at 06.00 h UTC. The ion concentrations measured in precipitation were: sulphate, nitrate, ammonium, magnesium, strong acid and the pH, as well as more recently calcium, chloride, sodium and potassium. The buckets were changed and washed with deionized water every morning. Sulphur dioxide and aerosol sulphate concentrations were measured from air samples of 2.5 m^3 per day. The sampling and analytical methods are listed in Table 2.

The hydrogen ion concentrations of titrated strong acids are systematically higher than the free acidities calculated from the pH. The reasons for this discrepancy arise from the analytical methods (Lindberg et al. 1984), with part of the weak acids being dissociated during the free acid titration, which leads to an overestimate of both strong and free acidity in precipitation samples (Keene and Galloway 1985). In this study we will give preference to H^+ concentrations calculated from the pH. Wet deposition values are calculated as concentration multiplied by the precipitation amount at the co-located meteorological station.

The ozone measurements were carried out using an ozone monitor 1003-RS manufactured by Environment SA under DASIBI license. It is based on UV radiation absorption by ozone at 240 nm and the principle is described in Hakola et al. (1987). The raw data consist of 1 min samples which are automatically averaged into hourly outputs. The measurement accuracy is better than 5 $\mu g\,m^{-3}$. Since the presence of the diesel generator on Utö introduces some perturbations into the ozone measurements, these effects were eliminated from the data by constraining the relative standard deviation, calculated from 1-min samples within 1 h, to be below 14% . This threshold corresponded best to those situations when the generator was upwind of the sampler and when NO_2 concentrations were also very high and fluctuating.

Measurements of nitrogen dioxide were performed using an automated version of the Saltzman method, developed at the FMI. The resolution is 0.2 $\mu g\,m^{-3}$ for 1 h sampling periods. The Nordic intercalibration of NO_2-sensors did not allow firm conclusions on their accuracy due to the high NO_2 concentrations used and the wide scatter between the measuring methods.

The terpene measurements, discussed in Sect. 5.4, were obtained from samples taken in a coniferous forest at an approximate distance of 10 cm from an old spruce every third or sixth hour with Tenax-GC polymer (150 mg) as sorbent. The samples were analyzed by a thermal desorption cold trap injector (Chrompack) connected to a gas chromatograph (Hewlett Packard 5890) equipped with a mass selective detector (Konttinen et al. 1989).

The Baltic cruise of spring 1985 included additional measurements of gaseous SO_2, ammonia, nitric acid and mercury, as well as particulate sulphate, nitrate, ammonium and chloride. Concentrations of the separate components of total nitrate and ammonium were obtained by the filter pack method. One should keep in mind that this method can lead to artifacts due to volatilization or reactions from or on the filters (Ferm et al. 1988), although these are not believed to be important under conditions of low temperature and moderate humidity such as during the cruise. No rain samples were collected during the cruise due to insignificant precipitation.

Chemical analyzers or monitors are very sensitive so that they require quite regular maintainance. Furthermore, they may be susceptible to many deficiencies such as shifts or pick up of interference, so that frequent intercalibration exercises are necessary.

Table 2. Sampling and analytical methods used in chemical measurements at EMEP stations

Species	Sampling	Sampling time (h)	Analysis
Gaseous compounds			
SO_2	H_2O_2 absorption	24	Ion chromatography (automatic Thorin)
O_3	continuous: Dasibi (RS-1003)	1	UV absorption (240 nm)
NO_2	continuous	1	Automatic Saltzman
Particulate			
$SO_4^=$	Whatman 40 filter	24	X-ray fluorescence
Precipitation			
$SO_4^=$	Collected	24	Ion chromatography
NO_3^-	in open	24	Ion chromatography
NH_4^+	cylindrical	24	Indophenol colorimetric method
Mg^{2+}, Ca^{2+},	polyethylene	24	Atomic absorption spectrometry
Na^+, K^+	buckets	24	Atomic absorption spectrometry
Cl^-		24	Ion chromatography
H^+ (strong acid)		24	Gran's titration
pH (free acidity)		24	Potentiometrically from pH electrode

3.2.2 Meteorological Data

As already stated above, it is very important to relate the chemical measurements to meteorological factors, since they all describe the state of the atmosphere. Meteorological observations at the synoptic stations of Utö and Ähtäri were used to characterize the air quality data. Since standard WMO measurements are performed at 3 h intervals, these data were merged into 24-h arithmetic means representing the corresponding chemical samples. These include wind speed and direction, air temperature and humidity, and cloudiness. Weather conditions, ground state and precipitation type are also deduced from the synoptic messages. At Virolahti, meteorological measurements were performed only three times a day, so that we completed them with synoptic data from the station of Rankki, located in the coastal area 40 km west of Virolahti. Moreover, ozone measurements at Utö and Ähtäri are supported by hourly wind and global radiation measurements.

Precipitation measurements also pose problems because rain events may be very short (especially in summer), and the use of 24-h bulk samples permits partial evaporation from the samples, a possibility of contamination by other radicals or inadvertent interference (e.g. birds, insects) and a possibility for reactions between the sampled components. Bulk samples also partly include dry deposition, so that theoretical studies aiming at determining the scavenging rate will be slightly biased.

There is a rather significant discrepancy between the sampling frequency of chemical and meteorological parameters. We saw in Fig. 2 that large fluctuations from one hour to another can occur, so that 24-h meteorological or chemical averages smooth actual variability very strongly. Moreover, certain phenomena such as precipitation or mesoscale dynamical patterns generally have a short lifetime, and by using long sampling times we merge together observations that have no interrelation. These difficulties should be borne in mind when interpretating concentration or deposition data.

4 Precipitation Chemistry

4.1 General Aspects

In Finland, about two-thirds of the total deposition of sulphur and nitrogen compounds occurs through wet deposition (Tuovinen et al. this Vol.), so that precipitation is the principal vehicle of pollutant deposition to the surface. Results on sulphate include the sea salt contribution because during the period 1980–86 only magnesium was measured, which does not describe well the marine origin. On the basis of 1 year of results (1988), when the most relevant marine indicator sodium was measured, marine sulphate was 11.7% of the total sulphur deposition on Utö but only 1.8% at Virolahti and 1% at Ähtäri. This is well within the accuracy of the measurements.

The precipitation weighted average (PWA) concentration $\langle q \rangle$ of an event j is defined as

$$\langle q \rangle = \frac{\Sigma p_j q_j}{\Sigma p_j}, \qquad (9)$$

where p is the daily precipitation amount. The averages of yearly PWA values and precipitation amount at the three stations of Utö, Virolahti and Ähtäri are shown in Fig. 6, together with minimum and maximum values during the studied period. It is interesting to notice that in molar units ammonium is the main compound at Virolahti.

It appears that the interannual variability due mainly to the meteorological conditions is significant, especially on Utö, where the absolute variation range is between 50 and 60% of the mean for all compounds. Elsewhere, it is generally 30%, except for the ion H^+ at Virolahti (80%) and nitrate at Ähtäri (50%). Because 6 years is not enough to look for trends, this issue will be addressed in a later report.

However, it is misleading to consider only yearly averages. In Fig. 7 is shown the annual cycle of precipitation at the three Finnish EMEP stations. One can note the clear difference between late winter-spring and late summer-autumn with a more than doubling of precipitation amount at all stations. This will lead to large deposition values in autumn or in summer (Ähtäri), although airborne pollutant concentrations are then generally lower. Moreover, the capacity of the water- and ecosystems to absorb air and precipitation pollutants depends strongly on their

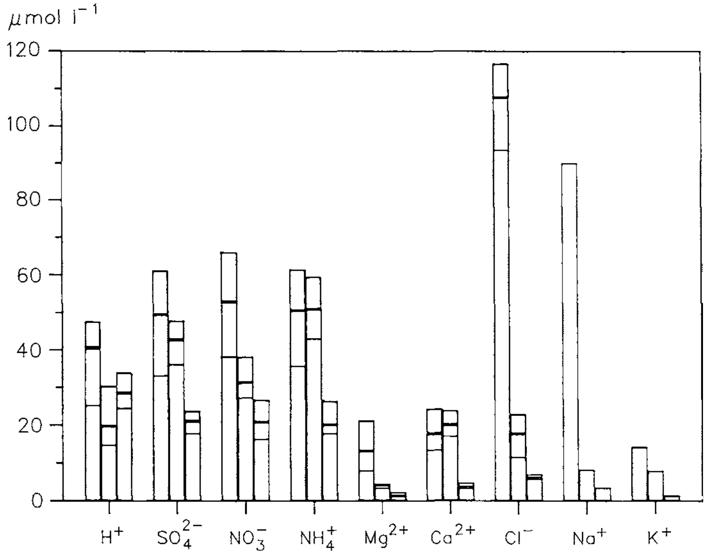

Fig. 6. Maximum, mean (*thick line*) and minimum yearly PWA concentrations (in μmol l^{-1}) at the three Finnish EMEP stations. The *three columns from left to right* depict for each ion the situation at Utö, Virolahti and Ähtäri, respectively

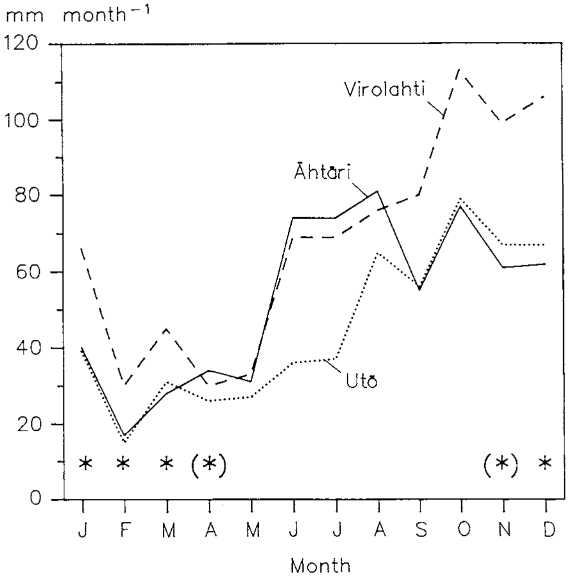

Fig. 7. Annual cycle of the montly precipitation sums at Utö (*dotted line*), Virolahti (*dashed line*), and Ähtäri (*continuous line*). The *stars* indicate the months when precipitation is on average in the form of snow.

seasonal cycle, so that it is the particular seasonal input at a particular stage of the water- or ecosystem's life which is the relevant factor to include in environmental studies.

4.2 Seasonal Variability

4.2.1 Concentrations

The distribution of PWA ion concentrations according to season are shown in Fig. 8 (a: Utö, b: Virolahti, and c: Ähtäri, respectively). Seasons are defined as: winter (December + January + February), spring (March–May), summer (June–August) and autumn (September–November). It can be seen that sulphate has the same seasonal trend at the three stations, with a clear maximum in spring, but very similar PWA-values during the other seasons. The annual amplitude is clearly smaller at the maritime site of Utö. Nitrate is less regular spatially with a maximum in winter for the Utö site, a spring maximum at Virolahti and a broad maximum in winter-spring at Ähtäri. At all sites the minimum occurs in summer.

Of the cations, ammonium is the main acid-neutralizing ion, having PWA-concentrations very similar to sulphate. Ammonium is closely associated with sulphate during all seasons but additionally with nitrate in winter. The yearly sulphate to ammonium molar ratio is around 1, except at Virolahti, where ammonium is more abundant ($SO_4^=/NH_4^+ \approx 0.83$). The sulphate/ammonium ratio

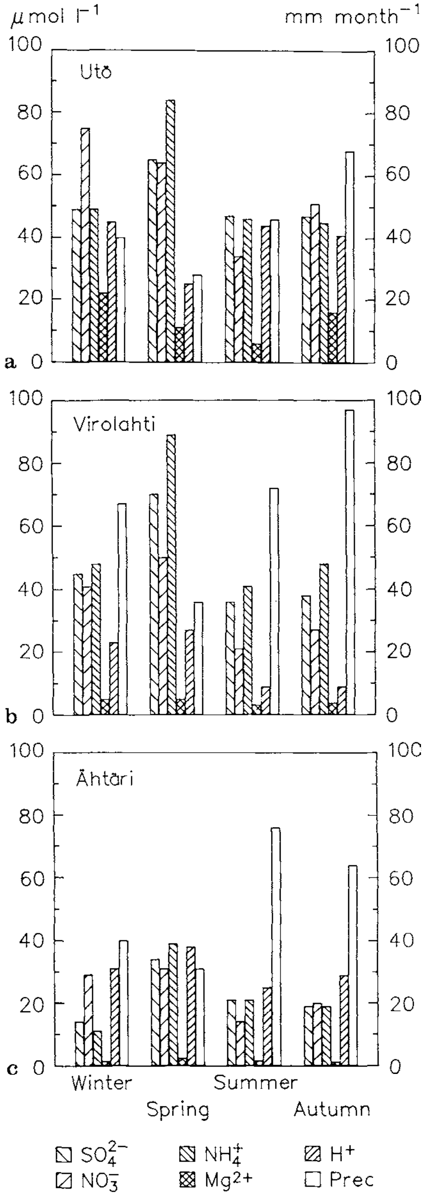

Fig. 8a–c. Precipitation-weighted average concentrations of sulphate, nitrate, ammonium, magnesium and H^+ ions according to season at the three Finnish EMEP stations of Utö (**a**), Virolahti (**b**), and Ähtäri (**c**) for the period 1980–85. The precipitation amount for the same period is also shown

does not vary much with season and has, as does sulphur, a clear maximum in spring at all stations. H^+ concentrations (from the pH) have a weak annual amplitude (20%) with a maximum in spring, except on Utö, where it is in winter. The high H^+ levels relative to the other ions at Ähtäri is noteworthy; H^+ is mainly associated with nitrate in all seasons and also with sulphate in spring and autumn.

In Fig. 9 are presented the PWA concentrations of Mg^{2+}, Cl^-, and Ca^{2+} during the period 1986–1988 as well Na^+ and K^+ for the year 1988. Chloride and sodium have a maximum during the stormy seasons of autumn and winter at all stations, (surprisingly it is not insignificant at the continental site of Ähtäri), but the relative concentrations are clearly the highest on Utö due to the mainly marine origin of these species. Potassium has a minimum in summer at all stations, while

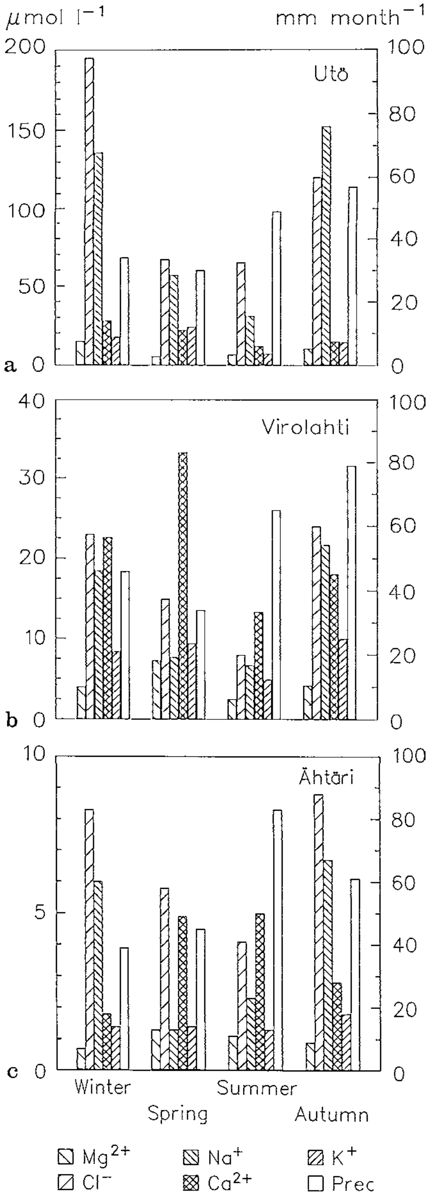

Fig. 9a–c. Precipitation-weighted average concentrations of magnesium, chloride and calcium for the period 1986–88 and of sodium and potassium for 1988 at the three Finnish EMEP stations. The precipitation amount for the period 1986–88 is also shown

the maximum occurs in autumn at Virolahti and Ähtäri but in spring on Utö. Calcium is not negligible and is often at the same level as nitrate except in winter, but has a very different behaviour at all three stations. The annual cycle is only clear at Virolahti and Ähtäri with a maximum in spring at Virolahti and in spring-summer at Ähtäri.

These three stations cannot represent the situation over the whole of Finland, and the differences between these stations already noted should restrain us from extrapolating these results to the whole country without caution. It is clear that more stations are needed for this. However, as discussed in Sect. 2.1, these stations have a mesoscale representativity, so that results can be representative of a domain of about 100 km radius around the stations. Nevertheless, geographical gradients can be discerned: there is a decreasing north-south gradient for PWA-concentrations in sulphate, nitrate and ammonium ions. This is in line with the increasing distance from the principal domestic and foreign sources. For the strong acid ion H^+, this is only partly true because although PWA concentrations are much higher on Utö, they are about the same at Virolahti and Ähtäri, probably due to the neutralizing effect of the large amount of ammonium and calcium at Virolahti. Additionally, we can notice a decreasing west-east gradient for nitrate and maybe also H^+. This is probably a consequence of the preponderance of nitrate in the anthropogenic sources of West European countries.

4.2.2 Ion Ratios

The higher likelihood of nitrate in air masses from western Europe can also be characterized by the PWA-concentration molar ratio of sulphate to nitrate, which is the lowest on Utö (0.94) and at Ähtäri (1.0) and much higher at Virolahti (1.3). This ratio is at its maximum in summer at all three stations, but with less interstation variation, and at its minimum in winter with large differences between the stations, Ähtäri having the lowest value (≈ 0.5). It should be also noted that for a given time period the ratio SO_4/NO_3 is always smaller in the case of snow than in that of rain, probably due to the preferential uptake of SO_2 by water droplets and the lack of dependence upon water form in the uptake of nitrate (Laurila and Joffre 1987).

The ratio of acidifying anions ($NO_3^- + SO_4^=$) to the main cation NH_4^+ illustrates the potential for neutralization (i.e. ratio = 1 in equivalents), assuming that other ions (Ca^{2+}, Mg^{2+}, etc.) have a smaller effect or compensate each other (Cl^- and Na^+). This ratio is at its minimum (i.e. closest to unity) in spring at all stations due mainly to agricultural activities after the snowmelt (e.g. Asman and Janssen 1987). The lowest values are, expectedly, found at Virolahti, although the difference between the stations is small (20%). The ratio is at its maximum in winter at all stations, being lowest at Virolahti (2.7 in equivalent) but very high at Ähtäri (5.2). This latter figure indicates a strong potential for acidification in forested Finland in wintertime, partly due to a lesser availability of neutralizing materials. This is confirmed by the fact that $[H^+]$ represents only 15–35% in equivalents of the sum $[SO_4^=] + [NO_3^-]$ at Virolahti and Utö (a minimum in spring, and at approximately the same level during the rest of the year, except for a slight maximum in summer), but rises to 40–50% at Ähtäri (maximum in winter, minimum in spring). At Ähtäri, furthermore, acidity is on the whole better related to nitrate (correlation coefficient $r \approx 0.6$) than to sulphate ($r \approx 0.45$), while at Virolahti there is no significant correlation (these correlations rest on about 850 events). However, if we consider low pH situations ($pH < 4.75$) only, both correlation coefficients increase at Ähtäri but the difference is reduced ($r = 0.78$ for nitrate, 0.72 for sulphate, with $n \approx 650$), while at Virolahti both anions also become significantly correlated with acidity ($r = 0.6$ for nitrate and 0.5 for sulphate; $n \approx 420$). Additionally, the high positive correlation between ammonium and H^+ ($r = 0.59$ and 0.45 at Ähtäri and Virolahti, respectively) indicates that a great deal of sulphate and nitrate is incorporated in salts like ammonium sulphate (Laurila and Joffre 1988).

We can study the efficiency for wet scavenging through the washout ratio W_R, which is the ratio of sulphate in precipitation to its concentration in air. If we again consider separately the cases with the air temperature lower than $-5°C$ (snow cases) or higher than $+5°C$ (rainwater) we find that on Utö W_R nearly doubles from 1050 to 1900 from the snow case to the rain case, and triples at the other two stations (from 550 to 1400 at Virolahti and from 400 to 1200 at Ähtäri). This shows that in-cloud SO_2 scavenging is at its most efficient in rain. The difference between stations might stem from a different contribution of particulate sulphate and SO_2, and also from local climatology characterized by different types of cloud. Aerosol nitrate concentrations were also measured during a short period in 1986 on Utö. The washout ratio for total nitrate ($NO_3^- + HNO_3$) was roughly the same (≈ 1700) for the two groups $T > +5°C$ and $T < 0°C$, indicating the indifference of nitrate wet scavenging to the phase of water.

4.3 Dependence on Air Mass Origin

Medians of concentration in precipitation according to the four main surface wind directions and seasons are presented in Fig. 10 for the three stations separately. Background support for the interpretation of this section's results can be found in the Appendix, in which wind direction statistics for the Finnish stations are presented. These statistics are based on surface observations, so that due to the clockwise veering of the wind vector with increasing altitude through the ABL, the wind direction of the upper winds (at about 1 km height) should be turned clockwise by about $+30°$.

Although the wind directions have been grouped into broad sectors in order to smooth out uncertainties connected with this coarse indicator of air mass origin, the different panels of Fig. 10 present some interesting variability. One notes that the wind direction dependence is especially marked at Virolahti for sulphate, ammonium and calcium, with maximum concentrations in the south sector, except in spring for sulphate with a maximum in the east sector. The fact that chloride

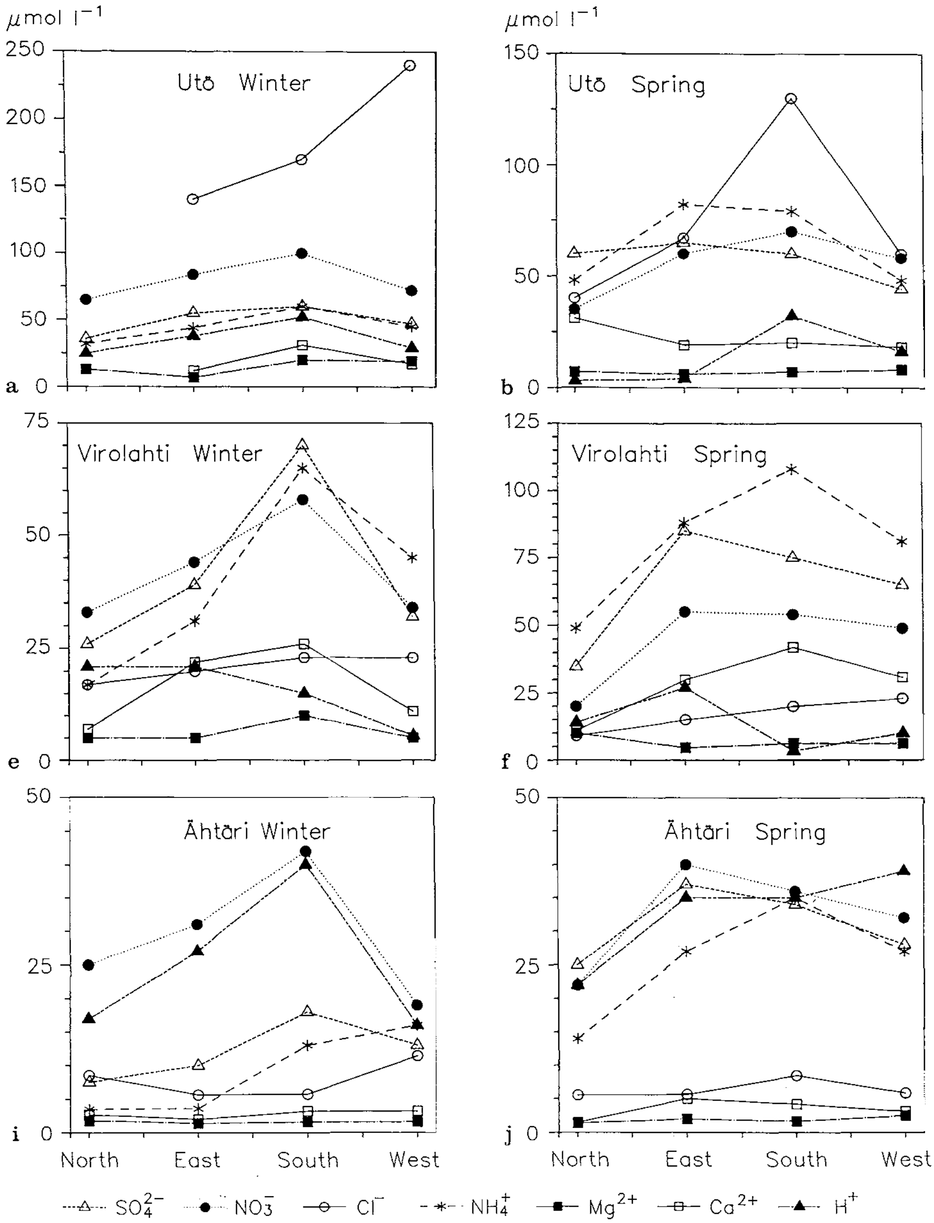

Fig. 10a–j. Dependence of ion concentration (in µmol l⁻¹) medians in precipitation on wind direction and season at the three Finnish EMEP stations (1980–85). Note the different scales

does not depend on the wind direction at this coastal site in winter would indicate the presence of anthropogenic hydrochloric acid. For the other components the amplitude of the wind direction variation is not so strong. On Utö, only chloride has a marked wind direction dependence which, moreover, depends on the season.

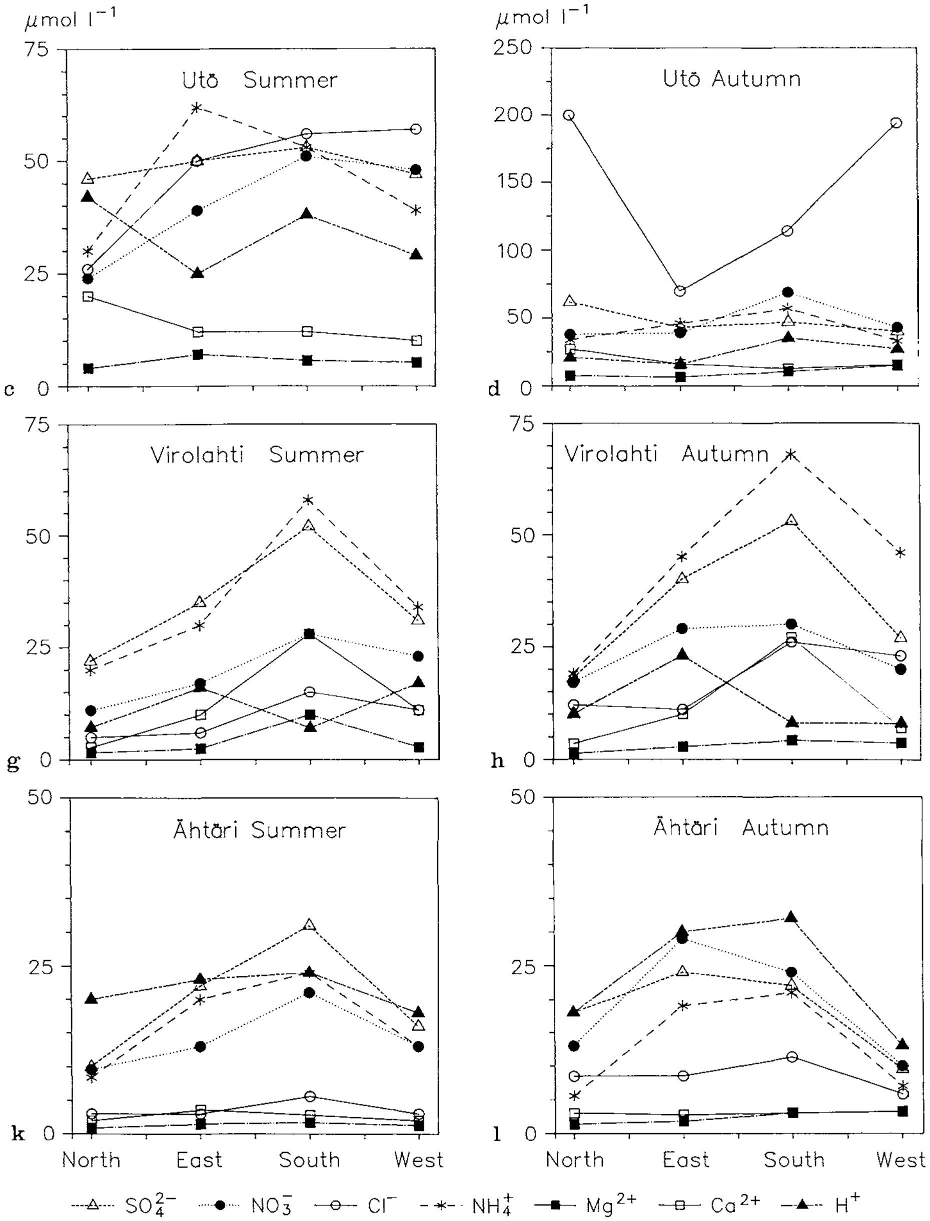

Fig. 10. (*Continued*)

4.4 Acid Deposition in Finland

The combination of precipitation (Fig. 7) and concentrations (Fig. 8) yields the wet deposition or airborne pollutants. The averaged total yearly wet deposition values for the different ions at the three Finnish EMEP stations are displayed in

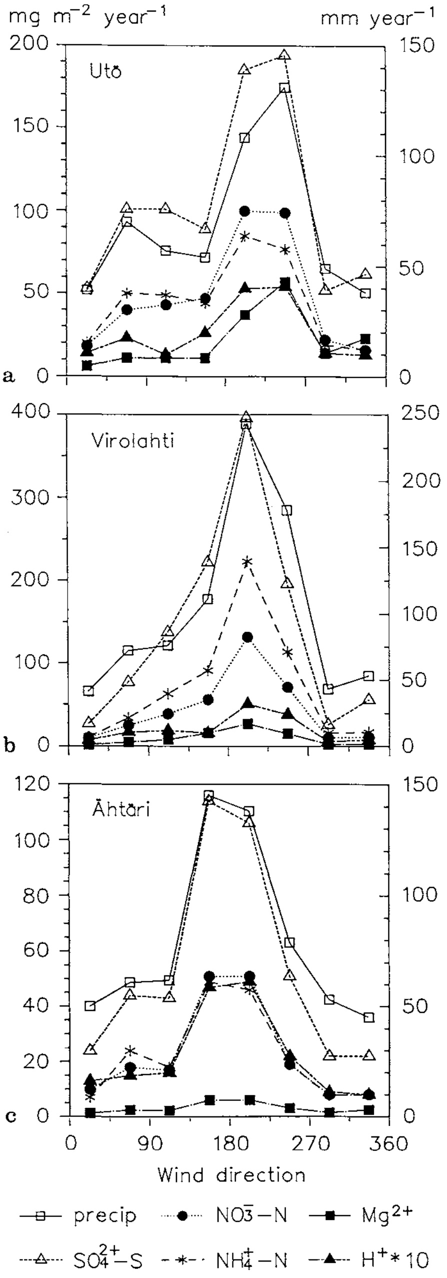

Fig. 11a–c. Dependence of annual deposition (in mg m^{-2} yr^{-1}) and precipitation amount (in mm yr^{-1}) on wind direction at the three Finnish EMEP stations (1980–85) for sulphate, nitrate, ammonium, magnesium and H$^+$ (× 10)

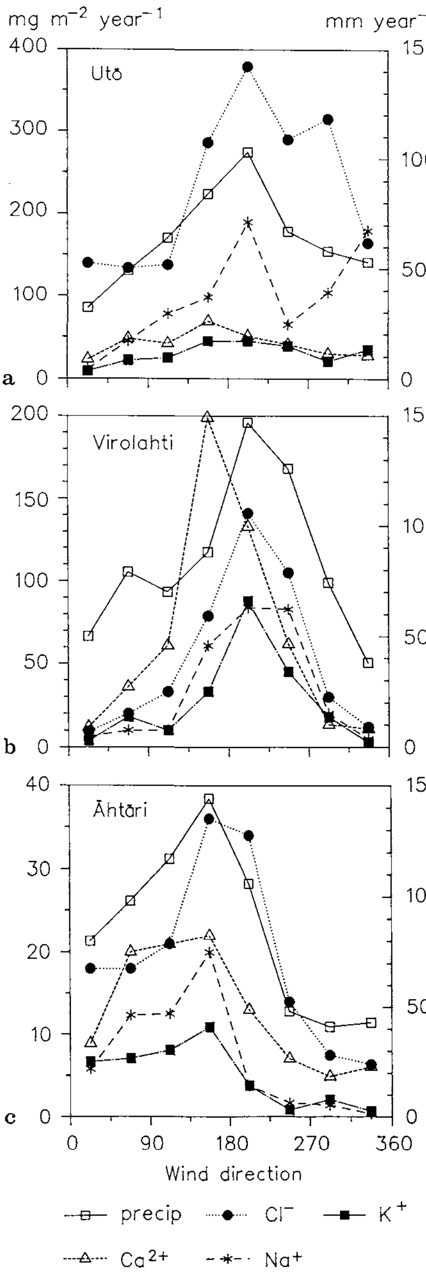

Fig. 12a–c. Same as Fig. 11 but for chloride, calcium and the precipitation amount (for the period 1986–88) and for sodium and potassium (1988)

Table 3. Mean yearly wet deposition with minimum and maximum values in parentheses (in mmol m^{-2} yr^{-1}) at the three Finnish EMEP stations during different periods, together with precipitation amount (in mm) during the same periods

	Period	Utö	Virolahti	Ähtäri
$SO_4^{=}$	1980–85	26.8 (20.7–40.8)	35.0 (26.1–40.8)	13.3 (10.4–14.6)
NO_3^-	1980–85	28.6 (22.1–40.1)	25.7 (21.1–31.1)	13.1 (9.2–16.1)
NH_4^+	1980–85	27.1 (21.0–37.0)	41.4 (35.1–54.4)	12.9 (10.0–15.9)
Mg^{2+}	1980–85	7.3 (3.6–14.1)	3.3 (2.9–3.7)	1.0 (0.6–1.3)
H^+	1980–85	22.0 (15.8–31.8)	20.1 (12.1–24.7)	18.2 (14.0–21.2)
Precip.	1980–85	545 (422–668)	815 (642–961)	633 (546–804)
Ca^{2+}	1986–88	8.8 (7.1–11.3)	13.4 (10.9–15.8)	2.6 (2.2–3.2)
Cl^-	1986–88	55.3 (44.6–68.8)	12.1 (7.4–15.2)	4.4 (4.3–4.5)
Precip.	1986–88	510 (463–590)	672 (632–723)	680 (631–733)
Na^{2+}	1988	41.7	10.1	2.5
K^+	1988	6.6	5.8	1.0
Precip.	1988	463	723	733

Table 3. The significance of these values with regards to acidification potential will be discussed in the next section (Sect. 4.5).

In Fig. 11 are shown the annual deposition (in mg m^{-2}) and precipitation amount (in mm) at the three Finnish EMEP stations according to wind direction for the period 1980–85. A noticeable feature is the strong maximum at all stations in wet deposition for air masses coming from the south-southwest sectors, as implied by the precipitation and concentration distributions.

At Ähtäri, the maximum sulphate deposition occurs in summer together with the precipitation maximum. At Utö and Virolahti both maxima occur in autumn. This may be explained by the relatively long and cold winter in Ähtäri, combined with the poor scavenging of sulphur dioxide by snow. At the southern stations, deposition is also significant in winter due to the emission maximum and also because precipitation occurs more frequently as rain. Winds are more frequently from the southern and western sectors in wintertime, while the eastern sector is especially reinforced in spring (see Appendix).

The nitrate deposition maximum is in winter (NO_x emission maximum), or in autumn if precipitation then is much higher than in winter. Ammonium deposition is high both in autumn and in spring. There is a summer maximum at Ähtäri due to the rainier summer season. The annual cycle of ammonium deposition exhibits a clear spring maximum and, due to the cold winters, a large annual amplitude. At the coastal stations magnesium deposition has a maximum during the stormy autumn and winter seasons, whereas the lower overall deposition level and the summer maximum at Ähtäri suggest an aeolian origin.

Hydrogen ion deposition most closely follows the precipitation amounts, with a spring minimum and a summer maximum at Ähtäri and an autumn maximum at

Utö and Virolahti. This means rather constant average concentrations throughout the year.

Complementary information on the wet deposition of other ions is presented in Fig. 12 for Utö, Virolahti and Ähtäri. Results for precipitation, Ca^{2+} and Cl^- are from the 3-year period 1986–88, while deposition of Na^{2+} and K^+ is based on the year 1988. We notice that due to their different origins (sea spray and crustal particles), leading to different incorporation into air masses, these species do not always follow the same behaviour as the typical anthropogenic compounds. An exception is calcium at Virolahti which closely follows sulphate and ammonium.

4.5 Critical Loadings and Acidification Potential

The concept of critical load has been introduced as "the highest load that will not cause chemical changes leading to long-term harmful effects on the most sensitive ecological systems". Critical load values for various ecosystems were reviewed in a recent expert workshop (Nilsson and Grennfelt 1988). For instance, critical loads for forest soils of the most sensitive classes 1 and 2 (quartz, granite and gneiss) between 20 and 50 mmol m^{-2} have been proposed, if all acidity comes from an equivalent sulphur deposition between 0.3 and 0.8 $g\,m^{-2}$. For aquatic ecosystems values of 15–40 mmol m^{-2} for sulphur have been proposed for Scandinavia. We thus notice that the mean annual deposition amount reported in Finland (Table 3) fluctuates around these critical load values.

Critical loads for nitrogen deposition are much more uncertain. However, according to the same meeting's recommendations, values between 21 and 36 mmol m^{-2} were proposed for sensitive raised bogs and dwarf shrub vegetation, and between 21 and 107 mmol m^{-2} for coniferous forests. Adding together the contributions to deposition from nitrate and ammonium listed in Table 3 leads to nitrogen loading well above the lowest critical value.

Several definitions have been proposed for defining the acidifying potential of atmospheric deposition for soil or lake surfaces: the pH (or $[H^+]$), $SO_4^=$, $AD = [H^+] + [NH_4^+] - [NO_3^-]$, and $AP = [SO_4^=] - [Ca^{2+} + Mg^{2+}]$. The acid deposition concept AD was introduced by Dillon (1983) to account for the production of H^+ in watersheds and lakes due to the biological uptake of ammonium and for alkalinity generation by the biological uptake of nitrate, assuming that all nitrate is taken up by the system. The acidifying potential AP introduced by Brydges and Summers (1989) takes into account that some of the sulphate in precipitation may be in the form of neutral salts such as calcium and magnesium sulphate, so that AP is the residual H^+. In their paper, Brydges and Summers argued why the acidifying potential of wet deposition should be as defined by AP, unless N leaches from the watershed in the form of nitrate, even though the pH may be increased by ammonia emission or lowered by NO_x emissions.

On the basis of deposition data at the three Finnish EMEP stations from the period of 1986–88, when all ion measurements were available, we tested the

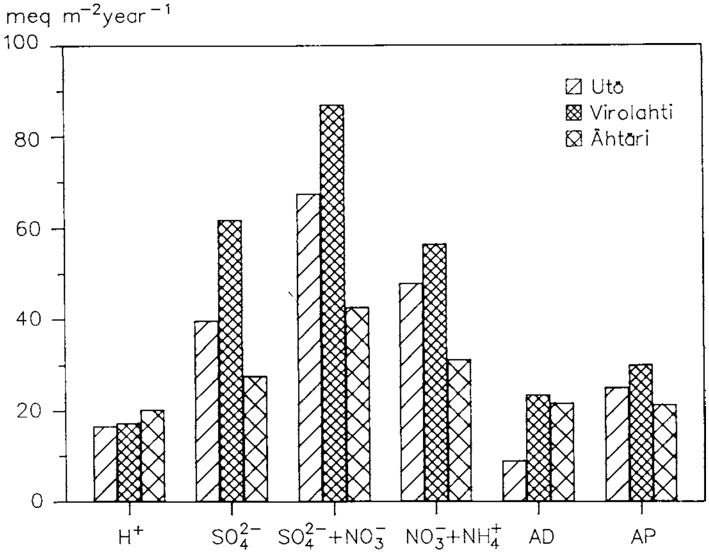

Fig. 13. Mean acid deposition at the three Finnish EMEP stations for the period 1986–88, as computed according to different definitions (see text)

differences introduced by these different definitions (Fig. 13). We note that H^+, AD and AP lead to very similar results, especially at Ähtäri, having around 20 mEq m^{-2} annually.

4.6 Acid Rain Episodes

Because of the strong link between deposition and precipitation amounts, it is relevant to study the correspondence between the cumulative percentage of deposition and the cumulative percentage of wet days, i.e. episodicity. For Ähtäri, 30% of the precipitation amount is reached on average after 12 of the largest precipitation days. Sulphate and ammonium are more episodic with 30% of the annual deposition reached after 9 and 6 days with the largest deposition, respectively, whereas nitrate and H^+ are less episodic, this 30%-amount being attained only after 12 days of the largest deposition.

Investigations on acidification effects may require not only a knowledge of mean concentration levels or the average deposition over a month or a year, but also a knowledge of how these levels are concentrated into episodes characterized by high concentrations above a certain critical value. Table 4 displays the annual distribution of days having deposition values in excess of 500 μEq m^{-2} d^{-1} for sulphate, nitrate, ammonium and H^+. This corresponds to 8 mg m^{-2} d^{-1} for sulphate as sulphur, and to 7 mg m^{-2} d^{-1} for nitrate and ammonium as nitrogen, respectively. Some events are lost if the sampling bucket is changed during the event (at 08.00 h.). The central part of the country receives far fewer episodes than the southernmost parts of Finland. At Ähtäri sulphate episodes occur mainly in summer, while at Utö and Virolahti they are observed during all seasons. Nitrate

Table 4. The number of days (from 08.00 h to 08.00 h) during the period 1980–1985 when deposition exceeded the given limit value of 500 μeq m^{-2} day^{-1}. Monthly and total numbers are given

Months	J	F	M	A	M	J	J	A	S	O	N	D	Total
$SO_4^=$–S > 500 μeq m^{-2} d^{-1}													
Utö	12	5	13	15	12	16	14	18	17	24	24	20	190
Virol.	24	10	23	14	21	21	20	20	18	38	41	31	281
Ähtäri		1	1	7	11	11	11	8	9	4	2	1	66
NO_3^-–N > 500 μeq m^{-2} d^{-1}													
Utö	7	3	7	1	2	2		8	7	5	11	16	69
Virol.	7	3	5	1			1	1	2	5	10	12	47
Ähtäri		1		1				2					4
NH_4^+–N > 500 μeq m^{-2} d^{-1}													
Utö	1		7	7	8	3	2	10	10	5	9	5	67
Virol.	8	3	13	8	14	11	11	14	8	22	26	19	157
Ähtäri				3	3	2	4	4	3				19
Titrated H^+ > 500 μeq m^{-2} d^{-1}													
Utö	4	3	6	3	1	10	8	11	11	10	15	16	98
Virol.	2	3	9	5	2	6	6	2	6	9	8	7	65
Ähtäri	1		2	2	3	10	1	8	7	3	5	4	46

episodes occurs both in winter and in autumn. Heavy deposition of ammonium takes place both in spring and in autumn. At Ähtäri acid deposition episodes occur in summertime and in autumn, while at the other stations they are more evenly distributed over the year.

The subgroup of acid precipitation cases, having a daily deposition of strong acid exceeding 500 μEq m^{-2} d^{-1}, had on average a precipitation amount of 11, 14.8 and 12 mm and a pH of 4.2, 4.4 and 4.3, at Utö, Virolahti and Ähtäri, respectively. This can be compared to a mean precipitation of 4, 4.7 and 4 mm with a pH of 4.5, 4.7 and 4.8 for all wet days.

The acid rain episodes were generally preceded by an extensive high pressure area over Russia. Pollutants from heavily industrialized European regions accumulated in a slow southerly flow on the western side of the stagnant high pressure area and were thus transported to northern Europe. Four types of precipitation systems caused the wet deposition episodes at Ähtäri (Laurila and Joffre 1989):

A) a low with a warm sector from the southeast;
B) disturbances coming from the southwest which were associated with a central low located to the west of Finland;
C) a cold front from the northwest causing precipitation through air that had lain over Scandinavia; and
D) two exceptional summer cases occurring when a central low was over Finland.

Class (B) cases were the most frequent (n = 29 episodes), and occurred throughout the year. They were characterized by southwesterly transport at 850 mb, indicated by southerlies at the surface. They had the lowest sulphate to nitrate molar ratio (median of 1.5) suggesting that the source area was western Europe with its high nitrogen oxide emissions. Very generally, the SO_2/NO_2 emission ratio ranges from 0.5 to 2 western Europe while it is typically over 3 in eastern Europe. Class (A) systems were of smaller dimensions, and occurred in summer (n = 5) and in autumn (n = 4). They came from the southeast and had a higher contribution of sulphate (sulphate to nitrate molar ratio ≈ 2) in accordance with high sulphur emissions in eastern Europe. Pollutants were rained out during the few (n = 4) cold frontal cases (C) occurring in summer and in autumn, and arriving from the northwest. The corresponding air masses had stayed over northern Europe, and had a relatively high sulphate concentration (sulphate to nitrate molar ratio ≈ 1.8).

5 Gaseous Compounds and Aerosols

5.1 Seasonal and Diurnal Variability

5.1.1 Comparative Behaviour

Although studies of sulphur compounds, such as sulphur dioxide and sulphate aerosol, are generally not connected with photochemical studies involving ozone and its related compounds, we present them here in a joint section for three reasons. First of all, both chemical families contribute to the composition of the atmosphere through their important coupling to aerosol formation, implying solar and atmospheric radiation modulation effects. Secondly, there is a direct linkage through homogeneous oxidation of SO_2 by the hydroxyl radical OH which is controlled by ozone (Calvert and Stockwell 1984), and finally heterogeneous oxidation of SO_2 by ozone proceeds with a strong dependence on the pH in the droplets.

In Fig. 14 is presented the annual cycle of sulphur dioxide and aerosol sulphate at Virolahti and Ähtäri. Utö data are not shown due to uncertainties in SO_2 values by local contamination. Sulphur dioxide has a clear February maximum, eight times higher than the summer minimum. The actual difference might be even larger if the detection limit of SO_2 measurements had been better. Almost all physical and chemical factors contribute to this difference: maximum emissions in winter, lower dilution, slower transformation, deposition and scavenging. Aerosol sulphate has a weaker maximum but it is delayed by 1 month from the SO_2 maximum. This may be due to the large reservoir of SO_2 accumulated during the winter ($[SO_2]/[SO_4^=] \approx 4$) which is not supplied so intensely as spring comes, while continuous sulphate formation is enhanced through oxidation (temperature-dependent) and indirectly through increased photochemical activity (ozone increases).

In Fig. 15 is shown the annual cycle of ozone, nitrogen dioxide and global radiation at Utö and Ähtäri. The striking feature is that, although ozone is a photochemical species, it is not in phase with the solar radiation curve's summer peak, especially at Ähtäri, where ozone has a marked peak in early spring (April) and decreases steadily until autumn. On Utö the maximum is more widely

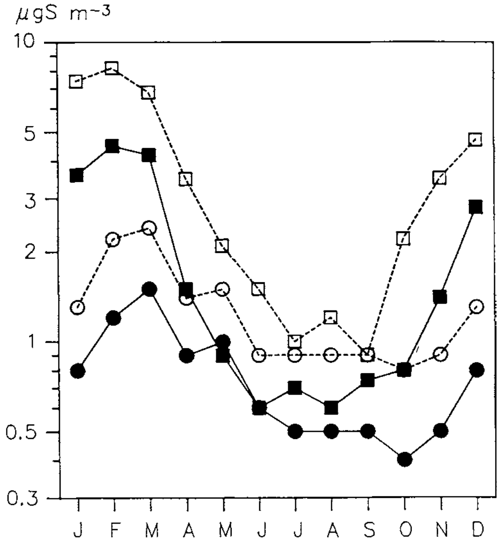

Fig. 14. Annual cycle of sulphur dioxide (*squares*) and aerosol sulphate (*circles*) monthly medians at Virolahti (*open symbols*) and Ähtäri (*full symbols*) for the period 1980–85

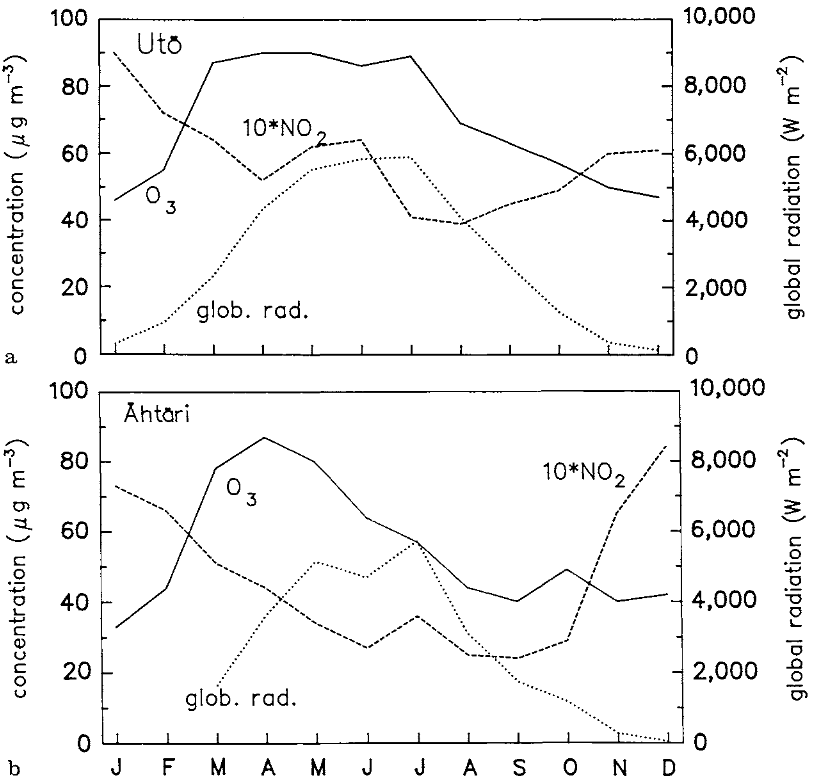

Fig. 15a,b. Monthly means of ozone (*continuous line*; 1986–88) and nitrogen dioxide (*dashed line*; 1987–88) at **a** Utö, and **b** Ähtäri. The annual course of global radiation (*dotted line*) at these stations is also shown

distributed with perhaps a bimodal structure (April and July), the later one corresponding to the radiation maximum. On the other hand, the ozone maximum corresponds to the spring precipitation minimum at both Utö and Ähtäri, when the uptake of precursor gases by cloudwater is less and photochemistry more active. Nitrogen dioxide has a very similar annual cycle at both stations, the minimum occurring in autumn and the maximum in winter.

5.1.2 Sulphur Dioxide and Aerosol Sulphate

The high concentrations of sulphur dioxide at Ähtäri in winter (Fig. 14) are partly due to its low uptake in clouds by snow (see above) whereas sulphate scavenging is not subject to this limitation (Barrie 1985). Additionally, SO_2 has a low deposition velocity to snow while sulphate particle deposition is not greatly affected by the type of surface. This has been confirmed by considering the dependence of SO_2 and sulphate concentrations on the state of the ground, which shows a clear increase of SO_2 from the situation when the soil is bare to the situation when the ground is snow-covered. Sulphate concentrations do not show such a clear increase. The ratio of sulphur dioxide to sulphate as sulphur has also an annual cycle, but depends additionally on the wind direction. The minimum is in May (≈ 1.8) and the maximum in January (≈ 7). On the other hand, the summer minimum varies from 3 in the northwestern sector to 1 in the southeastern sector, while the winter maximum is 6 in the northwestern sector and 3 in the southeastern sector. The southeastern sector minimum is due to aged long-range transported air masses from industrial Europe. The northwestern sector corresponds to close domestic sources with the conversion of SO_2 to sulphate still unaccomplished.

The mean yearly concentrations of SO_2–S are 4.5, 4.9 and 2.9 $\mu g\,m^{-3}$ at Utö, Virolahti and Ähtäri, respectively. However, the measurements on Utö are contaminated by a diesel generator on the north side of the sampler, so that by dealing with conditions only from the south sector 90°–270°, the annual mean becomes 3.5 $\mu g\,m^{-3}$. For particulate $SO_4^=$, the mean yearly concentrations are 1.4, 1.7 and 1.1 $\mu g\,m^{-3}$ at Utö, Virolahti and Ähtäri, respectively.

5.1.3 Ozone and Nitrogen Dioxide

The ozone levels on Utö (Fig. 15a) are higher due to the lower dry deposition of O_3 to the sea surface compared with deposition to vegetation, and the closer proximity of anthropogenic sources of precursor emissions. We notice also that there is a weak bimodal concentration maximum on Utö (spring and summer) but only one maximum in spring at Ähtäri (Fig. 15b). The daily maximum concentrations are about the same at both sites in winter and in spring. On the other hand, they are different in summer and autumn due to the active uptake of ozone by vegetation during summer days. A comprehensive search for the origin of ozone level increases during a 1-year period (1986–1987) showed only two, but these significant, spring episodes (35–60 $\mu g\,m^{-3}$ above the monthly mean) that could be attributed to stratospheric injections (Hakola et al. 1987).

The annual cycle of nitrogen dioxide presents a maximum in January–December (9 and 8.4 $\mu g\,m^{-3}$ at Utö and Ähtäri, respectively) and a minimum in August–September (3.9 and 2.4 $\mu g\,m^{-3}$, respectively), corresponding to maximum emissions in winter and photochemical destruction in summer. The annual amplitudes are approximately equal to Utö and Ähtäri. The NO_2 cycle is closer to the SO_2 cycle because they are both primary pollutants.

The amplitude of the diurnal variation of ozone is stronger at Ähtäri than on Utö (Fig. 16) due to a difference in stability conditions. On Utö, the hydrostatic stability is closer to neutrality due to persistent moderate winds, while the thermal inertia of the water surface smoothes out diurnal stability variations. On the other hand, stability has a typical strong continental oscillation at Ähtäri, with low wind and a thermal inversion at night and enhanced mixing during the day (in summer). The ozone maximum occurs in the evening on Utö but in the afternoon at Ähtäri. The diurnal cycle at Ähtäri is strongly dependent on the wind velocity, with an increasing diurnal amplitude as the wind speed decreases, i.e. as mixing from aloft

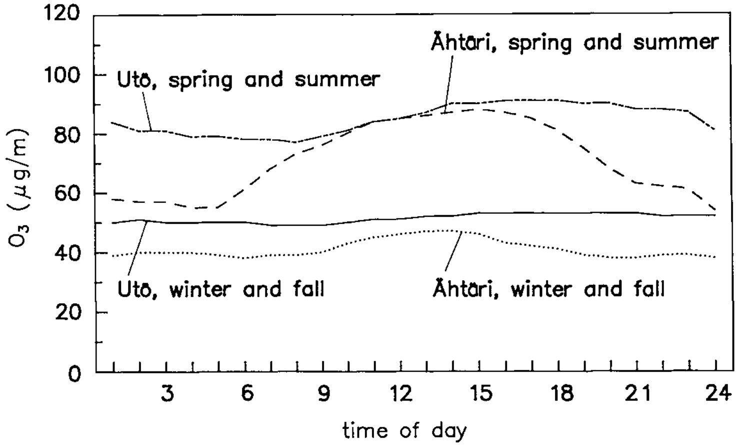

Fig. 16. Mean diurnal cycle of ozone averaged separately over winter + fall and spring + summer, at Utö and Ähtäri

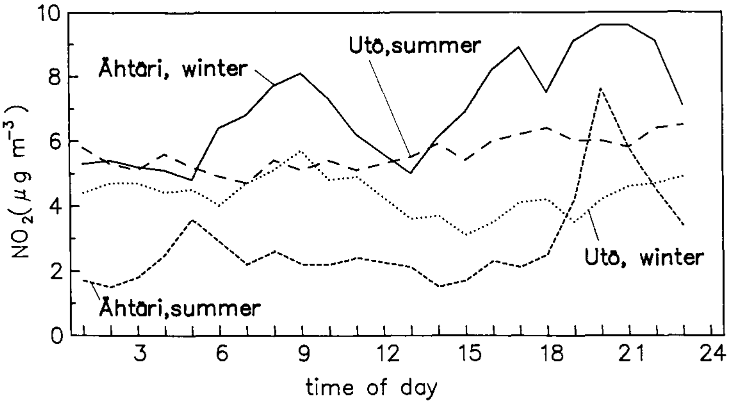

Fig. 17. Mean diurnal cycle of nitrogen dioxide in winter and in summer, at Utö and Ähtäri

decreases (Joffre et al. 1988). Furthermore, the concentration levels rise with increasing wind speed up to 3–4 m s^{-1}. These higher O_3 concentrations at stronger wind speeds should correspond to background atmospheric ozone levels, and depend on the season (95 $\mu g\,m^{-3}$ in spring, 50 $\mu g\,m^{-3}$ in summer). On Utö the ozone levels do not depend on the wind speed, except perhaps in spring with a slightly decreasing trend.

The diurnal cycle of nitrogen dioxide at the stations of Utö and Ähtäri is shown in Fig. 17, separately for winter and summer. We note that in winter NO_2 is higher at the continental station of Ähtäri than on the island of Utö, but that the reverse is true in summertime. There is practically no diurnal cycle on Utö except for perhaps the slight morning maximum in winter, probably due to the dissociation of NO_3,

N_2O_5 and PAN. This morning maximum occurs also in the winter cycle at Ähtäri, centred on the same time (09.00 h LT) but much broader. The same morning maximum can be observed in the summer curve at Ähtäri but earlier due to the early sunrise in these latitudes. The diurnal cycle at Ähtäri is also characterized by the strong evening maximum in both seasons.

5.2 Dependence on Air Mass Origin

The dependence of SO_2 and aer$SO_4^=$ on wind direction at the two Finnish EMEP stations of Virolahti and Ähtäri (Fig. 18) is very similar to the dependence of ion

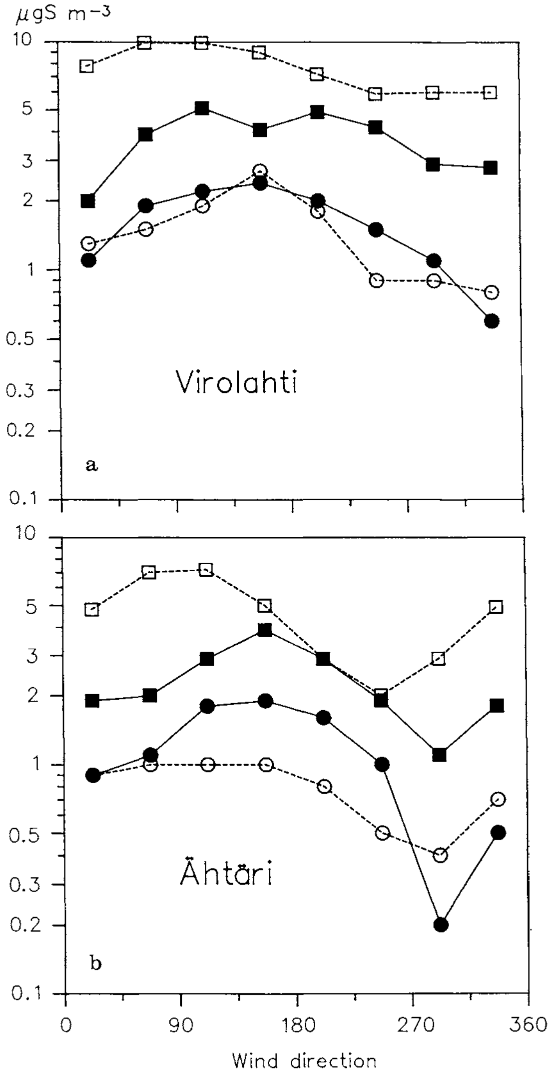

Fig. 18a,b. Dependence of sulphur dioxide (*squares*) and aerosol sulphate (*circles*) on wind direction in winter (*open symbols*) and in spring (*full symbols*) at Virolahti (**a**) and Ähtäri (**b**) concentrations in precipitation already discussed. Results from Utö are not shown here due to the problem of contamination from the nearby heating centre. We present the results separately for winter and spring, the period when SO_2 and aer$SO_4^=$ concentrations are the most significant. The origin of aerosol sulphate is not dependent on the season, while one can notice a shift of the SO_2 maximum from easterlies in winter to southerlies in spring at both stations.

Ozone concentrations have a clear dependence on wind direction according to season. On Utö, the spring and especially the summer concentrations have a clear maximum for the eastern to southwestern sector, the autumn concentrations have a clear maximum for the eastern to southwestern sector, the autumn concentrations have a maximum for westerly winds and a minimum for northeasterlies, while there is no directional variability in winter. At Ähtäri, the wind direction dependence amplitude is half the amplitude on Utö except for winter, when it is the same. Here also the spring and summer curves have the same shape with maxima in the south-southwestern sectors; the autumn curve has a broad maximum in the southwest-western and northwestern sectors, while the winter curve has a maximum in the west-northwest-northern sectors. This latter feature shows that during the dark period of the year ozone appears preferably in cleaner air masses, whereas chemical reactions act as a sink. On the other hand, nitrogen dioxide concentrations do not strongly depend on wind direction.

5.3 Episodicity

In Table 5 are given the medians and 97 percentiles of sulphur dioxide and aerosol sulphate at the three EMEP stations for the period 1980–85. We observe that the 97 percentiles are highest in Virolahti, for SO_2 being nearly doubled in the eastern sectors compared to the western sectors. The southeastern sector brings the highest sulphate episodes at all three stations. The ratio between the 97 percentile and the

Table 5. Medians and 97% percentiles of sulphur dioxide and aerosol sulphate concentrations (in $\mu g S m^{-3}$) at the three EMEP stations according to wind direction sectors

		Utö		Virolahti		Ähtäri	
	NE	4.8	20	3.2	26	1.8	10
S	SE	2.9	16	4.2	23	2.8	18
O	SW	2.0	9	3.3	15	1.8	10
2	NW	3.9	17	2.3	12	0.9	6
	All	2.9	16	2.9	18	1.8	12
	NE	1.0	4.9	1.0	5.4	0.8	3.0
S	SE	1.7	7.1	2.1	7.2	1.1	5.5
O	SW	1.0	5.2	1.3	5.9	0.8	4.0
4	NW	0.4	2.9	0.5	3.4	0.2	2.0
	All	0.9	5.1	1.1	6.0	0.7	4.1

median value was expectedly the highest at Ähtäri for SO_2 (≈ 6.1) while this ratio was about the same for all three stations for sulphate. Here also, the NW and NE sector results for Utö are not reliable due to probable local contamination.

Investigations for determining the lowest concentrations having harmful effects on vegetation are still preliminary and depend on the methods used and the combination of pollutants implicated. Nevertheless, according to WHO (1987), the lowest concentrations of ozone that have an effect can be estimated as an average 60 $\mu g\,m^{-3}$ over the growing season (100 days), 65 $\mu g\,m^{-3}$ and 100 $\mu g\,m^{-3}$ for an exposure of 24 h and 2 h, respectively. The relative contribution of different wind direction classes to high ozone concentrations (above 100 $\mu g\,m^{-3}$) at Utö and Ähtäri are shown in Fig. 19. From this figure it is clear that the highest concentrations occur for wind sectors corresponding to industrialized European sources.

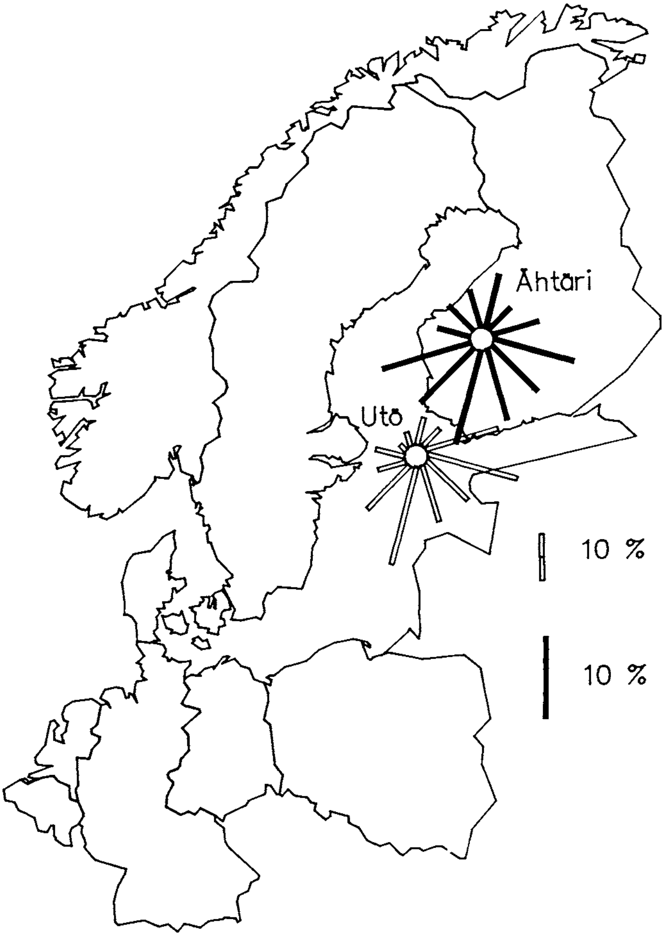

Fig. 19. Relative contribution of different wind direction classes to high ozone concentrations (> 100 $\mu g\ m^{-3}$) at Utö and Ähtäri

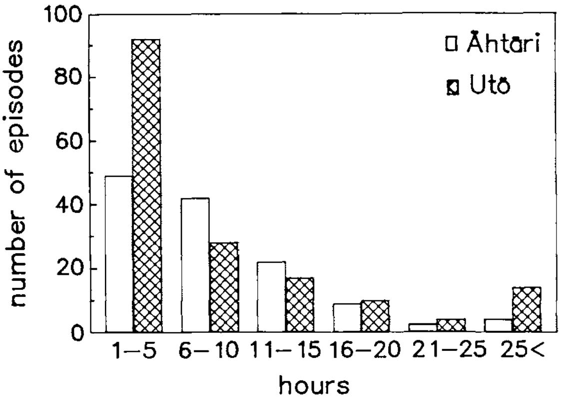

Fig. 20. Frequency distribution of high ozone events (> 100 µg m^{-3}) at Utö and Ähtäri, according to the duration of the episodes

The mean duration and the frequency of these high ozone episodes differ on Utö from those at Ähtäri. From Fig. 20 it can be seen, as expected, that the number of episodes is much higher on Utö.

5.4 Correlations Between Chemical and Meteorological Characteristics

As implied by the air chemistry diagram of Fig. 3, ozone concentrations are influenced by many factors. Table 6 shows significant correlation coefficients between hourly and daily ozone deviations δO_3 from their monthly mean, and some meteorological parameters.

The striking feature is that most relatively high correlations ($r \geq 0.4$) occur at Ähtäri, while on Utö only nitrogen dioxide seems to have some influence in winter and spring. This negative correlation between NO_2 and δO_3 probably reflects the oxidation of nitrogen oxide by ozone, leading to the formation of NO_2. The anticorrelation is stronger in autumn and winter and non-existent in summer. Expectedly, δO_3 is positively correlated with global radiation and air temperature, but this is significant only at the continental site of Ähtäri with its marked diurnal cycle. The effect of air pressure on δO_3 was also checked but no significant correlation was found, even slightly negative values occurring at Ähtäri, although ozone episodes in western Europe and North America are often connected with high pressure anticyclonic systems. This also confirms the large contribution of long-range transported ozone to Finland compared to the local build-up.

Using data on daily concentrations of sulphur dioxide and aerosol sulphate, it is interesting to notice that they are positively correlated with δO_3 in spring and summer at both stations but negatively correlated in autumn and winter. This implies that chemical sinks are effective in autumn and winter, whereas chemical production occurs in spring and summer. On the other hand, the negative correlation of δO_3 with SO_2 on Utö in summer might be due to a nearby polluting source.

Table 6. Correlation coefficients between ozone daily deviations from the monthly mean and different meteorological and chemical factors at Utö (7/85–3/88) and Ähtäri (9/86–3/88)

		Spring		Summer		Autumn		Winter	
		Utö	Ähtäri	Utö	Ähtäri	Utö	Ähtäri	Utö	Ähtäri
Hourly samples									
N	d	– 0.16	–	– 0.16	–	– 0.20	– 0.32	– 0.29	–
	n	–	0.24	– 0.13	0.23	– 0.21	–	– 0.24	0.16
WS	d	0.16	0.43	– 0.10	0.38	0.14[a]	0.41	–	0.41
	n	0.16	0.53	–	0.49	–	0.53	–	0.46
T	d	0.14	0.43	0.23	0.71	0.28	0.26	– 0.17	0.32
	n	0.11[a]	0.19	–	0.54	0.27	0.20	–	0.33
GR	d	0.14	0.28	0.10[a]	0.58	0.23[a]	–	0.31	0.26
RH	d	– 0.23	– 0.55	–	– 0.62	– 0.37	– 0.50	– 0.39	–
	n	– 0.12[a]	– 0.30	0.21	0.48	– 0.35	– 0.45	– 0.41	0.10[a]
NO_2	d	– 0.30	– 0.35	–	– 0.19	– 0.31	– 0.50	– 0.38	– 0.55
	n	– 0.41	– 0.30	–	–	– 0.29	– 0.52	– 0.50	– 0.65
Daily samples									
aerSO_4		0.50	0.46	0.59	–	–	–	– 0.41	– 0.33
SO_2		–	0.37	– 0.34	–	– 0.18[a]	–	– 0.45	– 0.23[a]

The reported correlations are significant either at the 1% level or at the 5% level.[a]
N is the cloudiness, WS the wind speed, T the air temperature, RH the relative humidity, and GR the global radiation. Results are differentiated according to the season and day/night (d/n).

Additional measurements of total nitrate (gaseous HNO_3 + aerosol NO_3^-), lead-210 and beryllium-7 from Utö were available during a few months in 1986. We noticed that ozone daily deviations from their monthly mean correlated with ^7Be and ^{210}Pb in summer ($r \approx 0.4$) but especially in spring ($r \approx 0.6$). Beryllium is a tracer for stratospheric air and thus these results would imply enhanced transport of ozone from aloft. On the other hand, lead as a decomposition product of radon would indicate a continental origin, i.e. mainly ozone formation in anthropogenic plumes. These parallel correlations indicate that very different processes can occur concomitantly.

Total nitrate was positively correlated with δO_3 in spring (≈ 0.4) but negatively correlated in February (≈ -0.5). This can be explained by the rapid formation of nitric acid in spring due to photochemical effects (availability of OH) together with ozone formation or transport.

Visibility has a high negative correlation with SO_2 and sulphate concentration at Utö and Virolahti, while the correlation is smaller at Ähtäri, where the air masses are cleaner.

5.5 Effects of Biogenic Volatile Organic Compounds on Ozone

The photochemical formation of ozone requires the presence of nitrogen oxides and hydrocarbons. The magnitude of the hydrocarbons to nitrogen oxides ratio has been shown to be an important factor in determining the rate of ozone formation, maximum ozone production occurring at ratios around 10:1 (Lurmann et al. 1983). The extensive forested areas in Finland probably imply relatively high natural hydrocarbon emissions (especially terpenes from conifers), which might influence ozone concentrations.

Terpene levels measured in the forest close to the EMEP station of Ähtäri showed a clear seasonal variation related to their emission rate dependence on temperature, with 3–37 $\mu g\,m^{-3}$ in July ($T \approx 11$–30°C) but only 4–7 $\mu g\,m^{-3}$ in April (T from -10 to $+10$°C), when the ground was snow-covered, and 1–4 $\mu g\,m^{-3}$ in September ($T \approx 4$ –11°C). They also displayed a strong diurnal cycle in summer with a maximum at night (Fig. 21). Thus, daytime chemical sinks, together with a more effective turbulent dispersion, compensate for higher emissions due to higher daytime temperature. These measured terpene concentrations are equivalent to or lower than those measured in neighbouring countries (Hov et al. 1983; Isidorov et al. 1985; Petersson 1988).

Ozone concentrations were measured at both the open field EMEP station and in the forest where the terpene measurements were performed. Ozone was systematically lower in the forest than in the open field (Fig. 22). The average ratio $[O_3(\text{forest})]/[O_3(\text{station})]$ was 0.8, 0.66 and 0.86 in April, July and September, respectively. This ratio also had a diurnal variation in July, with its minimum values appearing at night. This suggests that there exist processes depleting O_3 in the forest at night, and this more efficiently in the summer than in spring or autumn. The main sinks for ozone during the night are temperature-dependent

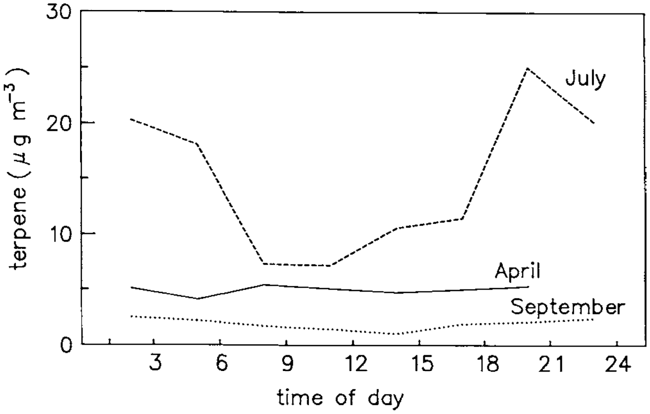

Fig. 21. Diurnal variation of total terpene concentrations in April, July and September 1988 at Ähtäri

chemical reactions and deposition. Reported ozone deposition velocities are 0.1 cm s^{-1} to snow, and 0.85 cm s^{-1} to vegetation in the daytime or 0.25 cm s^{-1} at night (Galbally and Roy 1980). Deposition is more efficient in the forest than in the open field due to stomatal activity. During windy nights the ozone-rich air from aloft can reach down to the surface. These intrusions probably occur at about the same rate above the forest and at the station, which is reflected in the stable and high ratio of ozone values at both sites during such conditions.

The role of terpenes in ozone destruction was studied by the reactivities of terpenes with OH, O_3 and NO_3. We took β-pinene and limonene as surrogates for terpene average behaviour because of their quite different reaction rates with these compounds (Atkinson et al. 1986). Terpenes react fairly rapidly with the OH radical during daytime, yielding lifetimes of β-pinene and d-limonene differing by a factor of 2. However, at night, they react mainly with ozone (due to the small amount of NO_3), leading to a β-pinene lifetime 30 times longer than for d-limonene. This should lead to a diurnal variation of the β-pinene to d-limonene

Table 7. Average percentage values with standard deviation of individual terpenes with respect to total terpenes during the different measuring periods separately for day (d) and night (n) conditions

	α-Pinene	Camphene	β-Pinene	3-Carene	Limonene
April					
d	46 ± 4	6 ± 1	9 ± 3	21 ± 6	18 ± 3
n	43 ± 5	8 ± 4	10 ± 3	23 ± 3	16 ± 3
July					
d	54 ± 9	10 ± 9	12 ± 5	12 ± 4	12 ± 7
n	47 ± 5	11 ± 7	10 ± 6	17 ± 5	15 ± 6
September					
d	48 ± 5	15 ± 3	11 ± 4	19 ± 12	7 ± 5
n	48 ± 4	14 ± 2	10 ± 2	19 ± 2	7 ± 5

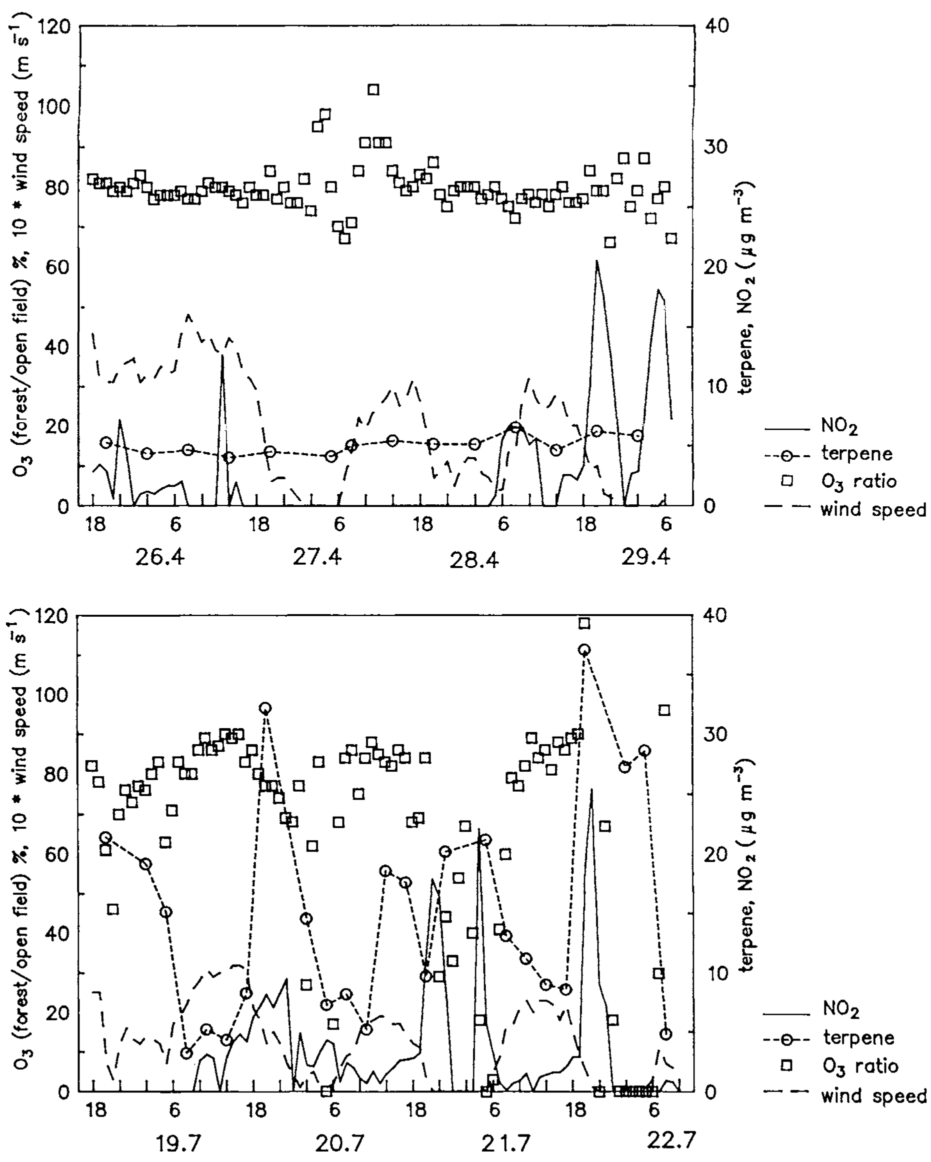

Fig. 22. Time variation of the ozone concentration ratio at the forest and at the Ähtäri station sites (*squares*) together with wind speed (*dashed line*) measurements (*left side ordinate*). The *right hand ordinate* refers to terpenes (*circles*) and NO_2 (*continuous line*) concentrations

ratio. However, we observed that, within the instrumental uncertainty, the ratio was nearly constant, thus suggesting that the terpenes do not react mainly with ozone (Table 7).

The ratio of terpenes to NO_2 had a maximum value of 5.0, occurring in July, suggesting weak ozone production potential. The low concentrations of nitrogen dioxide also probably made irrelevant the possibility of ozone depletion by NO_2. Consequently, we deduce that deposition related to meteorological conditions (wind speed, ABL height and thermal stability) was a more important sink for nighttime ozone during this short period, as was also observed by Roberts et al. (1983).

6 Variability over the Baltic Sea

6.1 Air Chemistry and Marine Meteorology

As illustrated in Fig. 1, Finland is half surrounded by the Baltic Sea, and what is more significant, on its southern side, the direction from which the major anthropogenic pollutant contribution arrives. It is thus very important to study the variability of airborne pollutants in the Baltic Sea Basin and try to infer the physical and chemical processes going on during transport over the sea area. Marine meteorology differs from the situation overland due to the different roughness conditions but especially due to the differing heat and moisture content of the surface, often yielding opposite stability conditions in overland and overwater areas, themselves characterized by very different ABL heights (Joffre 1985). For instance, one observes stably stratified conditions in spring and summer over the sea, concomitant with daytime unstable conditions overland.

Table 8 presents the statistics of daily chemical air concentrations obtained in spring 1985 during a cruise made in the Baltic Sea (see Fig. 1), as well as corresponding results from a previous Baltic cruise in spring 1983 (Korolev et al. 1985). The denomination $nssSO_4^=$ refers to non-sea-salt or excess sulphate, i.e. after the deduction of the marine sulphate component, on the basis of chloride concentrations (because sodium measurements were not available). Comparison of these data with other cruise results obtained from the Atlantic or the Pacific Ocean indicates that the Baltic Sea cannot be considered as a remote pristine region (Joffre and Lindfors 1989).

Correlation studies of the 1985 cruise results indicate that ammonia and chloride correlate positively ($r \approx 0.5$ and 0.4, respectively) with the wind speed on board the ship. Georgii and Gravenhorst (1977) have previously argued on a marine source of ammonia, but a closer inspection of our cases seems to indicate agricultural sources from the adjacent land areas. During the cruise, elevated ammonia levels did not occur in conjunction with other airborne pollutant episodes. On the other hand, the rather low correlation of chloride with wind speed might indicate that the sea is not the only source of chloride and that it can have an anthropogenic origin from decomposition of HCl. Since these results are based only on a limited amount of data, conclusions cannot be firmly established.

Correlation studies show that the most common anthropogenic airborne pollutants ($nssSO_4^=$, NO_3^- and NH_4^+) are very well correlated and probably exist under the form of salt, and are also well related to sulphur dioxide values (Joffre

Table 8. Statistics of concentrations of chemical compounds measured during the spring 1985 Baltic Sea cruise (in $\mu g\, m^{-3}$ except Hg in $ng\, m^{-3}$)

	nss$SO_4^=$-S	NO_3^--N	NH_4^+-N	SO_2-S	NH_3-N	HNO_3-N	Cl^-	Hg
Range	0.32–10.7	0.34–2.7	0.55–5.0	0.21–13.3	0.02–1.7	0.02–0.22	0.09–2.2	1.2–3.2
Median	2.26	0.76	2.08	1.48	0.20	0.04	0.52	2.0
Geom. mean	2.17	0.85	1.90	1.43	0.20	0.05	0.46	1.98
Mean	2.89	1.00	2.28	2.04	0.36	0.06	0.56	2.06
S.D.	2.25	0.60	1.32	2.39	0.43	0.05	0.40	0.61
Number	30	30	30	30	30	30	30	27
83 mean	1.86			1.81			0.40	1.65
83 S.D.	0.85			1.14			0.70	0.74

The 83 mean and standard deviation (S.D.) refer to the results of the April–May 1983 cruise (Korolev et al. 1985).

and Lindfors 1989). The more complex chemistry of nitrogen compounds is reflected in more variable and generally lower correlation coefficients. Nitric acid is well correlated only with SO_2. Gaseous mercury correlated significantly with $nssSO_4^=$ and NH_4^+, confirming its anthropogenic origin.

The ammonium to non-sea-salt sulphate molar ratio was very close to 2 for sulphate concentrations up to about 150 nmol m^{-3}, indicating the almost exclusive occurrence of $(NH_4)_2SO_4$ and full neutralization of H_2SO_4 particles. At higher sulphate concentrations, the ammonium concentrations seem to reach a saturation level and the $NH_4^+/nssSO_4^=$ molar ratio tends towards 1, indicating the presence of other compounds, such as NH_4HSO_4, NH_4NO_3 or $CaSO_4$. These results are somewhat at variance with data collected by Quinn et al. (1988) over the eastern Pacific, which indicate a molar ratio between 2 and 0.5 due to the lesser availability of total ammonium ($NH_3 + NH_4^+$) during their expedition. Joffre and Lindfors (1989) also observed the activation of the sulphur dioxide-sulphate conversion with increasing concentrations of both ammonia and water vapour. This stresses the environmental importance of ammonia and of having more measurements available.

6.2 Simulation of Episodes

On the basis of the 1985 cruise data, Salmi and Joffre (1988) showed that a very good linear correlation exists between SO_2 or aerosol sulphate and the sulphur emission, Q_S, integrated 48 h backwards along the air trajectories at the 850-mb level. Furthermore, the observed scatter for the sulphate relationship at low Q_S values was related to trajectories coming from the eastern sectors with their uncertain emission data. On the other hand, neither total nitrate nor total ammonium had any clear dependence on Q_N, the integrated NO_X emissions, the scatter being very large.

The importance of meteorology as a modulator of air concentrations is further demonstrated by applying a simple transport-scavenging model [see Eq. (1)] to the situations found during the 1985 cruise. Taking constant values for the scavenging rates (dry and wet deposition, chemical conversion) and integrating 99 h backwards from the ship's location yielded a fair agreement between observed and computed concentrations of SO_2 and $SO_4^=$ (Lindfors and Joffre 1989), as reproduced in Fig. 23.

6.3 Deposition Modelling

Dry deposition over the sea is strongly dependent on the wind velocity (Joffre 1988a,b). On the other hand, wind velocity has a known climatological distribution, so that if knowledge of wind speed statistics is used, the distribution of the dry deposition will also be available, and a weighted estimate of the deposition at a particular place can be obtained. This kind of exercise was performed by Joffre (1988b) and Joffre and Savunen (1989) for the location of the Ocean Weather Ship

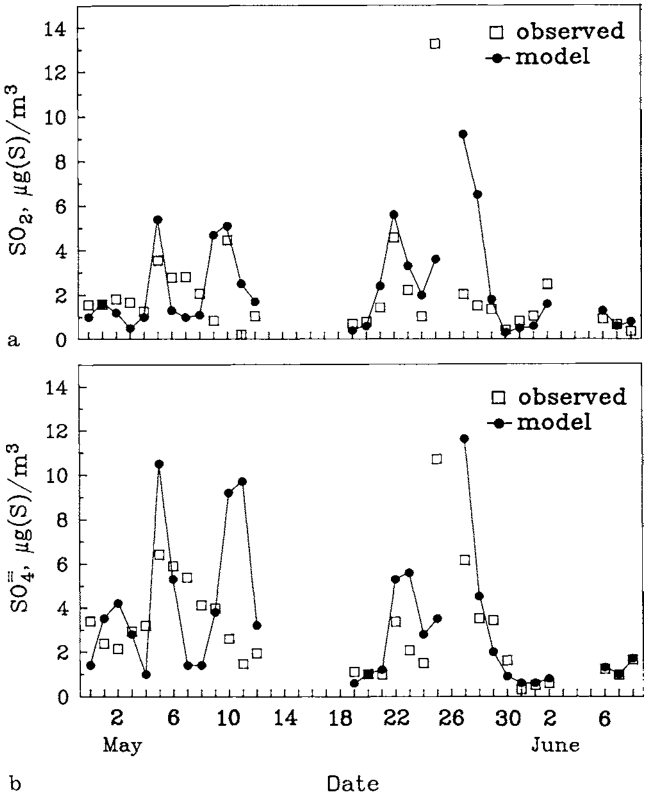

Fig. 23a,b. Comparison between the time variation of observed and simulated SO_2 (**a**), and nss$SO_4^=$ (**b**) concentrations (in µg S m^{-3}) during the Baltic Sea cruise of R/V Akademik Shuleykin in April-June 1985

M off the Norwegian coast. Both the wind velocity and dry deposition velocity frequency distributions followed a Weibull distribution quite accurately. The results also showed that distinctions between air mass origins (different meteorological conditions) and the seasons (different stability conditions) should be retained when computing average dry deposition velocities.

Using the data of the spring 1985 Baltic cruise, Lindfors and Joffre (1989) computed the dry deposition flux of some gaseous and particulate compounds onto different parts of the Baltic Sea (Table 9). They found that the Central Baltic (between Gotland and the Lithuanian coast) experienced a maximum deposition of gaseous SO_2 and NH_3, and particulate sulphate, nitrate and ammonium compared to the northern part (north of Gotland Island) and the southern part of the Baltic (Bornholm Island Basin). This tendency is also found in the distribution of nss$SO_4^=$, NH_4^+ and NH_3 concentrations.

On the other hand, the SO_2, HNO_3 and NO_3^- concentrations displayed the generally expected decreasing south-north gradient. One reason contributing to these slightly ambiguous results was the short duration of the cruise (30 daily

Table 9. Estimated dry deposition flux (in mg m^{-2} yr^{-1}) of airborne pollutants to different areas of the Baltic Sea according to Lindfors and Joffre (1989). The standard deviations are in parentheses

	SO_2–S	NH_3–N	$SO_4^=$–S	NO_3^-–N	NH_4^+–N
Northern	320	30	43	82	35
Baltic	(123)	(9)	(3)	(1)	(7)
Central	569	207	76	151	54
Baltic	(315)	(234)	(24)	(48)	(19)
Southern	336	64	38	131	38
Baltic	(186)	(44)	(28)	(77)	(23)

observations over a period of 6 weeks), during which we picked up spatially random samples, not representative of overall conditions. However, our results might also be partly explained by the stable stratification over the Baltic Sea, typical of springtime conditions, with the emitted pollutants staying a longer time aloft in a reservoir layer above the ABL and being finally deposited by slow turbulent transfers, as well as by mesoscale and synoptical scale instabilities only far away downstream of the coastal zone.

7 Conclusions and Further Work

In this article we have presented the major results from an analysis of monitoring air chemistry data from three Finnish EMEP stations and one cruise in the Baltic Sea. The dependence of air and precipitation concentrations on meteorological and climatological factors has been particularly emphasized. Meteorological variability forms the basis for understanding the source, path and fate of anthropogenic pollutants from the atmosphere to ecosystems. Indeed, it was demonstrated that meteorological conditions and air mass origins were the primary modulators of chemical concentrations, taking precedence above chemical reactions. Thus, abatement measures and impact studies should take these results into account.

The results presented in this article constitute a fair amount of new knowledge on air quality variability and air chemistry in northern European conditions. We have not touched upon the problem of temporal trends due to the shortness of the homogeneous time series. A wait of a few years more is necessary for this purpose. Nevertheless, these studies have allowed us to start an exhaustive analysis of air quality data together with meteorological data, providing a well-established climatological picture of the atmospheric environment of Finland. Moreover, these projects have in fact marked the start of atmospheric chemistry research in Finland. The results and the obtained database will be of great value for environmental modellers and for scientists from other fields needing values of pollutant concentrations and deposition to ecosystems in Finland.

Apart from the EMEP stations discussed in this chapter, other existing Finnish air quality monitoring stations are not adequate for estimating the origin of acid deposition, since they use sampling times much longer than the 12–24 h required for a reliable association of pollution episodes to defined air masses. The three EMEP stations, however, are not enough for a good coverage of deposition in Finland, and additional stations should be established in the Salpausselkä region (approximately at the barycentre of the triangle formed by the three existing stations) as well as in northern and eastern Finland. The issue of the influence of small-scale terrain features on deposition values has not been addressed here but should be the object of separate investigations. However, provided there is a similar geography at the extrapolated points, our results represent bulk deposition and concentrations within zones of several tens of kilometres around the sampling stations.

It is clear that chemical measurements should be performed with shorter sampling times in order to cope with the meteorological variability. Furthermore, chemical measurements should be extended to aerosol nitrate and ammonium, and to gaseous nitric acid and ammonia in order to understand the scavenging of inorganic nitrogen compounds. On the other hand, ozone chemistry would require measurements of PAN, methane, carbon monoxide, hydrogen peroxide and many hydrocarbon families. These lists show the distance still to go before one can hope to comprehensively explain air chemistry.

This work will be continued following the same methodology, in order to have more observed cases allowing the division of the broad classes presented here into finer classes, i.e. representing a better-defined set of common parameters. On the other hand, both development and acquisition of new and more powerful sampling and analytical methods such as remote sensing will contribute towards a better, more accurate and representative knowledge of the occurrence, transformation and deposition of air constituents.

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Appendix

Wind direction frequency distribution (in %) according to seasons at the three EMEP stations during the period 1980–85. The data are 3-hourly synop reports. Calm situations indicate no specific wind directions due to the low value of the wind speed. Rankki is the synop station closest to Virolahti (distance ≈ 40 km west)

Utö	NE	SE	SW	NW	Calm
Dec–Feb	21.0	23.8	30.7	24.3	0.2
Mar–May	21.1	26.6	28.4	23.7	0.2
Jun–Aug	16.0	17.6	35.0	31.2	0.2
Sep–Nov	17.2	18.3	39.8	24.6	0.2

Rankki	NE	SE	SW	NW	Calm
Dec–Feb	21.4	18.8	34.4	24.0	1.4
Mar–May	21.2	28.5	31.7	16.8	1.8
Jun–Aug	18.5	17.6	42.1	20.1	1.6
Sep–Nov	17.3	18.8	37.8	25.5	0.6

Ähtäri	NE	SE	SW	NW	Calm
Dec–Feb	17.0	21.2	26.8	13.1	21.8
Mar–May	17.3	23.0	22.8	17.6	19.3
Jun–Aug	18.2	18.5	21.7	22.7	18.9
Sep–Nov	15.0	26.0	25.8	20.0	13.2

Simulating The Formation of Acid Aerosols

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Summary

In the atmosphere new acid aerosol particles can form in water–sulphuric acid mixtures. In some practical conditions the formation of new particles will change the dynamical behaviour (growth, deposition) of pre-existing particles.

Introduction

Aerosols have a central role in the atmosphere. Their importance for cloud formation has been recognized for years. Furthermore, the aerosols participate in numerous chemical processes, and they also influence the visibility and the electrical properties of the atmosphere. In addition, they may affect the climate on earth by influencing the radiation budget.

The production and growth of particles in the presence of condensable vapours represent processes of major importance in aerosol dynamics. The formation of new aerosol particles will affect the composition of particles. The composition determines the growth rate, and this will determine the actual size and composition of particles. The size and composition of particles have an important effect on deposition.

In the present chapter, the formation of acid aerosols is investigated. The aim of the study is to show the significance of aerosol formation on aerosol dynamics and thereby on acid deposition.

The formation of aerosol particles (e.g. acid aerosols, particles containing acids, sulphates or nitrates) by gas-to-particle conversion can take place through several different mechanisms including: (1) reaction of gases to form low vapour pressure products (e.g. the oxidation of sulphur dioxide to sulphuric acid), (2) homomolecular or heteromolecular (in the atmosphere generally with water vapour) nucleation of these low pressure vapours, (3) vapour condensation onto surfaces of pre-existing particles (sometimes called heterogeneous nucleation), (4) reaction of gases with the surfaces of existing particles and (5) chemical reactions within particles.

The formation of new particles is a significant process, since it will change the dynamics (e.g. deposition) of aerosols. In cases where no new particles are formed,

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the dynamical behaviour of particles does not change very much. Thus the present study concentrates on nucleation and on the time variation of nucleating species. For generating the nucleating species, the gas phase reactions (step 1) are important. In the present chapter we shortly review the most important gas-phase reaction for aerosol formation. Nucleation (step 2) will follow gas phase reactions, if enough gas molecules exist for formation of new particles. The classical theory for heteromolecular homogeneous nucleation is reviewed. The condensation term (step 3) will decrease the concentration of the nucleating species. The continuum and transition regime condensation theory is presented. The other parts of gas-to-particle conversion (steps 4 and 5) will not affect the formation of new particles. Thus they are not included in the simulation.

Several binary gaseous mixtures have been studied for their possible implications in atmospheric processes. They include the study of homogeneous binary nucleation in the HCl–H_2O (Cocks and Fernando 1981), HNO_3–H_2O (Mirabel and Katz 1974; Mirabel and Clavelin 1978; Kulmala 1988), methane sulfonic acid (MSA)–H_2O (Hoppel 1987) and the H_2SO_4–H_2O (Doyle 1961; Jaecker-Voirol et al. 1987; Viisanen et al. 1987; Jaecker-Voirol and Mirabel 1988; Kulmala 1988) mixtures.

For formation of new acid particles the most important system is the H_2SO_4–H_2O mixture. Sulphuric acid molecules, together with water molecules, can form new particles in some practical situations in the atmosphere. These particles will grow to visible size through condensation and coagulation. In the growth process, the hygroscopic behaviour of acid particles is important. For example, nitric acid molecules in the troposphere can only absorb into or condense onto existing particles, and liquid phase chemistry will complete the gas-to-particle conversion of nitric acid molecules. In the stratosphere the nitric acid–water system will have a more important role (e.g. Crutzen and Arnold 1986; Toon et al. 1986; Molina et al. 1987).

Until approximately 1980, very little was known about liquid phase chemistry (step 5) including aerosol particles, clouds, fogs and rain (Finlayson-Pitts and Pitts 1986). Nowadays there is much evidence that liquid phase chemistry is in many atmospheric conditions many times as effective as gas phase chemistry for oxidation of sulphur dioxide. The relative importance of gas phase versus liquid phase oxidation is dependent on the particular meteorological conditions, e.g. relative humidity and whether clouds or fogs are present. Friedlander, McMurry and their co-workers have used the growth law technique to determine quantitatively the relative importance of gas and liquid phase reactions in SO_2 oxidation (Friedlander 1977; McMurry and Wilson 1982, 1983).

Theory

General

The formation and behaviour of aerosols in smog chamber experiments and in the atmosphere have been studied by physical and chemical models (e.g. Middleton and Kiang 1978; Bunz and Dlugi 1983, 1984, 1986, 1989).

In the present chapter, the formation of new acid aerosols is investigated. A simplified model is used for simulation. For atmospheric applications the most important system is the sulphuric acid–water system. In practice water vapour is always in equilibrium with water in particles and the changes in sulphuric acid vapour concentrations are significant.

The time dependence of sulphuric acid vapour concentration (N_b) can be presented by the following equation

$$\frac{d}{dt}N_b = Q_b - n_b^* I - C_b, \tag{1}$$

where I is the nucleation rate, n_b^* is the number of molecules (b) in the critical cluster, Q_b is the source term of gaseous sulphuric acid determined by the gas phase oxidation rate of SO_2, and C_b is the condensation rate of acid molecules (when particle concentration is N_p).

Gas-Phase Oxidation

The oxidation of sulphur dioxide in the gas phase has been widely studied (e.g. Atkinson and Lloyd 1984; Calvert and Stockwell 1983; Davis et al. 1979; Margitan 1984; Stockwell and Calvert 1983), and the main results are also presented in textbooks (e.g. Finalyson-Pitts and Pitts 1986; Seinfeld 1986). Although there are many possible reactions for the oxidation of ground state SO_2 in the gas phase, the only process which is fast and efficient enough is the reaction of SO_2 with the OH radical

$$OH + SO_2 + M \longrightarrow HOSO_2 + M. \tag{2}$$

$$HOSO_2 \longrightarrow \cdots \longrightarrow H_2SO_4. \tag{3}$$

The temperature and pressure dependence of the rate constant k_b used in the present study is adopted from DeMore et al. (1985) and is discussed elsewhere (see e.g. Finlayson-Pitts and Pitts 1986). The rate constants used in simulation are given in Table 1.

The concentration of OH radicals in ambient air depends on the intensity and wavelength of the actinic UV and on the absolute and relative amounts of

Table 1. The values of rate constant k_b as a function of temperature. The total pressure is 1 atm

Temperature (°C)	Rate constant, $k_b \times 10^{12}$ cm^3 $molecule^{-1}$ s^{-1}
−25	1.36
−15	1.30
−5	1.25
5	1.19
15	1.13
25	1.08

non-methane hydrocarbons and NO_x present in air, since it is connected to ozone concentration (Finlayson-Pitts and Pitts 1986).

The expression for the source term is

$$Q_b = k_b[OH][SO_2]. \tag{4}$$

Binary Nucleation

In homomolecular nucleation, formation of new particles does not occur unless the vapour phase is supersaturated. The situation changes when two or more vapour species are present, none of which is supersaturated: nucleation may take place as long as the participating vapour species are supersaturated with respect to a liquid solution droplet. Thus heteromolecular nucleation can occur when a mixture of vapours is unsaturated with respect to the pure substances.

One purpose of this study is to examine how certain kinds (i.e. acidic) of liquid aerosols can be generated under atmospheric conditions by heteromolecular nucleation. The classical hydrates interaction liquid–drop model (Jaecker-Voirol et al. 1987; Jaecker-Voirol and Mirabel 1988) is applied in investigating the formation of sulphate (binary system of H_2O–H_2SO_4 vapours).

The heteromolecular nucleation process was first studied by Flood (1934), and the kinetics of heteromolecular nucleation were first discussed by Reiss (1950). Reiss' theory was applied by Doyle (1961) to calculate the nucleation rate of sulphate particles. After his studies many scientists have examined the problem of sulphate formation. Theoretical investigations have been made with classical theory by e.g. Mirabel and Katz (1974) (they have also calculated nitrate formation), Nair and Vohra (1975), Stauffer (1976) (mainly kinetic part of the nucleation theory), and Yue and Hamill (Yue and Hamill 1979, 1980; Hamill and Yue 1980; Yue 1979, 1981). Reiss and his co-workers have considered the hydrate effect of sulphuric acid (Heist and Reiss 1974; Shugard et al. 1974; Shugard and Reiss 1976; Schelling 1980). In their current work, Jaecker-Voirol et al. (1987) have reexamined the hydrates interaction model. Suzuki and Mohnen (1981) have investigated the effect of cluster–cluster interaction on the nucleation rate. During recent years Wilemski (1984, 1987, 1988) has presented a revised classical binary nucleation theory considering the generalized Kelvin equation. On this subject there was a seminar at 1986 in Berlin, where the thermodynamics of binary droplets was studied.

According to the general formula of statistical physics, the probability of a fluctuation producing a condensation nucleus is proportional to $\exp(-\Delta G^*/kT)$, where ΔG^* is the minimum work needed to form the nucleus, k is the Boltzmann constant and T is temperature in Kelvin. The nucleation rate I can be predicted as

$$I = C \exp\frac{-\Delta G^*}{kT}, \tag{5}$$

where C is a (mainly) kinetic factor. It can be shown (e.g. Reiss 1950; Heist and

Reiss 1974) that in the three-dimensional space (n_a, n_b, ΔG), there exists a saddle point which corresponds to the minimum height of the free energy barrier, or $\Delta G^* = \Delta G_{sp}$ (sp = saddle point). Once a cluster reaches the saddle point, nucleation takes place and it can grow to a larger droplet. Hence, the radius and composition at this point (denoted by r^*, n_a^*, n_b^*) are called critical or equilibrium values.

The critical composition n_a^* and n_b^* at the saddle point can be calculated by solving the following simultaneous equations:

$$\left(\frac{\partial \Delta G}{\partial n_a}\right)_{n_b} = 0 \tag{6}$$

$$\left(\frac{\partial \Delta G}{\partial n_b}\right)_{n_a} = 0. \tag{7}$$

The Gibbs free energy of formation of a liquid cluster in a binary mixture of vapours is given by the expression (e.g. Yue and Hamill 1979):

$$\Delta G = n_a(\mu_{al} - \mu_{ag}) + n_b(\mu_{bl} - \mu_{bg}) + 4\pi r^2\sigma, \tag{8}$$

where n_i is the number of molecules of species i, μ_{il} and μ_{ig} are chemical potentials of species i in the liquid and gas phase, respectively, r is the radius of the cluster and σ is the surface tension. For the special systems of water and acid vapours, a refers to water and b refers to acid (sulphuric acid or nitric acid).

The change in the chemical potential during transformation from gas phase to liquid phase for each component is given by the following relationship

$$\mu_{il} - \mu_{ig} = -kT\ln\frac{p_i}{p_{i,sol}}, \tag{9}$$

where $p_{i,sol}$ is the partial vapour pressure of species i over a flat surface of the solution. The following quantities can be defined

$A_{ag} = p_a/p_{as}$ = water activity in the gas phase
$A_{bg} = p_b/p_{bs}$ = acid activity in the gas phase
$A_{al} = p_{a,sol}/p_{as}$ = water activity in the liquid phase
$A_{bl} = p_{b,sol}/p_{bs}$ = acid activity in the liquid phase

where p_{as} and p_{bs} are the respective equilibrium vapour pressures of water and acid vapour over a flat surface of pure substance.

Equation (8) can be rewritten

$$\Delta G(n_a, n_b) = -n_a kT\ln\frac{A_{ag}}{A_{al}} - n_b kT\ln\frac{A_{bg}}{A_{bl}} + 4\pi r^2\sigma, \tag{10}$$

and r is given by

$$\frac{4}{3}\pi r^3\rho = n_a m_a + n_b m_b, \tag{11}$$

where ρ is the density of the solution, m_a is the mass of a water molecule and m_b is the mass of an acid molecule.

The influence of hydrate formation on the energetics of nucleation is significant (Jaecker-Voirol et al. 1987). The nucleation rate can be calculated by the following equation

$$I_1 = 4\pi\alpha r^{*2} N_{a0} N_{b0} \frac{Z}{\sin^2(\theta)} \sqrt{\frac{kT}{2\pi m_b}} \exp\left(-\frac{\Delta G - kT\ln C_h}{kT}\right)^*, \tag{12}$$

where α is the sticking coefficient, N_{a0} is the total number of water molecules in gas phase, N_{b0} is the total number concentration of sulphuric acid molecules in gas phase, Z is the the Zeldovich nonequilibrium factor, θ is the angle between the direction of growth at the saddle point and the n_a axis, and m_b is the mass of sulphuric acid molecule. The correction factor C_h due to hydration (Jaecker-Voirol et al. 1987) is

$$C_h = \left[\frac{1 + K_1 p_{a,sol} + \cdots + K_1 K_2 \times \cdots \times K_h p_{a,sol}^h}{1 + K_1 p_a + \cdots + K_1 K_2 \times \cdots \times K_h p_a^h}\right]^{n_b}, \tag{13}$$

K_i is the equilibrium constant for hydrate formation, h is the number of water molecules per hydrate.

If the effect of hydrates is also included in the kinetics, the nucleation rate is (Shugard et al. 1974)

$$I_2 = \sqrt{8\pi kT}\, C_h N_{a0} \alpha \frac{Z}{\sin^2(\theta)} \sum_h (\delta^2 \mu^{-1/2} N_h) \exp\left(-\frac{\Delta G^*}{kT}\right), \tag{14}$$

where δ is the sum of radii of the critical nucleus and the hydrate (or a free acid molecule), μ is the reduced mass of the critical nucleus and the hydrate (or free acid molecule), and N_h is the number density of hydrates (see Jaecker-Voirol et al. 1987; Jaecker-Voirol 1988). The sum in Eq. (14) goes over all hydrates (h, 1) including $h = 0$.

Binary Condensation

The condensation rate (C_b) of acid molecules (monodisperse particle concentration N_p) is

$$C_b = N_p \frac{dn_b}{dt}, \tag{15}$$

dn_b/dt (for a liquid droplet of radius r) is obtained by two assumptions. First, since the concentration of water vapour is very high in comparison with sulphuric acid vapour concentration, the new solution droplet is quickly in equilibrium with the water vapour (see e.g. Hamill 1975). Thus the growth of the droplets depends on the absorption of H_2SO_4 molecules into the droplet. Once the absorption has taken place, the composition of the droplet changes. An increase in the weight percentage of H_2SO_4 in the droplet will cause the partial vapour pressure of water above the solution surface to become less than before the absorption. The droplet is now unsaturated with respect to water vapour, and more water vapour molecules can absorb into the droplet until a new equilibrium condition is reached. Secondly, the partial vapour pressure of H_2SO_4 over the surface of the solution droplet is negligible in comparison with the ambient vapour pressure of H_2SO_4.

Since pre-existing particles can be expected to be in the accumulation mode, the continuum and the transition regime condensation theory (see e.g. Wagner 1982) is adopted. Thus

$$\frac{dn_b}{dt} = 4\pi r \beta_M D N_b = B N_b, \tag{16}$$

with the transitional correction factor (Wagner 1982; Smirnov 1971)

$$\beta_M = \frac{K_n + 1}{0.377K_n + 1 + \frac{4}{3}\alpha^{-1}K_n^2 + \frac{4}{3}\alpha^{-1}K_n}, \tag{17}$$

where α is the sticking coefficient and the Knudsen number is

$$K_n = \frac{\lambda_v}{r}. \tag{18}$$

The mean free path of vapour molecules (λ_v) is connected with the diffusion coefficient

$$\lambda_v = 3 \times \sqrt{\frac{\pi m_b}{8kT}} \times D. \tag{19}$$

The diffusion coefficient can be estimated by the method of Fuller et al. (1966) (see also Reid et al. 1987).

Numerical Model

In conditions, where nucleation starts to be significant in the atmosphere, $C_b \gg n_b^* I$. Thus we obtain from Eq. (1)

$$\frac{d}{dt}N_b = Q_b - C_b = k_b[OH][SO_2] - BN_pN_b. \tag{20}$$

Integrating this, assuming B = constant, one obtains,

$$N_b = \frac{k_b[OH][SO_2]}{BN_p} \times [1 - \exp(-BN_pt)], \tag{21}$$

which in steady state gives

$$N_b = \frac{k_b[OH][SO_2]}{BN_p}. \tag{22}$$

In the numerical simulation the nucleation rate is calculated as function of N_b. The factors k_b and B are calculated as function of temperature and pressure. In practice, hydrates will decrease the condensation flux. After present calculations the effect will be 10–15%. The fraction $([OH][SO_2])/N_p(\equiv F)$ is estimated.

In order to calculate the nucleation rate, $\Delta G(n_a, n_b, T)$ at the saddle point has to be determined first. One can construct a table of ΔG as a function of n_a and n_b and the "pass" in the ΔG "mountain" can be found by visual inspection or calculated by a computer. To determine the saddle point one must remember that the factor C_h has also an effect on the location of the saddle point. After that the nucleation rate can be calculated using Eq. (12) or (14).

Values for activities, densities and surface tensions as functions of temperature are needed to calculate ΔG from the hydrates interaction model. In the present chapter, the values are calculated with the same methods that Jaecker-Voirol (1988) has used. The results are compared with the earlier study (Kulmala 1988). The inaccurancy of input parameters will cause the inaccurancy of nucleation rate to be of some orders of magnitude. The saturation vapour pressure measured by Ayers et al. (1980) has been used.

Results and Discussion

The Significance of Binary Nucleation at Atmospheric Conditions

In Finland, the atmospheric concentration of SO_2 in forest area can be around 1–10 μg m^{-3}; corresponding to number concentrations of SO_2 molecules of 10^{16}–10^{17} m^{-3}. According to numerical simulations, the average monthly noontime OH concentration will be from 2×10^{11} m^{-3} (November) to 11×10^{11} m^{-3} (May) at 60° N latitude (Isaksen and Hov 1987, Hov et al. 1988). The corresponding concentrations at 70° N are 0 from October to December, and then increase to 6×10^{11} m^{-3}. The number concentration of aerosol particles varies significantly. In the present chapter, accumulation mode particles ($r = 0.3$ μm) have been chosen to represent the whole aerosol distribution. The number of concentrations of these particles will be from 10^7 m^{-3} to 10^9 m^{-3}, which corresponds to a mass concentration of 1 μg m^{-3} to 100 μg m^{-3}. Thus F ranges between 10^{18} and 10^{22}. Typical noontime values will be from 10^{19} to 10^{21}.

The assumption of constant particle radius and constant B is sufficient, since the radius of the particle will increase less than 10% during more than 2 h. In this timescale (2 h) nucleation will be significant if the number concentration of particles is affected clearly. Thus the nucleation rate should be more than 10^3 m^{-3} s^{-1} if the number concentration of pre-existing particles is 10^7 m^{-3}.

According to the present simulations the formation of new particles by binary nucleation of sulphuric acid–water vapours will be effective enough in different atmospheric conditions (Figs. 1–7). The significance of the nucleation rate depends on F, relative humidity and temperature.

At −25°C a realistic value for relative humidity is from 80 to 100%. For new particle formation F must be about 10^{19} or more (Fig. 1).

At −15°C significant nucleation will occur when F is more than 10^{20} and relative humidity above 60%. At −5°C formation of new particles is notable at all relative humidities above 40% when F is 10^{21}. If F is 10^{20} and the sticking coefficient has a value of 0.06, nucleation will be important at relative humidities above 60% (Fig. 2).

At temperatures of 5 and 15°C (Fig. 3) and at 25°C (Fig. 4) nucleation will be significant at relative humidities above 40% if F is 10^{22} and the sticking coefficient has a value of 0.06. If F is 10^{21} and the sticking coefficient is 1.0 the nucleation is notable only at 5°C and at relative humidities of 60% or more.

The effect of temperature on nucleation is presented in Fig. 5. At −15°C and at 80% relative humidity significant nucleation occurs when F is about 10^{20} or more and at +5°C about 10^{21} (Fig. 5). At +25°C F must be at least near 10^{22}, which is an unrealistic value.

The nucleation rate depends strongly on F (see Figs. 6 and 7). When F increases by three orders of magnitude, the nucleation rate will increase by more than ten orders of magnitude.

The overall conclusion is that the most effective conditions for formation of new particles is during springtime, when [OH] and [SO_2] concentrations are high and temperature is low enough.

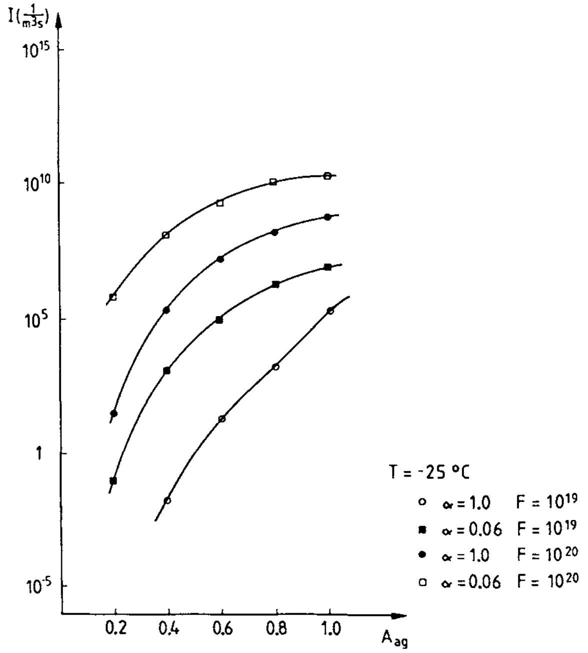

Fig. 1. Binary nucleation rate for water-sulphuric acid system as a function of water gas phase activity (A_{ag}) at −25°C. The values of F are 10^{19} and 10^{20} and the sticking coefficients 1 and 0.06

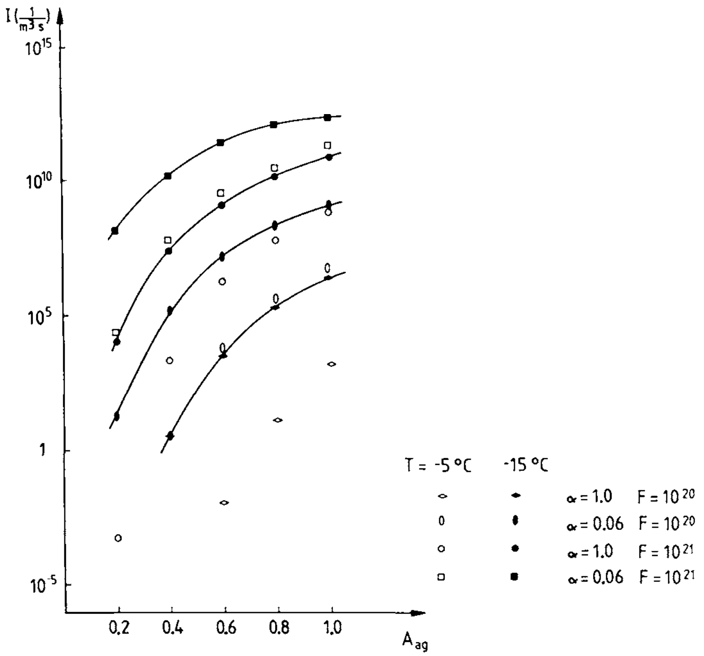

Fig. 2. Binary nucleation rate for water-sulphuric acid system as a function of water gas phase activity (A_{ag}) at −15°C and −5°C. The values of F are 10^{20} and 10^{21} and the sticking coefficients 1 and 0.06

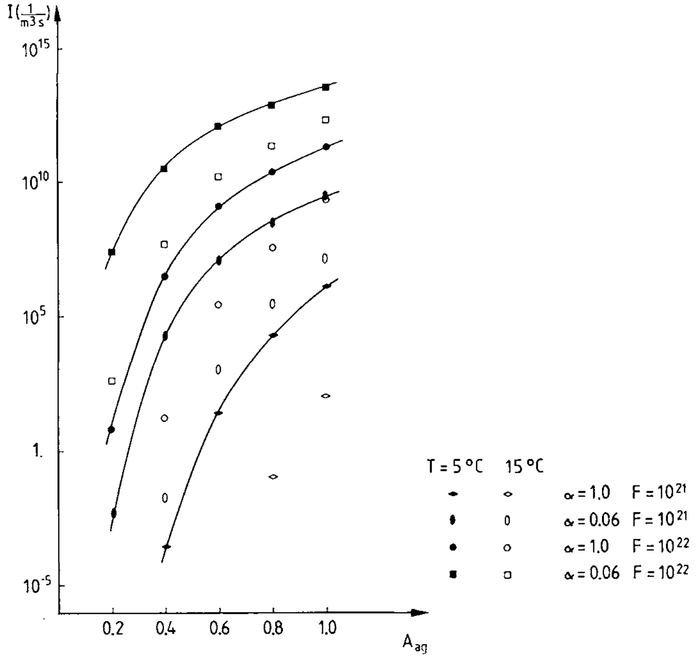

Fig. 3. Binary nucleation rate for water-sulphuric acid system as a function of water gas phase activity (A_{ag}) at 5°C and 15°C. The values of F are 10^{21} and 10^{22} and the sticking coefficients 1 and 0.06

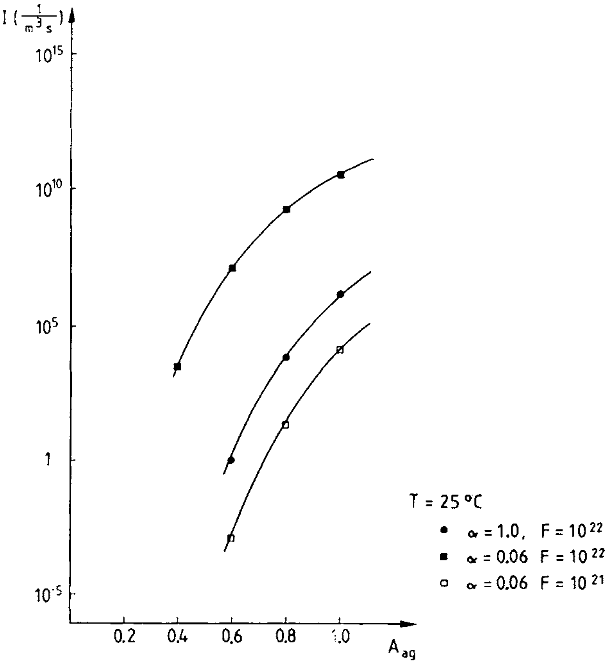

Fig. 4. Binary nucleation rate for water-sulphuric acid system as a function of water gas phase activity (A_{ag}) at 25°C. The values of F are 10^{21} and 10^{22} and the sticking coefficients 1 and 0.06

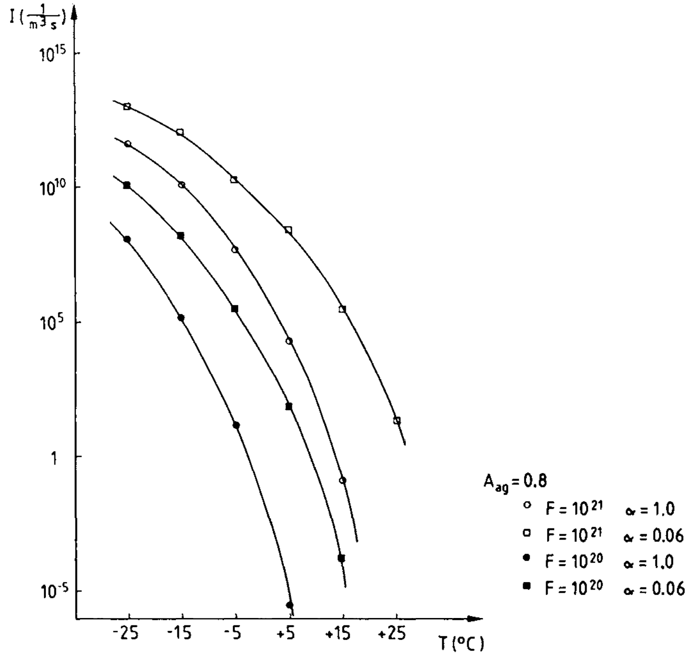

Fig. 5. The effect of temperature on the binary nucleation rate for water-sulphuric acid system at 4 different monomer concentrations. A_{ag}=0.8. The values of F are 10^{21} and 10^{22} and the sticking coefficients 1 and 0.06

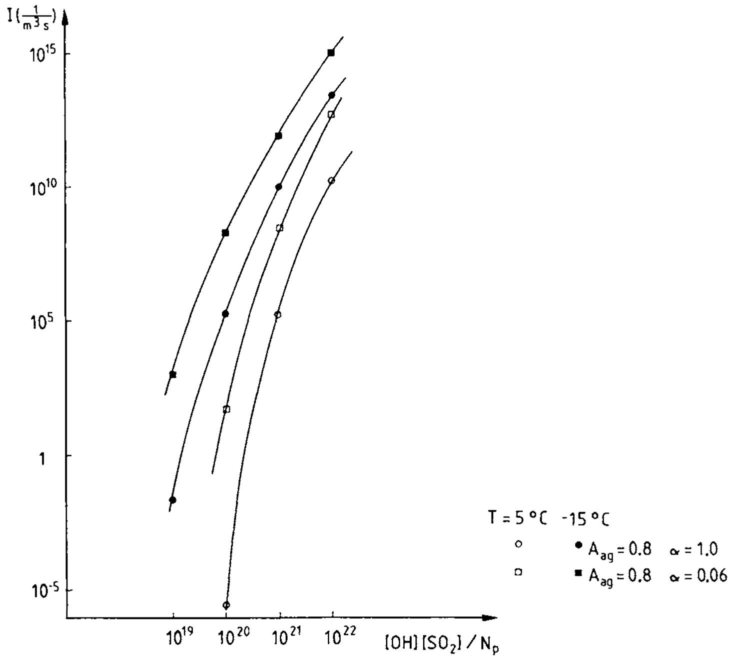

Fig. 6. Binary nucleation rate for water-sulphuric acid system as a function of F at −15°C and 5°C. A_{ag} is 0.8. The sticking coefficients are 1 and 0.06

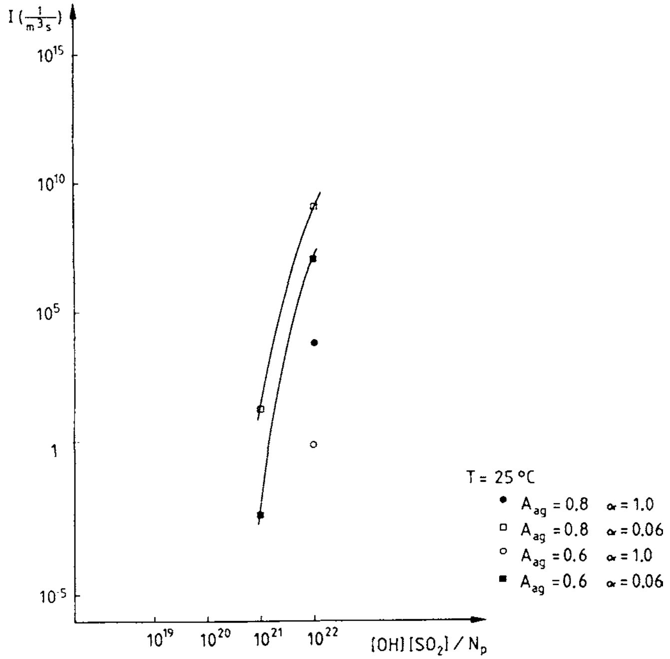

Fig. 7. Binary nucleation rate for water-sulphuric acid system as a function of F at 25°C. A_{ag} 0.6 and 0.8. The sticking coefficients are 1 and 0.06

The Sticking Coefficient

The value of the sticking coefficient for sulphuric acid is not well determined. However, recently Van Dingenen and Raes (1988) have measured the sticking coefficient to be 0.06. In the present simulations this value and the value 1.0 are compared. Although the same sticking coefficient works on both nucleation and condensation, the overall effect will be to increase nucleation rate when the sticking coefficient is decreasing. The reason for this is that the steady state sulphuric acid concentration is about five times higher, when α is 0.06.

The result of the simulation is clear. With a smaller sticking coefficient the significant nucleation will begin with a two or three times smaller value of F (see Figs. 1–7).

Nucleation Rate and Composition of New Particles

Nucleation rate increases very rapidly when gas phase activity increases. For example, at 248.15 K ($H_2O + H_2SO_4$) with $A_{bg} = 0.01$ and A_{ag} increasing from 0.2 to 0.8, nucleation rate increases by a factor of 3×10^6. When A_{bg} increases from 0.001 to 0.01 ($A_{ag} = 0.8$, $T = 248.15$ K) nucleation rate increases by a factor of 8×10^4.

According to the classical theory the physical diameter of critical clusters or new particles is 1–2 nm. The number fraction of sulphuric acid molecules in these particles varies from 0.15 to 0.25. The critical energy barrier at saddle point ($I = 10^6\ m^{-3}\ s^{-1}$) is 30–40 kT for sulphuric acid plus water system.

Conclusions

The above calculation is only a simple estimation of the real situation and more realistic simulations are needed. Nevertheless, the calculation shows that in some practical situations, sulphuric acid molecules may form new particles together with water molecules. The nucleation rate is high enough to double the number of particles during some hours. Thus the dynamical behaviour of acid aerosols and also the acid deposition will change. Especially in Southern Finland during springtime this process can be significant. On the other hand, e.g. nitric acid molecules can only absorb into existing droplets, since binary nucleation of H_2O–HNO_3 vapours is very unlikely in the lower atmosphere (see e.g. Kulmala 1988).

In conditions where OH and SO_2 concentrations are higher (e.g. at edge of plume and in the Central Europe) the formation of new particles will be more effective.

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Nomenclature

The following symbols are used in the text most frequently.

Symbol	Meaning
A_i	chemical activity
C	kinetic prefactor of nucleation rate
C_i	condensation rate
C_h	correction factor due to hydration
d	diameter of a particle
D	diffusion coefficient
F	fraction of OH + sulphur dioxide concentration per particulate number concentration
G	Gibbs free energy
I	nucleation rate
k	Boltzmann constant
k_b	rate constant of H_2SO_4 formation
K_n	Knudsen number
m	mass of a molecule
n	number of molecules in a cluster
N_b	number concentration of acid vapour molecules
N_p	number concentration of aerosol particles
p	vapour pressure
p_s	saturation vapour pressure
Q	source term
r	radius of a particle
R	gas constant, 8.314 J/mole K
t	time
T	temperature
Z	Zeldovich's nonequilibrium factor
α	sticking coefficient
β	transition coerrection factor for condensation flux
λ	mean free path
μ	chemical potential
ρ	density
σ	surface tension

subscripts

a	water
b	acid
d	droplet
g	gas
gtp	gas-to-particle
i	index
l	liquid
p	aerosol particles
s	saturation
sp	saddle point
v	vapour

superscripts

*	critical property

Characteristics of Alkaline Emissions, Atmospheric Aerosols and Deposition

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Summary

This chapter summarises the sources of alkaline aerosols in Finland. Annual total emissions are estimated in order to find the largest sources. For the use of receptor-oriented models the percent compositions of elements (source profiles) of the important sources are given.

The source apportionment of aerosols is examined in four case studies. Aerosol concentration measurements are combined with the source profiles with enrichment factors in order to find the possible sources of aerosols. The method of factor analysis is also used to study the source relationships between aerosol components. Finally, the deposition of alkaline substances is shortly discussed.

The main sources of alkaline aerosols in Finland are soil dust, energy production, industrial processes, traffic and seawater. Of the anthropogenic sources, combustion of wood and dust raised by traffic are the biggest single sources in Finland. However, in aerosol concentration measurements no significant deviations from well-mixed mineral aerosols was found. But in stations in southern Finland a strong connection between sulphate and alkaline aerosols was found. These preliminary data suggest that at least in the Helsinki region energy production may influence the circulation of alkaline aerosols, while in more remote parts of the country mineral background aerosol seems to be prevalent.

Introduction

Alkaline substances affect soil acidification in two ways. First they can significantly influence precipitation acidity by neutralizing some fraction of the acids. Secondly they are crucial elements in the modified cation exchange processes in soil caused by acidification. As water containing H^+ ions moves through soil, some of the hydrogen ions replace adsorbed exchangeable cations such as Ca^{2+}, K^+ and Mg^{2+}, which are macronutrients of vegetation. These species may eventually be leached into ground-water, thus resulting in a loss of these nutrients from the root zone of the soil. Weathering of soil particles and atmospheric deposition are sources of new cations. In soils where the mineral content and weathering rate are small, atmospheric deposition may be a considerable source of new base cations.

Kauppi et al. (Eds).
Acidification in Finland

Alkaline aerosols are introduced into the atmosphere from open sources like traffic, wind erosion and agriculture or from industrial sources like fuel combustion, sulphate pulping, clay products manufacture, cement and concrete processing, solid waste disposal and iron and steel manufacture. Emissions occur as aerosols of different sizes and shapes. The potential influence of this material on acidification depends on the chemical composition of the particles and their solubility and chemical stability in the atmosphere and in soil. In order to assess the significance of these questions it is important to obtain quantitative information about emissions, atmospheric concentrations and size fractions of alkaline aerosols, transport and wet and dry deposition flux.

Conventional dispersion models have been used to simulate the atmospheric behaviour of sulphur and nitrogen compounds. Base cations are emitted into the atmosphere as alkaline aerosols of various sizes and chemical composition. Dispersion models to simulate their behaviour should include emission rates of point, line and area sources, mathematical representations of meteorological dispersion and chemical reactions in the atmosphere, and all this for different size fractions and chemical compounds. No such models yet exist.

Source apportionment of aerosols is frequently made with receptor-oriented models (e.g. Henry et al. 1984; Stevens and Pace 1984). These models identify and quantify the sources of ambient aerosols at a receptor primarily on the basis of concentration measurements made at the receptor site. In these models valid source compositions (often called source profiles) for the specified sources and species are needed as input. The aerosol properties that are used as input to receptor models include particle size, usually divided into a fine and coarse fraction and elemental and ionic composition. Regional applications of receptor models are only now under development (e.g. Lowenthal and Rahn 1988; Dutkiewicz et al. 1987).

This chapter summarizes the sources of alkaline aerosols in Finland. The source inventory consists of two parts: Annual total emissions (source strengths) are estimated in order to find out the greatest sources. For the use of receptor-oriented models the percent compositions of elements (source profiles) of the important sources are given.

The source apportionment of aerosols is examined in four case studies. Aerosol concentration measurements at two urban and two rural sites are combined with the source profiles with enrichment factors in order to find the possible sources of aerosols. The method of factor analysis is also used to study the source relationships between aerosol components at these four sites.

Finally, the deposition of alkaline substances is shortly discussed.

Emissions of Alkaline Aerosols in Finland

This inventory includes energy production with coal, peat, wood and black liquor of sulphate pulping, clay products manufacture, cement and concrete processing, iron and steel manufacture, soil dust raised by traffic, wind-blown dust, dust from agricultural land and sea salt. For industrial sources the source strengths (on an annual basis) can be obtained, while for natural open sources in particular only percent composition of the emission is obtained. Source strengths are used to estimate the most important potential sources of alkaline deposition. Source profiles (percentage fraction of primary particle emission) are used in source apportionment of aerosols.

Industrial Sources

Fly ash emission from energy production was 63,000 tons in 1987 in Finland (Hupa et al. 1988). This estimate includes the emissions from oil, coal, peat and wood combustion and also the emissions from furnaces in the pulp industry, the sintering process in the iron and steel industries, cement and lime kilns and smelting furnaces of glass wool production.

Wood combustion in small (below 1 MW, including residential) heating ovens was the largest emission source of particles in Finland (Hupa et al. 1988). The total particulate emission from wood combustion was about 20,000 tons, emissions from black liquor combustion in the pulping industry was about 12,000 tons and fly ash emission from coal combustion was about 9000 tons. The remainder of the total emissions comes from oil and peat combustion and industrial furnaces.

The percent composition of particulate emission and annual elemental emissions from oil, coal, peat and wood combustion are presented in Table 1. Emission factors for coal and peat combustion are based on Finnish studies (Hupa et al. 1988, Pohjola et al. 1983) and emission factors for wood combustion are from Nilsson and Timm (1983). Emission factors for Cl and Si are from Javitz et al. (1988). For comparison, the emissions of gaseous nitrogen and sulphur are also given in Table 1.

The accuracy of the SO_2 and NO_2 emission estimates is about 10% and the accuracy of total particle emissions is about 30% (Hupa et al. 1988).

Total particle emissions of black liquor combustion in sulphate pulp mills were about 12,000 $t\ a^{-1}$ (Hupa et al. 1988). Na emission from this source can be as high as 5000–10,000 tons annually, while Ca, Mg and K are minor components. This estimate is based on the elemental concentrations of the fuel given in Hupa et al. (1988). However, no quantitative estimates can be made of the elemental percent composition of this source category. Total particle emissions from industrial furnaces like the sintering process in the iron and steel industry, cement and lime kilns and smelting furnaces of glass wool production were about 22,000 tons. In many of these processes Ca is used as a raw material or as an additive and these sources are potential sources of Ca-rich emissions. Based on the national emission inventories made at the end of the 1970's (Ministry of the Interior 1981) annual emissions are Ca: 2500 tons, K: 400 tons and Mg: 300. However, very few experimental data are available about the elemental emissions from these sources, and these figures should be regarded only as indicative.

Table 1. Percent composition (Hupa et al. 1988; Pohjola et al. 1983; Nilsson and Timm 1983; Javitz et al. 1988) of primary particulate mass emitted and total annual emission of elements from oil, coal, peat and wood combustion in 1987 in Finland

Element	Oil		Coal		Peat		Wood	
	%	t a^{-1}	%	t a^{-1}	%	t a^{-1}	%	t a^{-1}
Na	2.0–4.8	70	0.55–1.1	51	0.21–1.0	31		
Mg	0.03	6	2.2–4.5	210	1.3–3.6	110	2.1–5.2	1030
Si	2.8	93	21.9	2020				
Cl			0.052	4.8			0.51	102
K			1.3	120	1.7	50	7.0–15	3070
Ca			4.7	430	15.0	450	24 –29	4930
V	1.2	40	0.074	6.8	0.02	0.60	0.13	26
Cr	0.0012	0.04	0.018	1.7	0.0063	0.19	0.004	0.8
Fe	1.3	40	3.6	510	5.1	120	1.2	240
Ni	0.38	12.0	0.019	1.8	0.023	0.7	0.041	8.3
Zn	0.057	1.8	0.062	9.0	0.13	3.0		
As	0.0027	0.09	0.0060	0.55	0.011	0.33	0.0025	0.5
Cd	0.0001	0.01	0.0035	0.32	0.001	0.03	0.00095	0.19
Pb	0.027	0.9	0.054	5.0	0.02	0.60	0.034	6.8
N (gas)		2430		11470		3560		3260
S (gas)		16750		33050		4600		14600

The chemical compounds emitted from the industrial sources are numerous. For example fly ash from coal combustion is mainly silicate mineral particles with diameters around 1 μm (Mamane et al. 1986). Aerosol emissions from wood combustion are mainly silicates and oxides (e.g. Nilsson and Timm 1983) and emissions from industrial processes are sulphates, carbonates, oxides or organic material depending on the process. The dissolution of these particles into water is a function of time, solution pH and aerosol mass loading (Williams et al. 1988).

In summary, the greatest single industrial source of alkaline aerosols in Finland is wood combustion in small furnaces. The magnitude of industrial alkaline emissions is roughly one-tenth of the emissions of sulphur (Savolainen and Tähtinen this Vol.) and about ten times bigger than emissions of Pb and Mn (Hupa et al. 1988) in Finland.

Traffic

Particulate emissions from vehicle exhaust in 1987 in Finland were about 10,000 tons. This emission contains insignificant amounts of inorganic ash and alkaline aerosols.

More important in this connection is the soil dust raised by vehicles. The passage of a vehicle along a road can cause the surface material to be resuspended either by the shearing stress of the tires or by induced turbulence (Sehmel 1980). Barnard and Stensland (1986) present data which show that unpaved roads can be

Table 2. Percent composition (Koljonen et al. 1989) of primary particulate mass emitted and total annual emission of elements from road dust raised by vehicles in 1987 in Finland

Element	Road dust	
	%	$t\,a^{-1}$
Na	2.33	6100
Mg	1.04	2700
Al	7.42	19000
Si	29.8	77000
P	0.0695	200
S	0.0198	50
K	2.13	5500
Ca	1.81	4700
Ti	0.4	1000
V	0.0083	20
Cr	0.0091	20
Mn	0.0516	100
Fe	3.63	9400
Ni	0.0037	10
Zn	0.0094	20

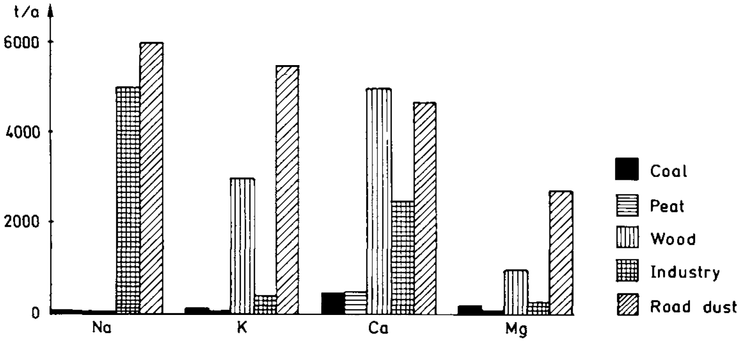

Fig. 1. The annual emissions of Na, K, Ca and Mg from coal, peat and wood combustion, industrial processes and road dust in 1987 in Finland

the most significant source of alkaline materials to the atmosphere in the U.S.A. In Finland this emission is estimated to be about 260,000 tons annually, of which about 100,000 tons is from gravel roads, about 70,000 tons from paved roads, and about 86,000 tons from sanding of roads (Ministry of Transport and Communications 1988).

The percent composition of this source category should be determined by using elemental concentrations of roads and urban soils (Batterman et al. 1988). In particular, concentrations of trace metals and carbon in road dust and urban soils are different from average soils, which should be taken into account in local scale receptor studies at least. In Finland this kind of data is not available; instead the elemental composition of average till in Finnish soils is used (Koljonen et al. 1989) (Table 2). The annual emissions of Na, K, Ca and Mg from coal, peat and wood combustion, industrial processes and traffic are summarized in Fig. 1. The accuracy of the emission estimates of coal, peat and wood combustion is about 50%, while estimates of industrial processes and traffic are more uncertain. According to this estimate, the greatest anthropogenic sources of alkaline elements are road dust emission and wood combustion.

Open Sources

The suspension of particulate material from soils into the atmosphere through erosion and soil transport has been known for a long time (e.g. Bagnold 1941). More recently, interest has centred on the resuspension of toxic or nuclear waste material rather than bulk soil erosion (Sehmel 1980; Nicholson 1988). Suspension of soil particles into the atmosphere is important for acidification processes in soils and in the atmosphere because certain alkaline and earth alkaline elements are very abundant in crustal dust. Material suspended from soil and again redeposited can form a great fraction of the total deposition of alkaline material to the soil. This small-scale resuspension and redeposition is a confounding factor in most acidification studies and needs to be understood. Suspension or resuspension of particles from soils and other surfaces like water and vegetation can be produced by wind and mechanical disturbances. Mechanical disturbances include, for example agriculture. Although a wide variety of resuspension experiments have been reported, there is no widely accepted way to calculate the environmental parameters of resuspension (Nicholson 1988). As a result, in this study only the percent compositions of the emissions can be given.

Soil Dust and Agricultural Dust

The outermost layer of the earth's surface consists of various sedimentary rocks whose elemental composition varies a great deal. For example, the Ca content in sedimentary rocks varies from about 30% in limestone to 1–2% in clay (Mason 1958).

It would be ideal to have detailed information of the local geochemistry in every study. This is seldom possible and a common approach in receptor studies is to use crustal averages (e.g. Javitz et al. 1988; Fidalgo et al. 1988; Schneider 1987; Braaten and Cahill 1986; Marshall et al. 1986). In this work it is possible to use Finnish crustal averages (Table 2), which are slightly different from global averages. Based on the national geochemical mapping of till made by The Finnish Geochemical Survey (Koljonen et al. 1989), K, Ca, Mg and Fe concentrations are slightly lower and Si concentrations higher than crustal averages.

Dust emissions from agricultural land cannot reliably be estimated with average till concentrations. Total elemental concentrations of cultivated soils in Finland have not been published. Erviö et al. (this Vol.) give extractable mineral element concentrations of Finnish agricultural soils. Their results show that cultivated lands are enriched with soluble Ca when compared to crustal averages. The concentration of soluble Ca is about ten times higher than that of K and Mg. This relation is different from the elemental relation in crustal averages (see Table 2). Cultivated lands in Finland are limed annually with about 1 million tons of calcium carbonate (J. Kivistö 1989) of which the Ca content is about 400,000 tons.

Vegetation

Most of the land area in Finland is covered by vegetation in summer and snow in winter. Lindberg et al. (1986) propose that K in particular has considerable in-canopy sources. The material emitted from vegetation could consist of weathered leaf cuticle, leaf hairs and pollen (Lindberg et al. 1986). Examples of the average elemental concentrations of vegetation are given in Table 3. Elemental concentrations of vegetation vary spatially and temporally a lot. These examples are averages from several hundred analyses, and show that K is enriched in vegetation when compared to crustal averages.

Sea Salt

Sea salt comprises a major fraction of the particulate material in the global troposphere. The tropospheric marine aerosol is composed largely of sea salt, but

Table 3. Percent composition of needles (Veijalainen 1977) and timothy (Kähäri and Nissinen 1978) in Finland

Element	Needles [%]	Timothy [%]
Mg		0.1
Al	0.028–0.064	0.001
Si	0.04–0.06	
P	0.09–0.17	0.3
S	0.09–0.13	0.1
Cl	0.04–0.08	
K	0.26–0.69	2.2
Ca	0.12–0.37	0.2
Mn	0.012–0.04	0.005
Fe	0.007–0.021	0.004
Cu	0–0.001	0.0004
Zn	0.0020–0.015	0.002

Table 4. Percent composition of sea salt (Mason 1958)

Element	[%]
Cl	55.05
Na	30.61
SO_4	7.68
Mg	3.69
Ca	1.16
K	1.10
HCO_3	0.41
Br	0.19
H_3BO_3	0.07
Sr	0.03

tends to show depletion of chloride and enrichment of sulphate relative to bulk seawater values. However, in source – receptor studies, the composition of bulk sea salt is often used (Table 4). Sea salt particles are produced by bubbles bursting at the sea surface.

Suspended Aerosol Particles: Measurements and Possible Sources

Concentrations of suspended aerosol particles were measured at two sites in southern and two sites in central Finland. The main characteristics of the sampling sites are the following:

Vuosaari, (here Urban 1) is a coastal suburban area in Helsinki. The largest emission sources in this area are energy production by coal and traffic. The annual average of the SO_2 concentration in this area is about 20 $\mu g\,m^{-3}$. The sampling site was on the eastern periphery of the town and the samplers were placed about 15 m above ground level. Measurements took place from August 14 to September 8, 1985. Twenty six daily samples were collected and analyzed. More details about the measurements can be found in Kulmala et al. (1986).

Site Urban 2 is not one specific sample area but a collection of separate sites, each of which is characterized by a strong influence of traffic. The samples were collected near the main roads of the region of Helsinki. Forty-two daily samples were taken between May 28 and June 26, 1986.

Vilppula (Rural 1) is located in a forested area in central Finland. This site is a field station of the Finnish Forest Research Institute (Pätilä 1987). The nearest significant industrial emission sources are 50 km east in the town of Mänttä. The pulp and paper industry in Mänttä is one of the greatest particle emitters in Finland (R. Pesonen 1989). The annual average SO_2 concentration in this area is about 2 $\mu g\ m^{-3}$ (R. Pesonen 1989). Possible natural emission sources in this area are soil dust and vegetative dust. The sampling site was inside the forest (mainly sparse pine trees), about 1.5 m above the soil level. Measurement dates were September 3–30, 1987. Twenty-nine daily samples were collected and analysed.

Hyytiälä (Rural 2), (Forest Field Station of the University of Helsinki) is located 50 km to the south of Vilppula. Nearest significant industrial emission sources are the towns of Mänttä, Jämsä and Tampere at distances of 30–50 km. When compared to the site Rural 1 this site is more affected by human activities. At this site also wood combustion and agriculture may have an influence on air quality. Natural emission sources are soil dust and vegetative emissions. Measurement dates were June 23–25 and August 11–13, 1986. Thirty samples were collected.

Suspended particles were collected on stacked filters. With this method particle concentrations of both fine (<2.5 μm) and coarse particles are obtained. Collection times were 8 h at urban sites and 12–24 h at rural sites. Elemental analysis of the particulate matter was done using the PIXE method at the Tandem van de Graaf accelerator of Helsinki University (Raunemaa et al. 1981, 1989). Arithmetic means of the elemental concentrations of fine and coarse particles are presented in Fig. 2.

Elemental detection limits in this analysis were 50 $ng\ m^{-3}$ for Si, 10 $ng\ m^{-3}$ for S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn and 100 $ng\ m^{-3}$ for Pb. Concentrations of Ni, Cu and Zn at site Urban 1 are at the detection limit of the method for both fine and coarse particles, and at the rest of sites these four elements were not detected at all. Also, the concentrations of fine K and Ca at both rural sites and Fe at site Rural 1 approach the detection limit. Elements listed in Fig. 2 constitute 12–25% of the total mass of their size fraction. The rest of the mass comes from lighter elements like C, N, Na, Al and O.

Average concentrations of Si, K, Ca and Fe are higher in the coarse particles than in the fine particles. Only for S the fine fraction concentration exceeds the coarse fraction concentration at all sites. These results are quite predictable and are due to the different processes leading to aerosol formation. Particulate sulphate is formed by gas to particle formation from gaseous SO_2 and is accumulated in the

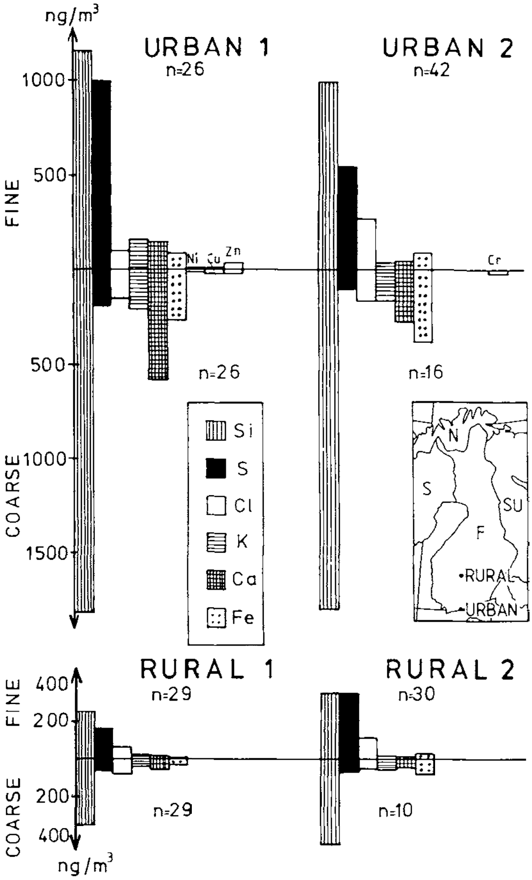

Fig. 2. Arithmetic means of the elemental concentrations of fine and coarse particles

fine particle fraction. Si, K and Ca are usually suspended from soil by mechanical agitation and are likely to be in coarse particles. Concentrations are higher at the coastal urban sites 1 and 2 than at the inland background sites Rural 1 and Rural 2.

Cl originates primarily from the sea and is usually found in coarse particles. The slightly increased Cl concentration in fine particles at site Urban 2 is evidently due to car exhaust. Particle-Cl concentrations as high as 4000–6000 ng m^{-3} are usual in coastal regions (McWilliams and Sealy 1987; Kronborg et al. 1987; Wiman and Lannefors 1985). The coastal sites Urban 1 and 2 were at the distances of 5–15 km from the coast and the chlorine concentrations were far below these maximum values. Surprisingly, the chlorine concentrations at sites Rural 1 and 2 are not negligible, but approximately half of the values found at the coastal sites Urban 1 and 2. Joffre et al. (this Vol.) present similar relationship of Cl-concentrations in precipitation at the coastal station of Virolahti and the inland station of Ähtäri.

Enrichment Factors

Although these data are limited and represent only summer and autumn seasons of the year, we shall examine some details of the relationship between emissions and aerosol concentrations. We shall start with crustal sources and use the data to investigate whether additional sources are important.

Soil particulate material within the size range $r < 10$ µm is rather homogeneously mixed and most elements are found in crustal proportions (Schütz and Rahn 1982). This result is often exploited by calculating so-called enrichment factors with respect to the earth's crust.

Enrichment factors ef_i are calculated from

$$ef_i = \frac{c_i/c_r}{a_i/a_r},$$

where c_i and c_r represent aerosol concentrations of an element i and reference element r, a_i and a_r are the concentrations of the elements in the earth's crust. Factors greater than 5–7 are considered to be evidence of other than crustal sources (Rahn 1976). Here we have calculated the enrichment factors with respect to the earth's crust for both fine and coarse particles. Fe is used as a reference element and the elemental concentrations in the Finnish till (Koljonen et al. 1989) (see Table 2) are used. Enrichment factors of all samples are given in Figs. 3–6.

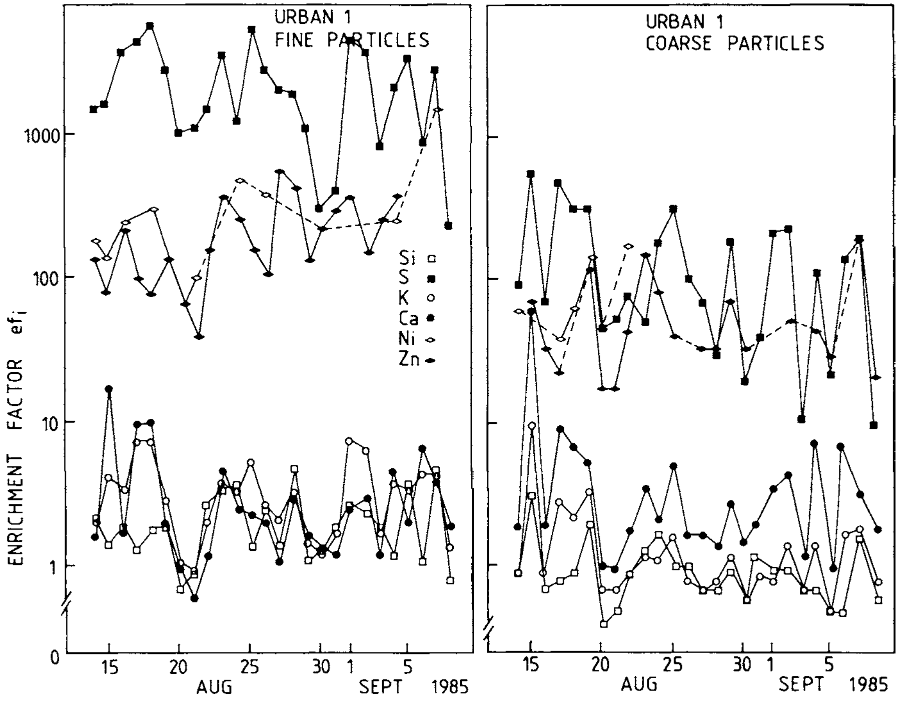

Fig. 3. Enrichment factors of elements with respect to the earth's crust at site Urban 1

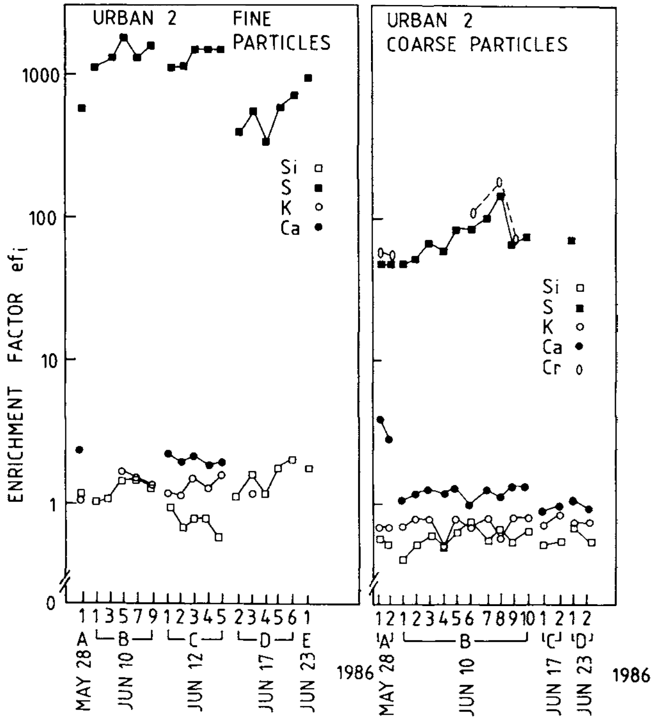

Fig. 4. Enrichment factors of elements with respect to the earth's crust at site Urban 2. Letters *A*, *B*, *C*, *D* and *E* refer to different sampling locations

In spite of the great differences between the sampling sites and concentration levels, the enrichment factors of elements behave very similarly. In all samples, S has distinguishably high enrichment factor values, 1000–3000 in fine particles and 50–400 in coarse. Also the enrichment factor values of Zn, Ni, Cr are high, 20–40, in both fine and coarse particles. These elements evidently have other than crustal sources.

Despite the enrichment factor of Si, K and Ca are clearly closer to unity. At sites Urban 2 and Rural 2 the limit value 7 is not exceeded at all. At site Rural 1 the limit value 7 is exceeded a few times (fine K twice, fine Ca once, coarse Ca four times). However, the concentration of the reference element Fe (see Fig. 2) at site Rural 1 is very close to the detection limit and the result should be considered with caution.

At site Urban 1 enrichment factors are on the average little higher than in the rest of the stations and especially Ca concentrations show little enrichment. In source-receptor studies of urban areas (e.g. Javitz et al. 1988; Kowalczyk et al. 1978) as much as 60–80% of the alkaline aerosol has been attributed to other sources than soil. Site Urban 1 is the place where such a situation could also be possible, as the main emission sources of this area are traffic and coal combustion. However, because coal fly ash is mainly alumino-silicate particles whose bulk is

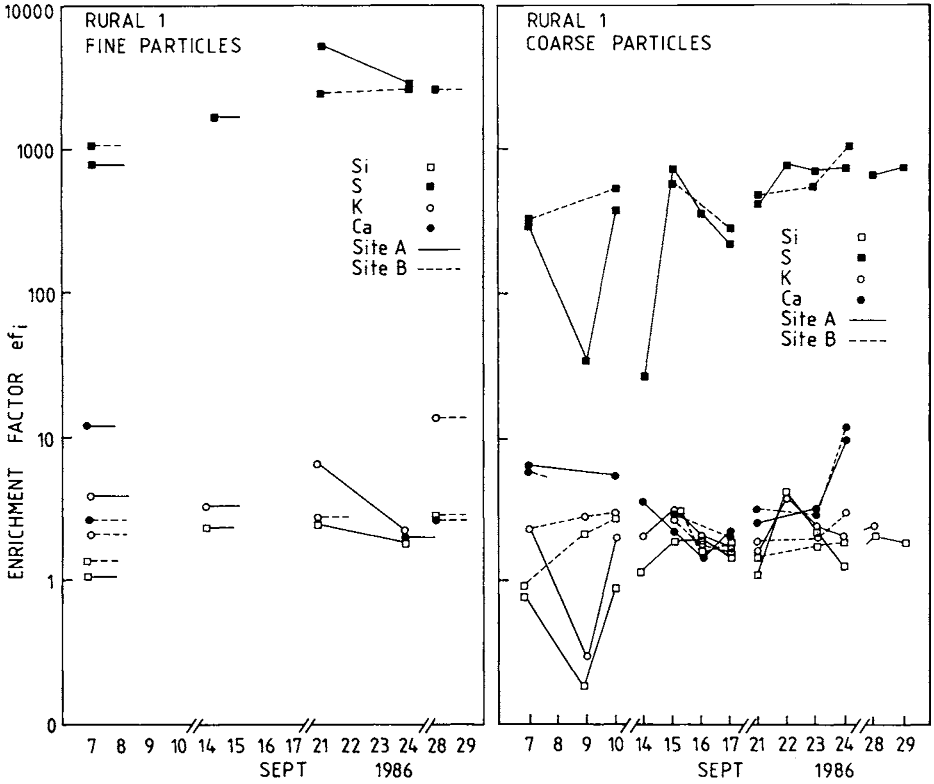

Fig. 5. Enrichment factors of elements with respect to the earth's crust at site Rural 1. Letters *A* and *B* refer to two different sampling locations

very similar to the earth's crust (see Tables 1 and 2), it is impossible to use only bulk compositional data to resolve coal fly ash from soil dust. So it is possible that alkaline aerosol here is a mixture of anthropogenic fly ash from coal combustion and soil dust.

Factor Analysis

A factor analysis of the element concentrations of fine and coarse particles was performed for all stations to investigate source relationships between aerosol components. The method of principal factor analysis (PFA) with Varimax rotation was used. Examples of the use of factor analysis methods in atmospheric applications are given by Hopke et al. (1976), Heidam (1981) and Marshall et al. (1986). Generally these studies attempt to classify elements into groups which, due to their composition, can be attributed to certain sources.

The calculated Varimax rotated factor loadings of elements are given in Tables 5, 6, 7 and 8. The number of factors retained was primarily decided so that it was

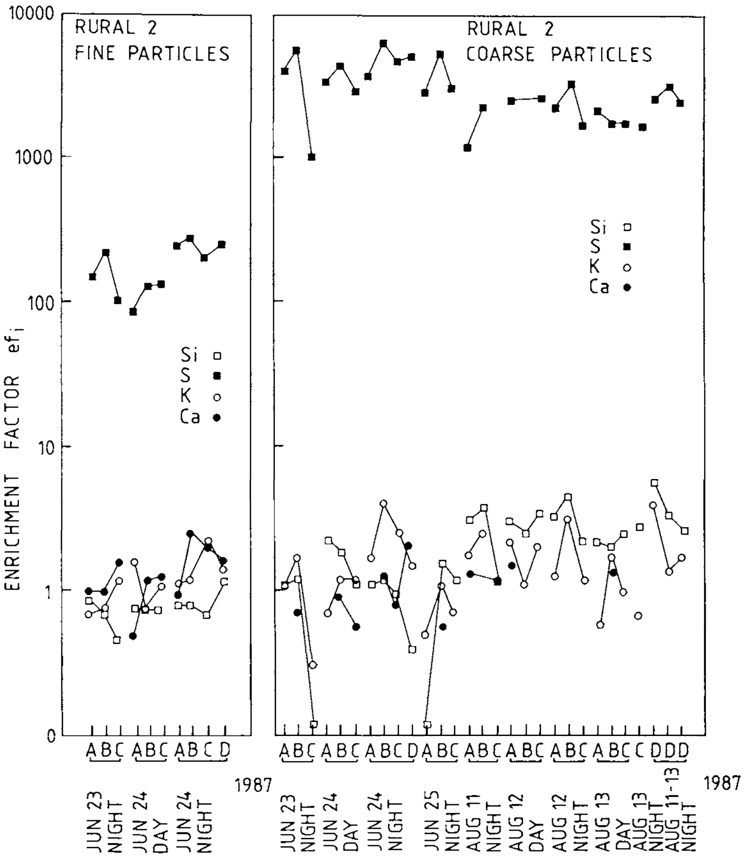

Fig. 6. Enrichment factors of elements with respect to the earth's crust at site Rural 2. Letters *A*, *B*, *C*, *D* refer to different sampling locations

possible to interpret the factors as sources pertinent to the physical environment, whereas statistical tests were considered secondary.

At site Urban 1 three factors are used to describe the fine particle data. From the estimated factor loadings it is seen that the total mass of suspended fine particles (TSP), S, K and Ca were highly correlated to the same hypothetical source. Energy production by coal and fuel oil is a source of TSP and S. However, as much as 85% of the total variance of K and 60% of the variance of Ca is explained by this *energy* factor.

The second factor correlated highly with Si and Fe and it is called *soil dust*. K and Ca have only low loadings in this factor. The third factor correlates highly with Ni and Cu which may be due to analytical uncertainty rather than sample by sample variations. The concentrations of Ni, Cu and Zn were at the detection limit of the analysis method. Cl does not correlate with any of these factors and it is presumably due to sea salt.

Table 5. Factor loadings and communalities for the elements at site Urban 1

	Fine particles				Coarse particles				
	Energy	Soil dust	Unknown	Comm[b]	Energy	Soil dust	Unknown	Sea salt	Comm
TSP	**0.87**[a]	0.030	0.08	0.77	0.46	**0.81**	−0.22	0.11	0.92
Si	0.30	**0.76**	0.35	0.79	0.37	**0.83**	0.26	−0.03	0.90
S	**0.85**	0.14	0.32	0.85	**0.90**	0.12	0.10	−0.08	0.93
Cl	−0.36	−0.15	0.02	0.15	0.12	−0.08	−0.00	**0.75**	0.58
K	**0.93**	0.24	0.17	0.96	**0.84**	0.46	0.13	0.14	0.97
Ca	**0.83**	0.28	0.23	0.72	**0.81**	0.32	−0.02	0.41	0.97
Fe	0.23	**0.85**	0.041	0.78	0.10	**0.74**	0.21	−0.4	0.75
Ni	−0.037	0.25	**0.72**	0.59	0.16	0.15	0.19	−0.04	0.09
Cu	0.21	0.04	**0.58**	0.39	0.11	−0.03	**0.69**	−0.16	0.54
Zn	0.085	−0.06	0.08	0.02	−0.02	0.16	**0.53**	0.18	0.37
Var[c]	3.27	1.55	1.19	6.02	2.58	2.29	1.00	0.9	7.02

[a] Confidence level over 99% bold type.

[b] Comm = communality.

[c] Var = variance explained by each factor.

The coarse particle data is described with four factors. The first factor correlates with S, K and Ca. This is the *energy* factor. The second factor correlates highly with the total mass of suspended coarse particles (TSP), Si and Fe and it is called *soil dust.* Cu and Zn are again related to their own factor and Cl to its own (*sea salt*).

At the site Urban 1 the high correlation of K and Ca with the same factor as S is striking. The data suggest that K and Ca are attributed to fossil fuel combustion at this site.

A similar pattern is seen in the fine particle data of site Urban 2: TSP, S, K and Ca correlate highly with the same factor. Here also Fe has high loading to this *energy* factor. The *road dust* factor contains Si and Fe but also Cl. Cl may originate from car exhaust or from resuspended soil material. Coarse particle data from site Urban 2 were not factored because of too few samples.

At site Rural 1 two factors are used to describe the fine particle data. The first factor, which explains about 80% of the total variance at this site, correlates highly with TSP, Si, K, Ca and Fe. This is the *soil dust* factor. The second factor correlates highly with TSP, S and also Cl. This is the factor called *long range.*

The coarse particle data from site Rural 1 is described with only one factor. This factor explains 95% of the total variation of the data and it contains TSP, Si, S, K, Ca and Fe, all elements analyzed except Cl. This factor could be *soil dust*; however, the high correlation of S with this factor is not clear.

At site Rural 2 two factors are used to describe the fine particle data. The first factor, which explains 62% of the total variation, correlates highly to K and Ca and less significantly to TSP and Fe. Si has negative loading to this factor so the factor can hardly be connected to mineral background aerosol. This is the only case where Si and Fe do not correlate highly to the same factor. The reason is not clear. S or Cl do not correlate with this factor. The enrichment factors of K, Ca and

Table 6. Factor loadings and communalities for the elements at site Urban 2

	Fine particles		
	Energy	Road dust	Comm[b]
TSP	**0.70**[a]	0.16	0.51
Si	0.10	**0.79**	0.63
S	**0.93**	0.13	0.88
Cl	0.00	**0.43**	0.19
K	**0.95**	−0.06	0.91
Ca	**0.94**	0.01	0.88
Fe	**0.77**	**0.58**	0.93
Var[a]	3.75	1.19	4.94

[a] Confidence level over 99% bold type.
[b] Comm = communality.
[c] Var = variance explained by each factor.

Table 7. Factor loadings and communalities for the elements at site Rural 1

	Fine particles		
	Soil dust	Long range	Comm[b]
TSP	**0.58**[a]	**0.62**	0.73
Si	**0.59**	0.13	0.36
S	0.15	**0.71**	0.53
Cl	0.06	**0.69**	0.48
K	**0.66**	0.38	0.59
Ca	**0.87**	0.04	0.76
Fe	**0.85**	0.17	0.74
Var[a]	2.63	1.57	4.20

[a] Confidence level over 99% bold type.
[b] Comm = communality.
[c] Var = variance explained by each factor.

Table 8. Factor loadings and communalities for the elements at site Rural 2

	Fine particles		
	Local dust	Long range	Comm[b]
TSP	**0.54**[a]	**0.62**	0.67
Si	−0.03	0.34	0.12
S	0.28	**0.76**	0.66
Cl	−0.01	0.09	0.01
K	**0.91**	0.09	0.84
Ca	**0.88**	−0.3	0.86
Fe	**0.54**	0.29	0.38
Var[a]	2.28	1.27	3.55

[a] Confidence level over 99% bold type.
[b] Comm = communality.
[c] Var = variance explained by each factor.

Si showed no significant deviation from soil dust composition (see Fig. 6). This factor may be a combination of vegetative or agricultural dust, fly ash from wood combustion and soil dust. It is called *local dust* to distinguish this factor from the typical soil dust component which was seen at the other sites.

The second factor, that explains 27% of the total variation, correlates highly with TSP and S and is called the *long range*. This factor has again only low loading on K and Ca.

At both rural inland sites a factor appeared related to S and TSP and to some extent to Cl. The presence of this factor can be thought of as a result of long-range transport. At these sites Si, K, Ca and Fe were related to other factors that can be attributed to soil dust, vegetative dust or agricultural dust.

In the factor solutions for the data sampled at the southern urban sites, a factor which correlated to both TSP, S and K and Ca was present. At these sites K and Ca must be attributed to fuel combustion as well, while Si and Fe originate from soil dust.

Deposition

The relation between atmospheric aerosol concentration and deposition is not at all simple. Deposition of aerosols depends on meteorological and surface variables, and on particle properties such as size, shape, density, hygroscopicity and solubility. Besides, there exists an analytical difference in the treatment of aerosol and deposition measurements. While aerosols are analyzed for the total concentration of each element in each sample, so far only the dissolved fraction (or ionic content) has been of interest in deposition samples.

The traditional deposition measurement technique is based on the collection of precipitation or bulk deposition by means of a gauge or funnel. The ionic concentration of the sample is usually analysed by atomic absorption, ion chromatography, plasma emission spectrometry or atomic emission (Schaug et al. 1988).

Here only a brief summary of the available information sources concerning base cation deposition is given. In Finland deposition of base cations in background areas has been measured routinely on a monthly, weekly or daily basis since the beginning of the 1970's (Järvinen and Vänni this Vol; Kulmala et al. 1982). The sampling sites belong to several monitoring programmes so that the sampling periods and sampling devices are of various kinds. The widest single network consists of about 40 stations at which the monthly bulk deposition is sampled (Järvinen and Vänni this Vol.). This network gives the geographical distribution of the bulk deposition of H^+, conductivity, S, Cl, total organic carbon, Na, K, Ca, Mg, nitrate nitrogen, ammonium nitrogen, total nitrogen and total P. Ca and Mg show clear decreasing gradients towards north and maximum deposition values are in the southeastern Finland (Järvinen and Vänni this Vol.). For K this pattern is not so clear. Detailed analysis of the relations of the elemental concentrations of the deposition has not been made.

Joffre et al. (this Vol.) give a more detailed analysis of alkaline deposition at three Finnish EMEP (The Co-operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe) stations. At these stations ammonium is the main acid-neutralizing ion. For Na^+, K^+ and Ca^{2+} the authors notice that due to their different origins (sea salt and crustal particles), these species do not always follow the same behaviour as the typical anthropogenic compounds. An exception is the deposition of Ca at the southeastern station Virolahti. There the deposition pattern of Ca closely follows that of sulphate and ammonium. Laurila (1989) has applied multivariate statistical methods to the observations carried out in 1988 at these three Finnish EMEP stations. He finds that correlations between sulphate and hydrogen ions are insignificant in the southern stations and are slightly higher between nitrate and hydrogen ions. These findings point out that sulphur or nitrogen deposition do not define the acidifying potential of wet deposition.

Several definitions have been proposed for defining the acidifying potential of atmospheric deposition for soil or lake surfaces (Dillon 1983; Brydges and Summers 1989). Joffre et al. (this Vol.) tested these different definitions and found that H^+, acid deposition concept (AD) given by Dillon (1983) and acidifying potential concept (AP) given by Brydges and Summers lead to very similar results when applied to the data of Finnish EMEP stations.

Annual wet deposition values of Ca and Mg in Europe based on the EMEP network (Schaug et al. 1988) are presented in Figs. 7 and 8. They show clear concentration gradients which to some extent differ from each other. Ca deposition is largest in Mediterranean countries and smallest in the Atlantic coastal countries like the U.K., the Netherlands, Norway, northern Sweden and Finland. The main feature of the pattern is that deposition values decrease from south to north and northwest.

Besides this main feature there are several smaller areas of increased deposition; one such area is in the Estonian SSR and it reaches out to southeastern Finland. In the Estonian SSR, on the south coast of the Gulf of Finland, there are

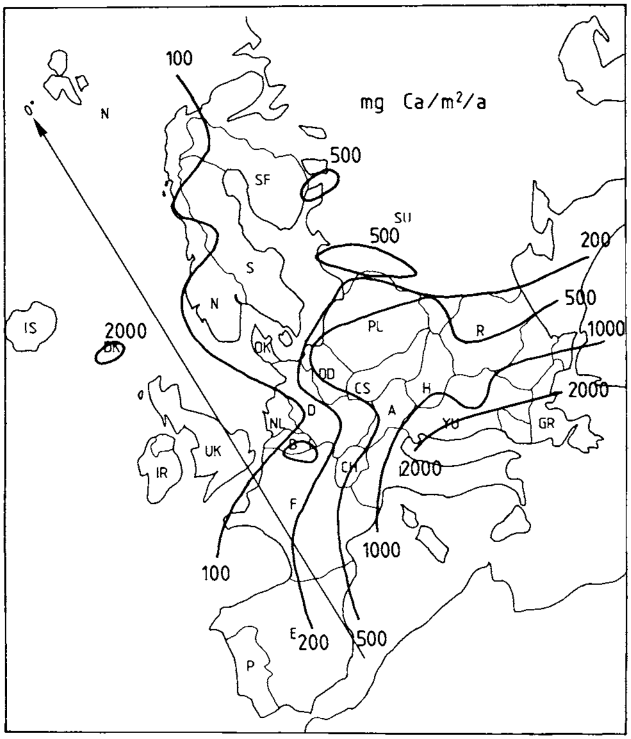

Fig. 7. Annual wet deposition of Ca^{2+} in Europe in 1986 (Original data from Schaug et al. 1988)

large oil shale deposits. Oil shale used at thermal power plants is a solid fuel with a high content of mineral matter (60–70% dry matter) (A. Ots 1988). Yearly about 30 Mt of Estonian oil shale is consumed to generate electric power.

Another area of increased Ca deposition is in the area of some east European countries e.g. Poland, Czechoslovakia, G.D.R. and Hungary. These countries use brown coal for energy production from which considerable emissions of CaO occur (Marquardt and Ihle 1988).

The main feature of the Ca deposition may be caused by soil dust. On the whole the soil dust component is a significant part of the total atmospheric aerosol burden. Especially the annual global natural production of desert mineral dust is comparable to the annual production of sea salt in the marine aerosol (d'Almeida and Jaenicke 1984; Deepak and Gerber 1983; Schütz and Sebert 1987). Deserts have a much higher productivity than oceans with regard to the active source area (Deepak and Gerber 1983). Thus the influence of the Sahara desert cannot be excluded here. With the large-scale wind systems of the lower latitudes dust from the Sahara is transported over long distances through the atmosphere. This phenomenon is responsible for episodes of so-called red rain or red snow which have been identified in various areas of the European continent (e.g. Loÿe-Pilot et al. 1986; Prodi and Fea 1979). Similar long-range transport of soil particles from Asian dust storms has been observed in remote areas like Hawaii (e.g. Braaten and Cahill 1986; Parrington et al. 1983) and the Arctic (Rahn et al. 1979).

Quartz is the dominant constituent of the Saharan dust; however, in the northern Sahara, calcite, and also dolomite in some regions, is a major compound of soil (Schütz and Sebert 1987), which makes this source very important for acidification studies. Its capability in neutralizing precipitation acidity is evident and this material also plays a certain role as a fertilizer for soil. Loÿe-Pilot et al. (1986) have studied the influence of Saharan dust on the rain acidity in Corsica and found that the incorporation into rain of Saharan dust is accompanied by a strong increase in the dissolved Ca content and an increase of the pH of rainwater. In Corsica red dust from the Sahara represents about 80% of the annual total deposition of solid particulate matter (Loÿe-Pilot et al. 1986). No such results are, to our knowledge, published from the rest of Europe, but the Ca-deposition map (Fig. 7) of Europe, with its strong decreasing gradient northwards, suggests that Saharan dust may be a significant source of alkaline deposition in extensive areas of Europe. Even though the European continent, with its industrial, agricultural and vehicular activities, is a source of alkaline dust, the residual Saharan aerosol background cannot be excluded.

In Europe the Ca deposition evidently is a mixture of emissions from industrial, agricultural and vehicular activities and soil dust.

The deposition of Mg shows a somewhat different pattern. The deposition is largest at the coastal regions of the Atlantic and the Mediterranean, which evidently is caused by the deposition of sea salt.

The significance of alkaline material in neutralizing precipitation acidity becomes evident by comparing the annual inputs of sulphur and calcium in Europe.

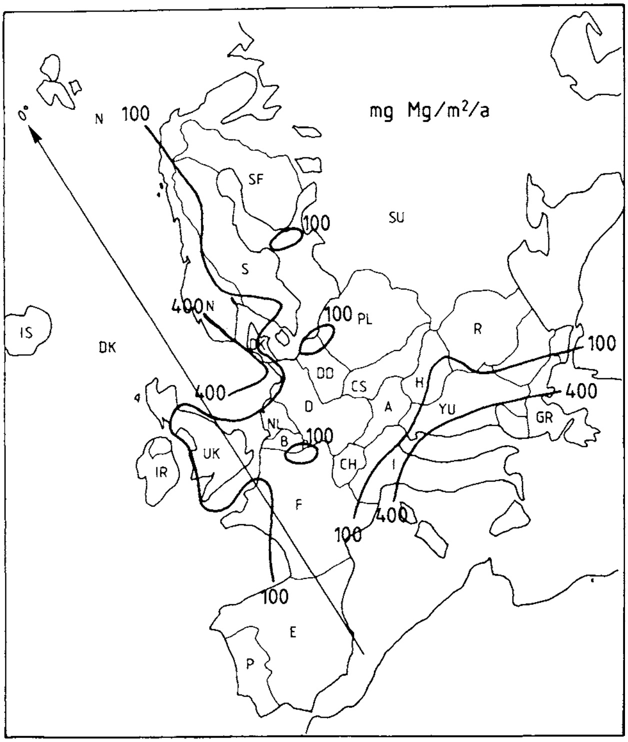

Fig. 8. Annual wet deposition of Mg^{2+} in Europe in 1986 (Original data from Schaug et al. 1988)

A representative value of annual Ca-deposition in east Europe is about 500 mg m^{-2} or 25 mEq m^{-2} which amount can neutralize about 1200 mg m^{-2} of H_2SO_4. Wet deposition of sulphate in the same area is annually about 4000 mg m^{-2}, of which about 30% is thus neutralized by the Ca deposition. Weathering rates of soils depend on soil types but typical values in Europe are 10–100 mEq m^{-2} (Swerdrup and Warfvinge 1988) which means that the atmospheric deposition can be a considerable source of acid neutralizing capacity and plants nutrients in extensive areas in Europe.

The maps presented here include only the wet deposition; dry deposition is not included. In soil acidification studies locally suspended and redeposited material is a disturbing factor which should be taken off the total deposition. Dry or bulk deposition measurements of alkaline materials are easily affected by locally suspended and redeposited soil dust. The most important factor influencing the suspension of soil dust is soil moisture content (Sehmel 1980). As long as soil is wet, suspension will practically not occur. The possibility that a deposition measurement is affected by locally suspended and redeposited soil dust is thus higher for dry periods than for wet periods. As a result, wet deposition is likely to contain less locally suspended soil dust than dry deposition. Thus it probably is justified to use only the wet deposition data of alkaline materials in acidification studies.

Conclusions

The main sources of alkaline aerosols in Finland are soil dust, energy production, industrial processes, traffic, agriculture and seawater. Of the anthropogenic sources, combustion of wood and dust raised by traffic are the biggest single sources in Finland. However, in aerosol concentration measurements no significant deviations from well-mixed mineral aerosols were found. At stations in southern Finland, however a strong connection between sulphate and alkaline aerosols was found. These preliminary data suggest that at least in the Helsinki region energy production may influence the circulation of alkaline aerosols while in more remote parts of the country mineral background aerosol seems to be prevalent.

In southeastern Finland there is an area of high deposition of Ca which evidently is caused by the use of oil shale for energy production in the Estonian SSR. In this area the southerly winds bring precipitation with highest Ca concentrations and the deposition pattern of Ca closely follows that of sulphate and ammonium (Joffre et al. this Vol.).

Wet deposition data from Europe show that alkaline deposition is an important factor in acidification studies both because of its acid neutralizing capacity and as a nutrient input.

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Characteristics of Sulphur Dioxide Monitors: Intercomparison

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Summary

The performance characteristics of five commercial sulphur dioxide monitors were studied. The experiments included both laboratory tests and field monitoring in an urban environment. According to the laboratory tests, the most sensitive concentration region was between 100 and 500 ppb [1 ppb(SO_2) = 2.86 $\mu g\,m^{-3}$ at NTP]. The lower detection limits were 2 to 5 ppb, and the precision varied from 1 to 26 ppb in the concentration range up to 500 ppb. The field data were analyzed with orthogonal regression and principal component analysis, and the results were less favourable than in the laboratory tests.

Introduction

Monitoring of chemical compounds in the atmosphere has increased due to increased concern for environmental protection. In the literature, development of different techniques for data collection of a variety of compounds seems to be very focussed. Nevertheless, problems associated with selectivity, detection limits, interfering substances, calibration and even automation need to be solved.

In this investigation, five commercial sulphur dioxide monitors were tested both in the laboratory and in field experiments. The laboratory results were evaluated on the basis of the relationship between the known calibration concentration and the concentration measured by each of the monitors. Additionally, other parameters, such as the standard deviation, the slope of the regression line, the sensitivity range, the linearity, the precision and the lower detection limit, were considered. Analysis of the field experiments was based on orthogonal linear relation (OLR) analysis (Heidam 1980), principal component analysis (PCA) (Carey et al. 1975; Lawton et al. 1979; Holland and McElroy 1986), time series analysis (Box and Jenkins 1976) and on an examination of deviations in the results of the monitors. We generally used hourly average values calculated from data sampled at a 1 min^{-1} frequency by an automatic data acquisition system.

Instruments and Methods

The laboratory arrangement for intercalibration experiments of the sulphur dioxide monitors is presented in Fig. 1. Steel and Teflon were used as tube materials in

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order to make the construction relatively inert to the SO_2-gas. The required dilution air, obtained from the laboratory compressed air system, is passed through a scrubbing system to act as reference zero air. Dilution is performed in two steps in order to obtain the concentration range of 0 to 1000 ppb, without having to raise the flow rates in conjunction with the higher concentrations. A permeation device was selected as a gas source, and much care was taken in handling of the permeation tubes, as recommended by Scaringelli et al. (1970). The permeation velocity was defined by weighing the tubes at certain time intervals (1–2 weeks), and the stability of the tubes was found to be within 4%.

In order to avoid the effect of induced perturbation signals from other electric equipment on the data signals, the mains system was designed and constructed as an isolated unit for the laboratory experiments and also for the field experiments. The noise of this electronic system was measured within the frequency bandwidth of the system (DC: 0–130 kHz) by terminating the signal lines with 100 Ω and 10 kΩ resistors and changing the amplifier coefficients in both cases over values one to ten times the value used during the intercalibration. The resultant noise (including also digitizing error) was at the most 0.5 mV (peak to peak). Thus we can affirm that the digitizing error (12 bit AD converter) is the only possible error in the results from the data collecting system. For more details of the laboratory arrangement the reader is referred to Walden et al. (1987).

The tested monitors were: Kimoto model 318 (Japan), Kimoto model 365 (Japan), Monitorlabs model 8850 (U.S.A.), Environnement AF20m (France) and Horiba Apsa 300E (Japan). The first monitor is based on a conductometric

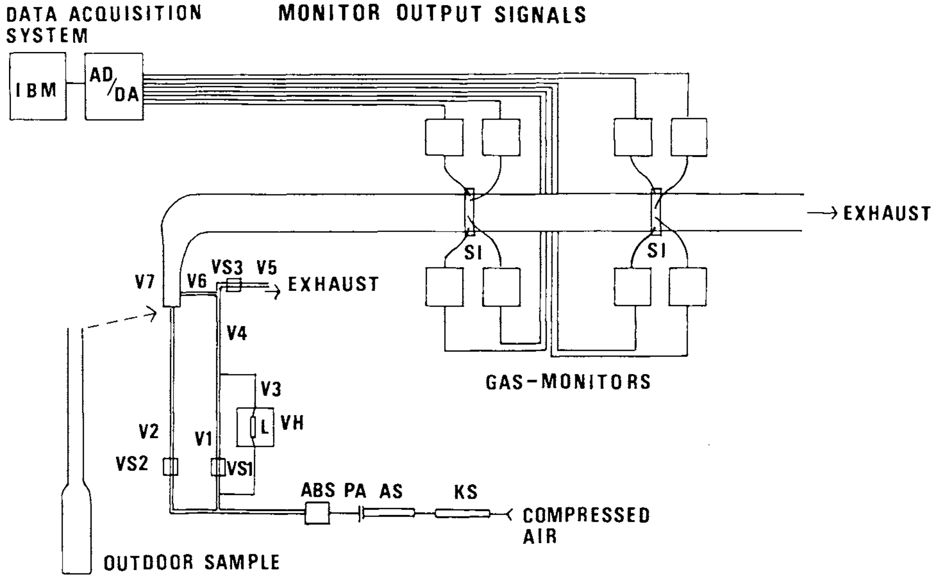

Fig. 1. Laboratory arrangement for the intercalibration of the SO_2 monitors. The mass flow controllers were made by Tylan, and the tube fittings were Swagelock and Teflon fittings

method, the others on a fluorescence method. In the text the monitors are referred to by numbers 1 to 5, not in the same order as above.

The calibration concentration can be calculated according to the equation

$$C = V_g(V1 + V3 - V5)[(V1 + V3)(V1 + V2 + V3 - V5)]^{-1}, \tag{1}$$

where C is the concentration by volume fraction (ppm), V_g is the permeation velocity (μl min^{-1}) and the flows V1 and V2 are the dilution flows, V3 is the constant flow (0.39 l min^{-1}) through the gas source, and V5 is the exhaust flow (see Fig. 1).

The calibration runs were performed by keeping the flows V1 and V2 constant and changing the flow V5 after a certain time period (normally 2 to 4 h) with a ten-channel clock controller.

The field experiments were carried out in two cities, Helsinki and Imatra, to demonstrate the characteristics of the monitors, when functioning in the ambient conditions.

In classical regression analysis (i.e. with a dependent and an independent variable) our model is linear: $y_{ik} = a_k + b_k x_{ik} + e_{ik}$, where y_{ik} is the i : th observation of the k : th monitor, a_k is the fixed bias and b_k is the proportional bias of the k : th monitor, x_{ik} is the true value for the i : th measurement and the random error e_{ik} is assumed to have a normal distribution with zero mean and with standard deviation σ_k. The unbiased estimate (S_{pk}) of σ_k is the precision of the k : th monitor. The exact equations for parameters a, b and S_{pk} are presented in many textbooks (Mandel, 1964). In this report we have included the 95% confidence limit into the precision at the point $x = \bar{x}$, and the precision takes the form:

$$dy = t_{gd} S_p [(n + 1)/n]^{1/2}, \tag{2}$$

where t_{gd} is the Student t-factor with the confidence limit d ($= 0.975$) and g is the degree of freedom ($= n - 2$), S_p is the precision and n is the number of observations. When n is large, we have approximately $dy = 2S_p$. The use of dy, instead of S_p, is a question of overestimating rather than underestimating the results.

When both variables are subject to errors, i.e. both variables are stochastic, we use orthogonal linear relation as proposed by Heidam (1980). In this case we seek a coordinate transformation where the orthogonal distance of the observations from the best fit line is minimized. This model is also linear and the same assumption about the error matrix of the variables x and y is made as in the case of classical regression analysis. The equations of the parameters a, b and S_p are somewhat modified, and they are presented by Mandel (1964) and Heidam (1980). In this case we also use a modified version for the precision, and the difference between dy_0 and S_{0p} is about a factor of 2.

According to regression analysis, parameters such as the regression line equation, the bias and the correlation coefficient, both in the classical form and in the orthogonal form, were used for comparison of the results, but also in calculating the lower detection limits and precisions. Linear dependence and strength factors were calculated with the PCA method from the field data, for which there was no other reference method for SO_2 concentration measurements. Spectral analyses were employed to determine any periodic features of SO_2 concentration and to estimate the white noise of the signals of the monitors.

Results and Discussion

At the beginning of the intercomparison test the signal wires were also tested after connecting the monitors into the mains system. Tests were made both against the signal lines (+ / −) and the signal against the earth. We found that the only disturbance signals occurring in the frequency range 0–150 MHz were caused by the monitors themselves. The disturbance signals found in monitors 1, 2 and 5 are presented in Fig. 2; monitors 3 and 4 were completely free from disturbances.

In the first laboratory period, measurements were made with the monitors calibrated by the Finnish representatives. The concentration ranges of 0–8 ppb,

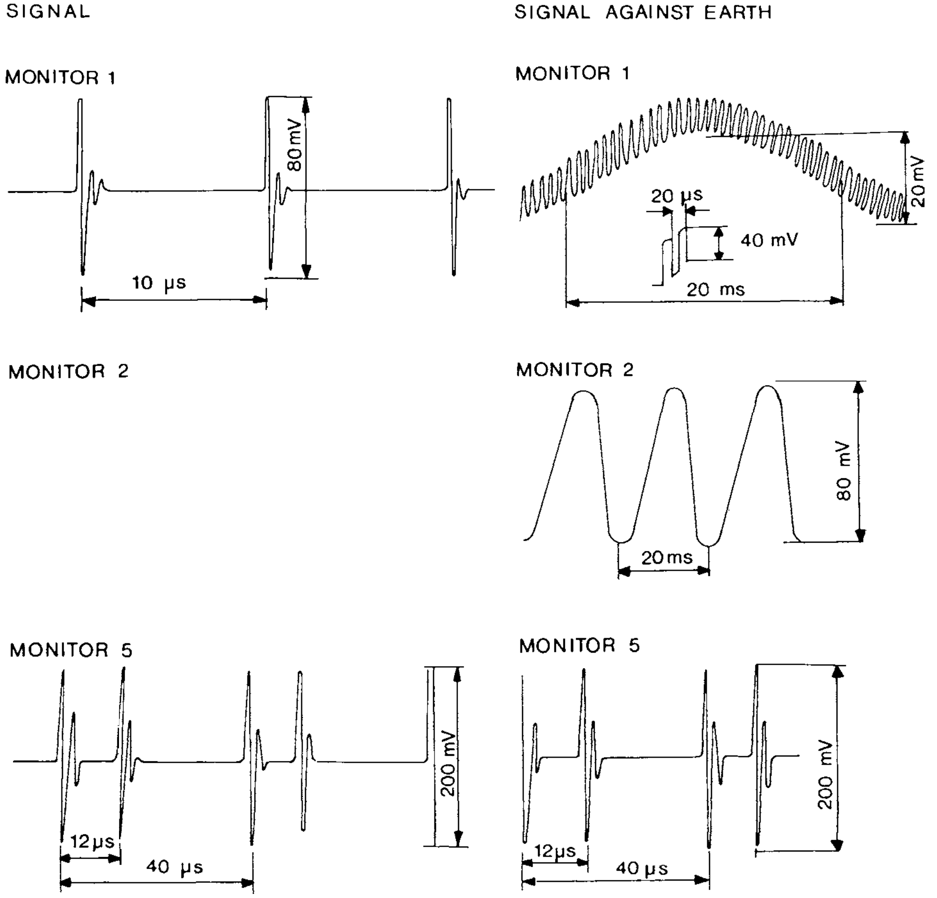

Fig. 2. Shapes of the disturbance signals found in monitors 1, 2 and 5

0–25 ppb, 0–250 ppb, 0–500 ppb and 0–500 ppb (10 levels/range, except five levels in the first range) were evaluated in both the increasing and the decreasing direction. The time lag for each concentration level was generally 2 h.

The relationship between the measured concentration of each monitor and the calibration concentration, calculated according to Eq. (1), from a calibration run (0–1000 ppb) is presented in Fig. 3 as a function of the concentration.

The linear regression parameters of the different calibration runs are shown in Table 1. Remarkable changes in numerical values were observed for parameters a, b and dy through the concentration. The variation of parameter a is mainly associated with the stability and the selected range in monitors. The zero level drift, measured by a three-step forward discretization method, was 0.3 ppb/h with monitor 5 and nearly zero for the others. Our great concern was, however, the behaviour of parameter b with monitors 3, 4 and 5, which indicated some unlinear feature of these monitors as a function of the concentration (see Table 1).

The precision (Pr = dy/b = modified bias/slope of regression line) is calculated from Table 1 and is presented in Fig. 4 as a function of the SO_2 concentration. The increasing value of this parameter is notable. The normalized bias (=dy/ȳ, where ȳ is the mean concentration of the calibration run) is also calculated from Table 1 and is presented in Fig. 5. The curves show that the most sensitive region seems to coincide with concentrations of 100 to 500 ppb.

The lower detection limits (LDL) were calculated according to the equation

$$\mathrm{LDL} = t_{gd}[S_0^2 + (S_{y0}/b)^2]^{1/2}, \qquad (3)$$

where t_{gd} is the Student t-factor at confidence level d (=0.975%) and g degrees of

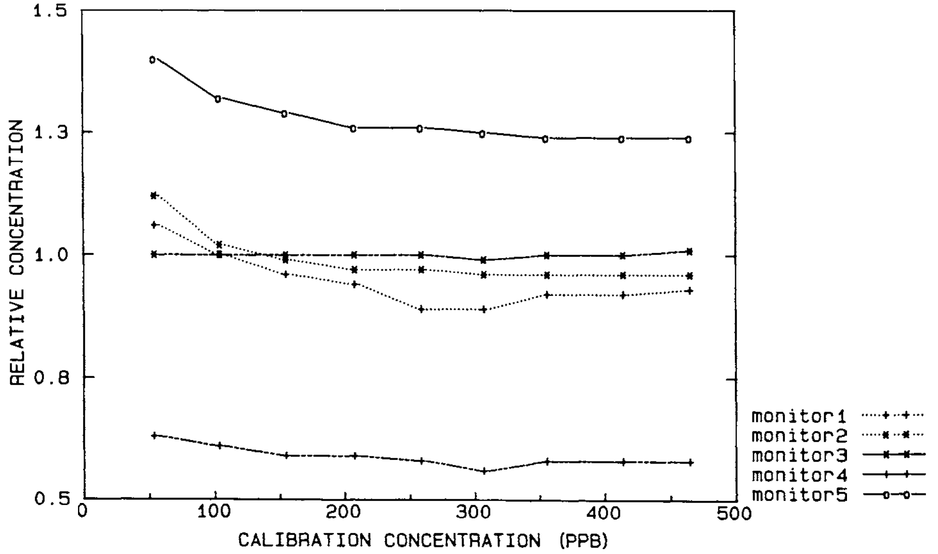

Fig. 3. Calibration run for monitors 1 to 5 in the concentration range of 0 to 500 ppb

Table 1. Linear regression parameters of the calibration runs; a is the y–intercept, b is the slope of the regression line and r is the correlation coefficient and dy is from Eq. (2)

Parameter	Monitor 1	Monitor 2	Monitor 3	Monitor 4	Monitor 5
0–8 ppb					
a (ppb)	4.66	4.70	− 4.57	0.43	29.0
b	0.65	0.68	0.88	0.65	1.70
r	0.899	0.942	0.963	0.930	0.960
dy (ppb)	1.67	1.28	1.28	1.34	2.60
0–25 ppb					
a (ppb)	3.17	3.09	− 5.91	0.23	32.7
b	0.97	0.99	1.22	0.71	1.38
r	0.994	0.996	0.996	0.994	0.936
dy (ppb)	1.81	1.48	1.84	1.36	8.86
0–250 ppb					
a (ppb)	3.17	4.65	0.32	0.40	68.4
b	0.92	0.95	1.08	0.79	1.01
r	1.000	1.000	0.999	1.000	0.998
dy (ppb)	5.15	1.88	2.43	2.00	11.6
0–500 ppb					
a (ppb)	6.33	6.77	− 3.33	1.46	11.14
b	0.90	0.94	1.01	0.58	1.21
r	1.000	1.000	1.000	1.000	1.000
dy (ppb)	9.63	3.31	3.38	5.37	5.38
0–1000 ppb					
a (ppb)	− 2.70	− 1.77	− 13.94	− 5.19	88.1
b	0.87	0.92	1.06	0.72	1.00
r	0.999	1.000	1.000	1.000	1.000
dy (ppb)	21.5	20.6	27.7	18.1	25.1

freedom. S_0 and S_{y0} are the deviation of the results with zero air, and the deviation of the results when the concentration is approaching zero, respectively, and b is the slope of the regression line. The calculated LDL values (see parameters in Table 1) are 2.3 ppb, 2.1 ppb, 1.6 ppb, 2.5 ppb and 4.7 ppb for monitors 1 to 5, respectively. The LDL values are approximately the same, except for monitor 5, for which it is about twice as high. This is mainly due to the rough filtering in the measured signals. These results and the use of parameter t_{gd} in Eq. (2) are discussed in more detail in Walden et al. (1987).

During the field period in Imatra the temperature varied between +4 and −22°C, the relative humidity between 80 and 96%, and the wind velocity between 0 and 8 m/s. The presence of other sulphur compounds due to the vicinity of the pulp mill produced quite extreme conditions for the monitors. The meteorological data during the field period in Helsinki were the following: the temperature between −2 and −17°C, the relative humidity between 70 and 98%, and the wind velocity between 0 and 7 m s^{-1}. In Helsinki there were two quite small industrial sources for sulphuric compounds in the surroundings of the measuring point.

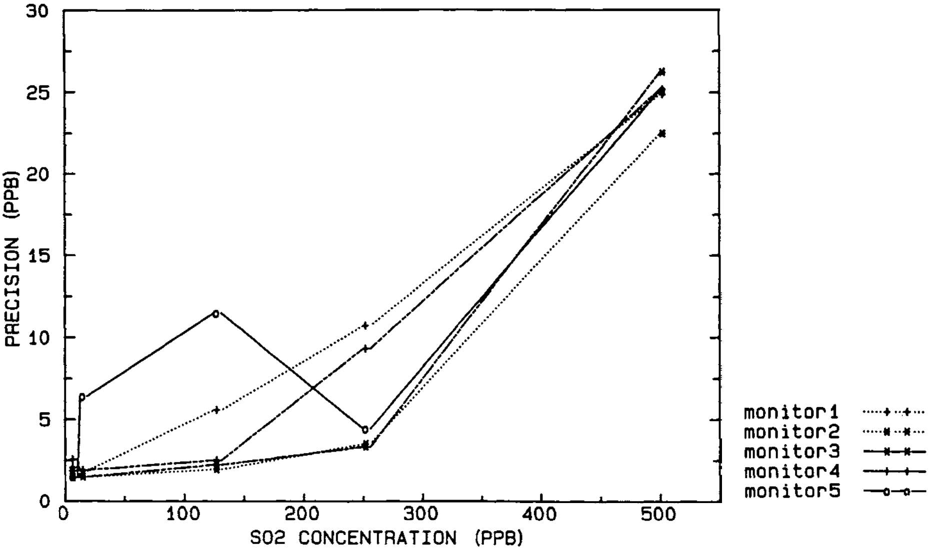

Fig. 4. Precision (= dy/b, parameters dy and b in Table 1) as a function of the concentration

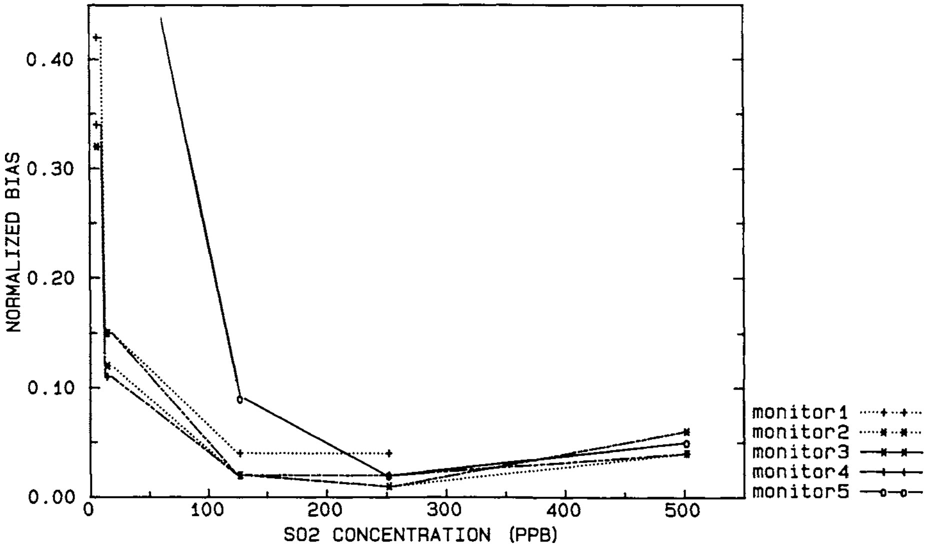

Fig. 5. Normalized bias (= dy/ȳ, parameters dy and ȳ in Table 1 and in text) as a function of the concentration

The daily average values of SO_2 concentration are shown in Fig. 6 for the field period in Imatra, and in Fig. 7 for Helsinki. In Fig. 6, three of the monitors seem to react similarly (monitors 1, 3, 4). Monitor 5 exhibits different values from these three but shows the same general tendencies. Monitor 2 reacted differently in the beginning of the period, but agreed with the three others at the end of the period.

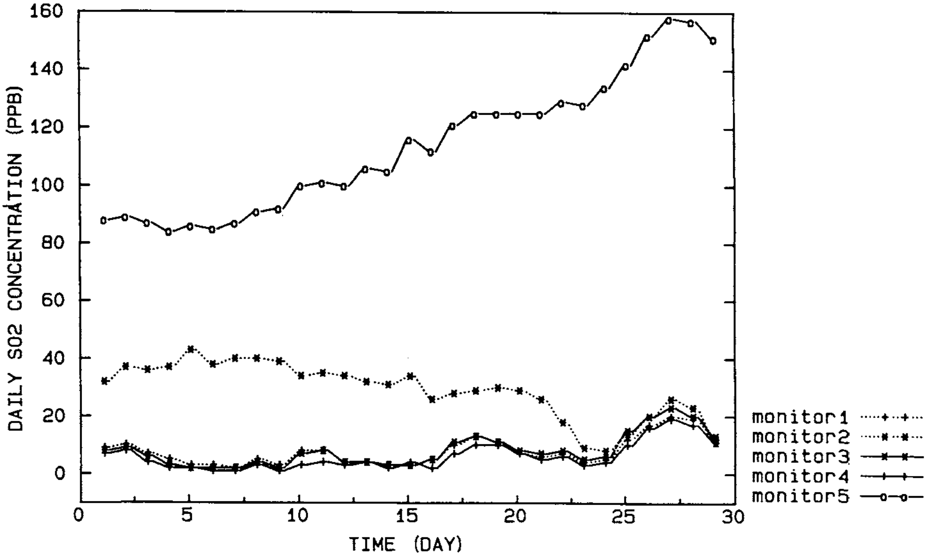

Fig. 6. The measured daily concentration of SO_2 during the field period in Imatra for monitors 1 to 5

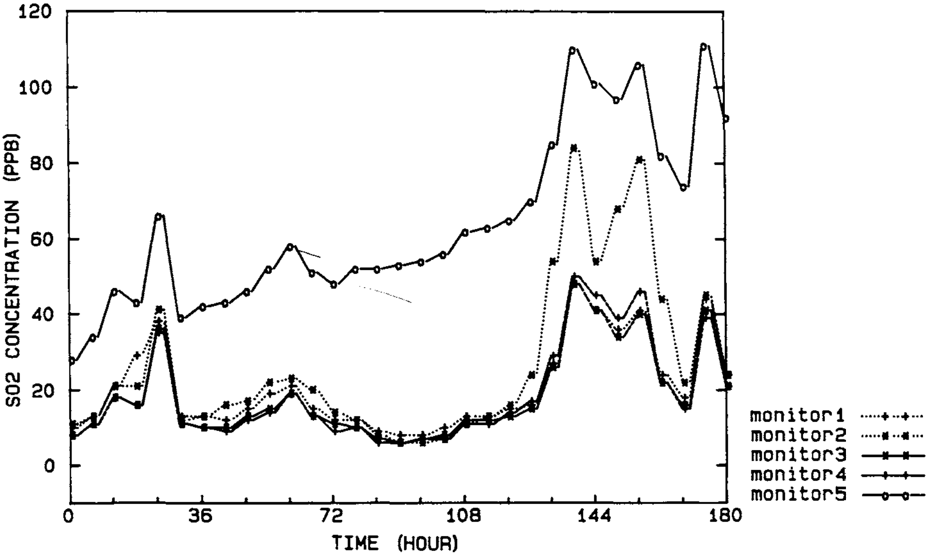

Fig. 7. The measured six hourly average concentration of SO_2 during the field period in Helsinki for monitors 1 to 5

At the beginning of the field period in Helsinki (see Fig. 7) all monitors show a similar concentration curve, except for the gap between monitor 5 and the other four monitors. However, in the middle of the period a sudden jump is seen on the curve of monitor 2. Without the first peak just after the jump, the shape of the curve is similar to the others. The drift of monitor 5 is clearly seen although a calibration check was made before these measurements. The arithmetic mean of SO_2 concentration was 8 ppb in Imatra and 22 ppb in Helsinki, calculated according to monitors 1, 3 and 4.

The orthogonal linear relation analysis of the data in Figs. 6 and 7 are shown in Tables 2 and 3, respectively. Because the model is linear, only half of the parameter matrix is presented. The regression equation, the correlation coefficient and the modified bias are calculated against the other monitors for each column. The slope of the regression equation and the correlation coefficient for monitors 1, 3 and 4 show that they are linearly related to each other. The modified precision (dy in ppb) is also very small with these monitors. From Table 3 we see that the correlation coefficient is rather close to 1, also with monitor 2 in relation to monitors 1, 3 and 4. However, the slope of the regression line and the modified precision of monitor 2 related to the other monitors indicates the differences, shown in Fig. 7.

The plot of the first two principal components from the daily average values in Imatra and in Helsinki is shown in Figs. 8 and 9. From Fig. 8 we see that monitors 1, 3, 4 and 5 give almost equal contributions to the first component and monitor 2 is mainly responsible for component 2. Although this analysis has found a linear relation between monitors other than number 2, it still shows that correlation, which is inversely proportional to the angle between the data points, is good between monitors 1, 3 and 4. These results suport the regression analysis in Table 2. From Fig. 9 we see that all the monitors give almost equal contribution to the first principal component but the correlation between the monitors 1, 3 and 4 is good. We also found the change in results between the field experiments in Imatra and Helsinki.

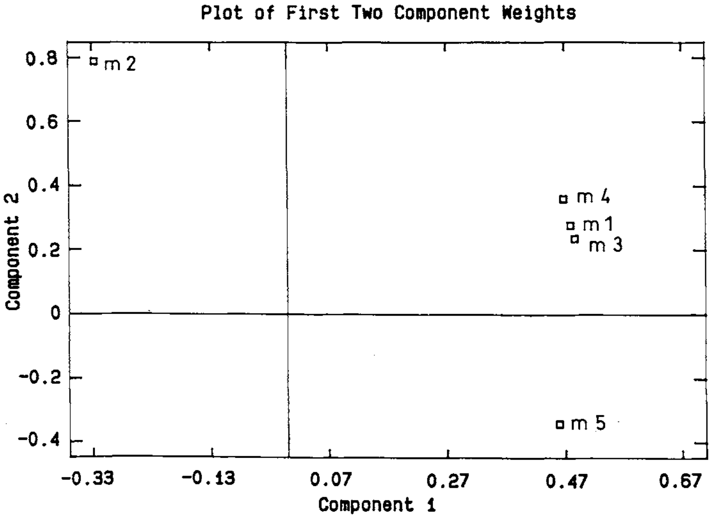

Fig. 8. Plot of the first two principal component weights for monitors 1 to 5 from the field period in Imatra

Table 2. Orthogonal regression analysis from the field period in Imatra. M1 to M5 refer to the monitors, and for definitions of the other parameters see Table 1 and the text

	M1	M2	M3	M4
M2	$y_2 = 61.2 - 4.16x_1$ $r = -0.371$ $dy_0 = 8.6$			
M3	$y_3 = -1.1 + 1.18x_1$ $r = 0.984$ $dy_0 = 1.4$	$y_3 = 18.9 - 0.38x_2$ $r = -0.473$ $dy_0 = 9.2$		
M4	$y_4 = -1.7 + 1.0x_1$ $r = 0.967$ $dy_0 = 1.8$	$y_4 = 13.8 - 0.27x_2$ $r = -0.424$ $dy_0 = 8.4$	$y_4 = -0.7 + 0.84x_3$ $r = 0.976$ $dy_0 = 1.7$	
M5	$y_5 = 62.6 + 6.61x_1$ $r = 0.718$ $dy_0 = 6.9$	$y_5 = 198 - 2.93x_2$ $r = -0.797$ $dy_0 = 11.2$	$y_5 = 73.7 + 5.01x_3$ $r = 0.806$ $dy_0 = 6.8$	$y_5 = 77.2 + 6.03x_4$ $r = 0.794$ $dy_0 = 6.0$

Table 3. Orthogonal regression analysis from the field period in Helsinki. M1 to M5 refer to the monitors, and for definitions of the other parameters see Table 1 and the text

	M1	M2	M3	M4
M2	$y_2 = -18.3 + 2.19x_1$ $r = 0.929$ $dy_0 = 11.3$			
M3	$y_3 = -2.3 + 1.01x_1$ $r = 0.998$ $dy_0 = 1.6$	$y_3 = 5.9 + 0.47x_2$ $r = 0.950$ $dy_0 = 9.7$		
M4	$y_4 = -3.8 + 1.09x_1$ $r = 0.991$ $dy_0 = 3.5$	$y_4 = 4.9 + 0.51x_2$ $r = 0.967$ $dy_0 = 8.5$	$y_4 = -1.3 + 1.08x_3$ $r = 0.996$ $dy_0 = 2.2$	
M5	$y_5 = 11.5 + 2.66x_1$ $r = 0.832$ $dy_0 = 15.9$	$y_5 = 35.5 + 1.15x_2$ $r = 0.775$ $dy_0 = 23.6$	$y_5 = 17.8 + 2.62x_3$ $r = 0.835$ $dy_0 = 15.9$	$y_5 = 21.0 + 2.42x_4$ $r = 0.830$ $dy_0 = 16.6$

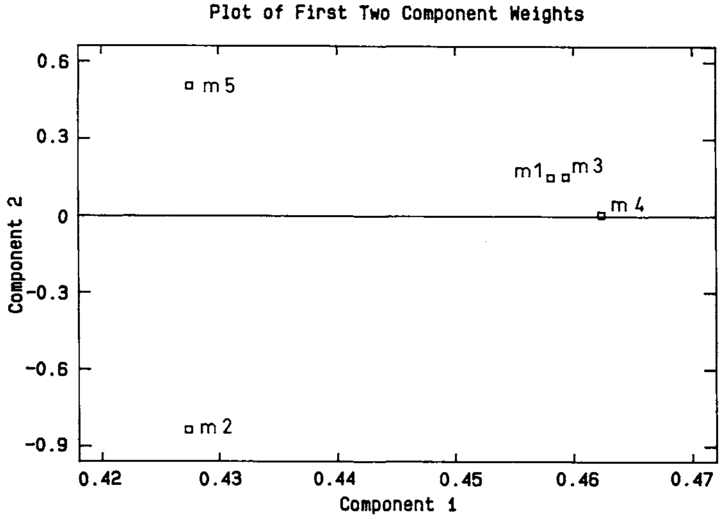

Fig. 9. Plot of the first two principal component weights for monitors 1 to 5 from the field period in Helsinki

Data obtained from the field experiments were also subjected to periodogram analyses. No clear periodicities were found, but the white noise was estimated from the spectral density figures to be 2.8 ppb, 2.5 ppb, 2.6 ppb, 2.6 ppb and 10 ppb for monitors 1 to 5, respectively. These values are reasonable in comparison with the LDL values obtained from the laboratory experiments.

Conclusions

These tests showed that although the monitors are continuously functioning, they need to be kept under surveillance: the maintenance schedules should be followed regularly according to the manuals. During the test periods, there were malfunctionings in the operation of the monitors. The zero level drift (monitor 5), electrical disturbances (monitors 2 and 5) and the slight decrease of zero level of monitor 4 at the end of the test period were noticeable. The worst problem was, however, the lack of reliablity when measuring at low ambient SO_2 concentrations in the presence of other polluting compounds, e.g. odorous sulphur compounds, hydrocarbons etc.

During the laboratory experiments the monitors correlated with the known concentrations and with each other. The slope of the regression line for monitors 3, 4 and 5 exhibits disturbing non-linear behaviour throughout the measuring range. The precision was constant (2 ppb) up to a concentration of 250 ppb for monitors 2 and 3, but beyond this concentration it increased to the same value as the others. The LDL values were between 2 and 5 ppb, which means that a reliable measured low concentration is about 4–15 ppb. For monitor 5 this is too high, if we compare this concentration to the background concentration.

The results obtained from the field period show that monitors 1, 3 and 4 agreed reasonably well. The zero level drift with monitor 5 has a somewhat ambiguous impact on the qualities of this monitor, but with monitor 2 the situation was more complicated. The results during the laboratory experiments were so promising that there is reason to believe that the poor agreement exhibited by monitor 2 during the field period in Imatra was due to a malfunctioning prescrubbing system. The rather low concentrations in Imatra made it quite difficult to analyze the results due to the rather high LDL values of the monitors. Clearly, improvements occurred in the field period in Helsinki where concentrations were higher, but still the results given by monitor 2 compared to other monitors were problematic.

The calibration of the monitors is a problem, which should be solved. At the beginning of these tests it was clear that the monitors were not well calibrated. The calibration concentrations must also coincide with the measurement concentrations and the selected range switch position should not change during operation. The linearity of the monitors should be checked over a large concentration range monthly, while a check of one calibration point and the zero level should be made weekly at the minimum.

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1.3 Deposition

Bulk Deposition Chemistry in Finland

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Summary

Continuous monitoring of bulk deposition has been made by the Water and Environment Research Institute (WERI) since 1971 in Finland. The results are mainly used in evaluating the deposition to watercourses and soil. The samples have been taken monthly.

There is quite often a clear geographical trend for the different components, i.e. the deposition in southern Finland is higher than in northern Finland. This trend is very strongly seen in sulphate sulphur, conductivity, total nitrogen and calcium. This phenomenon is not so clear in strong acids, ammonium nitrogen, total phosphorus and total organic carbon. pH, nitrate nitrogen, chloride, sodium, potassium and magnesium show no geographical trend at all.

When evaluating the representativeness of the deposition results of WERI, it can be seen that the local emissions have in some cases contaminated samples. For this reason the locations of the sampling stations are continuously observed, so that the results may be reliable and representative of unpolluted areas.

Introduction

The quality of rainwater has been monitored in Finland sporadically since the 1950's at a number of observation sites under the direction of Buch and Koroleff. The studies were based on monthly samples, and the first summary of the results was published in 1960 (Buch 1960).

A second examination of rainwater quality is to be found in Viro's series of observations from 1953 on the composition of snow at various locations throughout Finland in March 1952 and February 1953 (Viro 1953). In estimating the loading in water areas, the calculations used have as a rule been based on Viro's calculated average concentrations for the entire country. Viro's research also looks into nutrients, nitrogen and phosphorus, in rainwater.

City-based studies, for instance on sulphate and metal concentrations in rainwater, have been carried out by Laamanen (1969). Rainwater investigations began at the Water and Environment Research Institute in 1971. The same year also saw the start of the international OECD project (1977) which sought to throw

Kauppi et al. (Eds).
Acidification in Finland

light on the long-distance transportation of sulphur compounds. One aim of the rainwater quality monitoring activities at WERI was to complete the material balance investigations of small drainage basins with the information on loading resulting from precipitation. Another objective was to examine the overall direct loading on watercourses brought by rainfall, its regional differences, and changes over time. At that time particular attention was being paid to the quantity of nutrients being deposited via precipitation, since eutrophication was being singled out for special study. From the outset, however, the most important components have been monitored from the acidification viewpoint, such that it has been possible to make very good use of the results in acidification studies (Haapala 1972; Järvinen et al. 1980; Järvinen 1980).

WERI's rainwater research has been supplemented with snow studies which were started on a nationwide basis in 1975 (Soveri 1985). In 1986 work got under way at Vihti on throughfall studies which ended in 1988. Metals like Zn, Cu, Ni, Hg (Rekolainen et al. 1985), Pb, Cd and Al are analyzed from snow samples. Estimations of metal deposition in the winter period can be made through these results (Järvinen et al. 1986).

There are a number of aims in monitoring rainwater quality. In the first place one can follow changes in rainwater quality over long time-periods. There exists now a 18-year time series containing material covering the entire country. Then again, by looking into the quality of the rainfall, one can arrive at estimated figures for deposition in different parts of the country. Acidification researchers have often expressed their hopes for an expanded network of observation points, since they would like to get hold of increasingly detailed background information for their own impact studies. The quality of rainfall is of importance in all research into the effects of acidification, since it is the primary airborne input in material balance calculations (Järvinen 1985).

Sampling Devices

When the studies on rainwater quality were launched in WERI in 1971, there were no commercially available sampling devices on the market, so the device was designed within the Institute. Components of the sampler used and dimensions of the sampling equipment can be seen in Figs. 1 and 2. The sampling vessel has been modified over the years, so as to ensure in particular in cases of low rainfall that it is possible to obtain sufficient amounts of water for the purposes of all analyses, in order that the number of missing observations and data should remain as small as possible. An improvement was made in 1980 by altering the internal structure of the vessel. Collection efficiency was greatly improved by this means (Järvinen 1986). Some years later, at the beginning of the year 1986, a project was initiated in Vihti to test the optimum shape for the funnel element of the sampling vessel. The development work of the sampling equipment has been continued and last year birdrings were added to prevent the contamination caused by the birds. Also

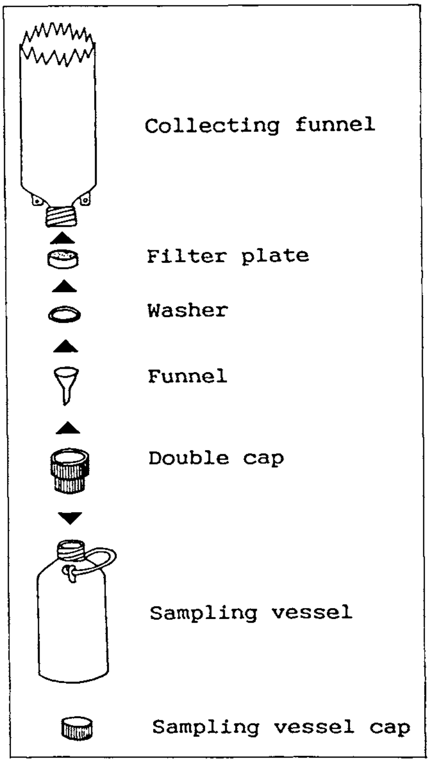

Fig. 1. Components of the sampler used

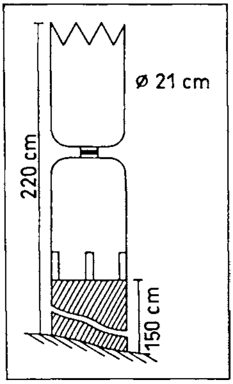

Fig. 2. Dimensions of the sampling equipment

minimization of evaporation from the sampling bottle is important; improvements in this field are being made all the time.

There is a large range of rainfall sampling devices in use. The end of 1987 saw the introduction of a comparative study arranged by the Baltic Sea Commission in Studsvik, Sweden, examining the vessels used by the various Baltic countries. WERI participated in this study with a bulk deposition sampler. Norway and Great Britain also took part in the comparative survey, which continued until the end of 1988. The results were handled in Stockholm in spring 1989. Special attention was paid to the collection efficiency of samplers. Evaporation is a serious problem in open models in summertime. It was also noticed that weekly and daily results gave the same conclusion. Also, results were quite equal, whether one used a complicated electrical sampler or a very simple one. All these results are tentative and they will be published later.

In 1980–1981 a comparative study was arranged in Finland embracing the sampling devices of WERI, the Finnish Meteorological Institute (FMI), and the Meteorological Department of the University of Stockholm (MISU), and the results were published in 1984. The results showed a fair measure of correlation, but certain differences were noted when the concentrations were near detection limits. Differences were also observed in the collecting efficiencies of the various devices (Haapala et al. 1984).

The sampling vessels are changed over on the first day of each month. Local observers have cleaned the funnel section in line with the directions given (Publs. of Nat. Board of Waters 1984).

Precipitation Stations

The network of observation points has from the earliest stages covered the entire country as can be seen by code numbers in Fig. 3A. The explanations of code numbers is seen in Table 1. The stations have been sited in order that the results gained from them represent clean areas, i.e. the quality of the background air. These background values can thus be used as reference values in the study of polluted areas (Järvinen 1986).

Recently there has been a growing need to increase the number of stations in the most critical areas of southwest Finland and particularly Lapland in the north. Studies in Lapland have shown that small lakes with poor buffering capacity are extremely sensitive to acidification. This sensitivity shows up especially in the spring season, when the impurities brought with the winter snow all enter the lake in a short period. In southwest Finland, the pH values for rainwater are the lowest in the country, and alarming news of damage to trees and forests has surfaced from this area in particular.

In Southern Finland it often difficult to find a completely ideal site for an observation station, since the entire coastal belt and particularly the Helsinki district is heavily industrialized.

Laboratory Analyses

In the Research Laboratory the monthly samples are analysed for pH value (SFS 3021 1979), conductivity (SFS 3022 1974), strong acids (Gran 1952), sulphate sulphur (Henriksen et al. 1974), total nitrogen (Henriksen 1969), nitrate nitrogen (Henriksen et al. 1970), ammonium nitrogen (SFS 3032 1976), total phosphorus (SFS 3026 1986), chloride (National Board of Waters, Report 213 1981), sodium

Table 1. Code numbers, names, establishment years and coordinates of the precipitation stations

Number	Name	Year	Coordinates	
1	Kevo	1971	69° 45′	27° 01′
2	Kilpisjärvi	1971	69° 03′	20° 48′
4	Nellim	1971	68° 51′	28° 18′
7	Kolari	1971	67° 24′	24° 11′
8	Sodankylä	1971	67° 22′	26° 39′
12	Juotas	1971	66° 19′	26° 58′
13	Kurvinen	1971	65° 35′	29° 31′
16	Viitamäki	1971	63° 56′	26° 25′
17	Kuhmo	1971	64° 16′	29° 50′
19	Valtimo	1971	63° 47′	28° 39′
20	Sulva	1971	62° 59′	21° 40′
21	Lestijärvi	1971	63° 27′	24° 27′
22	Kuopio	1971	63° 01′	27° 48′
24	Naarva	1971	63° 02′	31° 03′
25	Ylistaro	1971	62° 56′	22° 30′
26	Alavus	1971	62° 32′	23° 39′
27	Kuusjärvi	1971	62° 42′	28° 55′
28	Ylimarkku	1971	62° 41′	21° 21′
29	Laukaa	1971	62° 32′	26° 01′
31	Jämijärvi	1971	61° 44′	22° 43′
32	Sysmä	1971	61° 31′	25° 49′
35	Kotaniemi	1971	61° 22′	28° 40′
36	Lammi	1971	61° 03′	25° 03′
37	Oripää	1971	60° 54′	22° 42′
38	Jokioinen	1971	60° 49′	23° 30′
40	Virolahti	1971	60° 32′	27° 33′
41	Punkaharju	1971	61° 48′	29° 20′
42	Vihti	1971	60° 25′	24° 24′
43	Sipoo	1971	60° 24′	25° 14′
44	Jomala	1972	60° 11′	19° 59′
45	Espoo	1972	60° 13′	24° 36′
46	Hailuoto	1972	65° 02′	24° 48′
47	Korppoo	1972	60° 10′	21° 34′
48	Tvärminne	1972	59° 51′	23° 15′
52	Peipohja	1978	61° 16′	22° 15′
57	Rahja	1984	64° 13′	23° 42′
58	Jaurakkajärvi	1984	65° 10′	27° 37′
59	Hietanen	1984	61° 34′	27° 01′

(SFS 3017 1982), potassium (SFS 3017 1982), calcium (SFS 3018 1982), magnesium (SFS 3018 1982) and total organic carbon (National Board of Waters, Report 213 1981).

The methods for analysis have been presented in the publication of the National Board of Waters, Report 213. In addition, measurements are taken of the rainfall quantity in order to calculate the collecting efficiency of the devices.

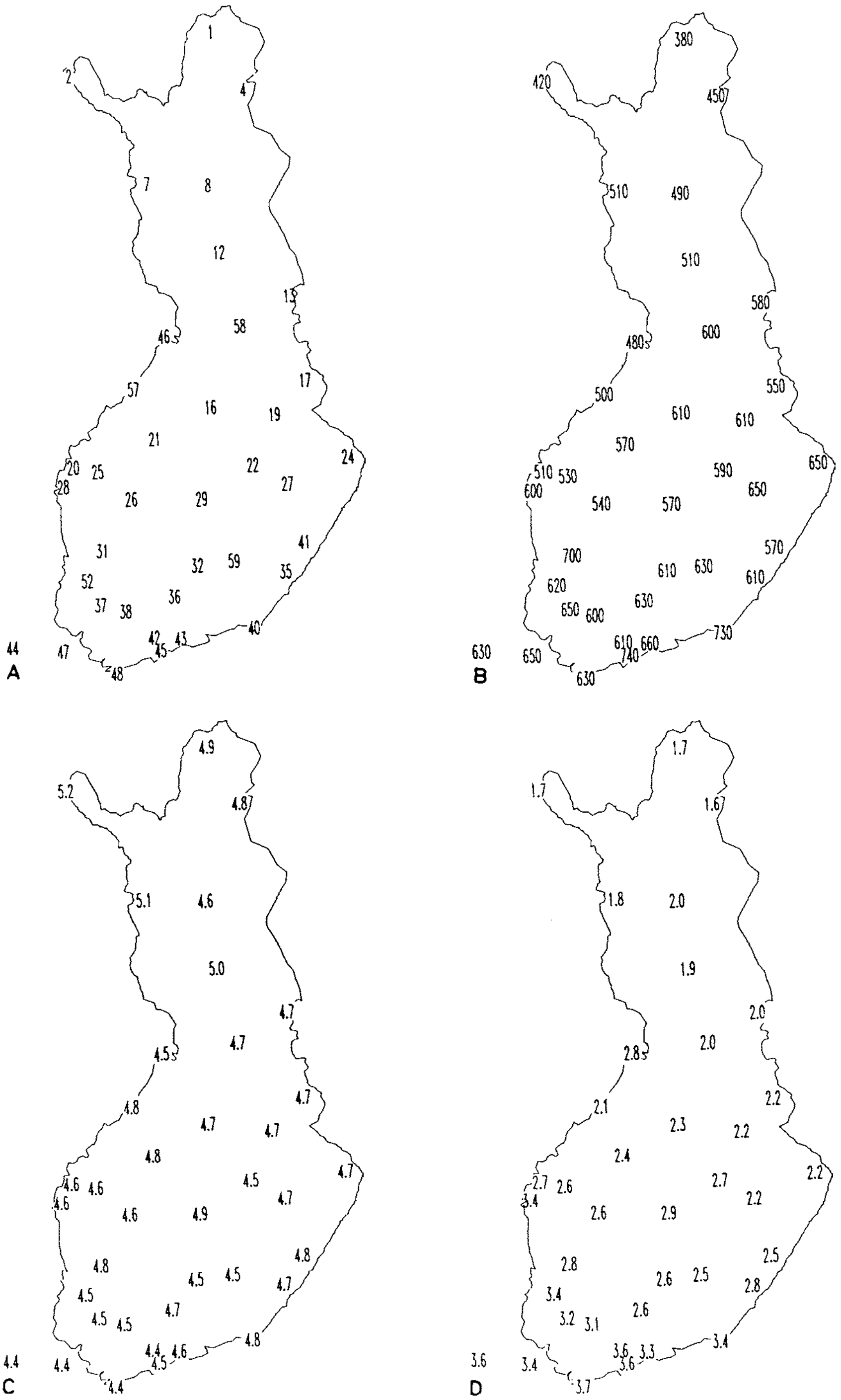

Fig. 3A–D. A Precipitation stations in 1988 (code numbers). **B** Average yearly precipitation in 1971–1988. **C** Median pH value in deposition in 1971–1988. **D** Yearly median deposition of strong acids in 1973–1988 (H^+ mmol $m^{-2} y^{-1}$)

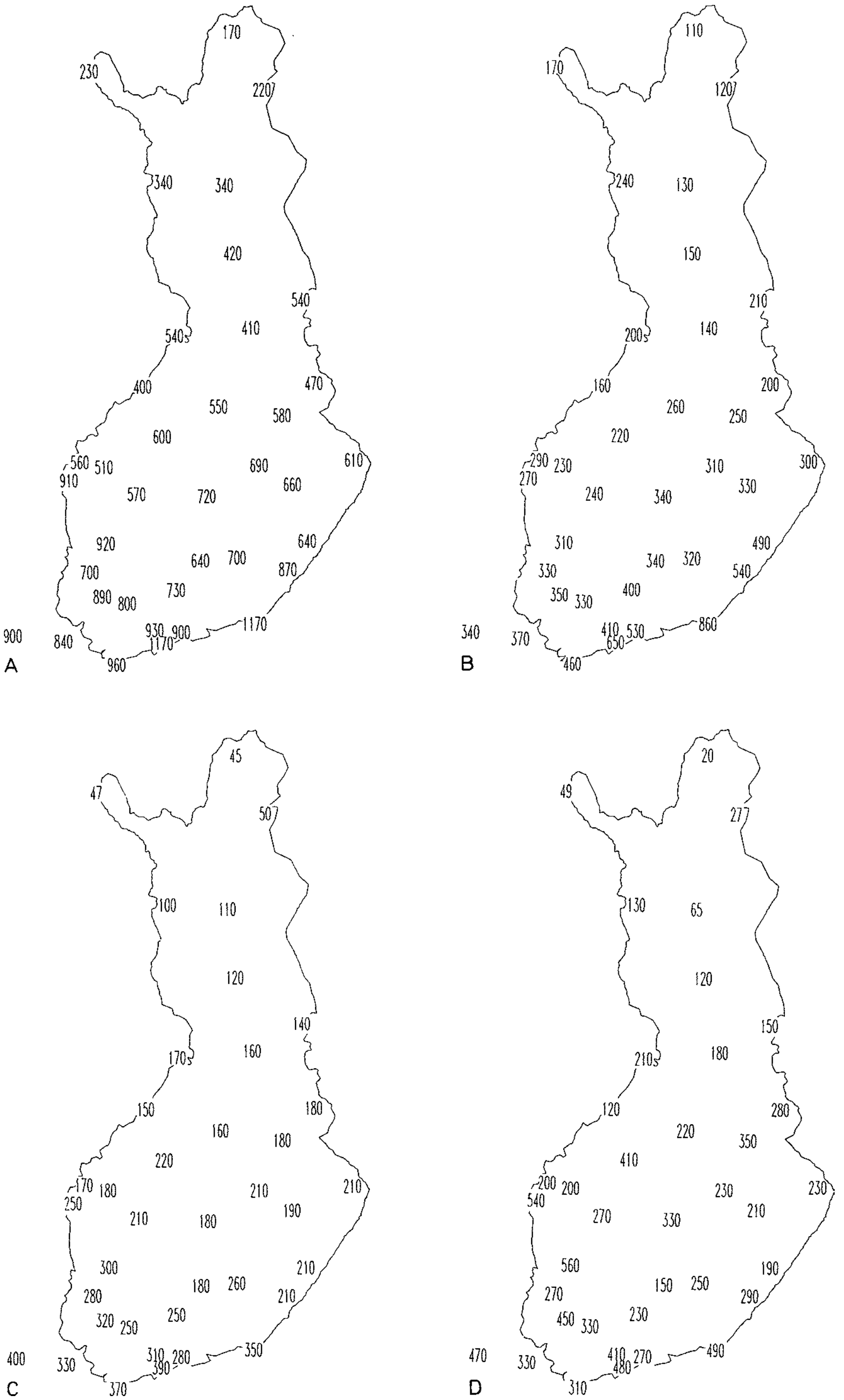

Fig. 4A–D. Yearly median deposition in 1971–1988 of: **A** Sulphate sulphur (SO_4–S mg m^{-2} y^{-1}). **B** Calcium (Ca mg m^{-2} y^{-1}). **C** Nitrate nitrogen (NO_3–N mg m^{-2} y^{-1}). **D** Ammonium nitrogen (NH_4–N mg m^{-2} y^{-1})

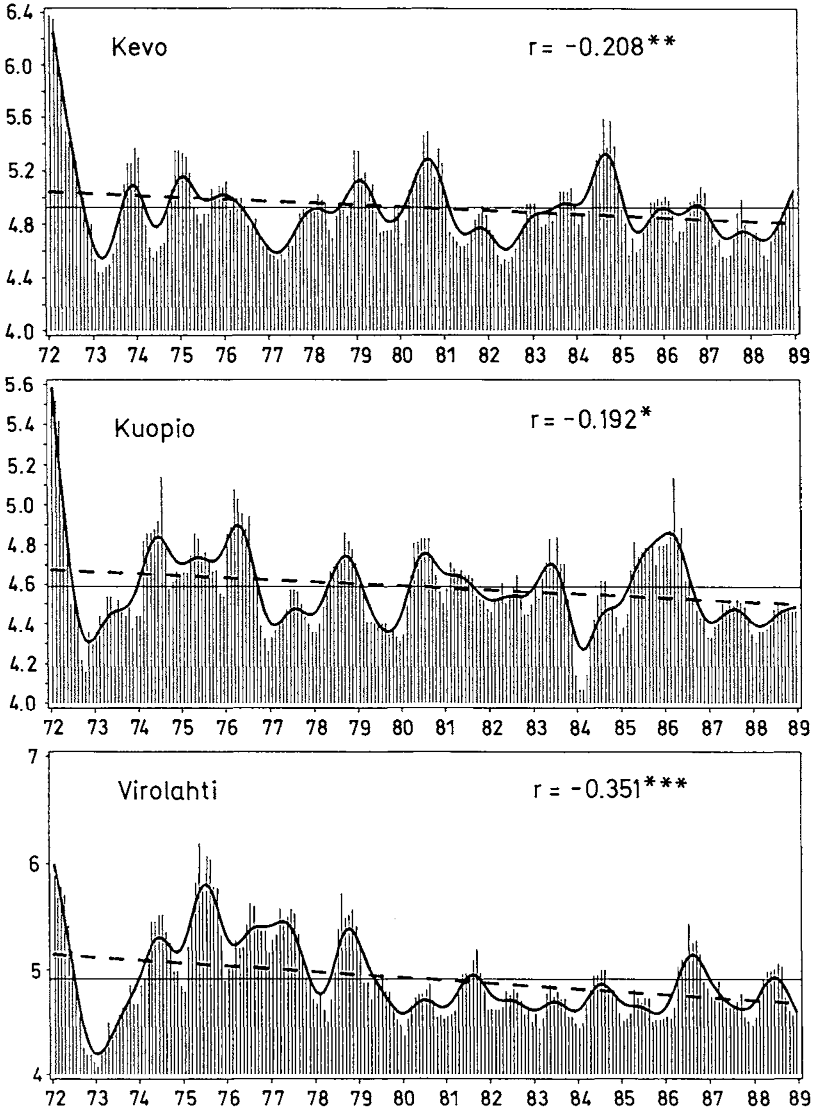

Fig. 5. Trend analysis of pH values

Results

After inspection of the results, all the data are recorded on the Precipitation Database in the National Board of Waters and the Environment's computer, which currently has more than 110,000 analysis results. The data are easy of access and combined with water quality data from the Board's other data banks.

The time series derived from rainwater investigations are now suitable for statistical treatment, since in the great majority of cases each station's series of

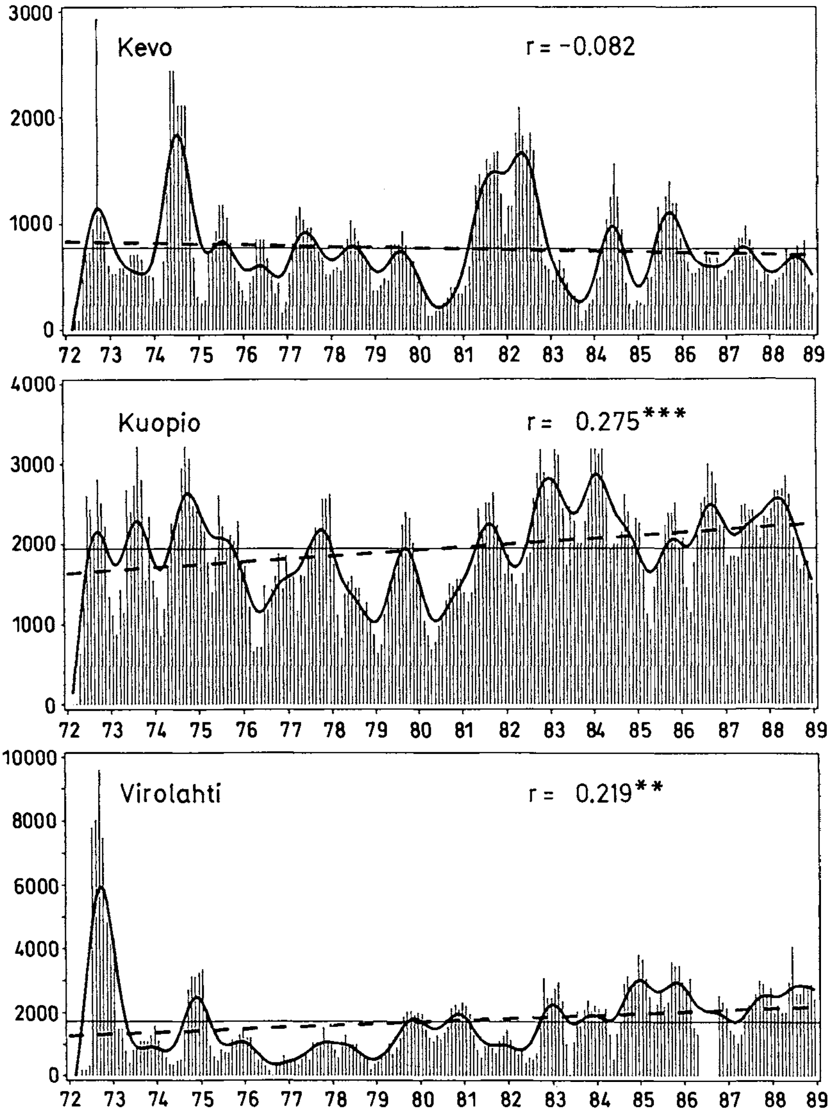

Fig. 6. Trend analysis of strong acids (mmol m^{-2})

observations now runs to more than 200 months. The yearly median deposition for each component is shown in Figs. 3–6. The yearly value has been calculated by multiplying the median value of the observations in 1971–1988 by 12. These maps provide a clear picture of the scale of deposition in different areas of Finland, i.e. they indicate in several cases a distinct north-to-south gradient, a so-called geographical trend, which means that in southern Finland the deposition levels are noticeably higher than in northern Finland. This is also to be seen in the trend analysis figures by calculating the sliding average (sliding average of 7 months and

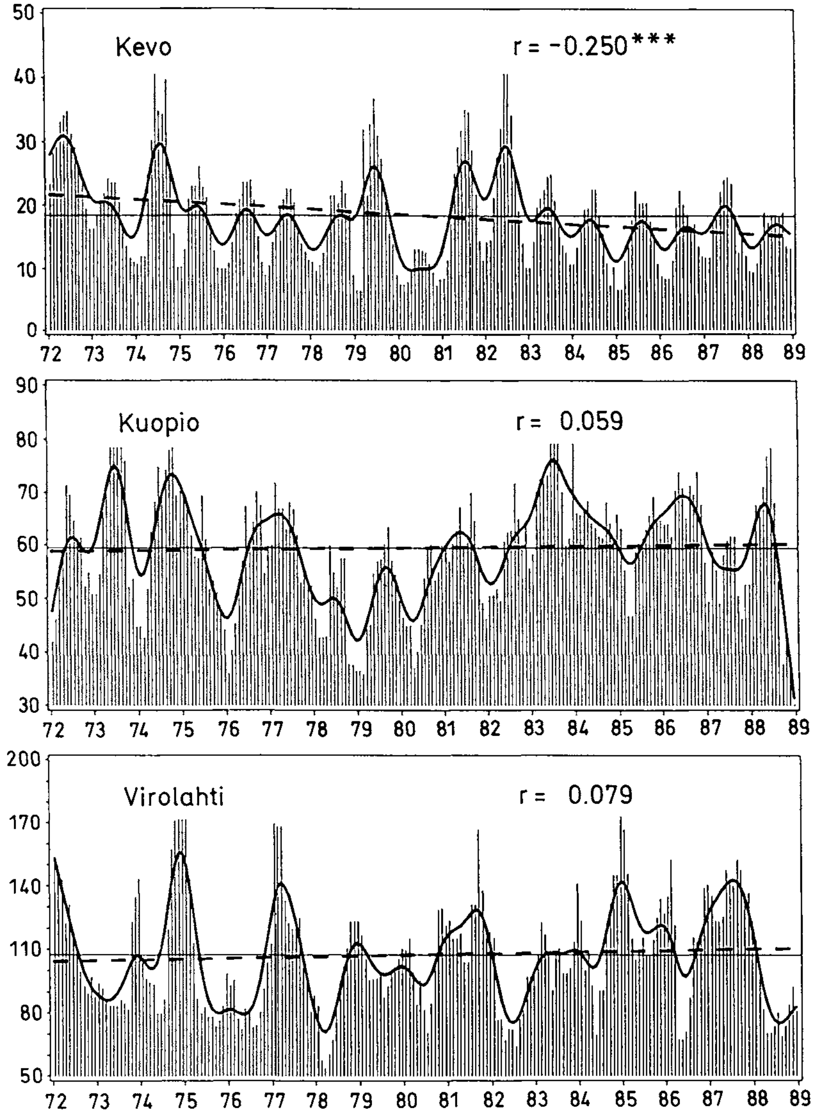

Fig. 7. Trend analysis of sulphate sulphur (mg m^{-2})

the highest and lowest value dropped) and based on figures from three observation stations, Kevo, Kuopio and Virolahti. In 1985 was published a study of the temporal development of acid deposition at Sodankylä, Jokioinen, Vihti and Virolahti stations in 1971–1982 (Järvinen et al. 1985).

In Figs. 5–10 one can see also the mean value line and the trend curves using spline interpolation. The figures contain linear regression lines (dashed line) which show the approximate trend in the time series in 1971–1988. It seems that the amount of precipitation is increasing, especially in southern Finland. This conclusion is the same as FMI's results.

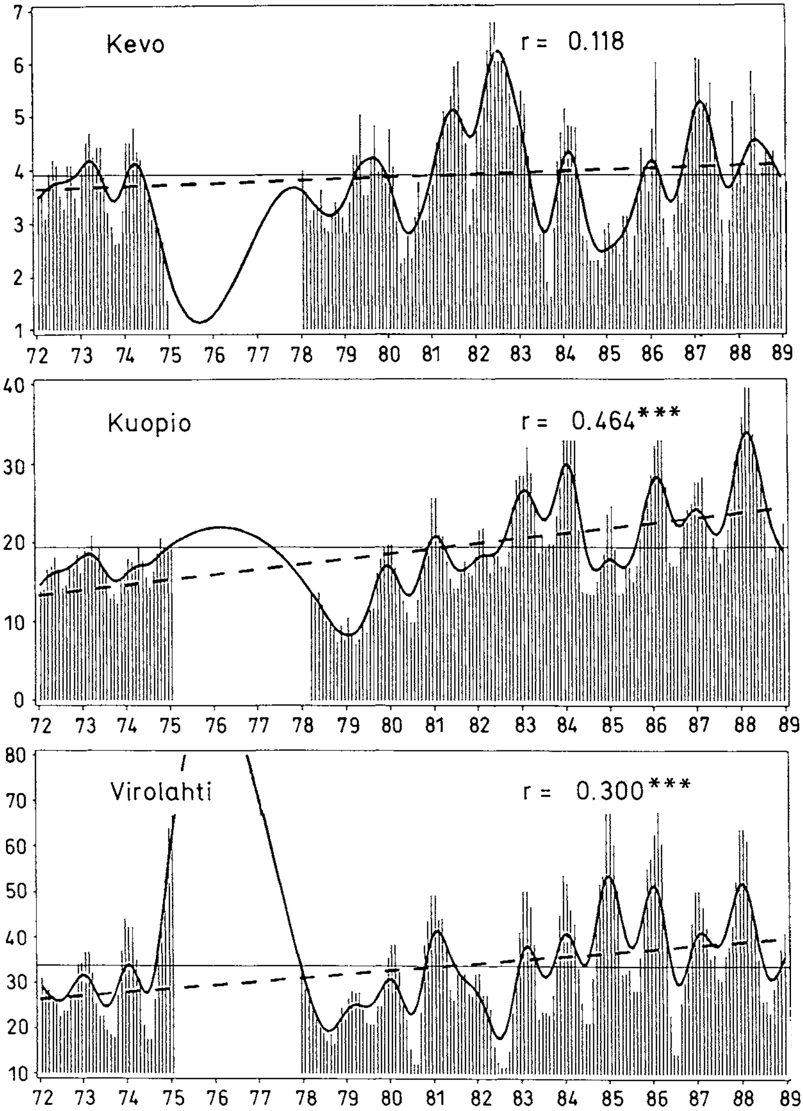

Fig. 8. Trend analysis of nitrate nitrogen (mg m^{-2})

In the figures for pH it can be seen that the trend lines are descending and this result does not agree with the Box-Jenkins method. Using the Box-Jenkins statistical method, a time series analysis was carried out of pH values, on the basis of which an attempt was made to forecast the development of future pH values over the following 5 years. On the basis of the pH values from 1971–1982 the situation has not materially worsened, nor does analysis of past pH values give cause to predict that values will decline in the immediate future (Järvinen 1986). In the

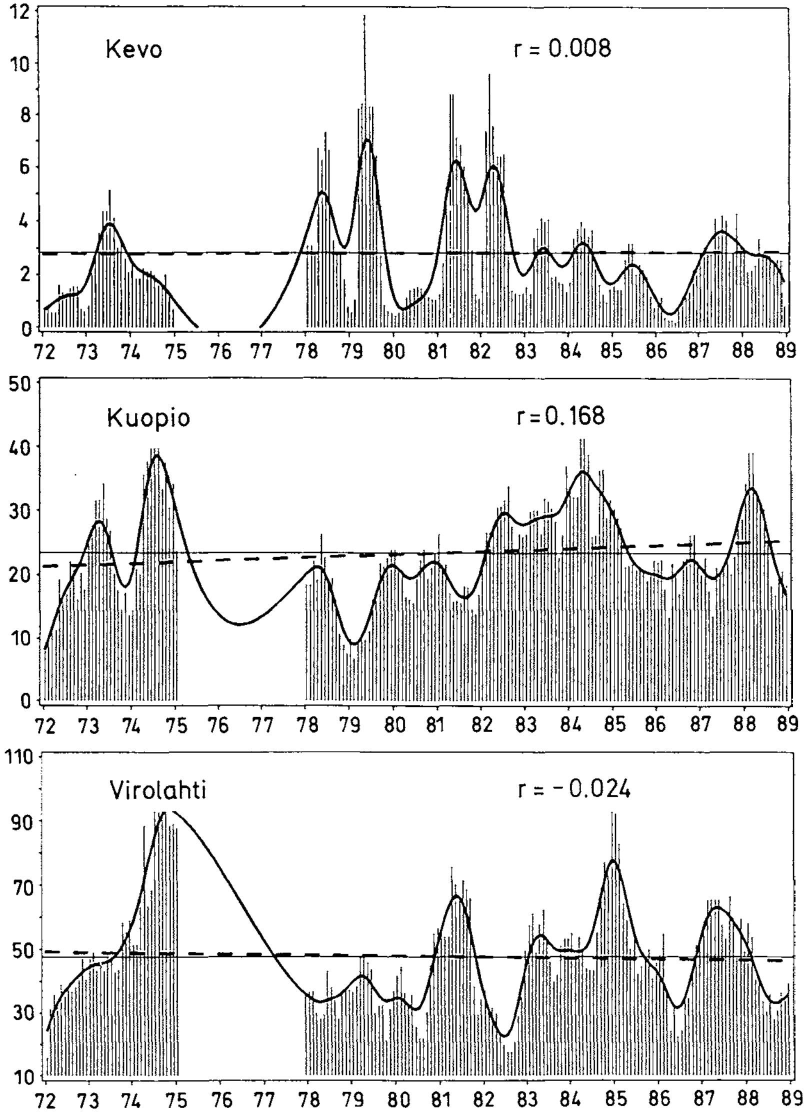

Fig. 9. Trend analysis of ammonium nitrogen (mg m^{-2})

beginning of the time series quite high pH values exist, probably due to contamination, and if one leaves the 2 first years away, the trend lines do not descend so much at all. The curves of strong acids agree quite well with pH curves, i.e. when the pH value is high then the strong acid value is low.

The trends in sulphate sulphur seem to stay stable and in the north it seems even to diminish. Maybe this is due to the phenomenon that sulphur emissions have decreased in Europe. Sulphur deposition has for some time now been a subject of great public interest. Here the north-south gradient is plain to see.

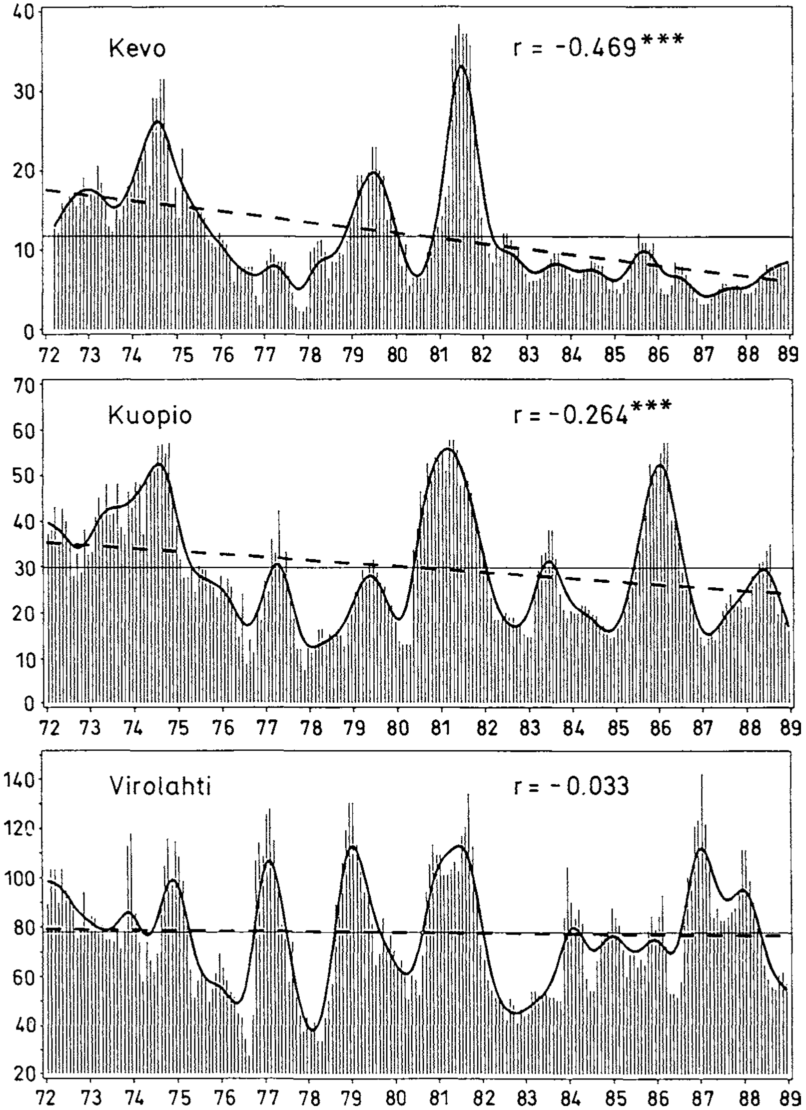

Fig. 10. Trend analysis of calcium (mg m^{-2})

From the perspective of natural tolerance levels, the critical figure has been found to be 0.5 g of sulphur m^{-2} per year. This figure is exceeded practically throughout the area south of Oulu. In the southernmost parts of Finland the highest values peak at around 1.2 g of sulphur m^{-2} per year. In general terms, the level of sulphur deposition in Finland is relatively low compared with that of other European countries. When comparing results with other nordic countries, it can be noticed that, for example, sulphate sulphur deposition is equal, but that strong acid deposition is only half of that which is deposited in the south of Norway and south Sweden (Järvinen et al. 1985).

In north and central Finland the calcium content of precipitation decreases clearly,but in south Finland no changes can be seen. Nitrate seems to increase quite strongly and at the same time also the emissions of nitrate have increased. Of nitrogen compounds it can be said there is more NH_4–N than NO_3–N in Finland, particularly in the more westerly observation stations. In Sweden the figures for the two compounds are roughly equal. Thus far it has not been possible to explain this divergence. The laboratory also determines the total nitrogen deposition from the samples. When we subtract from this total figure the values for NH_4–N and NO_3–N, we arrive at a value for organic nitrogen. Over the long term this organic nitrogen level has shown up as a mean value of around 28% of total nitrogen.

Conclusions

WERI's monitoring studies on rainwater quality are the most extensive and longest-running research investigations into air quality in Finland. The results have been shown to be comparable in a number of different contexts, and the level of analytical work has been charted in numerous comparative sample studies, where the success rate has been high.

The suitability of individual observation stations for the task of background air monitoring should be constantly checked. By developing the equipment used, we should try to optimize the reliability of the data produced. In future deposition studies it should be possible to estimate the relative shares of wet and dry deposition in the overall deposition figures and also metal deposition. The necessary ADP software for processing and working up results, which should be routinely available, will have to be continuously developed and upgraded.

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Model Calculations of Sulphur and Nitrogen Deposition in Finland

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Summary

The deposition and origins of sulphur and nitrogen in Finland have been calculated using LRT models developed within the ECE/EMEP project. In the sulphur calculations, new emission data from the Soviet Union were included. The results show that about 260 Gg of S was deposited in 1980 and 210 Gg a^{-1} in 1987–88. The indigenous fraction decreased from about 50 to 35% of the source-attributable deposition between 1980–88, mainly due to a national reduction in S emissions. There are two maxima in the large-scale S deposition field, one connected with the general south-north gradient, the other being due to the emissions in the Kola Peninsula. Nitrogen deposition was calculated at less than 50 Gg(N) both for NO_y and NH_z, the highest deposition flux occuring in south-east Finland. The USSR was found to be the major source of the N deposited. A comparison of calculations and observations revealed greater discrepancies at Finnish measurement sites than on the average in Europe, calculated concentrations being systematically lower than observed ones. The reasons underlying this were sought, but no definite answer found.

Introduction

The first findings regarding the link between the increased acidity of surface waters in southern Scandinavia and emissions of sulphur and nitrogen oxides in Central Europe were met with indifference and scepticism in the 1960's. In 1973 the OECD launched the LRTAP (the Co-operative Technical Programme to Measure the Long-Range Transport of Air Pollution) study, in which 11 European countries participated. This study provided a basis for the present understanding of the distribution of sulphur emissions and their transportation in Europe (OECD 1977). The study concluded that airborne pollutants can be transported by wind over long distances, and that air and precipitation quality in one country can be measurably affected by emissions in other countries, some countries being net importers and others net exporters of pollutants.

The OECD LRTAP study led to political initiatives, one of which is the Convention on Long-Range Transboundary Air Pollution supervised by the UN

Kauppi et al. (Eds).
Acidification in Finland

Economic Commission for Europe (ECE) which was signed by many European states, the United States and Canada in 1979. From the point of view of present air pollution research, it also provided the framework for the EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe) project run under the ECE Convention since 1977.

The main objective of EMEP is to produce information on the deposition and concentration of air pollutants, as well as on the quantity and significance of pollutant fluxes across national boundaries (Eliassen and Saltbones 1983). There are two ultimate methods for producing this information, viz. measurements and modelling. In practice, however, these methods are not applied independently of each other.

Based mostly on the calculations made with the EMEP Long-Range Transport (LRT) models, this chapter aims to give an overview of the long-term distribution of deposition of pollutants and their origin in Finland. Deposition of sulphur and nitrogen (both oxidized and reduced N) are considered, but no attempt is made to relate them to the acidity of deposition, or to the actual acidification processes going on in soils and waters. Nor are the features of short time scale or deposition episodes discussed. A more process-orientated atmospheric approach describing, for example, interactions between meteorology and air chemistry can be found in this volume in the chapter by Joffre et al.

Since the main results presented in this chapter are calculated using the EMEP models developed by the EMEP Western Meteorological Synthesizing Centre (MSC-W) at the Norwegian Meteorological Institute, EMEP publications are referred to whenever possible. The results of new calculations are given for Finland only, not for the whole of Europe.

Observed Levels of Sulphur and Nitrogen Deposition in Northern Europe

A general picture of the deposition levels in Northern Europe can be formed by inspecting briefly the observation data. There are roughly 90 EMEP stations in Europe, most of which sample on a 24 h basis. At the moment, only three of the stations are located in Finland, none of them north of 65°N. Thus, the estimates for the northernmost regions must be based on data points in Norway and in the Kola Peninsula in the USSR. For locations of and measurement programmes at the Finnish stations, see Joffre et al. (this Vol.). There are also a number of other stations, e.g. national networks, sampling on a weekly or monthly basis, but these are not considered here.

Wet Deposition

Over Finland, there is a considerable decreasing south-north gradient of sulphate, nitrate and ammonium concentrations present in precipitation. According to the

Table 1. Mean levels of excess (sea salt corrected) sulphur and nitrogen concentrations in precipitation in some regions of Europe during the mid-1980's (volume weighted arithmetic annual mean)

Region	Sulphate mg(S) l^{-1}	Nitrate mg(N) l^{-1}	Ammonium mg(N) l^{-1}
Northern Finland	0.3–0.5	0.1–0.2	0.1–0.3
Southern Finland	0.5–1.5	0.3–0.7	0.5–0.7
Central Europe (max.)	>2	>1	>2

EMEP measurement data (Schaug et al. 1987), an order of magnitude difference can be observed between the general levels in Northern Finland and the most polluted regions of Central Europe (Table 1).

The areas with the highest sulphate concentration are located in Eastern Europe, while nitrate is found more to the west, which reflects the emission structure. The distribution of nitrate concentration is rather uniform over Central Europe, with a plateau of ca. 0.7 mg(N) l^{-1} reaching from the Alps up to southern Fennoscandia and the southeastern United Kingdom, where the concentration decreases rapidly. The pattern for ammonium reveals a more uneven distribution, following the distribution of ammonia emissions. In the Netherlands, where emission density in certain areas exceeds 10000 kg(NH_3) km^{-2} a^{-1}, average annual ammonium concentrations as high as 3 mg(N) l^{-1} are observed in precipitation (Buijsman and Erisman 1986).

In terms of wet deposition flux, i.e. precipitation concentration multiplied by precipitation amount, the observed sulphur load varies spatially between 200–1200 mg(S) m^{-2} a^{-1} in Finland during the mid-1980's. Wet nitrogen deposition is roughly 400 mg m^{-2} a^{-1} of NO_3^--N and 500 mg m^{-2} of NH_4^+-N at maximum in southernmost Finland, and 50 mg(N) m^{-2} a^{-1} at minimum in the north for both nitrate and ammonium.

On a continental scale, the spatial variation in long-term precipitation quantities is relatively small in Finland, where the strong terrain-induced peaks are lacking. However, since a large proportion of long-term wet deposition is accumulated during a small fraction of rainfall events, the feature commonly called the episodicity of deposition, the mean rainfall is indicative only. Also the frequency in the occurrence of different types of precipitation and storm fronts plays a significant role (Bremer 1987).

Dry Deposition

There is no routinely applicable method for taking direct measurements of dry deposition. Dry deposition flux can be estimated from measured air concentrations in the same way as the dry deposition process is usually included in the transport models, i.e. by applying $F = v_d c$, where F is the flux of the compound with concentration c at a reference height (typically 1 m). The dry deposition velocity

(v_d) depends on chemical and biological interactions between the surface and the pollutant, and on aerodynamic factors (for discussion and typical values of v_d for various compounds, see Joffre et al. this Vol.).

Dry deposition of oxidized sulphur consists of gaseous SO_2 and particulate sulphates [e.g. $(NH_4)_2SO_4$]. Gaseous NO_2, gaseous HNO_3 and particulate nitrates should at least be taken into account when determining the dry deposition of oxidized N, while NH_3 and particulate ammonium (sulphates plus nitrates) are needed for reduced N. Unfortunately, measurements of concentrations in air are too sparse to provide a basis for a spatial estimate of dry deposition flux on a regional scale.

Even in unpolluted areas, dry removal makes a big contribution to total deposition. In sulphur, for example, it accounts for approximately 1/3-2/3 (Hov et al. 1987). Dry deposition makes a pronounced contribution in certain situations where high local deposition fluxes are encountered. Close to heavy ammonia sources, e.g. cattle and fur animal farms, dry deposition plays a very significant role because of low source heights and small surface resistance to the uptake of gaseous ammonia. At forest edges larger quantities of nitrogen are also received than deep inside the forest. Grennfelt and Hasselrot (1987) measured throughfall flows of $NO_3^- + NH_4^+$ at exposed forest edges in southern Sweden, which were two to five times those found inside the forest, because of the influence of dry deposition.

Model Calculations

To model atmospheric dispersion, transformation and deposition of reactive sulphur and nitrogen compounds, temporal and spatial scales spanning a few days and thousands of kilometres must be considered. There are a few models suitable for the long-term estimation of atmospheric loads of acidifying compounds in Europe. The Lagrangian trajectory models developed within EMEP are probably the best known of these; they are widely applied and frequently referred to. Eulerian models, using simple chemistry for S and NO_x, have been developed at the Danish Air Pollution Laboratory (Zlatev et al. 1985a,b), while the statistical trajectory model at the Harwell Laboratory in the U.K. includes a fairly comprehensive chemical description of nitrogen but very simple meteorology (Derwent 1987). Fisher (1978) and Klug and Erbshäußer (1988) have presented statistical sulphur models. These models have in common that they aim at repeated long-term calculations and, therefore, compromises between the complexity of a description of modelled processes, input data availability and computational efforts have been sought.

The EMEP models, which were used in the present calculations for Finland, are presented below in more detail. These models were chosen for the study because they are widely accepted, and have the status of furnishing results under the ECE Convention.

EMEP Models

The EMEP/MSC-W LRT models are described and evaluated in detail in the literature by their developers (Eliassen and Saltbones 1983; Eliassen et al. 1988; Hov et al. 1988). The sulphur model has also been subjected to extensive investigation by other groups, e.g. since it is used to provide the emission-deposition transfer matrices for the integrated acidification model RAINS of the International Institute for Applied Systems Analysis (e.g. Alcamo et al. 1987; Alcamo and Bartnicki 1987; Pitovranov 1988). In some studies it has been used as a frame of reference in the creation of more sophisticated parametrization (e.g. Joffre 1988a). In the following the formal basics of the models are given to provide a background against which the results presented in later sections can be understood.

Basic Formulation

For the sake of clarity, the basic formulation is presented here assuming that concentrations follow a linear system, although, strictly speaking, the nitrogen model includes a non-linear function in the chemistry section. However, the models are essentially linear. Thus, the basic mass balance equation (a set of ordinary differential equations) of the models can be expressed simply as

$$\mathrm{Dc/dt} = \mathbf{Sc} + \mathbf{R}, \tag{1}$$

where the state variable **c** is the N-dimensional vector of concentrations; N is the number of compounds modelled. **S** is a matrix describing chemical interactions and deposition processes (NxN elements). **R** is the N-dimensional source term. The operator D/dt denotes the total Lagrangian time derivative, i.e. $D/dt = \delta/\delta t + \mathbf{V} \cdot \nabla$ where **V** is the horizontal (non-divergent) wind field on an isobaric level chosen to represent the transport in the atmospheric boundary layer. In the present EMEP calculations, the 925 hPa pressure level, approx. 700 m above the ground, has been used.

The source term elements R_i can be expressed as follows.

$$R_i = \begin{array}{ll} (1 - \alpha_i - \beta_i)\, Q_i\, h^{-1} & \text{for primary emitted compounds} \\ \beta_j\, Q_j\, h^{-1} & \text{for secondary emitted compounds} \\ 0 & \text{for secondary non-emitted compounds} \end{array} \tag{2}$$

where Q_i is the areal emission flux of compound i. Division by mixing height h indicates that an instantaneous and complete vertical dilution is assumed. No external horizontal diffusion is included because of the inherent smoothing of the emission field in 150 km × 150 km grid squares. Emission strength is reduced by two factors: α_i takes into account the more effective removal of pollutants close to sources where dry deposition is enhanced; β_i is the fraction of Q_i that is assumed to be emitted as a secondary pollutant j.

The diagonal elements of S consist of sink terms due to chemical reactions and deposition:

$$S_{ii} = -(\Sigma k_{c_i} + k_{d_i} + k_{w_i}), \tag{3}$$

where k_c, k_d and k_w are first-order rate coefficients for chemical conversion, dry deposition and wet deposition, respectively. The chemical sink in S_{ii} consists of one or many reactions; the corresponding production rates are represented by the off-diagonal elements. Dry removal rate is expressed as $k_{d_i} = v_{d_i} h^{-1}$, where v_d is dry deposition velocity. Wet deposition rate is assumed to depend proportionally on precipitation intensity P, that is, $k_{w_i} = W_i P h^{-1}$ where W is an empirical scavenging ratio.

Trajectories are calculated to arrive at measurement stations and grid points covering Europe. Along the trajectories the mass balance Eq. (1) is solved. Deposition flux in the Eulerian framework is determined at every trajectory position by

$$F_i = (k_{d_i} + k_{w_i})\, h\, c_i, \tag{4}$$

or, in the sulphur model, calculated later from the Eulerian concentration fields formed by the values at trajectory arrivals.

In addition, background pollution and the exchange process between the boundary layer and the free troposphere are included in the models. In the sulphur model, constant background values are added to the calculated concentrations, giving rise to indeterminate deposition. In the nitrogen model, initial values are assumed at the beginning of the trajectories and in the free troposphere. Consequently, indeterminate deposition is formed more indirectly.

Chemistry

Sulphur dioxide and particulate sulphate are the compounds considered in the sulphur model. Most of the sulphur emissions are assumed to occur in the form of SO_2 [$\beta = 0.05$, see Eq. (2)]. Conversion of SO_2 is determined by the transformation rate, which depends on the time of year, reflecting in turn the variation of light and oxidant concentrations.

Several compounds have to be taken into account in the nitrogen model because of their different lifetimes with respect to removal. NO, NO_2, PAN, gaseous HNO_3 and particulate nitrates represent the total reactive oxidized nitrogen in the atmospheric boundary layer in the model. The sum of these compounds is expressed here as NO_y. Modelled reduced nitrogen (here NH_z) consists of NH_3 and particulate ammonium sulphates plus ammonium nitrate. Ammonium nitrate links the NO_y and NH_z chemistries. In addition, to estimate the amount of ammonia available for the formation of NH_4NO_3, the sulphate concentration must be known, i.e. sulphur must also be modelled in the nitrogen model. The chemistry module is described in detail by Eliassen et al. (1988).

In the nitrogen model, the chemical conversion rates are mostly calculated from reaction rates and related parameters. Three monthly and diurnally varying concentrations needed for conversion rates (O_3, OH and CH_3COO_2) are obtained from a two-dimensional global model (see Eliassen et al. 1988). These species are treated as having infinite reserves, an assumption which provides the linearity of the model (apart from the nitrate-ammonia link).

Present Calculations

Model Variants

For the present sulphur calculations, the description of source-receptor areas of the EMEP sulphur model was extended. The model formulation allows an arbitrary definition of the areas within the grid, the division bound to the country borders being the most obvious choice and the one of greatest political interest, since area-by-area pollutant budgets can be calculated. Nevertheless, it is clear that such country-by-country budgets cannot provide all the information that could be obtained by a more detailed definition of the areas. Also, the smaller the area the more reliably the effect of possible emission changes can be corrected simply by scaling deposition to the total emission rate of that area, without having to recalculate it.

This applies especially to the Soviet Union. Because of its large size and considerable emissions, results involving the Soviet Union have necessarily appeared highly integrated. It has not, for instance, been possible to attribute a fraction of the deposition to specific concentrated emission regions such as the Kola Peninsula in the very north of the USSR close to Finland. This has limited the applicability of the model in studies concerning the effect of emission reduction in the western Soviet Union.

To disintegrate the information and to make full use of the emission data presented in the next section, the Soviet Union was divided into several emitter-receiver areas. Nine new areas along the western border were defined based on administrative regions: (1) Murmansk Oblast (region), (2) the Karelian Autonomous Socialist Soviet Republic, (3) Leningrad Oblast, (4) Novgorod and Pskov Oblasts, (5) the Estonian Socialist Soviet Republic (SSR), (6) the Latvian SSR, (7) the Lithuanian SSR, (8) the Byelorussian SSR and (9) the Ukrainian SSR. Additionally, Finland was divided into three regions in a north-south direction.

Apart from the country extension, the model used for the sulphur calculations is the latest operational version of the EMEP sulphur model, as described in Eliassen et al. (1988). In principle, transports of sulphur could as well be calculated using the EMEP N model, since the formula for sulphur is basically the same in both models, the greatest difference probably being the treatment of background concentrations. The nitrogen calculations are made using the EMEP N model (Eliassen et al. 1988) with no changes apart from the technical treatment of input data.

Calculation Period

The calculation periods were determined mainly by practical considerations, including the availability of emission and meteorological input data and computing resources. The sulphur calculations were carried out for the years 1980, 1987 and 1988. Within the ECE/EMEP emission inventory, the most comprehensive estimate of sulphur emissions in Europe is available for 1980, which is the base year for SO_2 reduction within the ECE Convention. The new data described in the next section present the best coverage for 1987; 1988 was included to supply the latest possible estimate and indication of the extent of meteorological year-to-year variability.

The 6 h meteorological input (trajectories calculated from horizontal wind field, vertical velocity at the mixing layer top for the exchange between the boundary layer and free troposphere, the friction velocity and the turbulent heat flux for the dry deposition velocity, and the amount of precipitation) is obtained from the Norwegian Meteorological Institute's numerical weather prediction model, and the 24 h data (mixing height) from objective analysis of radiosonde observations (Eliassen et al. 1988).

The N model was run for 1985 because the extensive meteorological input needed for this model was not available for other years. Also emission data is much more sparse and uncertain for NO_x and NH_3 compared to SO_2.

Emission Data

New official estimates of sulphur emissions from western parts of the Soviet Union were obtained for the calculations (Kulmala 1989). Previously, only the total rates for the whole European part of Soviet Union, and Ukraine and Byelorussia were reported, and spatial distribution in the grid was estimated at the MSC-W. The

Table 2. Sulphur emissions in Finland and the Soviet Union in 1980 and 1987 [in 1000 tonnes or Gg(S) a^{-1}] (Kulmala 1989; Eliassen et al. 1988)

Region	Year 1980	1987
Finland	292	162
Kola	362	350
Karelia	85	85
Leningrad	125	112
Estonia	120	104
Total	692	651
European USSR total	6400	5100
Europe total	26,100	21,500

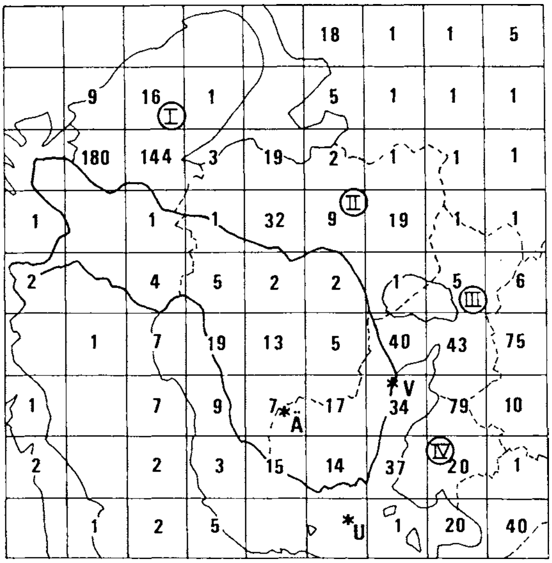

Fig. 1. Sulphur emissions in the EMEP grid over Finland and the nearby regions of the Soviet Union in 1987 [Gg(S) a^{-1}].The Soviet regions: *I* Kola Peninsula; *II* Karelia; *III* the Leningrad region; *IV* Estonia. The location of the EMEP measurement stations Ähtäri (*Ä*), Virolahti (*V*) and Utö (*U*) is marked with *stars*

new data include information on source distribution in the Kola Peninsula, Karelia, the Leningrad region and Estonia. Total S emissions for these regions are given in Table 2 and the distribution in the EMEP grid for 1987 in Fig. 1.

The Soviet data from the four regions near Finland presented in Table 2 differ significantly from the values obtained from the distribution used in the earlier calculations, the figures for Kola being more than 50% higher. On the other hand, the previous estimates for Leningrad and Estonia have to be halved. The strikingly large emissions in the Kola Peninsula originate almost entirely from two copper-nickel smelters, one located in Nikel and Zapolyarnyy, close to the Norwegian border, and the other in Monchegorsk (ca. 68°N, 33°E). These smelters contribute 80% of the total Kola emissions (Kulmala 1989). No quantitative information is available regarding the uncertainty in these new estimates.

In other parts of Europe, the official emission data reported to ECE/EMEP by the European countries by February 1989 have been used.

For the nitrogen calculations, the data employed by EMEP was used without any alterations. The estimated NO_x emissions were ca. 5900 Gg(N) in Europe in 1985, 73 Gg of which was emitted in Finland (Eliassen et al. 1988). No official estimate is available for ammonia, but according to the values used in the model 9100 Gg(N) a^{-1} were released in the mid-1980's. For Finland a value of 50 Gg(N) was applied, which compares well with the estimate of 43 Gg presented by Niskanen et al. (this Vol.).

Comparison of Calculated Concentrations with Measurements

Before presenting the deposition results obtained from the calculations, it is appropriate to see how the modelled concentrations compare with those observed. As far as model validation is concerned, the EMEP measurement programme provides data for sulphur compounds but very little for the nitrogen model, since NO_2 was practically the only component measured in air within the EMEP network in 1985. Nitrate and ammonium were measured in precipitation at a large number of stations, but the lack of measurements of these compounds in air makes it difficult to address uncertainty.

The words "underestimated" and "overestimated" are used throughout this chapter in comparing modelled values with measurements. Herewith it is assumed implicitly that the measured values are the correct ones. This is, of course, not always true. Validation of measurements is not, however, within the realm of this chapter.

European Stations

Throughout all the stations on average, sulphur dioxide concentrations are modelled very satisfactorily on a monthly basis (Eliassen et al. 1988). The same applies to particulate sulphate. Taking the averages for single stations over a period of 1 year, there is a considerable scatter in agreement between the stations. Mean annual sulphate in precipitation is slightly underestimated, the deviation between measurements and calculations being within a factor of 2 for all but a few. Since the measured wet deposition includes "contamination" by dry deposition, the systematic discrepancy is probably not so absolute.

With the exception of a few sites, observed and calculated mean annual NO_2 concentrations deviate from each other by a factor of less than 2, with a consistent pattern of underestimation emerging (Eliassen et al. 1988). Calculated values for nitrate in precipitation seem to be greatly (ca. 30%) underestimated, if no allowance is made for the effect of dry deposition. Nevertheless, the extent of this augmentative contribution is not known. According to Eliassen et al. (1988), dry deposition of HNO_3 gas is even significant in rainwater collected in a wet-only sampler, in which the funnel is open only during precipitation events. Dry deposition may be taken into account by adding the modelled dry deposition to the modelled wet deposition on days when wet deposition has accumulated in the model. This provides an estimate of the upper limit of the concentration. The upper limit concentration agrees much more closely, being an overestimate of less than 5%. This reasoning is hampered, however, by the inherent fact that the deposition velocities used in the model are not chosen for precipitation samplers but for natural surfaces.

Ammonium is underestimated even more in the calculations, even when dry deposition is totally included. However, as pointed out by Eliassen et al. (1988) and Buijsman and Erisman (1988), the particular problem with ammonium observations lies in the location of the background stations. The siting may be "background" with respect to sulphur and nitrogen dioxides though not with respect to ammonia, since the stations are typically located in agricultural areas or, in other words, in ammonia source areas. This means that in the case of NH_z many EMEP stations are influenced by local scale features not resolved in an LRT model.

Finnish Stations

Finland is located at the edge of the EMEP model calculation domain. Differences may, therefore, exist in the validity of the model calculations compared with those obtained in more central parts of Europe. Also, climatological and phytogeographical conditions in Finland differ from those in more southern and western parts of Europe, so that the assumptions in the model valid for Europe on the average are not necessarily applicable in Finland. Geographical and climatological characteristics have, however, been taken into account to some extent in the EMEP model by using local weather data, and space- and time-dependent parameterizations.

In the following the differences between observed and modelled data for sulphur and nitrogen compounds are studied in more detail. For brevity, only the year 1987 will be considered for sulphur. The other years modelled, 1980 and 1988, do not differ from 1987 as regards the agreement between observed and modelled data. For nitrogen, i.e. nitrate and ammonium, the comparison addresses the year 1985, which was the only one modelled.

Sulphur

Compared to the values observed at the Finnish EMEP monitoring stations, calculated sulphur dioxide concentrations are consistently underestimated (Fig. 2). The relative magnitude of the discrepancy is somewhat smaller in autumn than during the other seasons. At the Utö offshore station, the discrepancy is more pronounced than at Virolahti and Ähtäri. It is difficult to give any definite explanation for these discrepancies. Several possible reasons include, for example, underestimation of the sulphur emissions, the influence of local sources, and errors in the model simulations. The underestimations of SO_2 emissions are hardly large enough to account solely for the differences between observed and modelled SO_2 concentrations. At Utö, there is a local source to which the relatively high monthly mean concentrations at this offshore station can be attributed. At Virolahti and Ähtäri there are no substantial local sources. As to model errors, a possible faulty estimation of the vertical mixing may be significant. The average mixing depth in Finland is much lower than in more southern parts of Europe. In the EMEP model, a minimum mixing depth of 200 m is assumed, which may be too high for winter conditions in Finland. However, the high mixing depth does not explain the discrepancies during the summer months.

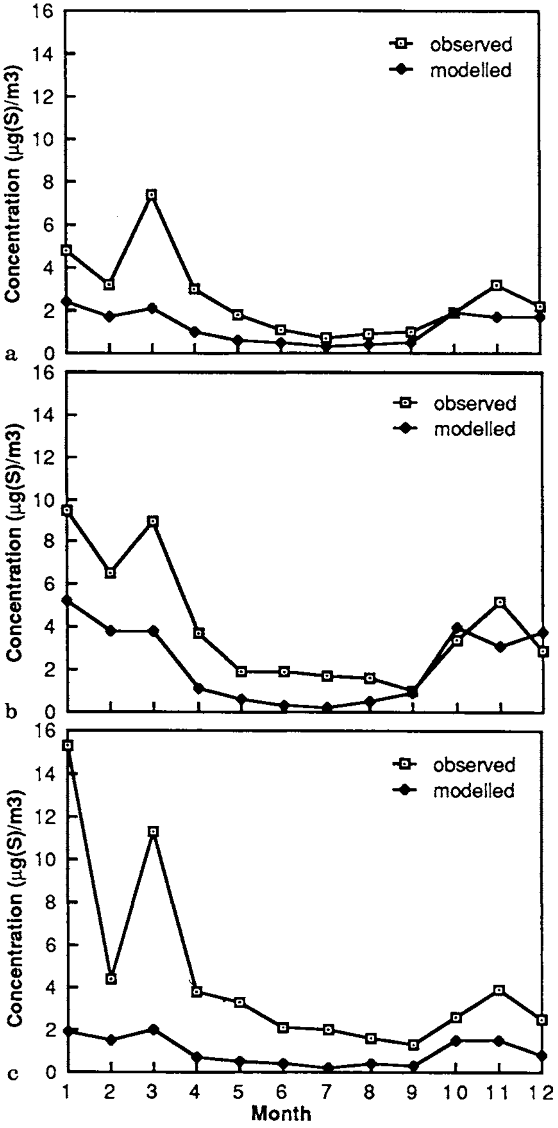

Fig. 2a–c. Calculated and observed monthly mean concentrations of sulphur dioxide at the Finnish EMEP stations in 1987 [µg(S) m^{-3}]. **a** Ähtäri **b** Virolahti **c** Utö

The modelled concentrations of particulate sulphate agree somewhat better with observations than the SO_2 concentrations (Fig. 3), but even for sulphate there is consistent underestimation. The reasons for this may be the same as for SO_2. The EMEP model includes as background assumed values for SO_2 and sulphate of 0.1 and 0.2 µg(S) m^{-3}, respectively. These values may be regarded as fairly low and contribute to the underestimation of air concentration values. For deposition, the

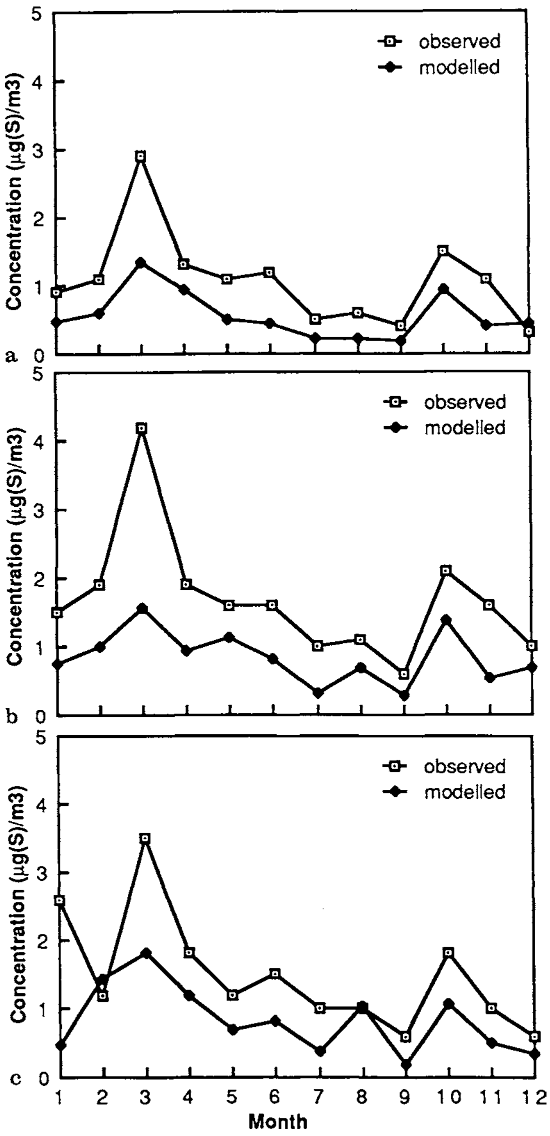

Fig. 3a–c. Calculated and observed monthly mean concentrations of particulate sulphate at the Finnish EMEP stations in 1987 [$\mu g(S)\ m^{-3}$]. **a** Ähtäri **b** Virolahti **c** Utö

background contribution [$0.3\ mg(S)\ l^{-1}$] is taken into account in a more realistic way.

Where sulphate in precipitation is concerned, which is directly reflected in the deposition quantities, the differences between modelled and measured values at Ähtäri change sign from winter to the other seasons (Fig. 4a). At Virolahti and Utö the modelled values are somewhat lower throughout the year (Fig. 4b,c). The annual means are presented in Table 3. One reason for greater agreement between

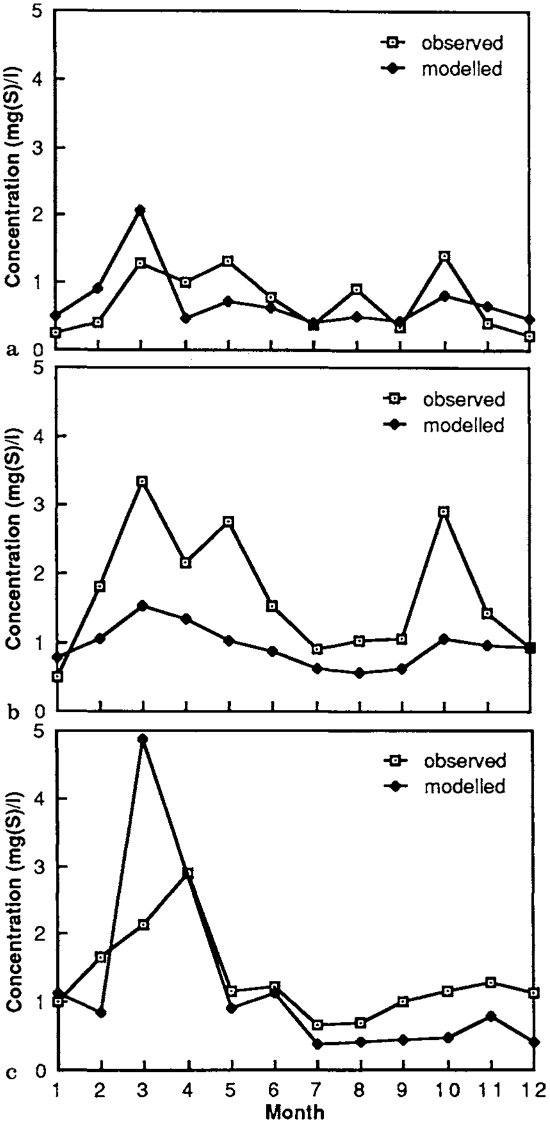

Fig. 4a–c. Calculated and observed precipitation weighted monthly mean concentrations of sulphate in precipitation at the Finnish EMEP stations in 1987 [mg(S) l^{-1}]. **a** Ähtäri **b** Virolahti **c** Utö

observed and modelled sulphate values in precipitation than for concentrations of SO_2 and sulphate in the air is that wrong estimation of vertical mixing does not affect concentrations in precipitation.

In the EMEP model, there is an additional removal factor α for deposition close to sources. This factor gives an additional deposition value which is not reflected in the SO_2 and sulphate concentrations. Thus, even when the concentration values are underestimated, the deposition is not necessarily as much in error.

Table 3. Calculated and observed precipitation weighted mean concentration of excess sulphate in precipitation at the Finnish EMEP stations in 1987 [mg(S) l^{-1}]

Station	Sulphate Obs./Calc.
Ähtäri	0.66/0.62
Virolahti	1.46/0.82
Utö	1.14/0.71

Further, due to the sampling technique, the observed values of sulphur in precipitation include dry deposition during precipitation days. This additional deposition, which is of the order of 10–30%, is not included in the modelled values.

Nitrogen

In Fig. 5 the calculated and observed precipitation weighted monthly mean nitrate concentrations in precipitation are shown for the Finnish EMEP stations. The annual means are presented in Table 4. As can be seen, there is pronounced underestimation in the model at the Finnish stations. However, the observed month-to-month variation is more or less followed by the calculations. There is some improvement when dry deposition is included in full, though the general picture does not change much.

The discrepancy is apparently greater at the coastal site Virolahti and at the marine site Utö than at Ähtäri. Poor agreement in the calculated deposition estimate for the Baltic Sea was also noted by Joffre (1988b), who compiled various observation-based estimates.

Ammonium in precipitation is modelled with a compatibility comparable to nitrate (Fig. 6 and Table 4); it appears to be underestimated. However, comparison of calculated and observed values of NH_z is not straightforward either. A couple of correction procedures presented in the literature will illustrate this. Buijsman and

Table 4. Calculated and observed precipitation weighted mean concentration of nitrate and ammonium in precipitation at the Finnish EMEP stations in 1985 [mg(N) l^{-1}]. The range of the calculated values indicates limit estimates of the influence of dry deposition (see text)

Station	Nitrate Obs./Calc.	Ammonium Obs./Calc.
Ähtäri	0.29/0.18–0.24	0.28/0.15–0.22
Virolahti	0.53/0.19–0.28	0.61/0.21–0.28
Utö	0.93/0.37–0.43	0.86/0.27–0.33

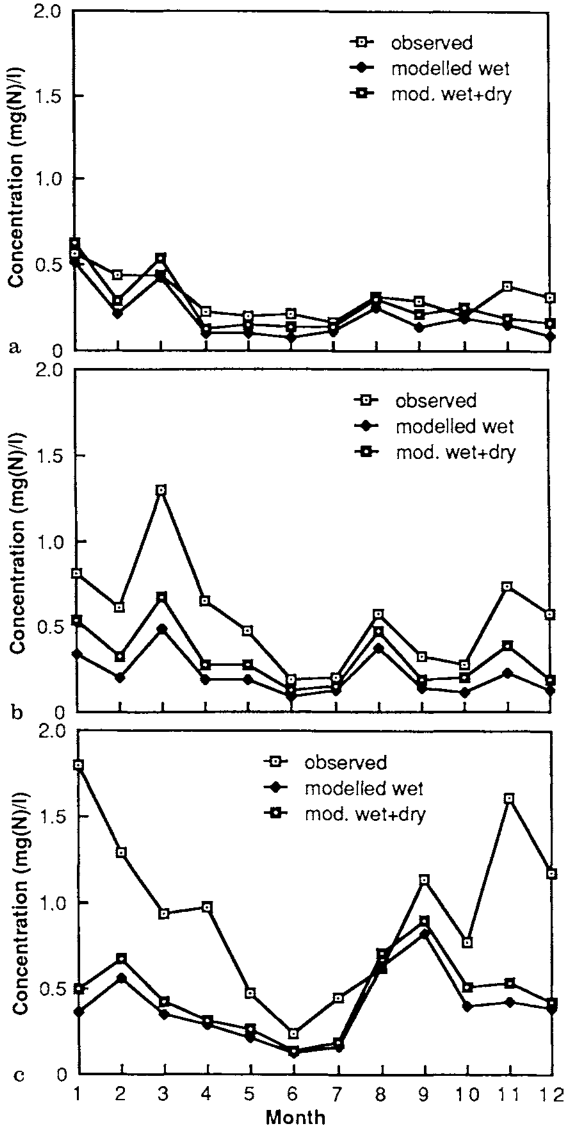

Fig. 5a–c. Calculated and observed precipitation weighted monthly mean concentrations of nitrate in precipitation at the Finnish EMEP stations in 1985 [mg(N) l^{-1}]. **a** Ähtäri **b** Virolahti **c** Utö

Erisman (1988) propose a correction factor of 0.8 for the EMEP ammonium data. This correction factor should take into account the influence of bulk sampling and the sampling period. Builtjes (1988) points out that the emission estimate used (the only one available) is now regarded as too low and gives a correction factor of 1.4 for the emission rates. The results presented here are not multiplied by these factors, but if they were taken as absolute the observations and calculations would deviate much less.

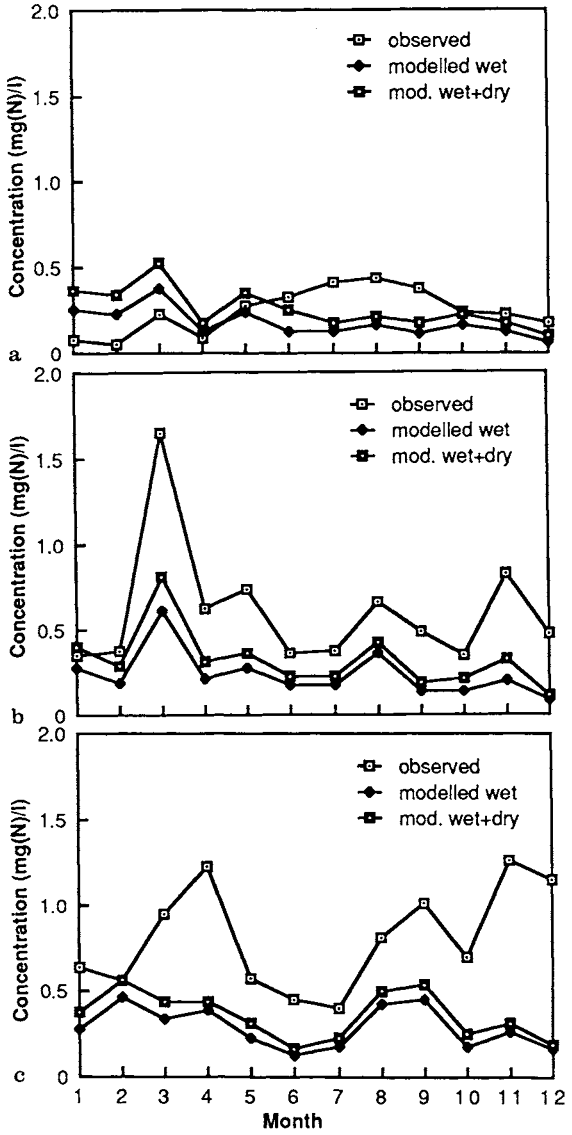

Fig. 6a–c. Calculated and observed precipitation weighted monthly mean concentrations of ammonium in precipitation at the Finnish EMEP stations in 1985 [mg(N) l^{-1}]. **a** Ähtäri **b** Virolahti **c** Utö

Due to shortage of measurements, the undeniable underestimation at the Finnish stations is difficult to explain. The only background measurements of inorganic nitrogen air concentrations in Finland in 1985 were made at Utö, where total (gaseous plus particulate) nitrate and ammonium were measured on a 24 h basis from August to October. During that period the calculated ammonium concentration was on the average about 20% lower than the observed one; this difference is less than that found in concentrations in precipitation (cf. Fig. 6). Strangely enough, somewhat higher nitrate concentrations were calculated than were measured in air. In precipitation, the reverse was true, but to a much less extent than in the annual mean.

The deviation between observations and calculations was also considered by splitting the observation data according to transport direction. Here the transport sector is determined by the trajectory positions between 100 and 1000 km from the station. The 925-hPa trajectories for 1985 obtained from EMEP/MSC-W were used in the sector analysis. At Virolahti, the relative difference in precipitation concentrations was greatest in the eastern and north-western sector for both NO_y and NH_z, although the influence and absolute deviation is greatest in the southern sectors. At Utö, the smallest deviation was in the eastern sectors but from west to north very small concentrations are calculated, contrary to observations. At Ähtäri, the most problematic directions were north and north-east for NO_3^-, and east and west for NH_z. No clear correlation could be observed between the discrepancy and emission density, or a factor of that kind in the corresponding direction.

Calculated Deposition

In this section, the results of the deposition calculations are presented. It should be noted that all numerical values and conclusions are restricted by the spatial resolution of the models employed. Local maxima and small scale features of the deposition patterns are smoothed out because of the 150 km x 150 km grid square size.

Sulphur

Spatial Distribution

The spatial distribution of the calculated sulphur deposition was analysed manually from the grid square values (Fig. 7). The deposition field includes two maxima, one connected with the general south-north decreasing gradient, the other being due to influence from emissions in the Kola Peninsula. The southern maximum is increased by the sources in Estonia and the Leningrad region of the USSR. The northern maximum is caused by two point sources, which makes it difficult to apply the calculated grid values. Therefore, the maximum region is not contoured but dotted in Fig. 7. The highest deposition values are roughly 2500 mg m^{-2} a^{-1} in one square so that the levels in Southern Finland are probably reached in eastern Lapland. More than half of Finland experiences sulphur deposition higher than 500 mg m^{-2} a^{-1}.

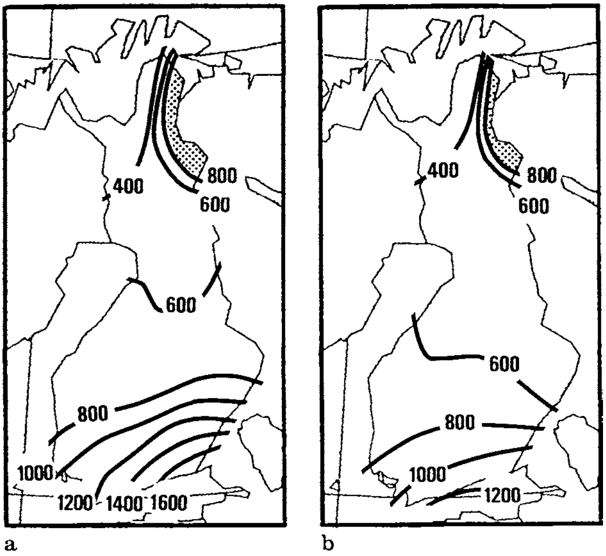

Fig. 7a,b. Sulphur deposition over Finland [mg(S) m^{-2} a^{-1}]. **a** 1980 **b** 1987 (see text for comments)

Integrated Deposition

According to the present calculations, 262 Gg of sulphur was deposited in Finland in 1980. Mainly due to a 45% national reduction in emissions, a 20% decrease in deposition has by now been achieved (Table 5).

The variation in the seasonal values shown in Table 5 reflects the influence of meteorological variability. Isolated weather events, e.g. strong pollution transport episodes or stagnant anticyclonic conditions, may have a predominant influence on the deposition values for a 3-month period. The low deposition in spring is partly due to the low precipitation typical of Finland during March and April. However, since the observed springtime maximum values for precipitation sulphate are not fully reproduced in the modelled values (cf. Fig. 4), the calculated deposition for this season is probably underestimated.

Table 5. Integrated deposition of sulphur in Finland [Gg(S) a^{-1}]

	1980	1987	1988
Winter (XII–II)	66	46	67
Spring (III–V)	53	47	48
Summer (VI–VIII)	60	64	56
Autumn (IX–XI)	82	53	44
Whole year	262	210	216

Dry and Wet Fractions

Dry deposition of air pollutants due to emissions from elevated sources typically attains a maximum when the plume "reaches" the ground. Close to the source there is a cavity zone, and further away a vertical concentration profile where the concentration decreases towards the ground in the atmospheric surface layer. Cavity effects are not included in the EMEP model since they are not important on the LRT scale. The decreasing concentration towards the ground is, however, taken into account by simulating the fluxes in the atmospheric constant flux layer. Dry deposition of particulate sulphate is lower than that of SO_2, which is another factor contributing towards less dry sulphur deposition with increasing distance from the source. Since precipitation scavenging is, in turn, faster for sulphate than for SO_2, the wet/dry deposition ratio will normally increase with increasing transport distance. This fact may also be observed in the model calculations. During the modelled period, between 55 and 65% of the total annual sulphur deposition in Finland was accumulated through precipitation. In northern Finland the wet fraction of precipitation was even larger than 75%.

Origin of Sulphur Deposited

In the calculations, concentrations in the air and in precipitation are split up according to the relative contributions of different source regions, i.e. countries, making it possible to estimate quantitatively the origin of pollutants. The country emitting the sulphur deposited throughout the whole of Finland is shown in Fig. 8 for the source attributable fraction; background deposition, which accounts for about one-third of the total deposition in Finland, is not included.

The striking feature of the results is that, if the unattributable deposition is ignored, three-quarters of the sulphur deposited in Finland originates from two countries only, i.e. indigenous sources and the Soviet Union. Since the beginning of the 1980's the Finnish contribution has decreased from roughly 50 to 35%, and the transport from the Soviet Union has become as important as Finnish sources in

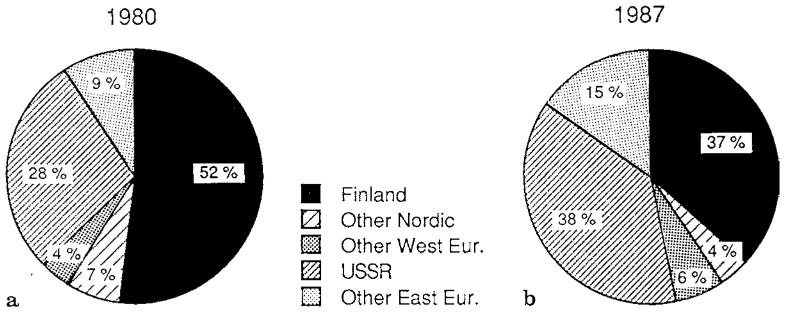

Fig. 8a,b. Origin of the source-attributable sulphur deposited in Finland. **a** 1980 [total deposition 262 Gg(S) of which 31% unattributable] **b** 1987 [total deposition 210 Gg(S) of which 32% unattributable]

Table 6. Sulphur budget between Finland and the Soviet Union in 1987 [Gg(S) a^{-1}]

Receiver	Emitter							
rec/em	NFI	CFI	SFI	KOL	KAR	LEN	EST	SUR
NFI	1	1	1	16	1	0	0	0
CFI	0	18	6	4	4	4	3	6
SFI	0	1	22	1	0	3	4	4
KOL	0	1	0	100	2	1	0	4
KAR	0	2	3	6	27	5	2	9
LEN	0	1	3	1	1	30	1	12
EST	0	0	3	0	0	2	23	6
SUR[a]	0	2	10	5	7	19	18	–

[a] Receiver area does not include the whole emitter area.
Abbreviations: NFI = Northern Finland, CFI = Central Finland, SFI = Southern Finland, KOL = Kola, KAR = Karelia, LEN = Leningrad, EST = Estonia, SUR = other parts of the USSR (see Fig. 1).

the deposition over Finland. This shift is partly induced by meteorological factors, since total deposition in Finland attributable to emissions in the Soviet Union has increased, though the Soviet emissions have decreased since 1980. More than two-thirds of the Soviet contribution comes from sources located in the regions near Finland, i.e. the Kola Peninsula, Karelia, the Leningrad region and Estonia, the Kola emissions accounting for 40% of total Soviet deposition in Finland. The sulphur budget between different parts of Finland and the Soviet Union is presented for 1987 in Table 6.

Other parts of Europe contribute annually ca. 40 Gg of sulphur, or one quarter of the total attributable deposition. The most important source countries are Poland (10 Gg in 1988) and the German Democratic Republic (9 Gg in 1988).

The spatial percentage of indigenous deposition is shown in Fig. 9. In 1980, Finnish sources dominated over large areas in southern and central Finland, but in 1987 this area was limited to regions on the west coast because of the lower indigenous emissions during this year. The Finnish contribution is smallest in eastern Finland and Lapland.

Nitrogen

Spatial Distribution

The calculated deposition of oxidized and reduced nitrogen is presented in Fig. 10. As for sulphur, the fields are analysed subjectively from the values obtained in 150 km × 150 km grid squares. The highest deposition occurs in the southeast corner of the country where 250 mg(N) m^{-2} a^{-1} is exceeded for both NO_y and NH_z deposition. Half of the country receives less than 150 mg(N) m^{-2} a^{-1} of both oxidized and reduced N. In Central Europe, the value of 1000 mg(N) m^{-2} is reached over areas the size of Finland for oxidized N, and in a small region close to the Dutch-German border for reduced N (Eliassen et al. 1988).

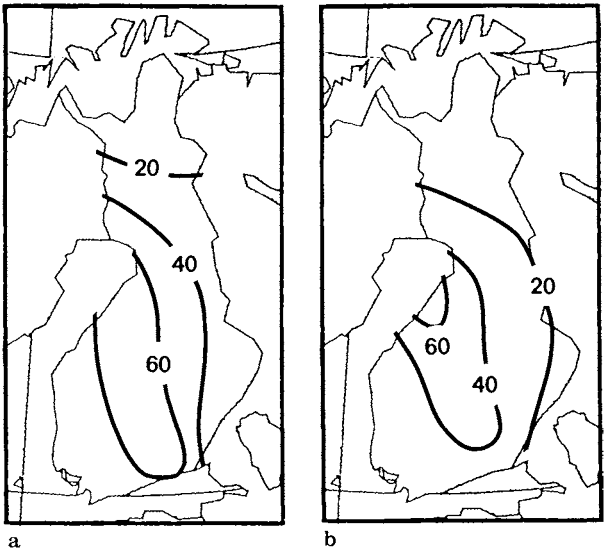

Fig. 9a,b. Indigenous fraction of the source-attributable sulphur deposited in Finland (%). **a** 1980 **b** 1987

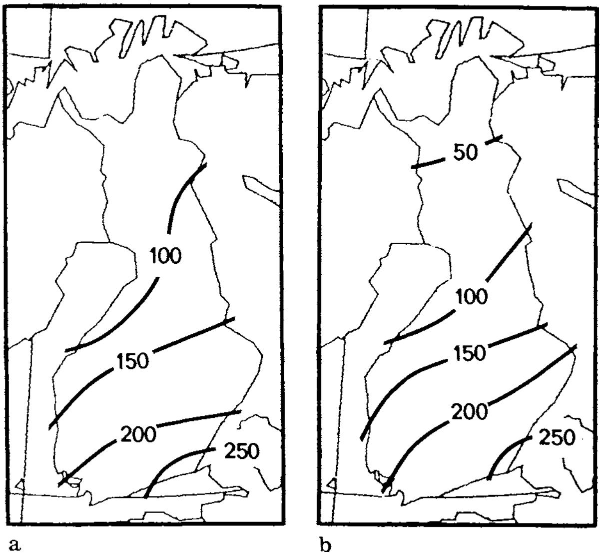

Fig. 10a,b. Nitrogen deposition over Finland in 1985 [mg(N) $m^{-2}a^{-1}$]. **a** Oxidized N **b** Reduced N

By plotting deposition as a function of latitude one can see that the load decreases systematically towards the north, the gradient being steepest between 60–62°N. The relatively rapid drop coincides with the edge of the plateau observed which was mentioned above although the concentration level is lower. There is a steeper gradient along Finland in deposition of NH_z compared to longer-lived NO_y.

Integrated Deposition

Integrated over the whole country, 49 Gg of oxidized N and 46 Gg of reduced N was deposited in 1985. While the nitrate deposition is relatively constant through the year, ammonium has a clear minimum in winter (Table 7).

The same annual value for NH_z was also obtained by Asman and Janssen (1987), who used a trajectory model very similar to the EMEP/MSC-W sulphur model. The parameter values were partly chosen on the basis of fitting calculations together with observations, and a constant mixing height was assumed. The emission data used was essentially the same as the NH_3 input to the EMEP model but meteorological input was for the year 1980.

Dry and Wet Fractions

Integrated over the whole of Finland, 65% of both NO_y and NH_z are deposited with precipitation. A consistent estimate of 67% can be calculated from the results presented by Asman and Janssen (1987) for NH_z. The spatial variation in the wet fraction of NO_y seems limited and rather inconsistent, while wet NH_z is negatively correlated with ammonia emissions because of the effective local dry deposition of NH_3.

According to the present calculations, dry deposition of NO_y in Finland occurs mostly as nitrogen dioxide and gaseous nitric acid. NO_2 concentrations have a very strong seasonal variation which is in phase with the emission strength amplified by the OH variation. Due to high concentrations, NO_2 is the predominant compound of dry deposition during wintertime although its dry deposition velocity is low.

Gaseous nitric acid is dry-deposited very effectively and thus not transported over long distances. During summer, roughly half of the dry deposition of NO_y originates from HNO_3. It is also removed very effectively by precipitation (residence time less than 1 h when precipitation intensity is higher than 1 mm h^{-1}).

Table 7. Integrated deposition of nitrogen in Finland in 1985 [Gg(N) a^{-1}]

	Oxidized	Reduced
Winter	10	7
Spring	11	13
Summer	13	14
Autumn	14	11
Whole year	49	46

Contrary to gaseous HNO_3, particulate nitrates are assumed to travel long distances before deposition. Highest NO_3^-/NO_y ratios are calculated over areas with small NO_x emissions. Aerosol nitrates are removed effectively by rain and they are also a significant component in dry deposition. Hardly any ammonium nitrate is formed under Finnish conditions. Thus the HNO_3–NH_3 link may be considered too weak to cause any important non-linear effect in the calculations.

Dry deposition of reduced nitrogen is dominated by gaseous NH_3 (more than three-quarters). Particulate ammonium sulphates have some effect, but ammonium nitrate does not seem to be important in Finland.

Origin of Nitrogen Deposited

According to the EMEP model, the USSR is the major emitter of the nitrogen deposited in Finland (Eliassen et al. 1988). Indigenous sources contribute only 16% of the annual areally integrated oxidized N deposition and 29% of the reduced N deposition (Fig. 11). Western Europe is a relatively more important source area of NO_x than NH_z. A fraction of ca. 8% of the NO_y deposition can be attributed to each of the Federal Republic of Germany and Sweden. The same amount of both NO_y and NH_z also originates from Poland.

The country allocation for ammonia deposition differs somewhat from the results obtained by Asman and Janssen (1987). Their choice of parameter values induces a shorter transport distance for ammonia, and hence a greater indigenous contribution compared to the EMEP model. As great a fraction as 53% can be obtained from these calculations for the Finnish NH_y deposition due to Finnish sources.

One of the different parameter values is the factor for local dry deposition [α in Eq. (2)], which not only determines the amount of pollutant that is added to the deposition in the same grid square as it is emitted but also how much material is left for further transport. Asman and Janssen used $\alpha = 0.24$ compared to $\alpha = 0.17$ in the EMEP model. If the higher value is used in the EMEP model (assuming the non-linearity to be negligible), the indigenous fraction is increased from 29 to 35%. Total areally integrated NH_y deposition remains practically constant.

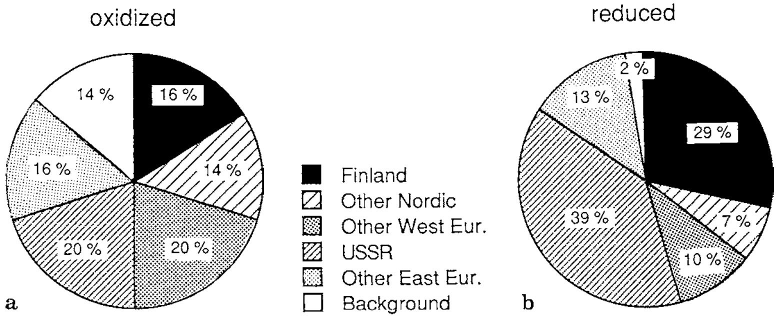

Fig. 11a,b. Origin of the nitrogen deposited in Finland. **a** Oxidized N **b** Reduced N

The fraction of deposition due to Finnish sources is smallest in northern Lapland as well as in eastern and southern parts of the country, mainly because of Soviet emissions (Fig. 12). Indigenous NO_y has a relatively constant fraction all over the country, whereas the fraction of NH_z varies between 0.1 and 0.6. Total ammonium deposition depends heavily on local scale dry deposition of NH_3 so that sources have a more local influence, and even higher relative contributions may occur in a subgrid scale.

The origin of the nitrogen deposition measured at the EMEP stations varies greatly from site to site in Finland. At Virolahti the Soviet contribution is high: more than 50% of the NH_z deposition and almost 30% of the NO_y deposition coming from Soviet sources. Nitrogen at Utö, especially NO_y, is characterized by about 55% probably originating outside Fennoscandia and the USSR. At Ähtäri, the country fractions of NO_y deposition are very close to the mean values calculated over Finland. For ammonium, the indigenous fraction at Ähtäri ($>$40%) is greater than the spatial mean over Finland.

A certain amount of deposition is not assigned to sources included in the model (denoted by "background" in Fig. 11). In northern parts of the country with lower absolute deposition, this indeterminate, or unattributable, background deposition becomes significant. Up to 30% of NO_y and 5% of NH_z depositing in the northern Lapland cannot be assigned to European emissions in the calculations. The sources of background deposition are discussed in the following sections.

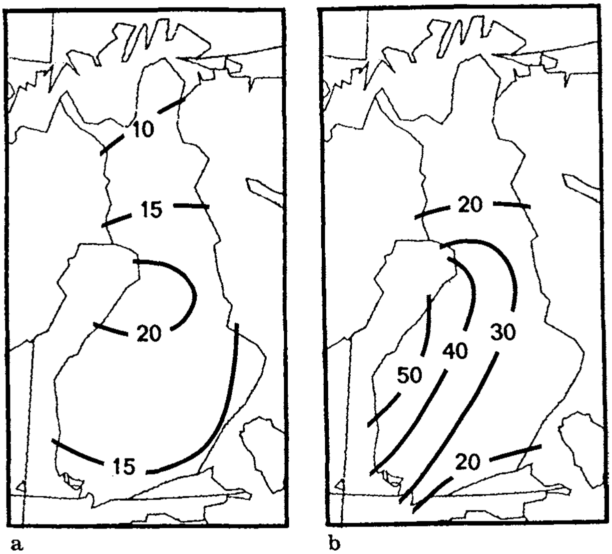

Fig. 12a,b. Indigenous fraction of nitrogen deposition over Finland (%). a Oxidized N b Reduced N

Interpreting the Results

In this section, two particular problems involved in the interpretation of the results are discussed. In addition to changes in emission rates, variable meteorological conditions greatly influence the deposition results even on an annual basis. For this reason the meteorological representativeness of the calculation period is studied. The possible origin of ambiguous background deposition is introduced briefly to shed light on this contribution, which in the northern areas, where pollution levels are relatively low, plays an important role.

Meteorological Representativeness

The interannual meteorological variability is typically fairly great in the zone of active cyclogenesis, to which Finland belongs. In addition to variability in wind conditions, differences in the occurrence of precipitation may cause significant variations in the deposition of long-distance transports of air pollutants. For Europe, Niemann (1988) has estimated that the year-to-year variability (as standard deviation divided by the average) in sulphur deposition is about 0.15, simply due to variations in precipitation. For the transboundary flux of sulphur between the United States and Canada, Olson and Oikawa (1989) have estimated an annual variability of 0.10 due to meteorological factors. In connection with an investigation of the deposition of nitrogen compounds in Europe, Bartnicki and Alcamo (1989) analysed roughly the interannual variability in deposition. For four selected locations they found a year-to-year variation of 6–10% in deposition due to the differences in dispersion conditions only.

In this article, depositions of sulphur for the years 1980, 1987 and 1988, and of nitrogen compounds for 1985 have been studied. From the weather statistics in northern Europe and Finland for these years, none were found to be exceptional. In 1980, there were relatively frequent southerly to southwesterly winds both in winter and in autumn, but not an exceptional number. In 1985 cold weather and northerly winds prevailed in January and February, but there was in turn much rain and southerly winds at the end of the year. The year 1987 was characterized by very variable weather throughout, and therefore on the average the year was quite normal. In 1988 there was somewhat more precipitation than usual but apart from the summer months, there were no long-standing blocking situations.

Because the deposition of nitrogen compounds was calculated using data from 1985 only, the dispersion conditions during this year were studied more carefully. From country-to-grid deposition matrices for the years 1979–1985, delivered by the EMEP project, the annual variability was studied in the contributions from Poland, the German Democratic Republic and Czechoslovakia, i.e. from countries for which the spatial distribution of emissions has been kept the same. Further, these three countries are at a typical LRT distance, 500–1000 km, from Finland. The mean relative deviation in the average contribution to Finland was 33%, but for the year 1985 only 16%. The deviations were, however, greater throughout for the northern parts of Finland than for the southern parts. In the already mentioned variability analysed by Bartnicki and Alcamo, single years were not specifically studied, but from the diagrams presented in their paper it may be observed that the year 1985 was close to the average for the whole period.

To conclude the analysis of the meteorological representativeness of the years used in the calculations, the modelled concentrations and deposition can be regarded as climatologically representative as far as yearly averages are concerned. None of the years 1980, 1985, 1987 and 1988 is either more or less representative than the others. The meteorological representativeness is weaker for the modelled monthly and seasonal values. Therefore, excess weight should not be placed on the values for single months or seasons, and especially not on month-to-month or season-to-season variations in single years.

Background Deposition

Background pollution can be defined as follows (EPA 1986): "Background air quality includes pollutant concentrations due to

1. natural sources;
2. nearby sources other than the one(s) currently under consideration; and
3. unidentified sources."

From the point of view of the EMEP models, background pollution can be interpreted in the following way. Natural sources are not included in the model and their importance must be considered. The sources other than those under consideration are located in the other continents, i.e. boundary conditions should be defined. The third class consists of sources that are not known to exist, or not considered in the emission inventory. More importantly, it should take into account the unidentified sources with respect to each trajectory, i.e. the emissions that are not reached by the 96 h trajectories. Some material is also transported back to the calculation domain although it has once flown out of it. The first and the second group are discussed in the next paragraphs.

Natural Sources

In addition to anthropogenic emissions mainly caused by combustion of fossil fuels, natural sources contribute to the global atmospheric budget of sulphur. Natural emissions of sulphur originate from volcanic activities, sea salt, wind-induced weathering of arid regions, and biogenic processes (Andreae 1985). On the global scale, the biogenic sulphur emissions equal the anthropogenic flux, ca. 100 Tg(S) a^{-1}, the total natural emissions being approx. 200 Tg(S) a^{-1}. Half of the biogenic sulphur emanates from oceans. The most important maritime compound is dimethylsulphide (CH_3SCH_3), or DMS, while inland soils are a significant source of H_2S. DMS emissions are likely to be related to plankton blooming during summer. Data on geographical distribution of the emissions is very limited. Nor is the fate of these compounds in the atmosphere unquestionable. According to Warneck (1988), one-half of DMS is oxidised to methanesulphonic acid and then to sulphate while the other half produces mainly SO_2.

Contrary to sulphur, oceans are a negligible source of NO_x, natural emissions of which originate from soils and lightning discharges. On the global scale these contribute with 10 Tg(N) a^{-1} both which is comparable with the emissions due to fuel combustion (Logan 1983). Soils are also a significant source of ammonia. However, NH_3 is removed from the atmosphere essentially in the regions of its origin (Warneck 1988).

Although quantitative estimates of the natural contribution to air and precipitation quality are rare, it seems reasonable to propose that roughly 1/3 of the background used for sulphate in precipitation in the EMEP sulphur model [0.3 mg(S) l^{-1}] is of natural origin (sea salt excluded). There are, of course, large spatial differences in the emission density of natural sulphur, the highest rates occurring in coastal regions. For nitrogen, no estimate can be presented here.

Anthropogenic Sources Located Outside Europe

A quantitative estimate of the transport of North American emissions across the North Atlantic Ocean to Europe has been presented by Whelpdale et al. (1988). They reviewed the available precipitation data from the North Atlantic and adjacent coastal regions to determine the change in precipitation composition as a function of distance from North America. An anthropogenic transatlantic sulphur flux of 0.3–0.4 Tg(S) a^{-1} was estimated from the measurements. An independent estimate was also made using a simple climatological transport model, and an agreeing value was obtained. In terms of concentration in precipitation these estimates correspond to ca. 0.06 mg(S) l^{-1}, while the natural marine background was found to be 0.1 mg(S) l^{-1}.

However, it is possible that a significant amount of sulphur is transported above the atmospheric boundary layer, and is thus not subject to dry deposition. Galloway et al. (1984) estimated that 48% of sulphur leaving the North American east coast is above 1500 m and 26% above 3000 m. For oxidized nitrogen, the respective percentages were 35 and 33%. A 15-day simulation by a detailed three-dimensional model including cloud transport yielded a consistent result with more sulphur in higher levels (Brost et al. 1988). Fisher's (1988) highly idealised analytical atmospheric circulation model proposes a very effective transport route between the continents via the mid-latitude free troposphere (flux entering Europe/flux leaving North America equals 0.2).

In the studies on Arctic air pollution it has been concluded that air quality in the Arctic is connected with large-scale atmospheric circulation patterns (Barrie 1986; Ottar et al. 1986). There is a strong transport from the Western Eurasian continent to the Arctic regions during winter but not so much in summer. This is due to the extent of the Arctic front and persistent blocking situations with meridional flow in winter. The modelling study of Iversen has suggested that the lowest layers in the Arctic are most polluted by the sources in the USSR (Ottar et al. 1986). As there are large source areas in the USSR outside of the modelling domain of the EMEP models (e.g. the Ural and Norilsk areas), it is possible that some sulphur is transported from the Asian Soviet Union to Northern Finland also. Sources located in the Far East seem to have no practical influence (Ottar et al. 1986).

Based on the literature mentioned above, it may be concluded that sources outside the spatial domain of the EMEP models may significantly contribute to background deposition. For sulphur, this contribution is probably of the same order as the natural one.

Final Remarks

Solely on the basis of the long-term deposition estimates, no sweeping conclusions should be reached on the impacts on ecosystems or even on their actual acid input. These absolute values do not tell the whole story because, firstly, deposition is usually more effective to vegetative surfaces than to open ground (so-called filtering effect), and because of the possible sources and sink of the compound in canopy. Secondly, the accumulation of deposition is fairly episodic. During episodes, both concentrations of pollutants in air and their deposition fluxes may be very high even in Finland (cf. Joffre et al. this Vol.), although the annual deposition levels in Finland for sulphur and nitrogen are one order of magnitude smaller than in the most heavily polluted areas in Central Europe. Nevertheless, in most parts of Finland, these quantities are, for sulphur at least, above the levels generally seen as the critical loads.

According to the present calculations of the origin of sulphur and nitrogen deposited in Finland, there are only a few predominant source areas: Finland itself, the northwestern parts of the USSR, and for sulphur the background "unattributable" contribution. Thus, the target areas where emission reduction measures should be allocated in order to diminish the acidifying load in Finland are obvious.

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List of Abbreviations

EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants
ECE	Economic Commission for Europe
LRT	Long-Range Transport
LRTAP	The Co-operative Technical Programme to Measure the Long-Range Transmission of Air Pollutants
MSC-W	Meteorological Synthesizing Centre, West
OECD	Organization for Economic Co-operation and Development
UN	the United Nations

List of Symbols

i, j	indices for compounds
$\mathbf{c}$	concentration vector
D/dt	total time derivative
$\mathbf{S}$	matrix describing chemical interactions and deposition processes
$\mathbf{R}$	source vector
$\mathbf{V}$	wind field
∇	operator $\delta/\delta x + \delta/\delta y$
α	correction factor for local dry deposition
β	correction factor for secondary emitting compounds
Q	areal emission flux
h	mixing height
k_c	coefficient for chemical conversion
k_d	coefficient for dry deposition
k_w	coefficient for wet deposition
v_d	dry deposition velocity
P	precipitation intensity
W	scavenging ratio
F	deposition flux

Deposition on Forest Soils – Effect of Tree Canopy on Throughfall

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Summary

Interception of the annual bulk precipitation by the canopy accounted for 27, 22 and 15% for Norway spruce, Scots pine and birch stands, respectively. The dominating ions in throughfall were H^+, K^+, Ca^{2+} and SO_4^{2-}. In 1986, estimates of annual H^+ throughfall deposition were 10–28 meq m^{-2} for spruce, 20 meq m^{-2} for pine, and 17–20 meq m^{-2} for birch. The canopies of all three tree species absorbed nitrogen. The average interception for ammonium was 37–43% and for nitrate 4–23% of bulk precipitation over the sampling period in 1986. The deposition of other elements, especially Ca, Mg, K and Mn, was higher in the throughfall than in bulk precipitation. Significant differences in canopy effects occurred between spruce and birch: the deposition of H^+ and SO_4^{2-} was greater in spruce-dominated stands.

Introduction

Precipitation passing through a forest canopy undergoes qualitative and quantitative changes. Some of the precipitation is intercepted by the canopy from where it is subject to evaporation and absorption by the foliage and bark, or continues its passage downwards as drip and stemflow. The chemical composition of the latter is modified by interaction with the tree during its passage downwards to the forest floor. The remainder of the precipitation reaches the forest floor directly through gaps and openings in the tree stand. In this chapter, throughfall refers to that part of the bulk precipitation that reaches the forest floor, both directly and through the canopy as drip (Fig. 1). Stemflow was not measured, but the amount is very small compared to throughfall and bulk precipitation under Finnish conditions, owing to the predominance of conifers. Päivänen (1966) found that stemflow during the growing season accounted for only ca. 2% of bulk precipitation in pine and birch stands, and as little as 0.1% in spruce stands.

The extent of the changes in the quantity and quality of throughfall depends upon many factors. Included are the characteristics of both the stand, e.g. tree size and density (Päivänen 1966), species composition (Cronan and Reiners 1983; Mahendrappa 1983), age (Miller 1984; Skeffington 1987) and physiological condi-

Kauppi et al. (Eds).
Acidification in Finland

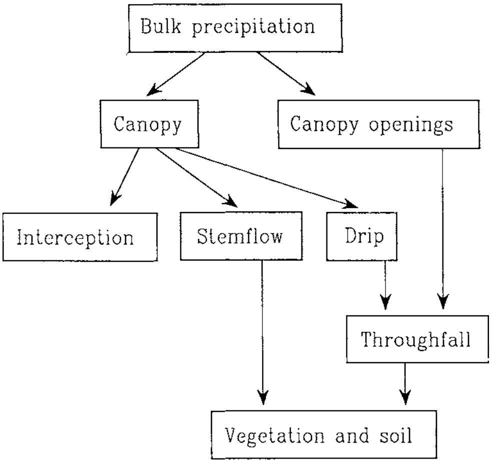

Fig. 1. Distribution of rain in stands. (Päivänen 1966)

tion (Ulrich 1983a; Miller 1984, 1985), and of the rainfall event, e.g. intensity and duration (Päivänen 1966; Leikola 1971), and also its chemical composition (Adams and Hutchinson 1984). In areas of acid deposition, the composition of the precipitation can have important repercussions in terms of damage to the forest, both directly to the canopy and indirectly through accelerating soil acidification (Ulrich 1983b). In polluted areas, wet deposition is most often dominated by sulphate, nitrate, hydrogen and ammonium ions. It has been shown that the acidity and deposition of Mg, Ca and Fe is greater from spruce canopies suffering from defoliation than from non-defoliated canopies; in contrast, deposition of Mn and K was less (Alenäs and Skärby 1988).

In addition to wet deposition, gaseous and particle substances may be deposited in varying amounts by impaction, sedimentation or gradual diffusion on the foliage and soil as dry deposition (Fowler 1980). The relative importance of dry deposition significantly increases nearer to the source of emissions (Acid Rain 1983). Measurements of the Finnish Meteorological Institute have shown that the contribution of dry deposition (mainly particulated material) to total deposition in open areas is of the order of 20% for S, 10–20% for NO_3-N, 50% for NH_4-N (southern Finland), 25–35% for Cl, 50% for K, and 25–50% for other alkali and alkaline earth metals (Kulmala and Leinonen 1983). Results concerning dry deposition in Finnish forests are not available. The decrease in throughfall pH in coniferous forest has been chiefly ascribed to the leaching of acidic dry deposition (Cronan and Reiners 1983; Ulrich 1983a).

Nutrients, especially nitrogen, and heavy metals deposited onto the canopy surfaces may be absorbed into the foliage and, in doing so, alter the chemistry of throughfall. In reverse, nutrients and metabolic products secreted onto the leaf surfaces may then be leached to the forest floor (Godt et al. 1986). Organic acids, e.g. malic and citric, and manganese bicarbonate salts secreted by hardwood canopies may be important neutralizers of strong acid deposition (Hoffman et al. 1980; Cronan and Reiners 1983; Adams and Hutchinson 1984). Cation exchange, involving the reciprocal exchange of hydrogen ions contained in precipitation with base cations in the cuticle and cell wall, is considered to be an important leaching and neutralization mechanism in the canopy (Ulrich 1983a). The exchange sites may be the hydroxyl and carboxyl groups of cellulose, hemicellulose, phospholipid and polyurinide molecules (Wood and Bormann 1975). The amount of base cations in the canopy is related ultimately to their availability in the soil. In sites with high soil and foliar alkalinities, throughfall pH may be higher than that of bulk precipitation (Bredemeier 1988). Variations in throughfall quality are thus related to the internal mobility and cycling of nutrients. The leaching of nutrient cations from the canopy would therefore be easiest when the internal nutrient cycle is most active, i.e. in early summer and spring (Bukovac and Wittver 1957).

Almost without exception, coniferous canopies, especially spruce, increase the amount of free H^+ ions in throughfall, whereas deciduous trees decrease the amount (Cronan and Reiners 1983; Bergkvist et al. 1986). Although the amount of H^+ in throughfall under spruce is high compared to deciduous species, spruce canopies also intercept proportionally more precipitation.

In this paper results are presented concerning throughfall anion and cation balances and the relative influence of canopy interaction on deposition quantity and quality in intensively studied sample plots in southern Finland. The stands investigated were dominated by Norway spruce, Scots pine, or birches, and receive bulk precipitation of varying quality.

Material and Methods

Experimental Design and Sampling

Bulk precipitation and throughfall were monitored during 1985 and 1986 at seven sample plots located in southern Finland (Fig. 2). The plots were situated so as to be in the vicinity of air quality observation stations operated by the Finnish Meterological Institute, and where possible also integrated into the network of permanent sample plots established by the eighth National Forest Inventory (NFI). The main tree species growing on the sample plots were Norway spruce (*Picea abies*), Scots pine (*Pinus sylvestris*) and birch (*Betula pubescens*, *B. pendula*). The forest stand data and site types of the plots are given in Table 1. The investigation on Plot 4 was interrupted in October 1985 because of forest fertilization.

Twenty throughfall collectors were located systematically in a ring of ca. 12 m radius around each plot (Fig. 3). In the case of the NFI plots (Plots 1, 2 and 5), the collectors were outside the permanent plot of 9.8 m radius. Some of the collectors were sited directly under the canopy and the rest under canopy openings. Three collectors were also placed in an adjacent open area to collect samples of bulk precipitation. The collectors consisted of a PVC funnel connected to a 1-l polythene sample collection bottle via polythene tubing. The funnel had a collecting

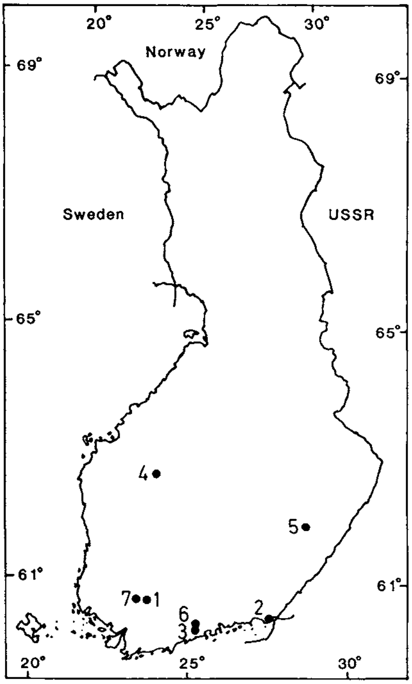

Fig. 2. Location of the sample plots

Table 1. Stand characteristics and site types (Cajander 1949) of the sample plots

Plot	Tree species composition % S	P	B	Stand volume m³ ha⁻¹	Age a	Mean height m	Basal area m³ ha⁻¹	Canopy coverage %	Site type
1	100	0	0	228	75	20	24	59	OMT
2	80	20	0	303	75	22	31	60	OMT
3	55	12	33	306	65	23	28	63	MT
4	0	99	1	169	95	21	17	35	VT
5	0	84	16	224	65	23	21	45	MT
6	0	0	100	164	40	16	22	64	OMaT
7	0	0	100	246	45	20	26	62	OMaT

Symbols: OMaT = Oxalis-Maianthemum site type; OMT = Oxalis-Myrtillus site type; MT = Myrtillus site type; VT = Vaccinium site type; S = Norway spruce; P = Scots pine; B = Birch

surface area of 307.91 cm^{-2} and a polythene mesh disk fitted into the neck to prevent litterfall and debris from falling into the sample bottle. The funnel was supported at a height of 1 m by means of a black PVC tube in which the sample bottle was also placed underground. The tube was perforated in the upper part to allow air to circulate. This ensured that the sample was kept cool and away from sunlight. In addition to wet deposition, the samples contained an unknown amount of dry deposition.

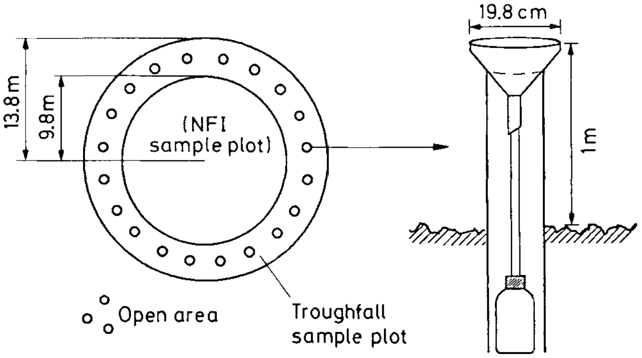

Fig. 3. Design and layout of the precipitation collectors

The establishment and start of sampling in 1985 varied considerably among the plots from June to September. The sampling period in 1986 was similar for all plots; May–June to November, and for this reason the 1986 results are analysed in more detail. The 1986 sampling period largely corresponds to the growing season when there is active nutrient uptake and translocation.

Samples were collected weekly, or more often depending on the rainfall. At the same time, the collection bottles and funnels of the collectors were replaced with acid-washed ones. Sample volume was recorded and an aliquot taken for pH measurement, after which the sample was filtered (Schleicher & Schüll filter paper 589[1]). The samples from each plot were then combined to form two samples for analysis according to whether the collectors were directly under the canopy or in canopy openings. Samples from the three bulk precipitation collectors were also combined for analysis. The samples were then frozen for storage.

Snow samples were taken once during weeks 11–13 in March 1986 from the snow cover in the immediate vicinity of the precipitation collectors in both the stands and open areas. Samples were taken using a plastic tube with inner diameter of 33.5 mm. The volume of the thawed snow samples representing points under the canopy, canopy openings and the open area were measured and then combined to form three samples for each site and analysed.

Laboratory Analyses

After thawing the samples, the following determinations were made: conductivity, K, Na, Ca, Mg, Cl, NH_4, NO_3, SO_4, PO_4, Al, Pb, Cu, Zn, Fe and Mn.

Sodium, chloride, ammonium, nitrate, sulphate and phosphate concentrations were determined using high performance HPLC/ion chromatography (Waters 430). Potassium, calcium and magnesium were determined by atomic absorption spectrophotometry (AAS, Perkin-Elmer 3030). Aluminium, lead, copper, zinc, iron, and manganese were determined by flameless AAS (Perkin-Elmer 3030, HGA-400). Hydrogen ion concentrations were calculated from the pH values.

Statistical Handling

The statistical differences in canopy effect between tree species were tested for amounts of precipitation and deposition values of H^+, SO_4^{2-}, NH_4^+, NO_3^-, K^+, Ca^+ and Mg^{2+} with one-way variance analysis and with pairwise t-tests using Bonferroni significance levels.

Area-specific depositions (mg m^{-2}) for the sampling periods were calculated from the concentrations and sample volumes. For the purposes of this paper the volume weighted mean deposition values of the throughfall-canopy and throughfall-openings were averaged to give the overall throughfall values presented. Estimates of annual bulk precipitation and throughfall amounts and deposition values were made for 1986 using the meteorological data from the nearby weather stations of the Finnish Meteorological Institute and the plot measurements of throughfall and water quality. It was assumed that the quantity and quality of deposition corresponds to the mean weekly values measured as rainfall (growing season) or as snow (winter). Annual Deposition (mg m^{-2}) was estimated as follows:

$$R = D_R/T_R$$
$$S = D_S/T_S$$
$$E = (R \times t_R) + D_R + (S \times t_S) + D_S$$

R = mean weekly deposition for the growing season
D_R = deposition sum measured during the growing season
T_R = number of sampling weeks during the growing season
S = mean weekly deposition for the winter period
D_S = deposition sum measured in winter
T_S = number of sampling weeks during the winter period
E = estimated annual deposition
t_R = number of weeks with no measurements during the growing season
t_S = number of weeks with no measurements in winter

Results and Discussion

Interception

Recorded precipitation amounts (mm) measured at the open areas of the sample plots in 1986 were similar to the long-term averages (1931–1960) of the corresponding nearby weather stations, except for Plots 1 and 7, which had 20% greater precipitation values.

Annual precipitation, canopy interception and throughfall amounts for 1986 are presented in Table 2. The three spruce-dominated stands were the most efficient interceptors of precipitation, intercepting 27% on average. Corresponding percentages were 22% for the pine stand and an average of 15% for the two birch stands. Päivänen (1966) reported greater quantities of canopy interception: 38% for spruce, 29% for pine and 23% for birch. In his study, interception clearly increased

Table 2. Estimated annual precipitation, throughfall (mm) and canopy interception (%) in 1986

Plot	Dom. sp.[a]	Precipitation Rain	Precipitation Snow	Throughfall Rain	Throughfall Snow	Interception %
1	S	493	206	395	92	30
2	S	379	228	265	167	29
3	S	465	246	395	154	23
5	P	357	190	300	128	22
6	B	465	246	422	194	13
7	B	501	210	424	165	17
Mean: Spruce						27
Pine						22
Birch						15

[a] Dominating tree species: S = Norway spruce; P = Scots pine; B = Birch

with increasing stand volume and basal area until stand volume reached 70 m^3 ha^{-1} or basal area 12 m^2 ha^{-1}, but thereafter interception remained constant. According to Päivänen (1966), the basal area of the stand best explained the variation in interception by the pine stands.

Throughfall Acidity

Precipitation acidity depends on its chemical properties and the ratio of acids to bases (Sequeira 1982). Figure 4 shows the frequency distributions of the precipitation pH values in 1986 for each of the three stand-dominating tree species. Throughfall in the spruce and the pine stands was more acidic than that in birch-dominated stands. Although the statistical differences were not tested, the throughfall in the spruce stands had pH values averaging 0.2–0.3 pH units less than that of bulk precipitation. In the birch and pine stands, however, the pH value of throughfall averaged 0.1 pH units higher than that of bulk precipitation. The variation in acidity was greater in the birch stands than in pine and spruce stands. The pH of throughfall in plots dominated by birch rose in September and October. Very high pH values were then recorded, even exceeding 6.0. These values were probably influenced by leaves and other forest litter falling into the precipitation collectors.

The highest mean pH value of bulk precipitation in 1985 (pH 4.42) and 1986 (pH 4.86) occurred in Plot 2, which is located in southeastern Finland. The lowest pH values in 1985 were measured in Plots 1 and 7 (pH 4.10–4.18), which are located in southwestern Finland. In 1986, the lowest mean pH was measured in Plot 5 (pH 4.23).

Throughfall Deposition

Measured deposition of various ions for the sampling period in 1986 only, as well as estimations for the whole year are presented in Tables 3 and 4, respectively. The

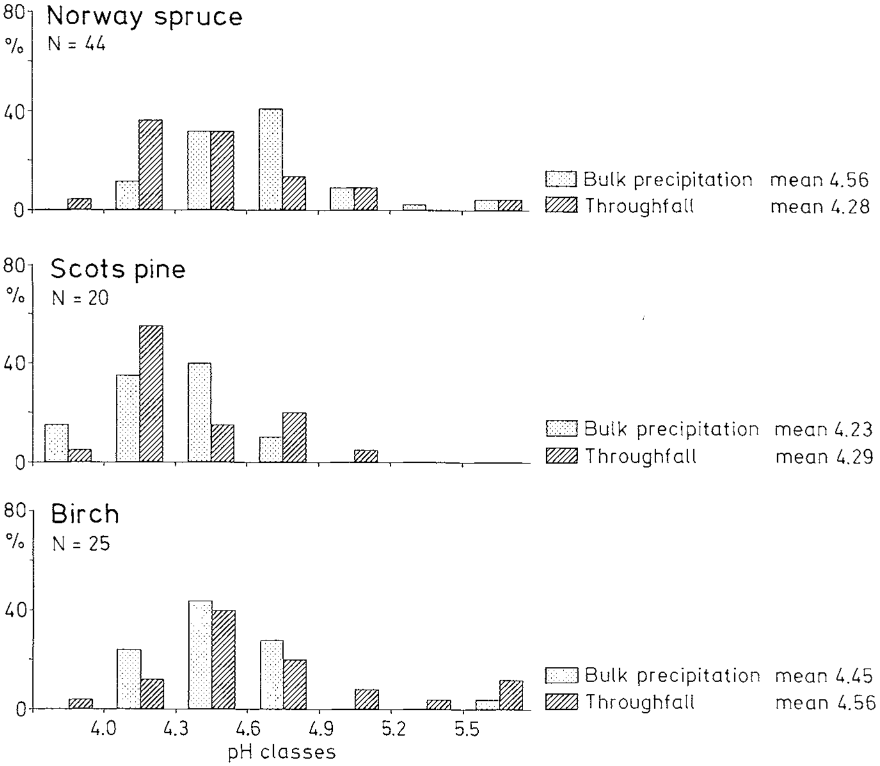

Fig. 4. Frequency distribution of 1986 bulk precipitation and throughfall into pH classes (% rainfall events)

highest amounts of alkali and alkaline earth metals, sulphur, and nitrogen in bulk precipitation occurred in the coastal areas of southern and southeastern Finland (Plots 2, 3 and 6). These plots also had lower proton depositions than the other plots.

Plots 3 and 6 are situated close to Helsinki-Vantaa airport and near to a major arterial road. Plot 2 is located in an extensively forested area near the country's eastern border. There is no industry or major road nearby, but some transboundary emissions including fly ash may reach the area. Fly ash of industrial origin, which contains alkali and alkaline earth metal oxides and carbonates, has been shown to be capable of neutralizing the protons in acid rain (Sequeira 1982).

In throughfall, the cation sum was greater than the anion sum for the sampling period 1986 (Table 5). The ratio of throughfall cation and anion sums varied between 1.1 and 1.7. In bulk precipitation, the two sums corresponded better to each other, the respective ratio varying between 0.9 and 1.4. The anion deficit is probably due to organic anions because phosphate concentrations in bulk precipitation and in throughfall were below the detection limit.

The overall anion and cation balances for throughfall and bulk precipitation for the 1986 sampling period are shown for each plot in Fig. 5. The dominant

Table 3. Bulk precipitation (B) and throughfall (T) deposition (mg m^{-2}) for the 1986 sampling period (May–June to November)

Plot	Dom.	H+		K		Ca		Mg		Na		Cl		NH_4–N		NO_3–N		SO_4–S	
	sp.[a]	B	T	B	T	B	T	B	T	B	T	B	T	B	T	B	T	B	T
1	S	12	14	25	575	78	221	15	57	45	77	81	230	91	55	86	60	231	438
2	S	4	5	78	603	201	407	24	67	70	111	218	333	149	80	150	81	372	639
3	S	10	20	106	753	212	477	34	112	70	111	142	335	187	159	130	178	424	893
5	P	17	12	43	450	107	247	21	69	36	48	66	121	99	62	85	65	276	349
6	B	10	8	106	782	212	415	34	138	70	87	142	227	187	109	130	122	424	507
7	B	12	7	20	303	73	169	13	94	68	65	93	158	106	59	97	93	247	258

[a]Dominating tree species: S = Norway spruce; P = Scots pine; B = Birch

Table 4. Annual bulk precipitation (B) and throughfall (T) deposition (mg m^{-2}) for 1986

Plot	Dom.	H+		K		Ca		Mg		Na		Cl		NH_4–N		NO_3–N		SO_4–S	
	sp.[a]	B	T	B	T	B	T	B	T	B	T	B	T	B	T	B	T	B	T
1	S	29	28	54	1034	173	422	32	107	101	155	312	482	216	136	253	156	507	860
2	S	15	10	152	927	430	755	52	119	154	192	394	528	311	194	308	198	771	1207
3	S	17	28	514	1115	458	831	88	191	390	228	280	711	370	305	330	345	840	1496
5	P	28	20	109	656	171	387	32	101	133	110	137	211	179	114	189	151	455	567
6	B	17	17	514	1213	458	756	88	210	390	300	280	773	370	259	330	289	840	781
7	B	30	20	44	531	169	348	28	169	149	145	323	430	240	167	265	258	537	551

[a] Dominating tree species: S = Norway spruce; P = Scots pine; B = Birch

Table 5. Cation (C) and anion (A) sums (meq m^{-2}) and their ratios for the 1986 sampling period (May–June to November)

Plot	Dom. sp[a]	Bulk precipitation C	A	C/A	Throughfall C	A	C/A
1	S	27	23	1.2	55	38	1.5
2	S	35	40	0.9	61	55	1.1
3	S	44	40	1.1	93	78	1.2
5	P	34	25	1.4	51	30	1.7
6	B	44	40	1.1	76	47	1.6
7	B	29	27	1.1	40	27	1.5

[a] Dominating tree species: S = Norway spruce; P = Scots pine; B = Birch

anion in both bulk precipitation and throughfall was SO_4^{2-}. The most abundant cations in bulk precipitation were H^+, Ca^{2+} and NH_4^+, and in throughfall H^+, K^+ and Ca^{2+}.

The effect of canopy interaction on deposition relative to bulk precipitation during the 1986 sampling period is shown in Fig. 6. Both ammonium and nitrate were absorbed by the canopy of all tree species. In 1986 canopy interception of the ammonium deposition averaged 37 to 43% of bulk precipitation, depending on the tree species, and that for nitrate 4 to 23%. Canopy interception of nitrogen would be even larger if gaseous deposition had been taken into account. Birch intercepted the most ammonium but the least nitrate. Forest growth in the boreal zone is mainly nitrogen-limited, and in other studies carried out in Sweden and Finland

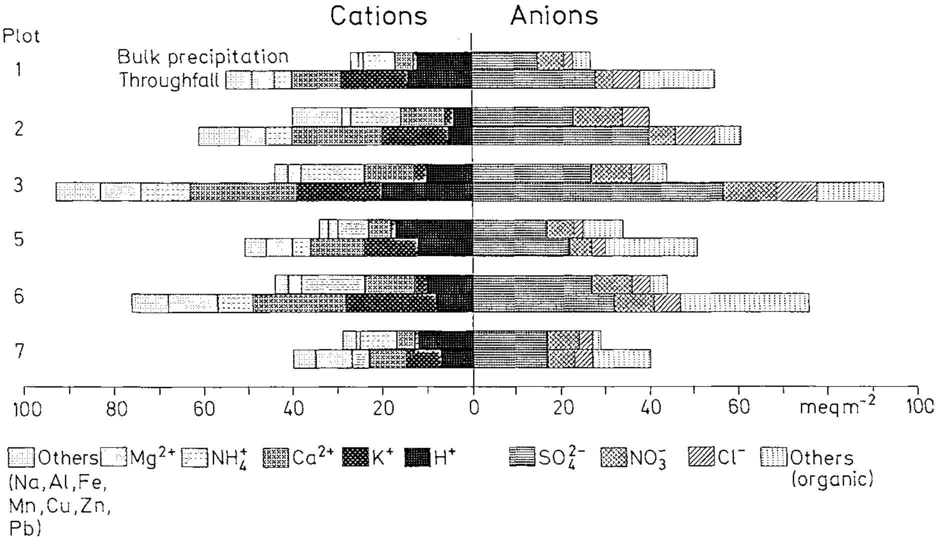

Fig. 5. The anion and cation balances for throughfall and bulk precipitation deposition for the sampling period, (1986 May-June to November). The anion deficit is assumed to be caused by organic substances

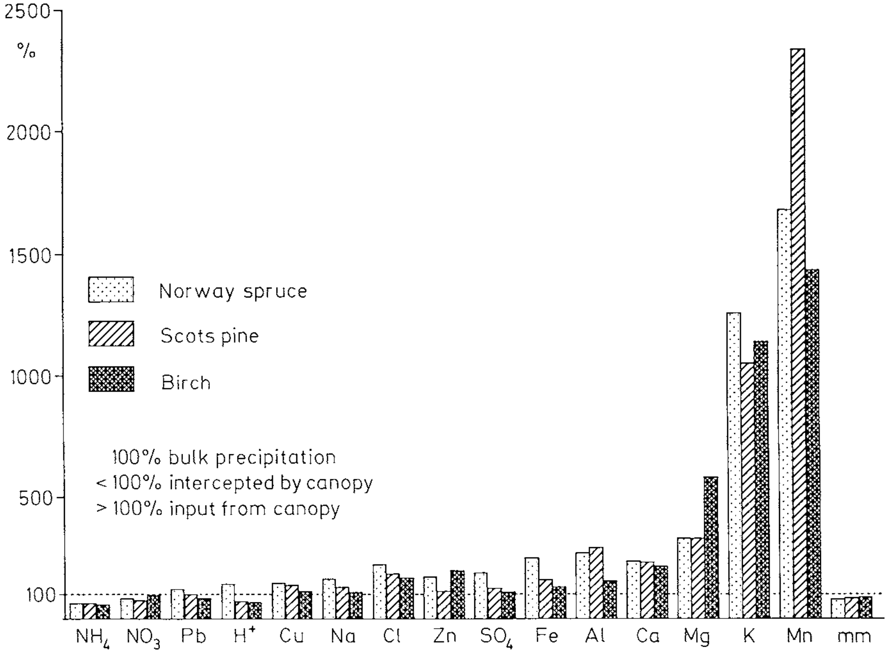

Fig. 6. Influence of canopy interaction on deposition quality (mg m^{-2}) and quantity (mm) relative to bulk precipitation for the sampling period in 1986 (May-June to November)

ammonium and nitrate have also been shown to be intercepted by canopies (Rosén and Lundmark-Thelin 1985; Grennfelt and Hultberg 1986; Helmisaari and Mälkönen 1989). Grennfelt and Hultberg (1986) state that absorption by the canopy may be 70% or more of the ammonium, and more than 50% of the nitrate in summertime precipitation. Interception of nitrogen, particularly NO_3–N, may also be partly due to the presence of epiphytes living on the surfaces of the canopy and trunk (Päivänen 1974; Rosén and Lundmark-Thelin 1985). Interception of the H^+ deposition averaged 31% for birch, and 26% for pine. Spruce canopies, in contrast, increased the H^+ deposition in throughfall reaching the ground by 41%.

There may be appreciable yearly variation in canopy interception. This was most apparent for nitrate and hydrogen ions. During the 1985 sampling period the relative amounts of ammonium and nitrate intercepted were roughly the same, whereas in 1986 more ammonium than nitrate was intercepted. In 1985 the canopy interception of ammonium averaged 42 to 56% and nitrate 39 to 57%. The H^+ interception capacity of pine varied slightly between the years; for the sampling period in 1985 (Plots 4 and 5) the H^+ deposition in the throughfall slightly increased, whereas in 1986 (Plot 5) the pine canopy clearly reduced the H^+ deposition in throughfall.

In contrast to nitrogen, the quantities of many other elements generally increased as the precipitation interacted with the canopy (Fig. 6). The greatest relative increases were for manganese, potassium, magnesium and calcium. For instance, in 1986 the amount of potassium in throughfall deposition, compared to bulk precipitation, increased by more than tenfold for each tree species. The manganese deposition from throughfall reaching the forest floor was as much as 15–20 times that from bulk precipitation. Some of the above increases may be due to the contribution of dry deposition from the surfaces of the canopy. However, Godt et al. (1986) found in wash-off experiments that while there is limited leaching of heavy metals from twigs of spruce, there was significant leaching (i.e. derived from internal nutrient cycling) of Mn, Mg and Ca compared to dry deposition wash-off. Matzner et al. (1984) also found increased concentrations of Mn and Ca in canopy drip from spruce due to leaching from the needles. Many studies have reported a corresponding leaching of nutrient cations in throughfall (Nihlgård 1970; Päivänen 1974; Adams and Hutchinson 1984; Rosén and Lundmark-Thelin 1985; Helmisaari and Mälkönen 1989).

Spruce and pine increased the quantities of several ions in throughfall more than birch. Magnesium was an exception; the magnesium enrichment of throughfall in birch stands was relatively greater than that in coniferous stands. The magnesium content of throughfall was at its greatest in autumn when pH values were elevated around the time of leaf fall. It is thus possible that the samples were further enriched with magnesium leached from leaves that had fallen into the collectors.

Compared to the bulk precipitation, the canopies increased the quantity of sulphate in throughfall. Birch stands, however, had only a slight effect. In 1986, the throughfall and bulk precipitation sulphate ratio was 1.7–2.1 in the case of the spruce stands. The respective ratio for the pine stand (Plot 5) was 1.3 (Tables 3 and 4), which compares well with the results of Helmisaari and Mälkönen (1989). The ratio for the birch stands was 1.0–1.2. The enrichment of sulphur in throughfall is undoubtedly due to the accumulation of dry deposition containing sulphur in the canopy.

One-way analysis of variance performed on the 1985 and 1986 weekly throughfall/bulk precipitation deposition ratios indicated significant differences among the stands related to dominant tree species. Spruce stand throughfall/bulk precipitation ratios for H^+ and SO_4^{2-} were found to be significantly ($P \leq 0.05$) greater than those of the birch stands.

A reduced amount of nitrogen and an increased amount of calcium was noted in throughfall in snow samples taken during late winter 1986 (data not presented). For other elements, however, the effect of the canopy was more variable than in samples taken during the growing season. The birch canopies tended to intercept potassium and sulphur from snowfall, whereas coniferous canopies increased the amounts in snow. Helmisaari and Mälkönen (1989) have also observed elevated concentrations of sulphate in snow samples from pine stands, and was considered it to be due to increased interception of sulphur-rich dry deposition in the canopy. The phenomenon was explained to reflect dry deposition accumulated in the canopy during winter.

Conclusions

The highest H^+ deposition in bulk precipitation occurred in plots located in southwestern (Plots 1 and 7) and eastern (Plot 5) Finland, and the lowest in the southerly located plots (Plots 2, 3 and 6). In the latter plots the sulphur and nitrogen contents are moderate with respect to the other sample plots, but these plots are also exposed to a significant base cation input which has a neutralizing effect. In contrast, the southwestern part of the country receives less base cation inputs. The correspondence between the sulphur and base cations in bulk precipitation may indicate that they could originate from the same emission sources.

Acid precipitation contains strong and weak acids. H^+ determinations based on pH values are a measure of the free dissociated H^+ ions only. However, the solution could contain a noticeable amount of undissociated acids. Titratable acidity would therefore be a better measure of precipitation and throughfall acidity.

The spruce, pine and birch canopies all reduced the ammonium and nitrate contents of the bulk precipitation, reflecting the low nitrogen levels prevalent in boreal forests. In contrast to nitrogen, the canopies of all three tree species increased the throughfall deposition of sulphate, magnesium, potassium and calcium ions. The throughfall/bulk precipitation SO_4^{2-} ratio was greater in spruce stands than in birch or pine stands, which largely reflects the difference in the amount of dry deposition trapped in coniferous tree canopies, especially spruce. The sum of cations in throughfall was greater than the sum of anions. The difference was assumed to be due to organic anions derived from the metabolic activity of the trees.

The amounts of most ions in throughfall deposition and bulk precipitation for comparable sampling periods are of the same order of magnitude as those reported for southern and western Sweden (Nihlgård 1970; Rosén and Lundmark-Thelin 1985). However, the deposition of sea salts, particularly sodium and chloride, were less.

The precipitation and snow sampling techniques are the most obvious sources of error. In addition to wet deposition, the open funnels collect an unknown amount of dry deposition and leachate from litterfall that accumulates in the collector funnel. Dry deposition to a bulk collector is probably very different than to a canopy. Because the samples may also have been influenced by evaporation, the sampling bottles were protected from the effects of direct sunlight. Further, the precipitation collectors were replaced each week with acid-washed ones. Precipitation collectors of this type are widely used in throughfall studies. The snow samples were taken only once in late winter, and may have been disturbed by litterfall, by ion migration in the snowpack as evaporation or with melting water passing into the ground. These factors may have influenced the great variation in the effect of the canopy on the results. In order to obtain more accurate knowledge about the effects of canopy on throughfall, sampling should be continued throughout the year.

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PART 2 TERRESTRIAL SYSTEMS

2.1 Soil Chemistry

Chemical Characteristics of Finnish Agricultural Soils in 1974 and in 1987

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Summary

Chemical analyses of the Finnish cultivated soils sampled in 1974 and in 1987 indicate, on average, that the pH level in 1987 was higher than that 13 years earlier. Concentrations of most of the AAAc-extractable macronutrients and AAAc–EDTA-extractable micronutrients in soils increased. Relatively great increases were observed, particularly in soil P, B, Co, Cr, Cu and Mo. Zn was the only nutrient that showed a decrease in the concentration. As to harmful heavy metals, the concentration of soil AAAc–EDTA-extractable Cd increased, whereas soil AAAc–EDTA-extractable Pb decreased from 1974 to 1987.

Introduction

Acidifying sulphur and nitrogen compounds mainly emitted into the air from energy production, traffic and industry are precipitated also onto the cultivated soils; also heavy metals originating from the same sources are deposited onto the fields. On the other hand, the physico-chemical properties of the agricultural soils are largely affected by the cultivation activities and the plant species to be cultivated. This study elucidates the chemical status of Finnish cultivated soils in 1987, and evaluates possible changes caused by agricultural and environmental factors over the 13-year period (1974–1987). Special attention has been focussed on the impacts of acid rain and heavy metal deposition on cultivated fields.

Materials and Methods

Soil Sampling

The majority (n = 1320) of the cultivated fields (n = 2000) sampled in summer 1974 throughout Finland were resampled in summer 1987 (Sippola and Tares 1978). Soil samples were collected from five plant cultivation zones (Fig. 1). The samples were taken from the plough layer (0–0.2 m). Each soil sample consisted of four subsamples collected from each of the four corners of the 10 × 10 m sampling area

Kauppi et al. (Eds).
Acidification in Finland

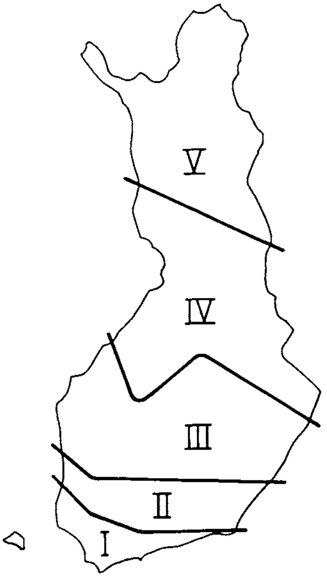

Fig. 1. The plant cultivation zones (I–V)

selected to represent the field. The samples were air-dried for analysis and the dried samples were passed through a 2-mm sieve.

Methods of Soil Analysis

Electrical conductivity (10^{-4} S cm^{-1}) was measured from a soil: water (1:2.5) suspension after letting the suspension settle overnight. Soil pH(H_2O) was determined conventionally with the pH meter from this suspension after stirring.

Organic carbon content was determined by an automated dry ashing method (Anon. 1979). Samples were combusted in an oxygen atmosphere and the CO_2 gas formed was measured by a solid-state infrared detector. In 1974, organic C content was determined by the colorimetric bichromate wet combustion technique (Graham 1948).

Bulk density was determined by weighing a 25-ml quantity of air-dried and ground soil.

P, K, Ca, Mg and S were extracted from the soils using a 0.5 N ammonium acetate 0.5 N acetic acid (AAAc) solution (pH 4.65), the extraction ratio being in a 1:10 volume ratio, the extraction time 1 h, and the shaking speed 27 r.p.m. (Vuorinen and Mäkitie 1955). P was measured from the soil extracts colorimetrically using the Mo blue method. K, Ca, Mg and S concentrations were measured from the soil extracts employing an inductively coupled plasma emission spectrometer (ICP).

Al, Cd, Cr, Co, Cu, Fe, Mn, Mo, Ni, Pb and Zn were extracted from the soil using a 0.5 N ammonium acetate 0.5 N acetic acid 0.02 N Na_2EDTA (AAAc–EDTA) solution (Lakanen and Erviö 1971). The extraction time and extraction ratio were the same as in the AAAc extraction. Mo concentrations were

Table 1. Mean soluble trace element concentrations (mg l^{-1}) in 27 soil samples collected in 1974 as well as measured by AAS in 1974 and by ICP in 1987

	1974	1987	
	Average by AAS	Average by ICP	Difference
Al	343.2	363.7	+20.5 NS
Co	0.56	0.60	+0.04 NS
Cr	0.36	0.40	+0.04 NS
Cu	1.65	1.58	−0.07 NS
Fe	721.0	780.8	+59.8 NS
Mn	91.9	95.5	+3.6 NS
Ni	0.56	0.54	−0.02 NS
Zn	5.60	5.72	+0.12 NS

determined from the soil extracts with a flameless atomic absorption spectrometer using a graphite furnace, whereas Cd and Pb concentrations were measured with an atomic absorption spectrometer using an air-acetylene flame. The concentrations of other trace metals mentioned above were determined with an ICP.

B was extracted from the soil with boiling water (1:2) and determined from the extract by the azomethine-H method (Sippola and Erviö 1987) with an ICP.

The extraction methods for the soil samples collected in 1974 were the same as in 1987. Chemical measurements from the soil extracts in 1974 were carried out as described by Tares and Sippola (1978). The levels of the analytical results on the same soil samples obtained in 1974 and in 1987 did not differ significantly from each other (Table 1). Statistical methods used for handling the results in the present study were T-test and variance analysis.

Results and Discussion

Soil Types and Some Other General Soil Characteristics

Classification of the soils was made in both years according to Aaltonen et al. (1949). Distribution of the soils into different soil type groups by the plant cultivation zones in 1974 and in 1987 are presented in Fig. 2. The organic carbon contents and bulk densities of the soil materials from the comparison years were very similar to each other (Table 2, Fig. 4). In 1987 the mean electrical conductivity was a little lower than in 1974 (Table 2).

Acidity

The mean pH(H_2O) of the soils increased from 5.57 in 1974 to 5.75 in 1987. The change was 0.18 pH-unit, on average (Table 2). An equal increase was observed

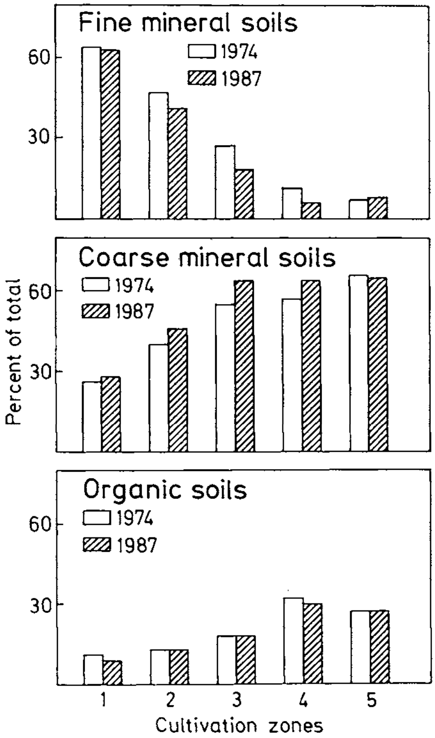

Fig. 2. Distribution of the soils into different soil type groups by the plant cultivation zones in 1974 and in 1987

also by the Soil Analysis Service (Kähäri et al. 1987), because the pH of the soil samples sent from the whole country for soil testing, averaged 5.66 in 1971–75 and 5.84 in 1981–85. Still, the most acidic fields of Scandinavia are cultivated in Finland (Kähäri 1989). In both years, soil pH varied areally so that it decreased from the south to the north (Fig. 3a). Furthermore, the greatest increase (0.34 pH-unit) occurred in southern and southwestern Finland.

The change in soil pH found here was most obviously due to liming. Total mean annual application rate of lime to the whole areal of cultivated fields approximately doubled from the early 1970's (4–500,000 tons) to the end of the 1980's (over one million tons), while the total areal of the cultivated fields slightly reduced from 2.4 million ha in 1974 to 2.1 million ha in 1987. The amount of lime as $CaCO_3$ used for fields in recent years has been 400 kg ha^{-1} per year. In order to eliminate the negative impact of acid rain (pH 4.5), no more than 25 kg of $CaCO_3$ is required annually per hectare. Instead, the amount of lime as $CaCO_3$ needed for neutralizing the acidifying effects of N fertilization is about 100–150 kg ha^{-1} yearly, when the calculations are based on the present annual application rate of N, 80–90 kg ha^{-1} (Anon. 1982). Furthermore, cultivated soils are acidified by the leaching of calcium and uptake of nutrients by the cultivated plants.

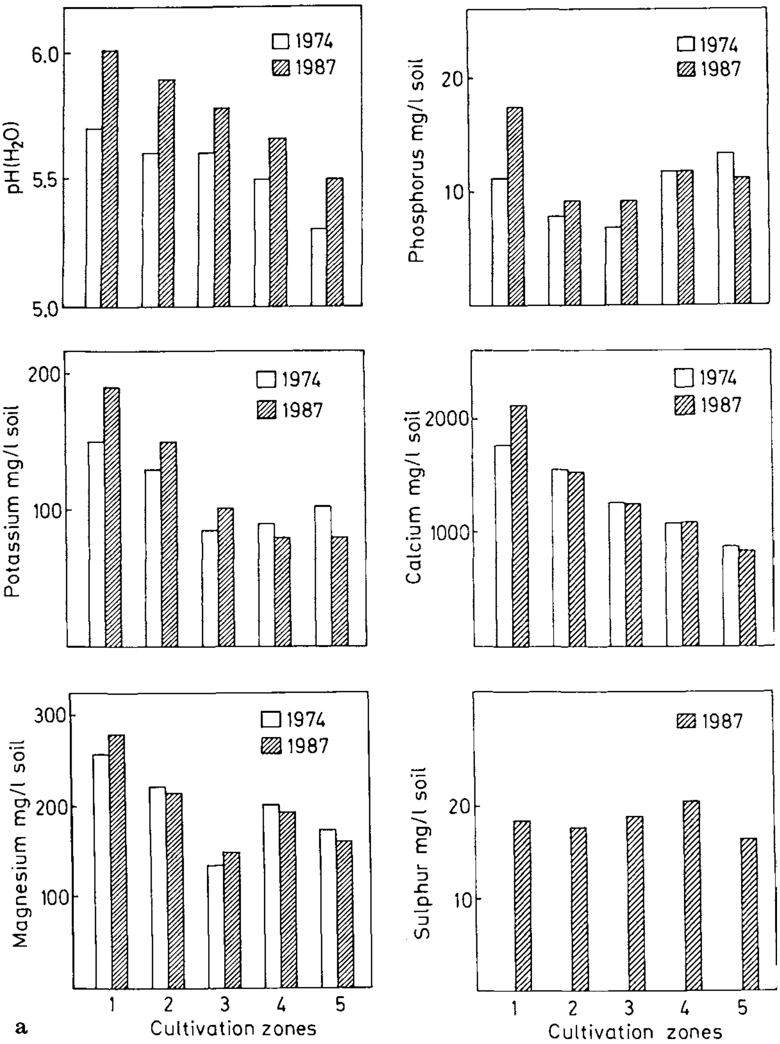

Fig. 3a. Means of pH(H_2O) as well as AAAc-extractable phosphorus, potassium, calcium, magnesium and sulphur of the Finnish cultivated soils (n = 1320) by the plant cultivation zones in 1974 and in 1987

Macronutrients

The mean of soil extractable phosphorus in 1987 was 10.3 mg l^{-1} and 1.4 mg l^{-1} higher than that in 1974 (Table 2). Especially the fields in the coastal area of southern Finland had about 50% more P than in 1974 (Fig. 3a). These fields contained P 17.5 mg l^{-1} and nearly twice that of other parts of the country. AAAc extracts only a small fraction of fertilizer phosphorus applied over several years (Tares and Sippola 1978). If it is assumed that only 1.5% of fertilizer P is extractable, the 1.4 unit higher value found in 1987 compared to that of 1974

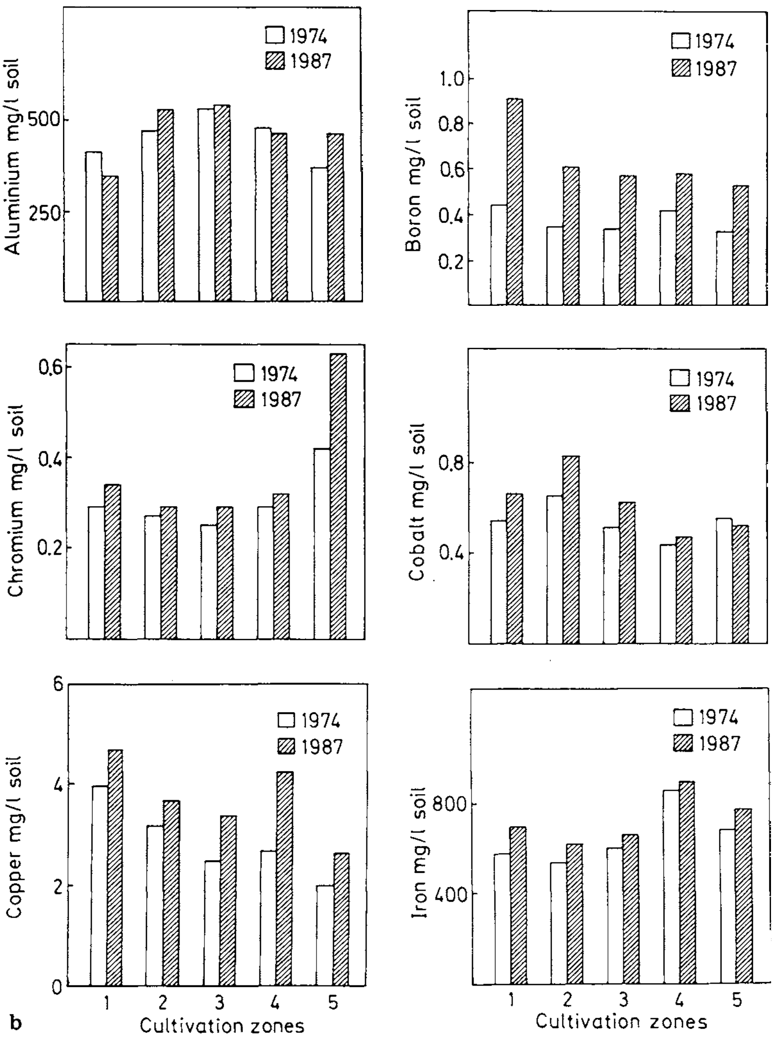

Fig. 3b. Means of AAAc-EDTA-extractable aluminium, chromium, cobalt, copper and iron as well as hot water-extractable boron of the Finnish cultivated soils (n = 1320) by the plant cultivation zones in 1974 and in 1987

corresponds to an increase of 186 kg ha^{-1} in total P. Compared to application rates of P in fertilizers and manure, as well as crop removal, this estimate can be considered to be reasonable.

The extractable potassium concentration of the soils was 109 mg l^{-1}, on average, increasing by 10% since 1974. The highest areal mean level, 191 mg l^{-1}, was in southern Finland, where the increase was 27% (Fig. 3a); the lowest areal value was in the north (80 mg l^{-1}). There soil K has reduced by 28%. Grass cultivation dominates in that area of Finland and relatively high rates of N-fertilizers have been applied to grasslands without sufficient addition of K-fer-

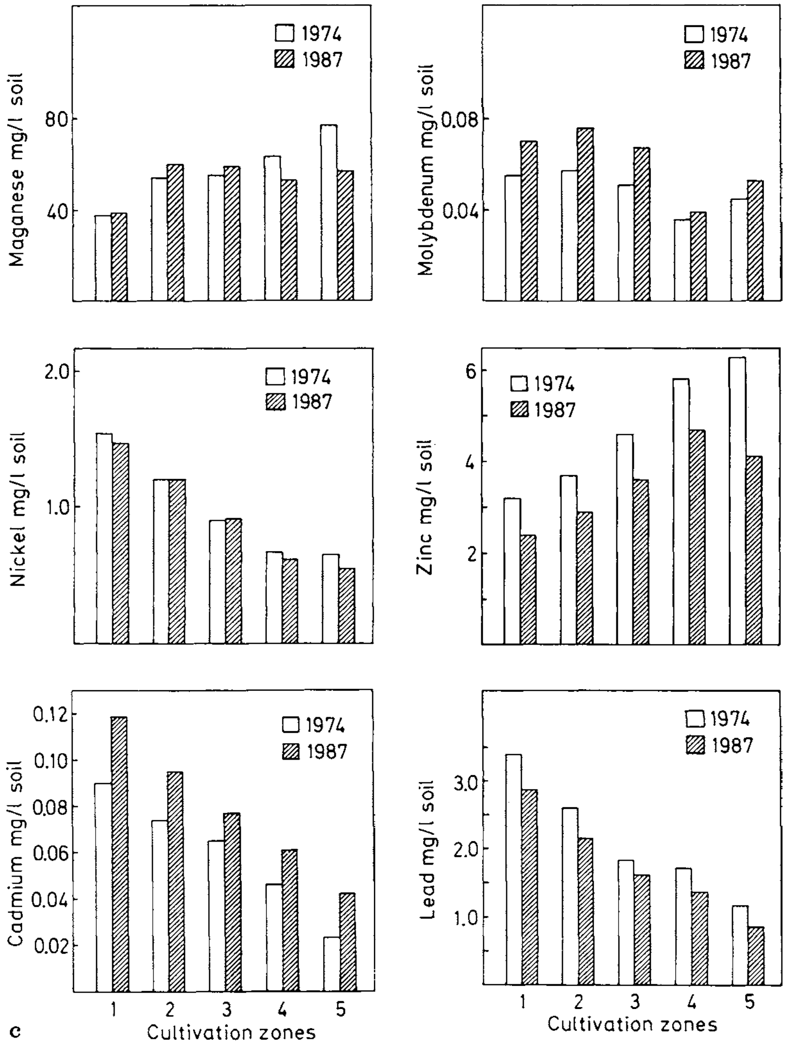

Fig. 3c. Means of AAAc-EDTA-extractable manganese, molybdenum, nickel, zinc, cadmium and lead of the Finnish cultivated soils (n = 1320, except in the case of cadmium in 1974, n = 142) by the plant cultivation zones in 1974 and in 1987

tilizers. This has apparently resulted in the decreased K levels found in these fields (Sillanpää and Rinne 1975).

The mean calcium level extracted from the soils in 1987 was 1277 g l^{-1}, similar to that in 1974 (Table 2). However, soil Ca increased in the southernmost fields by 21%. Areally, the highest concentrations were in southern Finland and the lowest ones in northern Finland (Fig. 3a).

Soil magnesium, on the whole, seemed to be unchanged from 1974. In 1987, the soils contained 178 mg l^{-1} extractable Mg (Table 2). Fields in southernmost Finland had to some extent higher Mg concentrations than those elsewhere (Fig. 3a). According to Kähäri et al. (1987) Mg has slightly increased in Finnish

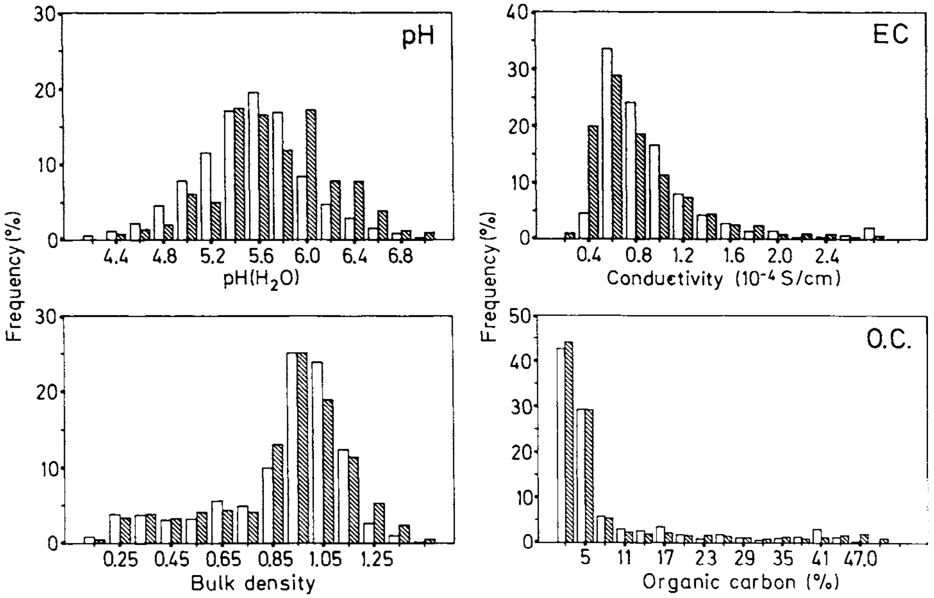

Fig. 4. Distribution of certain chemical characteristics of the soils (n = 1320) in 1974 (□) and 1987 (▨)

cultivated soils from the 5-year period of 1971–1975 to the 1981–1984 period. This has been due to the use of Mg-containing liming materials.

The soil AAAc extractable sulphur averaged 19.0 mg l^{-1} in 1987 (Table 2). The S concentration varied areally hardly at all (Fig. 3a). According to Korkman (1973), Finnish soil sample material collected in 1969 from the plough layer contained SO_4–S 12.1 mg l^{-1}, on the average, when extracted by the same method as employed in the present study. On the other hand, research results obtained by Kähäri et al. (1987), employing $CaCl_2$-extraction, indicated that the mean SO_4–S concentration in Finnish arable soils (n = 1394) was 12.9 mg l^{-1} in 1981–85. However, the $CaCl_2$-extraction method gave values which were only about two-thirds of the those obtained by the method used here (Yli-Halla 1986). Thus, the means presented here and by Kähäri et al. (1987) are quite similar.

Soil S concentrations were not measured in 1974. Thus, it was not possible to clarify the impacts of anthropogenic actions on the S levels of Finnish cultivated soils during the study period. Locally, high S concentrations may occur naturally in soils. For example, Erviö and Palko (1984) reported a mean SO_4–S concentration as high as 232 mg l^{-1} in acid sulphate soils located in the northwestern coastal area of Finland.

The annual atmospheric deposition of S in southern Finland is about 1000 mg per m^2 (Tuovinen et al. this Vol.). This amount corresponds to 5 mg l^{-1} of soil to a depth of 0.2 m. S is both easily leached from the soil and taken up by plants. Therefore, its accumulation in the soil was difficult to evaluate.

Macronutrients studied here are added annually through mineral fertilizers into the soils in the following amounts: P 30, K 50, Mg 4, S 16.5 kg ha^{-1} as well as

Table 2. Means of chemical characteristics of soils (n = 1320) in 1987 as well as their differences from 1974

	Mean 1987 (mg l^{-1})	Difference from 1974 (mg l^{-1})	(%)
pH(H_2O)	5.75	+0.18***	
Org. C, %	9.0	+0.38 NS	+4.4
Bulk dens.	0.90	0.00 NS	0.0
El. cond. 10^{-4}S cm^{-1}	0.84	−0.11***	
Ca	1278	+6.7 NS	+0.5
K	109	+9.6***	+9.7
Mg	178	+2.9 NS	+1.7
P	10.3	+1.43**	+16.1
S	19.0	–	–
Al	508	+19.4 NS	+4.0
B	0.59	+0.3***	+61.5
Cd	0.080[a]	+0.019***	+31.1
Co	0.62	+0.10***	+19.2
Cr	0.33	+0.05***	+16.9
Cu	3.68	+0.90***	+32.2
Fe	717	+64.1***	+9.8
Mn	57	−1.1 NS	−1.9
Mo	0.061	+0.013***	+27.1
Ni	0.90	−0.02 NS	−2.0
Pb	1.66	−0.31***	−15.5
Zn	3.70	−1.06***	−22.2

[a] (n = 142).
T-test:* = $(P > 0.05)$, ** = $(P > 0.01)$, *** = $(P > 0.001)$.

through liming materials, Ca 215 kg ha^{-1} (Mäkelä-Kurtto 1987) and Mg about 25 kg ha^{-1} (Jokinen 1981). In addition to this, they are deposited from the atmosphere as follows: P 0.04–0.24, K 1.0–4.8, Ca 2.4–15.2, Mg 0.6–2.0 and S 2.8–15.0 kg ha^{-1} per year (Mäkelä-Kurtto 1987). Thus, the importance of the atmospheric depositions on the macronutrient concentrations in the cultivated soils is minor, except in the case of S.

Means, minimum and maximum of the macronutrients of the soils studied as well as statistical significances of the differences by the cultivation zones in 1974 and in 1987 are presented in Table 3. Furthermore, distribution of the macronutrients of the soils into different concentration classes in 1974 and in 1987 are shown in Fig. 5a and b.

Microelements

The mean amount of aluminium extractable from the soils in an AAAc–EDTA solution was 508 mg l^{-1}, being unchanged since 1974 (Table 2).

The water extractable boron in the soils averaged 0.59 mg l^{-1} in 1987 (Table 2). The B concentration has significantly (by 62%, on average) increased all over the

Table 3. Means (x̄) as well as minimum (min) and maximum (max) of extractable mineral element concentrations (mg l^{-1}) of soils by plant cultivation zones in 1974 and 1987

Year		1974					1987				
Cultivation zone		I	II	III	IV	V	I	II	III	IV	V
No. of samples (if not mentioned)		64	249	614	305	88	64	249	614	305	88
pH	x̄	5.71^{c}	5.60^{bc}	5.61^{bc}	5.49^{b}	5.31^{a}	6.05^{c*}	5.79^{b*}	5.78^{b*}	5.65^{ab*}	5.49
	min	4.95	4.55	4.30	4.15	4.00	4.95	4.40	4.35	4.40	4.40
	max	7.20	7.15	6.90	6.75	6.50	7.45	7.60	7.00	6.90	6.25
Org. C, %	x̄	4.0^{a}	6.1^{ab}	7.6^{b}	12.6^{c}	11.9^{c}	5.0^{a}	6.3^{a}	7.7^{a}	13.1^{b}	14.4^{b}
	min	1.2	1.7	0.8	1.4	0.9	1.5	1.2	1.1	1.0	1.0
	max	17.9	47.4	46.2	47.2	43.9	25.7	48.1	51.3	51.9	50.6
Bulk dens.	x̄	0.96^{b}	0.92^{ab}	0.91^{ab}	0.85^{a}	0.88^{ab}	0.94^{b}	0.91^{ab}	0.94^{b}	0.83^{a}	0.85^{ab}
	min	0.62	0.29	0.11	0.06	0.11	0.38	0.30	0.27	0.11	0.14
	max	1.32	1.35	1.94	5.53	1.39	1.33	1.38	1.50	1.41	1.39
El. cond. 10^{-4}S cm^{-1}	x̄	0.78^{a}	0.79^{a}	0.84^{a}	1.26^{b}	1.22^{b}	1.07^{b*}	0.77^{a}	0.82^{a}	0.90^{a*}	0.89^{a*}
	min	0.49	0.37	0.36	0.39	0.51	0.31	0.36	0.23	0.21	0.20
	max	1.62	3.70	6.85	5.50	4.99	3.20	3.05	4.14	4.58	2.62
Ca	x̄	1763^{c}	1558^{c}	1260^{b}	1067^{ab}	874^{a}	2135^{d*}	1527^{c}	1249^{b}	1077^{b}	832^{a}
	min	550	250	100	50	25	201	296	139	117	146
	max	4900	4300	10250	3600	2100	5008	6062	5366	5050	2702
K	x̄	150^{b}	129^{b}	85^{a}	90^{a}	103^{a}	190^{c*}	150^{b*}	101^{a*}	81^{a*}	80^{a*}
	min	30	20	15	15	10	36	30	17	12	11
	max	380	720	600	700	580	328	418	393	418	340
Mg	x̄	265^{d}	223^{cd}	134^{a}	202^{bc}	174^{ab}	280^{c}	215^{b}	149^{a}	193^{ab}	159^{a}
	min	25	20	10	10	30	21	16	14	17	12
	max	1000	1150	620	680	810	1030	1118	748	852	655
P	x̄	11.2^{abc}	7.9^{ab}	6.9^{a}	11.8^{bc}	13.4^{c}	17.5^{b*}	9.2^{a}	9.2^{a*}	11.8^{a}	11.2^{a}
	min	1.9	0.9	0.4	1.2	0.8	2.6	0.1	0.5	0.1	0.5
	max	82.0	188.0	95.0	343.0	83.0	107.0	68.0	77.0	106.0	105.0
S	x̄	NA	NA	NA	NA	NA	19.1^{a}	17.9^{a}	18.9^{a}	20.5^{a}	16.3^{a}
	min						8.1	6.6	4.2	4.0	4.3
	max						64.0	149.9	199.6	269.9	38.6
Al	x̄	379^{a}	473^{b}	530^{b}	477^{b}	372^{a}	349^{a}	531^{b}	544^{b}	463^{ab}	466^{ab}
	min	85	140	1	7	17	77	122	68	14	11
	max	1400	1620	1650	1420	1550	1042	7746	8497	1376	1347

B	$\bar{x}$	0.44^{c}	0.35^{ab}	0.34^{ab}	0.42^{bc}	0.33^{a}	0.91^{b*}	0.61^{a*}	0.57^{a*}	0.58^{a*}	0.53^{a*}
	min	0.12	0.08	0.01	0.04	0.07	0.24	0.16	0.08	0.07	0.09
	max	2.21	1.56	2.17	2.96	0.96	3.19	1.91	2.58	3.03	1.84
Cd	$\bar{x}$	0.090^{c}	0.074^{c}	0.065^{bc}	0.046^{ab}	0.023^{a}	0.119^{e*}	0.095^{d*}	0.077^{c*}	0.061^{b*}	0.042^{a}
	min	0.030	0.036	0.020	0.011	0.008	0.060	0.010	0.010	0.010	0.010
	max	0.173	0.140	0.195	0.090	0.041	0.270	0.270	0.270	0.140	0.090
	n	13	19	64	38	8	64	249	614	305	88
Co	$\bar{x}$	0.54^{ab}	0.65^{b}	0.51^{a}	0.43^{a}	0.55^{ab}	0.66^{b}	0.83^{c*}	0.62^{b*}	0.47^{a}	0.52^{ab}
	min	0.14	0.10	0.01	0.20	0.40	0.17	0.09	0.03	0.02	0.02
	max	1.60	2.44	2.50	2.18	2.74	1.97	3.11	3.15	2.08	2.31
Cr	$\bar{x}$	0.29^{a}	0.27^{a}	0.25^{a}	0.29^{a}	0.42^{b}	0.34^{a}	0.29^{a}	0.29^{a*}	0.32^{a}	0.63^{b*}
	min	0.05	0.03	0.01	0.01	0.01	0.09	0.01	0.01	0.03	0.01
	max	0.63	2.00	1.38	1.68	5.35	1.20	1.11	1.78	1.23	3.66
Cu	$\bar{x}$	3.95^{c}	3.22^{bc}	2.59^{ab}	2.79^{ab}	2.05^{a}	4.73^{c}	3.70^{abc}	3.41^{ab*}	4.27^{bc*}	2.65^{a}
	min	0.73	0.42	0.01	0.15	0.25	0.60	0.41	0.29	0.13	0.15
	max	10.18	15.61	22.60	21.40	17.77	13.52	12.93	27.73	25.59	29.82
Fe	$\bar{x}$	573^{a}	536^{a}	602^{a}	857^{b}	684^{ab}	696^{ab}	621^{a}	663^{a}	892^{b}	774^{ab}
	min	160	81	1	17	60	131	113	92	103	117
	max	1340	3860	6300	4560	3440	2037	5407	5112	5353	3695
Mn	$\bar{x}$	38^{a}	54^{ab}	55^{ab}	63^{bc}	77^{c}	39^{a}	60^{b}	59^{b}	53^{ab*}	57^{b*}
	min	6.0	8.0	0.1	1.8	0.8	6.9	3.7	3.1	1.2	0.2
	max	224.0	204.0	590.0	424.0	690.0	165.0	202.2	581.2	650.2	610.4
Mo	$\bar{x}$	0.055^{a}	0.057^{a}	0.051^{a}	0.036^{a}	0.045^{a}	0.070^{b}	0.076^{b*}	0.067^{b*}	0.039^{a}	0.053^{ab}
	min	0.015	0.015	0.001	0.004	0.006	0.011	0.008	0.003	0.002	0.002
	max	0.829	0.824	2.561	0.228	0.314	0.257	1.110	1.080	0.530	0.830
Ni	$\bar{x}$	1.54^{c}	1.20^{b}	0.90^{a}	0.67^{a}	0.65^{a}	1.46^{c}	1.20^{bc}	0.91^{b}	0.61^{a}	0.54^{a}
	min	0.32	0.20	0.01	0.01	0.12	0.19	0.17	0.01	0.11	0.01
	max	9.20	6.00	7.20	4.92	2.44	4.55	6.22	6.72	3.76	3.39
Pb	$\bar{x}$	3.39^{d}	2.54^{c}	1.83^{b}	1.72^{b}	1.17^{a}	2.86^{d*}	2.14^{c*}	1.61^{b*}	1.36^{b*}	0.85^{a}
	min	1.50	0.40	0.01	0.10	0.10	1.25	0.05	0.01	0.10	0.05
	max	6.20	36.40	10.20	5.60	11.00	7.05	6.95	11.35	8.05	4.65
Zn	$\bar{x}$	3.19^{a}	3.73^{a}	4.60^{ab}	5.79^{b}	6.30^{b}	2.41^{a}	2.89^{ab}	3.60^{bc*}	4.68^{c*}	4.12^{c*}
	min	0.8	0.6	0.1	0.5	0.4	0.6	0.3	0.2	0.2	0.2
	max	14.2	32.3	74.8	89.2	44.7	11.3	14.1	22.0	28.8	23.4

Means in each row followed by a common index letter do not differ at $P = 0.05$ within the same year.
Means denote by (*) differ at $P=0.05$ from the respective ones in 1974. NA = not analyzed; n = number of samples

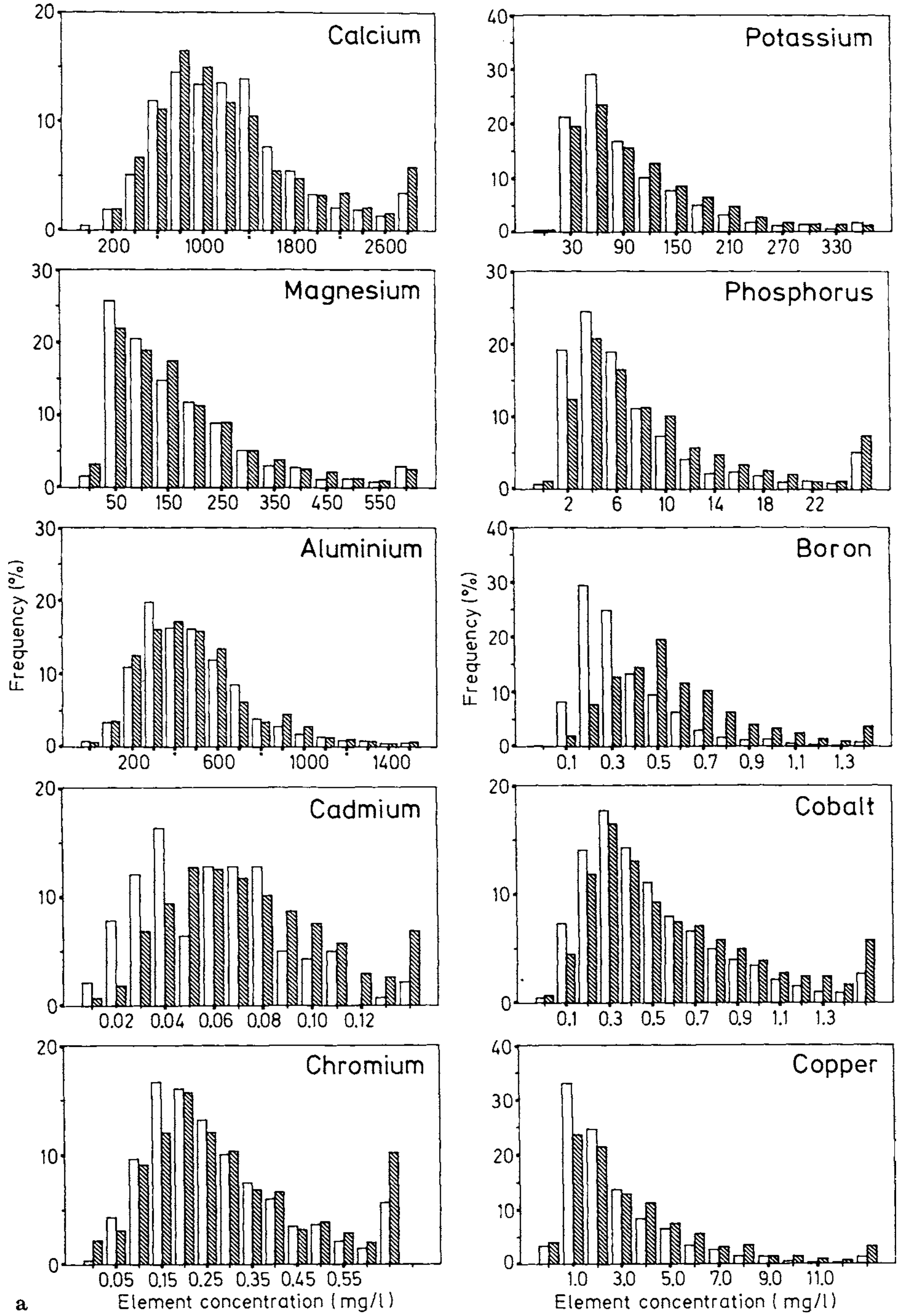

Fig. 5a. Distribution of mineral element concentrations of the soils (n = 1320) in 1974 (☐) and 1987 (▨) (in the case of cadmium in 1974, n = 142).

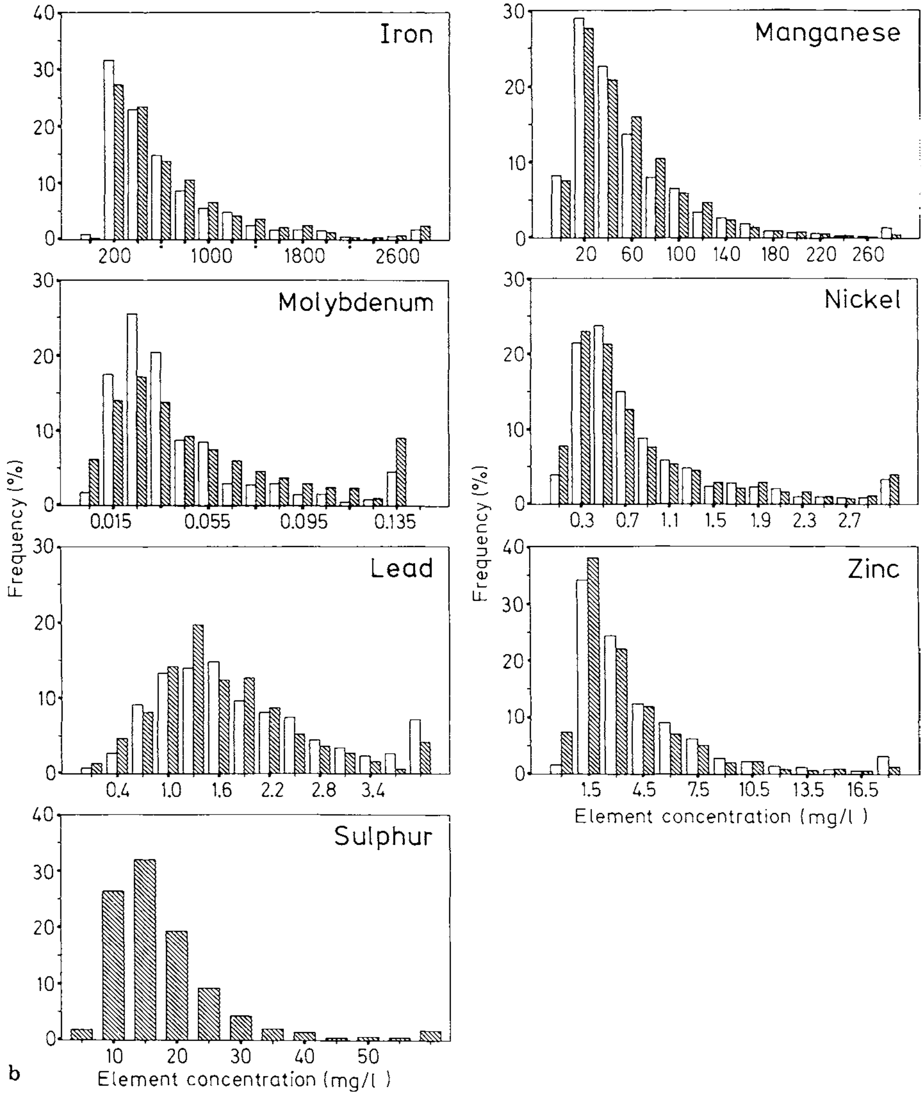

Fig. 5b. Distribution of mineral element concentrations of the soils (n = 1320) in 1974 (□) and 1987 (▨)

country since 1974. Fields in the south contained clearly more B than those in the north (Fig. 3b). Also the increase was greater in the south than in the north. Increased soil B was most obviously due to the application of B (200–400 g ha^{-1} per annum) into the soil as a component of all NPK-fertilizers since 1972.

The mean extractable cobalt concentration of the soils in 1987 was 0.62 mg l^{-1} and it was increased since 1974 by 19%, on average (Table 2). However, no change in the soil Co occurred in the north (Fig. 3b).

On the contrary, soil extractable chromium remarkably increased from 1974 to 1987, particularly in the north (Fig. 3b). The mean of soil Cr of the whole country was 0.33 mg l^{-1} in 1987 and it was 17% higher than that in 1974 (Table 2). Cr concentration in the north was about twice that in other parts of Finland and there also the emission of Cr from industry was reported (This is an unpublished work; should be cited in the text only, with name and initials of the author R. Valli 1989) to be great.

The extractable copper concentration of fields was 3.68 mg l^{-1} of soil, on the average. From 1974 to 1987, the mean of soil Cu rose by 32% (Table 2). Two times higher Cu values were detected in southern Finland than in northern Finland (Fig. 3b). The greatest increase, $>50\%$, was observed in the fourth cultivation zone. The most probable reason for the general increase in soil Cu is the fact that Cu fertilization (200–300 g Cu ha^{-1} per annum) has become more and more common since 1974. Cu deficiency recorded in peat soils as well as in coarse mineral soils has led to the increased use of Cu as a fertilizer. Small amounts of Cu are also deposited via the air. For example, in Sweden deposition of Cu was 10 g ha^{-1} in 1984 (Anon. 1987c). Measurements on the Cu deposition are not available in Finland.

In 1987, the amount of iron extracted from the soils was 717 mg l^{-1}, and seemed to be 9% more than in 1974, on average (Table 2). But when the difference in the level of analytical results on Fe between the 2 years (Table 1) was taken into account, no change in soil Fe could be detected from 1974 to 1987.

On the whole, the concentration of extractable manganese was 57 mg l^{-1} of soil and had not changed since 1974 (Table 2), although Mn has been annually added at about 200 g ha^{-1} in the fertilizers over the study period. Soil Mn had even decreased in the north.

Extractable soil molybdenum increased from 1974 to 1987 by 27% (Table 2) and particularly in central Finland (Fig. 3c). The mean of soil Mo in 1987 was 0.061 mg l^{-1}.

Nickel was one of the mineral elements whose concentrations remained unchanged between 1974 and 1987 (Table 2). The extractable Ni concentration of fields sampled in 1987 was 0.90 mg l^{-1} of soil. The highest concentrations occurred in the south (Fig. 3c) where also emissions of Ni into the atmosphere were the highest in the country (R. Valli 1989). Ni concentrations in the soil gradually decreased towards the north.

Cultivated Finnish soils contained in 1987 extractable zinc 16% less than in 1974 (Table 2). The mean concentration was 3.70 mg l^{-1}. Soil Zn decreased throughout Finland but the most in northern areas (Fig. 3c). However, the soils in 1987 still contained about twice as much Zn in northernmost Finland than in southernmost Finland. Zn has been added no earlier than since 1986 to the soils through fertilizers. However, no statistics on the amounts of Zn applied annually are yet available. According to fertilizer recommendations in use in Finland today, the rate of application could be 4–10 kg Zn ha^{-1} for several (3–5) years. This means 1–3 kg Zn ha^{-1} per year. A part of soil Zn originates from the air. Swedish measurements (Anon. 1987c) indicate that in 1984 the total deposition of Zn was 120 g in southern Sweden and 60 g in northern Sweden. Between the years 1985 and 1987 the total annual deposition of Zn in southeastern Finland was about 100 g ha^{-1} (Anon. 1986b–1988).

According to this study, input of most microelements to the soil from the atmosphere seemed to be smaller than from fertilizers. This means that the cultivation activities are, in general, more responsible for the changes in the microelement level in the agricultural soils than the atmospheric depositions.

Means, minimum and maximum of the studied microelements of the soils as well as significances of the differences by the cultivation zones in 1974 and in 1987 are shown in detail in Fig. 5a and b.

The AAAc–EDTA extractable cadmium concentration of all the soils studied in 1987 averaged 0.076 mg l^{-1}. The amount of Cd extractable with AAAc–EDTA solution is 40% of the total soil Cd (Sippola and Mäkelä-Kurtto 1986). Since 1974, the mean Cd concentration of soils from the same fields ($n = 142$) increased from 0.061 mg l^{-1} to 0.080 mg l^{-1} by about 30% (Table 2). Thus, the annual increase was 2.4%. During the 13-year period, the mean increases in the Cd levels in different parts of Finland were of the same magnitude, 0.02 mg l^{-1} (Fig. 3c). The total increase of AAAc–EDTA-extractable Cd in the volume (2 million liters) of the whole plough layer (0–0.2 m) in 1 ha during the study period was 38 g, on average. Obviously, the increase was mainly due to exceptionally Cd-rich phosphorus fertilizers in use during the period 1975–1981.

According to Kivioja (1982) and H. Hero (1988), the Cd load from fertilizers varied annually from 1974 to 1987 as follows: 1.7, 2.6, 2.3, 4.0, 4.6, 7.4, 6.2, 3.6, 1.8, 0.9, unknown, 1.6, 0.5, and 0.5 g ha^{-1}, respectively, being totally 37.7 g ha^{-1} during the study period and 2.9 g ha^{-1} annually, on average.

Another Cd source for cultivated soils is atmospheric deposition of Cd. Based on the measurements in southeastern Finland during the 1984–1987 period (Anon. 1985–1988), total Cd deposition was annually about 2 g ha^{-1} for the winter season and about 1 g ha^{-1} for the summer season, on average. If the Cd deposition is assumed to have been 1.5 g ha^{-1} over the study period, the total Cd load from the atmosphere was 19.5 g ha^{-1}. On this basis, Cd load from fertilizers was nearly twice that from the atmosphere.

The total amount of extractable Cd increase in the plough layer in 1 ha between the years 1974 and 1987 was approximately two-thirds of the total Cd input (57.2 g ha^{-1}) from fertilizers and atmosphere together. According to Andersson (1984), the input of Cd to Swedish soils is around three times the output. Hence, Cd is gradually accumulating in the soil, thus increasing the Cd content. Total concentrations of Cd are reported to increase in the cultivated soils annually by 0.3–0.4% in Sweden (Andersson 1984) and by 0.6% in Denmark (Tjell et al. 1981). Furthermore, it is assumed (Andersson 1984) that the more soluble and plant-available soil Cd fraction will increase at a higher rate than the total soil Cd.

Increased soil Cd will be reflected also in the Cd contents of the crops as well as in intake of Cd in human food. According to Swedish studies (Andersson 1984), the present Cd level in grain of winter wheat may probably increase by 0.5–0.7% annually. It is predicted in Denmark (Tjell et al. 1981) that daily human intake of Cd from food will increase from about 30 µg in 1980 to nearly 50 µg per person in 2080. The predicted increase was reported to be largely due to Cd inflows to soils by fertilizers and atmospheric precipitation.

Since 1986, P-fertilizers in use in Finland have been made mainly of the domestic, nearly Cd-free raw phosphate and consequently, the annual Cd load from fertilizers has been 0.5 g ha^{-1}, on average. Thus, it is expected that the rate of increase in soluble Cd in Finnish cultivated soils will be remarkably lower at the end of the 1980's than that found in this study.

The cultivated fields of southern Finland had significantly higher Cd levels than the fields of northern Finland (Fig. 3c). Furthermore, clays, which were dominant in southern Finland (Fig. 2), contained more Cd than other soil types, on average (Sippola and Mäkelä-Kurtto 1986). Most probably, there were also differences in the amount of Cd deposited onto the soils in southern and northern Finland. Based on the 1984 measurements in Sweden, the total Cd deposition in the south was 1.2 g ha^{-1} and that in the north 0.2 g ha^{-1} (Anon. 1987c).

It is not easy to make a comparison of the extractable Cd levels of the soils between Finland and other countries, since AAAc–EDTA is not a common extraction solution for soil Cd in the world. However, Sillanpää (1988) has reported on the AAAc–EDTA-extractable Cd levels in the agricultural soils of 30 countries under the FAO project. According to him, the national mean of AAAc–EDTA-extractable Cd concentration in Finnish soils in the middle of the 1970's was 0.11 mg l^{-1}. This was of the same low range as those of the developing countries, in general, and lower than the corresponding soil Cd concentrations of most of the developed countries in his study.

The AAAc–EDTA extractable lead concentration of cultivated fields sampled in 1987 was 1.66 mg l^{-1} of soil (Table 2). The mean Pb concentration of the soils decreased from 1974 by about 16%. The fields situated in southern Finland contained approximately three times more soluble Pb than those in northern Finland (Fig. 3c).

The significant decrease in the Pb level of soils throughout Finland was clearly due to the remarkable reduction in national as well as in international Pb emissions into the air from automobiles between 1974 and 1987. In the 1970's the highest permissible Pb concentration in petrol in Finland was 0.7 g l^{-1} and the total emissions of Pb from automobiles were annually about 1000 tons (Anon. 1981). The Pb concentration in petrol was gradually decreased in the 1980's, and since 1986, the Pb limit has been 0.15 g l^{-1}. In addition, Pb-free petrol has been available since 1985. In 1987, annual Pb emissions from traffic were 200–300 tons, but traffic was still the principal source of Pb emission into the air (Vornamo 1984). A positive effect by the effort to reduce lead emissions into the air was clearly observable also in pine needle samples collected from the Helsinki area (Mäkelä-Kurtto and Tares 1987). In 1986, the mean lead content (8.5 mg kg^{-1} DM) of one-year old pine needles was only one-third of that in 1970.

Measurements (Anon. 1987c) made in Sweden in 1984 show that the total deposition of Pb was 80 g ha^{-1} in the south and 15 g ha^{-1} in the northernmost region. Measurements of the total deposition of Pb in Finland have been carried out at only one meteorological station in southeastern Finland (Anon. 1985–1988). They indicate that between 1984 and 1987 annual Pb deposition was of a magnitude of about 50 g ha^{-1} for the winter seasons and about 20 g ha^{-1} for the summer seasons, on the average.

According to Sillanpää (1988), the mean of AAAc-EDTA-extractable Pb concentration of Finnish cultivated soils, 2.5 mg l^{-1}, in the middle of the 1970's, was distinctly lower than the national mean values of the other European countries compared: Malta 34, Belgium 13, Italy 12 and Hungary 6 mg l^{-1}.

Conclusions

This study indicates that the cultivated soils in Finland were not acidified during the 13-year study period. In 1987, the fields were less acidic than in 1974. They contained larger amounts of most of the extractable macro- and micronutrients in 1987 than in 1974. The only nutrients showing decreased concentrations were zinc in all parts of the country and potassium in the northern part of Finland. The depletion of these elements was most apparently due to intensive grass production and unbalanced fertilization. The increases in the concentrations of most of the nutrients studied were connected with application of these nutrients in fertilizers.

Changes in heavy metal concentrations were observed in soils. Although soil Cd increased, the Cd concentration was still low, compared internationally. However, this study indicates that Cd-rich P fertilizers, which were used exceptionally in 1975–1981, and also deposition of Cd from the atmosphere increased the Cd concentrations of agricultural soils by about 30%. Soil lead level was low in 1974 compared internationally. The level decreased further by 16% until 1987, most apparently as a consequence of reduction of Pb emissions into the air from traffic.

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A Survey of Forest Soil Properties Related to Soil Acidification in Southern Finland

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Summary

Parameters describing forest soil acidification status at 65 sites in southern Finland (61–63°N) are presented. pH_{aq} ranges were: 3.6–5.5 (humus), 3.6–5.4 (0–5 cm), and 4.9–7.4 (60–70 cm). Exchange acidity and total acidity in the humus layer averaged 7.0 and 65.6 me 100 g^{-1}, respectively. Corresponding values were 2.9 and 9.9 for the 0–5 cm layer, and 0.3 and 2.1 for the 60–70 cm layer. Aluminium (0.1 M $BaCl_2$) accounted for 32, 81, and 61% of exchange acidity in the humus, 0–5 cm and 60–70 cm layers, respectively. For the same layers, average $BaCl_2$ extractable Ca/Al molar ratios were 38, 1.5 and 11. Effective cation exchange capacity ($BaCl_2$) averaged 27.8 me 100 g^{-1} in the humus layer and decreased from 3.8 to 0.6 me 100 g^{-1} down the mineral soil profile. Corresponding base saturation values were 77%, and 21 to 42%. Different types of soil with respect to acidification could be distinguished.

Introduction

Forest damage and decline is now widely reported in central and northern Europe (Moseholm et al. 1988). This damage may be related indirectly to air pollution through increased levels of soil acidification, as suggested by Ulrich and his fellow-workers in West Germany at the end of the 1970's (e.g. Ulrich et al. 1979). According to the soil acidification hypothesis, base cations (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}) are irreversibly lost from progressively deeper in the mineral soil by leaching with SO_4^{2-} and NO_3^{-} as the accompanying anions. The net loss of base cations results in a reduced acid neutralizing capacity of the mineral soil, i.e. increased soil acidification (van Breemen et al. 1983, 1984). The detrimental ecological effects associated with soil acidification include: impoverishment of soil fertility and base saturation; increase in the amount and proportion of labile acid cations (Al^{3+}, Fe^{3+}, Mn^{2+}); and possibly a decrease in soil pH causing the development of toxic concentrations of Al and heavy metals in soil solution.

However, soil acidification arises naturally as a result of soil formation and development processes, particularly in the case of podzolization (Petersen 1980). Finnish mineral forest soils are mainly podzols or are podzolized, and derived

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from base-poor igneous and metamorphic rocks. However, soils are relatively young, < 10,000 years, and commonly less, depending on when the land emerged from the sea after the last glaciation (Jauhiainen 1973; Eronen 1983; Starr 1989). As a result, they may be expected to be less weathered than areas in central Europe. Acidification also arises as a result of forest growth and humus accumulation due to the uptake of nutrients (Hallbäcken and Tamm 1986). The acidification caused by growth is especially strong in the case of conifers (Nilsson et al. 1982; Bergkvist 1987a). Changes in soil acidification also result from forestry management practices such as thinning (Bringmark 1977; Nykvist and Rosén 1985), clearfelling (Rosén and Lundmark-Thelin 1987), soil cultivation (Starr 1987) and use of fertilizer (Nömmik and Möller 1981), all of which are generally carried out in Finland. Greatly improved wild fire control and the marked decline in the use of prescribed burning and shifting cultivation practices are additional factors affecting the development of acidification in Finnish forest soils (Kivekäs 1939; Viro 1969; Starr 1985).

It is thus important to distinguish between acidification possibly caused by an external proton input (i.e. acid deposition) and that caused internally by other anthropogenic and natural processes (Krug and Frink 1983). However, this is difficult to do in practice. One way is to calculate complete proton budgets for individual sites (van Breemen et al. 1983, 1984; Binkley and Richter 1987; Ulrich and Matzner 1986), but this involves considerable effort. On a regional scale, an attempt can be made to relate soil acidification parameters to external and internal soil acidification factors. The causality of soil acidification may then be assessed on the basis of the strength of these relationships, especially if regional gradients in acid deposition are present and the survey can be repeated (e.g. Troedsson 1985; Tyler et al. 1985; Tamm and Hällbacken 1988). Nevertheless, conclusions about the significance and contribution of acid deposition to soil acidification have been at odds. For example, while both Nilsson (1983) and Bergkvist (1987a) concluded that the most important causes of soil acidification in Sweden were more likely to be soil type, tree species and accumulation in plant biomass and humus rather than atmospheric deposition, Falkengren-Grerup (1987) and Tamm and Hallbäcken (1988) concluded that acid deposition was a significant contributor to the reduced soil pH observed in southern Sweden.

In Finland, the first signs of forest damage possibly caused by air pollution may have now become visible in southern Finland (Jukola-Sulonen et al. 1987; this Vol.). This is also the area receiving the most sulphur and nitrogen deposition (Järvinen 1986; Järvinen and Vänni, this Vol.). The proportion of *Calluna* and *Cladonia* forest site types (reflecting nutrient-poor, dry, coarse-textured soils low in organic matter) in the landscape and soil depth have been used to locate those areas having the least buffering capacity (Tamminen and Mälkönen 1986). However, empirical data specifically concerned with levels of forest soil acidification and acid neutralizing capacity are scarce.

The Department of Soil Science at the Finnish Forest Research Institute is currently carrying out a survey and sampling programme of forested mineral soils on a national scale. In addition to soil classification, the material is being collected to provide data about the levels of soil acidification and acid buffering in different site and soil types and regions. The first round of sampling (1986–89) will form the baseline data, while future repeated sampling is hoped to enable the rates of acidification and the contribution of acid deposition to be determined. In this chapter, the results presently available from selected sites in southern Finland are presented. The aim is to describe the levels and range in soil acidification and acid neutralizing capacity that are currently found in southern Finland using a variety of parameters. Emphasis is given to soil acidity, base and acid (especially aluminium) cations and heavy metals.

Material and Methods

Sample Plots and Soil Sampling

The sample sites were selected from the systematic network of permanent plots established by the eighth national forest inventory (NFI). The NFI network consists of clusters of four 300 m^2 circular sample plots; the clusters are spaced at 16-km intervals. From the 3000 NFI plots available, some 440 plots were selected to form a soil survey network covering the whole country. Of the 188 plots sampled in 1986 and 1987, a batch of 65 were selected to be analyzed first (Fig. 1). In seven cases, there were two plots from the same cluster.

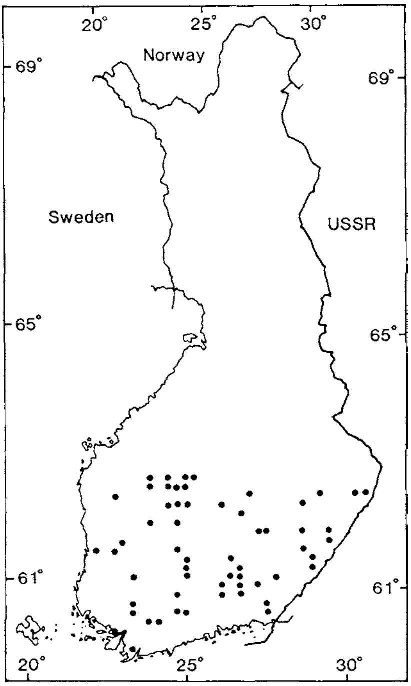

Fig. 1. Location of sample plots

Table 1. Distribution of sample plots according to site type and texture class

Site type[a]	Median grain size diameter, mm[b]					Total
	<0.02	0.02–0.06	0.06–0.2	0.2–0.6	>0.6	
OMaT		1	1	2		4
OMT	3	2	8	2		15
MT	1	2	13	10	1	27
VT			5	9		14
CT			2	2		4
CIT				1		1
Total	4	5	29	26	1	65

[a] Cajander (1949): OMaT – Oxalis Maianthemum type; OMT – Oxalis – Myrtillus type; MT – Myrtillus type; VT – Vaccinium type; CT – Calluna type; CIT – Cladina type.
[b] 5–20 cm layer.

The selection of these 65 sample plots was according to forest site type (site fertility) and soil texture so that rarer sites, i.e. both the most and the least fertile site types and the finest and the coarsest textured soils, were included (Table 1). Most of the soils were classified as podzols, but cambisols and gleysols are included.

Soil samples were taken from the humus layer and mineral soil at four depth intervals: 0–5, 5–20, 20–40 and 60–70 cm. For the humus sample, 10 to 30 subsamples, depending on humus thickness, were taken with a cylinder and combined into a single sample for the plot. The mineral soil samples for each layer consisted of a composite of five subsamples, except the 60–70 cm layer, which consisted of a single sample only. A sample of each genetic horizon was also taken, but these have not yet been analysed.

Sample Pretreatment and Analysis

The samples were dried at 50°C. Subsequently, the humus samples were milled, while the mineral soil samples were sieved to retain the < 2 mm fraction. The samples were then stored in closed plastic bags awaiting analysis.

Particle size analysis was performed by sieving and pipetting procedures after pretreatment with H_2O_2 and HCl (Elonen 1971). The particle size distribution of the 0–5 cm layer was not determined, but instead was given the same textural parameters as the next deeper, 5–20 cm, layer (Table 2). Total C and N were determined with a LECO CHN-600 analyser and organic matter (OM) content using a LECO TGA-500 analyser (Table 2). pH was measured in both water (pH_{aq}; 1:2 v/v) and 0.1 M $BaCl_2$ (pH_{ba}; 1:10 v/v) suspensions. Extractions were made with unbuffered 0.1 M $BaCl_2$ and buffered 1.0 M ammonium acetate pH 7.00 using a soil:solution volume ratio of 1:10. The suspensions were left to stand overnight before being shaken for 1 h and then filtered. Elemental concentrations

Table 2. Means of organic matter content (OM), C/N ratio and clay content by sampling layer. Ranges given in parentheses

Layer	OM %	C/N	Clay %
Humus	71.6 (32–95)	36 (20–90)	–
0–5 cm	7.0 (1.1–22.0)	21 (13–38)	2.8 (0.8–54.2)
5–20 cm	4.2 (1.4–11.2)	19 (8–60)	2.7 (0.7–54.3)
20–40 cm	2.5 (0.2–6.2)	17 (5–35)	2.0 (0.2–32.3)
60–70 cm	1.3 (0.3–5.6)	12 (0–40)	1.9 (0.1–28.5)

of Ca, Mg, K, Na, Al, Fe, and Mn were determined from both extractions using an inductively coupled plasma emission spectrophotometer (ICP, ARL 3580). Total and exchangeable acidities (TA and EA) were determined from the acetate and $BaCl_2$ extractions, respectively, by titration with NaOH to an endpoint of pH 7.00. Effective cation exchange capacity (CEC_e) was calculated as the sum of $BaCl_2$ extractable base (Ca^{2+}, Mg^{2+}, K^+, Na^+) and acid (Al^{3+}, Fe^{3+}, Mn^{2+}, H^+) cations (cf. Hendershot and Duquette 1986). The potential cation exchange capacity (CEC_p) was calculated as the sum of acetate-extractable base cations plus TA. BS_e and BS_p are the corresponding base cation saturations. Concentrations of Al, Cu, Zn, Cd, Pb, Cr, Ni, and Sr were determined by ICP after first dry ashing a subsample (LECO TGA-500) followed by digestion with HCl acid (Halonen et al. 1983). The metal dry combustion results mainly correspond to the total contents of the organically bound fraction. All concentration data have been converted to an oven-dry weight basis.

Results

Extractable Cations and Cation Exchange Capacities

The contents of 0.1 M $BaCl_2$ extractable cations are described in Table 3. Ca^{2+} was the dominant cation in the humus layer while Al^{3+} was in general dominant in the mineral soil, but especially in the 0–5 and 5–20 cm layers. Contents of all cations in the mineral soil clearly decreased with depth, with the exception of Na^+, and K^+ to a lesser extent, which remained relatively uniform down the mineral soil profile. Although contents of the base cations were rather similar to those extracted by neutral ammonium acetate, the acid cation contents were clearly not. For example, $BaCl_2$ aluminium contents were, on average, 17, 12, 4, 3, and 4 times greater compared with the acetate extraction for the humus to 60–70 cm layers, respectively. This difference is due to the difference in the acidity and buffering of these two extractants as the solubility of aluminium and iron is pH-dependent (Richburg and Adams 1970; Bache 1974; Andersson 1975). Amounts of cations extracted also vary with the effectiveness of the exchanging ion used (Tucker 1985; Baes and Bloom 1988), Ba^{2+} being particularly effective (Wiklander 1947). The values given in Table 3 are therefore probably higher than if KCl or NH_4Cl had been used instead of $BaCl_2$.

The means and ranges of effective (CEC_e) and potential (CEC_p) cation exchange capacity values, together with their respective base saturations, are given in Table 4. The average CEC_e/CEC_p ratios for the humus and mineral soil layers were 0.4, 0.4, 0.3, 0.3 and 0.3, respectively. However, the range in the CEC_e/CEC_p ratios increased with depth. In the 60–70 cm layer at three plots the ratio was 1.0. The average relative contributions of Ca^{2+}, other base cations, Al^{3+} and other acid cations to the CEC_e value for each layer are illustrated in Fig. 2. The relative contribution of the base cations to the CEC_e progressively increased with depth due to the larger reduction in the amount of acid cations (see Tables 3 and 4).

The cation exchange capacity and base saturation were correlated to the organic matter content and quality (C/N), clay content, and pH (Table 5). As has been generally found (e.g. Helling et al. 1964; Kalisz and Stone 1980), the organic matter content of the humus layer was strongly correlated to CEC_p but considerably less so to CEC_e. This was due to the strong relationship between organic matter and TA ($r = 0.89$). The CEC and BS parameters of the humus layer were only weakly related to the C/N ratio. This is presumably due to the fact that all C/N ratios for the humus layer were generally high (Table 2). Organic matter incorporated into the upper mineral soil has lower C/N ratios and has been shown to have higher CEC_e values per unit mass than for humus layer organic matter (Kalisz and Stone 1980). Organic matter content and the C/N ratio accounted for only 10% of the variation in the CEC_e values for the humus layer. When pH_{aq} was included in the regression model, the R^2 value increased to 39%.

In the mineral soil, pH_{aq} appeared to be more related to base saturation than to exchange capacity. Statistically significant ($p < 0.05$) correlations between CEC

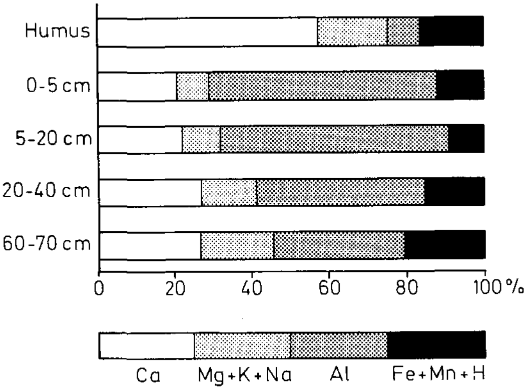

Fig. 2. Relative distribution of CEC_e components by sampling layer

Table 3. Contents of $BaCl_2$ extractable cations by sampling layer. Median and range in parentheses

Layer	Ca	Mg	K	Na	Al	Fe	Mn
	me kg^{-1} oven-dry soil						
Humus	157 (68–342)	29.2 (9.6–74)	17.4 (5.0–33)	1.2 (0.2–2.8)	18.9 (0.5–72)	4.4 (0.1–20)	10.1 (0.8–46)
0–5 cm	5.8 (0.4–110)	1.2 (0.2–51)	0.80 (0.29–6.3)	0.29 (0.06–1.4)	22.7 (3.9–93)	2.0 (0.1–16)	0.30 (0.01–8.1)
5–20 cm	2.9 (0.1–67)	0.51 (0.08–82)	0.29 (0.11–4.8)	0.24 (0.08–2.4)	9.3 (1.6–34)	0.49 (0.02–3.5)	0.18 (0–2.8)
20–40 cm	1.8 (0.1–78)	0.36 (0.02–95)	0.19 (0.01–4.9)	0.21 (0.07–4.2)	3.9 (0.1–17)	0.10 (0–1.9)	0.05 (0–1.3)
60–70 cm	1.1 (0.1–117)	0.25 (0–113)	0.23 (0.01–6.6)	0.18 (0.05–8.9)	1.7 (0.1–16)	0.05 (0–1.2)	0.01 (0–0.25)

Table 4. Acidity and cation exchange parameters by sampling layer. Median and range in parentheses

Layer	pH_{aq}	pH_{ba}	EA	TA	CEC_e	CEC_p	BS_e	BS_p
			me 100 g^{-1} oven-dry soil				%	%
Humus	4.17 (3.6–5.8)	3.15 (2.7–4.1)	7.0 (2.0–15.9)	65.6 (25.4–97.7)	27.8 (15.8–44.3)	82.8 (36.7–118.8)	77 (50–95)	20 (11–56)
0–5 cm	4.35 (3.6–5.4)	3.45 (3.0–3.9)	3.1 (1.0–10.9)	9.9 (3.1–28.4)	3.8 (1.9–14.8)	10.9 (3.5–30.2)	21 (5–93)	7 (2–51)
5–20 cm	4.94 (4.3–5.5)	3.76 (3.2–4.1)	1.2 (0.2–3.7)	5.9 (2.0–13.7)	1.9 (0.2–16.0)	6.5 (2.1–20.6)	27 (6–97)	7 (2–71)
20–40 cm	5.25 (4.8–6.6)	3.76 (3.2–4.2)	0.5 (0.0–2.2)	3.3 (1.2–8.2)	0.8 (0.2–18.3)	3.7 (1.4–23.0)	35 (10–100)	9 (2–88)
60–70 cm	5.56 (4.0–7.4)	3.76 (3.3–4.3)	0.3 (0.0–1.8)	2.1 (0.6–7.4)	0.6 (0.1–20.9)	2.5 (0.7–20.2)	42 (8–100)	13 (3–94)

Table 5. Correlations of CEC and BS to pH, organic matter and clay content by sampling layer

Layer		pH_{aq}	pH_{ba}	OM	C/N (humus) Clay (min.soil)
Humus	CEC_p	−0.63	−0.64	0.93	0.11
	BS_p	0.87	0.95	−0.58	−0.23
	CEC_e	0.33	0.40	0.22	−0.19
	BS_e	0.80	0.85	−0.50	−0.30
0–5 cm	CEC_p	0.11	0.01	0.95	0.54
	BS_p	0.61	0.17	0.43	0.49
	CEC_e	0.19	−0.05	0.87	0.61
	BS_e	0.64	0.26	0.49	0.37
5–20 cm	CEC_p	−0.17	−0.06	0.77	0.68
	BS_p	0.37	−0.07	0.25	0.80
	CEC_e	0.00	−0.05	0.52	0.79
	BS_e	0.56	−0.04	0.26	0.57
20–40 cm	CEC_p	0.21	0.09	0.67	0.79
	BS_p	0.56	−0.02	0.20	0.84
	CEC_e	0.43	0.07	0.41	0.85
	BS_e	0.63	0.10	0.13	0.65
60–70 cm	CEC_p	0.47	0.05	0.55	0.89
	BS_p	0.70	−0.02	0.22	0.80
	CEC_e	0.65	0.00	0.37	0.83
	BS_e	0.63	0.26	0.24	0.63

Critical r ($p \leq 0.01$) = ± 0.24

values and pH_{aq} were only found for the two deepest layers, which had the highest pH_{aq} values (Table 4). CEC and base saturation values were poorly correlated to pH_{ba} in all mineral soil layers. Organic matter and clay contents were clearly important in determining the CEC and base saturation values in the mineral soil. At least 70% of the variation in the CEC_e values for each mineral soil layer could be explained by the organic matter and clay contents. The relative importance of these two factors, however, changed from being organic matter-dominated in the surface (0–5 cm) layer to being increasingly dominated by the clay content in the deeper layers, even though the contents of both decreased with depth (Table 2).

Acidity and Aluminium

The pH_{aq} of the humus layer ranged from 3.6 to 5.5, and of the mineral soil from 3.6 (0–5 cm) to 7.4 (60–70 cm), and typically increased with increasing depth (Table 4). pH_{aq} values in all layers decreased with Al_{ba} contents ($p < 0.05$), the relationship being of most consequence in the humus and 0–5 cm layers (Fig. 3).

pH_{ba} values were lower than pH_{aq} values, as expected, but tended to remain low in the deeper mineral soil layers. Average pH_{ba} values showed no change from pH 3.8 below the 0–5 cm layer (Table 4). Why pH_{ba} did not increase with depth, as did

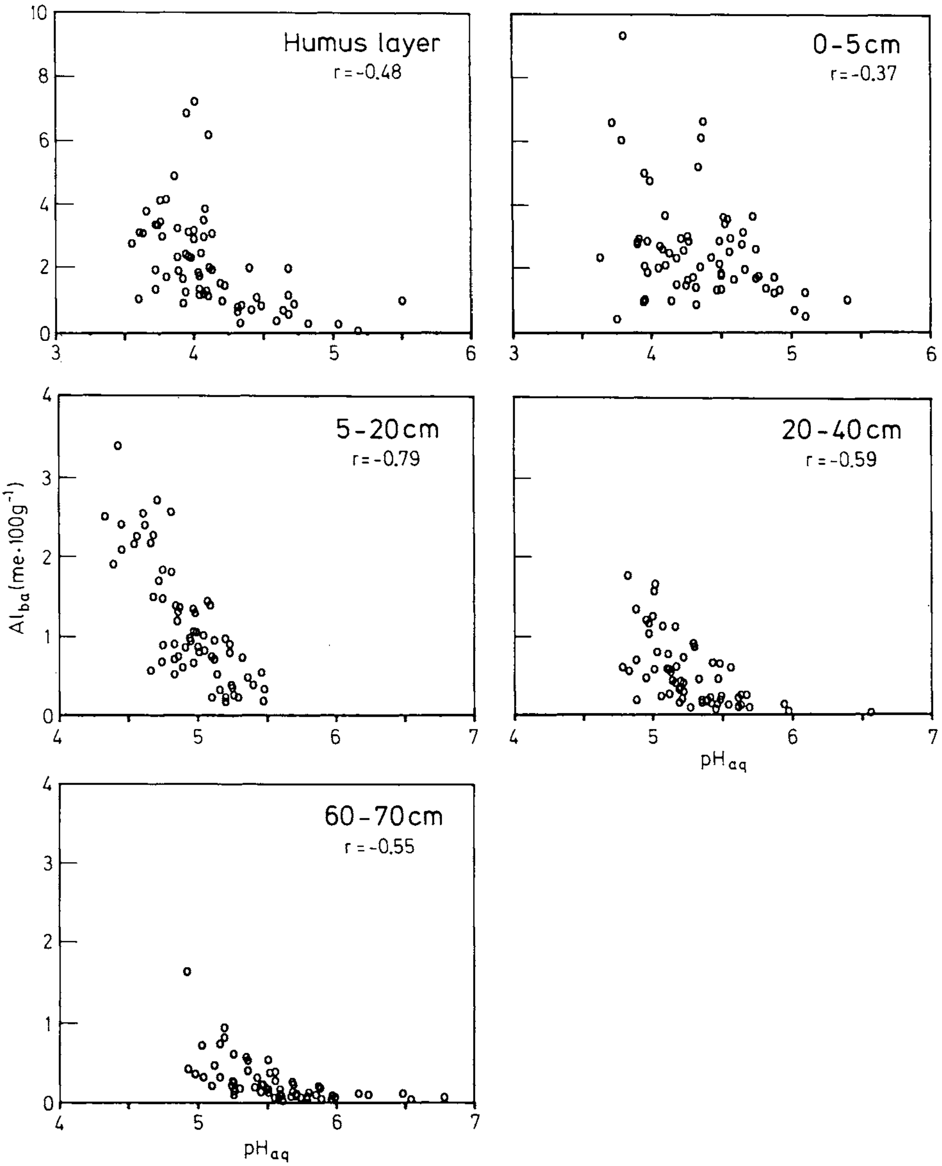

Fig. 3. The relationship between 0.1 M $BaCl_2$-extractable aluminium (Al_{ba}) and pH_{aq} by sampling layer

pH_{aq}, remained unclear. pH measured in a salt solution measures the acidity due to exchangeable H^+ ions, which is generally considered to be small and that fraction of displaced Al^{3+} ions which hydrolyses to produce H^+ ions. The fraction of the H^+ and Al^{3+} displaced depends upon the salt used, its concentration, and the soil:solution ratio (Thomas and Hargrove 1984), and the fraction of the displaced Al^{3+} that hydrolyses increases with pH (Lindsay 1979). pH_{ba} did not correlate with Al_{ba} contents in any of the mineral soil layers, even though Al_{ba} contents decreased with depth (Table 3). But clearly a sufficient amount of H^+ and Al^{3+} was displaced to produce low pH values even in samples with relatively low exchangeable Al (Al_{ba}) contents. In any event, pH_{ba} seemed to be a poor measure of mineral soil acidity.

Total acidity (TA) and exchangeable acidity (EA) both decreased with depth (Table 4). TA is largely comprised of the acidity which arises from the pH-dependent dissociation of organic acids and, in the case of the mineral soil, also Fe and Al hydroxides. Exchange acidity, in theory, largely consists of the acidity associated with the displacement and hydrolysis of acid cations, which is realized during titration. EA values in each mineral soil layer were highly correlated with Al_{ba} contents ($r > 0.90$), which formed a major component of EA (Table 6). The lower Al_{ba}/EA ratios for the humus layer may suggest that humus EA values (Table 4) are somewhat inflated. However, it appears that much of the exchangeable acidity of organic matter does arise from the hydrolysis of Al^{3+} but that the aluminium is difficult to displace with neutral salts (Thomas and Hargrove 1984). Inflated humus EA values could also arise due to the extraction and subsequent dissociation of organic acids during titration. In the 20–40 and 60–70 cm layers of one clay soil, where the pH_{aq} values were 6.6 and 7.4 respectively, there was no measurable EA.

The contents of Al_{ba} and total Al (Al_{tot}), together with the equivalent Al_{ba}/EA and molar Ca_{ba}/Al_{ba} ratios for each layer, are described in Table 6. The distribution of Al_{tot} contents in the mineral soil largely reflects the intensity of podzolization, i.e. the downward translocation of Al-organic complexes and Al hydroxides. Al_{tot} contents in each mineral soil layer increased with contents of organic matter and clay ($p < 0.05$); the correlation coefficient ranging from 0.42 (5–20 cm) to 0.75

Table 6. Aluminium contents, Al_{ba}/EA and molar Ca_{ba}/Al_{ba} ratios by sampling layer. Range in parentheses

Layer	Al_{ba}	Al_{tot}[a]	Al_{ba}/EA	Ca_{ba}/Al_{ba}
	mg 100 g^{-1}			
Humus	18 (4–59)	322 (130–1700)	0.32 (0.04–0.85)	38 (2–958)
0–5 cm	22 (3–80)	657 (70–3030)	0.81 (0.12–1.00)	1.5 (0.03–23)
5–20 cm	10 (1–30)	1218 (210–3240)	0.84 (0.33–1.00)	1.3 (0–31)
20–40 cm	4 (0–15)	1161 (460–2860)	0.73 (0.13–1.00)	14 (0–814)
60–70 cm	2 (0–14)	856 (260–2710)	0.61 (0.09–1.00)	11 (0–514)

[a] Al_{tot} = dry combustion + HCl digestion values.

(20–40 cm) for organic matter content, and from 0.64 (5–20 and 20–40 cm) to 0.76 (0–5 and 60–70 cm). Al_{ba} formed only a small fraction of Al_{tot}, and Al_{ba} contents increased with the amount of organic matter ($p < 0.05$) in each layer (humus, $r = 0.34$; mineral soil layers, $r = 0.50 \ldots 0.70$). The clay and Al_{ba} contents were poorly correlated.

Grouping Soils According to Soil Acidification Parameters

In order to assess the levels of acidification and neutralizing capacity of the soils from the sample of 65 plots with respect to each other, cluster analyses were performed (Engelman and Hartigan 1985) using variables describing the acidification of the mineral soil. Means, minimum and maximum values from the four mineral soil layers for a variety of parameters were evaluated as possible clustering variables after first being standardized to unit variance. Mean CEC_e, BS_e and molar Ca/Al ratio, together with the ratio of minimum to maximum Al_{tot} values, were selected as the most promising for our purposes.

A cluster analysis solution with five clusters of soils using the four selected variables is presented in Table 7. The number of clusters was chosen subjectively *a priori*, five being considered the maximum number of soil acidification types that could reasonably be interpreted. The first group was comprised of only one soil, a clay soil referred to earlier, with high pH, CEC_e and BS_e, and showing weak Al differentiation down the profile. This type of soil is not generally given over the forestry in Finland. The second group of soils had considerably lower CEC_e values, but which were still dominated by base cations; they represented fertile, weakly podzolized soils. Soils in the third group had low CEC_e values and distinct Al profile distributions, but relatively high base saturations and Ca/Al ratios. Soils in the fourth group contained more organic matter and consequently had higher CEC_e and total Al distribution values. However, they had lower BS_e and Ca/Al ratios than the third group. The biggest group, five, was clearly the most acidified

Table 7. Clustering of sample plots based on mineral soil profiles. Means of criteria variables and between-cluster F-values

Cluster	No. of plots	Variable			
		CEC_e me 100 g^{-1}	BS_e %	Ca_{ba}/Al_{ba}	Al_{tot} min/max
1	1	16.7	96	284	0.84
2	9	5.6	70	21	0.74
3	18	1.4	47	2.0	0.24
4	16	2.1	33	0.7	0.57
5	21	1.5	22	0.3	0.24
	F-value	66	75	82	60

and podzolized, having low values for all four criteria. According to a one-way analysis of variance, the Ca/Al molar ratio and base saturation were the best distinguishing variables in the cluster analysis (Table 7).

Trace and Heavy Metals

Increases in both the deposition and mobilization of trace and heavy metals in soils due to air pollution has aroused concern. Heavy metal pollution is often local, reflecting emissions from point sources (e.g. Erviö and Lakanen 1973; Rühling et al. 1987). Increased solubility of metals induced by acidification leading to both toxic concentrations of heavy metals and leaching of micronutrients may be of more concern over wider areas (Ulrich et al. 1979; Tyler 1981; Tyler et al. 1985; Bergkvist 1987a,b). Data on trace and heavy metal contents in Finnish forest soils are limited.

The contents of various metals in each layer determined by dry ashing and HCl digestion are presented in Table 8. Contents of Zn, Cd, Pb, Ni and Sr were clearly concentrated in the humus layer. In the mineral soil, Zn and Pb contents peaked in the 5–20 cm layer, contents of Cu and Ni continued to increase with depth, and contents of Sr, and to a lesser extent also Cd and Cr, remained relatively uniform with depth.

The results tended to confirm previous findings concerning the dependence of metal contents on organic matter and clay contents, and acidity parameters (Sillanpää 1962; Sillanpää and Lakanen 1966; Brümmer and Herms 1983). In the humus layer, only contents of Cr and Sr were significantly affected by acidity. Contents decreased with increasing acidity. In the mineral soil, contents of all metals were positively correlated to pH_{aq}, except Ni. The clay content had a strong positive correlation (0.46 . . . 0.65) with all metal contents, with the exception of Ni. Correlation coefficients between metal contents and organic matter contents were weaker. Only Cu in the humus layer showed a regional pattern. Contents were higher in the plots located in western Finland, where there are naturally high contents in the till parent material (Geochemical Atlas) and where metal industries are located, and in a plot located in eastern Finland near a copper mine (Lakanen 1965).

Table 8. Trace and heavy metal mean contents by soil layer

Layer	Cu	Zn	Cd	Pb	Cr	Ni	Sr
	mg kg^{-1} oven-dry soil						
Humus	7.4	54.7	0.47	38.3	9.4	5.1	27.7
0–5 cm	3.3	22.9	0.24	16.7	12.9	0.04	5.5
5–20 cm	4.0	28.1	0.32	20.6	19.9	0.13	5.0
20–40 cm	5.9	24.0	0.32	18.7	21.5	0.70	5.0
60–70 cm	7.8	19.0	0.28	14.2	18.3	0.72	5.5

Discussion

Acidification of forest soils is related to a number of soil factors. Important factors, as demonstrated in our material, are the soil organic matter and clay contents and their distributions within the profile. Acidification and acid neutralizing capacity thus varied considerably with soil type. Concerning the causes of acidification, it is not yet possible to determine the relative contributions of acid deposition, and other anthropogenic and natural causes of acidification such as podzolization, nutrient uptake and forestry practices. The sample plots are too sparse, their site histories unknown and soil types too diverse to allow any relationship between the spatial patterns of soil acidification and acid deposition to be discerned. Nevertheless, acid deposition in Finland is still low compared to other central European countries (Kauppi et al. 1987). Furthermore, the input of neutral salts along with precipitation will increase the base saturation of the soil through the "salt effect" and so help offset the acidification effect of proton deposition (Wiklander 1975).

The humus layers contained large amounts of "exchangeable" base cations (average 0.1 M $BaCl_2$ extractable Ca+Mg+K+Na contents = 21.5 me 100 g^{-1}), and effective base saturations were 50% or more. The humus layer may therefore be expected to have a substantial buffering capacity (Kalisz and Stone 1980; Krug and Isaacson 1984; James and Riha 1986). On the basis of limits for the total Ca/Ca+Al+Fe equivalent ratio given by Meiwes et al. (1986), the humus layers sampled would have been classified as having "very little likelihood of acid toxicity for fine roots and mycorrhizal fungi". On the basis of other soil acidification indices and their preliminary critical limits presented by Meiwes et al. (1986), some 40–50% of samples from the 0–5 and 5–20 cm layers would be classified as having a "low acid buffering elasticity to an input of protons", i.e., $(Ca_{ba}+Mg_{ba})/CEC_e < 0.15$ and $Al_{ba}/CEC_e > 0.6$. In deeper layers, low elasticity was due to low absolute CEC_e values. For example, the 60–70 cm layer in about 40% of the plots had CEC_e values of < 0.5 me 100 g^{-1}, the limit given for "very low elasticity". According to Berdén et al. (1987), a considerable proportion of soils in southern Scandinavia have exchangeable Ca/Al molar ratios < 0.1 in the 30–40 cm layer, representing advanced acidification and limited buffering capacity. In our material, 0.1 M $BaCl_2$ extractable molar Ca/Al ratios < 0.1 occurred in only 11, 14, 5 and 8% of samples in the 0–5 cm to 60–70 cm layers, respectively. It must be remembered, however, that such limits are only preliminary, and may be expected to depend on the methods of analysis and whether fresh, air-dried or oven-dried samples are used. It is also important to know the rate at which exchangeable cations are replaced by chemical weathering.

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List of Symbols used

CEC_e = effective cation exchange capacity
CEC_p = potential cation exchange capacity
BS_e = base saturation of effective cation exchange capacity
BS_p = base saturation of potential cation exchange capacity
Al_{ba} = 0.1 M $BaCl_2$-extractable aluminium content
Ca_{ba} = 0.1 M $BaCl_2$-extractable calcium content
Mg_{ba} = 0.1 M $BaCl_2$-extractable magnesium content
Al_{tot} = total (dry combustion +HCl digestion) aluminium content
EA = exchange acidity
TA = total acidity
pH_{aq} = pH of soil:deionized water suspension (1:2 v/v)
pH_{ba} = pH of soil:0.1 M $BaCl_2$ solution suspension (1:10 v/v)
OM = organic matter

Regional Acidification Model for Forest Soils

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Summary

Regional model calculations of forest soil acidification in Finland for different future energy use and emission reduction input scenarios are compared. The calculations have been made with the Finnish Acidification Assessment Model (HAKOMA) consisting of modules for emissions, emission abatement costs, atmospheric dispersion, transformation and deposition, and impacts on forest soils and lakes. The impact modules include time-dependent simulations of forest soil and lake acidification processes which consider the dynamic nature of ecosystems. The existing buffering capacity and its depletion are assumed to have ecological impacts. In forest soil acidification the depletion of the nutrient cation inventory in soil by acid deposition and through tree harvesting is considered. Cations are supplied by atmospheric deposition, estimated by measurements, and mineral weathering. The distribution of soil types is estimated on the basis of the national forest inventory. The cation contents for each soil class are derived from measurement programmes.

The results of the pilot studies show the most critical areas regarding acidification to be in the areas of high deposition in southwestern and southeastern Finland. To minimize the acidification, considerable emission reductions seem to be necessary both in Finland and in the areas of high emissions in the neighbouring countries. The results were also relatively sensitive to the parameter values in the soil model.

Introduction

Forest soil acidification has been considered as a function of possible future energy use and emission reductions. In this study the preliminary results obtained with the Finnish Acidification Assessment Model (HAKOMA) (Johansson et al. 1989) have been employed. The objective of the model is to assess various emission abatement policies and the importance of different factors related to acidification. The process of soils acidification is slow (decades) and, therefore, predictions with models are important.

Kauppi et al. (Eds).
Acidification in Finland

The HAKOMA system has modules covering energy use, emissions, emission abatement, atmospheric processes, and impacts on forest soil and lakes. The model system, when complete, will cover sulphur, nitrogen oxide and ammonia emissions, and their impacts. At present, the model is operational only for sulphur. The comprehensive model is in its pilot phase, and those modules already operational are being further developed. More data will be collected especially for the impact models.

The sulphur emissions are estimated separately for Finland and other European countries. In the emission submodel of HAKOMA there is a relatively detailed description of sulphur emissions in Finland compiled for the period 1950–2040 (Savolainen and Tähtinen this Vol.).

The results of two atmospheric models covering different transport distance scales have been employed in the calculation of sulphur deposition in the integrated model system. Both models assume linear transformation of sulphur dioxide to sulphate with empirical rate constants. The mesoscale model (Nordlund and Tuovinen 1988; Johansson et al. this Vol.) is used to estimate the deposition due to the emissions from Finland and areas close to Finland. The deposition due to emissions from the main part of Europe has been calculated on the basis of the results of the ECE EMEP programme (EMEP is an abbreviation from the Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe).

The reference energy use scenario for Finland is based on the long-term estimate published by the Ministry of Trade and Industry (1988). Two other scenarios, namely natural gas scenario and energy conservation scenario, have been developed using this scenario as a basis (Savolainen and Tähtinen this Vol.).

Five combinations of Finnish and European sulphur emission scenarios are considered. The Finnish sulphur emissions used in the soil acidification model have been calculated for three control strategies for the reference energy use scenario (Ministry of Trade and Industry 1988), and for one control strategy for the natural gas scenario and for the energy conservation scenario (Fig. 1). For the reference energy use scenario the strategies for emission controls were: (1) no reductions (theoretical case) as a reference, (2) current reduction plans by the Finnish government, and (3) maximum reductions to test the effect of the best available emission abatement measures. The fourth alternative for Finnish emissions used in the soil simulation is the energy conservation scenario with the maximum control strategy. The total emissions of the natural gas scenario with the maximum reductions are very close to those in the energy conservation scenario.

The sulphur emissions from the other European countries are mainly based on the emission scenarios of the code of the RAINS (Regional Acidification INformation and Simulation) of the IIASA (International Institute for Applied Systems Analysis) (Alcamo et al. 1987). These emissions are estimated on the basis of energy use and emissions statistics and emission control alternatives in various countries. Three alternative control policies have been considered: (1) no controls ("official energy pathway" in the RAINS code), (2) current reduction plans as

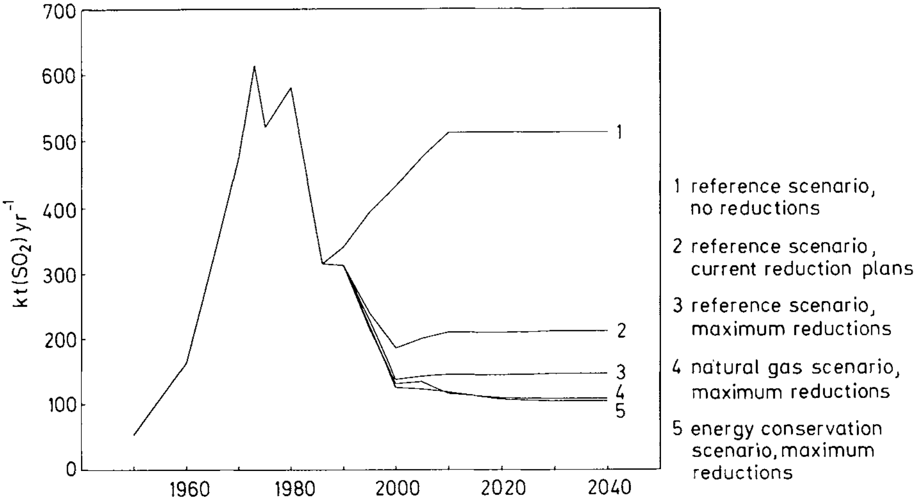

Fig. 1. Effects of different emission reduction measures on the total sulphur emissions in Finland. The reference energy use scenario is given by the Ministry of Trade and Industry (1988). The energy conservation and natural gas scenarios have been derived from the reference scenario

announced by various countries, and (3) the maximum reductions estimated by assuming that all potential emission reductions achievable with the present pollution control technologies are realized, but no measures are taken for energy conservation and fuel substitution.

In the pilot phase of the model system, it is important first to understand the behaviour and restrictions of the model and only then to apply more abatement strategy alternatives. Moreover the data on forest soils in this study are not yet comprehensive and the model validation is insufficient. Therefore, the sensitivity of the model to various parameter values has been emphasized.

The development of the model was part of the Finnish Research Project on Acidification (HAPRO). The work was carried out by the Technical Research Centre of Finland in co-operation with other institutes such as the Finnish Meteorological Institute, National Board of Waters and Environment, Helsinki University, Finnish Forest Research Institute, and Geological Survey. The RAINS model presented by Alcamo et al. (1987) of the IIASA is used as a basis for HAKOMA.

Soil Impact Model

The HAKOMA system has impact models for forest soil and lake acidification. The modules were originally developed for the RAINS model (Alcamo et al. 1987; Kauppi et al. 1986). The time span considered by both impact models is 50 years.

The calculations are made in a denser grid, in squares 0.25 (longitude) × 0.125 (latitude) degrees or about 14 km × 14 km in southern Finland, than in the RAINS code.

In the forest soil module the buffer range concept introduced by Ulrich (1983) is adapted. The model used in a regional application must be simple, suitable for long-term predictions, and the results should be descriptive and easy to use. The variables included in this model are: the carbonate and base cation contents in soil, and the rates of base cation weathering and aluminium remobilization. In Finland there are practically no calcareous soils and the carbonate content can be ignored.

There is a need to minimise input data requirements and complexity for applications at a regional scale. Therefore, the following assumptions, similar to the guidelines of de Vries et al. (1989), have been made:

- The soil chemistry depends solely on the net element input from the atmosphere, mineral weathering and the cation exchange. Exchangeable base cation content of soil is represented by one state variable, BC^{2+}. Apart from the net uptake of base cations, the influence of the nutrient cycle is not taken into account.
- Sulphate output is in equilibrium with sulphur input. Element budget studies in northern and western Europe indicate that the sulphate adsorption is generally neglible, however, it may become important in some areas.
- The effects of nitrogen compounds are not taken into account in the present phase of the model.
- Natural soil acidification is ignored.
- The weathering rate of base cations is independent of the soil pH.
- The soil to the depth of 50 cm is assumed to be homogenous with constant density. The element input mixes completely within the considered soil compartment.
- The water flow is stationary on a yearly basis, which corresponds to the time step of the model.

Most soils in Finland have a base saturation exceeding 5% and thus buffer primarily with cation exchange. The soils shift to the aluminium buffer range in low base saturation values. After the depletion of exchangeable base cations, aluminium remobilization is mainly responsible for acid neutralization. By then, base cation nutrients have become scarce and the vitality of forests is affected.

The most important factors presently considered in the module are the H^+ deposition (now calculated on the basis of sulphur emissions and atmospheric processes), base cation deposition, depletion of the base cation inventory through outflow with sulphate ions and net accumulation in tree stems, and supply of base cations from the weathering of minerals (Johansson et al. this Vol.). The model calculates the base cation content in soil and the soluble aluminium concentration in soil solution. The original RAINS values were used to estimate the geographical distribution of the net precipitation. The simulations are started at 1987, when the soil data were gathered, and are continued until 2040.

Ion Fluxes

Sulphur Deposition

The sulphur deposition is the main driving variable for the present version of the model. It is necessary to project sulphur emissions until the year 2040 for Finland and Europe, because soil acidification is a slow process. The current reduction plans scenario (Johansson et al. this Vol.) is considered as the reference case.

Forests gather more sulphur deposition than open areas (Kauppi et al. 1986). The filtering factor describes the effectiveness of the forest to increase dry deposition. The filtering factor is assumed to be 2 in the reference case, which means that forests gather twice as much deposition as an open area. The total deposition is kept constant within the grid square in the calculation, but it is distributed between forested and open area depending on the filtering factor and the fraction of the grid square that is covered by forests. Thus grid cells with little forests tend to receive more atmospheric deposition per square meter of forested land than grid cells that are largely covered with forests.

Base Cation Deposition

The geographical distribution estimate for the base cation deposition is based on bulk deposition measurements conducted in 1972–1981 at 38 stations over Finland (Järvinen 1986). At each station the values of calcium, magnesium, sodium and potassium expressed in eq m^{-2} yr^{-1} have been summed together. The effect of chloride is subtracted by assuming that an equivalent amount of base cations is bound to chloride compounds.

Because of the analyzing technique, all base cations in the sample have been measured. However, some of the base cation compounds are insoluble even in a long time scale and are not able to neutralize acidity. Moreover, a fraction of the measured base cation deposition may refer to internal circulation in the ecosystem and should not be considered as external input. The dry deposition consists of relatively large particles, for which the atmospheric transport distance is quite limited. It is assumed here that the wet deposition fraction better describes the external base cation deposition level than the bulk deposition (Anttila this Vol.).

The values based on Järvinen (1986), who measured bulk deposition, have been compared with preliminary results of the Finnish Meteorological Institute (FMI) of wet deposition. The measurements of FMI are from three to five stations and cover a period of 2 to 8 years depending on the cation considered. The levels of the base cation measurement results of Järvinen (1986) and FMI are consistently proportional, wet deposition being approximately 30 to 50% of the bulk deposition. Pending in-depth studies, an estimate of 30% of the measured values of Järvinen (1986) has been chosen as the value of effective external base cation deposition.

The base cation deposition value from the nearest station (Järvinen 1986) has been assigned to each model grid square. A 3 × 3 element moving average was cal-

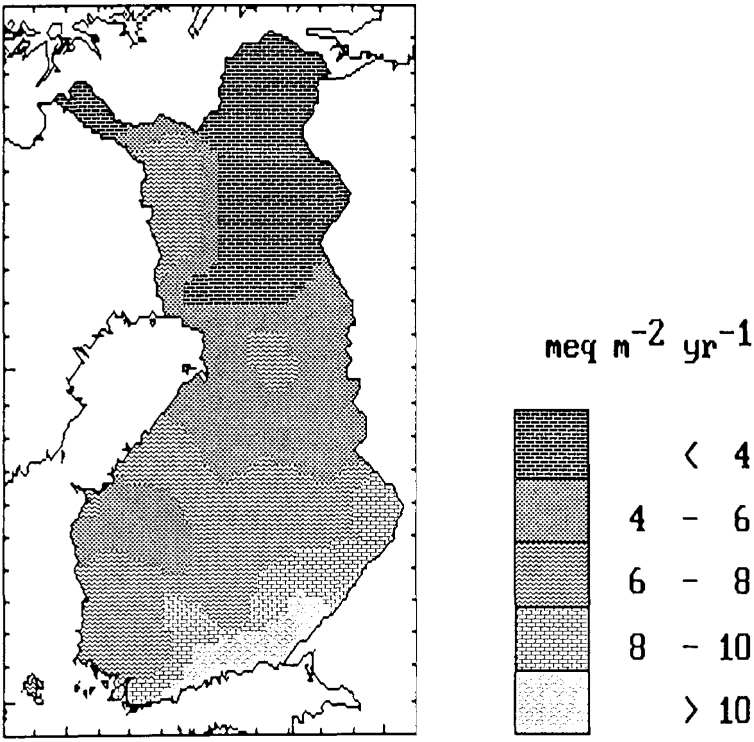

Fig. 2. The estimated effective base cation deposition in Finland (original measurements from 38 stations in a 1972–81 average)

culated over the whole grid. The resulting corrected effective base cation deposition distribution is shown in Fig. 2. The resulting values are kept constant with time. The forest filtering effect described earlier is assumed to affect base cation deposition also, and the same value as for sulphur deposition is used.

Mineral Weathering

The relative regional distribution of weathering rate values is taken from RAINS. The geological map of Europe (UNESCO 1972) has been used to determine the bedrock material in each grid square. Depending on the dominant bedrock the soil of each square was classified into one of four predetermined weathering rate categories. In Finland there are seven major bedrock types and they belong to the three lowermost weathering rate categories. They have been assigned to different categories mainly according to their classification to acid, acid to intermediate and basic rocks, which was interpreted from the map legend. Another definition made is that granites have been assigned to the lowest category. The values were first transferred from the RAINS grid to the HAKOMA calculation grid, and then a 3 × 3 element moving average was taken.

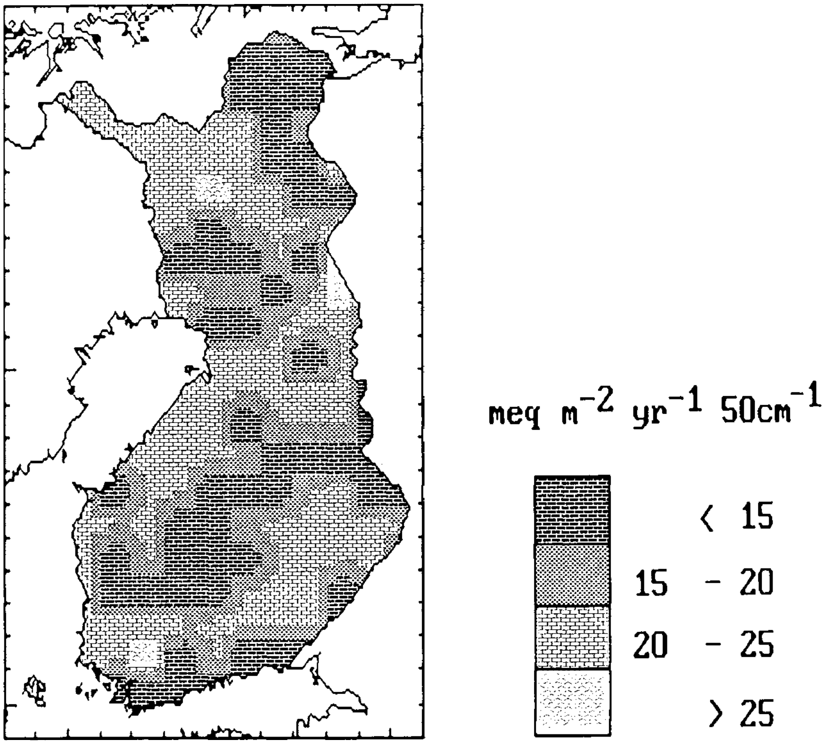

Fig. 3. The estimated weathering rates based on bedrock material types

The absolute values were scaled with the help of Swedish ion budget studies in various catchments (Sverdrup and Warfvinge 1988) and the lake model results by Kämäri et al. (in press). The assumed range of the weathering rate is mainly 10–20 meq m^{-2} yr^{-1} $(50\ cm)^{-1}$. The value is in a relatively good agreement with the catchment-wide testing of the lake model against the diatom analysis of the lake sediments (Kämäri et al. in press). The resulting mineral weathering map for Finland is shown in Fig. 3.

Base Cation Losses Due to Tree Growth

Trees consume base cations from soil. The nutrients are accumulated in stem, bark, branches and needles. In normal harvesting, cations in stem and bark are removed from the forest and thus from the ecosystem. This, then, assumes that all forest land is in production. In the soil model the cations accumulated in the average tree stem and bark growth was taken as a measure of the net uptake of base cations. The value was estimated as a function of forest site type and latitude.

For example, Rosén (1988) reported characteristics for a Norway spruce stand in the south of Sweden. The annual net uptake of potassium, calcium and magnesium is 21 meq m^{-2} yr^{-1} for a rotation period of 70 years. The relative equivalent proportions of the cations in stemwood are 17% for K, 61% for Ca and 22% for Mg.

Mälkönen (1975) has presented the base cation content in stemwood and bark for some Finnish stands. An annual growth of one cubic meter per hectare equals accumulation of potassium and calcium of about 2.7 meq m^{-2} yr^{-1}. If the proportion of magnesium estimated from values reported by Rosén (1988), the net uptake adds to 3.3 meq m^{-2} yr^{-1}. An average base cation accumulation could be defined for the whole of Finland on the basis of the average forest growth of 3 m^3 ha^{-1} yr^{-1}. This would result in an average loss of nutrients of about 10 meq m^{-2} yr^{-1}. However, forest growth depends on the fertility of the site and (Kuusela 1977) even more so on the effective temperature sum, which varies regularly with the latitude. Therefore, a linear dependency can be assumed between the growth and the latitude. Vuokila (1987) presents information on the growth for various temperature sum zones and different forest site types. Based on this information it is possible to construct separate linear combinations for forest site type groups for use in model simulations. The linear equation ranges are presented in Fig. 4 for three base cation content classes, which are considered in test simulations and explained later in the text. For the rich mineral soil types the annual base cation loss is about 5 meq m^{-2} yr^{-1} in northern Finland, increasing to 19 meq m^{-2} yr^{-1} in the south; for the poor mineral soils and the peat land the values are about half of these values. Because of the linearization there are errors in nutrient net uptake estimates in certain parts of Finland. These errors could be diminished by estimating the net uptake separately for each individual forest site type and mapping the temperature sums in more detail and not only as a function of the latitude.

Base Cation Contents For Different Forest Site Types

Data Sources

The base cation content, i.e. exchangeable nutrients, in forest soils and their geographical distribution can be estimated in two ways. First, the Finnish Forest

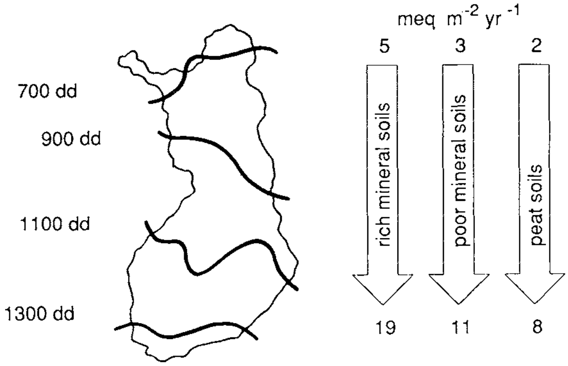

Fig. 4. The effective annual temperature sum (obtained by summing daily mean temperatures exceeding 5°C) zones in degree days (*dd*) and the average net accumulation in tree growth of base cation nutrients for three different forest site type groups as linear functions of the latitude

Research Institute has done an intensive survey of base cation contents and other important parameters for several plots of different forest site types. The distribution of forest site types in all of Finland is based on the Seventh National Forest Survey. Second, the Geological Survey has determined the base saturation at over two thousand measuring points in different soil parent types. The distribution of soil types in Finland is also available in map form.

The first approach was chosen for practical reasons. The forest soil data were measured recently in a consistent way. The forest site type distribution was already available in a digitised form and therefore was easier to convert into the HAKOMA calculation grid. The geological samples would have been more reliable because of the greater number of samples, but unfortunately the moraine is a dominating soil type in Finland and the values of its base cation content vary considerably. However, in the long term the data from the Geological Survey can be used to produce an alternative soil data file for comparison.

Input data for determining the base cation content in different soil types has been provided by the Finnish Forest Research Institute. From an intensive survey there were 27 samples with relevant measurement results available. The values from the intensive survey covering southern and central Finland have been compared with another data set of another survey mainly from southern Finland with 1246 measured sample plots. This data set was already calculated for humus and 30 cm mineral top soil. Therefore, for comparison all values are given for this soil profile (Fig. 5). The distributions are relatively wide and to some extent overlap

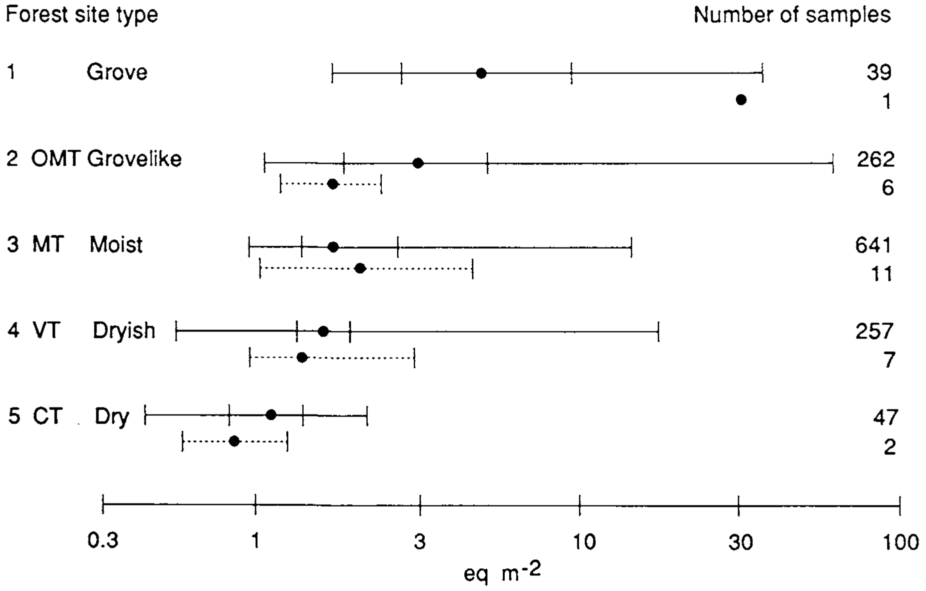

Fig. 5. The overall range, quartiles and median (●) of exchangeable base cation contents in forest soil per square meter. For comparison, these values were calculated for humus and top 30 cm of mineral soil. *Solid line* from extensive and *dashed line* from intensive survey of the Finnish Forest Research Institute

between the forest site types. The results, however, suggest that a forest site type satisfactorily describes the base cation content in soil. Less fertile forest site types dominate in the north of Finland and thus here the overall base cation content is also lowest.

Peat Soils

The exchangeable base cation values representing peat soils were derived from the results of the survey by Westman (1981). For peat land a soil layer of only 20 cm was considered. No additional chemical processes are included in peat land treatment. For peat soils the simulation programme applies the same chemical processes as for mineral soil.

No mineral weathering occurs in peat soils, but nutrients are released through decomposition of organic matter. The decomposition can be assumed to lead to a similar result as weathering, even though the processes are not similar. Therefore, the weathering rate has also been applied to peat soils, scaled to a value for the 20-cm profile. Because mineral soil is more sensitive to acidification than peat, this simple way to describe peat soil was selected. This assumption will have only a marginal effect on the final results.

Values for Simulation

Three exchangeable base cation (BC) classes for the test runs were selected from the results of the intensive survey. The selection was based on the characteristics of poor and rich forest site types and peat land. The rich and poor types of the mineral soil are grouped into two BC-classes, representing site types 1–3 and 4–8 respectively. Peat land is considered in one BC-class only. All peat soil types were grouped in one as they are not very sensitive to acidification.

Table 1. Forest soil parameters used in the test simulation

Base cation class number	1	2	3
Soil type	Mineral	Mineral	Peat
Representing forest soil site type	Rich	Poor	All
Percentage of all forest soils in Finland, %	37	34	29
Layer thickness, cm	50	50	20
Total cation exchange capacity, meq m^{-2}	15,300	13,000	13,600
Exchangeable base cations (BC), meq m^{-2}	2300	1300	6100
Base saturation, %	15	10	45

The soil layer thickness examined is 50 cm including humus, except for the 20 cm depth for peat land. Median values were used for calculations. The parameters representing the BC-class for the rich mineral soils are the exchangeable base cation content of 2300 meq m^{-2} and the base saturation of 15%. For poor mineral soils these values are 1300 meq m^{-2} and 10%, and for the peat land 6100 meq m^{-2} and 45% (Table 1).

Regionalization of Base Cation Content Classes

The geographical distribution of the exchangeable base cation content and total cation exchange capacity in soil is estimated on the basis of forest site type distribution. The distribution was derived from the Seventh National Forest Survey (conducted in 1977–1984) information provided by the Finnish Forest Research Institute. This survey is based on field work in 8 × 8 km squares covering most of Finland. The northern part of the country has been investigated by aerial photographs and verified by a field survey. The relative proportions of different forest site types are assumed to remain constant in time and space in Finland.

Because of different grid element size the data had to be converted from the Forest Survey grid to the HAKOMA calculation grid. There were from one to four Forest Survey squares falling in one HAKOMA grid element considered at a time. The forest site type data were transferred by weighing the values according to the Forest Survey grid square area falling on the target grid element.

For each grid cell the percentage of forested area was divided into mineral and peat land. Both of these two types are further divided into up to eight different forest site types. The geographical distribution of these three different soil type groups obtained this way is shown in Fig. 6. The percentages represent the forest soil portions of the total grid element area.

Simulation Results

Scenario Comparison

The preliminary results from five different combinations of the Finnish and European sulphur emission scenarios have been compared. The percentage of forest soils falling under base saturation of 5% has been used as a criterion. This base saturation value corresponds to a soil solution pH value of about 4.2, an acidity value implying an increased risk of forest damage (Kauppi et al. 1986). The main results of the five cases are as follows: without restrictions 57% of the Finnish forest soils would reach this base saturation value in the year 2040. If current reduction plans were followed, this figure would drop to 38%. If Finland would apply as strict controls as possible and the rest of Europe would continue on their current reduction plans, the value would decrease to 36%. If the Finnish emissions

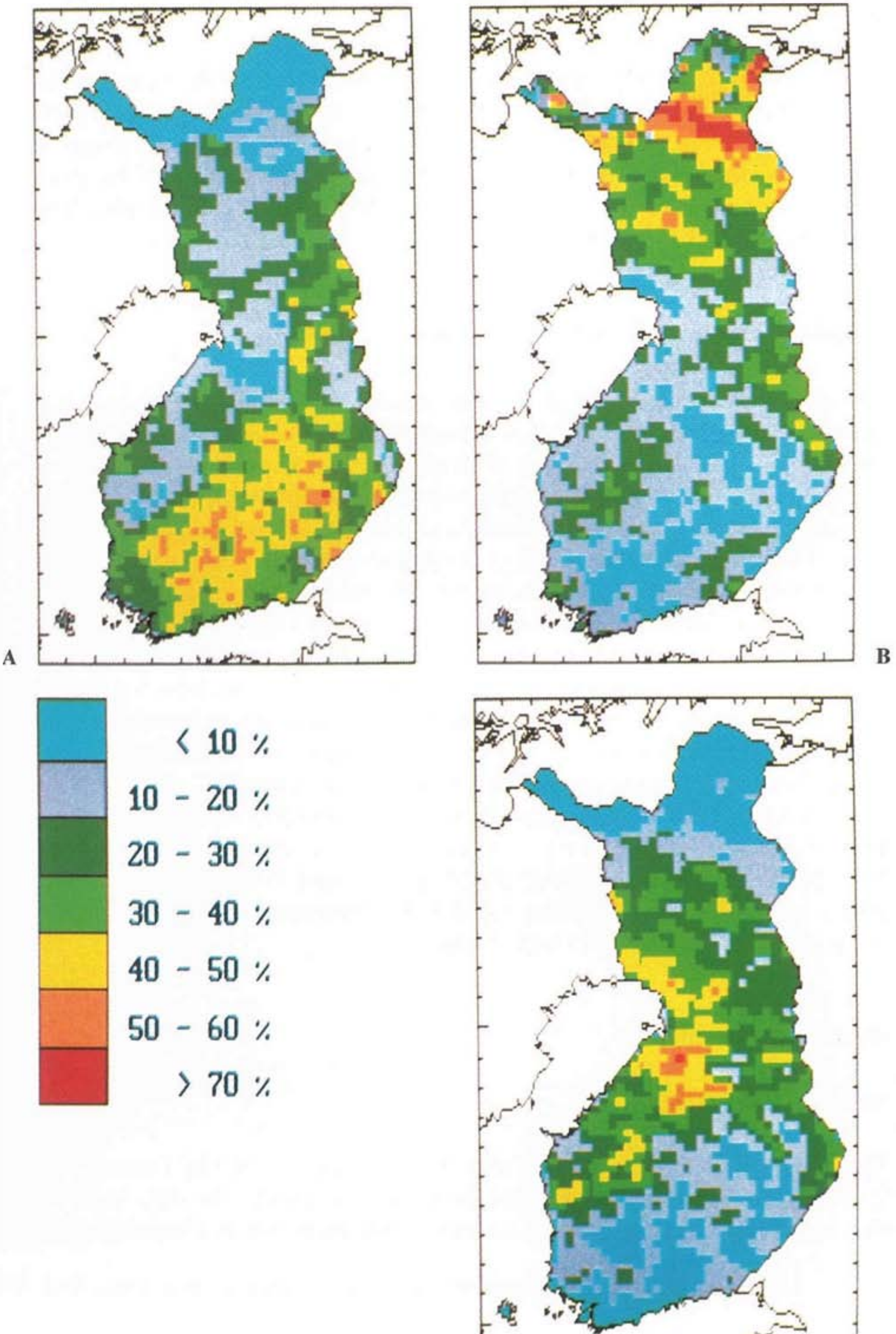

Fig. 6A–C. Soil type group maps representing the portion of **A** rich mineral soils, **B** poor mineral soils, and **C** peat land of the total area in each calculation grid element would correspond to the energy conservation scenario with the maximum emission reductions (curve 5 in Fig. 1), and the emissions from other countries would correspond to the current reduction plans, 35% of the forest soils would fall in the high risk category. The case of the maximum reductions applying the best technology available gives a reduction to 12%.

The maps of affected areas with three different sulphur emission reduction strategies are shown in Fig. 7. These distributions could be employed in the planning of countermeasures to prevent further acidification.

Uncertainty Analysis

A number of test simulations may clarify the importance of various parameters in the soil module. The factors considered in the sensitivity study are forest filtering effect, base cation deposition, weathering rate, net removal of base cations due to harvesting, and a more detailed classification of the soil exchangeable base cation content. The results of the parameter studies are compared against the reference case corresponding to the current emission reduction plans.

To test the sensitivity of the filtering factor, a factor of 1.6 was used for coniferous forests, based on the studies by Ivens (1988). The use of this lower factor resulted in continued but slower acidification of forest soils. The effect is marginal compared to the uncertainty of some other parameters.

The base cation deposition measured is probably the maximum deposition conceivable. In Lapland the present deposition is low but sufficient to slow down acidification. In southern Finland it is relatively high and thus helps to compensate high acid loads. Reducing the base cation deposition to half resulted in some local acidified areas in Lapland. The southwestern part of the country was strongly affected, worsening quite rapidly. Doubling cation deposition leads to slower acidification than in the reference case, with mostly local effects.

Weathering rate is one of the more difficult parameters to validate. Its importance to the simulation model was studied by using values half or double the reference values. Using 50% lower weathering rates resulted in a rapid deterioration of soils in most of Finland. Doubling the rates compared to the reference values caused very few and restricted areas to lose the cation buffering capacity, and large areas even showed increased base saturation values on soils.

The base cation classification was refined by considering five instead of three classes, by splitting each mineral soil class into two. For the lower third of the original class a boundary value at the first quartile of the original class was used. For the remaining two thirds the median of the original class was used. Compared to results with three classes the use of five classes produced a larger area of soils below base saturation value of 5% in the south.

When no net uptake of base cations by vegetation would occur, model predicts that large areas with considerable buffering capacity remain in the cation buffering range, particularly in the south of the country.

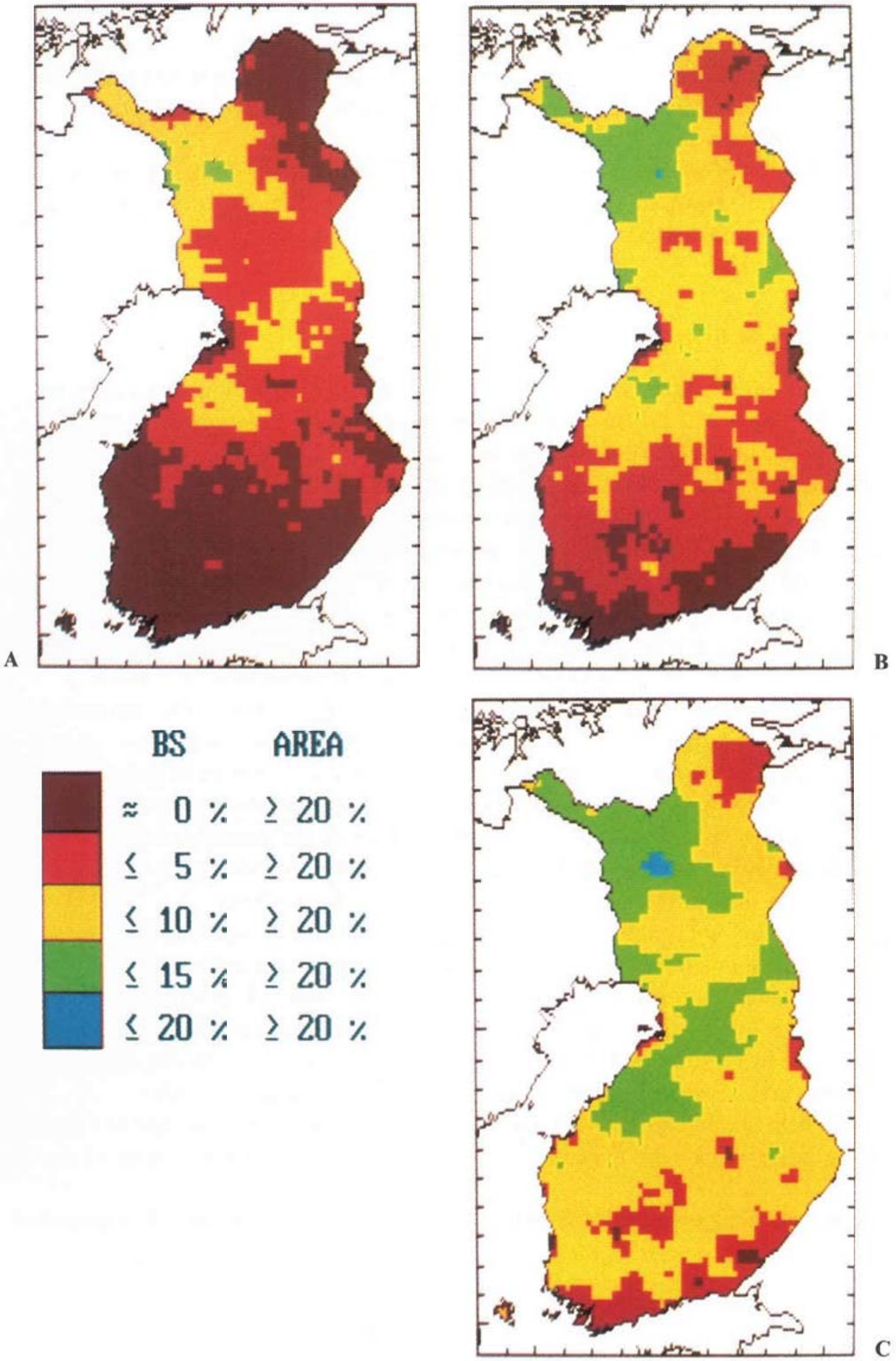
A
B
C
BS
AREA
≈ 0 % ≥ 20 %
≤ 5 % ≥ 20 %
≤ 10 % ≥ 20 %
≤ 15 % ≥ 20 %
≤ 20 % ≥ 20 %

Table 2. Results of the sensitivity analysis in terms of the forested land area with base saturation smaller than 5% in the year 2040. The results are given in percentage of the total forested area and as relative units compared with the reference case

Reference case	38%	1.00
Filtering factor = 1.6 (reference 2.0)	35%	0.92
Base cation deposition × 0.5	46%	1.21
Base cation deposition × 2.0	18%	0.46
Weathering rate × 0.5	57%	1.48
Weathering rate × 2.0	11%	0.27
More detailed base cation classification	43%	1.12
No base cation removal by harvesting	13%	0.35

The relative importance of the different factors can be seen in Table 2. The results of the calculation seem to be quite sensitive to the choice of many parameters. Most of these are not well known. The weathering rate needs more refining and the base cation deposition should be further analysed. The net uptake of the base cation nutrients by tree growth and loss through harvesting is an important factor and is included already in the reference case. More research should be concentrated in determining the main factors of the soil acidification. If the range and type of the uncertainty of these factors were known, a statistical uncertainty analysis could be made to obtain quantitative information on the uncertainty distribution of the results.

Validation Considerations of the Assessment

There is uncertainty from other sources also including emissions, atmospheric transportation, sulphur deposition and sulphate adsorption in the soil. The uncertainty of the other submodels is considered by Johansson et al. (this Vol.). For soil models validation data are still very scarce.

Soil chemistry data from southern Sweden have recently been used to test two soil acidification models (Posch et al. 1989). The first samples date back to 1949/50; samples were retaken in 1984/85. The first model is the current RAINS soil model used presently in HAKOMA system. The second model, which features a more detailed description of the cation exchange processes, is SMART (Simulation Model for Acidification's Regional Trends). It has been used already in the lake model and is described in more detail by Johansson et al. (this Vol.). Results of validation studies show that the change in the amount of exchangeable base cations is predicted fairly well, while the changes in soil pH could hardly be

Fig. 7.A–C. Results of three test simulations showing the areas in the year 2040 where over 20% of the forest soils in Finland have base saturation values lower than the value indicated in the legend. The emissions from both Finland and the other countries correspond to **A** no reductions, **B** the current reduction plans, and **C** maximum reductions. For Finland the reference energy use scenario is assumed.

reproduced by the first soil model, but reasonably well by the SMART model. These findings support the idea that the changes in the soil chemistry due to the deposition of acidifying compounds should be characterized not only by pH but by base saturation and other soil property changes, such as calcium-aluminium ratios.

Conclusions

A comprehensive model system is being developed both for the assessment of importance of different factors related to acidification and for the assessment of various emission abatement policies. The model system presented here also includes time-dependent simulations of forest soil and lake acidification processes when the dynamic nature of ecosystems is considered. The existing buffer capacity and its depletion can be assumed to have an effect on the ecological impacts of acidic deposition.

The results from the pilot phase of the soil acidification model using various sulphur emission control scenarios can be considered only preliminary and of relative nature. This is due to the uncertainty and incompleteness of the parameters. For Finnish conditions, the model is about equally sensitive for many important parameters, i.e. they are of about the same magnitude. Therefore, validation of each of them is important. One result of the modelling is the identification of the various parameters causing uncertainty. The net uptake of base cations by trees seems to contribute greatly to the development of the base cation content in forest soils.

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Buffering Capacity of Finnish Soils and its Dependence on Geological Factors in Relation to the Acidification Sensitivity of Lakes

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Summary

The role of geological factors in the neutralization of the acid deposition of a drainage area was studied with the aid of soil samples (podzol samples in particular) taken from various parts of Finland and the properties determined from them in the laboratory (grain size, pH, humus, exchangeable base and acid cations, CEC, BS). The influence of the deposition on the chemical properties of the soil was clearest in the very topmost part of the podzol profile (A_0, A_{1-2}). In the deeper soil layers, the differences in chemistry are due to variations in geological factors such as grain size and lithology. The length of time the runoff water and soil are in contact with each other proved to be the dominant factor affecting the neutralization efficiency of the runoff water.

Introduction

The environmental effects of acid rains have been recorded in northern Europe only during the last two decades (Oden 1968; Wright et al. 1980; Kämäri 1985). In Finland, the first observation was the acidification of small oligotrophic forest lakes in the south of the country (Kämäri 1985, 1988). The geological properties of the drainage area have a marked impact on the hydrologic pathways of pollutants and on the extent of acidification of the waterways. The chemical and mineralogical composition of soil, the grain size distribution of mineral matter and the composition of organic matter are known to affect dissolution and ion exchange reactions, which are capable of neutralizing the acids of the runoff in soil and waterways (cf. Norton 1979).

Finnish soils derive mainly from Precambrian siliceous rocks and have developed predominantly on till, which covers more than half the surface area of the country. Sand/gravel and clay deposits each account for less than 10% and geological peatlands for about 15%, the remainder consisting of exposed bedrock or overburden less than 1 m thick. These inorganic surficial materials were emplaced 8000 to 10,000 years ago during deglaciation.

Because areas were deglaciated or emerged from water as a result of uplift at different times, there is considerable variation in the degree of soil development,

Kauppi et al. (Eds).
Acidification in Finland

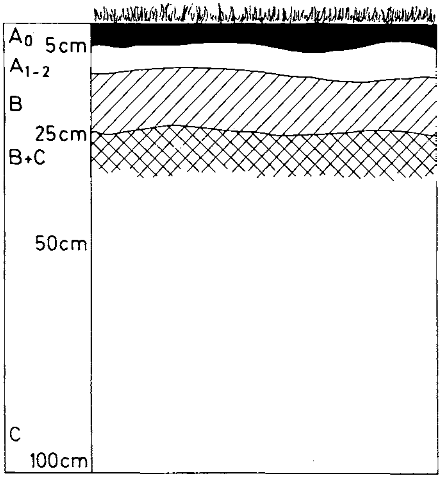

Fig. 1. A typical podzol profile in Finland (Ilomantsi, eastern Finland) developed over 10,000 years. A_0 humus layer; A_{1-2} eluvial layer; B illuvial layer; $B+C$ weakly changed layer; C parent glacial material

dominantly podzolization. The soil structure also contributes to podzolization. Figure 1 illustrates a typical Finnish podzol profile. In Finland studies of podzols have been conducted by Aaltonen (1939, 1941), Jauhiainen (1969), Nuotio et al. (1985), Räisänen (1987) and Nuotio (1988). Studies on recent acidification of soils have been carried out in Central Europe by Ulrich (e.g. 1983a,b).

Our study of Finnish podzol soils concentrates mainly on the buffering properties of podzol soil and bedrock in the drainage areas of small oligotrophic forest lakes known or assumed to be acidified. Follow-up studies based on extensive sampling have been conducted to establish the overall buffering capacity of the Finnish soil and bedrock against fallout pollutants. Using the data obtained we sought to establish whether there were any regional differences in the chemical properties of the podzol profiles and, if there were, to find out whether they were partly due to atmospheric impurities or were caused solely by geological variables.

Study Areas

One hundred and fifty drainage basins located in various parts of Finland, and proposed by the National Board of Waters and Environment (NBWE), were originally chosen as study areas. These watersheds, which are relatively undisturbed, are forested; their lakes are small and, according to long-term measurements made by the NBWE, assumed to be acidified. The drainage areas are characterized by conifer (Picea abies, Pinus silvestris) and shrub and heather vegetation (Vaccinium sp., Ericaceae sp). Because these sites had rather uniform geological properties, the number of study areas was increased, and at the same time their geographical representativeness was improved. Areas underlain by mafic rocks, under-represented in the original study plan, were included, as were areas with podzol profiles developed in fine-grained till. Supplementary samples were collected from

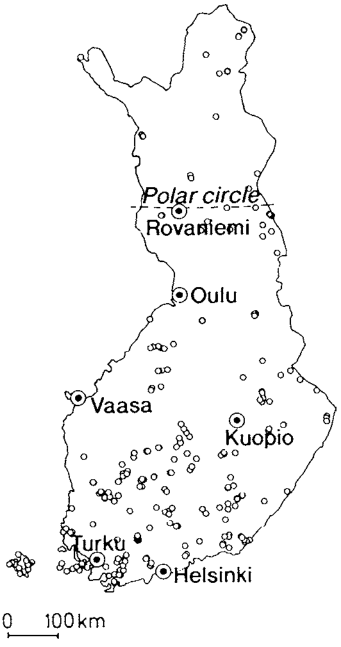

Fig. 2. Location of the study areas

the Åland and Turku archipelagoes, Ostrobothnia and northern Finland. Four drainages in southern Finland were sampled for soil monitoring purposes in the course of three field seasons (summers 1986–1988). The whole sampling took place from summer 1984 to summer 1988 and study areas totalled about 240 (Fig. 2).

Materials and Methods

The soil and bedrock of the drainage areas were determined with the aid of map interpretation and field studies. A set of soil samples was taken from all the different soil type sites in each drainage area. Samples were not taken when it was raining. At least 24 h passed before sampling started again. In this way the chemical equilibrium in the soil had time to stabilise. Samples from mineral soil were taken from the A_0, A_{1-2} and B podzol horizons (see Fig. 1) and from constant depths of 50–60 cm and 90–100 cm. The podzol horizons were identified mainly on the basis of colour. The surfaces of exposures were sampled for humus. At 71 study sites, soil samples were taken from deeper than 1 m either with a percussion drill or from the wall of a dug pit. The samples were taken at intervals of 0.5–1.0 m to an average depth of 4 m (the deepest sample was from 10.5 m). The peat samples (in 1984–86) were taken from constant depths of 0–10 cm, 50–60 cm and 90–100 cm. The representativeness of single samples in relation to the other samples of the same soil type and area was tested with repeated sampling.

The four special drainage areas in southern Finland (see Fig. 9) are mainly composed of glacio-fluvial sediments ranging from fine sand to coarse gravel.

Podzol profile samples were collected three to six times during a field season (May–September). Each sample set was taken from as close as possible to the previous sample sets, yet from an undisturbed podzol profile.

From 240 study areas and altogether 320 sampling sites, 850 till samples and 910 sand/gravel samples were taken from mineral soil, 400 from peat and 140 from bedrock terrain.

Fresh samples were measured for pH (H_2O, 1:1) in the field. In the laboratory the mineral soil samples were sieved, and the grain size distribution of the fine grained samples was determined either areometrically or with a pipette technique (e.g. Head 1984). The chemical analyses were made on <2 mm fractions. The humus content was determined with a wet combustion method (Hesse 1971). The exchangeable and readily soluble base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) essential for plants were determined from an acetic acid–ammonium acetate solution (pH 4.65) by AAS. The acid Al^{3+} and H^+ cations were extracted into KCl titrations. The first titration gives the concentration of exchangeable hydrogen in the soil sample:

$$\mathrm{HCl + NaOH = H_2O + NaCl}$$
$$\mathrm{AlCl_3 + 3\ NaOH = Al(OH)_3 + 3\ NaCl.}$$

The addition of NaF solution (KF solution in Thomas' method) results in formation of a stable fluoroaluminate complex and liberation of hydroxyl ions:

$$\mathrm{Al(OH)_3 + 6\ NaF = NaOH + Na_3AlF_6.}$$

The concentrations of exchangeable Fe^{2+} and Mn^{3+} were determined for about 700 samples from an NH_4OAc acetic acid extract by AAS.

The sum of base and acid cations, the cation exchange capacity (CEC pH 4.65), is expressed in milliequivalents/100 g of dried soil sample. The base saturation degree (BS) is the percentage of base cations of the CEC. The base saturation degree was chosen to describe buffering capability, because a number based on percentage is easy to use when comparing the analytical data on different soil types and depths with each other.

Results

Sample Representativeness

The soil samples collected from the soil monitoring areas during a field season did not show any consistent variation in chemical composition attributable to seasonal variation (spring-summer-autumn). Samples (specially from A_0 and A_{1-2} horizons) taken during cool, wet weather (1987) had slightly lower base saturation and higher CEC. Correspondingly, in an exceptionally warm, dry summer (1986) the base saturation was slightly higher. The chemical properties of the samples taken from a greater depth showed less difference from year to year. The variations in chemical properties were higher in areas composed of coarser sediments.

The representativeness of individual samples was tested by comparing the averages and standard deviations of multiple samples taken from the same depth at a sampling site. The percentage of the standard deviation of the average was calculated from the data and used as a measure for the representativeness of the average (Table 1). The average cation concentration and the values of BS and CEC fluctuated by about 25% around the mean value, whereas the pH varied at each depth by less than 10% on average. When the extreme values were omitted from the distributions, thus leaving only 90% of the data for consideration, the scatter was reduced markedly. We assume that the average obtained at a 90% level of probability describes the general level of the chemical properties of the individual soil type areas fairly reliably. The significance of the differences between the areal or soil type values grows with the increase in the volume of data.

Buffering Properties of the Podzol Profile

Averages and medians were calculated from the data (pH, exchangeable cations) for each horizon and depth (Figs. 3–6) for 1760 soil samples from 240 study areas. The podzol profiles (altogether 320) were classified into two soil types – sorted sand/gravel soils and till soils – on a genetic basis. If the soil material changed vertically, all the samples were included in the soil type that predominated down to a depth of 0.5 m. In some cases the sandy interlayers in till or the uneluviated, till-like interlayers in sand/gravel soils level out the differences in the chemical data on these soil types. The differences in chemistry are also levelled out by the weathering and eluviation of the fine material from the A_{1-2} horizon and its migration to the B horizon; these processes are typical of podzolization.

pH and Exchangeable Cations

Shown in Fig. 3 are the median pH values for podzol profiles, peats and sorted fine-grained clay/silty soils. The pH for the sand/gravel and till soils increases fairly regularly down to a depth of about 1.5 m, below which it stabilizes at between pH 6 and 6.2. Our data differ from that reported by Bache (1984) mainly in terms of the values of the topmost horizons. According to Bache, the pH in the humus horizon is 3.5 and in the eluvial horizon 3.8, in Finland 4.1 (standard deviation 0.446) and 4.3 (SD 0.406) respectively. However, Bache measured pH in salt solution extract, which yields lower pH than water suspension. Acidity rises with increasing age of the podzol profile (Troedsson 1980). We also noted that in subaquatic areas submerged after deglaciation, pH was by 0.2 pH units higher on average than in the predominantly supra-aquatic areas in Lapland and eastern Finland, which were not submerged.

The pH curve of the clay/silt soils follows fairly closely the curves of the sand/gravel and till profiles. Thus, the pH of the soil seems to depend more on the

Table 1. An example of testing sample representativeness. pH, CEC and BS values in each sampling depth taken in various dates. Samples were taken from drainage area of Lake Tourijärvi, Pernunnummi monitoring area (Fig. 7)

Sampling date	pH					CEC (mequ/100 g)					BS (%)					
	Sampling depth/Podzol profile															
	A_0	A_{1-2}	B	50–60 cm	90–100 cm	A_0	A_{1-2}	B	50–60 cm	90–100 cm	A_0	A_{1-2}	B	50–60 cm	90–100 cm	
29.5.86	3.70	4.50	4.55	4.70	4.85	16.42	3.99	4.16	0.87	0.62	45.2	11.0	9.4	63.2	56.5	
2.7.86	3.75	3.75	4.50	4.70*	4.95	27.75	4.98	1.74	0.60	0.67	54.7	15.9	12.1	53.3	55.2	
22.9.86	3.55*	3.65*	4.05*	4.95	4.75*	23.02	5.89	2.36	1.33*	1.76*	60.8	12.9	10.6	24.8*	31.3	
28.5.87	4.10	4.40	4.95	5.75	5.85	43.87*	5.84	3.60	1.03	0.72	49.5	12.3	9.4	34.9	45.8	
16.7.87	4.05	4.60	4.60	5.55	5.80	32.01	3.97	6.17*	1.22	1.03	45.1	8.4	11.7	32.8	29.1*	
7.9.87	3.95	4.05	5.00	5.40	5.70	37.03	6.01	3.15	0.78	0.83	43.2*	12.6	12.4	30.8	30.1	
23.5.88	4.10	4.35	4.80	5.75	5.85	30.85	5.77	1.51	0.74	0.62	58.9	12.7	21.2*	35.1	40.3	
22.6.88	3.70	4.35	4.90	5.45	5.60	17.07	5.64	1.42	0.52	0.57	54.2	9.2	19.7	50.0	47.4	
19.7.88	3.90	4.25	4.70	5.25	5.40	17.58	5.15	1.21	0.79	0.70	57.3	17.8*	16.5	32.9	42.9	
30.8.88	4.10	4.40	5.05	5.50	5.80	26.88	2.74*	1.73	0.66	0.58	51.3	16.5	20.2	51.5	58.6	
	3.89	4.23	4.71	5.30	5.46	27.50	5.00	2.71	0.85	0.81	52.0	12.9	14.3	40.9	43.7	$\bar{x}_{100}$[a]
	0.19	0.30	0.29	0.37	0.42	8.60	1.04	1.50	0.25	0.34	5.9	2.9	4.4	11.9	10.5	SD_{100}[b]
	4.9	7.1	6.2	7.0	7.7	31.3	20.8	55.4	29.4	42.0	11.3	22.5	30.7	29.1	24.0	$\%_{100}$[c]
	3.93	4.29	4.78	5.37	5.53	25.40	5.26	2.32	0.80	0.70	53.0	12.4	13.6	42.7	45.3	$\bar{x}_{90}$[d]
	0.16	0.24	0.19	0.33	0.37	6.90	0.76	1.00	0.20	0.14	5.3	2.5	3.9	11.1	9.8	SD_{90}[e]
	4.1	5.6	4.0	6.1	6.7	27.1	14.4	43.1	25.0	20.0	10.1	20.4	29.1	26.0	26.0	$\%_{90}$[f]

[a] $\bar{x}_{100}$ = the average value (all equal samples included).

[b] $SD._{100}$ = the standard deviation (all equal samples included).

[c] $\%_{100}$ = the percentage of the SD. of the average value (all equal samples included).

[d] $\bar{x}_{90}$ = the average value with 90% probability (the omitted value marked with *, thus leaving 90% of the data for consideration).

[e] $SD._{90}$ = the standard deviation (all equal samples included).

[f] $\%_{90}$ = the percentage of the $SD._{90}$ of the $\bar{x}_{90}$ (all equal samples included).

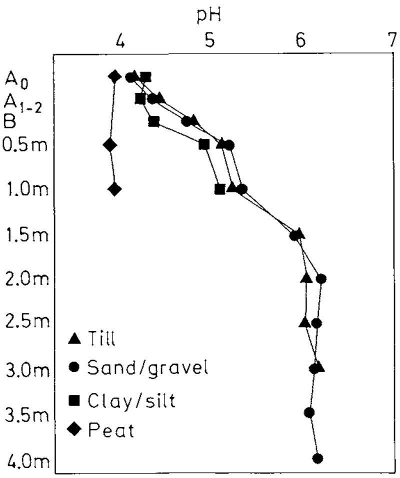

Fig. 3. Median pH for various soil types. pH values along the x-axis, sampling depth along the y-axis

evolutionary stage of the podzol profile and the sampling depth than on the grain size distribution in the soil. Furthermore, most of the clay/silt areas included in the present study are located in paludified forest land, where the thick humus layer clearly promotes natural acidification. The exchangeable cation concentration of the podzol profile is more closely related to the grain size of the soil than is pH.

The average pH values of the peat samples do not vary much as a function of depth. The pH in *Sphaqnum* and *Eriophorum* peats is distinctly lower by up to 1–2 units than in *Bryales* or *Carex* peats.

The vertical variations in the concentrations of exchangeable Ca^{2+} and Mg^{2+} and Al^{3+} and H^+ in the podzol profile are shown in Figs. 4 and 5. In till the concentration of exchangeable cations is slightly higher than in sorted sand/gravel soils. The high cation exchange capacity of the surficial podzol horizon is due to the negative surface charge of humus (COO^-- and 0^--groups) that attracts cat ions. The concentration of exchangeable aluminium in humus and eluvial horizons

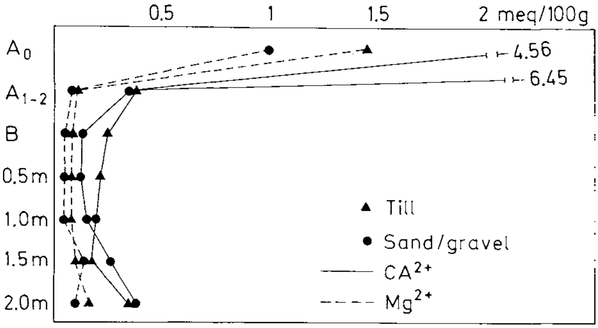

Fig. 4. Median concentrations of the exchangeable Ca^{2+} and Mg^{2+} base cations in sand/gravel and till soils. The concentration in milliequivalents/100 g of dry soil sample along the x-axis, sampling depth along the y-axis

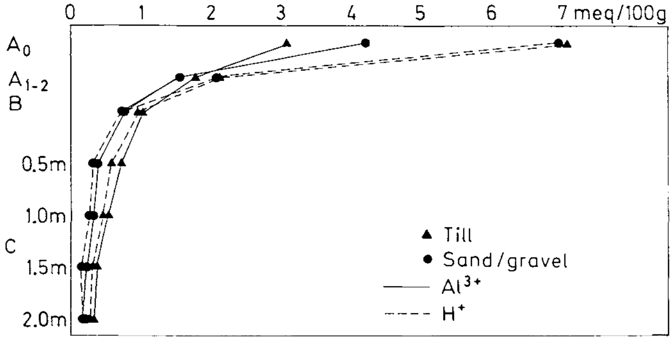

Fig. 5. Median concentrations of the exchangeable Al^{3+} and H^+ acid cations in sand/gravel and till soils. Concentration in milliequivalents/100 g of dry soil sample along the x-axis, sampling depth along the y-axis

is almost ten times higher in Finland than in the data of Bache (1984). The large differences may be due to the fact that the aluminium adsorbed on hydroxides, oxides and clay minerals or bound to insoluble marcomolecules of humus as complexes may be ionized if conditions are sufficiently acidic (Bache 1986; Kinniburgh 1986). In the course of the titration procedure applied in the present study, the KCl solution probably leaches not only the exchangeable Al^{3+} ions (Räisänen 1988) but also some of the other Al compounds and complexes (titratable acidity). The concentration of this non-exchangeable aluminium is highest in the organic matter of podzol horizons A and B. This aluminium does not promote acidification of the surficial waters; on the contrary, it is an important pH buffer in the soil (Kinniburgh 1986).

At greater depths the soluble compounds derived from organic matter form complexes with metals, which are retained in the B horizon of the podzol profile (Evans 1980). The precipitation process has been attributed to the biological decomposition of organic molecules (Petersen 1976, 1978) and to the inorganic precipitation of Fe–Al–Si sols (Farmer et al. 1980; Farmer 1984). The aluminium ion concentrations in leachates in deeper soil levels agree with the values reported by Bache (1984).

According to Cresser et al. (1986) and Wilson (1986), the character of weathering in the surficial part of the podzol profile is changing to some extent. It has been proposed that weathering, which was initially controlled by organic acids, is gradually changing into a reaction between mineral acids (H_2SO_4, HNO_3) and mineral matter. This results in more acidic podzol profiles and may contribute to the elevated concentration of the readily soluble Al^{3+} ion in soil solutions in general.

The concentrations of exchangeable base cations agree with those reported in the literature (Bache 1984). The concentrations decrease rapidly downwards due to the decrease in humus abundance. Below a depth of about 0.5 m, the total abundance of base and acid cations, CEC, is fairly constant. At greater depths the

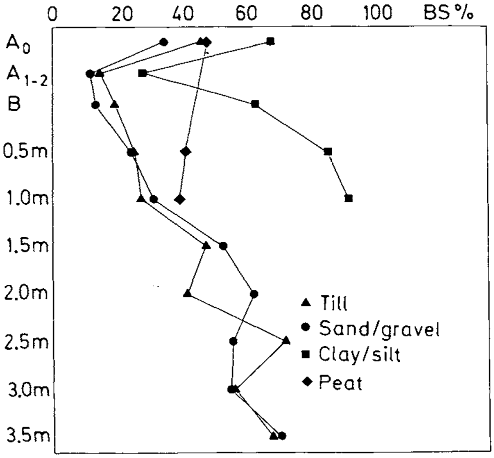

Fig. 6. Median values of the base saturation degree for various soils

contribution of acid cations to the cation exchange capacity clearly diminishes, i.e. the base saturation increases (Fig. 6).

Regional Variation in CEC and BS

The data were divided on the basis of eight equal areas with different soils, bedrock and precipitation (Tuovinen et al. this Vol.). The geological typical features of each subarea are given in the legend to Fig. 7. As the number of soil samples is not evenly distributed over Finland, the small regional differences in the analytical data may not necessarily be significant. Also differences in vegetation cause areal variation. Another factor hampering interpretation of the results is the predominance of samples from sand/gravel and bedrock terrain in southern and southeastern Finland (regions 1–3) and of samples from till terrain in central and northern Finland (regions 4–8).

Figures 8 and 9 show the median values of the cation exchange capacity and base saturation level, respectively, in various areas (1–8) and in the whole of Finland (region 0).

The cation exchange capacity values are markedly higher in southern and central Finland than in eastern and northern Finland. The large differences are mainly due to differences in the extent of podzolization. Large areas in eastern and northern Finland (regions 6–8) were supra-aquatic immediately after deglaciation, with the consequence that podzolization has been proceeding there for longer than in the south-coastal areas (regions 1, 2, 5). Therefore the A_{1-2} horizon in eastern (region 6) and northern Finland (regions 7–8) often shows sharp boundaries, is grey or white in colour, quartz in mineral composition and almost exclusively sand in grain size. In the younger podzol profiles the boundaries are more indistinct due to humus that has infiltrated the A_{1-2} horizon. Also the mineral composition is more complex and the grain size distribution wider. Owing to the more advanced leaching in eastern and northern parts of Finland (regions 6–8), the topmost part

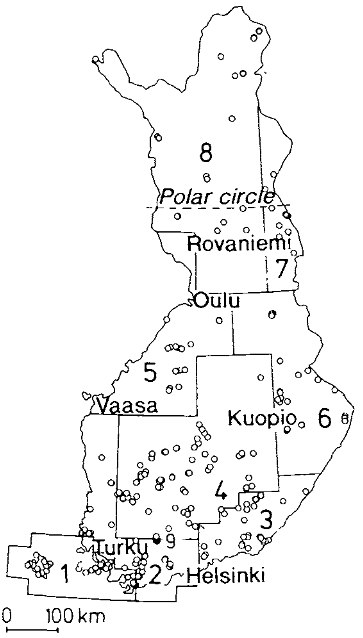

Fig. 7. Subareas based on map sheet division. The geological features characterizing the subareas, *1 Åland and Turku archipelagoes.* Small-scale topography, shallow till deposits, abundant bedrock terrains. Bedrock composed of rapakivi granites or granites, small limestone occurrences. *2 Southwestern and Southern Finland.* Small-scale topography, moraines overlain by ablation till, poor in fines, littoral deposits on hill slopes, abundant clay deposits and bedrock terrains. Bedrock composed of granites, mica gneisses and migmatites. *3 Southeastern Finland.* Small-scale topography, moraines shallow and overlain by ablation till, abundant bedrock terrains, clay and littoral deposits. Bedrock predominantly rapakivi granite. *4 Central Finland.* Varying topography, moraines moderately thick, drumlin fields, bedrock terrains here and there are abundant lakes. Bedrock composed of granite, granodiorites, quartz diorites and mica schists. *5 Ostrobothnia.* Flat topography, moraines often fairly thick and rich in fines, bedrock terrains rare, sulphide-bearing clays. Bedrock composed of granites, quartz diorites, granodiorites, mica schists and mica gneisses with occasional amphibolites and gabbros. *6 Eastern Finland.* Varying topography, rare bedrock terrains, moraines thick on average, drumlins. Bedrock predominantly gneisses, mica schists, quartzites and granites. *7 Kuusamo-salla.* Varying topography, moraines thick, rare bedrock terrains. Bedrock composed of gneisses, quartzites and gabbros with some limestone occurrences. *8 Lapland.* Large-scale topography, bedrock terrains on fells, moraines often thick with till intermixed with weathered bedrock. Bedrock composed of gneisses, quartzites, granulites and mica schists. In places dolomitic limestones, amphibolites and greenstones. *9 Pernunnummi Monitoring Area*

of the profile may be more sensitive to changes caused by deposition because only almost insoluble, base-poor minerals are left in the eluvial horizon.

The low CEC in the samples taken from a depth of 1 m in southern, southwestern and southeastern Finland (regions 1–3) is due to the granitic characteristic of these areas; the chemical weathering of the minerals and release of base cations is slow. The high CEC in the samples from Ostrobothnia (region 5) is ascribed to the tills rich in fines (<0.063 mm mineral fraction) and humus typical of the area

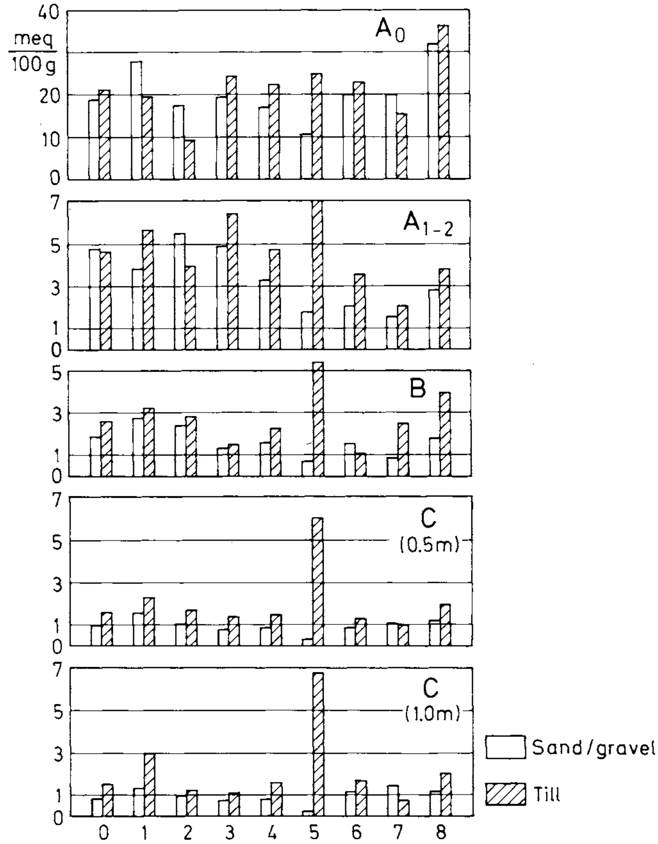

Fig. 8. Median cation exchange capacities of the subareas according to the podzol horizon or sampling depth. For subareas see Fig. 7. 0 = the corresponding values for the whole country

and to the mafic rocks that occur here and there. Since the area has been supra-aquatic only for a relatively short time since the deglaciation, the leaching of cations from till has not been as effective as elsewhere in Finland.

The CEC values of the samples from the Åland and Turku archipelagoes (region 1) are slightly higher than the average for Finland, although the Mg^{2+} concentration is many times higher than elsewhere in the country. Owing to the surrounding sea, the Mg^{2+} and Na^+ ions carried by precipitation maintain the relatively base cation concentration (high BS) in the top soil. The local high Ca^{2+} values are due to the fine dust from the limestone quarries and cement plants in the area. At greater depth, the sediments, initially deposited in water and fairly rich in fines, contain abundant exchangeable Mg^{2+} ions. In this area the influence of the occasionally very acidic precipitation on the soil is not immediate, as a persistent load is needed to cause changes in the buffering capacity.

The base saturation degree in the A_0 horizon increases fairly clearly from southern Finland via southeastern and central Finland to Ostrobothnia, and on

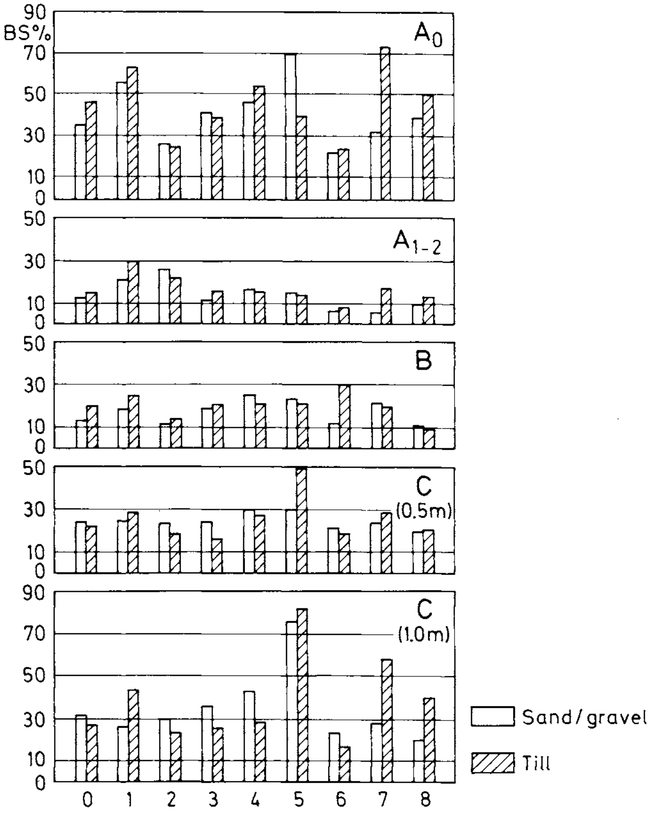

Fig. 9. The medians of the base saturation degree of the areas according to the podzol horizon or sampling depth. For subareas see Fig. 7. 0 = the corresponding values for the whole country

the other hand the low BS in eastern Finland rises gradually northwards. These areal differences in surficial soil layers are partly due to the variation in acid deposition (Tuovinen et al. this Vol.). Southern and southeastern Finland are areas of high fallout, and attention has recently been paid to the local impact of industrial emissions from the Kola peninsula in the USSR on the vegetation, soil and waterways of eastern and northern Lapland. The difference in vegetation and in climate (precipitation, temperature) between eutrophic and oligotrophic habitats also causes areal variations in the base saturation and the cation exchange capacity.

The areal differences in the CEC and the BS in the B horizon or in samples from a depth of 0.5 m are not distinct or statistically significant.

Reflection of Buffering Capacity in the Quality of Runoff

The lowest base saturation and CEC values in the podzol were recorded from southern and southeastern Finland and parts of eastern Finland and northern

Lapland (Figs. 8, 9). Very low pH values have also been noted in lakes of the same areas (Forsius 1987; Forsius et al. this Vol.). However, these acidified lakes occur in subareas where the overburden is thin and the bedrock mainly composed of granite or other acidic silicic rocks. The neutralization of the acidic deposition in these areas takes place exclusively in the humus layer or at most in the podzol profile, and the retention time of the runoff, or the reaction time between water and mineral matter, is short.

The buffering capacity of the drainage area as well as the retention time of the runoff, however, increases along with the thickness of overburden. For instance, in the Pernunnummi glaciofluvial delta area in southern Finland (follow-up region 9), the BS values in the A_0 and A_{1-2} layers of the soil were as low as 5–20%, but, since the thickness of overburden is locally 20–30 m and the sand layers are intercalated with fine-grained silty layers, as was observed in the drill holes and in the walls of the dug pits, they were not reflected in lake water as low pH values. Nevertheless, in these areas the total buffering capacity of the drainage area is high and the migration time of the runoff waters fairly long. Farrel et al. (1980) have also demonstrated that sorted sand fractions have a marked capability to adsorb sulphur compounds such as sulphate.

Clay and silt layers have a very high buffering capacity, which, however, does not manifest itself in the study areas as high pH values in lake water. The low permeability of tight clay/silt layers increases the surface runoff and thus shortens the reaction times between the mineral grains and the runoff water; the pH of the water decreases.

Water percolating through peatlands and surface runoff carry acid humus compounds dissolved from organic matter, thus further increasing the acid load of water. The influence of the ground vegetation in the drainage area on water quality is complex. On the one hand, trees and ground vegetation retain part of the impurities, but on the other, the nutrient intake by plants (cation exchange between root tubers and mineral grains) and the humic acids generated during humification change the chemical equilibrium in the soil.

With the decrease in size of the drainage area, an ever-increasing proportion of hydrogen ion load precipitates directly into the lake, with the consequence that both the average flowing distance of rainwater to the waterways and the neutralization time are short.

Conclusions

The chemical properties of the soil samples did not show any clear seasonal variation. However, the analytical data demonstrated that data on an individual sample describe the chemical properties at the sampling site fairly reliably, i.e. the observed variation and standard deviations were moderately low. Therefore, even one set of samples taken from one soil subarea of a drainage area reveals the buffering capacity of the surficial layer of this soil type.

On the basis of about 320 podzol profiles, we obtained information about the average chemical properties affecting the buffering capacity of the Finnish top soil. The study confirmed the increase in pH with depth, which is typical of the podzol profile. The concentration of the base cations was also in agreement with the average values reported in the literature. The aluminium concentration in the surficial parts of the podzol profile was many times higher than the values given by Bache (1984). The extraction used in our analysis (1N KCl) also leaches the aluminium that is loosely bound to organic matter or that occurs as complexes on the surfaces of clay minerals, if the pH of the sample is low. This non-exchangeable aluminium does not, however, increase the abundance of harmful aluminium in waterways; rather, it acts as a pH buffer in soil.

Examination of the areal differences between the podzol profiles shows that the chemical properties of the topmost soil layers (A_0, A_{1-2}) are particularly affected by vegetation, the thickness of the humus layer, the evolutionary stage of podzolization and the quality and quantity of atmospheric impurities. In the samples collected from depths below 0.5 m the buffering properties are controlled by the lithologies of the bedrock and the grain size and mineral composition of the soil. The high deposition values in southern, southeastern and northern Finland are reflected in the surface layers as low base saturation values and as high H^+ concentrations. The low buffering capacity, slow weathering and low base cation production rate of the granitic mineral matter manifest themselves as low CEC values in the samples taken at a depth of 1 m from southern and southeastern Finland. The low outwash degree of fines from till in Ostrobothnia and the archipelago has increased the CEC significantly. The vicinity of the sea also increases the exchangeable base cation concentration in the topmost layers in these areas.

To be able to assess the sensitivity of a lake to acidification, it is not enough simply to know the chemical properties that affect the buffering capacity of the topmost soil layer in the drainage area. The thickness of the soil layers and the grain size distribution (the deeper earth layers included), the hydrological conditions in the soil, and the size, topography, elevation, vegetation, lithological composition, resistance to weathering and base cation production of the drainage area must also be known to obtain an overall picture of the neutralization capacity of a drainage area. The chemical behaviour of nitrogen and sulphur also contribute to the acidification reactions. However, the key factor controlling the acidification of lakes turned out to be the contact time between runoff water and soil: the longer the retention of water in the soil, the more effective the neutralization.

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Effects of Acid Deposition on Exchangeable Cations, Acidity and Aluminium Solubility in Forest Soils and Soil Solution

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Summary

The responses of two forest soils on 100/50 successive treatments with three solution H^+ concentrations (pH 3.3, 3.8, 4.6) were studied in laboratory conditions. The higher the H^+ concentration of the treatment solution, the greater the amount of H^+ retained in all soil layers. The released base cation amount was 90% of the retained H^+ amount (meq) in humus layer. For Ca and Mg in humus and eluvial layers and for H^+ in all soil layers there was a strong positive correlation between the released amount of cation to treatment solution and the decrease in the amount of exchangeable cation. In the end of the treatment the ratio between base cations and H^+ on soil exchange sites corresponded that in equilibrium solution. The major part of the H^+ retention occured in the illuvial layer and the dissolution of Al ions was the most important H^+ consuming reaction. The solubility of Al was near that of gibbsite and the highest Al concentration found in equilibrium solution was 5 mg Al l^{-1}.

Introduction

The emissions of sulphur and nitrogen oxides have increased. In atmosphere the reactions of these compounds lead to nitrous and sulphuric acid formation and to an increased inflow of anions and protons into the soils.

When water filtrates through a soil profile, the anions not retained on soil particles or taken up by plants transport an equivalent amount of cations away from the topsoil to groundwater (Reuss 1977; Johnson and Cole 1980). Protons in the soil solution take part in cation exchange reactions, reactions with aluminium, weathering and decomposition of organic material. The cation exchange and reactions of aluminium provide a buffer against changes in the soil solution chemical properties. Weathering of minerals common in the Finnish topsoils does not increase considerably with decreasing solution pH (Huang et al. 1968). The increased proton inflow into the soil thus leads to cation exchange and accelerated leaching of base cations as well as to increased aluminium solubility (Ulrich 1983). The reduction of pH and the amount of exchangeable base cations of forest

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soil has been observed in the field data by Hallbäcken and Tamm (1986) and Falkengren-Grerup et al. (1987).

The aim of this chapter is to examine what effects successive acid solution inputs have on

- cation exchange reactions and base cation leaching
- the equilibrium between H^+ and Al^{3+} in soil solution
- the amounts exchangeable base cations in different podzol soil layers.

The changes in the amounts of exchangeable cations are compared with the total changes in the treatment solution concentrations. The results are discussed in comparison with the basic assumptions used in some soil models, and in connection with probable effects of acid precipitation on tree growth.

Material and Methods

The soil samples were treated with solutions having different concentrations of H^+, i.e. pH 3.3, 3.8 and 4.6, in vacuum filtration equipments installed on a shaker (Fig. 1). The treatment solution was first applied to the humus layer samples (10 ml). The volume ratio between the soil sample and the treatment solution was 1:5 in all layers. The humus samples were shaken for 10 min. with 50 ml of treatment solution and the leachates were then separated with vacuum. Forty-two ml of the leachate was further used in the treatment of the soil sample of eluvial layer (8.4 ml) while the rest of the leachate was taken to the analyses. The treatment of the other layers was continued in the same manner. The leachates

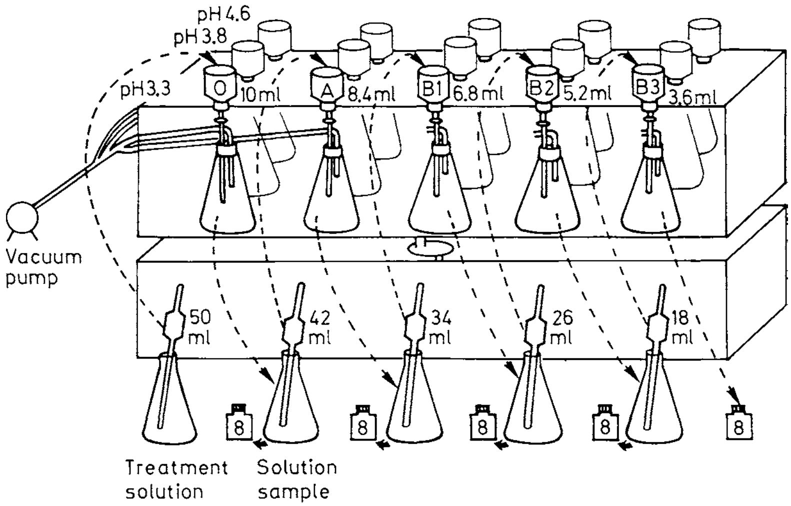

Fig. 1. The shaking and filtration unit used in the treatments and in the CEC measurements. The soil volumes used are shown in the filtration unit and the TS volumes used in each layer are given in the pipettes

from five successive shakings were combined and later in the text this combination is called a sample: Two treatment series with different solution base cation concentrations were done, applying 100 successive shakings to series I and 50 to series II.

The treatment solutions contained cations occuring in natural rain water, namely NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+} (Table 1). Two levels of cation concentrations were used. In series I, in treatments pH 3.3 and 4.6, the concentrations were adjusted to double of the level measured in rainwater at the Jokioinen field station of the Finnish Meteorological Institute (FMI) in summer 1985 (Ilmatieteen laitos 1986). In series II and series I pH 3.8, these levels were those measured by the FMI.

The treatment solutions were prepared by first adding salts [$(NH_4)_2SO_4$, $CaSO_4$, $MgSO_4$, K_2SO_4, Na_2SO_4 and $Ca(NO_3)_2$] to distilled water, then regulating the pH of the solution. This was done using HCl, HNO_3 and H_2SO_4, the molar proportions of Cl^-, NO_3^- and SO_4^{2-} being 1:6:12, respectively. Owing to the salt application, the pH measured was higher than that calculated from the acid concentrations, and an extra amount of acid mixture was added so as to reach the required pH levels. The treatment solutions were allowed to stabilize with the ambient CO_2 concentration.

The cation exchange capacity (CEC) and the amounts of exchangeable cations were determined by extracting the soil sample with 1 M NH_4Cl solution for 1 h (Table 2, Table 5). The soil sample: treatment solution volume ratio was 1:10. The CEC was determined of both untreated samples and samples treated with acid solutions.

The activity of protons was measured with a pH meter, Na and K were determined with flame spectrophotometer and Ca, Mg, Fe, Al and Mn with atomic absorption spectrophotometer. The BS, base saturation, of soil exchangeable cations and of solution cations was calculated by dividing the amount of base

Table 1. The ionic concentrations (µeq l^{-1}) of the TS and the total deposition divided by the volume of precipitation (µeq l^{-1} and mg l^{-1}) in the FMI's field station Jokioinen in summer 1985 (Ilmatieteen laitos 1986). The amounts of cations in the TS except NH_4^+ are measured and the amounts of anions and NH_4^+ are calculated from salt additions

Treatment	H^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-
1. pH 3.3	510	20	12	58	9.5	90	442	221	37
2. pH 3.3	495	9	6	27	6.5	45	372	186	31
1. pH 3.8	158[a]	9	6	36	7.0	45	165	82	14
2. pH 3.8	168	9	6	30	6.7	45	167	84	14
1. pH 4.6	27	25	15	68	10.9	90	149	75	12
2. pH 4.6	27	10	7	30	6.8	45	79	40	7
Jokioinen summer 1985		6	6	23	5.3	45			
mg l^{-1}		0.13	0.22	0.46	0.065	0.63			

[a] For Parkano this was actually 190 µeq l^{-1} (pH 3.72).

Table 2. Properties of the soil samples

	Koski				Parkano				
	Humus	Eluvial	Illuvial		Humus	Eluvial	Illuvial		
	O	A1	B1	B2	O	A1	B1	B2	B3
Depth (cm)	4.1	2.9	3.4	4.3	2.4	3.0	5.0	5.1	5.8
$pH(H_2O)$	3.7	3.8	4.1	4.4	3.7	4.0	4.5	4.6	4.7
Loss on ignition (%)		4.7	5.3	5.3		4.7	3.3	2.4	1.4
Clay (%)		4	5	6		1	1	1	1
Silt (%)		43	46	43		9	7	6	6
Fine sand (%)		39	33	33		45	46	50	53
Coarse sand (%)		14	16	18		45	46	43	40
CEC (meq l^{-1})	48.0	37.6	50.7	31.4	34.8	32.6	16.9	8.1	5.3
CEC (meq kg^{-1})	222.0	35.7	49.6	29.5	137.0	31.6	13.5	5.8	3.8
Base saturation (%)	69	17	9	13	51	12	13	23	32

cations Ca, Mg, K by the sum of Ca, Mg, K, Al and H. The amount of exchangeable H^+ was calculated from the pH in the NH_4Cl solution.

The soil samples used in the experiment were taken in October–November 1986 from two experimental sites of the Finnish Forest Research Institute (FFRI) located in Koski and Parkano. Twenty soil profiles were taken from both sites. The thickness of each layer was measured and the profiles were divided into humus (O), eluvial (A), and illuvial (B) layers. The illuvial layer was further divided into two (Koski) or three (Parkano) parts. In laboratory all sub samples of each layer were combined. The soil samples were air-dried for three days at 50°C. The volume-weight, the texture (Elonen 1971) and the amount of organic material of the mineral soil samples (Allen 1974) was determined.

The soil texture of mineral soils was fine sand in Parkano and sandy moraine in Koski, and the CEC of soil layers was greater in Koski than in Parkano material (Table 2).

Results

The Retention of H^+ Ions in the Soil Profile

The higher the H^+ concentration of the treatment solution (TS), the greater the amount of H^+ retained in all layers of soil samples (Table 3). In the treatments pH 3.3 and 3.8 the retention of H^+-ions occured in all of the soil layers whereas in the treatment pH 4.6 the acidity of the TS increased in humus and eluvial layers. Because of H^+ retention in illuvial layer, the net change in the H^+-concentration of the solution that percolated through the whole profile was small in this treatment. In all treatments the major part of the H^+ retention occured in the illuvial layer (Fig. 2).

Table 3. The retention of H^+ in soil layers during the treatment series. The amounts of H^+ retention are given as meq/l soil in layers O and A and in layer Koski B as meq/2 l soil and Parkano B as meq/3 l soil. Negative values denote release of protons from soil to solution. H^+ input to humus is the total amount of protons added to humus (1 l)

Koski						Parkano					
H^+ input to humus	H^+ retention meq			Through		H^+ input to humus	H^+ retention meq			Through	
meq	O	A	B	meq	%	meq	O	A	B	meq	%
253	22	18	157	56	22	256	10	25	195	26	10
125	21	12	72	20	17	123	20	20	73	10	8
79	8	4	55	12	15	96	3	12	66	14	15
42	9	0	24	9	22	42	10	5	21	6	14
14	−9	−8	19	12	87	14	−9	−2	18	7	50
7	−3	−3	7	6	79	6	−4	−1	8	4	55

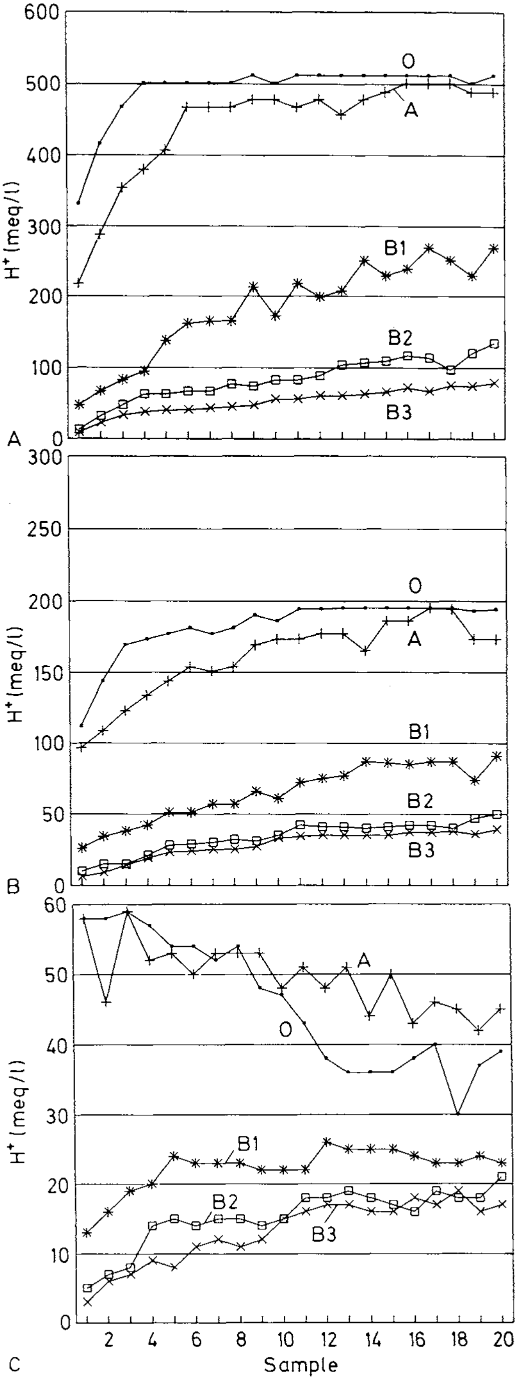

Fig. 2A–C. The H^+ concentrations of the EQS in each layer of Parkano material in samples from 1 to 20, treatment series 1. pH 3.3. **B** treatment 1. pH 3.8. **C** treatment 1. pH 4.6

Table 4. The EQS cation concentrations in the lowest illuvial layers in the first and last samples of the treatment series (see also Table 1)

Sample	First	Last	First	Last	First	Last	First	Last	First	Last
Treatment	H^+		K^+		Ca^{2+}		Mg^{2+}		Al^{3+}	
Koski	μeq l^{-1}									
1. pH 3.3	43	120	220	23	224	108	118	18	334	527
2. pH 3.3	43	125	149	9	147	47	107	8	333	455
1. pH 3.8	18	41	140	20	66	57	58	15	231	199
2. pH 3.8	43	44	109	10	70	47	59	13	244	152
1. pH 4.6	15	19	123	26	55	64	49	18	220	94
2. pH 4.6	41	19	86	9	69	21	46	11	200	50
Parkano	μeq l^{-1}									
1. pH 3.3	9	79	106	13	152	58	82	11	68	555
2. pH 3.3	10	52	97	10	176	42	71	8	77	644
1. pH 3.8	6	39	102	9	94	38	51	6	–	247
2. pH 3.8	8	36	82	8	49	38	35	10	55	100
1. pH 4.6	3	17	83	13	75	64	52	13	–	53
2. pH 4.6	3	18	68	12	39	21	23	9	–	–

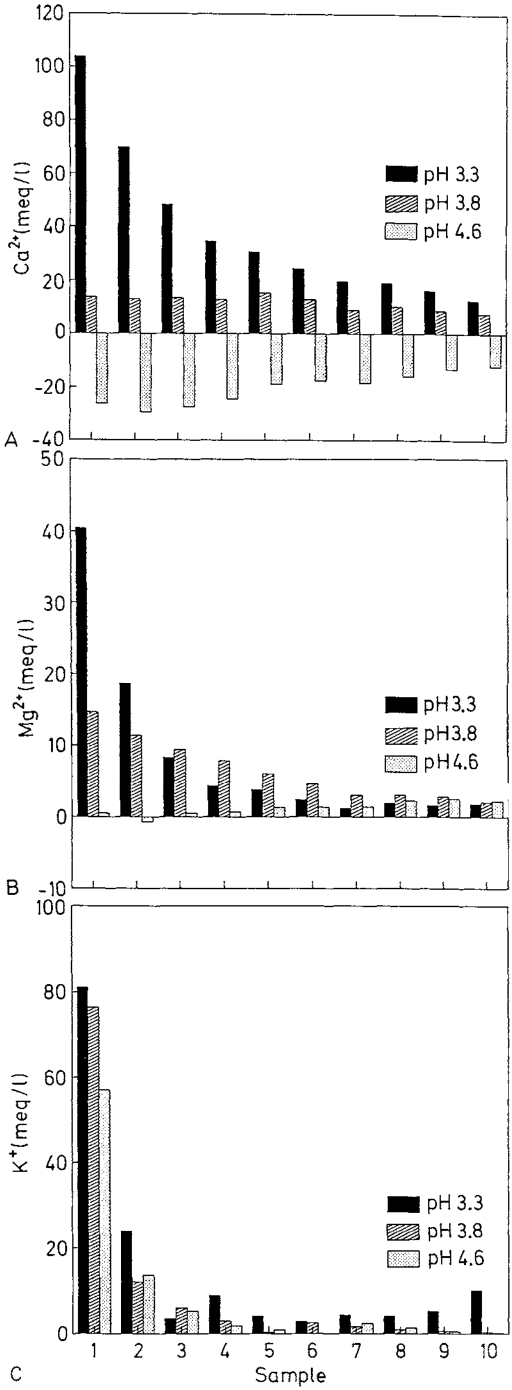

Fig. 3A–C. The change in the TS Ca^{2+} concentration in the humus layer of Parkano material. **B** The change in the TS Mg^{2+} concentration in the humus layer of Parkano material. **C** The change in the TS K^{+} concentration in the humus layer of Parkano material

The ability of humus layer to retain H^+ was greatest in the beginning of the treatment series: the retained amount in the first three samples was around 60 and 50% of the total amount of H^+ retained in this layer in treatments pH 3.3 and 3.8, respectively. In the last samples of the treatment series the H^+ concentration of the EQS in humus and eluvial layers was nearly the same as that of the TS (Fig. 2).

Although a substantial amount of H^+ was retained in each sample in the illuvial layer, the ability of this layer to retain H^+ did not decrease remarkably during the treatment series. In the illuvial layers the H^+ concentration of the EQS increased only slowly during the treatment series (Fig. 2), at the end of the treatment series being 25–30% (Koski material) and 10–20% (Parkano material) of the Ts H^+ concentration in treatments pH 3.3 and 3.8 (Table 4, 1).

Reactions of Treatment Solution H^+-Ions with Soil

Humus Layer

The release of Ca and Mg was much smaller in the treatment pH 3.8 than in the treatment pH 3.3, and in the treatment pH 4.6 the humus layer even retained Ca (Fig. 3). For K the differences between the amounts released in different treatments were small. The release of base cations from the humus layer was largest at the beginning of the treatment series and for K the release occurred in all treatments mainly during the first two samples. In the last samples of the treatment series, the humus layer had only minor or no effects at all on the TS base cation concentration.

A linear regression between the cumulative retention of H^+ and the release of base cations was found. Calculated from the cumulative changes in the first three samples the slope of the regression equation was 0.63, if Ca alone was taken into account. When Mg was added, the slope was 0.79 (Fig. 4), and further after the addition of K it was 0.91. When examining this regression in the first sample, the

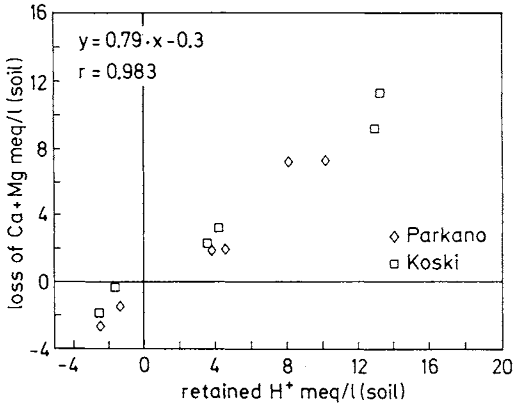

Fig. 4. The correlation between the retained amount of H^+ in humus layer (=x) and loss of Ca and Mg from humus layer (=y) in the first three samples. The amounts are given as meq l^{-1} (soil)

significance of K and Mg in the cation exchange reaction with H^+ was greater than in the first three samples on an average.

Mineral Soil Layers

In mineral soil the main reaction consuming H^+-ions from solution was aluminium dissolution, and only in the eluvial layer some base cation exchange was detected to consume H^+-ions from the solution. The amount of dissolved Al in the uppermost illuvial layer was about the same as the H^+ retained. In the lower illuvial layers of Parkano material, H^+-ions, aluminium and base cations were retained at the beginning of the treatment series. After the first samples, aluminium dissolution started to consume H^+-ions from solution also in these layers.

In the illuvial layer the correlation between solution H^+ and Al concentration was strong (Fig. 5). The Al concentration of the EQS as a function of the H^+-concentration was highest in the samples of the deepest layer. The solubility of Al was quite near that of gibbsite in the lowest layers of Parkano material. The solubility of Al as a function of solution H^+ concentration decreased during the

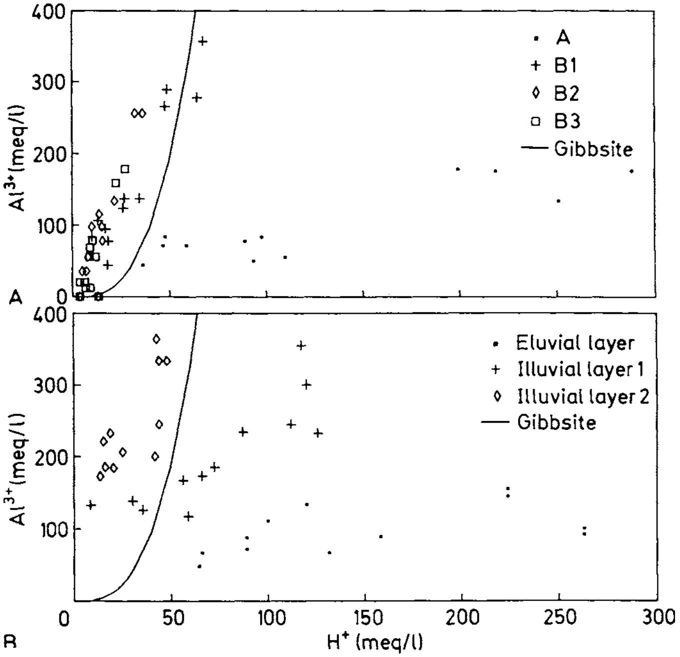

Fig. 5A,B. The EQS Al^{3+} concentration as a function of the EQS H^+ concentration in samples 1 and 2 in mineral soil layers of Parkano material. The solubility of gibbsite ($K = 10^{8.7}$) is drawn in the Figure. **B** Koski material treatment series in eluvial and uppermost illuvial (B1) layers, being unchanged in the samples of lower illuvial layers (B2 and B3).

Soil Exchangeable Cations

When compared to the initial amounts of exchangeable cations, the treatments differed from each other in the amounts of H^+ in all soil layers, and in the amounts of Ca and Mg in the humus and eluvial layers (Table 5). The exchangeable amount of Mg in humus after the treatments pH 3.3 and 3.8 was only about 15 and 40% of the initial, respectively. The amount of soil exchangeable K decreased essentially in all the treatments.

The CEC of the humus layer is reduced by 10–40% in the treatments pH 3.3 and pH 3.8. In the illuvial layer the CEC is increased in the treatment pH 3.3 and reduced in the treatment pH 4.6, the changes being strongly correlated with the changes in amounts of exchangeable Al.

The changes in the amounts of exchangeable Ca and Mg in humus and eluvial layers were for Ca 70–90% and for Mg about 50–80% of the changes measured from the treatment solutions (Table 6). In the illuvial layer there was no correlation

Table 5. The amounts of exchangeable cations in untreated soil samples, and the changes in these due to the treatments. Positive values denote increased, negative values decreased amounts. The results of K are given as a mean of all the treatments (soil volumes as in Table 3)

Treatment	Koski			Parkano		
	Humus	A	B 1,2	Humus	A	B 1,2,3
H^+	meq	meq	meq	meq	meq	meq
1. pH 3.3	9.6	2.9	3.1	4.7	4.0	1.4
2. pH 3.3	4.5	0.0	1.1	3.3	1.6	0.2
1. pH 3.8	5.4	0.9	0.7	3.8	1.4	0.3
2. pH 3.8	0.3	−1.6	−0.3	−0.3	−0.5	−0.3
1. pH 4.6	−3.3	−1.5	0.0	−2.5	−0.4	−0.1
2. pH 4.6	−2.7	−2.1	−0.4	−2.2	−0.8	−0.3
Untreated	9.0	6.0	1.9	8.2	2.9	0.7
Al^{3+}	meq	meq	meq	meq	meq	meq
1. pH 3.3	2.8	−0.8	8.3	0.1	−5.0	8.7
2. pH 3.3	0.4	1.8	12.2	0.4	4.9	13.3
1. pH 3.8	1.1	−0.5	2.3	0.6	−2.6	2.9
2. pH 3.8	−0.9	2.5	−0.4	−0.9	1.8	3.0
1. pH 4.6	−1.1	−3.7	−1.9	−1.1	−1.3	−0.9
2. pH 4.6	−2.2	0.5	−5.2	−2.2	−14.8	−3.0
Untreated	5.6	24.8	71.2	8.2	25.5	23.7

Table 5. (continued)

Treatment	Koski			Parkano		
	Humus	A	B 1,2	Humus	A	B 1,2,3
Ca^{2+}	meq	meq	meq	meq	meq	meq
1. pH 3.3	−15.2	−2.2	−2.9	−8.2	−1.6	−0.7
2. pH 3.3	−17.6	−2.7	−3.7	−9.4	−2.0	−1.4
1. pH 3.8	−8.4	11.5	−1.1	−4.1	−1.6	−0.8
2. pH 3.8	−9.9	0.2	−3.1	−3.0	−1.5	−1.2
1. pH 4.6	4.4	6.2	−1.6	9.4	1.2	−0.6
2. pH 4.6	−0.3	1.2	−3.2	2.1	−0.7	−1.1
Untreated	24.9	3.5	4.6	13.1	2.4	1.6
Mg^{2+}	meq	meq	meq	meq	meq	meq
1. pH 3.3	−3.2	−0.8	−1.0	−1.4	−0.3	−0.2
2. pH 3.3	−3.4	−0.9	−1.1	−1.4	−0.3	−0.3
1. pH 3.8	−2.5	−0.7	−0.9	−1.0	−0.3	−0.2
2. pH 3.8	−2.4	−0.6	−1.0	−0.8	−0.3	−0.3
1. pH 4.6	−1.5	0.0	−0.9	−0.3	−0.2	−0.1
2. pH 4.6	−0.5	0.2	−0.9	0.5	−0.2	−0.3
Untreated	3.9	1.0	1.2	1.7	0.4	0.4
K^{+}	meq	meq	meq	meq	meq	meq
Mean (n=6)	−3.7	−1.5	−1.5	−2.5	−0.9	−1.8
Untreated	4.2	1.9	2.3	2.9	1.1	2.4

for Ca and Mg. In the measurements concerning K there was no correlation in any layer.

A strong positive correlation could be found in each soil layer between the retained amount of H^+ and the change in exchangeable H^+ (Table 6). The increase in the exchangeable H^+ amount was ca. 30% and 15% of the amount retained in the humus and eluvial layers, respectively. In the illuvial layers the amounts of retained protons were two decades higher compared to the change in the amount of exchangeable H^+. Opposite to other cations, the amount of exchangeable Al increased as the leached Al amount increased in the illuvial layer.

The equilibrium between the cations in solutions and the soil exchangeable cations was studied by comparing the properties of the last samples of the treatment series with the amounts of exchangeable cations in soil samples. The BS of humus was nearly the same as that in EQS (Fig. 6A). However, when the BS in EQS increased to values greater than 60%, the increase in soil BS seemed to be slower than the increase in EQS BS. In mineral soil the corresponding correlation

Table 6. The regression equation and the correlation coefficient (r) between the losses of cations from soil (=x, measured from the EQS) and the decrease in the amounts of exchangeable cations (=y)

	Koski		Parkano	
	r	Regression equation	r	Regression equation
Humus				
H^+	0.885	y=0.36*x−0.6	0.715	y=0.21*x+0.07
Ca^{2+}	0.805	y=0.71*x−2.8	0.950	y=0.92*x+0.5
Mg^{2+}	0.729	y=0.54*x−0.7	0.951	y=0.79*x+0.4
Eluvial layer (A)				
H^+	0.869	y=0.17*x−0.9	0.938	y=0.16*x−0.7
Ca^{2+}	0.979*	y=0.75*x+0.3	0.971*	y=0.69*x−0.7
Mg^{2+}	0.845	y=0.46*x+0.2	0.402	y=0.12*x−0.2
Illuvial layer (B)				
H^+	0.994	y=0.024*x−0.6	0.992	y=0.009*x−0.4
Al^{3+}	−0.698	y=−0.08*x−2.9	−0.624	y=−0.05*x+1.3

* n=5

was weak in the eluvial and uppermost illuvial layers (B1). However, between the ratios $base^+/base^+ + H^+$ in the EQS and on the mineral soil exchange sites (Fig. 6B) there was a strong positive correlation in all mineral soil layers.

Discussion

In this study, the response of different soil layers to acid precipitation was studied in circumstances where decomposition, nutrient uptake and weathering were nearly totally excluded, and hydrology was simplified. Thus the results are describing the reactions of actual soil profiles within these limitations, which have to be taken into account when, for example, making forecasts of the reactions of soils under acid load.

The cation exchange theory (e.g. Gaines and Thomas 1953) implies that the increase in H^+input into soil solution, e.g. by increased H^+deposition leads to cation exchange between solution H^+ and soil exchangeable base cations, until the relation of base cations and H^+ on soil exchange sites correspond that in equilibrium solution. In this study the detected linear regression between H^+retention and base cation release, together with the detected dependence between soil and solution BS, are in accordance with this theory.

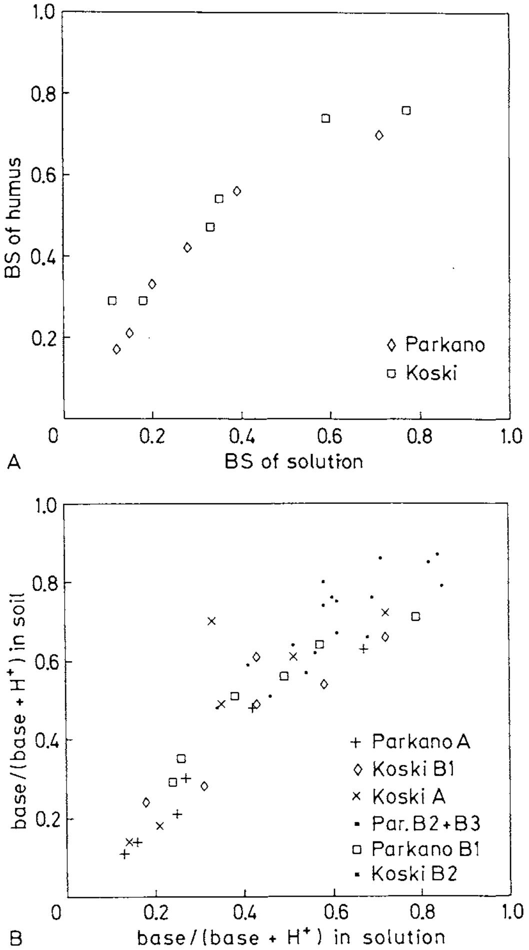

Fig. 6A,B. The correlation between BS in the equilibrium solution and BS of humus at the end of the treatment series. **B** Mineral soil otherwise same as **A**, but the relative base cation amounts in the soil and in the solution in the mineral soil layers are calculated as: base cations/(base cations $+H^+$)

In this study the acid added caused in humus and eluvial layers an increase in the soil solution Ca and Mg concentrations and a decrease in the amounts of exchangeable Ca and Mg. In the illuvial layer this effect could not be detected, even if the ratio between the soil exchangeable base cations and H^+ was seen to correspond to that of the EQS.

It has been found also in many lysimeter studies that in humus and eluvial layers the leaching of Ca and Mg increases (e.g. Abrahamsen 1983; Bergkvist 1986; Freiesleben and Rasmussen 1986; Skeffington and Brown 1986) and the exchangeable amounts of these cations decrease (e.g. Abrahamsen 1983; Skeffington and Brown 1986; Kelly and Strickland 1987) due to acid load. Wright et al. (1988) have conducted manipulation experiments on whole catchments in which the leaching of Ca and Mg was found to increase due to acid deposition, and to decrease following acid deposition exclusion.

For K it seems that the leaching is not a pH-dependent reaction at the pH levels used in this study. This observation is supported, for example, by the observations of Bergkvist (1986) and Brown (1987), the latter proposing that the ready exchange of K at the pH values typical of acid forest top soils explains the mobility of this element as a consequence of water flow.

When studying the base cation losses from (or retention to) soils it seems that in the humus and eluvial layers the extraction of exchangeable cations with unbuffered salt solution gives good estimates of the actual changes. The changes in the exchangeable amounts of Ca^{2+}, Mg^{2+} and H^+ were not the same as those measured from the leachates, but there was a good positive correlation between these measurements. So it seems evident that in time series analysis of soil samples, the exchangeable amounts of these ions can be used to indicate the effects of acid precipitation.

From the strong correlation between the retained H^+ amount and the change in the exchangeable H^+ in all soil layers it can be implied, that the increase in exchangeable H^+ and the decrease in soil salt pH should be useful indicators of acid load in all soil layers. This is supported also by e.g. Abrahamsen and Stuanes (1986), who found that acid load affected the pH-value of the whole 0.4-m-deep soil layer used in the lysimeter study, and by Brown, who found that pH of the soil was affected by the treatment pH 3.0 (compared to distilled water) to a deepness of 0.8 m, and also by Hallbäcken and Tamm (1986), who found changes in soil pH in a time series of Swedish soils.

In the humus layer the CEC decreased as a result of H^+ adsorption, because the increase in the exchangeable H^+amount was only about 30% of the adsorbed amount. Compared to a situation where all of the adsorbed H^+ would be effectively exchangeable, the BS does not decrease as fast and the ability of the humus layer to decrease soil solution H^+ concentration remains longer. However, this means that the amounts of exchangeable base cations decrease more than in a situation in which all the adsorbed H^+ would be effectively exchangeable. James and Riha (1986) have suggested, that each equivalent of Ca released by H^+ might decrease CEC of the organic horizon by the same amount, so that the Ca saturation percentage would remain unchanged as the soil pH decreases which, according to the results of this study, is an over estimation.

The reduction of the H^+ concentration of the TS occurred mainly in the illuvial layer due to the reactions with aluminium compounds, the finding of which is supported also by studies of e.g. Brown (1987). In the first sample of the lower illuvial layers of the Parkano material the reduction of total cation concentration indicates sulphate adsorption (Chao et al. 1964) or precipitation of aluminium sulphate (Prenzel 1983), later the reactions were Al dissolution reactions. The dissolution of Al was highly dependent on EQS H^+ concentration, shown also by e.g. Tyler et al. 1987. The solubility of aluminium was quite near that of gibbsite, which is suggested, e.g. by Reuss and Johnson (1986) and by Schecher and Driscoll (1987) to regulate the concentrations of aluminium and H^+ in soil solutions of many soils. In the eluvial and the uppermost illuvial layers a reduction in the amounts of dissolved Al in the soil solution at a high EQS H^+ concentration was found during the treatment series, showing a reduction of easily soluble Al compounds in these layers.

The results of this study can be used in evaluating the assumptions used in models describing the effects of acid deposition on soils (Cosby et al. 1985; Holmberg et al. in press; Johansson et al. this Vol.; Posch et al. in press; Reuss and Johnson 1986). It is evident that in order to obtain a good estimate of the effect of acid deposition on the soil exchangeable base cation amounts and the soil solution base cation and Al concentrations in Finnish conditions , the soil reactions should be divided to occur at least in two vertically separate layers instead of one. In humus and eluvial layers the most important reaction depending on solution H^+ concentration is cation exchange. In the illuvial layer this is dissolution of aluminium compounds, which occurs simultaneously with exchange reactions.

The highest aluminium concentrations found in EQS in illuvial layer were around 5 $mg\,l^{-1}$, when pH of the incoming solution was 3.3. In studies concerning Al toxicity on Scots pine and Norway spruce, concentrations as low as this did not affect the growth of these trees (e.g. Eldhuset 1988; Arovaara and Ilvesniemi this Vol.), when other cations were available in optimal amounts.

It is evident that the increased input of H^+ to forest soil solution causes increased leaching of base cations. Especially the leaching of Mg is proposed to cause deficiency symptoms in trees (Mayer and Ulrich 1977). In connection with the decreased exchangeable base cation amount the increase in nitrogen input to forests can lead to unbalanced nutrition of plants.

List of Abbreviations

FMI	Finnish Meteorological Institute
FFRI	Finnish Forest Research Institute
CEC	Cation exchange capacity
BS	Base saturation of soil exchangeable cations and solution cations
TS	Treatment solution
EQS	Equilibrium solution
Sample	Combined EQS of five successive shakings of treatment series
O	Humus layer
A	Eluvial layer
B	Illuvial layer, this is further divided to layers 1, 2, 3

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Buffering of Peat and Peaty Soils: Evaluation Based on the Artificial Acidification of Peat Lysimeters

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Summary

Sphagnum peat, ligneous sedge peat and ash fertilized (10 t ash ha^{-1} in 1937) *Sphagnum* peat profiles were irrigated over a 16-month period in the laboratory with acidified (H_2SO_4) water at pH 4, 3 and 2, using deionized water as control. Total sulphur (H^+) deposition during the study period was $0.8\,g\,S\,m^{-2}$ ($0.051\,eq\,H^+\,m^{-2}$) at pH 4, $10.6\,g\,S\,m^{-2}$ ($0.663\,eq\,H^+\,m^{-2}$) at pH 3, and $115.7\,g\,S\,m^{-2}$ ($7.233\,eq\,H^+\,m^{-2}$) at pH 2. Outflow of elements was measured after each irrigation, and the peat profiles were analysed at the end of the experiment. Irrigation at pH 4 and pH 3 did not considerably change either the outflow of elements or peat quality compared to the controls. In the outflow from the *Sphagnum* and ligneous sedge peat profiles at pH 2 and pH 3 sulphate was the dominating anion, thus superceding the role of organic anions. From the ash fertilized profiles sulphate outflow was lowered owing to the probable immobilization of sulphur as calcium sulphate. It was concluded that further acidification of naturally acid peat soils at realistic acid loads is improbable. However, sulphur inputs might be effectively retained in anaerobic peat layers and, when oxidized to sulphate, take over the role of organic anions with a resulting increased strong acid input into watersheds.

Introduction

Peatlands in humic regions are naturally acidic soils where acidity itself is an important parameter reflecting the trophic character and the productivity of the site type (Kivinen 1932; Holmen 1964). The nature of the acidity in peat was quite early connected with the acids synthesized from the living and dead remains of mosses, especially *Sphagnum* species, forming peat (e.g. Kivinen 1932). However, the chemistry and the ecological role of these acids, which were identified as uronic acids, were not recognised until much later (Theander 1954; Knight et al. 1961; Clymo 1963). Formation of these acids during the growth and decomposition of *Sphagnum* also explained the high cation exchange capacity and high acidity of peat (Spearing 1972; Clymo 1984).

Kauppi et al. (Eds).
Acidification in Finland

Owing to the chemical nature of peat, i.e. high acidity and high CEC, peatlands should theoretically be rather tolerant to air pollutants or at least to further acidification. During the past decade, however, the adverse effects of air pollutants on peatland vegetation (Ferguson and Lee 1978) and chemistry (Gorham et al. 1985) have been documented and speculated on. Peatlands which are sensitive to acidification, defined here as a loss of acid neutralizing capacity, should be those with a high base saturation or bicarbonate buffering capacity, i.e. minerotrophic mires. However, peatlands in Finland typically consist of highly acidic ombrotrophic mire complexes and more interest has been paid to runoff and surface water acidification caused by peaty soils (e.g. Kortelainen and Mannio 1988) than to further acidification of peatlands themselves. This is fully understandable considering that more than half of the Finnish peatland area is drained.

In spite of the complex hydrological and chemical nature of peat soils, four major buffering systems can be distinguished in mires (Anderson 1986; Urban et al. 1987);

1. Bicarbonate buffering; active in minerotrophic mires $pH > 5$.
2. Ion-exchange reactions; molar exchange of ions between the organic exchange complex (mainly carboxyl groups) or assimilatory uptake of ions by vegetation. Acid production due to cation exchange may be relatively high, but the acidity will mainly be neutralized during the breakdown of organic matter.
3. Redox processes at or below the groundwater table; biochemical sulphate and nitrate reduction may be very efficient (e.g. Bayley and Schindler 1987) producing alkalinity. If S compounds are oxidized, they produce an equivalent amount of acidity.
4. Production of organic acids as a result of incomplete aerobic decomposition of organic matter. This acidity originates from the humic and fulvic acids which have a high content of carboxylic and phenolic groups.

To be able to calculate the buffering capacity of these systems, detailed mass-balance studies are needed. Mass-balance techniques have been successfully utilized in Thoreau's Bog (Hemond 1980; McKnight et al. 1985) and in Marcell Bog (Urban et al. 1987), both in the U.S.A. These studies have revealed that the main source of acidity in these bogs is the production of organic acids. The acids buffer the systems at the low pH values characteristic of the bogs, even in the case of the bog with a relatively high atmospheric acid input (Thoreaus's Bog) where the external acidity was neutralized by anion (SO_4, NO_3) reduction.

The area of peatlands in Finland is about 9 million hectares, covering one third of the total land area. The volume of the standing crop in peatland forests is 18%, and the annual increment 22% of the total stand volume and growth in Finland (Paavilainen and Tiihonen 1988). Thus peatlands play an important role in Finnish forest production, and the need for evaluating the sensitivity of peaty soils to air pollutants is well justified.

Materials and Methods

Laboratory Lysimeters

The effect of simulated increased acidification on the elemental composition of peat was assessed by supplying artificial rain to peat lysimeters in the laboratory using methodology presented by Braekke (1978). The results of elemental analysis carried out during and after irrigation were utilised in assessing the sensitivity of peat soils to an acid load.

The peat samples studied in the laboratory experiment were collected from Jaakkoinsuo experimental drainage area (62°04'N, 24°34'E, 120 m asl). They consisted of the following:

1. Ombrogenic ligneous *Sphagnum* peat from a drained (in transitional state) low shrub pine bog (denoted later as S peat).
2. Ligneous *Carex* peat from an old peatland forest intermediate between the herb-rich type and the *Vaccinium myrtillus* type (LC peat)
3. Same as peat 1, but fertilized with wood ash (10 t ha^{-1}) in 1937 (S peat + ash).

The elemental composition of the wood ash is unknown, but average values can be estimated on the basis of ca. 150 wood ash analyses summarized by Silfverberg (unpubl.) as follows: phosphorus 10–20 kg t^{-1}, calcium

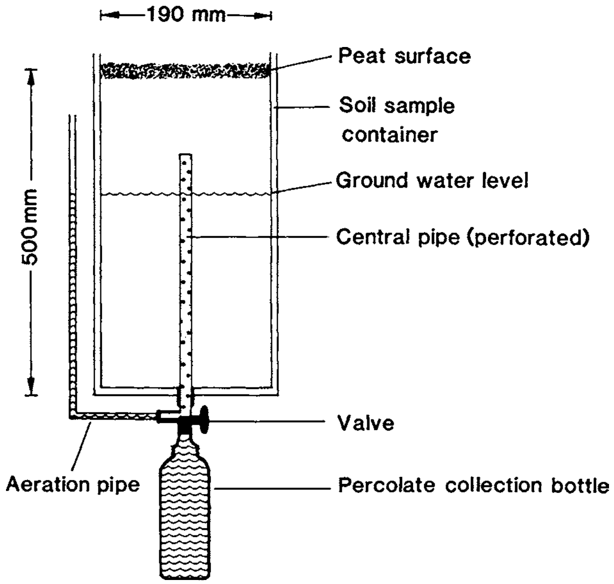

Fig. 1. Diagram showing construction of lysimeter

200–300 kg t^{-1}, magnesium 20–50 kg t^{-1}, potassium 50(−100) kg t^{-1}, iron ca. 15 kg t^{-1} and manganese ca. 15 kg t^{-1}.

The laboratory lysimeter study was carried out by irrigating originally 72, and to the end of the experiment 36 lysimeter cells, each containing a 50-cm-long peat profile (Fig. 1) with deionized water (control) and deionized water acidified with sulphuric acid to pH values of 4, 3 and 2 during a 16-month period. The number of replications for the peat analyses per peat type and pH treatment was three. Irrigation was normally done biweekly or monthly with 35 mm of artificial precipitation. The sulphur load at each irrigation was 0.048 g S m^{-2} at pH level 4, 0.622 g S m^{-2} at pH level 3 and 6.786 g S m^{-2} at pH level 2. The corresponding proton loads were 0.003, 0.039 and 0.424 eq H^+ m^{-2} respectively. The total amount of artificial precipitation added during the 16-month period was 600 mm. Total sulphur deposition (H^+ deposition) was thus 0.8 g S m^{-2} (0.051 eq H^+ m^{-2}) at pH level 4, 10.6 g S m^{-2} (0.663 eq H^+ m^{-2}) at pH level 3, and 115.7 g S m^{-2} (7.233 eq H^+ m^{-2}) at pH level 2.

After each irrigation the percolating water was allowed to flow into a sampling bottle until the original groundwater level, 20–30 cm from the surface, was reached. Evaporation from the lysimeters was assumed to be small because of the low temperature (5–7°C) in the laboratory.

Chemical Analyses

Percolate water samples were filtered through filter paper [Schleicher & Shull 589(3)] and frozen until analyzed. The following analyses were performed: Na, K, Ca, Mg, Al, Fe, Mn, Cu, S, P, Zn by ICP/AES (ARL 3580), NH4–N according to the ammonia gas diffusion method by FIA, COD(Mn) according to SF Standard 5504, colour with a comparator according to SF Standard 3023, and pH with a combined glass electrode. The concentration of organic anions was calculated according to the method of Oliver et al. (1983) using TOC instead of DOC. TOC values were obtained indirectly from the regression equation between COD and TOC; TOC = 4.0 + 0.334* COD, (r = 0.982***) determined in peat groundwaters of the Jaakkoinsuo experimental drainage area.

The soil samples were dried at 70°C, milled to pass a 2-mm sieve and dry digested in HCl for elemental analysis by ICP/AES. Boron was determined following separate digestion. Soil pH was measured in deionized water and in 1 M KCl (1 : 25). Total carbon, nitrogen and sulphur were determined by LECO analyser. The reliability of the LECO total S values was assessed by analysing peat samples also by the wet combustion method (HNO_3, H_2O_2 digestion).

Exchangeable cations were extracted using acid (pH 4.65) 1 M NH_4OAc and neutral (pH 7.00) 1 M NH_4OAc. Potential exchangeable acidity and base saturation were determined from neutral NH_4OAc extracts according to a modified method of Brown (1943). Potential exchangeable acidity determined from the NH_4OAc extract (pH 7.00) was compared with total H^+ in carboxylic groups titrated by the modified calcium acetate method (Holtzclaw and Sposito 1979).

Table 1. Leaching losses of elements from irrigated *Sphagnum* peat (S peat), ligneous sedge peat (LC peat) and ash fertilized *Sphagnum* peat (S peat + ash) profiles during the 16-month irrigation period (irrigation: C = control, 4, 3, 2 = respective pH levels). Values are in g m^{-2}

	S peat				LC peat				S peat + ash			
	C	4	3	2	C	4	3	2	C	4	3	2
NH_4-N	1.10	1.40	1.92	7.03	1.76	1.21	2.23	7.11	1.60	2.84	3.25	4.59
P	0.19	0.15	0.17	0.39	0.14	0.08	0.07	0.08	1.77	1.15	1.19	2.41
Ca	0.73	0.83	1.04	20.93	4.86	6.18	7.21	50.57	8.70	5.54	4.83	37.40
Mg	0.16	0.20	0.29	4.44	0.27	0.30	0.42	3.58	1.89	1.27	1.35	7.23
K	0.46	0.54	0.88	2.34	0.68	0.58	0.89	2.07	1.86	1.36	1.24	3.28
Na	0.26	0.79	0.57	0.65	0.30	0.75	0.55	0.54	0.61	1.22	0.74	0.93
Fe	1.14	1.04	1.03	15.76	0.35	0.31	0.22	0.44	2.17	2.26	3.07	5.26
Mn	0.01	0.01	0.02	0.41	0.00	0.00	0.00	0.12	0.06	0.11	0.04	0.22
Al	0.11	0.12	0.10	0.29	1.47	1.40	1.25	0.90	0.13	0.21	0.18	0.09

Results

Chemical Properties of the Peat in the Lysimeters

The chemical properties of the peat in the lysimeter cells was measured only on the 0–40 cm layer because the peat profiles had become compressed during irrigation, and sampling down to the original depth of 50 cm was no longer possible. Thus the actual element contents in the profiles based on mean values per treatment (Fig. 2) may be somewhat higher than the calculated ones. Direct comparisons between different irrigation treatments within the same peat type may also be uncertain because of spatial variation in the chemical composition of the peat. This was especially true in the ash fertilized peat profiles.

Nitrogen and Phosphorus

Nitrogen in peat is mainly organically bound, and almost all the inorganic N is present as ammonium nitrogen (Waughman 1980). Changes in the total contents of N in the lysimeter cells brought about by acid irrigation were small, although total N values in profiles irrigated with the strongest acid were lower than in the control lysimeters (Fig. 2a). Leaching losses of N as NH_4–N from lysimeters treated with water at pH 2 were 5–7 g NH_4–N m^{-2} compared to 1.1–1.8 g m^{-2} for the controls (Table 1).

However, losses of ammonium nitrogen even at pH 2 were so small that they do not explain the lowered total N values in peat.

The total phosphorus contents in the lysimeters did not change significantly as a result of acid irrigation (Fig. 2b). Fertilization with ash in 1937, which may have been at the level of 10–20 g P m^{-2}, was still visible in the peat. Leaching losses of phosphorus were also small (ca. 0.2 m^{-2} at pH 2), except from the ash fertilized peat profiles where large amounts (1.2–2.4 g m^{-2}) of P were leached regardless of acid irrigation (Table 1).

Calcium

The total contents of calcium were clearly dependent on the peat type (Fig. 2c). The calcium contents in LC peat were 4–5 times higher than those in the S peat. In the ash fertilized S peat, the addition of calcium (200–300 g m^{-2}) about 50 years ago was still clearly visible as elevated Ca contents that were of the same order as those in LC peat. Ash fertilization also caused variation in the chemical quality of the peat, which was reflected in varying element contents of peat cores used in the lysimeters. In these lysimeters, about half of the total Ca content was derived from the uppermost 10-cm-thick layer, except in lysimeters given the highest acid load at pH 2 where calcium has been displaced to a greater depth.

Leaching losses of calcium were, on an average, proportional to the total Ca contents in the peat (Table 1). Irrigation with acid at pH 2 resulted in a loss of

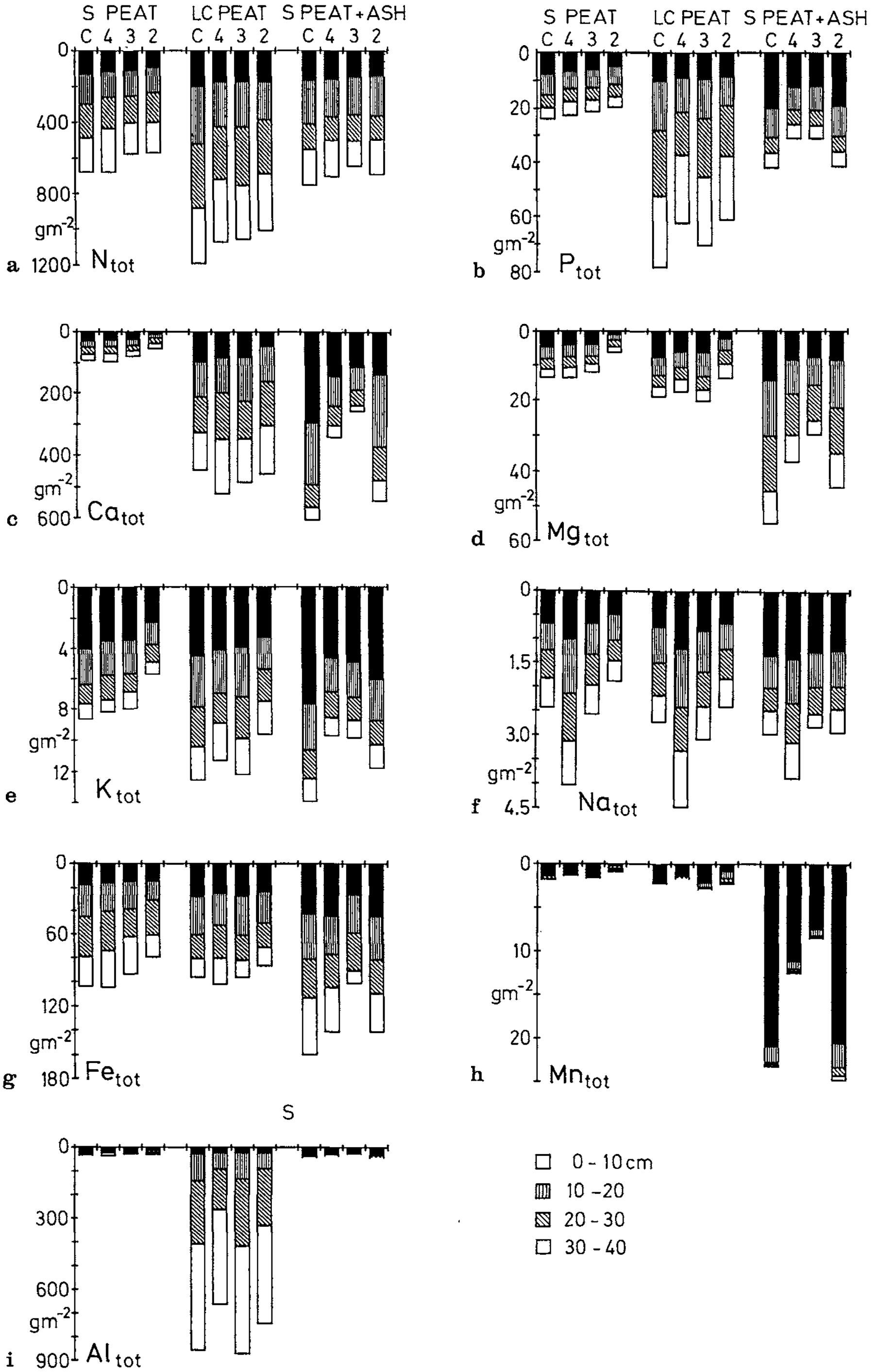

Fig. 2a–i. Element content of *Sphagnum* peat (S peat), ligneous *Carex* peat (LC peat) and ash fertilized *Sphagnum* peat in different layers. *4,3,2* indicate the pH of the artificial; *C* control

22% of the total amount of Ca in the S-peat compared to the control lysimeters during the study period. The corresponding value for the LC peat was 11%, and for the ash fertilized peat 6%.

Magnesium

The magnesium contents in the S and LC peat profiles were 12–20 $g\,m^{-2}$, and in the ash fertilized peat 30–55 $g\,m^{-2}$ (Fig. 2d). The magnesium content of the ash fertilized peat was rather high considering the assumed amount of Mg added (20–40 $g\,m^{-2}$) and Mg leaching (control: 1.9 $g\,m^{-2}$) during the 16-month irrigation. Downward leaching of magnesium due to acid irrigation was more pronounced than that of calcium. Magnesium losses at pH 2 were 47% of the total Mg contents in the control lysimeters for the S peat, 19% for the LC peat and 13% for the ash fertilized peat.

Potassium and Sodium

The potassium contents in the profiles of all peat types were quite similar and the contents were only influenced by acid irrigation at pH 2 (Fig. 2e, Table 1). The sodium contents in the profiles of the different peat types were also almost the same (Fig. 2f). Irrigation with acid did not significantly increase leaching of sodium (Table 1).

Other Metals

Changes in the total contents of iron, manganese and aluminium due to acid irrigation were hardly detectable (Fig. 2g–i). Only the iron contents at pH 2 slightly decreased; this was evident as increased Fe losses especially in the S-peat profiles. Irrigation at pH 2 also resulted in increased manganese losses, but losses of aluminium were small (Table 1). Neither boron, zinc nor lead contents differed in the acidified lysimeters compared to the controls.

Acidity and Base Saturation

The pH values within the same peat type only differed in those profiles with the pH 2 treatment. The average pH in the 0–20-cm-thick layer of the control lysimeters was 3.4 for the S peat, 3.7 for the LC peat and 4.4 for the ash fertilized peat. After 16 months irrigation at pH 2 the pH values decreased by 0.5–0.7 units throughout the whole S peat profile. In the LC peat this pH decrease took place in the uppermost 30-cm-thick later and in the ash fertilized peat only in the uppermost 10-cm-thick layer (Fig. 3). In percolate waters the sharpest decreases in pH at pH 2 took place in 50 days after the commencement of irrigation (Fig. 4) and were followed by an increased outflow of most elements.

The values of potential exchangeable acidity (PEA) were more related to peat type than to the acid treatment. PEA values for the S peat and the LC peat ranged

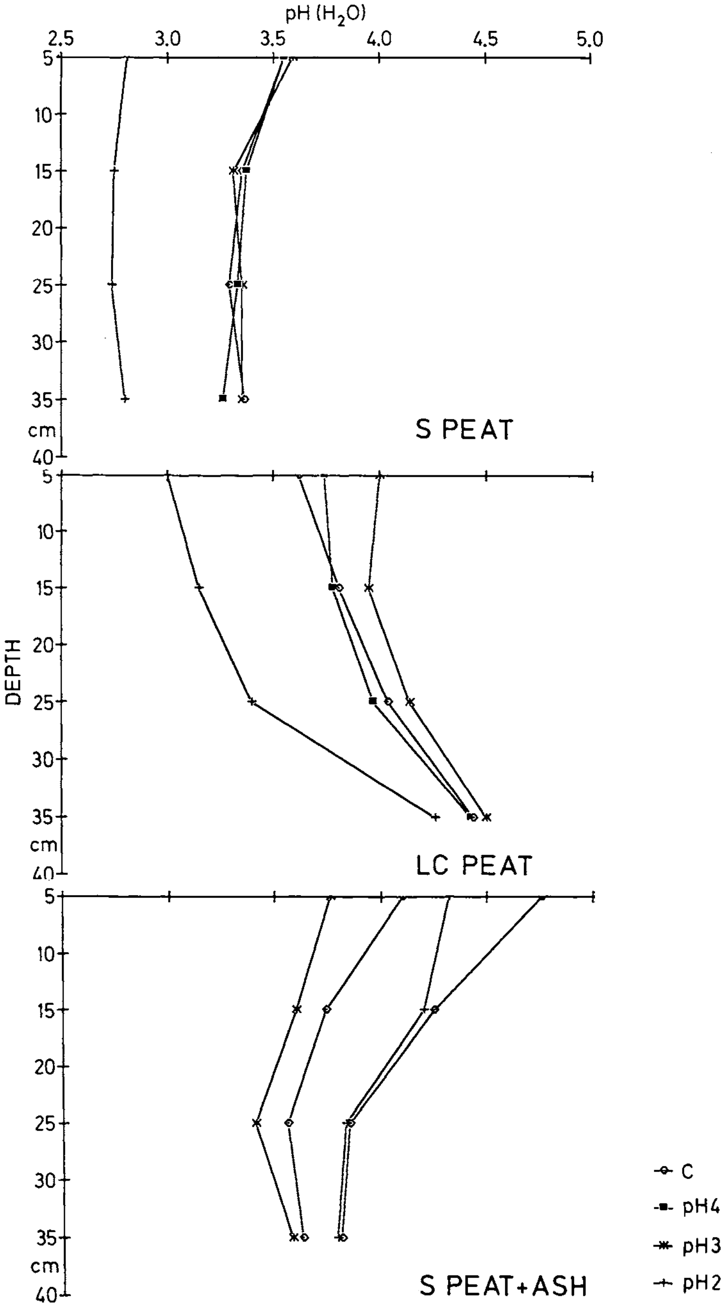

Fig. 3. Vertical distribution of pH (H_2O) in S peat, LC peat and ash fertilized peat after the 16-month irrigation. *4,3,2* indicate the pH of the artificial rain; *C* control

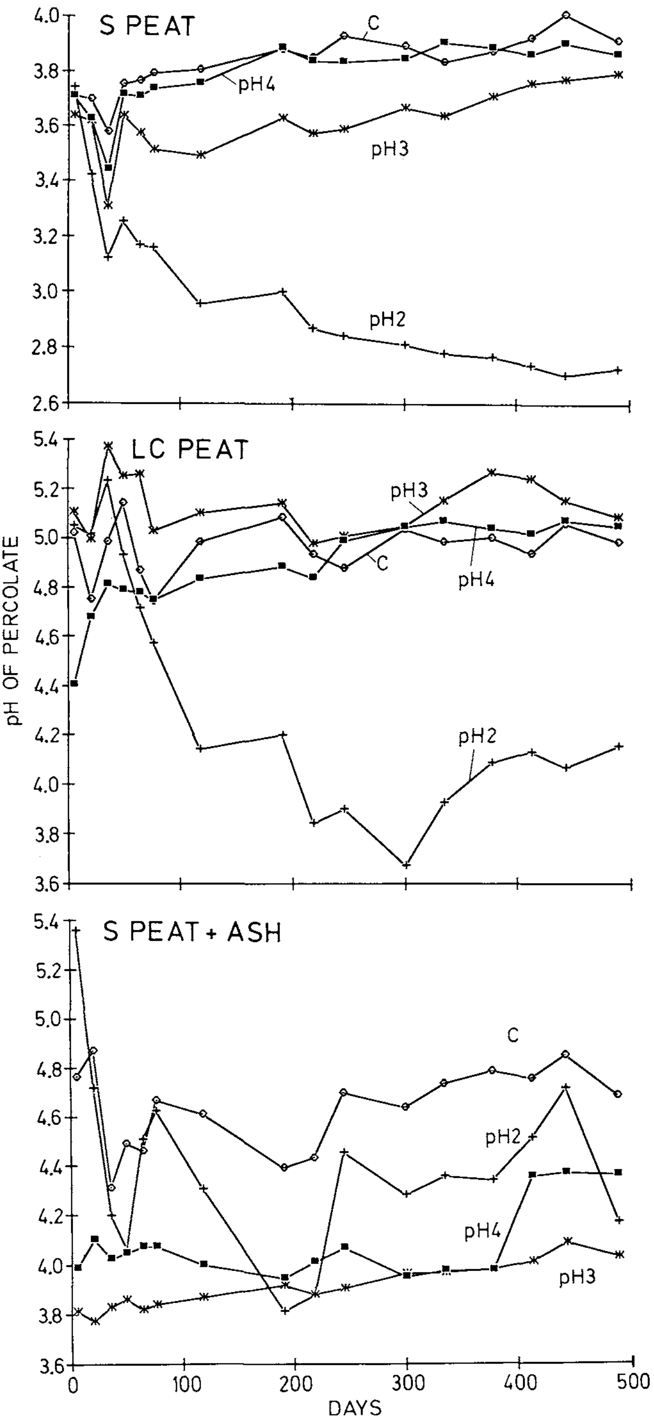

Fig. 4. pH of the percolate from S peat, LC peat and ash fertilized peat profiles during the 16-month irrigation

between 0.7–0.9 meq g^{-1} d.w., and for the ash fertilized peat between 0.4–0.7 meq g^{-1} d.w. Titrated carboxylic H^+ values in the S peat did not correlate very well with PEA, but were of about the same magnitude as PEA (PEA ca. 0.8 meq g^{-1} d.w., titrated H^+ ca. 1.0 meq g^{-1} d.w.).

Base saturation (BS) in the surface (0–10 cm) of the S peat was 15–17%, and decreased to about 10% in the lysimeters irrigated at pH 2. Changes caused by acid irrigation were small in the deeper layers because the original BS of peat was low 7–8%. The BS of the LC peat surface (0–10 cm) fell from 26% to 12% at pH 2, but no corresponding decrease was visible in the other layers. Base saturation in the 0–10 cm layer of the control lysimeters containing ash fertilized S peat was as high as 65%, and in the 30–40-cm layer 20%. Irrigation at pH 2 decreased BS to 28% in the 0–10-cm later but in deeper layers changes could not be detected.

Sulphur Budget

The mean amount of sulphur in the control S peat profiles was 100 g m^{-2}, in the LC peat profiles 284 g m^{-2}, and in the ash-fertilized S peat 86 g m^{-2} (Table 2). The effect of H_2SO_4 irrigation on the sulphur contents of the peat was clear only in the ash fertilized S peat profiles receiving the highest sulphuric acid load (Fig. 5).

The highest sulphur contents normally occurred in the deeper layers, except for the ash fertilized S peat where sulphur was concentrated in the 10–20-cm layer. This was also the layer with the highest calcium content.

Sulphur leaching from the control lysimeters ranged between 0.4 and 0.9 g m^{-2} during the 16-month period. Sulphur added at pH 4 (0.8 g m^{-2}) appears to have passed through the system unaffected (Table 2). At pH 3 (10.6 g S m^{-2} added) 70 to 50% of the added sulphur appears to have been retained. At pH 2 (115.7 g S m^{-2} added) ca. 50% of the added sulphur was retained in the S peat and LC peat, and ca. 70% in the ash fertilized peat. This suggests that the calcium originating from the wood ash was instrumental in retaining the added sulphate.

Comparison of the amounts of sulphur added, retained and present in the peat profiles at the highest H_2SO_4 load with the controls, revealed a deficit in the sulphur budget especially in the case of S peat and LC peat. In some cases, this

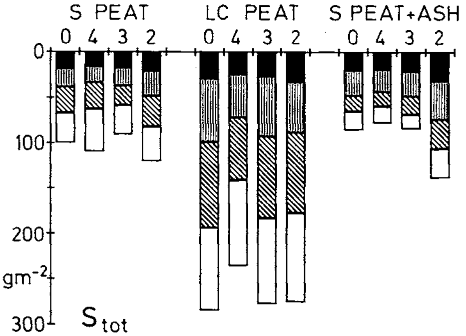

Fig. 5. Total sulphur of S peat, LC peat and ash fertilized peat in different layers

Table 2. Sulphur balance (g S m^{-2}) in S peat, in LC peat and in ash fertilized S peat subject to different sulphuric acid treatments

	Control	pH 4	pH 3	pH 2
S peat				
S in peat	100.0	110.4	91.0	120.6
S added	—	0.8	10.6	115.7
S in leachate	0.4	1.3	3.8	51.5
S deficiency	—	—	?	30–50
LC peat				
S in peat	284.4	240.1	276.9	274.7
S added	—	0.8	10.6	115.7
S in leachate	0.9	2.4	5.3	54.2
S deficiency	—	—	?	20–50
S peat + ash				
S in peat	86.0	78.4	84.2	138.4
S added	—	0.8	10.6	115.7
S in leachate	0.9	1.9	2.8	38.3
S deficiency	—	—	?	15–25

deficit was as much as 20–50 g m^{-2} (in the ash fertilized peat 15–25 g m^{-2}) of the added sulphur. The deficit could not be explained by losses in total S analysis because of the rather small difference between LECO ($\bar{X} = 0.210\%$) and wet combustion S ($\bar{X} = 0.195\%$) determinations.

Cation Budget

Exchangeable bases (Ca, Mg, K, Na) in the peat samples were extracted as "potential exchangeable bases" using neutral 1 M NH_4OAc. The amounts extracted with this method were almost the same as values as obtained with acid 1 M NH_4OAc (pH 4.65) (cf. Vuorinen and Mäkitie 1955). There was also a high correlation between total bases and potential exchangeable bases, the values of exchangeable/total being 0.52 for calcium, 0.73 for magnesium and 0.97 for potassium (cf. Starr and Westman 1978).

Calcium and magnesium accounted for most of the total base content of the peat. Calcium comprised between 70–80% of the total exchangeable bases in the different layers of the S peat, 80–95% of the LC peat and 65–90% of the ash fertilized peat. The proportions for magnesium were 20–25%, 5–15 and 10–30% respectively. The higher amounts of exchangeable magnesium were found in the deeper soil layers of the ash fertilized peat, indicating a higher translocation rate for magnesium compared to calcium, similar to that found in limed mineral soils (Hallbäcken and Popović 1985).

The total amount of exchangeable bases remaining in the peat profiles and the relative leaching losses after treatment with acid indicate the sensitivity of the peat profiles to acidification.

About 30% of the exchangeable base content in S peat, 20% in the LC peat and 12% in the ash fertilized S peat was leached at pH 2, i.e. at an acid input of

Table 3. Total amounts of exchangeable bases (Ca + Mg + K + Na) in peat profiles (0–40 cm) after 16-month irrigation (control, pH levels 4,3,2) and total leaching losses of bases + NH_4 and Fe. Values are in meq m^{-2}. Total leaching losses of bases are also expressed as a percentage of the total amount of exchangeable bases present in the peat of the control lysimeters

	Control	pH 4	pH 3	pH 2
S peat				
Bases in peat (0–40 cm)	5250	5430	4470	3070
Leached Ca	36	41	52	1044
Leached Mg	13	16	24	365
Leached K	12	14	23	60
Leached Na	11	34	25	28
Leached bases total	72	105	124	1497
+ leached Fe^{3+}	59	54	54	849
+ leached NH_4^+	78	100	137	501
Leached total	209	259	315	2847
Leached bases % (vs. control)	1.4	2.0	2.4	28.5
LC peat				
Bases in peat (0–40 cm)	14240	16170	14760	13740
Leached Ca	243	308	360	2523
Leached Mg	22	25	35	294
Leached K	17	15	23	53
Leached Na	13	33	24	23
Leached bases total	295	381	442	2893
+ leached Fe^{3+}	19	17	12	24
+ leached NH_4^+	125	86	159	507
Leached total	439	484	613	3424
Leached bases % (vs. control)	2.1	2.7	3.1	20.3
S peat + ash				
Bases in peat (0–40 cm)	21500	14870	11720	19480
Leached Ca	434	276	241	1868
Leached Mg	155	104	111	594
Leached K	48	35	32	84
Leached Na	27	53	32	40
Leached bases total	664	459	416	2586
+ leached Fe^{3+}	116	121	165	282
+ leached NH_4^+	114	202	232	327
Leached total	849	782	813	3195
Leached bases % (vs. control)	3.1	2.1	1.9	12.0

7233 meq H^+ m^{-2} (115.7 g S m^{-2}). The corresponding values for pH 3 (acid input of 633 meq H^+ m^{-2}, 10.6 g S m^{-2}) were 2.4%, 3.1% and 1.9% which did not differ essentially from those of the control lysimeters (Table 3).

The other main cations (except H^+) in the percolates were iron and ammonium. Leaching of iron from S peat at pH 2 was rather high compared to the leaching of base cations. Ammonium was also exchanged by H^+ or produced and leached as a result of acid catalyzed reactions (cf. Braekke 1978).

Cation/Anion Budget

The cation/anion budget calculated on the basis of the concentrations in the percolate is presented in Table 4. This budget contains several uncertainties; the hydrogen ion loss is based on pH, not on titrations, organic anions (A^-) are determined indirectly, and chloride has not been measured. However, the budget reveals that the organic anions, which were predominant anions in the percolate

Table 4. Cation/anion budget for the percolate from the peat lysimeters during 16 months irrigation (control, pH levels 4,3,2). Values are in meq m^{-2}

	Control	pH 4	pH 3	pH 2
S Peat				
Ca, Mg, K, Na, Fe, NH_4 loss	209	259	315	2847
H^+ loss	88	99	143	658
Total cation loss	297	358	458	3505
Sulphur loss	25	81	238	3219
Organic anion loss	225	228	135	44
Total anion loss	250	309	373	3263
LC peat				
Ca, Mg, K, Na, Fe, NH_4 loss	439	484	613	3424
H^+ loss	8	8	5	41
Total cation loss	447	492	618	3465
Sulphur loss	56	150	331	3388
Organic anion loss	229	196	140	55
Total anion loss	285	346	471	3781
S-peat + ash				
Ca, Mg, K, Na, Fe, NH_4 loss	849	782	813	3195
H^+ loss	29	56	71	60
Total cation loss	878	838	884	3255
Sulphur loss	56	119	175	2394
Organic anion loss	341	374	345	167
Total anion loss	397	493	520	2561

from the control and pH 4 irrigated lysimeters, were partially replaced by sulphate as the acid load increased. This was especially apparent in the percolate from the S and LC peat profiles where A^- loss was of the same magnitude; ca. 230 meq m^{-2} in the control lysimeters decreasing to ca. 140 meq m^{-2} in the pH 3 and to ca. 50 meq m^{-2} in the pH 2-irrigated lysimeters.

The cation/anion budget also reveals that different mechanisms are responsible in the S peat and LC peat for neutralization of the added acid. In the percolate from the S peat, H^+ accounted for about 30% of the total cation loss (except at pH 2), but in the percolate from the LC peat and ash fertilized peat cation losses mainly consisted of basic cations (see also Table 3). This also means that more H^+ are leached out from the S peat profiles compared to the peat of other types.

The transmission of sulphur through the LC profiles was somewhat higher than for the S peat profiles probably because of a higher original S content of the peat. The higher capacity of ash fertilized peat to retain sulphur could be due to inactivation of sulphate by calcium and magnesium. This was also reflected in S retention at pH 3 and pH 2 compared to S peat and LC peat (Table 4).

The deficit of anions, which in the ash fertilized peat was rather high (ca. 700 meq m^{-2}), may partly be due to chloride, which was not analysed.

Discussion

General Remarks

The trends in ion leaching from the peat profiles in this study were rather similar to the lysimeter experiment of Braekke (1978) on oligotrophic *Sphagnum* peat and eutrophic sedge peat. The changes in the peat and percolate quality caused by irrigation by acid were the most pronounced at pH 2 treatment as was expected, and irrigation at pH 4 and pH 3 caused only minor changes in peat or percolate quality. As Braekke (1978) points out, element fluxes in peat are largely governed by sulphur dynamics, which are very complex in waterlogged organic soils.

Sulphur Dynamics

The increase in the peat sulphur content was small and the amount of transmitted and retained sulphur did not balance inputs at high sulphur load – 115 g S m^{-2} (Table 2). Peatlands should be rather effective at retaining sulphate by incorporating it into the organic matrix after reduction by anaerobic sulphate reducing bacteria (Brown 1986; Wieder and Lang 1986), and this mechanism seems to work well at least when smaller amounts of sulphur are added (Brown 1985; Bayley et al. 1986; Urban et al. 1987). One possible reason for the undetermined losses of sulphur in this study could be the release of hydrogen sulphide gas, although Brown and Macqueen (1985) have postulated that the volatilization of H_2S from peat should be insignificant. The undetermined losses of sulphur at the highest acid load (pH 2) ranged between 15 and 50% depending on the peat type and could not be explained by analytical errors. These were higher values than those obtained in Braekke's lysimeter study (Braekke 1978), who reported an undetermined sulphur loss of ca. 17%.

The highest proportions of added sulphur were retained by the ash fertilized profiles, probably as a result of precipitation as calcium sulphate. This assumption is supported by the results from the Finnish liming experiments (Derome and Pätilä this Vol.), although in a Swedish study on the liming of mineral soils, however, no differences in sulphur content were found in either the humus layer or the upper mineral soil layers of the limed plots (Hallbäcken and Popović 1985).

The chemical reduction of sulphate produces alkalinity, which in turn results in elevated pH values in anaerobic peat layers (Ødelien et al. 1975). However, such a phenomenon was not detected in this study. On the contrary, under aerobic conditions, the sulphides and sulphur produced during the breakdown of organic sulphur compounds are oxidized to sulphate and sulphuric acid, which might be an important source of acidity, e.g. in humic lakes (Braekke 1981b; Brakke et al. 1987).

Leaching of Cations

The loss of cations involved in the neutralization of protons in acidic peat soils is dominated by calcium and magnesium (Braekke 1978). High acidity is needed before aluminium is mobilized (cf. Hargrove and Thomas 1981). The leaching of cations is dependent on their adsorption strength which is lower for mono- or divalent alkali and earth-alkali metals than for trivalent metals (cf. Stevenson 1982, p. 325). This was seen as an increased outflow of basic cations (Ca, Mg, K, Na) from the lysimeters irrigated especially with the strongest acid; the outflow of the other metallic cations (Fe, Al, Mn) was small. At pH 2, however, the mobilization of iron from the S peat significantly increased.

Thus the risk of considerable base cation loss or release of inorganic aluminium in toxic amounts from peaty soils at ambient maximum strong acid loads in Finland (ca. 0.025 $\mathrm{eq\,m^{-2}\,a^{-1}}$) is improbable. Even at higher acid load (simulated with irrigation at pH 3 giving 0.663 $\mathrm{eq\,H^{+}m^{-2}}$), the base cation loss should not have any drastic effects on peat soils because the loss is mainly compensated by annual base cation deposition (cf. Hyvärinen this Vol.).

Cation Exchange Capacity and Base Saturation

Cation exchange capacity, exchangeable acidity or base saturation are rather uninformative measures of the acid neutralizing capacity of peat. This is due to the protons, which dissociate from the functional groups of the organic matter as the pH rises, giving higher values for exchangeable acidity and lower values for base saturation in neutral or alkaline solution compared to acidic solution (cf. Helling et al. 1964; Thomas and Hargrove 1984). This difference between "effective"(acidic extraction) and "potential" (neutral or alkaline extraction, used in this study) CEC was also seen when comparing the base saturation values obtained with those of Westman (1981) who measured "effective" CEC. In this study base saturation of the S peat was less than 20%, compared to Westman's 43% for ordinary sedge mires. The reason for this difference is dissociation of H^+. The former value represents a situation where H^+ is mainly dissociated and it should be closer to the "absolute" base saturation value. This is because H^+ in neutral solution was of the same magnitude as the titrated carboxylic total H^+ by the calcium acetate method. Thus, when assessing the buffering capacity of peat, available base reserve should be considered more than method-dependent CEC or base saturation.

Nitrogen and Phosphorus

Although the increased leaching of ammonium as a result of irrigation with acid might be due to ion exchange, it could also be due to acid catalyzed chemical processes which decompose amino compounds (Braekke 1978). In the former case the maximum losses at pH 2 (ca. 7 $g\,m^{-2}$ from S and LC peat) could be significant for the nitrogen economy of peat soils, assuming that less than 1% of the total nitrogen in peat is readily available NH_4–N (e.g. Waughman 1980).

Phosphorus, an essential nutrient in peatland forests, is not leached from peat at ambient acid load. The reason for the mobilization of P in the ash fertilized profiles could be the decrease or total cessation of uptake of phosphate phosphorus by the vegetation caused by the experimental conditions. Similar findings are reported by Haveraaen (1986) from an ash fertilization experiment.

Organic Anions

Leached cations must be balanced by equivalent amounts of anions which, in peatlands, are usually predominantly sulphate, organic anions (A^-) and sometimes also chloride (Gorham et al. 1985; Wieder 1985; Blancher and McNicol 1987). The outflow pattern of sulphur and organic anions clearly showed that A^- dominated over sulphate in the absence of an acid input, but when the acid load was increased A^- was replaced by SO_4^{2-} (Table 4). An opposing cyclic pattern of sulphate and organic anions similar to the one recorded in this study has also been found in the discharge from peat soils (Braekke 1981a) and in coloured streams (Kerekes et al. 1986) where the outflow of sulphur from the watershed is governed by local hydrology. It thus seems possible that runoff from peaty soils in certain conditions may introduce considerable amounts of sulphate and strong acidity into streams and lakes, although under normal conditions weak acids dominate. In areas of high atmospheric sulphur load, the probability of such acid pulses increases although acidification of peat soils would not be expected.

Effect of Ash

Ash fertilization brought about a long-lasting neutralizing effect in the peat which was still clearly evident 50 years after the treatment. These findings are in a good agreement with other studies concerning the effects of ash fertilization on the acidity of peat soils (Merisaari 1981; Silfverberg 1988). If we also consider the increased immobilization of sulphur by ash, liming with ash seems to be a rather effective means of preventing strong acid outflows from peaty soils.

Relevance of the Lysimeter Study

The laboratory lysimeter techniques adopted in this study is subject to criticism because the results are obtained from peat profiles which were isolated from their natural environment. The stabilised groundwater level and the use of deionized water for irrigation are perhaps the most important differences compared to field conditions. A field trial with plots irrigated with either natural rainwater, natural rainwater acidified (H_2SO_4) to pH 3 or natural rainwater acidified (H_2SO_4) to pH 2 was carried out in order to compare results with the laboratory results. The only peat type studied in the field experiment was S peat (as in the laboratory experiment). After irrigation with 630 mm at pH 2 (140 $g\,S\,m^{-2}$ added) the base cation and sulphur content of the peat was of the same order of magnitude as found in the laboratory study with pH 2 treatment (Pätilä unpubl. data). This suggests that results from the laboratory study, at least concerning peat quality, are comparable to field conditions.

Conclusions

Naturally acidic peat soils are rather well buffered against further acidification, judged on the basis of base cation losses. The organic acids produced in peat are the main contributors to the H^+ balance of peaty soils. This is reflected in a high organic anion outflow. Increased sulphur inputs could however, be, retained in the anaerobic layers of peat, and they can be transformed into sulphate. This sulphate displaces organic anions in the outflow, resulting in an increased base cation loss from peat and a mineral acid input into watersheds. Liming of peat with ash will reduce sulphate release from peat, and alleviate the possible adverse effects on watersheds.

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Effects of Nitrogen Inputs on Forest Ecosystems Estimation Based on Long-Term Fertilization Experiments

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Summary

The material consists of 40 fertilization experiments in Scots pine and Norway spruce stands. The total amount of nitrogen applied during a 20-year period averages 315 kg ha^{-1}, which is equivalent to the total atmospheric nitrogen load in central Finland during a single rotation period according to current deposition levels.

Nitrogen addition significantly increased the amount of organic matter and nitrogen in the humus layer. However, the C/N ratio decreased only in surface soil of the pine experiments. Nitrogen addition did not affect soil pH. The concentrations of available base cations did not change to any appreciable extent.

Nitrogen addition caused the greatest relative growth changes on the least productive sites, although the absolute increase was greatest on the sites of medium productivity. On the most productive sites the growth response was negligible.

Introduction

Nitrogen cycling in forest ecosystems is almost completely based on biological processes which are, in turn, regulated by the chemical and physical properties of the soil (Fig. 1). The low rate of decomposition caused by the cool and humid climate and naturally acidic nature of forest soils means that nitrogen cycling in Finnish forest soils is slow. A deficiency of available nitrogen is therefore usually the factor limiting tree growth (e.g. Aaltonen 1926; Viro 1967; Kukkola and Saramäki 1983). Even though forest soils in Finland usually contain large amounts of nitrogen (2000–5000 kg N ha^{-1}), normally only about 1% of this is present in a mineralized form (e.g. Nömmik 1968; Viro 1969). Input and turnover of nitrogen are therefore very important factors for the production and maintenance of forest ecosystems.

Fungi, which are mainly responsible for decomposing organic matter, are important in maintaining a tightly closed nitrogen cycle. The dense mass of fungal mycelia and plant roots effectively prevent the leaching of nitrogen. The amount of nitrogen leached under natural condition in Scandinavia has been estimated as

Kauppi et al. (Eds).
Acidification in Finland

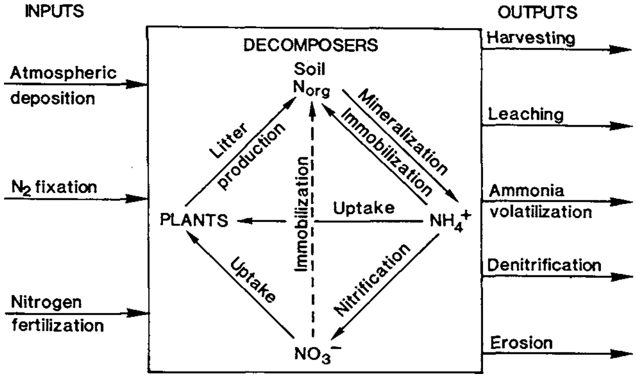

Fig. 1. A simplified model of nitrogen cycling in forest ecosystems. (After Vitousek 1981)

1–2 kg N ha^{-1} a^{-1} (Nilsson and Grennfelt 1988). In undisturbed forest ecosystems leaching losses of nitrogen are lower than the nitrogen input (e.g. Viro 1953).

The frequent forest fires in the past, as well as the silvicultural practice of prescribed burning, considerably influence the nitrogen reserves of forest soils. The nitrogen bound in the burnt material is lost to the atmosphere as gaseous nitrogen. Moreover, owing to the changed physical and chemical properties of the soil, mineralization of nitrogen is increased (Viro 1969). Although the availability of nitrogen for plants is temporarily improved after burning, the risk of nitrogen leaching is increased at the same time.

The amount of atmospheric bulk nitrogen deposition in open collectors is about 10 kg N ha^{-1} a^{-1} in the southernmost parts of Finland, and about 1 kg N^{-1} a^{-1} in the northernmost parts of the country (Fig. 2). The nitrogen load in southern Finland, which is the most important region from the point of view of timber production, is about 5 kg N ha^{-1} a^{-1} (Fig. 2). The trend of nitrogen deposition during the last decades is not very clear (e.g. Järvinen 1986; Rodhe and Rood 1986). Atmospheric deposition contains approximately equal amounts of ammonium and nitrate. During the long winter period the nitrogen deposition accumulates in the snow cover, and about half of the annual nitrogen load passes into the soil in the spring when the snow melts (Helmisaari and Mälkönen 1989).

In forest ecosystems where nitrogen is a growth-limiting factor, an extra input of nitrogen through deposition will increase biomass production (Kenk and Fischer 1988). Further increases in the nitrogen input may alter the biotic composition of ecosystems and may bring about a number of other effects. In forest soils these may include soil acidification, the release of aluminium into the soil solution, and nutrient imbalances.

The complexity of nitrogen turnover makes it difficult to evaluate critical loads for nitrogen deposition. Based on present-day knowledge, a critical load of 3–15 kg N ha^{-1} a^{-1} has been proposed for coniferous forests in Scandinavia (Nilsson and Grennfelt 1988). Nitrogen loads exceeding the critical load are assumed to cause chemical changes in the soil leading to long-term, harmful effects on forest ecosystems, for which natural processes cannot compensate.

No field experiments have been established in Finland with the express purpose of investigating the effects of nitrogen deposition. However, long-term nitrogen fertilization experiments can be used for estimating the changes taking place in forest soils exposed to elevated nitrogen loads. According to Skeffington and Wilson (1988), the major drawbacks of utilizing such experiments in investigating the effects on forest ecosystems are that:

–they do not take into account the direct effects of nitrogen on the foliage,
–nitrogen fertilization is given in relatively large doses at fairly infrequent intervals, and
–the composition of the nitrogen fertilizers is not necessarily the same as that of nitrogen deposition.

It should also be kept in mind that after several nitrogen applications the development stage of the tree stand may differ greatly between control and nitrogen-fertilized plots. This makes it difficult to interpret the current growth differences.

Despite these shortcomings, long-term nitrogen fertilization experiments provide the only means currently at our disposal of obtaining empirical data about changes taking place in the nitrogen balance of forest ecosystems as a result of increased atmospheric nitrogen deposition.

The aims of this study are to determine, through nitrogen fertilization experiments, the long-term changes caused by nitrogen inputs on:

- the chemical composition of the humus layer and uppermost mineral soil layers,
- the reaction of tree stands on sites of naturally varying site fertility in terms of growth and nutrient status.

This information is used to estimate the effect of current levels of nitrogen deposition on nutrient availability and stand development.

Material and Methods

General Features

A total of 40 nitrogen fertilization experiments in Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* (L.) Karst.) stands representing a range of site types were used in this study (Table 1). The experiments were established during the period 1958–1962. General information about the tree stands is given in Appendix 1, and their geographical location in Fig. 2. Although the experiments were laid out using a factorial design employing three or four nutrients, only the data from the control and N-fertilized plots are examined here. The size of the plots was, in most cases, 30 × 30 m^2.

Nitrogen fertilization was repeated several times (Appendix 1) using ammonium sulphate, urea and ammonium nitrate with lime (27.5% N, 4.0% Ca,

Table 1. Distribution of the nitrogen fertilization experiments used in this study according to site type (Cajander 1949) and tree species

Tree species	Site type				
	OMT	MT	VT	CT	Total
Scots pine		12	10	4	26
Norway spruce	8	6			14

Symbols: OMT = *Oxalis-Myrtillus* type
MT = *Myrtillus* type
VT = *Vaccinium* type
CT = *Cladonia* type

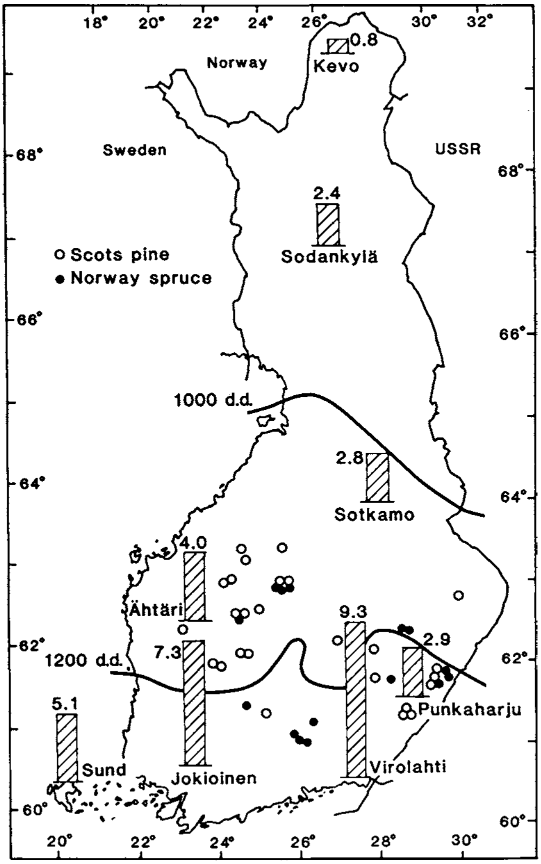

Fig. 2. Location of the fertilization experiments and annual nitrogen deposition (kg $ha^{-1} a^{-1}$) based on data collected in 1986 by The Finnish Meteorological Institute

2.2% Mg). The first nitrogen application was given as ammonium sulphate. Urea was used especially in the first refertilization, and the most recent ones were done with ammonium nitrate with lime.

In many of the experiments the nitrogen fertilizers were applied at shorter intervals at the beginning than at the end of the study period. After the first few years, however, an attempt was made to keep the time interval between refertilizations constant in each experiment. The nitrogen doses used at the time the experiments were established were below 100 kg N ha^{-1}. Since then, the doses have been gradually increased and 180 kg N ha^{-1} was used in the most recent refertilizations.

The mean total amounts of nitrogen applied in the Scots pine and Norway spruce experiments are approximately the same, 310 (range 174–566) and 317 (174–498) kg N ha^{-1} respectively. The distribution between site types is also very even:

	OMT	MT	VT	CT
N	334 (174–498)	304 (174–498)	309 (174–444)	317 kg ha^{-1} (174–566)

Since the ammonium nitrate used in the most recent refertilizations contains 4.0% Ca and 2.2% Mg, the following amounts of Ca and Mg were added to the plots in conjunction with N fertilization:

	OMT	MT	VT	CT
Ca	10.9	9.7	10.9	16.4 kg ha^{-1}
Mg	6.0	5.3	6.0	9.0 kg ha^{-1}

The mean amounts of calcium and magnesium applied are approximately the same in the pine experiments (11.7 kg Ca ha^{-1} and 6.5 kg Mg ha^{-1}) and in the spruce experiments (9.4 kg Ca ha^{-1} and 5.1 kg Mg ha^{-1}).

Soil Samples and Analyses

Soil samples have been taken from these experiments after certain intervals, but not at the time of establishment. The experiments used in this study have been selected so as to provide material representing a time lag of ca. 20 years between establishment and soil sampling.

Samples of the humus layer were taken systematically along three lines running parallel across each plot. Humus samples were taken at 15 sampling points per plot using a sampler with diameter of 56 mm. A total of four mineral soil samples were taken along two transects running from the corners of each plot. The samples represented the 0 to 10-cm-thick mineral soil layer.

The samples were taken to the laboratory, air-dried and weighed. The humus samples were milled to pass through a 1-mm sieve, and the mineral soil samples sieved to remove roots and gravel (>2 mm). The moisture content of the air-dry samples was determined by oven-drying at 105°C.

pH_{KCl} was determined from a slurry consisting of 10 ml air-dry sample and 25 ml of 1.0 M KCl.

Total C, H and N were determined on an automatic CHN analyser (LECO). Organic matter content was calculated by multiplying the carbon content by the Van Bemmelen factor of 1.72.

Available nutrients were extracted by shaking 5 g air-dry humus or 15 g air-dry mineral soil for 1 h (after standing overnight) with 150 ml of 1 N NH_4OAc, pH

4.65. After filtering, Ca, Mg and K were determined by inductively coupled plasma atomic emission spectrophotometry (ICP/AES) (ARL, model 3580 OES).

Needle Samples and Analyses

Needle samples were collected from the same fertilization experiments as the soil samples. Five sample trees per sample plot were selected from the dominant crown layer using a relascope. The needles were collected during the winter, in most cases in March, from among previous years' needles growing in the third to fifth branch whorl (counting from the top) on the southern side of the crown. The samples were taken, depending on the height of the tree, using long-handled pruning shears or by shooting off the branch with a shotgun. The needle samples were analysed separately for each tree in accordance with the methods currently in use at the Finnish Forest Research Institute (Halonen et al. 1983).

Measurement and Calculation of Stand Parameters

The tree stands were measured at intervals of about 5 years. In many cases thinnings were also carried out in conjunction with the measurements.

The breast height diameter of all the trees on the sample plots was measured. Some of the trees were selected as sample trees for estimating the parameters of height and volume equations.

The measurement methods changed somewhat during the study period. When the experiments were being established, the sample trees were selected to represent different diameter classes. From 1963 onwards the sample trees were selected by a relascope. After 1977, the sample trees were selected in most cases using a DBH cumulator (Laasasenaho 1973). In addition, the five tallest trees were taken as sample trees.

Up until 1978 the diameters were measured to an accuracy of 1 cm from one direction, and after that to an accuracy of 1 mm from two directions. The height of the sample trees was measured to an accuracy of 0.1 m.

A function based on breast height diameter and height (Laasasenaho 1982) was used for calculating the volume of the sample trees. The volume increment was calculated as the difference between the volume estimates of successive measurements (the removals being taken into account).

Results

Effect of Nitrogen Fertilization on Soil Properties

Organic Matter

The amount of organic matter in the humus layer of the experimental stands was rather similar on different site types except for the poorest one (Table 2). On the

Table 2. The amount of organic matter in the humus and mineral soil (0–10 cm) layers by site type and tree species ca. 20 years after establishment of the experiments

Site type or tree species	Treatment	Humus layer		Mineral soil		Number of exper.
		Organic matter				
		t ha^{-1}	Change, %	t ha^{-1}	Change, %	
OMT	0	20.6		76.5		8
	N	30.0	+ 58*	86.3	+ 14	
MT	0	23.6		52.8		18
	N	28.3	+ 31**	48.6	− 6	
VT	0	23.2		43.1		10
	N	32.1	+ 55**	42.4	+ 3	
CT	0	12.3		43.6		4
	N	17.6	+ 47***	46.2	+ 13	
Scots pine	0	21.9		44.9		26
	N	28.1	+ 42**	43.8	+ 2	
Norway spruce	0	21.6		70.9		14
	N	29.3	+ 46**	73.7	+ 4	

Statistically significant differences refer to the percentage change compared to the control plots, determined using the t test. The percentage change has been calculated as the mean of the percentage change values for each of the individual experiments.

Symbols: * = significant (5% risk level),
** = very significant (1% risk level),
*** = highly significant (0.1% risk level).

other hand, the uppermost mineral soil layer of the most fertile site types (OMT) contained large amounts of organic matter.

Nitrogen fertilization significantly increased the amount of organic matter in the humus layer of all site types (Table 2). Although the mean amounts of nitrogen given as fertilizer were approximately the same on all four site types, there was considerable variation in the response of the individual experiments. The spatial variation in soil properties is considerable on *Oxalis-Myrtillus* sites, and the effect of nitrogen fertilization on the amount of soil organic matter in this group has probably been overestimated. There was no clear relationship between the magnitude of the change in the amount of organic matter and the amount of nitrogen added as nitrogen fertilizer. Neither were there any differences in response between the pine and spruce stands.

Nitrogen fertilization had no significant effect on the amount of organic matter in the uppermost mineral soil layer.

Total Nitrogen

The mean total amount of nitrogen given as fertilizer was approximately the same as the amount of total nitrogen in the humus layer on the control plots in the pine stands, and about 75% of that in the spruce stands. As would be expected,

Table 3. The amount of total nitrogen in the humus and mineral soil (0–10 cm) layers by site type and tree species ca. 20 years after establishment of the experiments

Site type or tree species	Treatment	Humus layer Total nitrogen kg ha^{-1}	Humus layer Change, %	Mineral soil Total nitrogen kg ha^{-1}	Mineral soil Change, %	Number of exper.
OMT	0	461		1953		8
	N	682	+ 61*	2371	+ 23	
MT	0	384		1148		18
	N	462	+ 33*	1179	+ 7	
VT	0	316		700		10
	N	471	+ 72*	837	+31**	
CT	0	147		786		4
	N	231	+ 61*	811	+24*	
Scots pine	0	310		812		26
	N	425	+ 55***	883	+ 23**	
Norway spruce	0	448		1810		14
	N	595	+ 43**	1976	+ 10	

See Tables 1 and 2 for explanation of symbols.

nitrogen fertilization has therefore brought about a statistically significant increase in the amount of total nitrogen in the humus layer of all the experiments (Table 3). The change in the amount of total nitrogen in the humus layer followed to some extent that for the amount of organic matter.

Although there also appeared to be an increase in total nitrogen in the mineral soil on all sites, only that in the pine experiments was statistically significant.

C/N Ratio

There is a very clear difference between the mean C/N ratio of the control plots in the pine and spruce stands (Table 4). Nitrogen fertilization significantly reduced the C/N ratio in both the humus layer and the uppermost mineral soil layer of the pine experiments. The marked reduction in the C/N ratio in the pine experiments is undoubtedly due to the rather high initial C/N ratios on sites occupied by pine.

The absence of a significant decrease in the C/N ratio on the more productive sites is primarily caused by the fact that the accumulation of organic matter has been matched by an equal rate of accumulation of total nitrogen.

Soil Acidity

Exchange acidity has not been determined on the samples in this study. Although pH_{H_2O} is a widely used parameter, it is only a measure of the concentration of hydrogen ions free in soil solution at the measuring instant, i.e. the effective pH.

Table 4. The C/N ratios in the humus and mineral soil (0–10 cm) layers by site type and tree species ca. 20 years after establishment of the experiments

Site type or tree species	Treatment	Humus layer C/N	Humus layer Change	Mineral soil C/N	Mineral soil Change	Number of exper.
OMT	0	26.1		23.4		8
	N	26.3	+ 0.2	22.1	– 1.3	
MT	0	36.8		29.7		18
	N	35.9	– 0.9	26.6	– 3.1	
VT	0	43.9		41.8		10
	N	40.0	– 3.9*	32.5	– 9.3**	
CT	0	48.7		45.5		4
	N	44.2	– 4.5*	40.8	– 4.7*	
Scots pine	0	42.4		38.2		26
	N	39.1	– 3.3**	31.8	– 6.4***	
Norway spruce	0	28.7		23.4		14
	N	29.8	+ 1.0	22.6	– 0.8	

See Tables 1 and 2 for explanation of symbols.

pH_{KCl} (sometimes called potential pH), which is a measurement of the concentration of exchangeable and free hydrogen ions, provides more information about the total amount of hydrogen ions in the soil and is more comparable to exchange acidity than pH_{H_2O}.

The pH_{KCl} shows that the levels and types of nitrogen fertilizer used here had no significant long-term decreasing effect on the potential pH, irrespective of whether the data are grouped according to site type or to tree species (Table 5).

In order to determine whether the size of the nitrogen dose has had an effect on soil acidity, the regression between total nitrogen dose and the change in hydrogen ion concentration (pH_{KCl}) was calculated separately for each site type. The regression was statistically significant only in the 0–10-cm-thick mineral soil layer of the spruce experiments. The highest total nitrogen application (over 400 kg N ha^{-1}) resulted in a slight decrease in the pH (about 0.1 pH unit) of the uppermost mineral soil layer in the spruce stands.

Base Cations

Although it has not been possible to calculate base saturation values because cation exchange capacity data were not available, the total sum of base cations is used here as an approximate estimate of the base status. Sodium has not been included in total available base cations because the levels of Na in Finnish forest soils are negligible (e.g. Derome et al. 1986). Interpretation of the results concerning the effect of nitrogen fertilization on the amount of base cations (Table 6) is

Table 5. The pH_{KCl} values of the humus and mineral soil (0–10 cm) layers by site type and tree species ca. 20 years after establishment of the experiments

Site type or tree species	Treatment	Humus layer		Mineral soil		Number of exper.
		pH_{KCl}	Change ($H^+ \times 10^{-5}$)	pH_{KCl}	Change ($H^+ \times 1^{-5}$)	
OMT	0	3.46		3.70		8
	N	3.52	− 3.7	3.65	+ 2.1	
MT	0	3.09		3.79		18
	N	3.17	− 14.8	3.84	− 1.9	
VT	0	2.86		3.96		10
	N	2.86	+ 0.6	3.97	− 0.2	
CT	0	2.87		4.29		4
	N	2.78	+ 29.7	4.15	+ 2.0	
Scots pine	0	2.94		3.91		26
	N	2.96	− 5.6	3.92	− 0.4	
Norway spruce	0	3.32		3.73		14
	N	3.33	− 1.9	3.73	− 0.1	

See Tables 1 and 2 for explanation of symbols.

a little difficult because ammonium nitrate used in the most recent refertilizations contains some calcium and magnesium.

Nitrogen fertilization significantly increased the amount of available Mg in the humus layer of the pine and spruce experiments. Although there is a similar increase in the amounts of Ca, the change is statistically significant only in the pine experiments. Both Ca and Mg have been added in small amounts with the nitrogen fertilizer, but the overall increase in the amount of these elements in the humus layer was much larger than that added in the fertilizer. The amount of potassium also increased significantly in the humus layer of the pine and spruce experiments. The increase in total available base cations is correspondingly statistically significant on all the site types. The amounts of basic cations in the uppermost mineral soil layer have remained fairly constant (Table 7).

Effect of Nitrogen Fertilization on the Nutrient Status of the Trees

The foliar nutrient analyses depict the nutrient status of the trees on the average 20 years after establishment of the experiments. Since nitrogen has been applied at different doses at varying intervals in the experiments, it is difficult to estimate the effect of nitrogen fertilization on the nutrient status of the trees.

The results presented here represent the foliar nutrient concentrations at least 5 years after the last refertilization, and hence only long-lasting effects will still be visible (Tables 8 and 9). Nitrogen fertilization significantly increased foliar nitrogen concentrations only on the least productive site type. The significant increase in magnesium concentration is connected with the small amounts of magnesium

Table 6. Total amounts of available base cations Ca, K and Mg in the humus layer

Site type or tree species	Treat-ment	Ca kg ha^{-1}	Change, %	K kg ha^{-1}	Change, %	Mg kg ha^{-1}	Change, %	Ca + K + Mg keq ha^{-1}	Change, %	Number of exper.
OMT	0	134		22.7		12.8		8.52		8
	N	214	+ 73*	32.8	+ 61*	21.5	+ 91*	13.28	+ 74*	
MT	0	99		28.3		11.0		6.57		18
	N	118	+ 30	31.8	+ 15*	14.2	+ 41	7.87	+ 29*	
VT	0	56		24.2		8.1		4.25		10
	N	80	+ 62**	27.4	+ 22*	10.9	+ 73**	5.61	+ 55*	
CT	0	17		10.1		2.6		1.33		4
	N	26	+ 42	16.3	+ 62	4.1	+ 68	2.06	+ 49*	
Scots pine	0	72		22.9		8.4		4.85		26
	N	95	+ 47**	26.4	+ 24*	12.0	+ 62**	6.42	+ 45**	
Norway spruce	0	120		26.7		12.6		7.70		14
	N	169	+ 49	35.4	+ 43*	18.1	+ 60*	10.82	+ 50*	

See Tables 1 and 2 for explanation of symbols.

Table 7. Total amounts of available base cations Ca, K and Mg in the mineral soil (0–10 cm) layer

Site type or tree species	Treat-ment	Ca kg ha^{-1}	Change, %	K kg ha^{-1}	Change, %	Mg kg ha^{-1}	Change, %	Ca + K + Mg keq ha^{-1}	Change, %	Number of exper.
OMT	0	287		42.0		40.8		1.88		8
	N	329	+ 25*	49.2	+ 15*	51.0	+ 48*	2.19	+ 29**	
MT	0	160		35.8		19.2		1.05		18
	N	120	− 17	34.8	1	16.5	− 4	0.82	− 15	
VT	0	65		26.8		9.3		0.47		10
	N	58	− 5	26.1	− 2	9.6	+ 4	0.44	− 3	
CT	0	20		26.7		5.2		0.21		4
	N	23	+ 16	26.9	+ 5	7.9	+ 47	0.25	+ 18	
Scots pine	0	115		29.3		13.0		0.75		26
	N	91	− 6	30.0	+ 4	13.1	+ 12	0.64	− 4	
Norway spruce	0	205		42.0		31.6		1.39		14
	N	220	+ 8	43.1	+ 2	35.1	+ 17	1.49	+ 8	

See Tables 1 and 2 for explanation of symbols.

Table 8. Dry weight and nutrient concentrations of Scots pine needles. Sampling ca. 20 years after establishment of the experiments

Site type	Treatment	Dry wt. of 1000 needles, g	N	P	K	Ca	Mg	B	Number of exper.
					$g\ kg^{-1}$			$mg\ kg^{-1}$	
MT	0	13.9	12.4	1.46	4.93	2.24	1.07	11.3	12
	N	15.1	12.8	1.46	4.95	2.22	1.05	10.2	
VT	0	12.7	12.4	1.45	4.98	2.23	1.09	13.0	10
	N	13.1	12.6	1.37*	4.63*	2.17	1.13	7.2**	
CT	0	11.0	11.5	1.27	5.03	2.29	0.99	16.0	4
	N	13.0*	12.6**	1.34	4.38**	2.12	1.17***	10.0***	

See Tables 1 and 2 for explanation of symbols.

Table 9. Dry weight and nutrient concentrations of Norway spruce needles. Sampling ca. 20 years after establishment of the experiments

Site type	Treatment	Dry wt. of 1000 needles, g	N	P	K	Ca	Mg	B	Number of exper.
					$g\ kg^{-1}$			$mg\ kg^{-1}$	
OMT	0	4.1	14.1	1.76	4.86	5.62	1.46	6.0	7
	N	4.3	14.0	1.74	4.77	5.88	1.45	6.1	
MT	0	3.9	12.6	1.73	4.78	4.23	1.31	6.2	6
	N	3.7	12.5	1.73	4.32	4.89	1.50*	6.5	

See Tables 1 and 2 for explanation of symbols.

added in refertilization. The "dilution effect", which is frequently observed in stands given nitrogen fertilization during their maximum growth stage, was clearly apparent as decrease in the boron concentrations in the pine stands.

Effect of Nitrogen Fertilization on Stand Growth

The effect of nitrogen addition on tree stand production was examined on the basis of the total volume growth following establishment of the experiments (Table 10). The varying production capacity of the different sites was clearly evident in the results. The most fertile sites produced 213 $m^3 ha^{-1}$ during the 20-year period, and the least productive only 14% of this level, i.e. 31 $m^3 ha^{-1}$. The greatest relative growth increase was found on the least productive sites. The absolute growth reaction was, however, the greatest on medium sites, i.e. on VT and MT sites. On the most fertile sites the effect of nitrogen addition was negligible. The growth reaction of spruce stands was lower than that of pine stands, which is partly due to the site type distributions (see Table 1).

Discussion

General Remarks

The material is, as regards nitrogen application, rather heterogeneous owing to the variation in intensity and type of fertilizer applied during the course of the

Table 10. Volume growth by site type and tree species during the ca. 20 years period after establishment of the experiments

Site type or tree species	Treatment	Volume growth $m^3 ha^{-1} a^{-1}$	Volume growth Relative difference, %	Number of exper.
OMT	0	10.64		8
	N	10.75	5	
MT	0	6.05		18
	N	7.84	32***	
VT	0	4.66		10
	N	6.06	35**	
CT	0	1.54		4
	N	2.67	147	
Scots pine	0	4.71		26
	N	6.27	51**	
Norway spruce	0	8.88		14
	N	9.68	16	

See Tables 1 and 2 for explanation of symbols.

experiments. The total amount of nitrogen added is not very large, but corresponds approximately to the current nitrogen deposition load during one rotation period in the area where the experiments are situated. Although the results obtained from these experiments cannot be directly compared to the effects of nitrogen deposition on forest ecosystems, it can be assumed that fertilizer nitrogen and nitrogen deposition would have a similar effect on many processes in forest soil. Further variation is caused by the fact that no soil data are available for the time when the experiments were established, but this has been partly compensated for by the relatively large number of experiments.

Changes in the Soil

Nitrogen addition has brought about a considerable increase (over 30%) in the amount of organic matter in the humus layer, but no change in the uppermost mineral soil layer. The trend is the same in both the pine and spruce experiments on all site types.

The amount of organic matter in the soil is affected by the amount and quality of the litterfall and the activity of the decomposing microorganisms (e.g. McClaugherty and Berg 1987). The increased biomass production brought about by nitrogen addition leads to increased litterfall with a time lag of 2 to 4 years in the case of pine, and 6 to 8 years in spruce (Albrektson et al. 1977). Nitrogen fertilization can also increase the litterfall of the ground vegetation already during the year of application, although this component is usually of less importance as a litter producer (e.g. Mälkönen 1974). The increase in the litterfall from the ground vegetation may be especially significant in the pine stands.

Nitrogen fertilization has been found to change the composition of the decomposers to such an extent that the rate of decomposition of organic matter may even decrease (e.g. Bååth et al. 1981; Söderström et al. 1983; Fog 1988). However, the results presented refer to studies made under varying conditions with different amounts and types of nitrogen fertilizer (e.g. Schalin 1967; Salonius and Mahendrappa 1975). In contrast to urea applications, ammonium salts appear to decrease microbial activity in the humus (e.g. Roberge 1976). The plots in this study have received both types of nitrogen fertilizer: ammonium salts [$(NH_4)_2SO_4$, NH_4NO_3] and urea at different times.

Nitrogen fertilization significantly increased the amount of total nitrogen in the humus layer on all site types. Total nitrogen in the uppermost mineral soil layer of the pine experiments also increased significantly. Studies carried out with ^{15}N have shown that the vegetation utilizes only a relatively small proportion of the N added as fertilizer and most of it is immobilized in an organic form in the different layers of forest soil (e.g. Melin and Nömmik 1988). Most of the fertilizer nitrogen taken up by the vegetation is gradually returned to the humus layer in the litterfall. More of the nitrogen given as urea is immobilized in the soil than that applied as ammonium nitrate (Melin and Nömmik 1988).

The proportion of organically bound nitrogen that is mineralized as nitrate is of decisive importance from the point of view of the risk of soil acidification and nitrogen leaching. The ability of soil to nitrify depends on several factors, of which the C/N ratio of the organic matter may be the most important (Gundersen and Rasmussen 1988). It would appear that relatively infertile soils with a C/N ratio of > 25–30 in the humus layer are unable to nitrify (Zöttl 1960; Kriebitzsch 1978). The C/N of the humus layer on the control plots of only the most fertile sites included in this study were below this critical limit. On the other hand, nitrogen fertilization decreased the C/N ratio on the least fertile sites. It would thus appear that there is little likelihood of nitrification taking place following nitrogen fertilization in these conditions. However, the accumulation of nitrogen in forest soil may subsequently increase nitrogen mineralization and the risk of nitrate leaching after final cutting (Wiklander 1981).

The effect of nitrogen addition on soil acidification depends on the conditions prevailing in the soil, as well as on the type of nitrogen compounds applied (e.g. Binkley and Richter 1987). Of the nitrogen fertilizers used in these experiments, ammonium sulphate is considered to have a strong acidifying effect. In theory, ammonium nitrate should also have an acidifying effect in forest soils, primarily through the leaching of accompanying base cations (Nömmik and Wiklander 1983). In contrast, urea is considered to have no acidifying effect, especially in naturally acidic forest soils.

According to the results of this study, nitrogen addition has had no significant effect on the pH_{KCl} of the humus or uppermost mineral soil layers on any of the site types in either the pine or spruce experiments. Annual nitrogen additions of 60–80 kg N ha^{-1} over 14 years increased the pH of the humus layer, but acidified the mineral soil (Tamm and Andersson 1989). In this case there was little difference if the nitrogen was given as ammonium nitrate or urea.

Nitrogen fertilization increased the amounts of available base cations (Ca, K, Mg) in the humus layer, but had no appreciable effect on their concentrations. Thus the addition of nitrogen has apparently no negative effect on base cation availability.

Nutrient Status of the Trees

Normal levels of nitrogen fertilization usually increase the needle nitrogen concentration for a period lasting for a few years, without having any clear effect on the concentration of the other macronutrients. Needle phosphorus concentrations in the spruce stands were acceptable, but in order to achieve a satisfactory growth increase on the most fertile spruce sites, phosphorus must be given together with nitrogen (Kukkola and Saramäki 1983).

The clearest detrimental effect of nitrogen fertilization on the nutrient status of tree stands growing on mineral soils is the "dilution effect" on micronutrients (e.g. Alberktson et al. 1977; Möller 1983). Growth disturbances caused by this phenomenon are mainly restricted to northern Finland. The growth disturbances recorded in young, fertilized pine stands take the form of leader damage of various degree, or merely needle browning. Young pine stands in the vigorous growth stage are clearly more susceptible than mature stands. No damage symptoms of this sort have been found in mature stands. The cause of these growth disorders is considered to be deficiency of boron (e.g. Aronsson 1983), since there is a significant decrease in needle boron concentrations with increasing levels of N fertilization. A needle B concentration of about 5 mg kg^{-1} is considered to be the limit below which there is a risk of damage.

Stand Growth

The growth reaction to nitrogen fertilization varied considerably between different sites and tree stands. On the most fertile sites the response to nitrogen fertilization was negligible or even negative. However, these have shown a positive response to NP applications (Kukkola and Saramäki 1983). The increased nitrogen availability following fertilization increased growth the most on the medium sites of fertility. The greatest relative change in stand growth after nitrogen addition was obtained on the least productive sites. Although the relative response of individual trees was considerable, the total growth response remained small. The accumulation of humus following nitrogen additions may be especially beneficial for productivity on dry site types.

There is also variation between the responses to subsequent fertilizations in the same stand. The pattern of this variation depends on the development stage of the tree stand and the nitrogen status of the site. In young stands the volume growth response to subsequent fertilizations increases with time due to increasing stand volume and amount of foliage. Finally, however, the optimum level is reached and the productivity of fertilization starts to diminish. In old stands the growth and also the growth response to subsequent nitrogen fertilizations are diminishing slowly.

Conclusions

The effects of nitrogen fertilization on forest ecosystems are not directly comparable to the effects of nitrogen deposition. From the point of view of the forest soil, however, the effects of adding nitrogen as either fertilizer or nitrogen deposition may be similar. The main difference naturally lies in the dynamics of the changes in soil processes. This aspect cannot, however, be examined on the basis of this material.

In nitrogen-deficient forest ecosystems where nitrogen deposition has a fertilizing effect, the amount of organic matter in the humus layer will increase. This increase in the humus reserves can be considered to be beneficial for the nutrient status and water regime of the soil, especially on dry and relatively infertile sites.

A high proportion of the nitrogen added to forest ecosystems accumulates as organically bound nitrogen in the humus layer. The mineralization of this nitrogen may, however, increase to an appreciable extent following final cutting, when the risk of nitrate leaching will also be greater. The nitrogen doses used in this study did not have any detrimental effects on pH or the amounts of base cations in the humus layer and uppermost mineral soil. However, the stage following final cutting may be decisive also in this respect.

The growth reaction of the tree stand to nitrogen applications is connected to the natural fertility of the site and the development stage of the stand. Nitrogen addition caused the greatest relative growth increase on the least productive sites. However, the absolute growth increase was greatest on the medium sites, where the added nitrogen is better utilized by the larger biomass and better availability of water. On the most fertile sites the trees are not nitrogen-deficient and the growth reaction of the tree stand is negligible.

Appendix 1. Information about the experimental stands in the year when fertilized

Exp. No.	Location					Climate 1941–70		Site					Tree stand					Date of first fertilization	Study period	N applications
	N		E		Alt. a.s.l.	Temp. sum	Precp.	H_{100}	Fert. class	Soil texture class		Humus layer	Age	Stem number	H_{dom}	V	I_v			
	°	′	°	′	m	d.d.	mm	m				cm	a	per ha	m	m^3ha^{-1}	$m^3ha^{-1}a^{-1}$		a	
Scots pine stands																				
26	61	24	25	2	115	1226	553	26	3	FS	M	3.2	12	2647	2.7	1.1	6.8	25.6.58	20	4
33	61	52	29	20	80	1245	585	27	3	CS	M	5.5	20	3822	8.1	32.9	4.7	10.6.59	22	6
37	61	25	28	32	90	1207	580	20	4	FS	S	2.3	25	4286	5.5	18.1	3.8	13.6.59	20	2
38	61	25	28	32	100	1200	580	22	4	CS	S	2.6	25	3611	6.5	19.9	4.1	13.6.59	20	2
52	62	1	24	48	120	1184	589	27	3	FS	S	2.2	9	2860	1.6	0.5	5.2	3.7.59	19	4
53	62	4	24	29	150	1172	587	26	3	CS	S	5.3	12	2833	2.4	1.3	6.3	23.7.59	19	4
55	61	39	29	18	90	1222	581	27	3	FS	S	3.6	14	3289	3.6	5.4	8.5	7.7.59	19	2
56	62	56	25	36	170	1072	574	22	4	FS	M	2.2	27	2136	7.5	25.52	3.6	11.7.59	19	4
59	62	55	25	29	165	1079	578	26	4	CS	M	9.3	34	702	13.4	59.0	5.1	15.7.59	19	4
64	61	29	29	4	90	1224	580	20	5	CS	M	1.8	33	1912	8.7	22.9	3.8	23.7.59	19	2
67	61	32	29	4	120	1203	579	20	4	FS	S	4.6	24	2361	4.7	7.8	7.0	7.8.59	19	2
68	61	57	27	34	120	1081	585	20	4	CS	M	3.6	35	2431	9.9	45.8	7.2	11.6.60	18	3
69	62	17	27	37	115	1136	571	27	3	CS	M	2.8	10	2650	2.0	1.1	5.1	13.6.60	18	3
71	62	12	27	25	105	1149	580	21	4	FS	S	2.5	17	2303	2.4	1.3	3.0	14.6.60	18	3
73	62	46	24	45	200	1062	586	26	3	FS	M	1.5	6	2596	0.7	0.2	4.4	17.6.60	18	3
82	63	17	25	21	185	1044	517	17	5	FS	S	1.4	10	8935	0.8	0.4	0.5	2.7.60	21	3
97	62	34	24	7	170	1098	571	26	3	CS	S	2.8	13	2703	2.7	3.2	6.5	9.6.61	20	2
98	62	34	24	7	170	1098	571	26	4	FS	M	1.7	12	3173	2.6	3.3	5.1	10.6.61	20	4
100	62	0	23	42	175	1123	576	26	3	FS	M	2.2	9	4638	2.0	2.2	4.6	29.5.61	20	2
101	62	0	23	41	175	1123	576	26	3	FS	M	2.8	9	5223	1.8	2.4	5.6	30.5.61	20	2
103	63	12	24	37	180	1039	516	23	4	CS	S	2.1	10	3722	1.2	0.3	2.1	7.6.61	20	2

Appendix 1. (contd.)

Exp. No.	Location					Climate 1941–70		Site				Tree stand						Date of first fertilization	Study period	N applications
	N		E		Alt. a.s.l.	Temp. sum	Precp.	H_{100}	Fert. class	Soil texture class		Humus layer	Age	Stem number	H_{dom}	V	I_v			
	°	′	°	′	m	d.d.	mm	m				cm	a	per ha	m	m^3ha^{-1}	$m^3ha^{-1}a^{-1}$		a	
106	63	23	24	17	160	1040	490	15	5	CS	S	1.2	25	2303	3.7	1.9	1.2	5.6.61	20	5
107	63	6	24	16	180	1041	523	16	5	FS	S	1.0	15	2548	2.2	0.8	0.7	8.6.61	20	2
108	63	0	24	12	195	1035	529	24	4	CS	S	2.9	15	2514	4.3	5.7	5.6	8.6.61	20	4
110	62	27	22	38	145	1105	533	27	3			3.2	7	2606	1.8	0.9	4.3	15.6.61	20	2
131	62	48	30	26	170	1070	598	25	3	FS	S	1.6	45	636	16.5	97.3	8.0	1.6.62	18	3
Norway spruce stands																				
31	61	51	29	22	85	1251	585	28	2	FS	S	3.6	26	1797	7.9	21.9	12.4	11.6.59	21	5
34	61	54	28	16	130	1120	576	25	3	FS	S	4.0	22	1948	4.7	3.7	8.1	12.6.59	20	2
35	62	24	28	42	120	1183	581	22	3	FS	M	3.5	27	2197	3.6	4.0	6.6	15.6.59	20	2
36	62	24	28	42	120	1183	581	23	3	FS	M	3.1	27	1186	3.8	3.2	5.8	15.6.59	20	2
57	62	56	25	41	200	1051	572	22	3	FS	M	3.9	28	1836	4.3	3.4	4.7	14.7.59	19	4
58	62	56	25	41	195	1054	572	23	3	FS	M	2.8	26	1634	4.8	4.8	7.3	14.7.59	19	4
60	62	56	25	40	200	1051	572	24	3	FS	M	4.8	28	1881	6.1	13.6	6.8	16.7.59	19	4
66	61	34	29	8	140	1194	579	28	2	FS	M	4.0	21	1375	4.3	3.9	10.4	8.8.59	19	2

111	61	11	26	1	130	1238	583	30	2	FS	S	2.6	50	800	20.3	200.1	8.9	20.6.61	18	3
113	61	10	26	3	115	1249	585	28	2	FS	M	1.5	12	1980	1.6	0.4	5.1	13.6.61	17	4
121	62	30	24	22	190	1083	588	21	4	FS	M	4.2	28	3277	5.6	15.6	4.3	6.7.61	19	5
138	61	25	24	24	110	1237	543	28	2	FS	M	1.3	30	2658	8.9	53.8	14.1	28.5.62	20	4
152	61	12	26	0	100	1260	582	32	1	FS	M	2.8	31	1830	12.7	109.0	18.9	19.7.62	19	2
155	61	10	26	2	120	1244	584	29	2	FS	M	3.9	13	2103	1.6	0.3	6.4	13.7.62	20	3

Temperature sum:

Estimated annual effective temperature sum (d.d.) based on the effective minimum temperature 5°C.

Fertility classes:

1 = grove (*Oxalis-Maianthemum* type)
2 = grove-like site (*Oxalis-Myrtillus* type)
3 = moist site (*Myrtillus* type)
4 = dryish site (*Vaccinium* type)
5 = dry site (*Calluna* type)

Abbreviations for the soil texture classes are as follows:

FS = Fine sand 0.02–0.2 mm,
CS = Coarse sand 0.2–2.0 mm,
M = till,
S = sorted.

Stem number, dominant height (H_{dom}) and volume (V) are mean values from plots. Iv is the mean volume growth during the course of the experiments on the control plots.

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2.2 Soil Microbiology

Microbiological and Chemical Properties of the Forest Humus Layer at Four Sites in Southern Finland

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Summary

The current microbiological and nutrient status of the humus layer of four forest site types, Myrtillus (MT), Oxalis-Myrtillus (OMT), Vaccinium (VT) and Calluna (CT) types in southern Finland were determined during two growing seasons. C/N ratio was highest, pH lowest on the poorest, CT, site. The nutrient content between sites differed clearly, year to year variation was normal. The physiological capacity of microorganisms was more complex in early summer than in the autumn in 1987. In 1988, the pattern was reversed except for the CT site. Seasonal variation in microbial and fungal amounts and activity was alike in both years. The weekly microbiological dynamics reflected the variation in humus moisture and temperature. This emphasizes the importance of sampling time and frequency in the future screening of the impact of acid atmospheric load, i.e. factors other than climatic, on the microbiological characteristics of the forest humus layer.

Introduction

Bacteria and fungi are key components in the biochemical turnover of plant nutrients in the soil, and the productivity of the forest ecosystem is thus highly dependent on the diversity and the rates of soil microbial processes.

An important hypothesis concerning the effects of acid load on forest soils is that it affects the functions of micro-organisms. Changes in the decomposition of organic matter and turnover of C and N may alter the release and availability of plant nutrients (e.g. Abrahamsen et al. 1976; Tamm 1976; Bååth et al. 1978; Hovland et al. 1980; Strayer et al. 1980; Firestone et al. 1984).

Our knowledge of the effects of increasing rates of acidification on the soil microbiota in northern coniferous forest soils is still limited. Most reports on this topic deal with simulated soil acidification experiments done in controlled laboratory or field conditions (e.g. Bååth et al. 1980; Hovland et al. 1980; Killham et al. 1983; Lee et al. 1983; Bewley et al. 1983a). The parameters of microbial activity commonly dealt with in such experiments include respiration, decomposition of leaf or needle litter, the nitrogen cycle, enzyme activities, and bacterial and fungal numbers and biomass. However, no common pattern has yet been noted

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with regard to the response to acidification. The conflicting data about specific microbial processes from many experiments are most probably due to differences in experimental design (i.e. intensity of acid treatment, anionic component, soil type etc.).

The results from intensive, short-term acidification experiments cannot be extrapolated to predict the long-term effects of actual acidic precipitation in the field because the interactions between soil acidity and microbial, chemical, and physical components of the soil are extremely time-dependent. Effects observed in accelerated treatments may not occur at the slower ambient rates of acidification.

The lowering of soil pH attributable to acid atmospheric input is one obvious way in which micro-organisms are affected. Other effects of an increased acid load are still inadequately documentated, but the mobilization of toxic metals including aluminium may be the most important. Aluminium inhibits the germination of fungus spores (Ko et al. 1972) and has a detrimental effect on soil bacteria (Zwarun et al. 1971). Cadmium and zinc may also have a similar effect (Bewley et al. 1983b). Even if changes in the overall acidity of soil cannot be recorded, a shift in the pollution pattern (i.e. decreasing SO_2 levels, increasing NO_x levels) may nevertheless affect the activities of soil micro-organisms (Söderström et al. 1983).

Very acid soils are thought to have stable acidophilic microbial populations and they may also cope better with "natural" acidification, i.e. the long-term input of small amounts of hydrogen ions (Wainwright 1980). According to Alexander (1980), the elimination of the activity of one heterotrophic population by a stress factor will most probably result in its replacement by another population that is not affected by this stress factor, or is adapted to it. Such a change is not necessarily harmful. On the other hand, if only a single bacterial population is responsible for carrying out a specific process (e.g. nitrification), the depression of the population responsible for that process could have serious consequences for the whole ecosystem.

The aim of this study is to establish base level data for judging acidification effects in the future. The current microbiological properties of forest humus layers of varying chemical composition at four sites subjected to continuous, intensive, and comprehensive monitoring have been investigated using clearly defined bacterial and fungal parameters. The results from 2 years are presented in this chapter. The emphasis in this study is mainly on microbiological dynamics with reference to qualitative and quantitative characteristics. A comparison of the microbiological dynamics during 2 consecutive years is briefly outlined. Follow-up studies on the same sites may subsequently reveal changes in the qualitative and/or quantitative parameters of the microbial populations which may possibly be addressed to shifts in the chemical status of the humus layer.

Material and Methods

Experimental Plots and Sampling

General Description

Humus samples were collected from four of the permanent sample plots established by the Finnish Forest Research Institute as part of the ILME Project (Effects of Air Pollutants on Forest Ecosystems). All four plots are situated in southern Finland on iron podzolic soil (Fig. 1), and cover the range of important forest site types (Table 1).

Ten humus samples were taken systematically from each plot with a soil auger (50 mm in diameter) at monthly intervals during two successive growing seasons : 18.5.1987–12.10.1987 and 3.5.1988–24.10.1988 (Fig. 2). In 1988, sampling on the MT plot started immediately after snowmelt but before the humus layer had completely thawed (i.e. 3.5.1988). It continued weekly until the end of June and terminated in mid-October (17.10.1988) after occasional snowfalls when the humus layer started to freeze (Table 2). The samples were transported within 1 day to the laboratory in insulated boxes. Parts of the samples were used for the determination of pH, dry weight, nutrient analyses, and the microbial screening, while the reminder was frozen to be used as reference material for future studies.

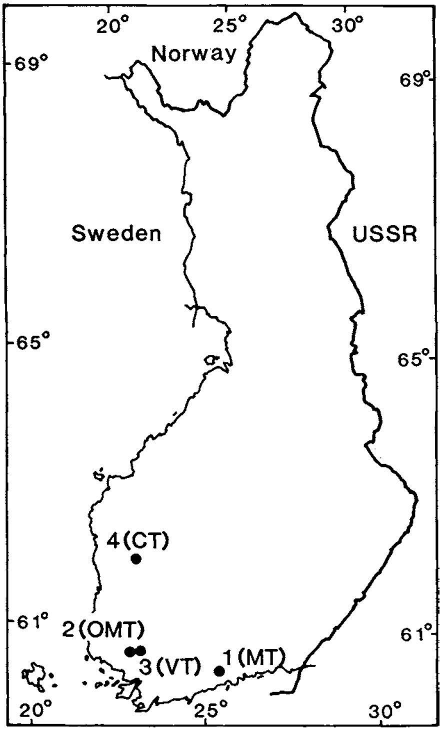

Fig. 1. Geographical location of the experimental plots representing four different forest site types (see Table 1)

Table 1. Characteristics of the four experimental forest site types in southern Finland used for studying soil microbiota

Plot	Location	Site type	Dominant tree species	Age of the tree stand, a	Soil texture class	Humus layer Type	Humus layer Thickness, cm
1	60°21'N 25°00'E	MT	*Picea abies* (55%), *Pinus silvestris* (12%), *Betula* sp. (33%)	65	Fine sand	Moder	4
2	60°55'N 23°11'E	OMT	*Picea abies* (66%), *Betula* sp. (34%)	60	Sand moraine	Mor	4
3	61°04'N 23°10'E	VT	*Pinus silvestris* (100%)	25	Sand moraine	Mor	5
4	61°45'N 22°44'E	CT	*Pinus silvestris* (100%)	95	Coarse sand	Mor	2

For the geographical location of plots, see Fig. 1
Symbols: MT = Myrtillus type, OMT = Oxalis-Myrtillus type, VT = Vaccinium type, CT = Calluna type (Cajander 1949)

Table 2. Number of humus layer sampling times for each plot during 1987 and 1988

Plot and site type		May	June	July	August	September	October
1 MT	1987	1		1[a]	1	1	1
	1988	5	4		2	1	2
2 OMT	1987	1	1	1	1	1	
	1988	1	1		1	1	1
3 VT	1987	1	1	1	1	1	1
	1988	1	1		1	1	1
4 CT	1987	1	1	1	1	1	1
	1988	1	2		1	1	1

[a] Results shown in Fig. 8.

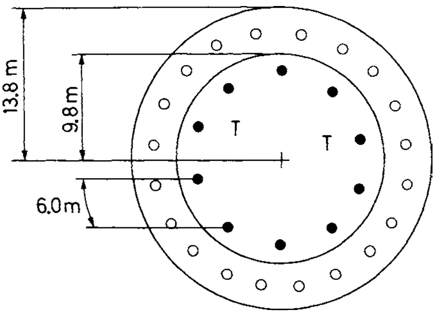

Fig. 2. Design of the humus sampling area. ● = sampling site located 20 cm in from the boundary of the permanent sample plot at 6 m distance from each other. *T* = thermographs; O = rainwater gauges

Soil Properties and Climatic Data

The humus samples were analysed for total nitrogen and carbon by the dry combustion method (LECO). Ammonium acetate (pH 4.65) extractable P, K, Ca, Mg, Na, S, Mn, Fe, Al, Zn, and Cd were determined by inductively coupled plasma atomic emission spectrophotometry (ICP/AES) (ARL, model 3580 OES), and pH(H_2O) was determined from a slurry of 10 ml air-dry sample and 25 ml of deionized water.

Some results of the nutrient analyses for humus samples taken in 1987 are presented in Table 3. The nutrient status of the OMT plot by far exceeded that of the others. The most obvious differences with respect to total nitrogen and the C/N ratio were found on the CT plot. Some differences between years were recorded. However, these cannot yet be regarded as significant changes in the over-all

Table 3. Soil properties on the experimental plots representing four different forest site types. Mean values for samples taken in May, June and September 1987

Characteristic	Plot and site type 1 MT	2 OMT	3 VT	4 CT
N_{tot}, %	1.17 ± 0.03	1.31 ± 0.13	1.27 ± 0.13	0.81 ± 0.02
C/N	27.6 ± 1.1	29.6 ± 1.0	32.4 ± 1.3	41.0 ± 1.9
P, mg kg^{-1}	26.1 ± 4.7	108.5 ± 7.0	53.4 ± 5.5	52.3 ± 4.6
K, "	170 ± 4	330 ± 26	145 ± 8	220 ± 40
Ca, "	725 ± 54	1220 ± 101	875 ± 44	550 ± 56
Mg, "	99 ± 8	196 ± 18	109 ± 8	84 ± 9
S, "	49 ± 0	71.4 ± 4.4	32.7 ± 2.4	52.8 ± 13.5
pH(H_2O)	4.01 ± 0.04	4.06 ± 0.02	3.99 ± 0.09	3.73 ± 0.16

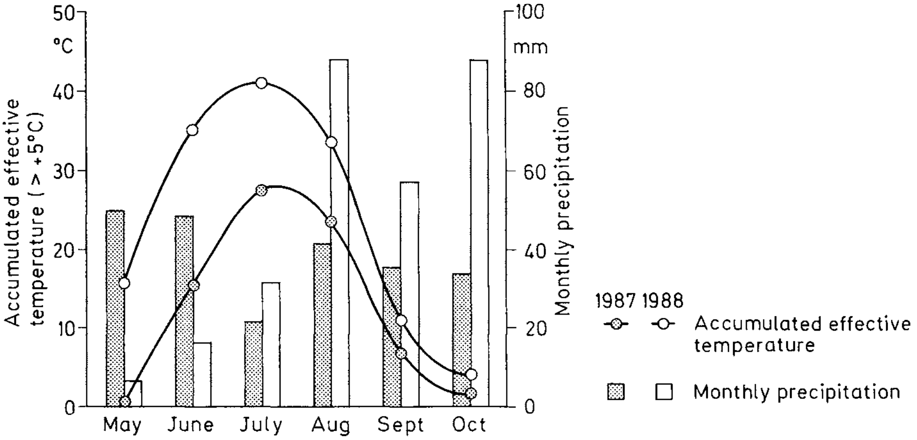

Fig. 3. Accumulated effective temperature (above + 5° C) and monthly precipitation in 1987 and 1988 on the Myrtillus site type (60°21′N, 25°00′, E) with Norway spruce, Scots pine and birch (see Table 1)

nutrient status of the humus layer, but may be attributable to normal year-to-year variation.

The temperature in the humus layer was recorded continuously with thermographs, and the precipitation collected in rain-water gauges and measured weekly. Values for the mean temperature in the humus layer and the total amount of precipitation during 1 week prior to sampling were used in the statistical treatment. The precipitation and the accumulated effective temperature ($> +5°C$) in the humus layer on the MT plot in 1987 and 1988 are shown in Fig. 3. Temperature and precipitation stayed within the normal range in 1987. Summer 1988 was exceptionally warm, the temperature in the humus layer was on an average + 3°C higher in 1988 during most of the monitoring period. It was also very dry up until mid-July.

Microbiological Analyses

Counts and Activity of Heterotrophic Bacteria

The batches of ten subsamples per plot were randomly combined to form five composite samples. Dead and living roots larger than 1 mm in diameter were removed before the samples were sieved (mesh size 2 mm) and then homogenized in sterile water with an Ultra Turrax homogenizer for 1.5 min. Total bacterial numbers were obtained by standard plate counts on soil extract agar (Taylor 1951) using three serial dilutions and five replicates. Ammonifying bacteria were estimated as Most Probable Numbers (MPN) from ten serial dilutions and five replicates (Pochon et al. 1962). Numbers (g humus dw)$^{-1}$ were transformed to logarithms for statistical analyses. The humus samples for the measurement of enzymatic activity and respiration were pooled to make three composite samples. Removal of dead and living roots larger than 1 mm in diameter was performed over an ice bath. Rates of soil respiration were estimated by the alkali absorption method at + 12°C and reported as mg CO_2 (g humus dw)$^{-1}$ h^{-1} (Heinonen-Tanski et al. 1984; Ohtonen 1990a). Dehydrogenase activity (DHA) was estimated as the reduction of 2,3,5-triphenyl tetrazolium chloride (TTC) and reported as uMol triphenyltetrazolium formazan (TPF) (g humus dw)$^{-1}$ 24 h^{-1} (Ohtonen 1990b).

Total and Active Fungal Mycelium

The total length of fungal mycelium was estimated by the membrane filter method using samples prepared as for the activity measurements (Hansen et al. 1974; Sundman and Sivelä 1978). Active fungal mycelium was estimated by the fluorescein diacetate (FDA) method on samples taken in 1988 only (Söderström 1977, 1979a). Lengths of total and active fungal mycelium were measured by the intersection method and reported as m mycelium (g humus dw)$^{-1}$ (Olson 1950).

Physiological Characteristics of the Bacterial Population

The tests were performed using the multipoint inoculation technique as described by Bowie et al. (1969). The modified inoculator used in our laboratory operates with autoclavable 25-compartment plastic trays (65 × 65 × 15 mm, ELESA-Milano) or with sets of 25 glass tubes (10 × 45 mm) in racks that fit the inoculator. Stainless steel inoculation needles (75 × 1 mm), each with a groove 5 mm from its tip, were sterilized after being dipped in alcohol by flaming.

Thirty to fifty colonies were randomly isolated from each humus sample grown on soil extract agar, recultivated and maintained (+ 4°C) on slants containing 1% tryptic soy broth (Difco) + 0.3% agar (TSA). Cultures were transferred at most twice after isolation before submitting them to various tests (Table 4). The test substrates were designed to separate bacterial populations with simple nutritional requirements from those with more complex nutrient requirements (e.g. tests 13–16). Other selective criteria were e.g. enzymatic capacity (tests 3, 6, 7), and capacity to produce acid from sugars (tests 10–12). Tests 4 and 8 were designed to detect organisms taking part in the nitrogen and sulphur cycle respectively.

Twenty-four randomly chosen isolates grown for 3–4 days on semi-solid TSA (+ 28°C) in glass tubes, served as so-called master cultures. Number 13 on the tray or in the rack was left uninoculated as a control throughout the testing procedure on all substrates. Test 1 was incubated at room temperature for 2–3 days, test 2 for at least 2 weeks at + 28°C. Tests 3, 4, 5, 6, 7, and 9–12 were incubated for 5 days at room temperature, test 8 for 6–7 days, and tests 13–16 for 4–5 days at + 20°C.

Table 4. Test substrates used in the screening of the physiological capacity of pure cultures isolated from the humus layer at four different forest site types

Test number	Function
1	Hydrolysis of casein. Tryptic soy agar + 0.7% skim milk
2	Decolorization of humic acid (SERWA) (Clarholm and Rosswall 1973)
3	Phosphatase production (Sundman 1970)
4	Ammonification (Niemelä and Sundman 1977)
5	Formation of pigment on any of the media used
6	Oxidase production on semi-solid trypone soy agar (Kovacs 1956)
7	Urease production (Christensen 1946)
8	Sulphide produced from cystein (Skerman 1967)
9	Formation of protochatechuic acid from quinic acid (Stewart 1965)
10–11	Acid production from xylose and cellobiose (Goodfellow 1968)
12	Oxidative production of acid from glucose (Hugh and Leifson 1953)
13	Growth on the Basal medium according to Taylor (1951) with 0.5% tryptone, 0.3% yeast extract and 25% (v/v) soil extract
14	Growth on the basal medium with amended carbon source: glucose, acetate, lactate, glycerole, and citrate, 0.05% respectively
15	Growth on basal medium with vitamin-free casamino acids
16	Growth on basal medium with 0.1% glucose, 0.05% $(NH_4)_2HPO_4$ and minerals

Statistical Treatment

Measurements of fungal mycelium and biological activity were normalized using logarithmic transformations prior to analyses of variance. Measurements of bacteria were subjected to analyses of variance and Bonferroni t-tests. Correlations were examined using multiple regression analyses. Physiological characteristics were tested by analyses of variance, and by grouping parameters according to relative frequencies.

Results

Comparison Between Plots and Years

Table 5 summarizes annual average values for all sampling events of the qualitative and quantitative microbial and fungal mycelium estimates made in 1987 and 1988. Respiration rates, dehydrogenase activity, and total length of fungal mycelium were clearly higher on the OMT plot than on the MT, VT and CT plots. Contrasts between plots were most distinct in 1987. Differences in dehydrogenase activity and total fungal mycelium on the OMT plot in 1987 and 1988 were significant ($p < 0.001$; < 0.01 respectively). Generally, there was more total fungal mycelium in 1987 than in 1988. There was a distinct pattern for bacterial counts in the pooled data. In both years there was a significantly larger bacterial population on the OMT and VT plots than on the MT and CT plots. Compared on a yearly basis, total counts were higher in 1987 on the MT and CT plots than in 1988 ($p < 0.05$; $p < 0.05$ respectively). Ammonifiers were more abundant on all plots in 1987 than in 1988. The difference was greatest on the CT plot ($p < 0.01$).

Seasonal Variation

Numbers of ammonifiers and total count of bacteria generally increased towards the end of the growing season in both years. Exceptions to this trend were total bacteria on the CT plot, and the ammonifiers on the OMT and CT plots in 1987 and on the OMT plot in 1988, all of which were fairly stable.

The biological parameters measured in 1987 have some aspects in common (Fig. 4). Especially on the OMT plot, bacterial numbers were high in early summer and autumn. This coincided fairly well with high respiration rates, dehydrogenase activity, and with a high total amount of fungal mycelium. The ammonifiers and total count of bacteria, as well as respiration rates, significantly correlated on this plot ($r = 0.72^*$; $r = 0.65^*$ respectively). The large number of bacteria on the VT plot were not, however, reflected by high activity values. Peak values in fungal mycelium were as expected: a smaller one in spring and a larger one in late summer.

The activity on the CT plot differed much from those for the other plots. Fungal mycelium amounts were always low, and there were no marked seasonal

Table 5. Annual mean estimates for 1987 and 1988 of quantitative and qualitative microbial characteristics in the humus layer at four different forest site types in southern Finland

		1987					1988					
Plot	Site type	a	b	c	d	e	a	b	c	d	e	f
1	MT	0.015	1.169	7.4	5.4	4993	0.014	0.984	6.7	4.9	3416	395
2	OMT	0.028	1.674	7.6	5.9	6089	0.022	0.985	7.9	5.6	3586	488
3	VT	0.010	0.803	7.8	5.8	4414	0.013	0.755	7.9	5.4	3239	329
4	CT	0.017	0.894	7.3	5.3	2558	0.019	0.767	6.8	4.6	2289	419
		1–2*** 1–3* 2–3*** 2–4** 3–4*	1–2* 1–3* 2–3*** 2–4**	1–2*** 1–3*** 2–4*** 3–4***	2–4* 3–4*	1–4* 2–4*** 3–4*	1–2* 2–3**	2–3*	1–2*** 1–3*** 2–4*** 3–4***	2–4** 3–4*	1–4* 2–4* 3–4*	2–3* 3–4*

Significant differences: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.
a = respiration, as CO_2, mg (g humus dw)$^{-1}$h^{-1}, b = dehydrogenase activity, as TPF, µmol (g humus dw)$^{-1}$ 24^{-1}, c = total count of bacteria (log), g humus dw^{-1}, d = most probable number of ammonifying bacteria (log), g humus dw^{-1}, e = total length (m) of fungal mycelium, g humus dw^{-1}, and f = length (m) of active fungal mycelium, g humus dw^{-1}.

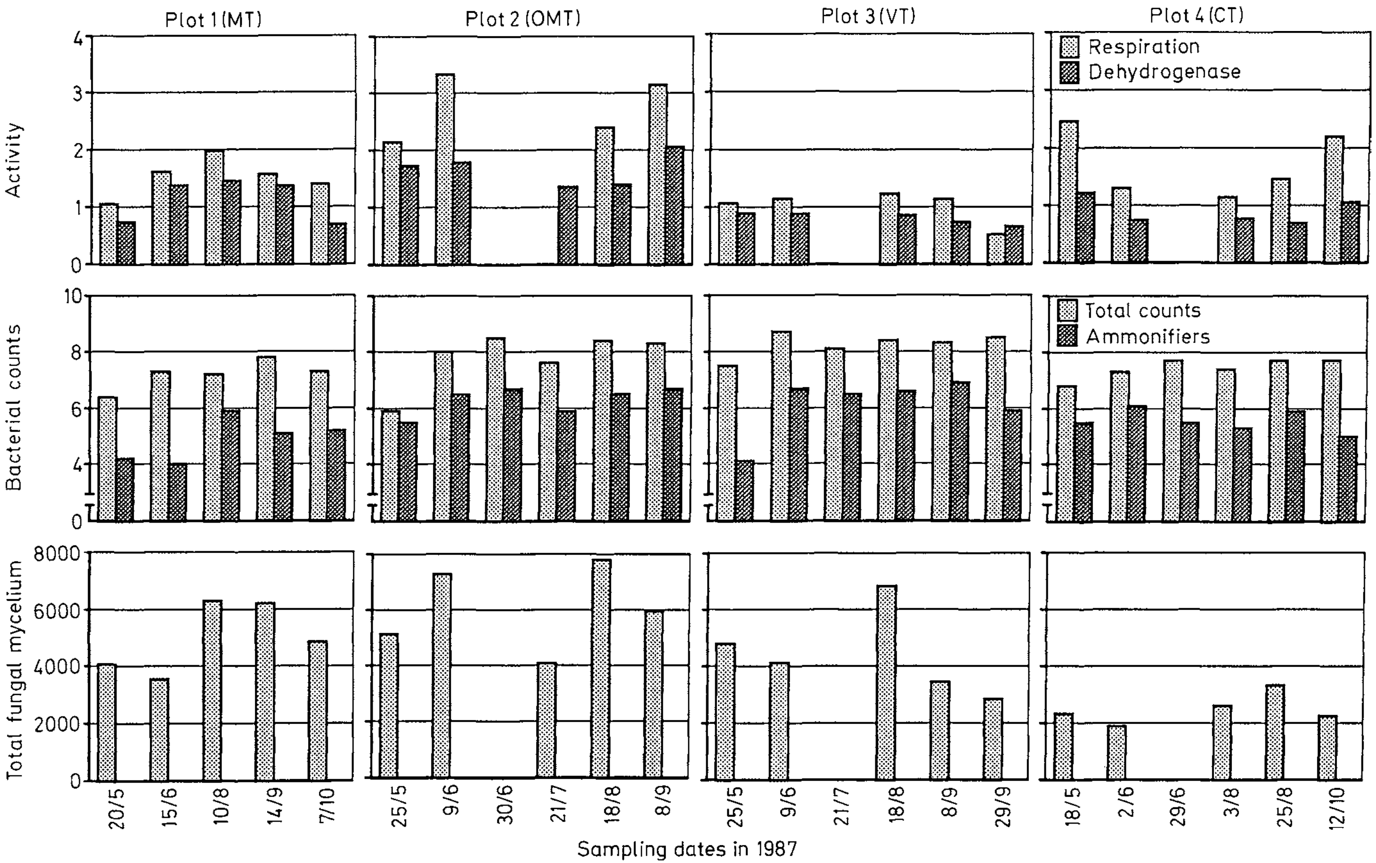

Fig. 4. Biological activity recorded as respiration rate [mg CO_2 $(\times 10)^{-2}$ (g humus dw)$^{-1}$ h^{-1}] and dehydrogenase activity [µmol TPF (g humus dw)$^{-1}$ 24 h^{-1}], total count of bacteria and number of ammonifiers (log. values), and total length (m) of fungal mycelium in the humus layer on the Myrtillus (MT), Oxalis-Myrtillus (OMT), Vaccinium (VT), and the Calluna (CT) sites types (see Table 1) as determined monthly in 1987

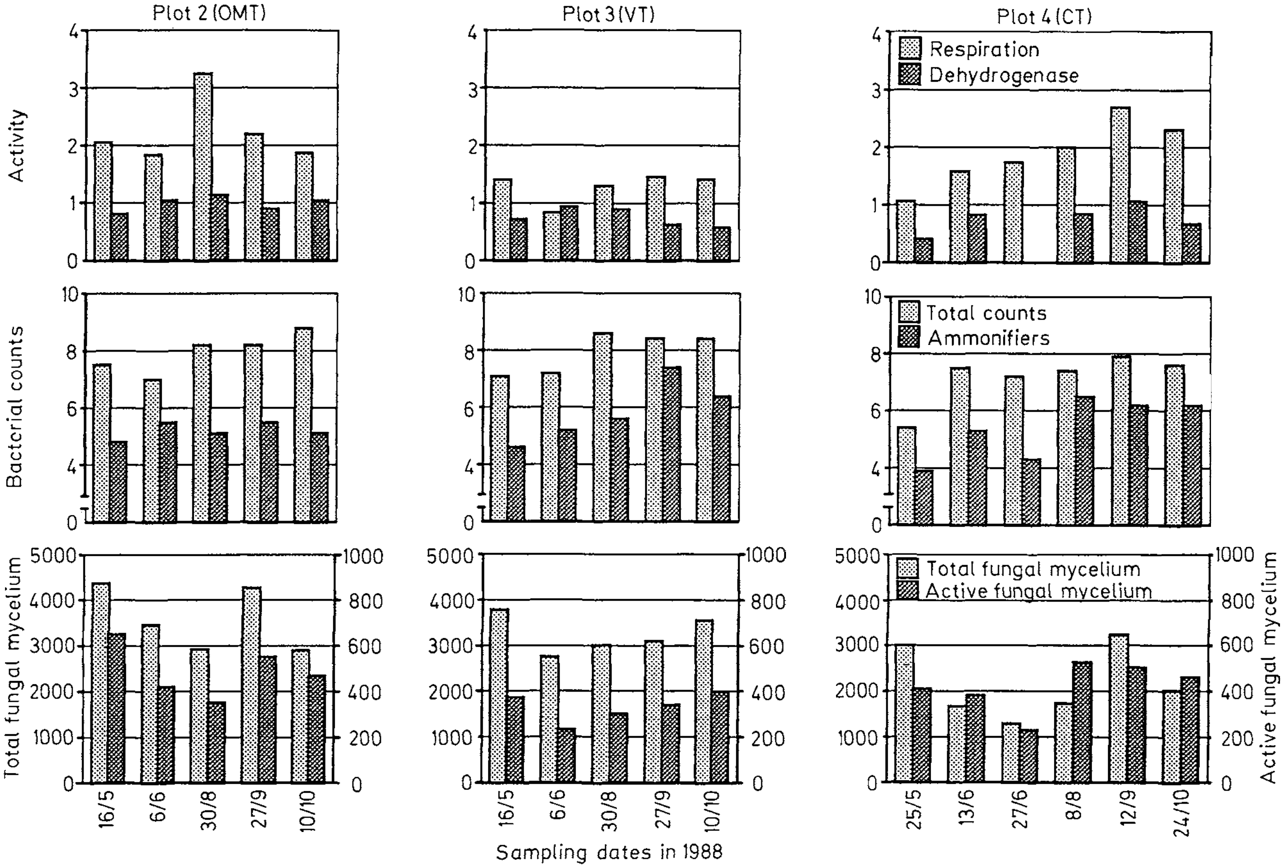

Fig. 5. Biological activity recorded as respiration rate [mg CO_2 ($\times$ 10)$^{-2}$ (g humus dw)$^{-1}$ h^{-1}] and dehydrogenase activity [µmol TPF (g humus dw)$^{-1}$ 24 h^{-1}], total count of bacteria and number of ammonifiers (log. values), total length (m), and length (m) of active fungal mycelium on the Oxalis-Myrtillus (OMT), Vaccinium (VT), and Calluna (CT) site types (see Table 1) as determined monthly in 1988

changes in bacterial population size or in amount of fungal mycelium. The respiration rates were unexpectedly high compared to the estimates of dehydrogenase activity. The timing of the respiration peaks (mid-May and mid-October) is also unusual. The correlation between bacterial counts and respiration rates, and with dehydrogenase activity, was significant (r = 0.81*; r = 0.86* respectively).

Observations of fungi and bacteria for the OMT, VT and CT plots in 1988 are shown in Fig. 5. Separate estimations were made for this year of active, and total fungal mycelium. The typical growth rhythm for fungal mycelium, i.e. spring and autumn peaks, was clear on all plots. The total amount of fungal mycelium correlated with that of the active mycelium on the OMT and VT plots only (r = 0.84**; r = 0.89** respectively). The active part of the fungal mycelium correlated with respiration on the VT plot (r = 0.85**), and also significantly but negatively with the dehydrogenase activity on this and the OMT plot. (r = − 0.98***; r = − 0.89**). The normal seasonal changes in numbers of bacteria, i.e. spring and autumn peaks, were obvious also in 1988. Total bacterial counts and the amount of ammonifiers on the CT plot highly correlated with respiration rates (r = 0.91**; r = 0.84** respectively), and with dehydrogenase activity as well (r = 0.96***; r = 0.92*** respectively). Corresponding correlations for the VT plot were weaker.

Weekly Variation

The correlations between climatic data and microbiological parameters during the period of intensive monitoring on the MT plot in May-June 1988 are shown in Table 6, and the dynamics of the microbiological parameters in Fig. 6. The drying out of the humus layer after snowmelt significantly decreased the biological activity. Fungal mycelium increased rapidly during the 3-week period and stabilized until mid-June. High counts of bacteria were observed from the onset of sampling. The respiration rate was negatively correlated to the total fungal mycelium and, as was the case with dehydrogenase activity, positively correlated to total counts of bacteria. Towards the end of the growing season, from mid-September to mid-October, total fungal mycelium accumulated in the humus layer. The increase generally, and the shift in the ratio notably between bacterial groups, was remarkable. These changes in composition and size of the microbial population are evidently reflected in the high activity values recorded at the same time, but this is not verified statistically. The favourable temperature and moisture conditions that prevailed in the humus layer during autumn, coupled with good availability of easily decomposable organic matter, might explain this.

Physiological Characteristics

When the results from all the sampling events in 1987 and 1988 were pooled together, and presented per plot, the out-come of the tests on the 16 test substrates listed in Table 4 shows that there are very low positive responses (>20%) in tests

Table 6. Correlations between moisture, temperature, and biological characteristics in the humus layer of the intensively monitored MT plot. Values based on results from an 8-week sampling period: May 3–June 27 1988

	1	2	3	4	5	6	7
1 Moisture, % fw			* N			***	*
2 Mean temperature, °C			*		**	* N	
3 Total length (m) of fungal mycelium, g humus dw^{-1}						** N	
4 Length (m) of active fungal mycelium, g humus dw^{-1}							
5 Bacteria, total count (log), g humus dw^{-1}						*	**
6 Respiration, as CO_2, mg (g humus $dw)^{-1}$ h^{-1}							*
7 Dehydrogenase activity, as TPF, μmol (g humus $dw)^{-1}$ 24 h^{-1}							

Significant differences: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.
N = negative correlation.

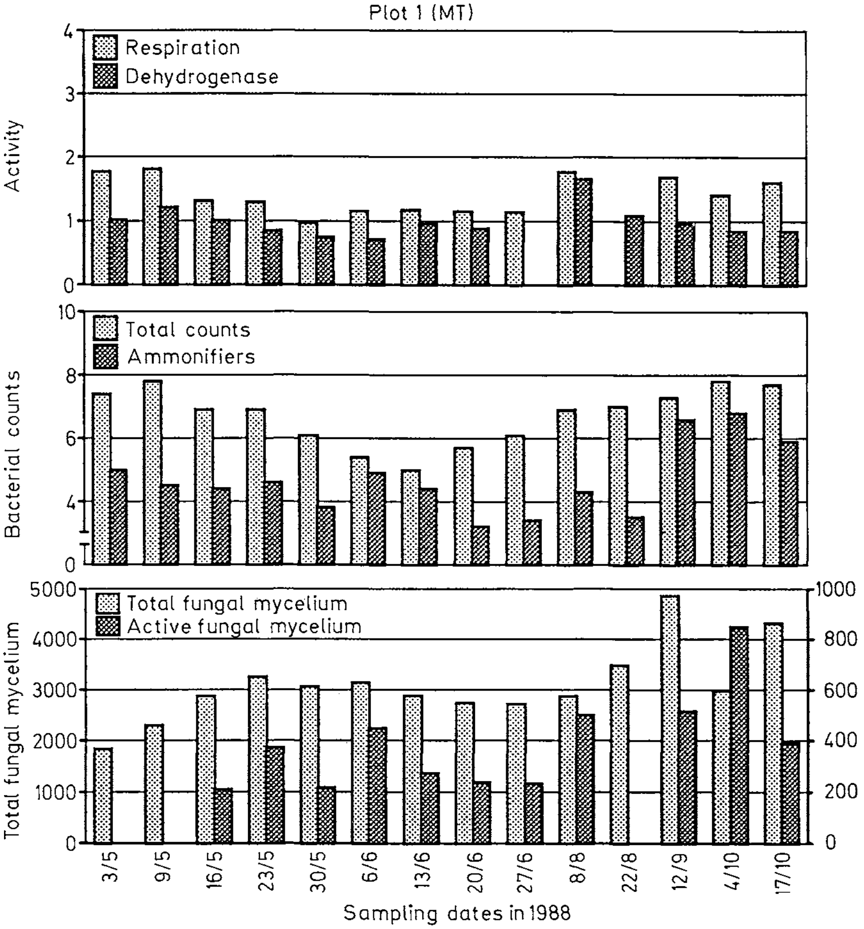

Fig. 6. Biological activity recorded as respiration rate [mg CO_2 (× $10)^{-2}$ (g humus dw)$^{-1}$ h^{-1}] and dehydrogenase activity [μmol TPF (g humus dw)$^{-1}$ 24 h^{-1}], total count of bacteria and number of ammonifiers (log. values), total length (m), and length (m) of active fungal mycelium on the intensively monitored Myrtillus (MT) site type (see Table 1) as determined weekly and monthly in 1988

2,5, and 8, i.e. tests designed to detect bacteria with the capacity to discolour humic acid, to form pigments, and to mediate in the sulphur cycle (Table 7). In 1987 a medium positive response, less than 40%, was recorded for the OMT and MT plots for the majority of the substrates. The CT and VT plots showed most substrate-positive isolates on the 40–60% level. Test substrate 13, which provides micro-organisms with complex essential nutrients, showed a very high positive response on all plots except on the MT plot.

In 1988 the frequency pattern was different from that of 1987 in the sense that positive results higher than 60% were never recorded. On the other hand, many of the tests were positive at the same percentage level (<40%) as in 1987. The tests with a low positive response were also the same as in 1987. On the OMT plot,

Table 7. The percentage distribution of the test substrates that were positive after inoculation with humus sample isolates for each of the four plots in 1987 and 1988. Results are calculated from all samples taken in each sampling season (see Table 2)

Plot	Site type	1987				1988			
		< 80%	< 60	< 40	< 20	< 80%	< 60	< 40	< 20
1	MT	–	13,15, 16[a]	1,3,4,6, 7,10,11, 12,14,	2,5,8,9	–	1,12,14, 15,16	3,4,6 7,10,11, 13	2,5,8
2	OMT	13	14,15	1,3,4,6, 7,10,12, 16	2,5,8,9 11	–	12,14	1,4,7, 13,15, 16	2,3,5, 8,9,10, 11
3	VT	13,15	3,4,6, 9,10,12, 14,16	1,5,7,8, 11	2	–	12,13, 14,15	1,3,4, 6,9,10, 16	2,5,7, 11
4	CT	4,6,13 14,15,	1,9,10, 11,12	3,5,7, 8	2	–	1,12,14, 16	3,4,6, 9,11,13	2,5,7, 8,10

[a] Test substrates listed in Table 4.

however, as much as half of the batch of tests gave a positive result lower than 20%. A statistical comparison between plots indicated that there were some tests that clearly distinguished plots from each other (Table 8). As an example of this, the result for the urease activity test is shown in Fig. 7. Only two tests, 1 and 11, distinguished between the most and the least productive (OMT-CT) plots.

Seasonal Variation

In the case of urease activity, some variation was noted on the OMT plot in 1987 and the MT plot in 1988 (Fig. 7). Considering the material as a whole, the seasonal variations were small in both years for tests 2, 5, 8, 11, and 14, as was the case for test 9 in 1987, and tests 3 and 10 in 1988. There were notable seasonal variations in both years in the remaining batch of tests.

The results of the tests reveal some distinct features when sampling events are grouped according to season (spring + early summer, and late summer + autumn). Significantly higher positive percentage values were recorded for most tests on cultures isolated from humus samples in May and early June 1987 than in samples taken in late summer and autumn the same year. In 1988 this pattern was the same for the CT plot only.

Weekly Variation

The weekly variation in the physiological characteristics of the microbial population on the MT plot in 1988 is shown in Fig. 8. The first two samples were taken while the temperature in the humus layer was still around zero, and the last

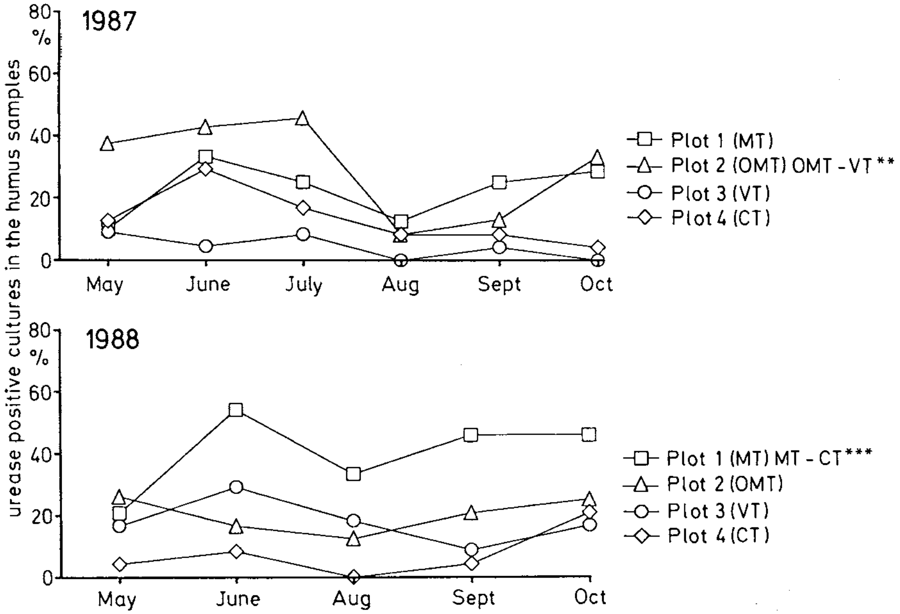

Fig. 7. Seasonal variation of the urease active isolates in the humus samples from the Myrtillus (MT), Oxalis-Myrtillus (OMT), Vaccinium (VT) and the Calluna (CT) site types (see Table 1) in 1987 and 1988. Significant differences between plots: ** $p < 0.01$, *** $p < 0.001$

Table 8. Test substrates with a positive response that separates the four different forest sites from each other in 1987 and 1988

Year	Test substrate[a]	Site types between which there were significant differences
1987	1	MT–CT**
		OMT–CT*
	4	MT–CT*
	7	MT–VT**
		OMT–VT***
	11	MT–OMT*
		OMT–CT*
1988	1	MT–VT*
		OMT–CT*
		VT–CT*
	3	OMT–VT**
	4	MT–CT*
	7	MT–OMT*
		MT–VT**
		MT–CT***

[a] Test substrates listed in Table 4.

Significant differences: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

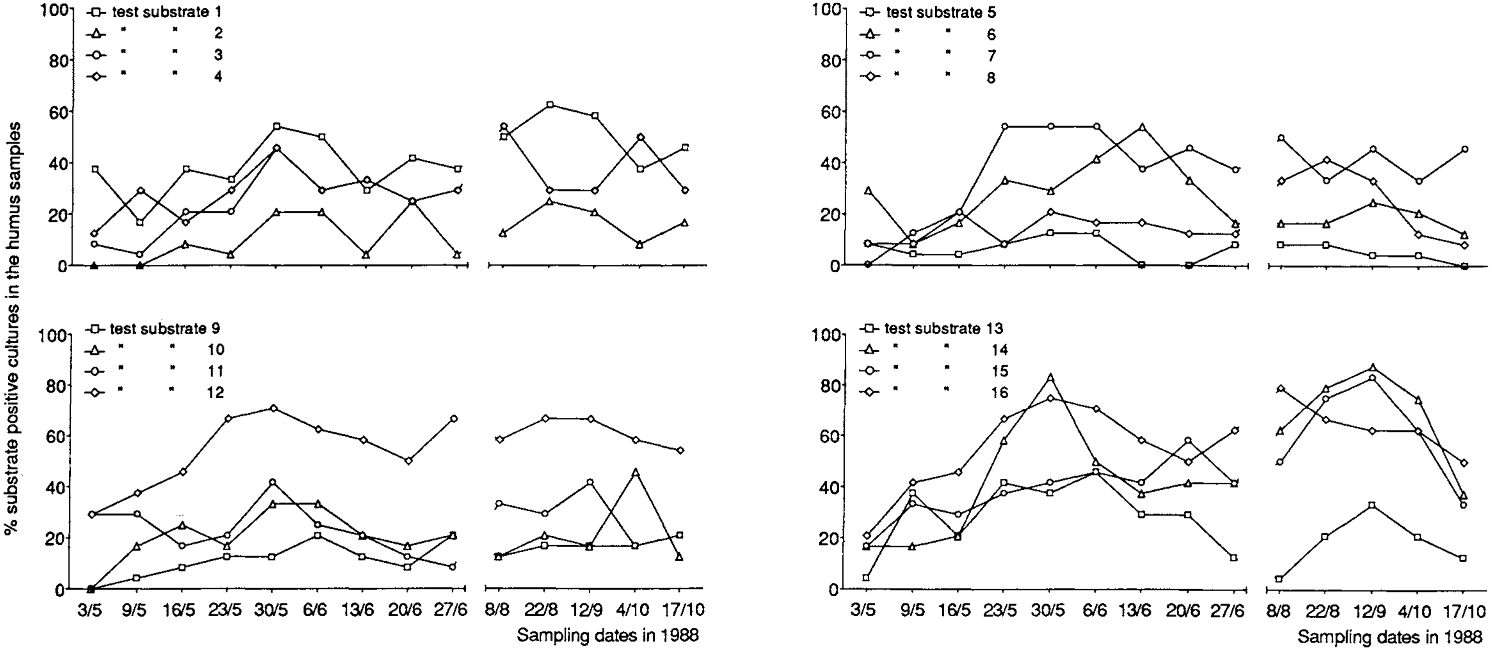

Fig. 8. Weekly and monthly variation in responses to 16 different test substrates (see Table 4) of the isolates in the humus samples from the intensively monitored Myrtillus (MT) site type (see Table 1) in 1988.

samples when the temperature was at an average + 5°C. The low initial positive responses at the start are to some extent an effect of temperature. Some of the tests (5, 8, 9, 12, 15) remained substrate-positive and at constant percentage throughout the 8-week period of intensive sampling. As soon as the temperature stabilized above + 6°C, urease activity remained constant. The outcome of tests 1, 3 and 4, all of which differentiated the plots from each other, varied considerably during the intensive sampling period, as well as later on in the season.

Discussion

Under natural conditions and in the absence of anthropogenic pollutants, organic matter decomposition is primarily ruled by climate and substrate quality. Although bacteria are the most abundant soil organisms, they do not generally form the major part of the soil biomass due to their small size. However, they play a primary role in the transformation of organic matter. Nevertheless, in acid soils fungi are at least as, or more important than bacteria (Flanagan and Van Cleve 1977). On the other hand, Persson et al. (1980), referring to bacterial/fungal biomass ratios, suggested that the role of bacteria in acid forest soils has been underestimated.

The conclusion of Ausmus (1973) that it is too simplistic to use only one or two parameters for describing the biological status of the soil seems justified. In this study, a variety of methods has been used to characterize the current microbial status of the forest soil. The primary data can thus serve as reference data when judging the effects of acidification on the microbiological status of the forest humus layer in the future.

The method of estimating bacterial numbers by plate counts is criticized because it is impossible to isolate a representative, unbiased sample of micro-organisms from natural environments. Whatever substrate is used, it acts as a filter: only a fraction of the micro-organisms will proliferate. However, if this limitation is kept in mind, the method can still serve as a means of estimating sizes of microbial populations. Furthermore, as colonies on plates are isolated for the functional description of microbial populations, the above limits seem acceptable. This type of approach has several merits: it permits a quantitative and qualitative assessment of functional shifts in microbial populations in changing soil environments, it provides estimates of population diversity and dynamics, and the method of multi-point inoculation lends itself to a certain degree of automation which enables the handling of adequate numbers of replicates made on large numbers of samples (Niemelä and Sundman 1977; Rosswall and Kvillner 1978; Kauri 1980).

The physiological tests of the isolated micro-organisms have revealed some unusual features. These may be indicative of the prevailing situation, or a sign that the tests in question are irrelevant. In both years and on all plots some of the 16 tests had a very low positive response percentage. In 1988 the species diversity appeared to be smaller than in the previous year. This outcome might be explained by the exceptional warm and dry growing season in 1988. As far as the seasonal variations are concerned, the years differed considerably. The frequency of substrate-positive cultures was much higher in spring samples than in autumn samples in 1987. In the following year this pattern was reversed except for the poorest, CT, plot. Some of the tests clearly distinguished between plots. Some of them were the same in both years, which increases their value in the screening of the population diversity.

The natural seasonal variation was clearly observed as peaks in bacterial counts and acitivity, and in the amount of fungal mycelium early and late in the summer especially on the most productive, OMT, plot. (cf. e.g. Söderström 1979b). Also on the intensively monitored MT plot in 1988, a short interval dynamic pattern was observed (cf. Tiwari et al. 1987). Although the 2 years differed climatically in that the growing season 1988 was very dry and warm, the estimates of respiration and dehydrogenase were equally low and constant on the VT plot. Comparing the four site types in both years, the OMT plot generally showed the highest values for the bacterial parameters. The nutrient content and C/N ratio were also the best. On the CT plot, the activity estimates and the bacterial counts seemed to be least effected by climate. On sites like this, with high C/N ratio, poor nutrient content, and low pH, changes due to acid atmospheric load may be recognized earlier than on more productive sites. Generally fungal biomass exceeds that of bacteria in acid forest soils owing to the lower pH optimum of the fungi. Changes in the amount of fungal mycelium may thus reflect changes in the pH of the humus layer. Indications of such a process were observed on the MT plot in 1988: the pH decreased about 0.5 pH units from May through October while the amount of active fungal mycelium simultaneously increased.

The positive correlation noted for respiration rate and length of active fungal mycelium during spring and autumn on some of the plots is in accordance with the findings of Ingham and Klein (1984), but contradictory to those of Bååth et al. (1978). The negative correlation between the active fungal mycelium and dehydrogenase activity observed on the OMT plot may indicate competition between fungi and bacteria in which the bacterial activity increases at the expense of fungal activity. The response of respiration or dehydrogenase activity to changes in the microhabitat moisture status is immediate, whereas there is a time lag before the effect can be recorded in bacterial and fungal counts (Nannipieri et al. 1979; Tiwari et al. 1987). This fact highlights the importance of sampling time and frequency. The gross results from the MT plot sampled in 1987 compared to those from the weekly sampling in 1988 exemplifies the difference in the value of information thus obtained and the difficulties in interpreting the results.

Cronan (1985), who examined the carbon cycling and precipitation acidity, concluded that the biologically mediated mineralization of organic matter in forest soils is relatively unaffected by acid precipitation at $\mathrm{pH} > 3.0$. The pH of the forest humus at the different sites in the present study ranged between 3.5 and 4.3. So far, it has not been possible to prove that the pH of these plots has changed, or that the microbial characteristics have been affected by any acid load. The statement of Cronan should, however, not pass unchallenged because it would mean that the variety of complex interactions between soil micro-organisms and their environment are ignored. Small changes in microbial characteristics that are difficult to detect with existing methods may still have important effects in the long run. This should be kept in mind because of the long rotation period in the northern coniferous forest ecosystem.

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Soil Biological Parameters as Indicators of Changes in Scots Pine Forests (*Pinus sylvestris* L.) Caused by Air Pollution

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Summary

Certain soil parameters were studied in three areas of Scots pine (*Pinus sylvestris* L.) forests subjected to long-term stress from industrial air pollution by different point sources. In the Oulu area the status of mycorrhizal fungi, soil biological activity and the amount of fungal mycelium, in the Kuopio area cellulose decomposition and in the Harjavalta area the decomposition of green Scots pine needle litter were studied. Long-term deposition of a variety of air pollutants will lead to severe changes in soil biology, of which sporophore production of mycorrhizal fungi, number of mycorrhizal types, number of root tips per soil volume, biological activity of soil and green needle litter decomposition seemed to be suitable parameters for detecting depressive changes.

Introduction

The forest soil, as a part of the whole forest ecosystem, is a complex system comprising biological, chemical and physical phenomena. The podzolization process is pronounced in the Nordic coniferous forests, and soil microorganisms, especially fungi, play a major role in the decomposition of organic matter and in the formation of soil. Five to ten years ago very little was known about the effects of air pollution on the biology of forest soils. Soil biology, which is nowadays considered in many large projects on air pollution, has recently increased our understanding of the processes involved.

Measures of biological activity, such as respiration rate, the activity of certain enzymes or the rate of decomposition of organic matter, are commonly used as indices of the functioning of microorganisms in soil, and these are found to be depressed by air pollution stress (Vogt et al. 1980; Bååth 1985; Prescott and Parkinson 1985). The nutrient uptake of forest trees greatly depends on the symbiotic fungi in the mycorrhizal fine roots. When the roots of forest trees are subjected to stress by air pollution, changes may occur in the status of the mycorrhizae (Jansen 1988; Meyer 1984; Meyer 1988). The production of

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sporophores by certain mycorrhizal fungi is drastically reduced in the Netherlands in declined forests (Arnolds 1985).

In general, because of the high diversity among organic forest soils, no single ideal method exists for measuring changes due to air pollution in soil microbial communities. Many methods are used, and the sensitivity of different methods is one critical point when looking for small, slow changes in the ecosystem. One problem concerns the differences between fungi and bacteria, or ecological or physiological groups of these, in their responses to air pollution stresses. In all cases a variety of tests should be carried out to find any imbalances in energy or nutrient cycles of the soil or in the biological structure of soil communities. Both long-term and short-term changes should be considered.

Sporophore production and mycorrhizal status do not necessarily correlate well with each other in a forest ecosystem, where a number of fungal symbionts is present. It is therefore important to evaluate the usefulness of parameters measured above and below ground level. The relationship between biological activity and mycorrhizal parameters in a forest stand should also be studied and their indicative value in a changing forest ecosystem discussed.

The research taking place in Oulu, Kuopio and Harjavalta is concerned with soil biology and, in the absence of a time perspective, represents attempts to reveal the effects of air pollution on a spatial scale around one source of emissions or a cluster of such sources. In each of these places local deposition of a variety of pollutants has been affecting the pine forests for some decades, and it is difficult to point to any single stress factor. Each field study is unique in kind because of local differences in the composition of emissions and in climatic and vegetational factors.

The status of the mycorrhizal fungi, soil biological activity and the amount of living mycelium in the pine forests around Oulu are measured and discussed in relation to chemical and physical parameters describing the mor humus layer. Some preliminary results have been published in Markkola and Ohtonen (1988) and Ohtonen and Markkola (1989).

The data regarding seasonal variations of biological activity and the mycelium (Ohtonen 1990) and changes in the vegetation and fungal flora, together with descriptions of the mycorrhizal types, will be published elsewhere.

Cellulose decomposition in the pine forests around Kuopio is discussed in relation to the nitrate, ammonium and sulphate content of the mor humus. Cellulose decomposition is a common, rapid process in soil, resulting from enzyme systems of many kinds maintained by a great diversity of fungi and bacteria (Ljungdahl and Eriksson 1985), and as cellulose is the main component of dead plant material, its decomposition can provide an impression of general microbial activity in the soil.

The Harjavalta research is based on investigations carried out in Helsinki in 1987–88. The pollution pattern in the area surrounding the city of Helsinki resembles that prevailing in the Oulu area. A field study in a coniferous forest revealed lower soil respiration and a lower amount of total fungal hyphae in a polluted part of the area than in a less polluted one, but no difference in the length of the fluorescein diacetate-active (FDA) fungal hyphae (Fritze 1987). Neither did the pollution significantly lower the decomposition rate of the green coniferous needle litter, but a significantly higher release of Mn from the decomposing needle litter and an enrichment of heavy metals in the needle litter were detected in the polluted area (Fritze 1988). Urban air pollution had no effects on the Ca, Mg and K content in the decomposing needles. To test the decomposition rate and the leaching pattern of nutrients from the needles in an environment polluted with heavy metals, green Scots pine needle litter was buried in the soil mor horizon surrounding a Cu-Ni smelter at Harjavalta. The data concerning its effects on the vegetation and the soil microbiology will be published elsewhere (Fritze et al. 1989). The mass loss data regarding the decomposing needle litter are again presented here, together with new data on the dynamics of Ca, Mg, K, Mn and N in the decomposing needle litter as well as the enrichment of Cu, Ni, Cd and Zn into them.

The Areas Studied

The three areas studied are all located around industrialized communities. The city of Oulu is located on the Gulf of Bothnia coast at lat. 65°N, 25°30′E, the second area is in the lake region of eastern Finland near Kuopio (63°N, 27°45′E) and the third is in southwestern Finland around the town of Harjavalta (61°19′N, 22°9′E). The areas all fall within the middle boreal vegetation zone (Ahti et al. 1968).

The study sites examined in all three areas are mature forests of Scots pine (*Pinus sylvestris*). The stands close to Oulu and Kuopio contain a small amount of spruce (*Picea abies*) and birch (*Betula* spp.) and the field layer consists mainly of *Vaccinium vitis-idaea*, *Empetrum nigrum coll.* and *V. myrtillus*. The central sites in Oulu are more grassy, with *Deschampsia flexuosa* and *Trientalis europaea*, for example, while *Calamagrostis* sp. and *Epilobium angustifolium* were encountered at the sites in Kuopio. The sites at Harjavalta are located in a pine forest of the dry Calluna type (CT, Cajander 1926).

In the Oulu area the main sources of sulphur and nitrogen emissions are a pulp mill and a chemical factory, the local heating plant and traffic. Local deposition is quite variable (Table 1). In the Kuopio area the main air pollution since the late 1960's has been caused by a birch pulp and corrugated medium mill using ammonium sulphite as the cellulose reagent (Table 1). At Harjavalta the Cu-Ni smelter has been polluting the environment with Cu, Ni, Zn and Cd since the mid-1940's (Hynninen 1986; Table 1).

In the Oulu area 20 forest sites about 10 m in diameter situated between about 1 and 40 km from the main sources of emissions were selected for study (Ohtonen 1990). The tendency for the S content of pine needles to increase towards the city centre was one criteria when selecting the sites and another a quite narrow pH range in the mor humus layer, pH (H_2O) from 3.8 to 4.3. The thickness of the mor

Table 1. Principal emissions and depositions in the areas studied. In the Oulu area the main sources of S and N are a pulp mill, a chemical factory, a local heating plant and traffic, in the Kuopio area a birch pulp and a corrugated medium mill and in the Harjavalta area a Cu-Ni smelter

Emissions	Oulu[a] $t\ yr^{-1}$	Kuopio[b] $t\ yr^{-1}$	Harjavalta[c] $t\ yr^{-1}$
SO_2	6275	13,700–14,300	6900
NO_x	7010	890[d]	nd
NH_3	nd	16	nd
H_2S	507	nd	nd
Cu	nd	nd	140
Ni	nd	nd	100
Zn	nd	nd	160
Pb	20	nd	90
Cd	nd	nd	4
As	nd	nd	19

Depositions	Oulu[e]		Kuopio[f]	Harjavalta
	S	N		
	$g\ m^{-2}\ yr^{-1}$		$g\ m^{-2}\ yr^{-1}$	
SO_4-S	0.8–1.0	3.6–5.6	2.3–3.7	nd
NH_4-N	nd	nd	1.2–1.7	nd

[a] Air quality in Oulu measurements in 1988 (The municipality of Oulu publications 2/1989).

[b] According to the Provincial Administration of Kuopio (Kuopion lääninhallitus, päätös 2Y 1989).

[c] In 1987 according to the authority of the mill (Kupari-nikkeliryhmän tiedotuslehti 1/1989).

[d] Measured as NO_2.

[e] In 1986–88 according to the municipal authority in Oulu (unpublished 1989)

[f] Monthly means between December 1987 and April 1989 in points 400 m NW and 400 m N from the mill.

S = the southern part of the city centre in 1987, the main deposition level in the city centre.

N = the nothern part of the city centre in 1987, the most polluted sites within a 5 km radius of this point.

nd no data available.

humus layer was from 2.3 to 8.9 cm, and increased towards the central areas (Ohtonen et al. 1989). Total N, S and ammonium N in the mor humus also increased towards the city centre, while the C/N ratio, which varied from 24 to 43, was decreasing towards the city centre. The chemical characteristics of the sites are presented in detail elsewhere (Ohtonen et al. 1989; Ohtonen 1990). Ten of the sites are referred to as the outer or cleaner sites and the other ten as the central or more polluted sites according to the S content of pine needles (Ohtonen et al. 1989).

The four forest sites studied in the Kuopio area are situated from 0.3 to 22 km N or NW of the mill. The soil pH was approximately 4.0 in the control areas but

5.3 nearer to the source of emissions partly due to liming, which also increased Ca and Mg contents from 400 to 2000 and from 40 to 110 mg l^{-1}, respectively.

At Harjavalta, ten sites were established on a transect south of the smelter running from close to the smelter to a distance of about 20 km from the industrial zone. The soil type is a podzol on moraine, with a well-developed mor layer, except at the study sites nearest to the smelter, where the mor layer was almost absent. There were no clear pollution-related differences in pH or the C/N ratio between the sites, the values being around 4.00 and between 32 to 48, respectively. A clear reduction in the nutrients Ca, Mg, K and Mn and an increase in the heavy metals Cu, Ni, Zn and Cd was recorded in the soils towards the smelter (Fritze et al. 1989).

Material and Methods

The Oulu Area

Sporophore inventories of the mycorrhizal fungi were made in September 1987 and August–September 1988. The fungal flora was studied over a larger area than the sites themselves (within a radius of about 50–100 m from the site), and the species observed in both years are summed. Sporophore production was estimated along a 50 m^2 transect. The sporophores of all mycorrhizal species were counted twice, at the beginning and in the middle of September 1988. The sporophores were collected and their dry weights determined once in September 1988.

The general sporophore parameters include
- biomass of all mycorrhizal species (g dw m^{-2})
- numbers of sporophores of all mycorrhizal fungi (number m^{-2})
- number of mycorrhizal species per site.

The numbers of sporophores of the dominant species (*Cortinarius* spp., *Suillus variegatus*, *Lactarius rufus*, *Chroogomphus rutilus*, *Paxillus involutus*) per m^2 were also included in statistical analysis.

The samples for mycorrhizal analysis were taken from the whole depth of the mor humus layer with a stainless steel coring tool 3 cm in diameter in September 1987. Fine roots (diameter < 1 mm) were carefully collected and mycorrhizae from five replicate cores per site examined under a dissection microscope. Eighteen types of mycorrhiza were characterized (Markkola and Ohtonen unpubl.).

The general mycorrhizal parameters include
- total number of root tips per soil volume unit
- number of mycorrhizal types in a sample
- ramification index (number of root tips per cm of long root)
- condition of the mycorrhizae according to the appearance of the mantle (Lehto 1984) examined under a dissection microscope (number of well-developed mycorrhizae per soil volume unit).

Frequencies and percentages of nine dominant mycorrhizal types were also included in the statistical analyses, as well as their actual numbers per soil volume unit.

Humus samples for the other analyses were taken as described in Ohtonen (1990) and all of the following analyses were done in the laboratory from homogenized humus samples with the thick roots removed. Soil respiration was measured by the alkali absorption method (Coleman 1973) at 12°C. Dehydrogenase activity (DHA) was measured by the TTC method (von Thalmann 1968). The amount of living fungal mycelium present was measured by the FDA method (Söderström 1977). Because of seasonal variation, only the autumn period, averaged over the 2 years, was chosen to represent the level of biological activity and amount of hyphae at each site. The other soil analyses comprised pH (H_2O), total N, ammonium and nitrate N, exchangeable acidity (Ohtonen 1990), total S (Ohtonen et al. 1989) and the total amounts of Cu, Cr, Zn, Pb, V and Cd determined in duplicate by wet combustion with HNO_3 and plasma emission spectrometry at the Department of Chemistry, University of Oulu.

Descriptive statistics (mean and standard error), one-way analysis of variance (ANOVA), simple correlation coefficients and linear and logarithmic regression models, were performed for statistical analysis.

The Kuopio Area

Cellulolysis was determined by the polyester-bag method monitoring weight losses in a filter paper for 11 months from autumn to autumn. Twenty-five bags, each containing a piece of paper of weight 5.0 g, were buried in the mor humus horizon at each site in October 1987 and harvested in September 1988. Nitrate N, ammonium N and sulphate S in the mor humus was determined from a soil-water extract with an ion selective electrode (Orion). A one-way analysis of variance (ANOVA) as Tukey's test and correlation analysis were used to compare the results.

The Harjavalta Area

Green Scots pine needles from the growth for 1985 were collected in March 1986 in a background area 150 km NE of Helsinki, weighed into litter bags and buried in the mor horizon of the soil as described by Fritze (1988). Twenty litter bags were buried at each site in July 1987 and harvested 1 year later.

Following mass loss determination for each litter bag, the 20 bags from each site were randomly combined to form four composite samples. A 0.5 g portion of the dried needle material from each of the composite samples was then analysed for Ca, Mg, K, Mn, Cu, Ni, Zn and Cd by atomic absorption spectrophotometry as described by Fritze (1988). The total N content of the needles was analysed by the Kjeldahl method using a Tecator Kjeltec Auto 1030 Analyser.

A one-way analysis of variance (ANOVA) was used to evaluate the litter decomposition data. Regression analysis was performed to ascertain whether either the nutrient or heavy metal content of the needle litter was correlated with the mass loss percent.

Results

The Oulu Area

Chemical Background Data for the Biological Analyses

The chemical background data will be published elsewhere (Ohtonen et al. 1989; Ohtonen 1990), except for that concerning the heavy metals. The concentrations of Pb, Zn, V, Cr and Cu were between 45 to 290, 40 to 85, 10 to 55, 10 to 35 and 5 to 35 μg g^{-1}, respectively, the concentrations generally increasing towards the city centre. Cd was below the detection level. Many of the chemical parameters showed positive correlations with each other (Table 2). The nature of the various factors and their mutual correlations enable them to be divided into two groups: primary air pollution parameters, i.e. total S, total and ammonium N and the heavy metals, and secondary air pollution parameters, i.e. pH and exchangeable acidity. Nitrate N, being an easily leachable ion, did not accumulate towards the centre of the city despite the nitrogen deposition.

Sporophore Production

Both the number of sporophores and the number of mycorrhizal species were distinctly lower at the central sites than at the outer sites (Table 3). The biomass production of mycorrhizal fungi averaged 0.29 ± 0.06 g dw m^{-2} at the outer sites but only half of this, 0.15 ± 0.04 g dw m^{-2} at the central sites. The difference,

Table 2. Significance of the coefficients of correlation between the chemical analyses of the mor humus at the mature Scots pine stands ($n = 20$) in the environs of Oulu, Finland

	S	N	NH_4-N	Cu	Cr	Zn	V	Pb	pH	exchangeable acidity
N	***									
NH_4-N	*	*								
Cu	**	*								
Cr				***						
Zn	*	*		*						
V	*			***	***	**				
Pb	*	**		*						
pH	*	**	*	*	*			*		
exchangeable acidity				--	---		-		--	

Positive correlations: * = $p < 0.05$; ** = $p < 0.01$; *** = $p < 0.001$; negative correlations: - = $p < 0.05$; -- = $p < 0.01$; --- = $p < 0.001$.

Table 3. Development of mycorrhizal fungi and mycorrhizae, in association with Scots pine, and biological activity in terms of soil respiration and DHA (dehydrogenase activity) in mature Scots pine stands near to (1–5 km) and at a distance from (5–40 km) industrial sources of atmospherically dispersed pollutants in the environs of Oulu, Finland. Mean ± standard error (SE) and the significance of the differences between the stands by ANOVA. Number of stands in both groups is 10.

	Distance from sources of emissions		
	5–40 km	1–5 km	Significance
Mean numbers of species of mycorrhizal fungi producing sporophores (no. per site)	21 ± 2	6 ± 1	$p < 0.001$
Mean numbers of sporophores of mycorrhizal fungi (no. m^{-2})	1.74 ± 0.30	0.39 ± 0.13	$p < 0.001$
Mean numbers of root tips (no. cm^{-3} of humus)	35.8 ± 4.5	16.4 ± 3.5	$p < 0.01$
Mean numbers of different types of mycorrhizae (no. per soil core)	4.52 ± 0.35	3.59 ± 0.21	$p < 0.05$
Soil respiration (μg CO_2 g^{-1} h^{-1})	51.5 ± 9.3	30.8 ± 7.0	$p < 0.01$
DHA (μmol TPF g^{-1} 24 h^{-1})	1.52 ± 0.26	1.17 ± 0.24	$p < 0.01$

however, was not significant. All these general sporophore parameters correlated well with each other, and were negatively related to the total S content of the mor humus ($p<0.01$, $p<0.001$ and $p<0.01$, respectively), the number of mycorrhizal species showing the highest correlation coefficient (Fig. 1). The sporophores of *Cortinarius* spp., *Chroogomphus rutilus* and *Suillus variegatus* showed the same decreasing trend with respect to S ($p<0.001$, $p<0.05$ and $p<0.05$, respectively).

The general sporophore parameters showed a negative correlation with the total N content of the mor humus ($p < 0.001$), and the number of mycorrhizal species had the highest correlation coefficient (Fig. 1). The numbers of sporophores of *Cortinarius* spp. and *Suillus variegatus* decreased with increasing N content ($p < 0.01$ and $p < 0.05$, respectively). The ammonium N content of the mor humus also showed a negative correlation with the general sporophore parameters, although this was significant only with the number of species of mycorrhizal fungi ($p < 0.05$). In this case the logarithmic regression model was better than the linear model (Fig. 1).

The general sporophore parameters tended to decrease with increasing Cu and Pb content of mor humus, the correlation with the number of mycorrhizal species being the closest (Cu: $p < 0.01$; Pb: $p < 0.05$). This parameter in relation to Cu is presented in Fig. 1. The number of sporophores of *Cortinarius* spp. showed a negative correlation with Cu ($p < 0.05$). As in the case of ammonium, the logarithmic model describes the relation of the sporophore parameters to Cu better than the linear model.

Although the pH of the humus varied within quite a narrow range, the general sporophore parameters, except for the biomass of mycorrhizal fungi, decreased

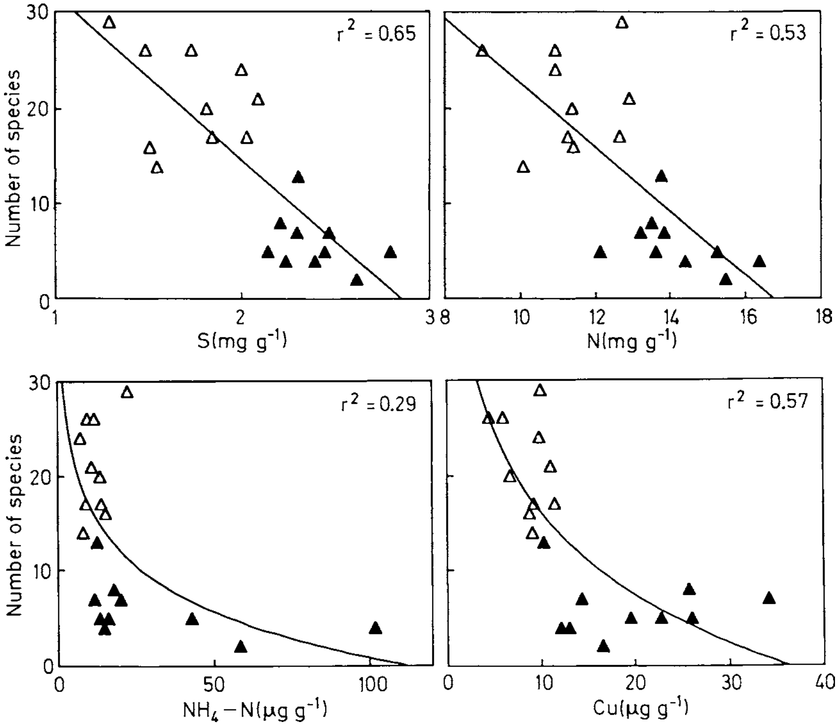

Fig. 1. Association between numbers of species of mycorrhizal fungi producing sporophores and humus layer concentrations of S, N, NH_4–N and Cu in stands of mature Scots pine 1–5 km (▲) and 5–40 km (△) from industrial sources of atmospherically dispersed pollutants in the environs of Oulu, Finland

with the slight increase in pH towards the centre ($p < 0.01$). The same was true with numbers of *Cortinarius* spp. and *Suillus variegatus* ($p < 0.05$).

Mycorrhizae

The total number of root tips per soil volume unit and the number of mycorrhizal types per site were lower at the central sites than at the outer ones (Table 3). Both of them correlated well with the sporophore parameters and also showed a rather similar pattern with them to the chemical parameters. All the general mycorrhizal parameters showed significant negative correlations with the total S content of the mor humus (Figs. 2 and 3). *Dermocybe* mycorrhiza and "type 2" mycorrhiza were the only ones whose frequencies showed a significant negative correlation with S ($p < 0.01$), and the actual numbers of *Dermocybe* and smooth, brown mycorrhizae per soil volume correlated negatively with the humus S content ($p < 0.001$ and $p < 0.05$, respectively). The latter type accounted, however, for an increasing proportion of all mycorrhizae as the total number of types decreased towards the city centre. The numbers of smooth, brown mycorrhizae were significantly lower in the central than in the outer sites ($p < 0.05$).

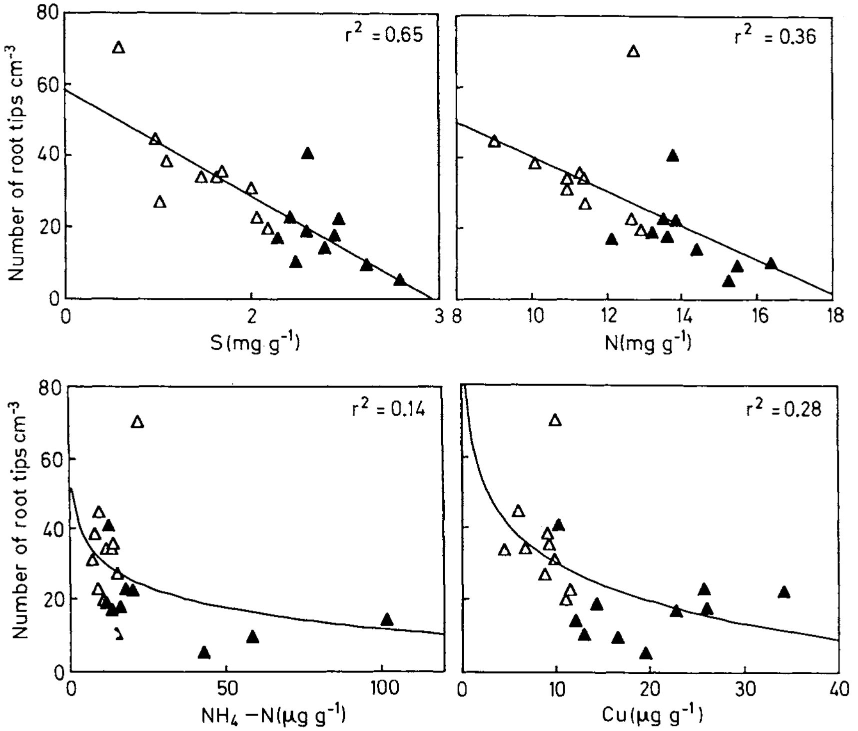

Fig. 2. Association between numbers of root tips cm^{-3} and humus layer concentrations of S, N, NH_4-N and Cu in stands of mature Scots pine 1–5 km (▲) and 5–40 km (△) from industrial sources of atmospherically dispersed pollutants in the environs of Oulu, Finland

The negative relation of the general mycorrhizal parameters to total N in the mor humus was weaker than that to total S, only the number of root tips per soil volume and mycorrhizal types showing a significant correlation ($p < 0.01$) (Figs. 2 and 3). The numbers of mycorrhizae of several individual types per soil volume, however, correlated negatively with total N. Significant correlations were showed by *Piloderma croceum* ($p < 0.05$), *Dermocybe* ($p < 0.01$), "type 1" ($p < 0.05$) and "type 9" ($p < 0.05$). Also the frequencies of *Piloderma* and *Dermocybe* decreased with increasing total N content of the mor humus ($p < 0.01$ and $p < 0.001$, respectively). Ammonium N content showed a similar logarithmic model with respect to the number of root tips and mycorrhizal types (Figs. 2 and 3) as it did with the number of sporophores of mycorrhizal fungus species. The frequency of *Piloderma croceum* also showed a negative correlation with ammonium N ($p < 0.05$). The frequency of damaged root tips increased with increasing ammonium N content in the mor humus ($p < 0.05$).

The correlations of general mycorrhizal parameters with heavy metals in the mor humus were negative, Cu (Fig. 2) and Pb showing significant correlations ($p < 0.05$) with the total number of root tips and the condition of mycorrhizae, and Cu also with the ramification index ($p < 0.05$). The numbers of *Piloderma*

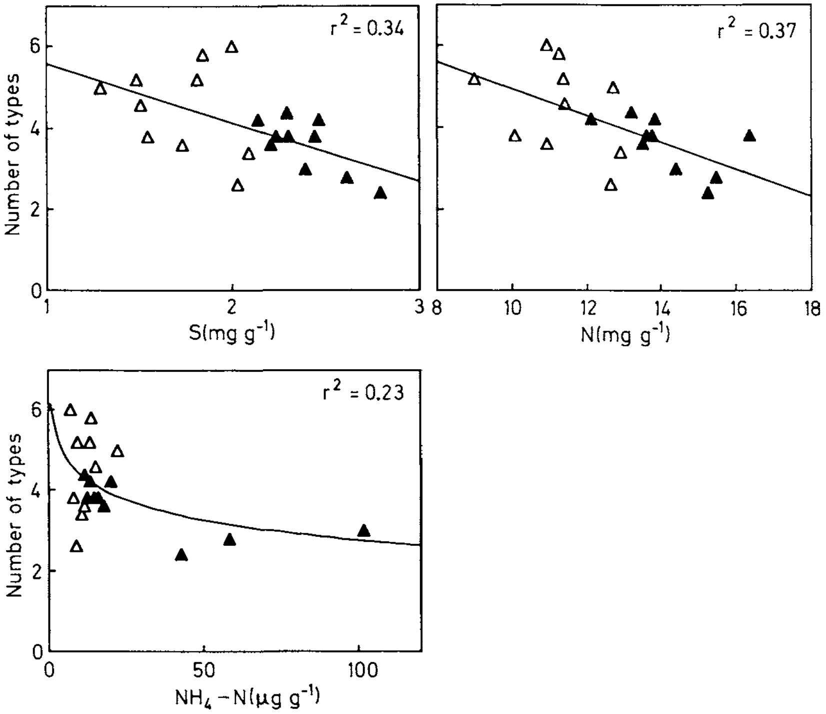

Fig. 3. Association between numbers of different types of mycorrhizae and humus layer concentrations of S, N and NH_4–N in stands of mature Scots pine 1–5 km (▲) and 5–40 km (△) from industrial sources of atmospherically dispersed pollutants in the environs of Oulu, Finland

croceum and *Dermocybe* decreased with increasing Zn content of the mor humus ($p < 0.05$), and the frequency of "type 7" with increasing Cu ($p < 0.05$). The frequency of damaged root tips showed a positive relation to Cu and V ($p < 0.01$ and $p < 0.05$, respectively).

Hyphal Length and Biological Activity

The average length of living mycelium at the outer sites was 710 ± 150 and at the central sites 680 ± 360 m g^{-1}. The length showed no clear trend towards the city centre, and no clear relationships to the chemical parameters of the mor humus were found.

The two soil activity parameters, respiration and DHA, correlated with each other ($p < 0.001$) and both decreased distinctly towards the city centre (Table 3). Negative correlations with total S ($p < 0.001$ and $p < 0.01$, respectively) and Cu ($p < 0.05$) were obvious (Fig. 4). In addition, respiration showed negative relation to total N ($p < 0.01$) and ammonium N ($p < 0.05$) (Fig. 4) and DHA to V ($p < 0.05$) concentrations in the mor humus.

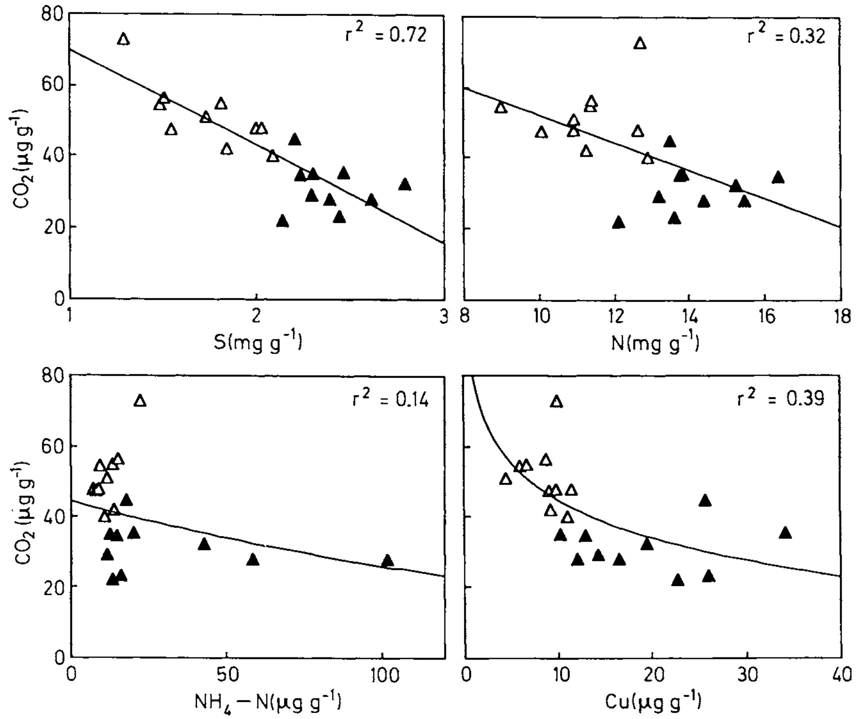

Fig. 4. Association between biological activity of the mor humus measured as respiration and humus layer concentrations of S, N, NH_4–N and Cu in stands of mature Scots pine 1–5 km (▲) and 5–40 km (△) from industrial sources of atmospherically dispersed pollutants in the environs of Oulu, Finland

The Kuopio Area

The percentage decomposition of cellulose over eleven months related to soil nitrate N, ammonium N and sulphate S is presented in Table 4. Cellulose decomposition significantly increased towards the pulp mill ($p < 0.05$) and showed

Table 4. Cellulose decomposition (% of initial dry weight) in the course of 11 months and soil NO_3–N, NO_4–N and SO_4–S content in Scots pine stands at different distances from the pulp mill in Kuopio, Finland

Distance, km	Cellulose decomposition, % Mean	SE	NO_3–N $\mu g\ g^{-1}$	NO_4–N	SO_4–S
0.3	81.4	2.5[c]	25	35	11
0.6	93.7	2.5[d]	29	18	26
1.8	67.7	3.2[b]	11	22	11
22.0	26.8	2.2[a]	0.4	8.1	8

The values of decomposition indicated with the different letters differ at least with $p < 0.05$ from each others.

a significant positive correlation to soil nitrate and ammonium N contents ($p < 0.001$). There was no correlation between cellulose degradation and soil sulphate S or pH.

The Harjavalta Area

Decomposition of the green Scots pine needle litter was retarded significantly ($p < 0.001$) towards the smelter (Fritze et al. 1989), the mass loss being 34.0% near the smelter (<4 km), 39.4% at the distance of 7 km and 43.7% at 20 km (Fig. 5).

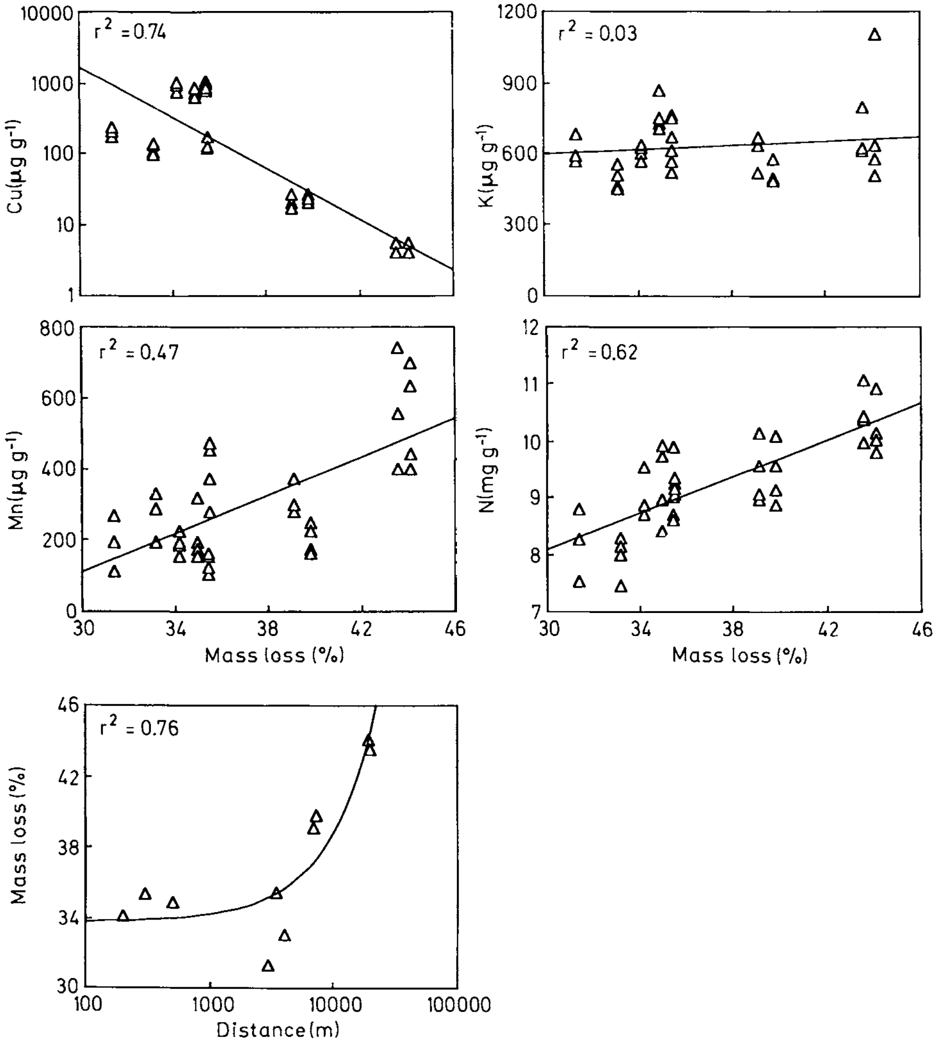

Fig. 5. The relative concentration changes (µg g^{-1} dry weight) of the different elements in relation to Scots pine needle litter mass loss % and increase in this mass loss % with distance from the smelter at Harjavalta, Finland

The relative amounts of the nutrients K, Ca and Mg in the needle litter showed no linear relation to the mass loss percentage. This is illustrated for K in Fig. 5. Close positive correlations with mass loss ($p < 0.001$) were found for the relative amounts of Mn and total N (Fig. 5). The highest Mn and N concentrations were found in the best decomposed needle litter at the unpolluted sites. All the heavy metals measured, Cu, Ni, Zn and Cd, reacted in the opposite manner to Mn and N ($p < 0.001$), being very high in the least decomposed needle litter near the smelter, as seen for Cu in Fig. 5.

Discussion

Main Pollutants and Their Relations to Biological Status of the Soil

The harmful effect of air pollution on the ecosystem is explained by several individual factors, including extra amounts of S, N and metals, which will be discussed separately here. In fact, however, there is a composite effect of various stress factors, e.g. nutrient imbalance, soil acidification, extreme weather conditions, pathogens or insects affecting the forest tree physiology and the soil biology.

Sulphur

Increasing S content has often been found responsible for failures or imbalances in ecosystems, although most of the research concerned has been carried out near factories emitting mainly SO_2, or with artificial acidification treatments using sulphuric acid.

Total S in the mor humus increased towards the centre of the Oulu area, and bore a negative relationship with many of the biological parameters. The most distinct effect was seen in the biomasses of the mycorrhizal fungi, numbers of sporophores of mycorrhizal species, numbers of *Cortinarius* sporophores and soil respiration. Sulphur has been suggested to take part in the disturbances of mycorrhizal symbiosis according to some studies, although the mechanism of this process is not known. In Scots pine forests in the Netherlands numbers of mycorrhizal species and sporophores have been found to decrease, associated with increasing SO_2 concentrations in the air (Termorshuizen and Schaffers 1987), and H_2SO_4 treatment has been shown to alter the type composition of Scots pine mycorrhizae (Dighton et al. 1985).

A decrease in soil respiration rate and in microbial biomass and a lower rate of mass loss of decomposing pine needles were also found at polluted forest sites. These may indicate a reduction in decomposition activity in response to elevated levels of S (Bååth et al. 1980; Prescott and Parkinson 1985; Bewley and Parkinson 1986). This reduced rate of litter decomposition is thought to be a factor linking S pollution to reduced forest productivity (Prescott and Parkinson 1985), and is often associated with increasing acidity in the environment of the decomposing microorganisms or alterations in element concentrations, perhaps to toxic concentrations, due to the change in acidity. However, in Oulu and Kuopio the acidity of the mor humus layer has not increased at the sites having the highest S or sulphate S concentrations, which means that the pH of the mor humus depends more on the other factors than on S.

Nitrogen

Nitrogen compounds have been identified in recent years as an environmental problem and an important stress factor in forest ecosystems (Nihlgård 1985). N is nowadays claimed to be one of the major factors causing the changes in the status of mycorrhizal fungi (Meyer 1988). In forest fertilization studies excess N seems to cause changes in the morphology (Ahlström et al. 1988) and the anatomy (Laiho et al. 1987) of Scots pine mycorrhizae. These results may indicate functional disturbances, and according to the theory of Slankis (1973), changes may be due to reduced auxin production of the fungi in elevated N concentrations. In the polluted Scots pine forests in the Netherlands the numbers of mycorrhizal species and sporophores showed a significant negative correlation with the NH_3 emissions (Termorshuizen and Schaffers 1987), as they did also with SO_2. Also the ramification index for mycorrhizae was found to decrease with increasing soil N content (Meyer 1988) and the tips of the mycorrhizae became increasingly damaged (Blaschke 1981). The mycorrhizal status in the Oulu area seems to agree well with these observations, as well as the observations about mycorrhizae in the study area of Kuopio (Holopainen and Vaittinen 1988).

The soluble nutrients in soil are a result of the activity of the decomposing microflora as well as deposition, but any point estimate of soluble nutrients cannot represent the mineralization process, i.e. the activity of micro organisms. The negative relation of ammonium N with microbial activity in the Oulu area may have arisen from a direct negative effect of ammonium N at the highest levels affecting three sites. At the other sites the ammonium N content does not exceed the natural values of forest soil. On the other hand, the ammonium N content of the soil showed a close correlation with total S and N, and the correlations of biological parameters with ammonium N may be connected with all these elements.

The effect of N depositions on biological parameters of forest soils is unclear, e.g. N fertilizers have decreased microbial activity calculated per gram of C, but increased C content of soil and thus the microbial activities of control and fertilized plots on an area basis have not differed from each other (Nohrstedt et al. 1989). A depressive effect of nitrate N on microorganisms has been observed when using N fertilizers in conjunction with artificial acidification (Popovic 1984), indicating a drastic effect of a N surplus on soil microorganisms. This may be an especially serious problem in northern forests, which have adapted to low nutrient levels and slow nutrient cycling.

The cellulose decomposition results in Kuopio showed the opposite trend to many of the biological parameters measured in Oulu. In a laboratory experiment, added N, either as ammonium sulphate, potassium nitrate or ammonium nitrate, enhanced the cellulose degradation (Ljungdahl and Eriksson 1985), as happened in the Kuopio study area. This may indicate that N becomes to a limiting factor when excess carbon is added to a normally carbon limited system. N at least is a possible reason for the increased degradation activity in the Kuopio area and provides an explanation for the close correlation of nitrate and ammonium with the degree of cellulose degradation.

Metals

Heavy metal pollution is a special problem of greater local importance than S and N depositions. A retarding effect of heavy metal deposition on the rate of decomposition of needle litter has been observed before (Tyler 1975; Williams et al. 1977; Strojan 1978; Coughtrey et al. 1979; Freedman and Hutchinson 1980) and the Harjavalta results confirm this. The pollution pattern associated with the smelter is clearly reflected in the heavy metal content of the decomposing needles, Cu, Ni, Cd and Zn being found in much higher concentrations in the needles near the plant than in those at the more remote sites. The pattern for Cu in Fig. 5 is representative for that of all heavy metals considered, although long-distance trends were more gradual for Zn and Cd.

In artificial acidification treatments a significantly higher release of the nutrients Ca, Mg, K and Mn from decomposing litter has been found in the most acidic treatments. Berg (1986a) reported a greater release of Mn and Mg from decomposing pine and spruce needle litter when the soil was acidified with sulphur. Hovland et al. (1980) and Brown (1985) demonstrated that release of K, Mg, Ca and Mn from spruce needle and bracken litter, respectively, can be induced by acidic treatment. Experiments with attached foliar needles also showed leaching of K and Mg (Waldman and Hoffmann 1988) and Ca and Mg (Joslin et al. 1988) induced by acidic cloudwater.

The Harjavalta experiment showed no linear relations between the relative concentrations of Ca, Mg and K and mass loss in the needle litter, implying that these nutrients are released at rates mostly similar to the organic matter weight loss (Staaf and Berg 1982). A higher release rate was obtained for Mn and total N at lower rates of mass loss. In the case of Mn this is believed to be a leaching effect, because the relative amount of Mn issuing from decomposing needle litter is negatively related to the litter mass loss (Staaf and Berg 1982). In the case of total N it may also be a leaching effect, since the litter used was green and therefore rich in N, but it is also generally known that total N is immobilized in the early stages of coniferous needle litter decomposition (Berg 1986b). The results thus confirm those of Fritze (1988) that Mn is leached from decomposing green needle litter in relation to the pollution gradient.

Like needle decomposition, the soil respiration rate has been shown to decrease in soil contaminated with metals (Nordgren et al. 1986). This is also in agreement with the observations in Oulu, where Cu was one of the most important environmental parameters with respect to biological variation.

Indicative Values of the Parameters

Three groups of soil biological parameters were found here, distinguished by their patterns of correlation with the main pollution agents, S, N and the heavy metals: those which were markedly depressed by this air pollution, those which increased in the polluted sites, and those which were indifferent to it.

The general sporophore parameters all showed negative correlations with total S and N and certain metals. Sporophore production could thus be a suitable parameter for use in evaluating the biological status of forest mor humus. It turned out to be a good bioindicator also in an artificial acidification study in Norway (Høiland 1988). Suitable indicator species could be *Suillus variegatus* and *Chroogomphus rutilus*, which decreased most markedly with increasing S and N deposition. Sporophores of *Cortinarius* spp. were also reduced in number, but this group consists of several species, not all of which are necessarily sensitive to air pollutants. Sporophore production varies greatly from year to year, however, and usually 3 successive years are needed to study it adequately at a Finnish forest site (Ohenoja and Koistinen 1984).

A suitable method for determining the response of the mycorrhizae could be the counting of both the number of root tips and the number of mycorrhizal types, which in the Oulu study correlated well with the general sporophore parameters. The most powerful indicators among the mycorrhizal types may well be the pollution-sensitive types *Dermocybe* and *Piloderma croceum*. A rough counting of types using the characterizations and identification keys already published (e.g. Agerer 1986; Jansen and de Vries 1988) could be done fairly quickly. For greater reliability, however, descriptions of mycorrhizal types should include light and electron microscopy and chemical analyses (Agerer 1986; Haug et al. 1986). One disadvantage of this approach is that the fungus symbiont remains unidentified in many cases, and the composition and number of types do not necessarily correspond to the composition and actual number of mycorrhizal fungus species.

The effects of air pollutants on mycorrhizal fungi and mycorrhizae of forest trees are now being critically discussed. Controversial results have also been published, partly due to varying methods. Jansen (1988) summarized the effects as decreases in sporophore production, in the number of species fruiting and the number of mycorrhizal types as well as in mycorrhizal infection. On the other hand, Haug et al. (1986) found no differences in the anatomy of mycorrhizae in healthy and damaged spruce and fir trees in the Black Forest, nor did Dighton and Skeffington (1987) with Scots pine.

Soil respiration and DHA are common indicators of the activity of the whole microflora and react in this way to many disturbances in the ecosystem. These parameters may thus serve as useful indicators of pollution. Because they vary temporally and spatially in response to many ecological factors (Ohtonen 1990), some care is needed when using them as indicators in forest ecosystems of varying nutrient status, for instance. DHA, an indicator of non-specific decomposition activity in biological material (Moore and Russel 1972), sometimes poorly correlates with other parameters describing the biological activity in soil (Nohrstedt 1985). Others (Stevenson 1959; Ohtonen 1990) found a good correlation between DHA and soil respiration rate, and DHA has been found to correlate better with soil pH than many other soil parameters (Nohrstedt 1985). DHA could thus serve as a valuable index for assessing soil acidification. The negative correlation with sulphur in the Oulu area supports the findings of Nohrstedt. Soil respiration nevertheless seems to be a more sensitive parameter than DHA.

Results of the needle decomposition experiment at Harjavalta confirm the observation of Fritze (1988) that Mn is leached from decomposing green needle litter in relation to the pollution gradient. The rate of decomposition of needle litter, and especially the leaching of Mn from the needles, could thus be valuable pollution indicators. The decomposition rate, however, is not always changed in the polluted environment (Fritze 1988).

Cellulose degradation is one of the parameters showing positive correlations with at least one of the pollution agents. In agricultural soil, Vörösbaranyi (1984) has showed that the function between cellulose decomposition and N fertilization is a parabolic curve with maximum at 140 kg N ha^{-1}. A pronounced increase in cellulose decomposition may be a symptom of an imbalance in microbial activity, and the effect of this on the quality of the humus, for instance, needs further investigation.

The changed balance of microbial ecosystems is seen also in the changes in the diversity of mycorrhizal fungi. The increasing frequencies of smooth, brown mycorrhizae and *Lactarius rufus* sporophores imply their greater resilience in polluted soil, where they may replace the more sensitive fungi. Such changes in diversity have been observed in several studies (Dighton et al. 1985; Holopainen and Vaittinen 1988; Jansen 1988). In addition, changes in species composition of microfungi or analysis of the whole community (Bååth et al. 1984) could be good indicators of air pollution stress.

Parameters showing no response to the main pollution indexes evaluated here, and thus are with little value as pollution indicators, included the condition of the mycorrhizae as determined under a dissection microscope. More exact microscope examinations would thus be needed (Laiho et al. 1987). FDA-stained mycelial length in the Oulu area did not seem to react to air pollution. The same has been noticed by Fritze (1987) and Nordgren et al. (1986), although indications to the opposite were observed by Bååth et al. (1984). The method may be insufficiently accurate to reveal any differences present.

Mycorrhizal and macrofungal parameters and microbiology of forest soils can provide a good insight of changes taking place in the soil under the effect of airborne pollutants. Different elements and their different chemical natures will cause varying reactions in the microflora, and no one single parameter can tell us everything about soil changes. Parameters may be concerned with single species or with the whole microflora, and with particular physiological, ecological or systematic groups of microflora. Some parameters are clearly better indicators than others. Further basic research is still needed into the complex mechanisms by which individual chemicals exert their effects and the interactions between them.

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2.3 Vegetation and Insects

Epiphytic Lichens on Conifers in the 1960's to 1980's in Finland

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Summary

The frequencies of three lichen species or genera have been studied in litter samples from seven permanent litterfall collection plots located in different parts of the country. The frequencies of pollution-sensitive *Usnea* and *Bryoria* species have decreased between 1967 and 1985 in the southernmost sample plots, while the frequency of fairly tolerant *Hypogymnia physodes* has remained stable.

The occurrence and abundance of 13 common epiphytic lichen species or genera have been mapped in a survey of basal trunks and branches of 6526 coniferous trees (*Picea abies* and *Pinus sylvestris*) on 2333 systematically selected plots throughout Finland in 1985 and 1986. The average number of species and IAP values of the sample trees, as well as the distribution maps of eight species or genera and their abundance and occurrence on stands of different age groups, are presented.

In the southern parts of the country the low IAP values, the present scarcity of *Usnea* and *Bryoria* species and the decreased frequencies of these species in the litter samples may indicate the effects of increased sulphur deposition. Among other significant factors correlating with the distribution and abundance of the studied lichens are climate, tree species and stand age.

Introduction

Lichens have been used extensively as biological indicators of air pollution, especially sulphur deposition, during the last few decades. The most commonly used method in lichen studies is the mapping of the distribution of the total epiphytic lichen flora, or some well-known indicator species, at different distances from a pollution source. Mapping studies of this sort have been carried out in several hundred urban and industrial areas in Europe and North America since the earliest studies of the 1930's (Hawksworth 1973, Showman 1988). Most of the studies have been concentrated in relatively small areas, but systematic, large-scale mapping studies have recently been carried out in some European countries.

One of the most extensive studies is the Atlas of the Lichens of the British Isles in 10 × 10 km grids. The first published part of this Atlas contains a total of 176

Kauppi et al. (Eds).
Acidification in Finland

species mapped in over 2900 grid units (Seaward and Hitch 1982). In the Netherlands the effect of air pollution on epiphytic lichen flora has been studied in 5 × 5 km grids (de Wit 1976). The first results of the lichen mapping in Austria have been published (Türk and Wittmann 1986). In West Germany the detailed distribution of numerous lichens has been mapped in Baden-Württemberg (Wirth 1987), for instance.

In Sweden the distribution and abundance of four common epiphytic lichens (*Hypogymnia physodes, Platismatia glauca, Usnea* spp. and *Bryoria capillaris*) on twigs and branches of *Picea abies* have been studied on ca. 80 plots throughout the country (Westman 1986). In addition, the maximum thallus length of *Usnea* spp. and *Bryoria capillaris* has been measured.

The studies described above indicate that air pollution is one of the main factors explaining the present distribution of many species. Some very sensitive species (e.g. *Lobaria* spp., *Bryoria* spp., *Usnea* spp.) have decreased or vanished over wide areas. In the most severely polluted regions the epiphytic lichen flora is distinctly impoverished, consisting mainly of the most toxitolerant species (e.g. *Lecanora conizaeoides, Scoliciosporum chlorococcum*).

It is well known that many epiphytic lichens have decreased in towns, cities and around industrial plants in Finland due to pollution (see e.g. Laaksovirta and Silvola 1975; Laaksovirta and Olkkonen 1977, 1979; Kauppi and Mikkonen 1980). However, it is not known to what extent the increased level of sulphur deposition has affected the lichen flora throughout the whole country, and especially the most severely polluted southern Finland. The main objectives of this study are to investigate trends in the frequency of occurrence of lichen species in litter samples over the period 1967–1985, and to describe the regional distribution of the most common epiphytic lichens in Finland. The time evolution and regional patterns in relation to air pollution are discussed.

Material and Methods

Permanent sample plots for monitoring litterfall were established by Professor Risto Sarvas in the 1960's. Since then some of the plots have been continuously monitored by the Finnish Forest Research Institute. Here we report the results for the period 1967–1985 on seven plots.

Litter has been collected on each plot with 8–15 funnel-shaped collectors (area 0.5 m^2) made of galvanized steel sheet. The collectors were placed systematically or randomly on 50 × 50 m or 100 × 100 m plots. Litter accumulates in the small canvas bags tied to the bottom of the collectors. The bags were emptied four or five times a year, with a frequency of once a month during the summertime (May-August). The litter samples were dried at room temperature and sorted into the following components: seeds, flowers, cones, needles or leaves, bark, epiphytes (mainly lichens), insect remains etc.

The frequencies of some epiphytic lichens in the litter samples, e.g. *Hypogymnia physodes*, *Bryoria* spp. and *Usnea* spp., were studied from samples collected every third year on seven *Pinus sylvestris* plots (Fig. 1) between 1967 and 1985. Only the litter samples collected between September and May were utilized.

Over 3000 permanent sample plots were established by 13 field groups in conjunction with the 8th National Forest Inventory (NFI-8) in 1985 (southern and central Finland) and 1986 (northern Finland). The sample plots were clustered: four per cluster in southern and central Finland and three in northern Finland. The clusters were located in a 16 × 16 km grid in the south and 24 km × 32 km in the north (Fig. 1).

Epiphytic lichens were studied on 6526 conifers on 2333 plots; 4075 of the trees were Scots pine (*Pinus sylvestris*) and 2451 Norway spruce (*Picea abies*). Lichens were studied on the trees closest to the mid-point of the plot. Lichens were recorded on both the trunk and branches between a height of 0.5 and 2.0 m on all sides of the tree. Only trees with a breast height diameter of over 4.5 cm were

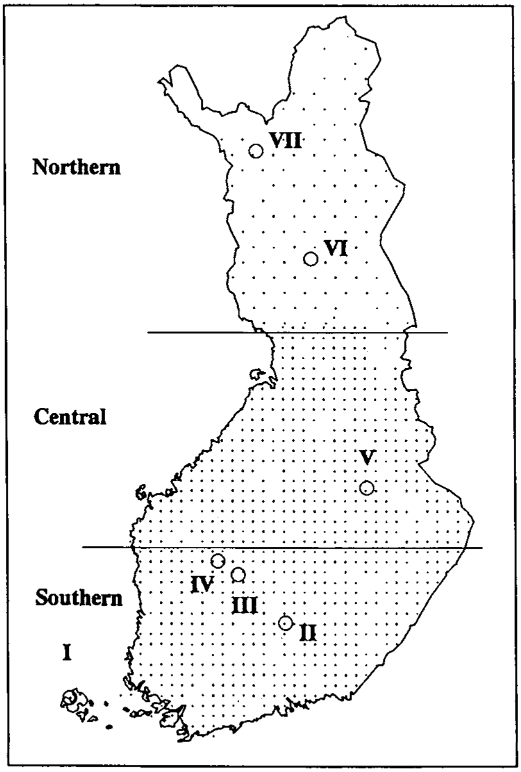


Fig. 1. The network of lichen-tree sample plots established in the 8th National Forest Inventory. Each *point on the map* represents 1–4 sample plots and 1–12 trees. Note that the western parts of northernmost Finland lack sample trees. The Roman numerals *I–VII* depict the litter collection plots. The areal division into southern, central and northern Finland has been used in Figs. 4, 5 and 6

included. In some stands dominated by deciduous trees only one or two conifers were available for sampling.

The abundance of 13 lichen species or genera which vary in sensitivity to sulphur dioxide (Table 1) was estimated using a four-step abundance scale (Table 2). Whether the lichens grew more dominantly on the trunk or on the branches was also estimated. The species or genera were selected so that they were (a) easily identifiable even by people not acquainted with lichens, (b) common and widely distributed in Finland, and (c) common on conifers.

A wide range of background information about the stand, individual trees, field vegetation and soil were collected during the inventory. In particular, the tree species composition, the age, and the basal area (m^2 ha^{-1}) of the stand were available for this study.

Table 1. The 13 lichen species surveyed in the 8th National Forest Inventory (1985–1986) divided into groups according to their presumed sensitivity to sulphur dioxide. The nomenclature follows Santesson (1984)

Sensitivity	Species
Tolerant	*Scoliciosporum chlorococcum* incl. green alga *Desmococcus olivaceus* *Hypocenomyce scalaris*
Fairly tolerant	*Hypogymnia physodes* *Parmeliopsis ambigua* *Cetraria chlorophylla* *C. pinastri*
Moderately sensitive	*Parmeliopsis* spp. (*P. hyperopta* and *P. aleurites*) *Platismatia glauca* *Pseudevernia furfuracea* *Parmelia sulcata* *Evernia prunastri*
Sensitive	*Bryoria* spp. incl. *Alectoria sarmentosa* *Usnea* spp.

Table 2. The abundance scale used in the field survey. Classes 3 and 4 were pooled in the data analysis

Abundance class	Definition
0-absent	
1-sparse	At most two small individuals
2-fairly abundant	3–7 individuals or if less, tall individuals
3-abundant	More than 7 individuals or wide cover with indistinct limits between individuals
4-abundant outside the sampling level	Abundant on the sample tree, but only above or below the sampling level (0.5–2.0 m height). Used mostly in reindeer grazing areas

Data Analysis

Distribution maps were produced by program MAPP using an moving averages algorithm which generates raster surface maps with a 50 × 50 km grid according to the smoothed mean values of the observations in each grid quadrat.

IAP (Index at Atmospheric Purity) is commonly used for summarizing information about species pollution tolerance and their spatial variation of abundance

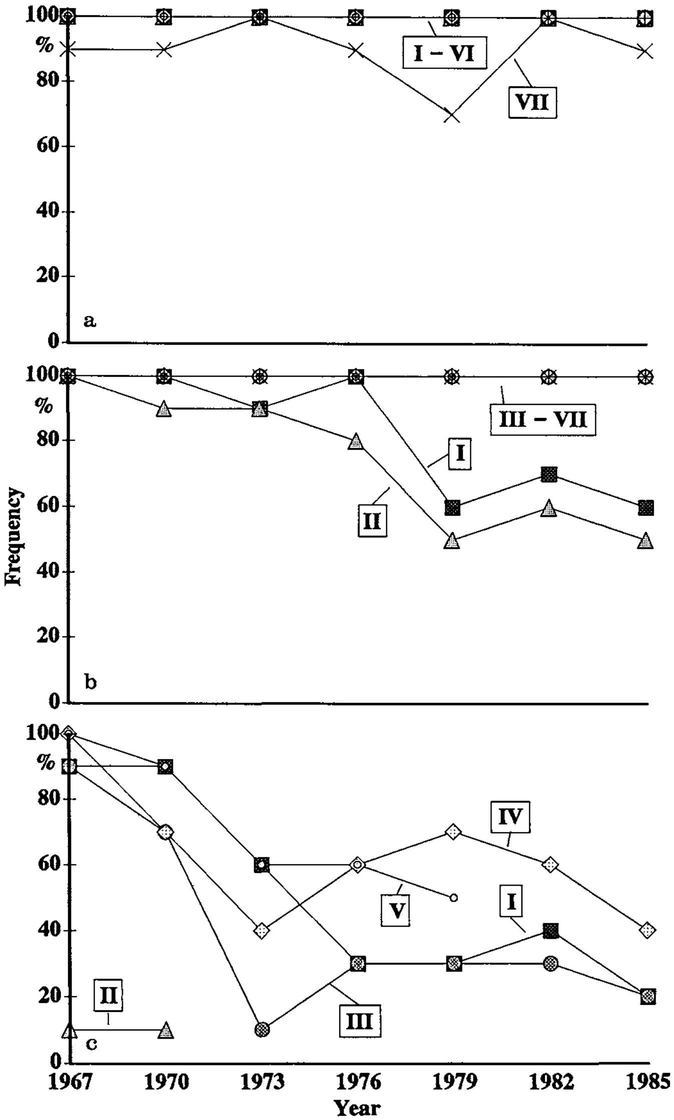
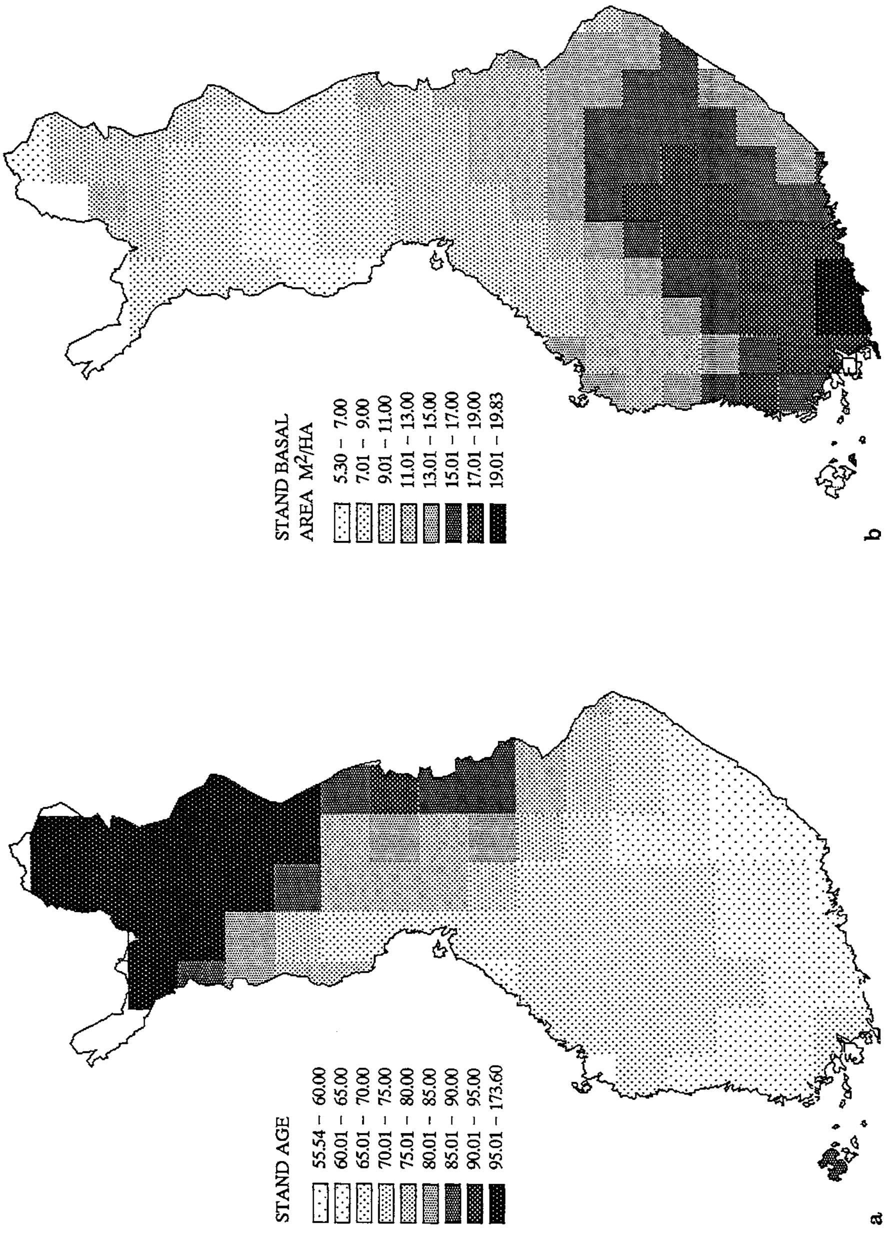


Fig. 2a–c. The frequencies of *Hypogymnia physodes* (**a**), *Bryoria* spp. (**b**), and *Usnea* spp. (**c**) in the samples from the litterfall collection plots (I–VII, see Fig. 1) every third year between 1967 and 1985. Note that litter collection on plot V was interrupted in 1979


STAND AGE
55.54 - 60.00
60.01 - 65.00
65.01 - 70.00
70.01 - 75.00
75.01 - 80.00
80.01 - 85.00
85.01 - 90.00
90.01 - 95.00
95.01 - 173.60
a
STAND BASAL AREA M²/HA
5.30 - 7.00
7.01 - 9.00
9.01 - 11.00
11.01 - 13.00
13.01 - 15.00
15.01 - 17.00
17.01 - 19.00
19.01 - 19.83
b

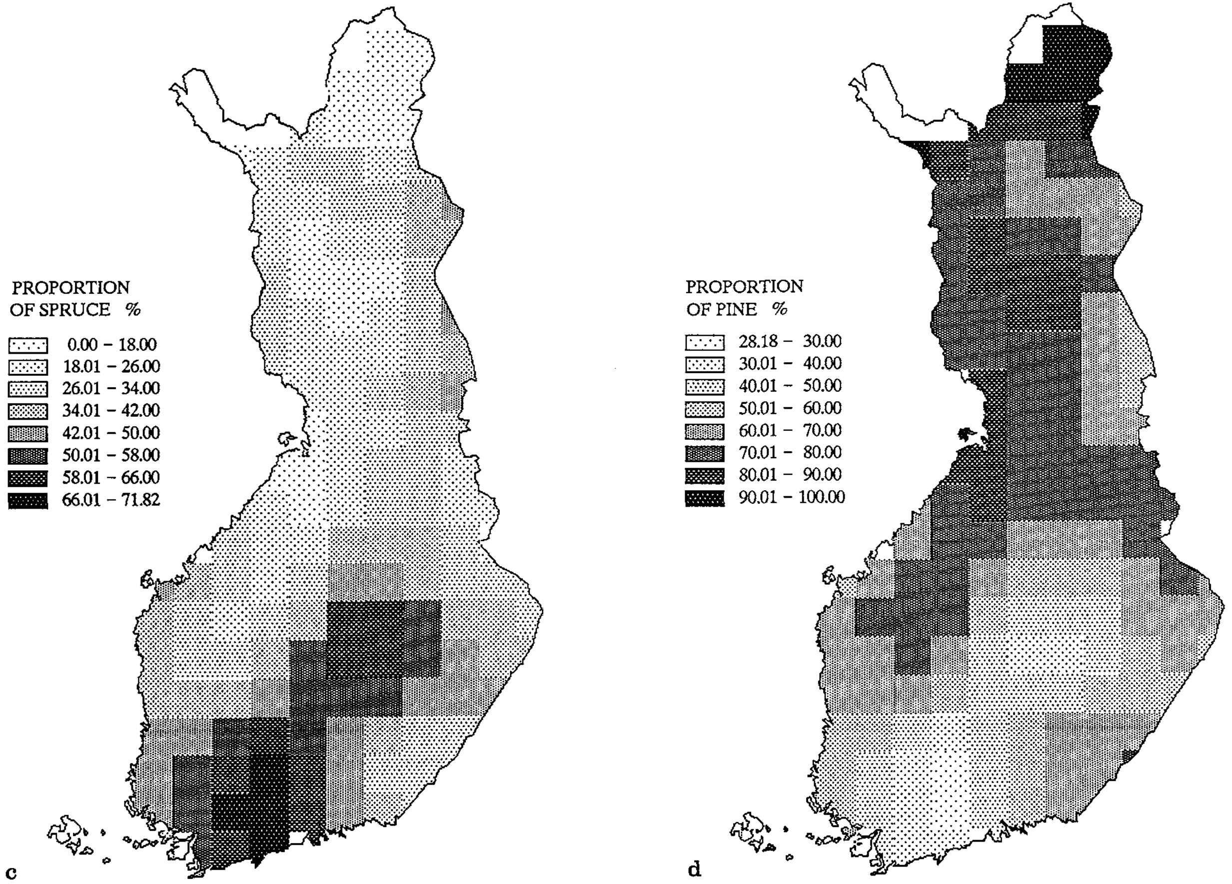


Fig. 3a–d. The mean age (**a**), mean basal area ($m^2 ha^{-1}$) (**b**) and proportions (%) of Scots pine (**c**) and Norway spruce (**d**) in the stands of the 8th National Forest Inventory plots

(LeBlanc and DeSloover 1970). It is assumed that the more tolerant the species, the lower is the average number of its companion species.

$$\mathrm{IAP} = \sum_{n}^{1} (Q * f) * 10^{-1},$$

where n = species number on a tree, Q = average number of other species growing with the target species, and f = abundance (0–3) of the target species. The IAP values were calculated for every sample tree.

Results

Long-Term Changes in Litter Lichen Composition

Hypogymnia physodes, which is a very common species in southern and central Finland, was detected in all litter samples from all the sites except the northernmost site VII, where the frequency of this species remained rather stable at around 80% (Fig. 2a). The frequencies of sensitive *Bryoria* species in the litter samples decreased during the collection period on the two southernmost sample plots (sites I and II, Fig. 2b). In southern and central Finland the frequencies of sensitive *Usnea* species decreased in a consistent fashion (sites I–V, Fig. 2c). In northern Finland *Usnea* species are rare and did not occur in the litter samples on sites VI and VII.

Observations Made on NFI-8 Sample Plots

Stand age and basal area were not evenly distributed. The oldest stands were found in the eastern and northern parts of the country (Fig. 3a). Stand ages in northeastern Lapland were on an average 100–150 years higher than those in southern Finland. The stand basal area was highest in southern Finland, decreasing gradually northwards (Fig. 3b).

The mutual relationships between the proportions of spruce and pine also showed distinct spatial patterns (Figs. 3c,d). Spruce is dominant in the southern and central parts of the country, whereas pine is more common in the western part of central Finland and in northernmost Finland.

The most abundant species throughout the country both on pine and spruce were *Hypogymnia physodes* and *Parmeliopsis ambigua.* In northern Finland *Bryoria* species were very common, particularly on spruce. *Usnea* spp., *Platismatia glauca, Cetraria chlorophylla* and *C. pinastri* were fairly common throughout the country on spruce, as well as *Parmeliopsis* spp. and *Cetraria pinastri* on pine. The least common of the studied species were *Scoliciosporum chlorococcum, Hypocenomyce scalaris, Evernia prunastri* and *Parmelia sulcata* (Fig. 4).

Hypogymnia physodes was abundant in stands of all ages (Fig. 5a). *Bryoria* species (Fig. 5b), *Parmeliopsis ambigua* (Fig. 6a) and *Platismatia glauca* (Fig. 5d)

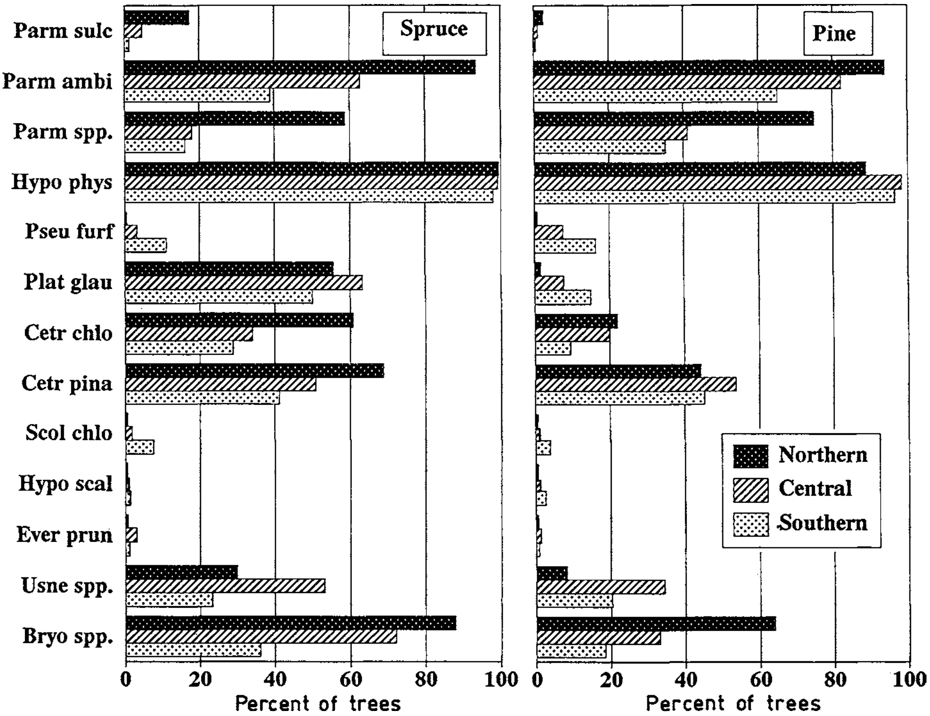


Fig. 4. The frequencies of lichens on sample trees of the 8th National Forest Inventory plots in southern, central and northern Finland (cf. Fig. 1)

were species that clearly favoured old forests, and also *Usnea* species (Fig. 5c) and *Scoliciosporum chlorococcum* (Fig. 6b) were most abundant in relatively old stands. *Cetraria chlorophylla* (Fig. 6c) and *Cetraria pinastri* (Fig. 6d) are species that were most common in relatively young stands. All the other species tended to favour old forests.

All the lichen species occurred on both spruce and pine. *Platismatia glauca, Cetraria chlorophylla, Usnea* spp., *Bryoria* spp., *Evernia prunastri* and *Parmelia sulcata* were spruce-favouring species. *Parmeliopsis* spp. (especially *P. aleurites*), *Pseudevernia furfuracea* and *Hypocenomyce scalaris* favoured pine. There were also areal differences in the preference for the host tree: *Hypogymnia physodes* and *Parmeliopsis ambigua* were more abundant on spruce in northern Finland, although in southern Finland they were equally common on both trees.

The distribution maps of the eight most common or otherwise interesting species are presented in Figs. 7 and 8. *Hypogymnia physodes* (Fig. 7a) and *Platismatia glauca* (Fig. 7d) are somewhat southern species, although they were also found especially in the eastern parts of northern Finland. *Bryoria* spp. (Fig. 7b), *Parmeliopsis ambigua* (Fig. 8a) and *Cetraria chlorophylla* (Fig. 8c) had a more or less northern distribution although they did occur throughout the country. *Usnea* species were most common in the western parts of central Finland, rarer in

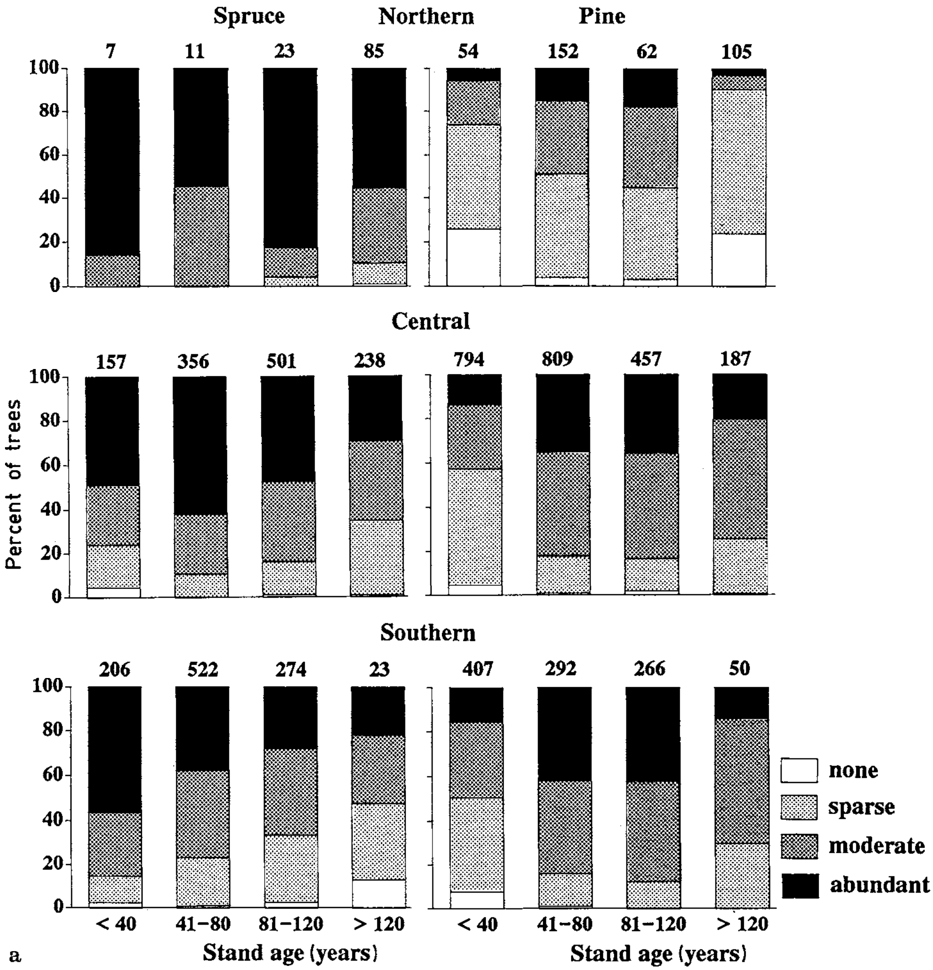


Fig. 5a

southern Finland, and almost totally absent in northern Finland (Fig. 7c). *Scoliciosporum chloroccocum*, and its algal partner *Desmococcus olivaceus*, which are southern species, were not found in this material in northern Finland (Fig. 8b). *Cetraria pinastri* (Fig. 8d) was very common throughout the country, although its spatial abundance pattern was somewhat uneven.

Pseudevernia furfuracea is a southwestern species, its northernmost occurrence in this material being in the northern parts of central Finland. The distribution of *Evernia prunastri* resembled that of *Usnea* spp., although it is a markedly less common species on conifers. All *Parmeliopsis* species had a distribution similar to that of *P. ambigua*. *Parmelia sulcata* is a northern species on conifers, and was found at only a few localities in southern Finland. *Hypocenomyce scalaris* was fairly common only in southern Finland.

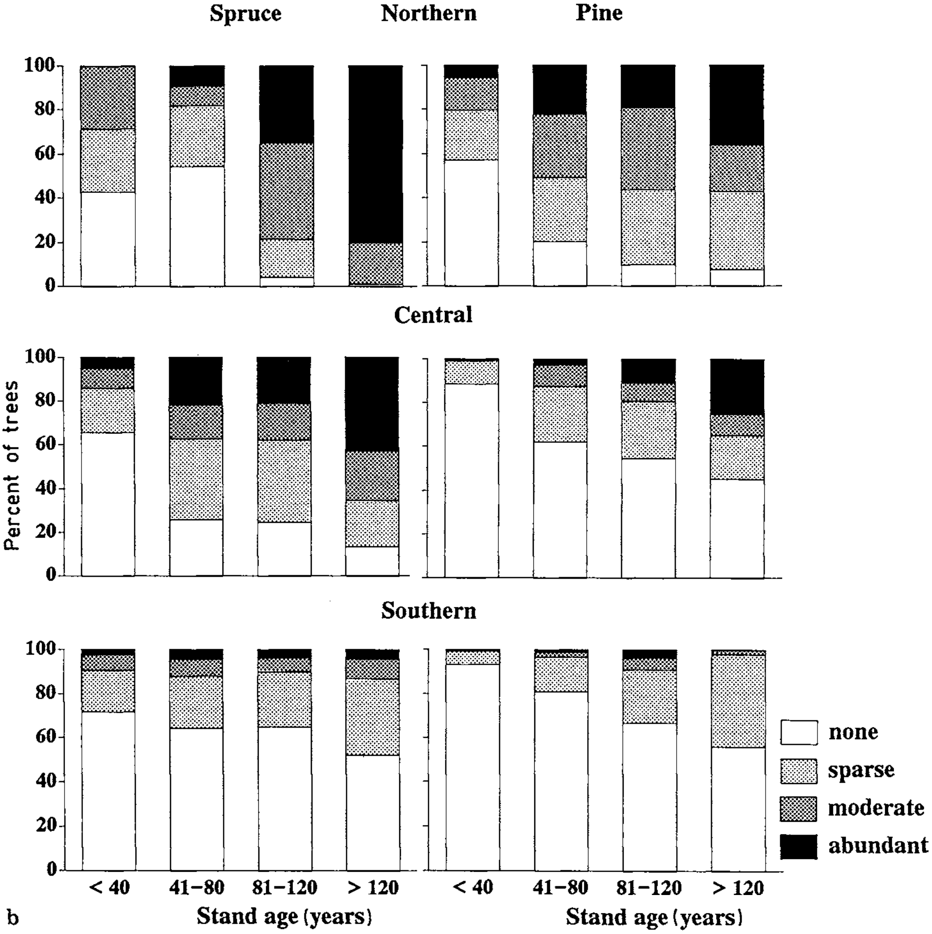


Fig. 5b

Both the average number of species and the IAP values were lowest in southeastern Finland (Fig. 9a, b). On an average, the values increased gradually on moving northwards. Low IAP values also occurred in certain parts of southern and central Finland, particularly around industrialized areas. In the eastern parts of northernmost Finland the average number of species and the IAP values were distinctly low.

Discussion

The biomass of the lichens in the litter samples could have been measured more reliably than the frequencies. However, biomass was not measured because of the

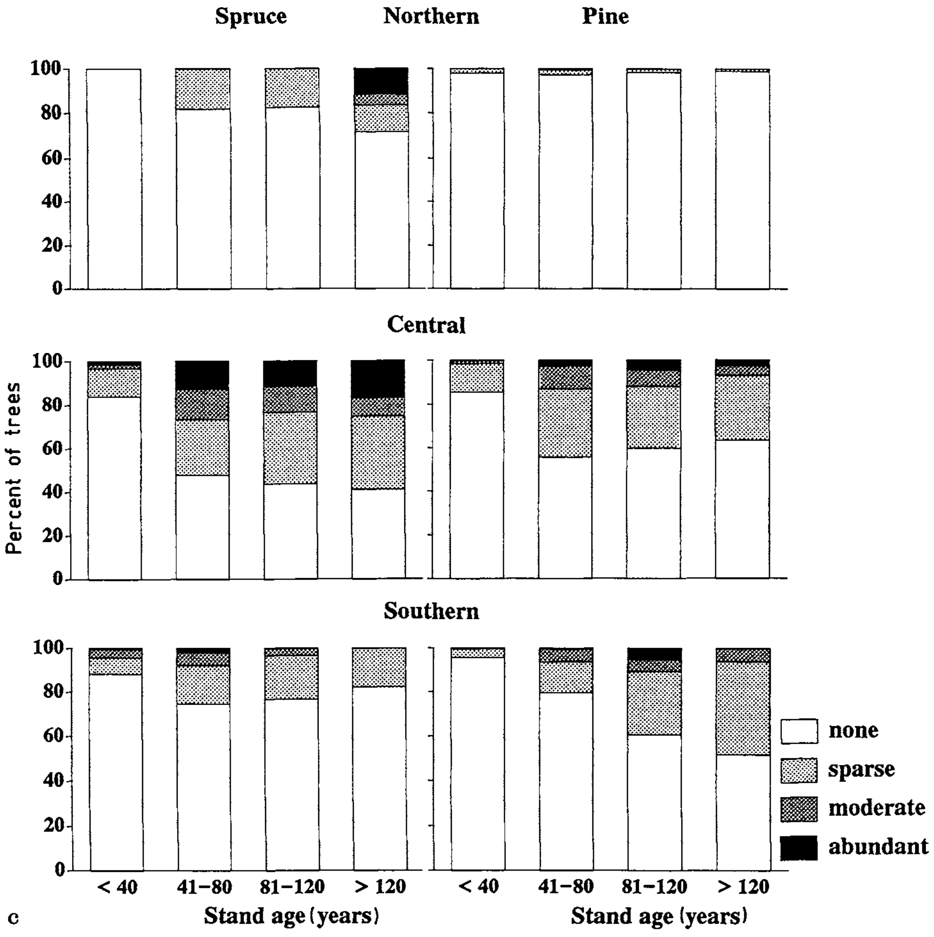


Fig. 5c

laboriousness of sorting the litter samples. The small number of collectors per sample plot meant that the effect of random fluctuation on the frequencies can be considerable. Thus the magnitude and exact time of the changes in the frequencies of *Bryoria* and *Usnea* species are not as meaningful as the distinct decreasing trend on several plots. The biomass already has to be very low before the frequency begins to fall.

The study area is especially wide in the south-north direction, ranging from the hemiboreal to the northern boreal zone (Ahti et al. 1968). Although we tried to select as widely distributed and common species as possible, most of them still exhibit a clear south, or north-centred, distribution pattern. In fact *Cetraria pinastri* seems to be the only species that is approximately equally common throughout the country.

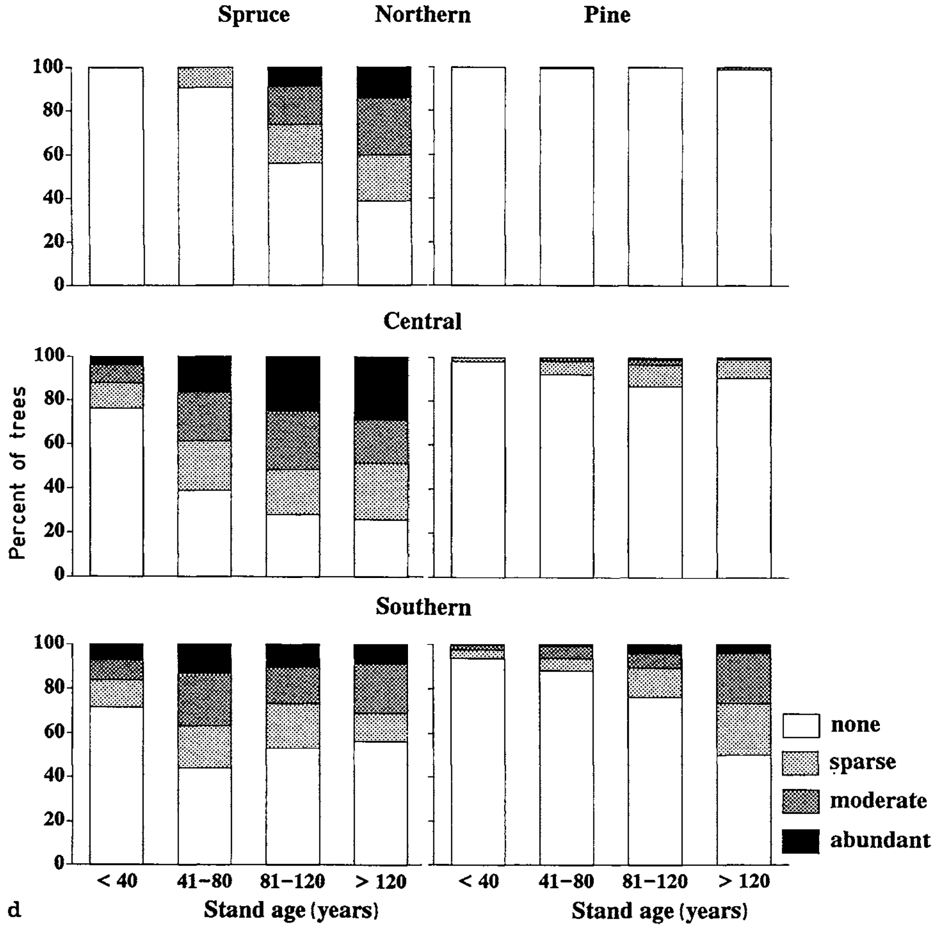


Fig. 5a–d. The occurrence and abundance of *Hypogymnia physodes* **a**, *Bryoria* spp. **b** *Usnea* spp. **c** and *Plastismatia glauca* **d** on sample trees of different stand age classes in southern, central and northern Finland (cf. Fig. 1). The *values above the columns* **a** denote total sample tree frequencies in each age class

The distribution of *Bryoria* species in Finland is predominantly northern boreal. The biomass of *Bryoria* species on trees is largest in old, mesic coniferous forests on the hills of northern and northeastern Finland. The most common species in these areas are *Bryoria fuscescens, B. simplicior, B. fremontii* and *Alectoria sarmentosa.* In southern and central Finland the dominant species are *B. capillaris, B. fuscescens* and *B. furcellata,* the large species *B. fremontii* and *Alectoria sarmentosa* being fairly rare. Moreover the specimens in southern Finland are often small and of poor condition compared to the large, vigorous and sometimes fertile specimens collected at the beginning of this century.

The distribution of *Usnea* species in Finland is floristically interesting. They appear to be most common in the middle boreal zone, and their abundance

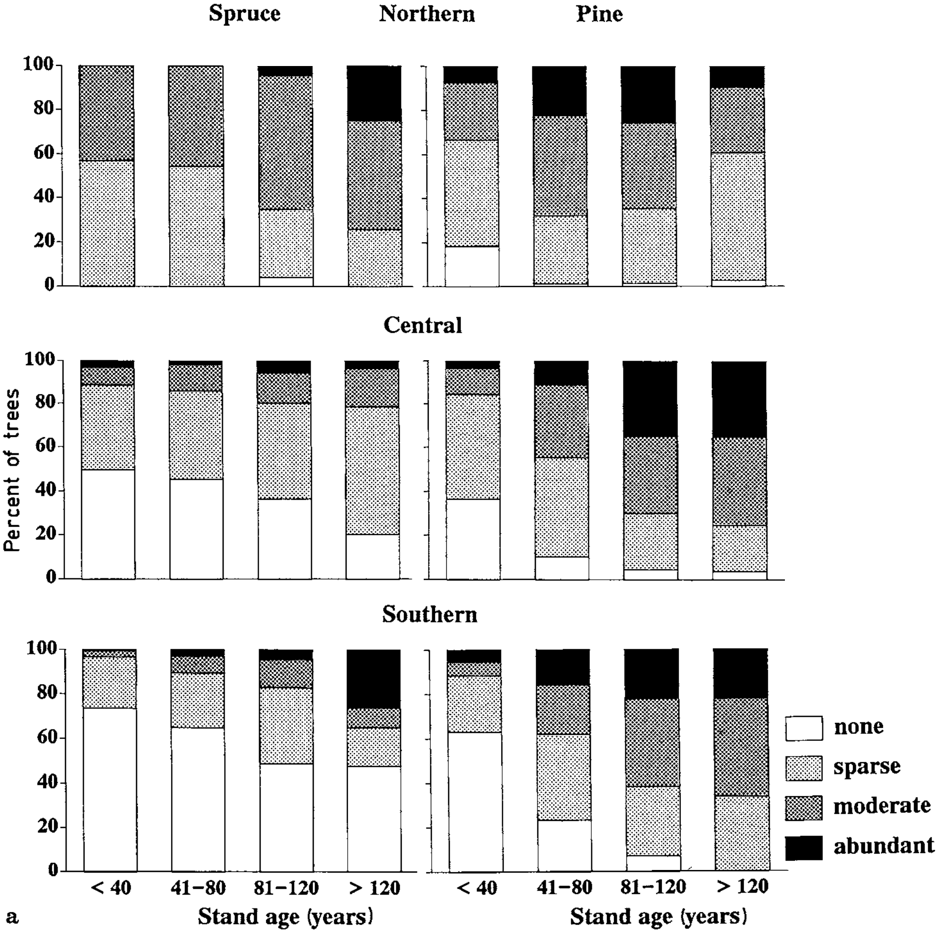


Fig. 6a

decreases both to the north and to the south. *Usnea* species are apparently rare in northern Finland for climatic reasons. Their scarcity in southern Finland is, however, due to other reasons: museum collections dating from the late 19th and the early 20th century show that they have been common and abundant on conifers in this area. In Sweden too, *Usnea* species are most abundant on spruce in the central parts of the country (Westman 1986).

The particular abundance of *Usnea* species in the western parts of central Finland is unusual. One reason may, however, be the lower humidity and smaller amount of rainfall in the area (Alalammi 1988) that is favourable to these lichens.

There may be marked differences between the different *Usnea* species as regards their sensitivity to air pollution. One of the most common species, the small fruticose *U. hirta*, seems to be more tolerant than most larger species, e.g. *U. filipendula, U. glabrescens*, and especially *U. scabrata.*

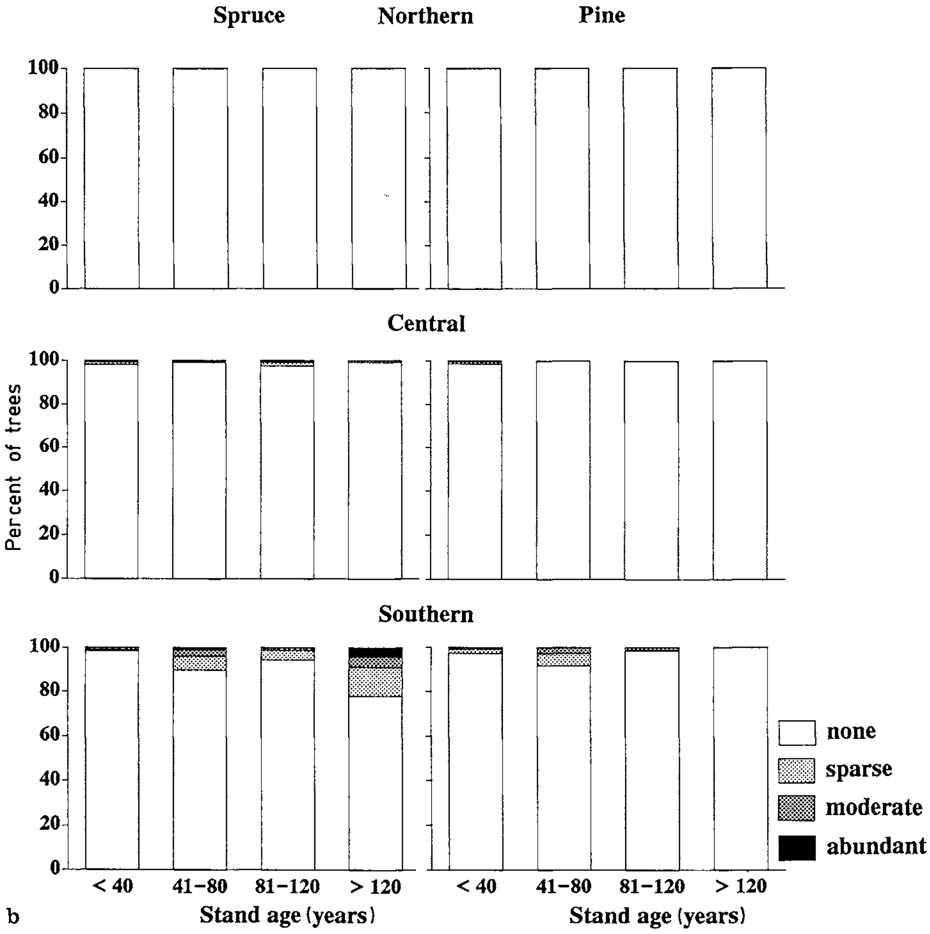


Fig. 6b

The distribution of *Evernia prunastri* on conifers resembles that of the *Usnea* species. Although this species is still a common epiphyte on deciduous trees in southern Finland, it occurs only sporadically on conifers. It may be more sensitive to sulphur deposition on conifers than on deciduous trees, whose bark is generally less acidic.

The pollution-tolerant *Scoliciosporum chlorococcum* and its free-living algal partner *Desmococcus olivaceus* are very common in Finland on trees in urban areas, where most other lichens are absent. *Scoliciosporum chlorococcum* is a predominantly southern species in Finland, which may have increased lately (Ahti and Vitikainen 1974). This is the only one of the species studied that has been interpreted as a positive indicator of air pollution.

According to our results, *Scoliciosporum chlorococcum* is most common in the dense, shady spruce forests of southern Finland, with a scattered distribution in

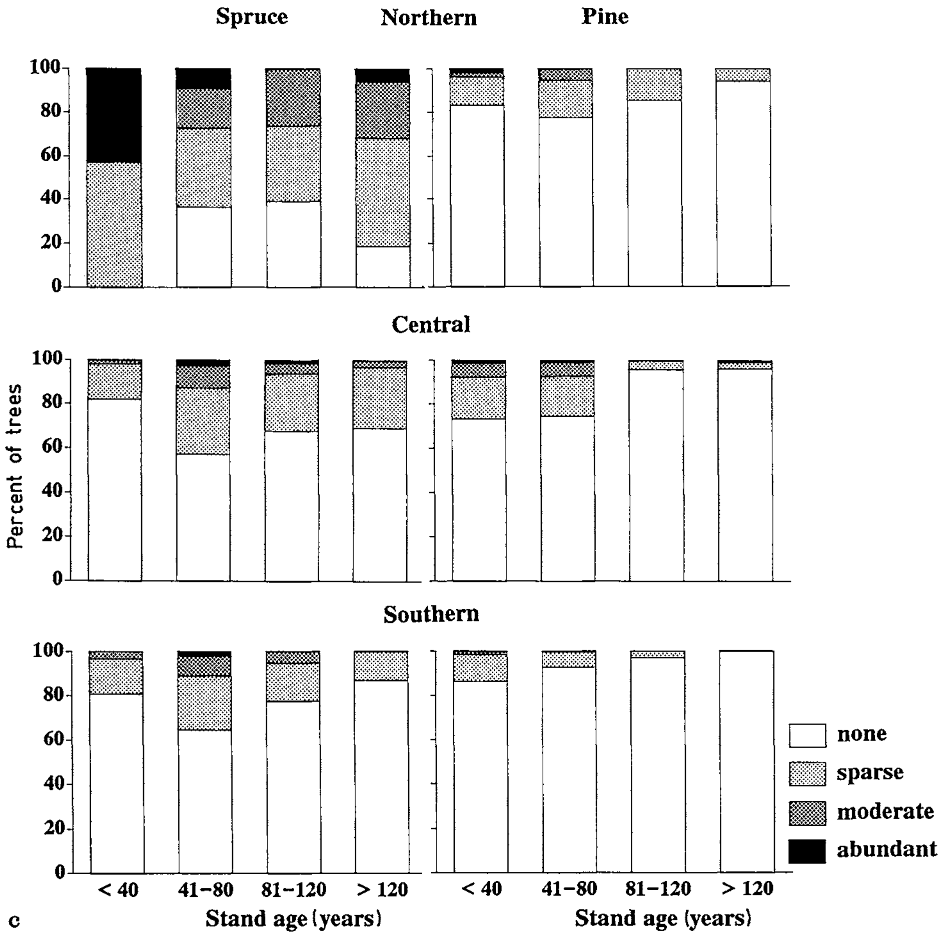


Fig. 6c

other parts of the country primarily around industrial areas. It seems to be a weak competitor that is easily overgrown by other species and thus most common in areas unfavourable to other lichens as a result of air pollution or other environmental factors. This species may also benefit from high nitrogen concentrations (Barkman 1958).

Parmeliopsis ambigua is a photophilic species growing especially on the base of the trunk and lower branches of trees below the level of maximum annual snow cover. It is most common in areas with a thick snow cover and relatively open forests in eastern and northern Finland. In parts of southern and central Finland with a thin snow cover it may be more concentrated on basal parts of the trees below the survey height (0.5–2.0 m).

The highest species numbers and IAP-values occur in old spruce forests of northern Finland. These forests are particularly favourable to epiphytic lichens,

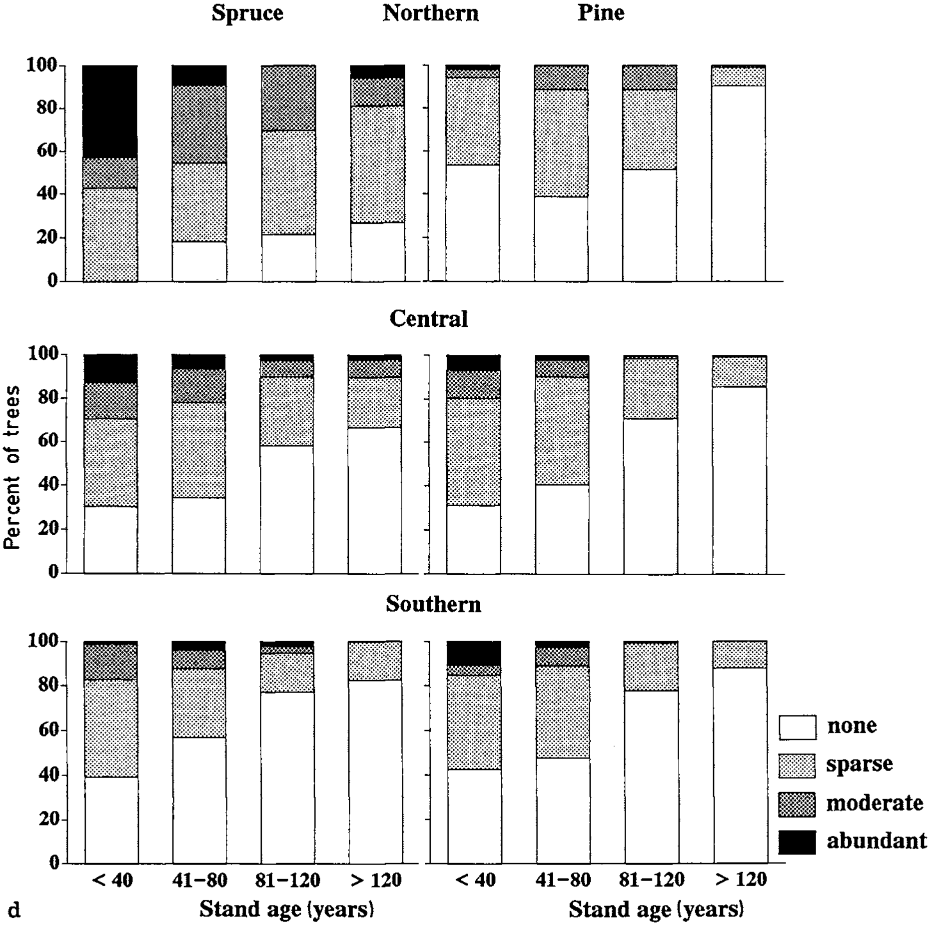
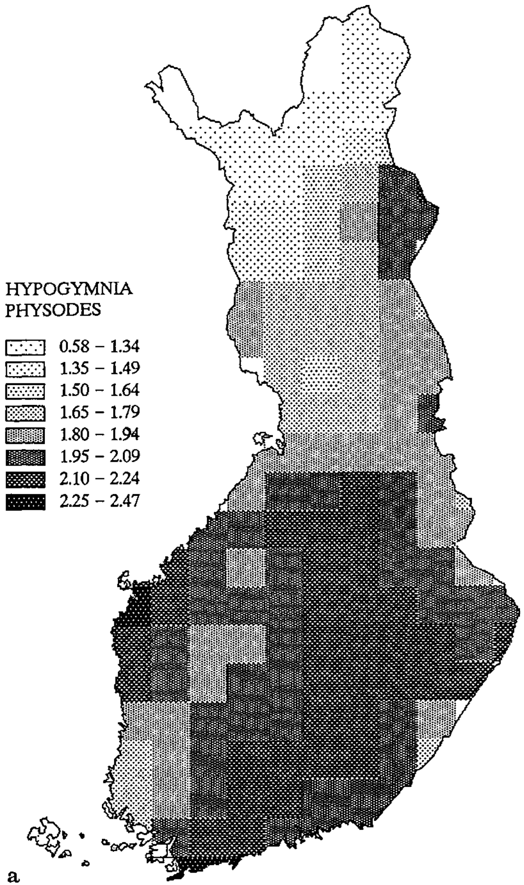


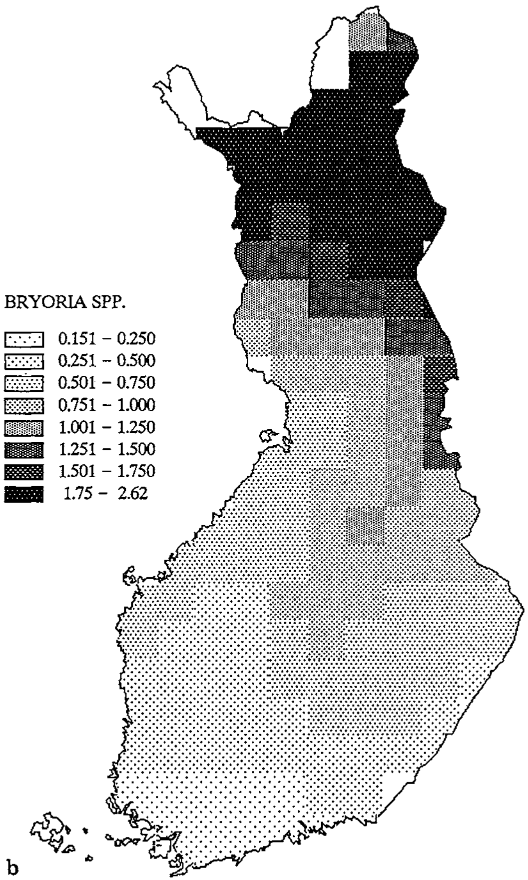
Fig. 6a–d. The occurrence and abundance of *Parmeliopsis ambigua* **a**, *Scoliciosporum chlorococcum* with green alga *Desmococcus olivaceus* **b**, *Cetraria chlorophylla* **c** and *Cetraria pinastri* **d** on trees of different stand age classes in southern, central and northern Finland (cf. Fig. 1)

because they are well-lit, moist and grow very slowly. The morphology of *Picea abies* in northern Finland is different to that in southern Finland. The northern spruce form (subsp. *obovata*) has a long, narrow crown with living branches often near the ground. Low and dense branches offer a suitable habitat for many epiphytic species.

The basal area of the trees in a stand reflects relatively well the light conditions in the stand. Stands with a large basal area usually have a high crown cover and thus poor light conditions. The amount of light reaching the basal trunk of the trees is relatively small in the spruce forests of southern Finland. Their epiphytic lichen flora can be very scanty, consisting mainly of some crustaceous species, especially *Lepraria incana*.


HYPOGYMNIA PHYSODES
0.58 – 1.34
1.35 – 1.49
1.50 – 1.64
1.65 – 1.79
1.80 – 1.94
1.95 – 2.09
2.10 – 2.24
2.25 – 2.47

a


BRYORIA SPP.
0.151 – 0.250
0.251 – 0.500
0.501 – 0.750
0.751 – 1.000
1.001 – 1.250
1.251 – 1.500
1.501 – 1.750
1.75 – 2.62

b

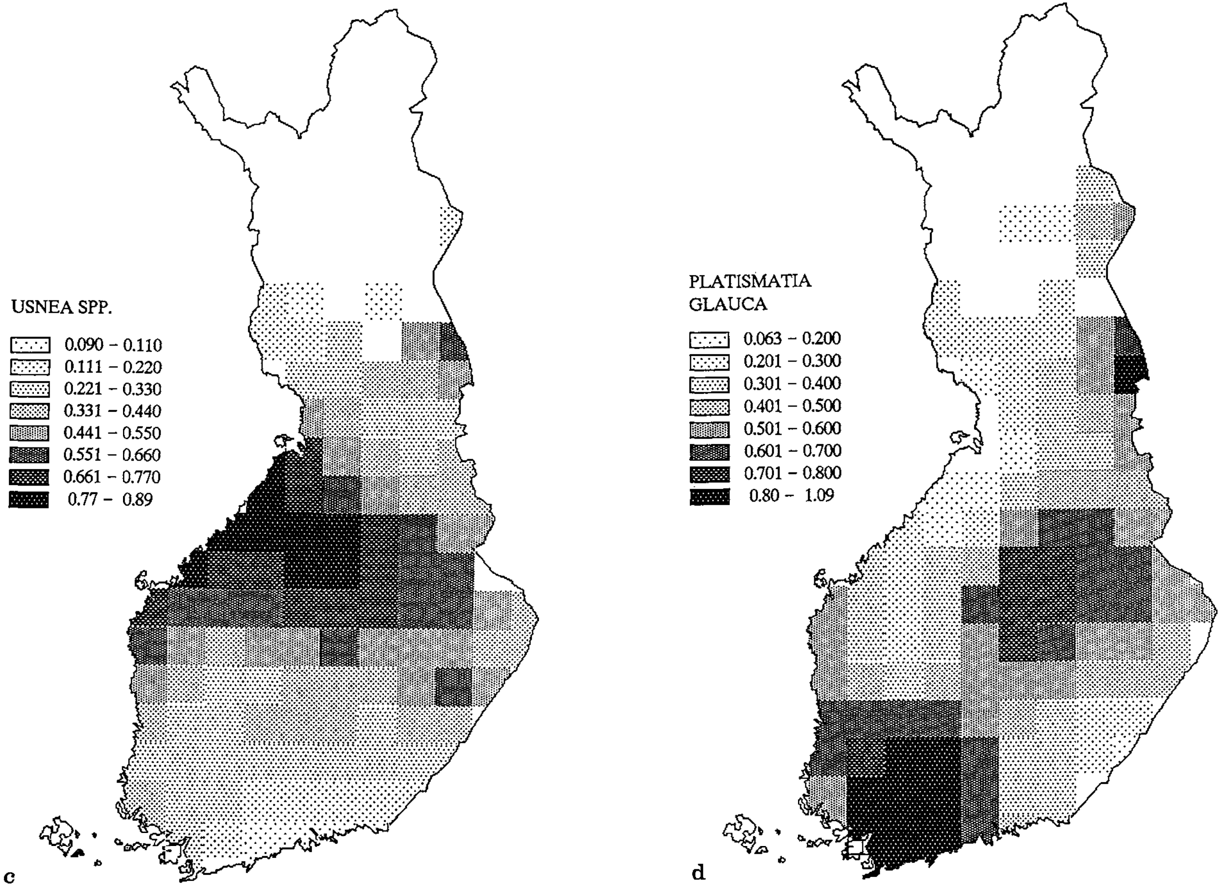
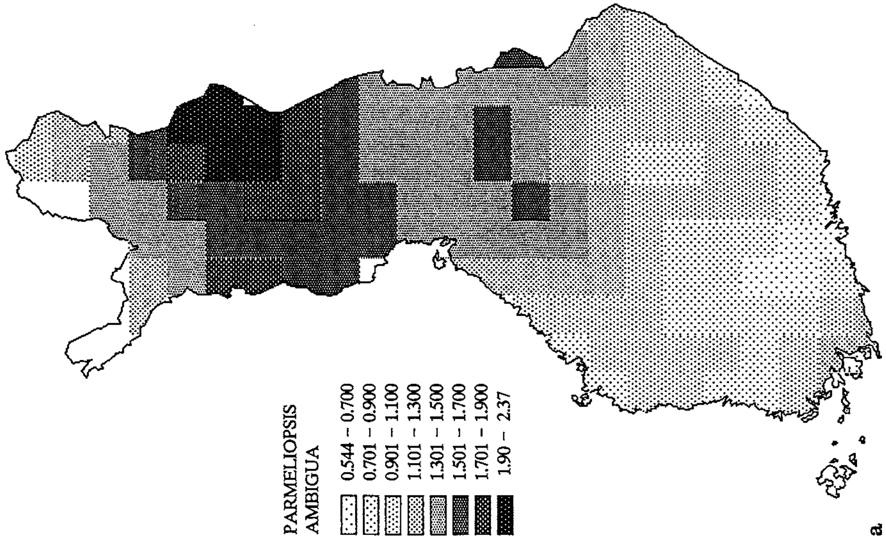
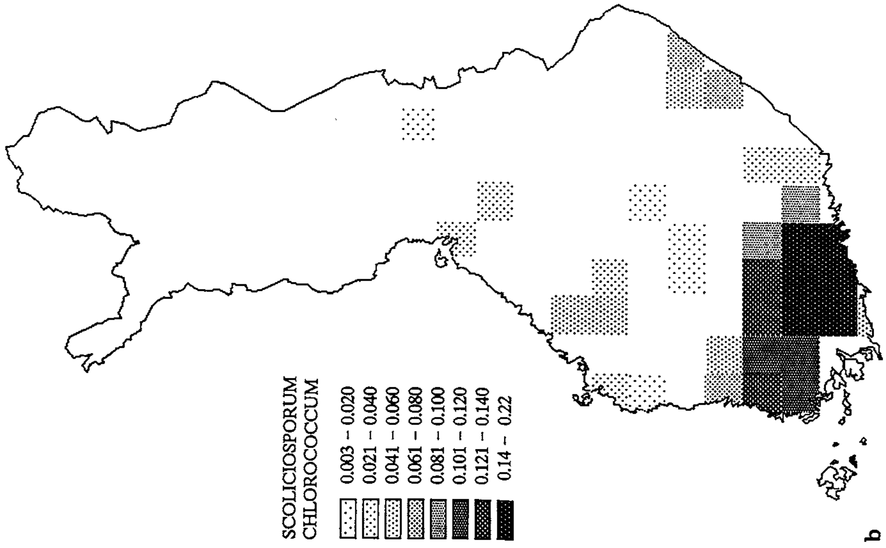


Fig. 7a–d. The occurrence and average abundance of *Hypogymnia physodes* **a**, *Bryoria* spp. **b**, *Usnea* spp. **c** and *Platismatia glauca* **d** on sample trees of the 8th National Forest Inventory plots


PARMELIOPSIS
AMBIGUA
0.544 - 0.700
0.701 - 0.900
0.901 - 1.100
1.101 - 1.300
1.301 - 1.500
1.501 - 1.700
1.701 - 1.900
1.90 - 2.37
a


SCOLICIOSPORUM
CHLOROCOCCUM
0.003 - 0.020
0.021 - 0.040
0.041 - 0.060
0.061 - 0.080
0.081 - 0.100
0.101 - 0.120
0.121 - 0.140
0.14 - 0.22
b

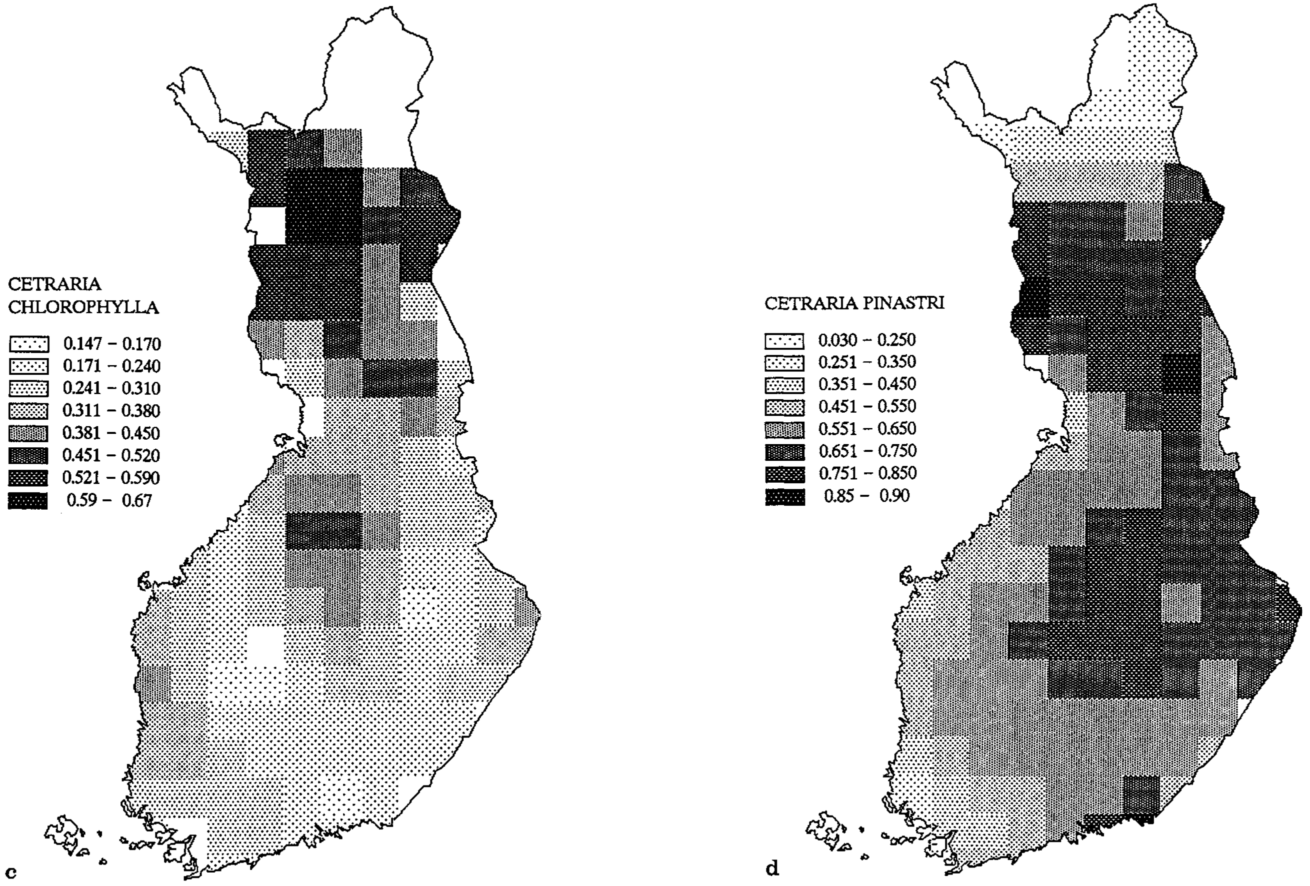


Fig. 8a–d. The occurrence and average abundance of *Parmeliopsis ambigua* **a**, *Scoliciosporum chlorococcum* with green alga *Desmococcus olivaceus* **b**, *Cetraria chlorophylla* **c** and *Cetraria pinastri* **d** on sample trees of the 8th National Forest Inventory plots

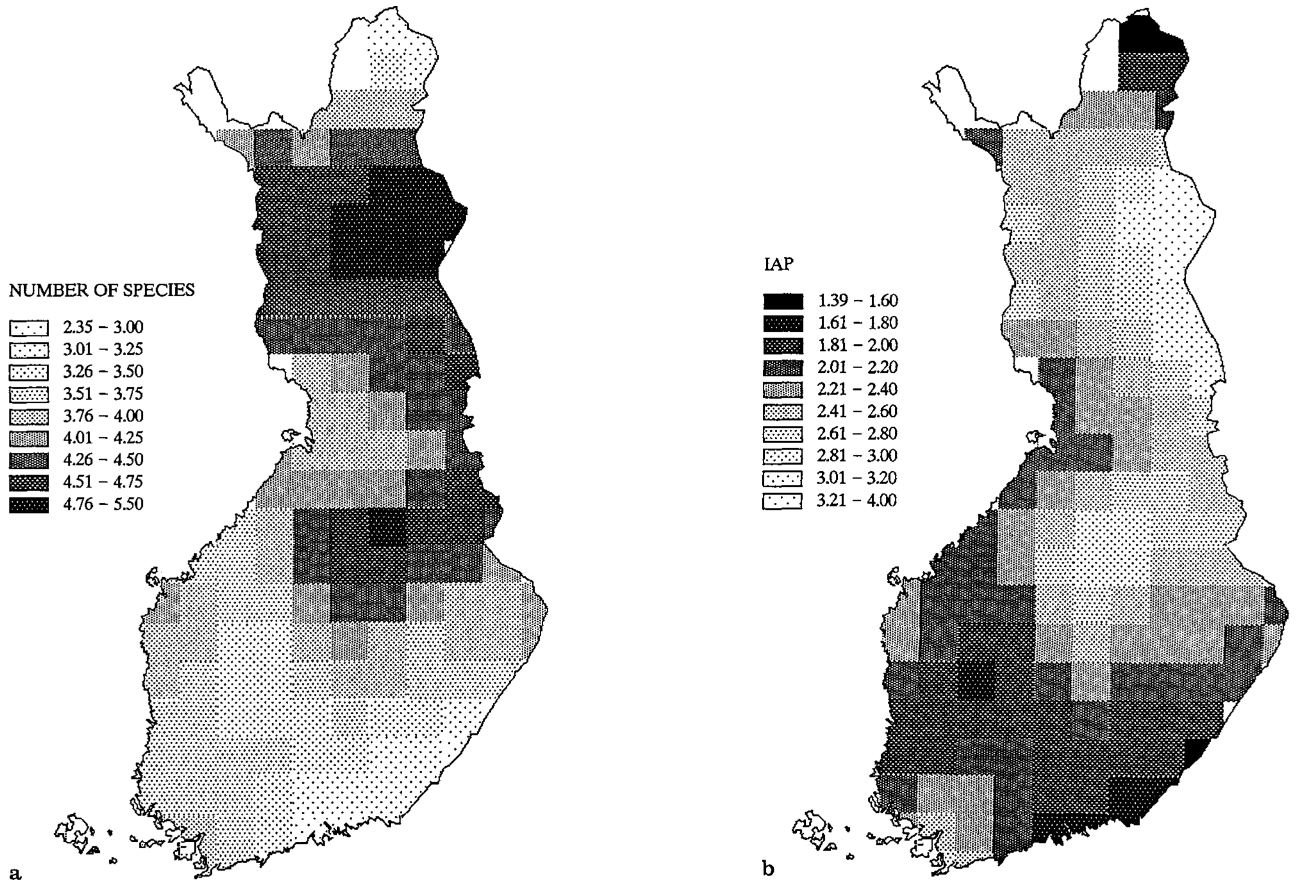


Fig. 9a,b. The average number of species **a** and the Index of Atmospheric Purity **b** on sample trees of the 8th National Forest Inventory plots

Most of the studied species favour at least moderate light conditions, only *Scoliciosporum chlorococcum* apparently tolerating dimly lit stands. Thus the low species numbers and IAP values in the spruce forests of southern Finland may be partly due to the poor light conditions. However, the spruce forests of southeastern Finland are not particularly dense, and yet it is the area with the lowest IAP values. The amount of illumination is not likely to be a limiting factor in pine forests, because they are more open than spruce forests.

All the species studied here are also quite common on deciduous trees, especially on *Betula* spp. If deciduous trees had been included then more complete distributional patterns of some species could have been obtained, at least for *Parmelia sulcata* and *Evernia prunastri* – species particularly favouring deciduous trees in Finland. Some species, especially *Cetraria pinastri, Hypogymnia physodes* and *Platismatia glauca*, are even common on rocks and cliffs.

Stand age seems to be only a secondary factor affecting the average number of species and the IAP values. The IAP values of a subgroup of 60- to 80-year-old stands was studied in order to determine whether stand age explains the high IAP values in northern Finland. The resulting pattern was, however, quite similar to that of all stands.

No doubt there are some differences between the personnel carrying out the species abundance estimation, in spite of their comprehensive training prior to the survey. These differences must, however, be slight, because the boundaries of different survey sections are not visible in the distribution maps.

In addition to the factors previously mentioned, there must be some other important factors, so far undetected, which still need further study. These factors could explain the somewhat unusual distribution patterns of certain species. Among the factors that appear not to have any clear correlation with the distribution and abundance of the studied species are exposition, angle of the slope, area of the stand, site quality and defoliation.

The decreased frequencies of the *Bryoria* and *Usnea* species in the litter samples during the past few decades are most probably associated with changes in air pollution. The forest management practised on the plots during the monitoring period has not been such that it could have affected the frequencies of epiphytic lichens. The ageing of the stands hardly explains the results, because *Usnea* and *Bryoria* species favour old forests (cf. Fig. 5a,c). As there has been no decrease in the frequency of *Hypogymnia physodes* during the monitoring period, the observed changes are not likely to be due to differences in collecting or handling the litter samples.

Usnea and *Bryoria* species are known to be very sensitive to sulphur dioxide (Hawksworth and Rose 1970). The sulphur pollution levels in southern Finland increased the most during the 1950's and 1960's (Kulmala 1985), about a decade before the observed decrease in the frequencies. This well supports the results obtained here – there has to be a certain time lag before the frequencies of even the most sensitive species begin to decrease.

No effects of air pollution are evident in the distribution patterns of the other less sensitive species. The marked decline of moderately sensitive species is limited only to small areas around cities and industrial centres. This phenomenon does not show up in large-scale mapping. Instead of pollution-derived distribution patterns, there are complex relationships between lichen abundance and stand age and structure, as well as mere sampling noise.

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A Survey of Element Concentrations in the Epiphytic Lichen *Hypogymnia physodes* in Finland in 1985–86

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Summary

A total of 2385 samples of *Hypogymnia physodes* were collected systematically from sites distributed over the whole country and analysed for Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, N, Na, Ni, Pb, S, Ti and Zn, chiefly for the purpose of tracing areal variations in the deposition of airborne metal elements.

The determinations showed this lichen species to be well suited for monitoring relative differences in deposition. High copper concentrations were recorded close to a copper mine and a copper refining plant, for example, and corresponding results were obtained for many other metals. The occurrence of high concentrations of certain elements in eastern Lapland is interpreted as implying long-distance transport from the Kola Peninsula. High concentrations of sulphur and nitrogen were observed predominantly in the south of Finland.

Introduction

As one part of the Finnish Research Project on Acidification, a programme of research was set up by the Forest Research Institute to study the effects of air pollution on the forests of Finland. Since the aim was to gather as wide a body of data as possible to cover changes detectable in the forests throughout the country, a set of 3009 secret monitoring sites were established (Valtakunnan 1986) at which measurements regarding the forests and individual trees were taken, observations made on various parts of the forest ecosystem and moss, bark and lichen samples collected (Reinikainen and Nousiainen 1985). The lichen selected for sampling was *Hypogymnia physodes*, which is commonly found on the trunks and branches of trees. Since the epiphytic lichens receive the majority of their nutrients from rainwater, they are particularly suitable for the analysis of airborne substances.

Hypogymnia physodes is a widely distributed epiphytic lichen which is relatively resistant to impurities in the air, as seen from the fact that in experiments on the effects of sulphur dioxide on lichens (O'Hare and Williams 1975), changes appeared in the chlorophyll of *Usnea subfloridana* after only two days, whereas the time lag was 24 days *Hypogymnia* and 21 days in *Pseudevernia furfuracea*. All the species studied had a higher sulphur dioxide content after the experiment than did

Kauppi et al. (Eds).
Acidification in Finland

the control samples. In transplant experiments (O'Hare 1974) both *Usnea subfloridana* and *Hypogymnia physodes* accumulated sulphur in proportion to the mean ambient level of sulphur dioxide. Griffith (1966, cit. Hawksworth 1973) similarly observed that the sulphur content of specimens of *Hypogymnia physodes* was related to that of the ambient air.

In addition to experiments of the above kind, the concentrations of certain substances in *Hypogymnia physodes* have been examined with the aim of tracing the proportions of these in depositions from the air both locally (Seaward 1974; Olkkonen and Takala 1975; Laaksovirta and Olkkonen 1977, 1979; Lodenius and Laaksovirta 1979; Addison and Puckett 1980; Kauppi and Mikkonen 1980; Takala and Olkkonen 1981; Nygård and Harju 1983; Huttunen et al. 1983; Huttunen 1988) and regionally (Pilegaard et al. 1979; Takala and Olkkonen 1985; Takala et al. 1985; Westman 1986). Most of these surveys conclude that concentrations are highest close to known sources of pollution or in places where regional deposition is high. This has led to general acceptance of the suitability of the species as a regional indicator of airborne pollution. Guderian (1977) goes so far as to note that it is of particular value for this purpose in places where the concentrations of pollutants in the air are low.

Samples of *Hypogymnia physodes* for chemical analysis were collected here in a systematic manner, to cover the whole of Finland. Although lichens have been used a great deal to study air pollution in this country, no national survey with the same sampling density had previously been carried out, nor has any report come to light of such a project existing in any other country.

Materials and Methods

Collection of the Samples

A set of 12 teams of research workers, which differed from those usually employed on forest inventories in that each included a biologist specialized in botany, were set up for the purposes of establishing the monitoring sites, taking the samples and performing the field measurements. The majority of the sites were established in summer 1985, the teams operating simultaneously in different parts of the country. It was only in the northernmost area that the work was left until the following summer (Fig 1). The locations of the actual sites are kept secret as they are to be used in future for monitoring tree growth, and knowledge of their selection could cause forest owners to intensify their silvicultural methods.

The sites were defined on the basis of the nationwide grid employed in the 5th National Forest Inventory (Kuusela and Salminen 1969), in which sampling was performed at points located at particular distances along transects defined with respect to the index points on this grid, the whole system being integrated with the national network of map coordinates. The index points on the grid were located 16 km apart in a N-S and E-W direction, except in the northernmost part of the

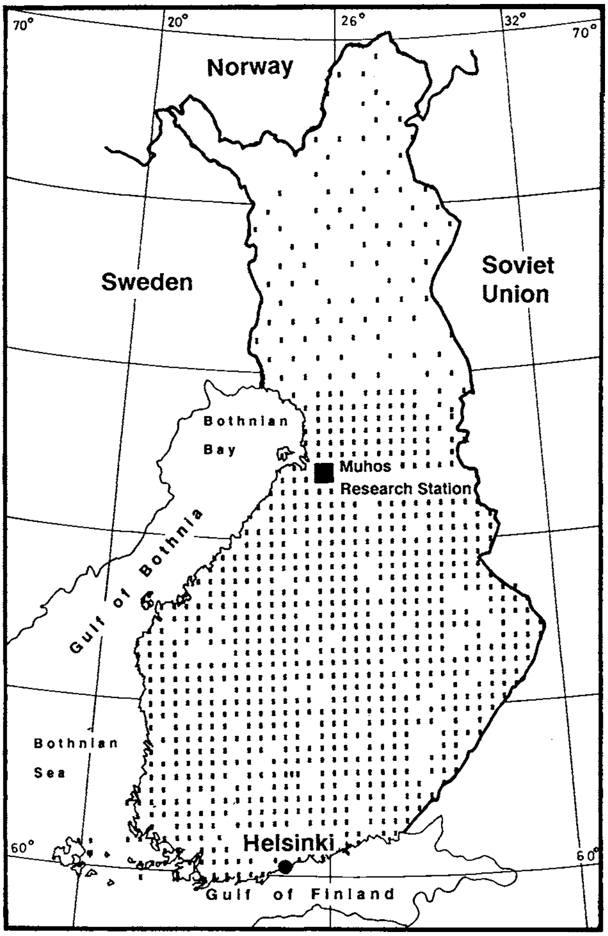

Fig. 1. Location of the clusters of monitoring sites. Sampling took place in summer 1985 in the area with the denser network, where each cluster comprised four sites, and in summer 1986 in the less dense area, where the clusters were of three sites each. The samples were collected together and stored at the Muhos Forest Research Station

country, where they were 32 km apart in an E-W direction and 24 km apart from N to S (Fig. 1). The monitoring sites themselves are arranged in clusters of four associated with each index point, 400 m apart in the denser grid area and 600 m on the sparser grid.

Lichen samples were collected from every site in each cluster, except where a site fell within 300 m of a main road, built-up area or factory or 100 m from the nearest local road, forest road, winter road, house or country cottage. Similarly, instructions were issued that no samples were to be taken from closer than 20 m to the tracks of a forestry machine or the site of a lumbermen's campfire. Care was also taken that (1) the sample should be from above the highest point reached by the snow, (2) the site should be as open and well-ventilated as possible, (3) the sample should for preference be taken from one of the principal forest tree species, and (4) it should not be taken from amongst dense branches at a point affected by water dripping from the tree. The samples were never touched with bare hands, but were removed using rubber gloves and placed directly in a paper bag, or a polythene bag when it was raining.

A total of 3009 permanent monitoring sites were set up at secret locations, observing the conditions mentioned above, although on account of sporadic absences of lichen the total number of lichen samples obtained was only 2401. Deducting from this the ten samples of *Pseudevernia furfuracea* collected as a substitute for *Hypogymnia physodes*, the samples that contained too little lichen for analysis or remained unanalysed for some other reason, a final figure of 2385 samples covering the whole country was reached.

The above system for creating a network of randomly chosen monitoring sites meant at the same time random variations in the structure of the growing sites represented. Thus the lichen samples were not all obtained from the same type of surface, or even from the same species of tree. The distribution of the eventual material by tree species was as follows:

Pinus silvestris	1413 samples
Picea abies	689 samples
Betula pendula	11 samples
Betula pubescens	252 samples
Populus tremula	5 samples
Alnus incana	6 samples
Not indicated	9 samples

Thus the majority of the samples were taken from pine trees, this being the predominant forest tree species in Finland rather than spruce.

Among the pine samples, 1286 were taken from the trunk of the tree, 25 from living branches, 83 from dead branches and 19 from points unspecified at the time of collection. Correspondingly, 72 of the samples taken from spruces represented the trunk of the tree, 314 live branches, 296 dead branches and 7 were unspecified. The higher proportion of samples collected from the branches of the spruces is due to the frequent occurrence of these lichens on the low branches of this species. No account was taken of the tree species or position of the lichen on the tree when analysing the material at the national level, as any deposition of pollutants is assumed to affect the results more than these factors.

Storage of the Samples

The samples were sent to the Muhos Forestry Research Station (Fig. 1) immediately after collection, where they were kept in an even-temperatured storeroom specially fitted out for the purpose. Before the final long-term storage at room temperature, they were dried at +30°C until no further loss in weight occurred. Temperature and relative humidity in the storeroom were controlled by means of a plotting thermohygrograph.

Chemical Analyses

Once the dried samples had been cleaned, the whole thalli were ground to a fine powder and 1 g of this powder from each sample placed in a 250-ml Kjeltec tube, to which 10 ml concentrated nitric acid was added. After standing overnight, 4 ml of 70% perchloric acid was added to each sample, which was then shaken and transferred to a 20-tube Tecator Digestion System, in which the temperature was raised in steps to 225°C. The total digestion time was 3 h 15 min. After cooling, the solution was diluted to a volume of 25 ml in a graduated flask.

The above stages, performed in the laboratories of the Muhos Forest Research Station, were then followed by determination of the element concentrations by ICP plasma emission spectrophotometry at the central laboratories of the Finnish Forest Research Institute. The only exception was nitrogen content, which was determined entirely at Muhos by an adaptation of the micro-Kjeldahl method (Kubin 1978) as shown in earlier research (Kubin and Siira 1980) to be particularly suitable for the determination of the nitrogen content of lichens, in this case *Cladonia stellaris.*

The chemical analysis procedure was carefully tested before any of the actual samples were run (Kubin 1987). The reliability of the determinations was assessed using an accepted international standard for which a certain level of reliability is guaranteed by the manufacturer. These methodological trials, conducted under the direction of the chemist Harri Lippo, showed that wet digestion with perchloric acid combined with ICP determination yielded reliable results for Ca, Mg, S, Fe, Mn, Zn, Cu and Pb. Marked discrepancies relative to the standard existed in the case of chromium, cadmium, nickel and vanadium, but the reproducibility of these determinations was nevertheless good, and they were therefore included among the analyses to be performed.

The least comparable of all the determinations performed was that of titanium, although even in this case the reproducibility of the results was satisfactory. No tests for Na and B determinations against the international standard were attempted, as these elements are known to appear as contamination. The concentrations in the present lichen samples were analysed, but the results for boron had to be rejected because of this contamination problem. The vanadium concentrations, on the other hand, were well below the ICP detection limit, so that determinations were only made on a small number of samples. Molybdenum was measured in all the samples, but its concentrations were again below the ICP detection limit in the majority of cases, so that the results were omitted from the final evaluation. The elements for which figures are quoted here are therefore Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, N, Na, Ni, Pb, S, Ti and Zn.

The wet digestion stage is probably the most demanding part of the analytical procedure of all as far as reliability is concerned. Inadequate digestion is liable to leave some of the element concerned in an undecomposed form, while excessive digestion may cause some of it to evaporate out of the solution. The demanding nature of this stage in the procedure is also accentuated by the fact that samples representing the same series of tests have to be digested many times over, in the present case 161 times.

Particular care was taken to obtain control values for this stage and many others in the present chemical analyses. Every individual wet digestion included three blanks, i.e. tubes containing solution but no sample, the results obtained indicating a need to subtract the values for Cr, Cd, Mo and Ni contamination arising from the reactions themselves before indicating the final results.

Similarly, a large quantity of lichens of the same species was collected and prepared to form a control sample for use in setting up the analytical routine, and aliquots of the same sample were analysed repeatedly after that in order to check the reproducibility of the measurements and the digestion efficiency of the various tubes. Quantities of this same sample were also introduced among the field specimens for control purposes. Unfortunately, however, this material ran out eventually and new control lichens had to be collected on two subsequent occasions. Even so, a good picture was obtained of the reliability of the method in spite of using three batches of control lichen, since the scatter in the results from one digestion to the next was always small compared with that observed between the actual field samples. It may thus be concluded that the samples proper really do reflect the variations in element concentrations prevailing in nature at the time when they were collected.

Presentation of the Results

The material on which this report is based consists of the results of chemical analyses performed on 2385 individual samples of *Hypogymnia physodes.* Since these samples originated from monitoring sites arranged in clusters, mean values for the clusters were calculated for presentation on standardized maps of Finland. The method serves to smooth out the influence of individual high values, and at the same time improves the reliability of the data from each of the 908 clusters (Fig. 1) for representing the particular characteristics of the area concerned.

When constructing the areal maps, the original 908 irregularly distributed data points were redesigned to form a regular grid containing 8100 points (60 × 135), which was then used for plotting purposes. The element concentration classes depicted on the maps were obtained by dividing the observations for each element into five groups of equal size, hence the somewhat irregular distribution of boundary values.

The order of presentation of the elements follows the division into macro and micronutrients and inessential substances with respect to the higher plants (Allen 1974; Larcher 1975; Mengel and Kirkby 1979). The latter category comprises substances found in plants but upon which they are not dependent. Many of these are toxic metals, which are dealt with here under the heading of heavy metals, aluminium and titanium.

Results

Sulphur and Nitrogen

Sulphur and nitrogen are both crucial nutrients which plants consume in large amounts, and both make an essential contribution to the structure of enzymes and protoplasm, for example. Correspondingly, both play a similar role in the development of acid rain, since their oxides form chemical compounds which, via a number of intermediate steps, serve to increase the acidity of water, i.e. the numbers of hydrogen ions present. Even though nitrogen accounts for 78% of the composition of the atmosphere and sulphur is encountered in both living and non-living forms of nature, their significance for the natural environment has come to the fore especially clearly in the form of pollution generated by human activity, chiefly industry and traffic.

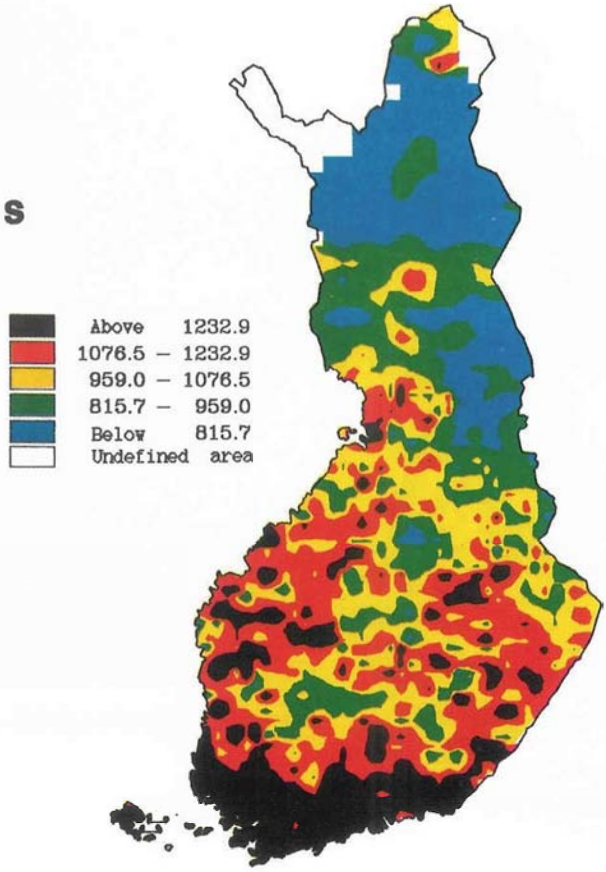

Fig. 2. Sulphur content ($\mu g\,g^{-1}$ dry wt.) of *Hypogymnia physodes in* 1985–86

The mean sulphur content of the lichen samples for the whole country was 1092 μg g^{-1}, range 599–2610 μg g^{-1}, with the highest concentrations to be found over a broad area of southern Finland (Fig. 2). Local points of high concentration also exist, however, and it is noticeable that areas with values similar to those recorded in southern Finland are still to be found even close to the Bothnian Bay coast north of the city of Oulu. Northern Finland in general and Lapland in particular form regions of lower sulphur concentrations, however, with the exception of the northern tip of Lapland, where the higher concentrations are evidently attributable to pollution entering the area from the east, since there are no local sources of emissions there, and no real built-up areas. No actual samples were obtained from the area along the eastern border of Finland at this point, however (Fig. 1), so that no figures are available to support this assumption.

The mean nitrogen concentration of the lichens was 1.3% dry weight, and the range 0.75–2.56%, the areal distribution of the highest figures being to a large extent similar to that for sulphur (Fig. 3). Again a local occurrence of higher

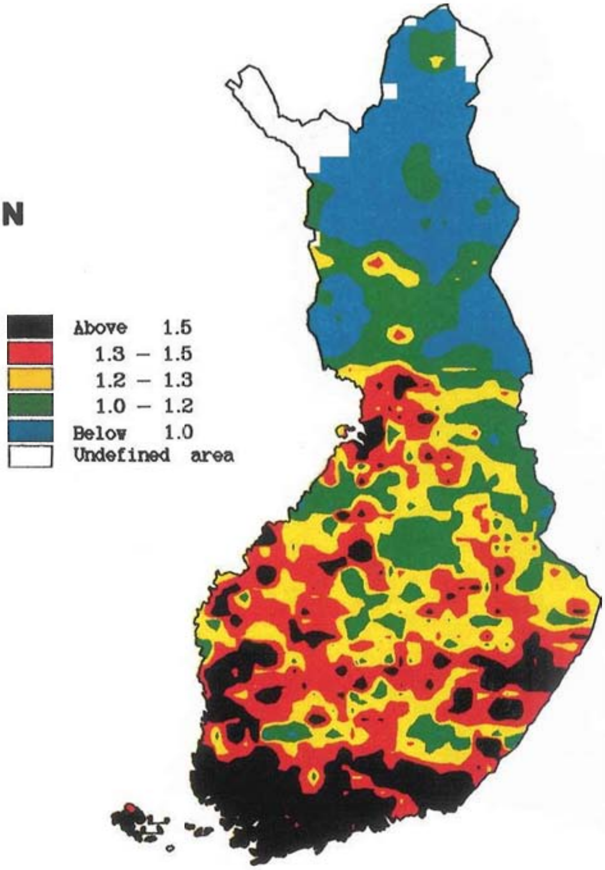

Fig. 3. Nitrogen content (% dry wt.) of *Hypogymnia physodes* in 1985–86

concentrations was recorded in the far north of the country, although the difference was not so pronounced as for sulphur.

Other Macronutrients

Calcium, magnesium and potassium are nutrients which plants require in relatively large amounts, the first two being mostly of structural significance to the plant, while potassium is best known as a functional nutrient, which in the higher plants, for example, is engaged in a rapid cyclic circulation between the living plant tissues and the soil. *Sodium* is mentioned as an essential nutrient for plants, but less emphasis is placed on its functional significance. These substances are probably not of any direct significance as air pollutants, unless one considers direct fall-out in the form of dust. A particularly high incidence of calcium will have the effect of neutralizing acidity, of course.

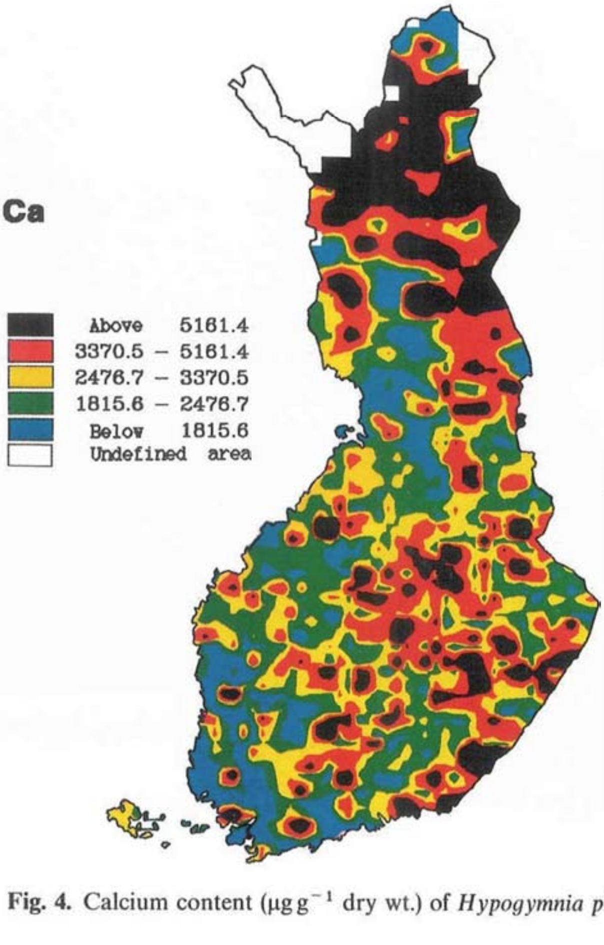

Fig. 4. Calcium content ($\mu g\,g^{-1}$ dry wt.) of *Hypogymnia physodes* in 1985–86

The mean potassium concentration obtained here was 2751 $\mu g\ g^{-1}$ dry weight of lichen, range 1448–6045 $\mu g\ g^{-1}$, that of calcium 3344 $\mu g\ g^{-1}$, range 388–33375 $\mu g\ g^{-1}$, that of magnesium 399 $\mu g\ g^{-1}$, range 210–989 $\mu g\ g^{-1}$, and that of sodium 42 $\mu g\ g^{-1}$, range 21–521 $\mu g\ g^{-1}$. Apart from the very high maximum figure recorded here, the interesting point about the calcium concentrations is the occurrence of high figures in central and south-eastern Finland and over wide areas of Lapland (Fig. 4). Magnesium concentrations (Fig. 5) are also high in Lapland and on the coast of the Gulf of Bothnia.

Sodium concentrations (Fig. 6) were high on the coast of the Bothnian Bay and in the north of Lapland. It is possible that deposition in both of these areas may be due to the effects of seawater, but it must also be borne in mind that the determination of sodium is liable to run into contamination problems. Considerable local accumulations of potassium are observed (Fig. 7), but in view of its rapid biological cycle, it is possible that local conditions at the time of sampling, and also the surface on which the lichen was growing, may have been responsible for the differences to a greater extent than other factors.

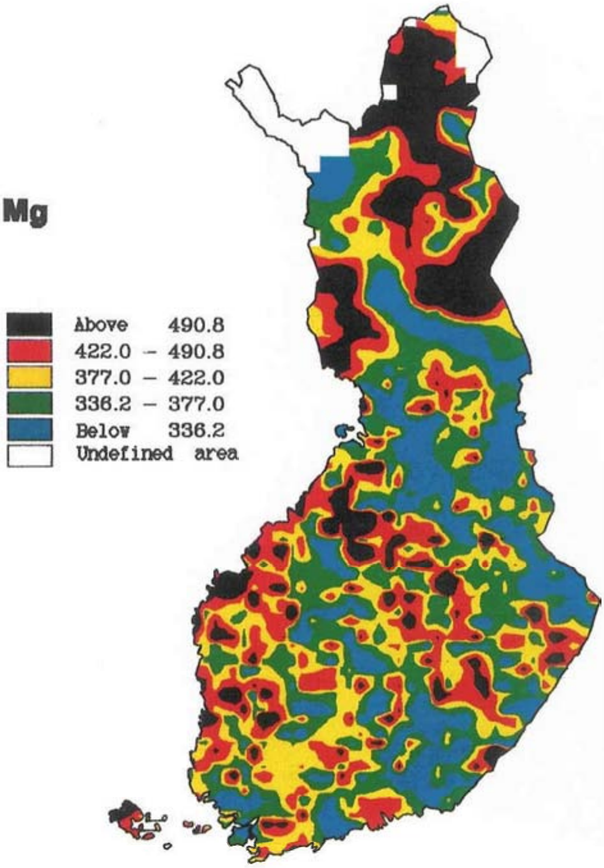

Fig. 5. Magnesium content ($\mu g\, g^{-1}$ dry wt.) of *Hypogymnia physodes* in 1985–86

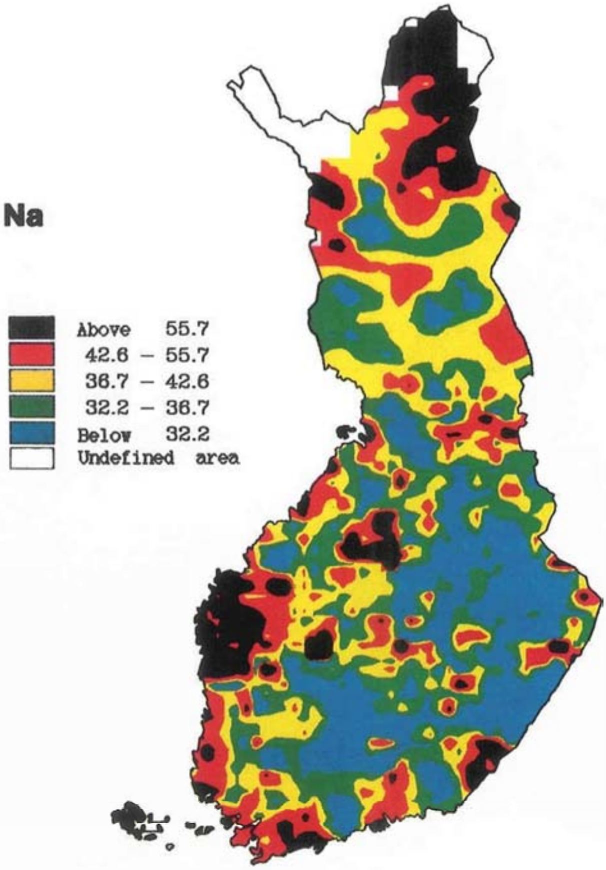

Fig. 6. Sodium content (µgg dry wt.) of *Hypogymnia physodes* in 1985–86

Micronutrients

Copper, iron, manganese and zinc. These are the chief micronutrients of significance for the basic metabolism of plants and other reactions. With the exception of iron, they are frequently mentioned as environmental pollutants if they occur in nature in high concentrations, and since they tend to form complex compounds in soil solutions, deficiency symptoms with respect to one or more of these can appear in plants under certain conditions.

The mean copper content of the present lichen samples was 7.3 µg g^{-1} of lichen, range 3.5–199.6 µg g^{-1}. The areal distribution of high values forms an interesting pattern (Fig. 8), with an extensive accumulation of such values in the west of Finland, close to the coast of the Bothnian Sea, evidently attributable to the presence of a copper refinery in the region, and another in eastern Finland, around a copper mine. The high figures recorded in the north of Lapland are

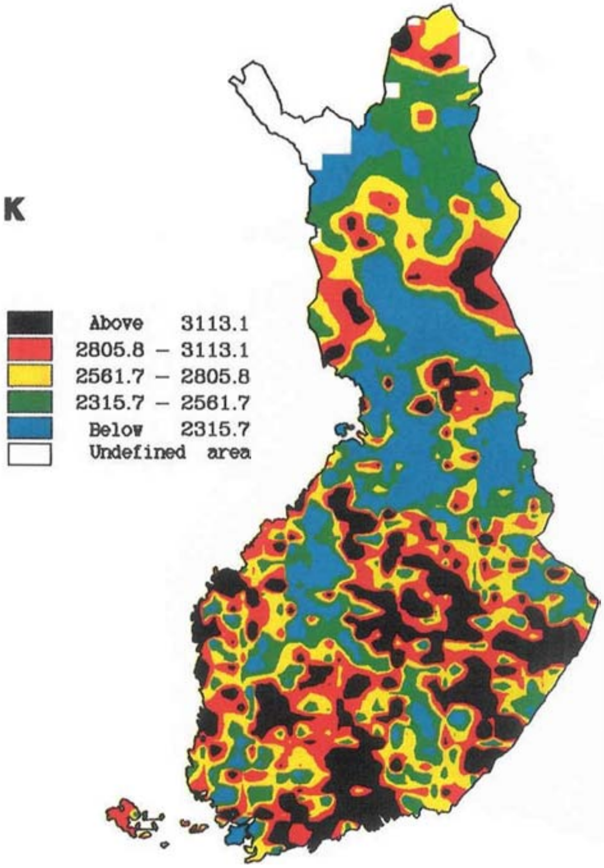

Fig. 7. Postassium content (μg g^{-1} dry wt.) of *Hypogymnia physodes* in 1985–86

evidently the result of long-distance transport, as there are no local sources of emissions.

Iron content gave a mean value of 544 μg g^{-1} of lichen for the whole country, with a range of 180–3759 μg g^{-1}. It is significant that the high concentrations are located predominantly in the south (Fig. 9), with a further area close to the Bothnian Bay coast, marking the sphere of influence of a major iron works. The mean for the whole country in the case of manganese was 131 μg g^{-1} of lichen, and the range 20–693 μg g^{-1}. In this case the high concentrations were found in central Finland and Lapland (Fig. 10). Zinc gave a mean concentration of 86 μg g^{-1}, range 38–216 μg g^{-1} (Fig. 11). The area of high values in southwestern Finland coincides with that for copper, while other high points occur around certain mining districts. Long-distance transport is also possible in northern Finland. The high maximum concentrations of both zinc and manganese point to relatively pronounced local emissions.

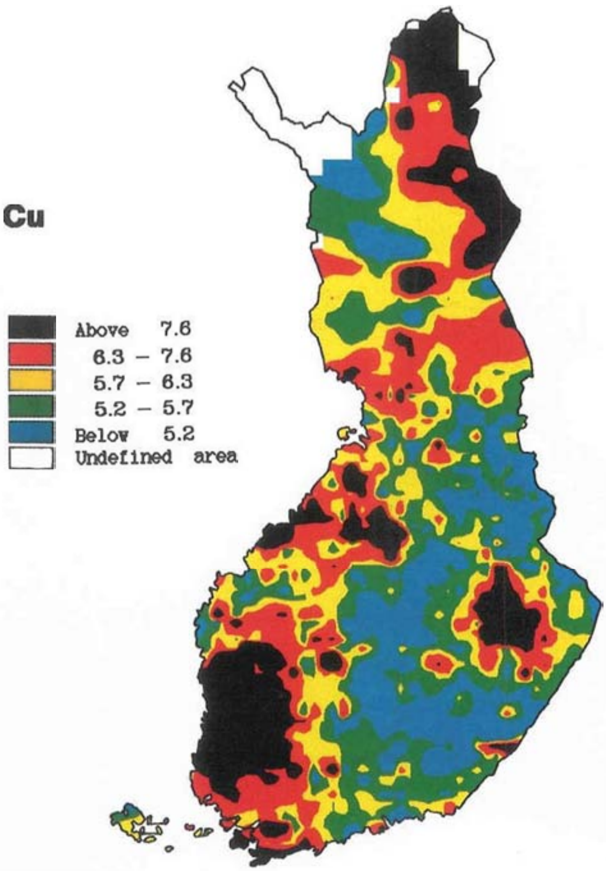

Fig. 8. Copper content (μg g^{-1} dry wt.) of *Hypogymnia physodes* in 1985–86

Heavy Metals, Aluminium and Titanium

The elements determined here which fall into the class of heavy metals in terms of their chemical character and biological effects are cadmium, chromium, lead and nickel. Although these are to be found in plants, they are not mentioned as being in any way essential elements for plant life. In the same way, plants take up aluminium and titanium, but it is not entirely known what significance these have for the plant. Aluminium can easily be toxic for plants, while titanium determinations are often used as indicators of industrial emissions.

Cadmium is a detrimental substance for both human and plant life. Its effect on plants is derived from its ability to block the involvement of zinc in enzymatic reactions, while in humans it has been shown to have a cumulative toxic effect. Plant cells normally contain 0.1–1.0 μg g^{-1} cadmium (Mengel and Kirkby 1979), but this figure can easily be exceeded where cadmium is readily available. The

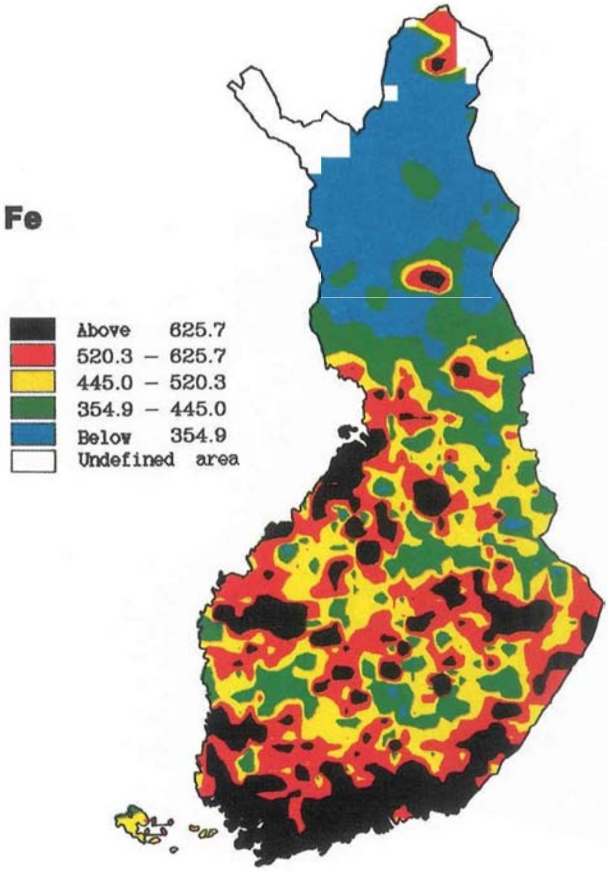

Fig. 9. Iron content ($\mu g\,g^{-1}$ dry wt.) of *Hypogymnia physodes* in 1985–86

mean cadmium content of the present lichen samples was 0.70 $\mu g\,g^{-1}$, with a range of 0.12–4.25 $\mu g\,g^{-1}$. Bearing in mind that lichens usually require little in the way of nutrients by comparison with higher plants, the maximum values recorded here may be regarded as extremely high.

The fairly broad area of high cadmium concentrations in the western part of the country (Fig. 12) coincides with those for copper and zinc, while another such area is found at the northern tip of the Gulf of Bothnia, and high values are also recorded in Lapland at a latitude at which a substantial mining industry is found across the border in the Soviet Union. The extent to which the high concentrations of cadmium conform geographically with those of other elements originating from industrial emissions supports the interpretation that local cadmium emissions must also take place.

The significance of *Chromium* for the metabolism of plants is as yet unresolved, and it does not occur in any very large quantities in plant tissues, being present in the soil in a highly insoluble form. It is generally regarded as a toxin. The mean

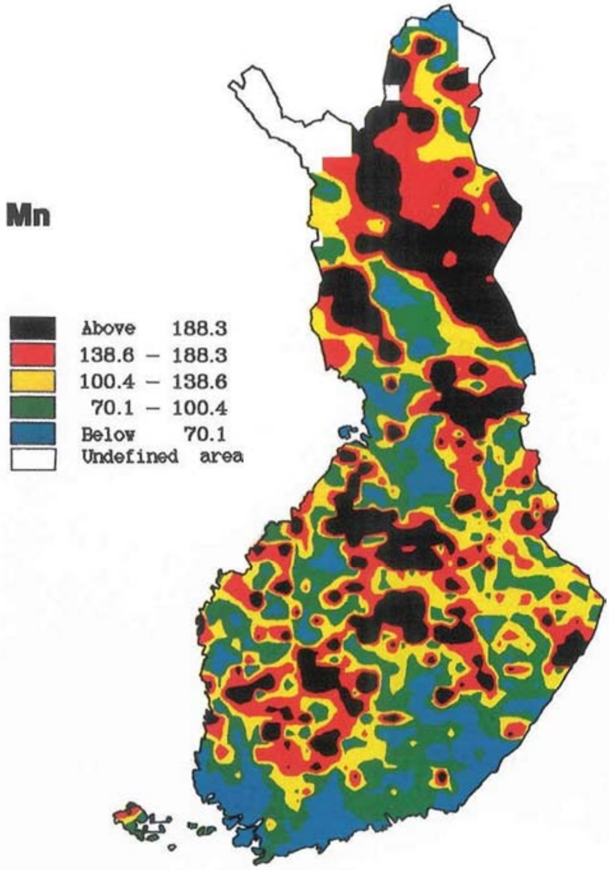

Fig. 10. Manganese content ($\mu g\, g^{-1}$ dry wt.) of *Hypogymnia physodes* in 1985–86

chromium content recorded here, 2.13 $\mu g\, g^{-1}$ of lichen, with a range of 0.30–56.00 $\mu g\, g^{-1}$, is high in relation to the values of 0.02–1.00 $\mu g\, g^{-1}$ customarily reported in plants (Mengel and Kirkby 1979). The method employed here (Kubin 1987) does give slightly higher chromium concentrations than usual, but with a determination limit as low as 0.75 $\mu g\, g^{-1}$ the high values in particular must be regarded as reliable as far as their reproducibility is concerned. The highest values are grouped in a single broad area (Fig. 13) which may be linked locally with a major precision steel works.

Lead is above all a roadside pollutant (Ruhling and Tyler 1968; Takala and Olkkonen 1981) and is highly toxic to humans. The toxicity of its effects on plants is not fully understood, however. The mean lead concentration in the present lichen samples was 18 $\mu g\, g^{-1}$ and the range 1–62 $\mu g\, g^{-1}$. The major areas with high concentrations occurred in the more industrialized south of the country (Fig 14), although local occurrences of high values were also found in the north, associated at least in some cases with mining.

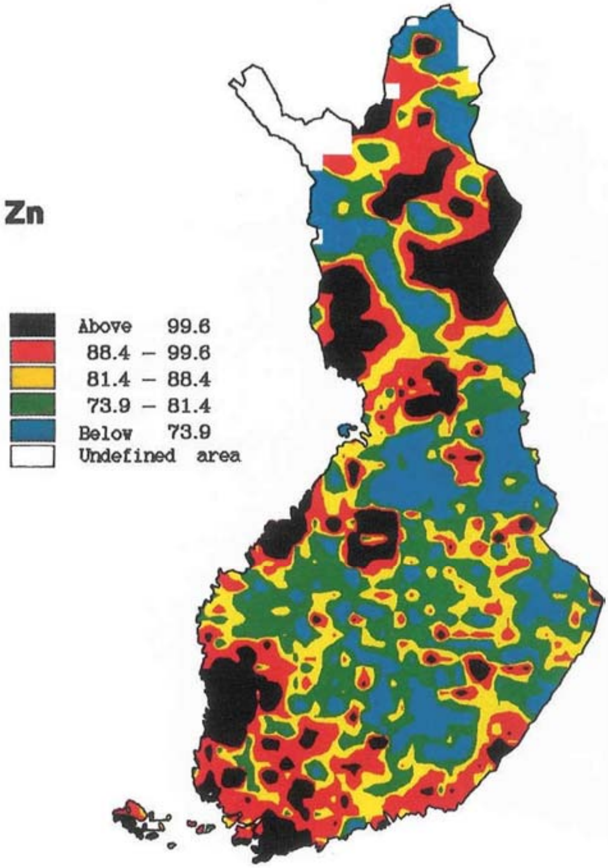

Fig. 11. Zinc content ($\mu g\,g^{-1}$ dry wt.) of *Hypogymnia physodes* in 1985–86

Nickel is known to be toxic to plants, even though it is normally to be found in their tissues to the extent of 0.1–5 $\mu g\ g^{-1}$ dry weight. Where large amounts of nickel are present in the soil, however, its concentrations in plants can be very much higher. The mean nickel content of the present lichen samples was 2.62 $\mu g\ g^{-1}$, with a range of 0.00–51 $\mu g\ g^{-1}$, so that the maximum values at least may well be derived from local sources of pollution. The large area of high values close to the Bothnian Sea coast in south-western Finland (Fig. 15) coincides again with the pattern obtained for copper and zinc, while the broad zone in Lapland is confined to the eastern part of the region and in all probability is attributable to the major industrial areas on the Kola Peninsula in the Soviet Union.

Our knowledge of the function of *aluminium* in plants and of its necessity for plant life is still incomplete. It exists in the soil in large quantities and increases in solubility with increasing soil acidity, so that its toxic effects have been associated primarily with acid soils. The amounts encountered in plants vary within the range 100–1000 $\mu g\ g^{-1}$ (Allen 1974).

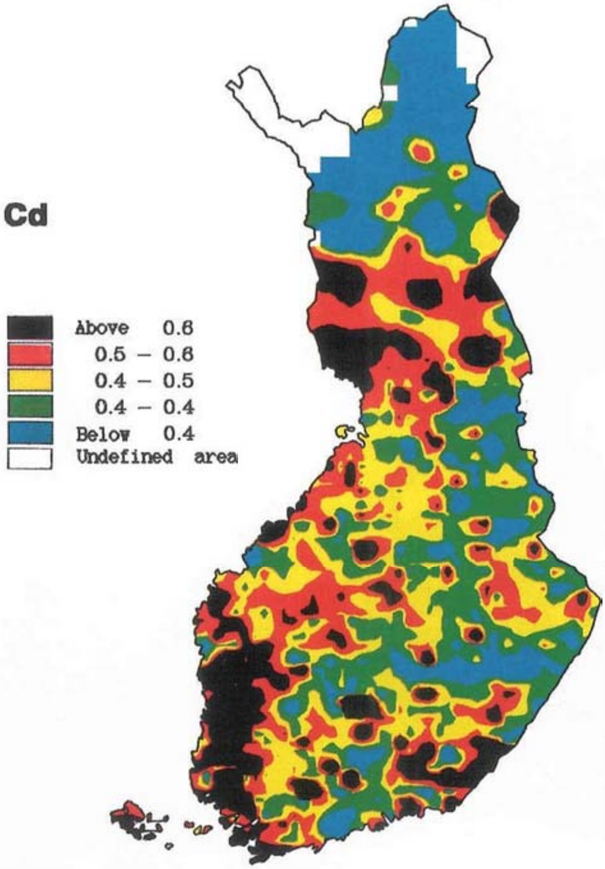

Fig. 12. Cadmium content ($\mu g\,g^{-1}$ dry wt.) of *Hypogymnia physodes* in 1985–86

The mean aluminium concentration of the present lichens was 480 $\mu g\ g^{-1}$, range 119–1358 $\mu g\ g^{-1}$. The major area of high concentrations was in south-eastern Finland (Fig. 16) and the next highest classes also tended to occur towards the south and southeast.

Titanium is an element about which little is known in relation to its effects on plants, and few analyses are available of its content in plant tissues. According to Allen (1974), its concentrations in plants vary in the range 0.4–8.0 $\mu g\ g^{-1}$; representing considerably lower figures than those recorded here, where the mean was 25.9 $\mu g\ g^{-1}$ and the range 18.0–49.4 $\mu g\ g^{-1}$. The main areas with high concentrations were in the south and west (Fig. 17), while the figures for Lapland were in general low except for an area of high concentrations coinciding with the results for sulphur and nitrogen.

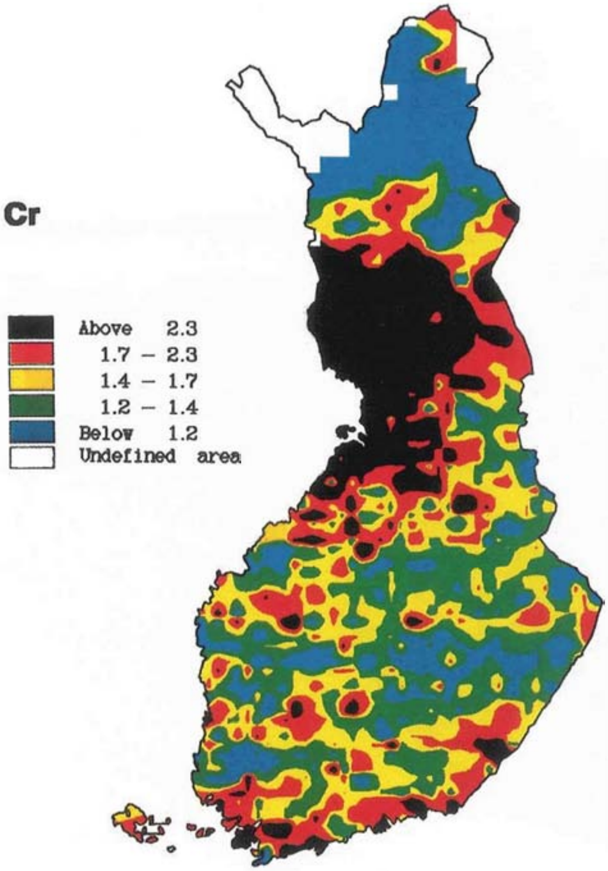

Fig. 13. Chromium content (μg g^{-1} dry wt.) of *Hypogymnia physodes* in 1985–86

Discussion

Many extensive series of tests have shown that lichens are particularly sensitive indicators of air pollution and can be used for this purpose in a variety of ways (see Ferry et al. 1973; Kauppi 1980; Nash III and Wirth 1988). Other plants used in the Nordic countries for mapping the distribution of heavy metals in particular are mosses, by means of which Ruhling and Tyler demonstrated as early as 1971 that concentrations of certain heavy metals were as much as ten times greater in the southern parts of Scandinavia than in the north. New moss samples were then collected in all the Nordic countries in 1985 and a set of maps published jointly to show the distribution of depositions of heavy metals over the whole region (Ruhling et al. 1987). The present lichen-based survey is linked with this work insofar as the lichen samples were collected at the same time and from the same sites as the mosses.

Comparison of the lichen results with those obtained from the mosses (Ruhling et al. 1987) shows a high measure of correspondence in the areal patterns for

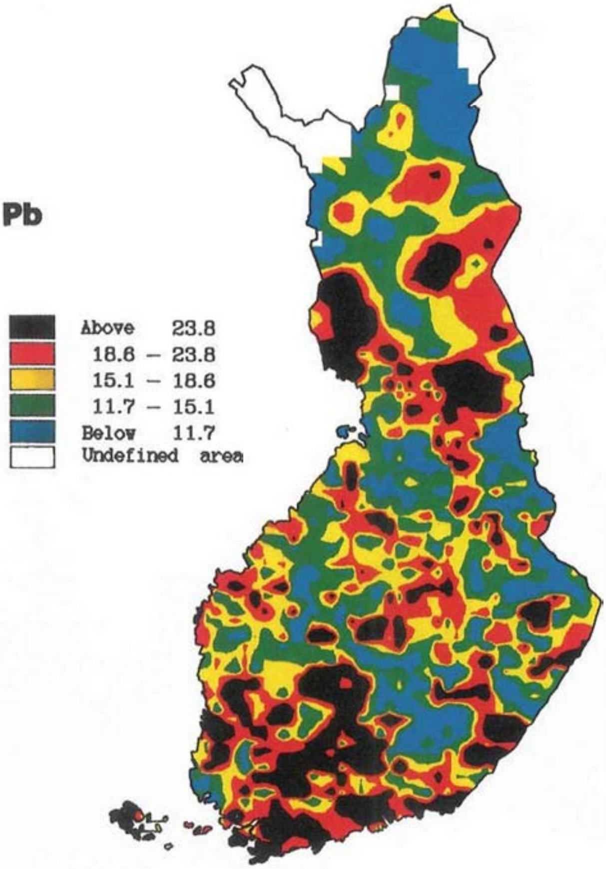

Fig. 14. Lead content ($\mu g\, g^{-1}$ dry wt.) of *Hypogymnia physodes* in 1985–86

chromium, iron and nickel concentrations, and also for copper, except that the area around the copper mine in eastern Finland was depicted more clearly in the lichen results. At the same time the maps for cadmium, iron and lead were much more detailed when based on the lichen samples, perhaps because there were more than four times more lichen samples available and twice as many means for clusters were available as there had been moss collection sites.

Consecutive moss surveys in Sweden have shown lead concentrations, for instance, to have decreased from 1975 onwards (Ruhling et al. 1987), and similar results can now be presented for Finland by comparing the present variations in lead content (1–88 $\mu g\, g^{-1}$) with the results obtained by Mäkinen and Pakarinen (1977) using the same species, *Hypogymnia physodes* (35–124 $\mu g\, g^{-1}$). On the other hand, the maximum zinc concentration recorded here (326 $\mu g\, g^{-1}$) was higher than earlier (119 $\mu g\, g^{-1}$), whereas in Sweden zinc concentrations have also been shown to have declined.

Apart from the metals, the concentrations of sulphur and nitrogen in the lichens offer some points of interest. The range of variation in sulphur content in

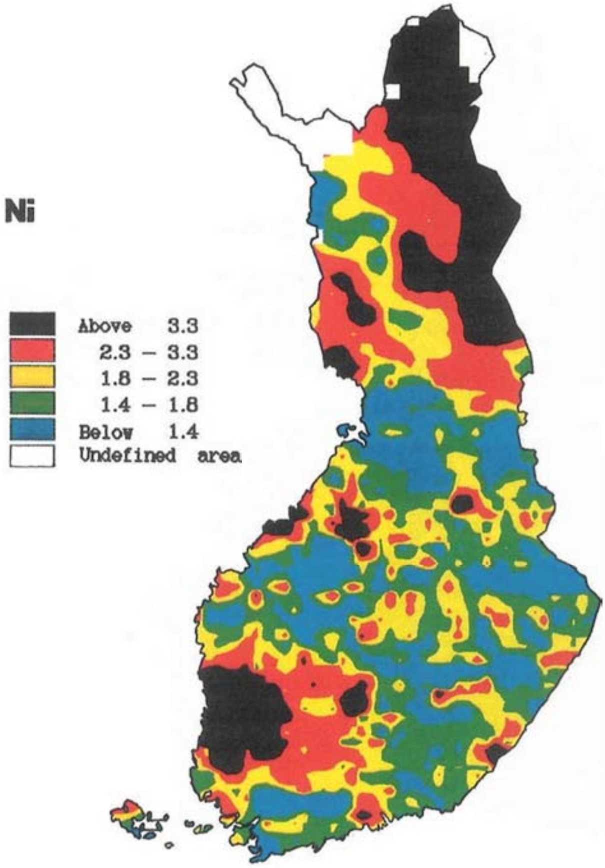

Fig. 15. Nickel content ($\mu g\,g^{-1}$ dry wt.) of *Hypogymnia physodes* in 1985–86

a set of 31 samples taken in different parts of Finland in 1979–81 (Takala et al. 1985) was 370–1830 $\mu g\ g^{-1}$, whereas that reported here for the means of the clusters was 599–2610 $\mu g\ g^{-1}$. Since both surveys included some obvious "background samples", sulphur concentrations in general may be said to have increased in the early 1980's. The areal patterns were to a great extent similar in both surveys, with the highest figures recorded in southern and south-eastern Finland.

Comparison of the present results with locally measured sulphur concentrations in *Hypogymnia physodes* shows the latter to include both larger maximum figures (Huttunen et al. 1983) and lower ones (Olkkonen and Takala 1975; Laaksovirta and Olkkonen 1977, 1979). Although these figures combined with the present results do not allow direct statement of the trend prevailing between the 1970's and the mid-1980's, sulphur deposition may be said to have increased rather than decreased over this period.

The highest sulphur concentrations recorded in the lichens also coincide well with the highest deposition of sulphur as determined in the model for this constructed for southern Finland (Kulmala 1985). As far as northern Finland is

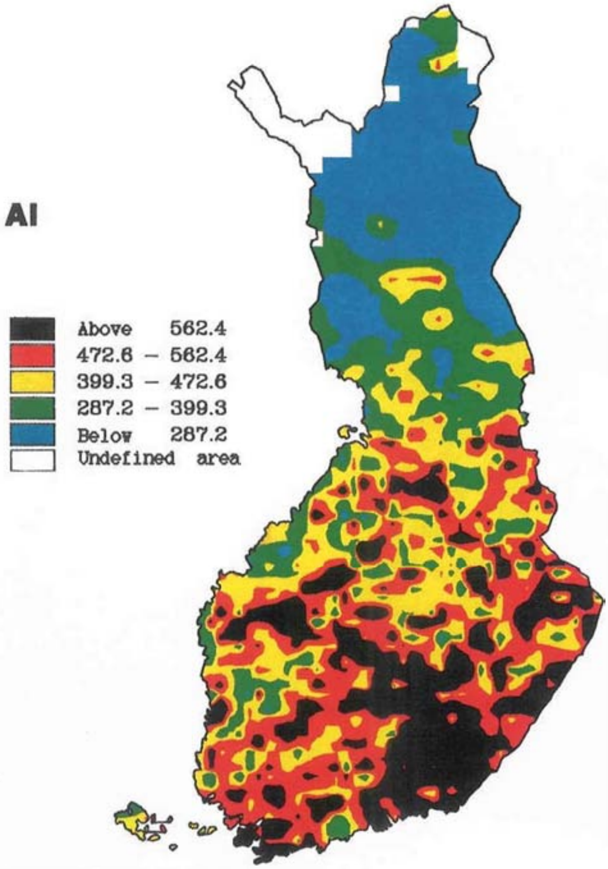

Fig. 16. Aluminium content ($\mu g\,g^{-1}$ dry wt.) of *Hypogymnia physodes* in 1985–86

concerned, unofficial maps have been published in the press suggesting that deposition over extensive areas of eastern Lapland is of the same order as in the south of the country. The present results do not support this suggestion, however, but indicate that the highest figures in the region are to be found in the extreme north, beyond Lake Inari, as also shown in the most recent models produced (Savolainen and Tähtinen this Vol.). An index of air pollution calculated from the occurrence of lichen species similarly shows pollution to be less serious in Central Lapland than in Inari Lapland (Kuusinen et al. this Vol.).

Since it is nevertheless possible that the differences in climatic conditions between Lapland and the remainder of Finland may have affected the results, a separate regional analysis was performed for Lapland alone (Kubin 1989), but this again did not show the figures for eastern Lapland to be any greater than elsewhere, but rather pointed to areas with high values on the Bothnian Bay coast and in the extreme north. Westman (1986) has specifically shown sulphur concentrations in *Hypogymnia physodes* to be high in places where deposition is high and low in places where this is low.

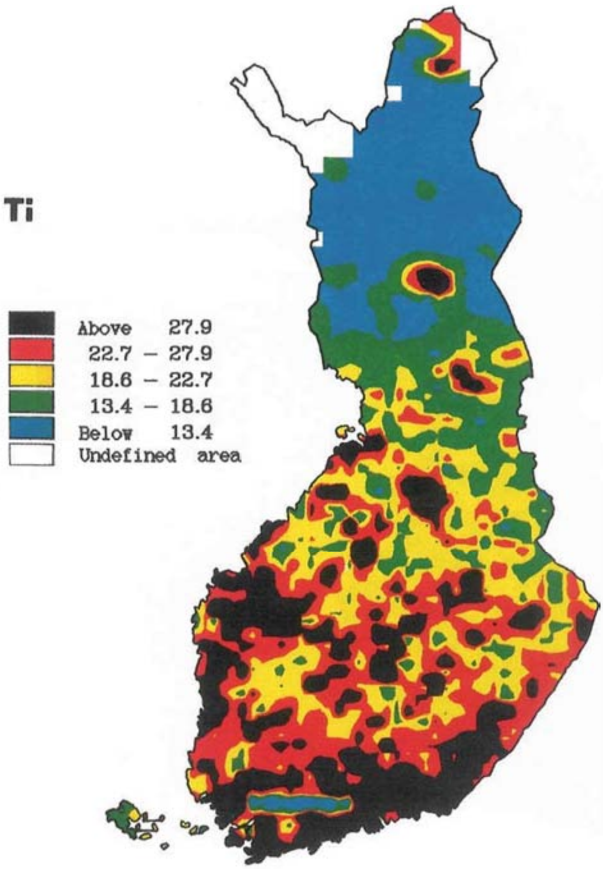

Fig. 17. Titanium content (µg g^{-1} dry wt.) of *Hypogymnia physodes* in 1985–86

It would seem, therefore, that since the predominant wind directions in northern Finland are towards the northeast, with a much lower frequency of winds blowing from the Kola Peninsula into Lapland or along the Finnish-Soviet border, sulphur does not accumulate in the lichens of eastern Lapland to the same extent as it does in the southwestern corner of Lapland or in southern Finland. There is indeed some deposition from the Kola area on the Finnish side of the border, as observed here in the case of some of the metals, but the distribution of airborne metal dusts would seem to be quite different from that of the predominantly gaseous sulphur and nitrogen emissions. Although the areal patterns for sulphur and nitrogen concentrations are similar, even to the occurrence of a peak in the extreme north of the country, it would be useful to conduct further experiments on the accumulation of sulphur in lichens under varying ambient conditions.

Takala and Olkkonen (1985) published results on titanium concentrations in *Hypogymnia physodes* using the same samples as in Takala et al. (1985), and showed the highest values to occur in the southeast, with levels in the south of the country in general being higher than in the north. This pattern conforms well with the distribution found here, where the zone of high concentrations covered both southern Finland and an extensive area on the west coast. Again attention is drawn to the extreme north of Lapland and the influence of the Kola Peninsula in this area, since titanium is generally defined precisely as an indicator of industrial emissions.

A still more pronounced accumulation of high concentrations in the southeast is observed for aluminium, whereas in this case Lapland falls to a great extent into the area of low values.

The distinct peaks in magnesium and potassium content in the north of Lapland represent a deviation from the pattern depicted by Ruhling and Tyler (1971), and sodium also reaches its highest concentrations in the far north and on the west coast, evidently more on account of the marine influence than of any other factor. Potassium was highest of all in southern and central Finland, although the areal distribution would seem to be somewhat accidental and may have been dependent more on material dropping from the crowns of the trees than on any other factor. This effect may also be present in the distribution of calcium and magnesium as well, but it is noticeable that no connections with the occurrence of rich grass-herb forests can be detected. Although the areal variations in the occurrence of these elements which are of importance as plant nutrients are not of such immediate interest as those in detrimental substances, the major areas of high calcium and magnesium concentrations in Lapland must be of some significance and call for further investigation.

The elements determined here which are not essential for plant life are Cd, Cr, Ni, Pb, Al and Ti, of which the highest concentrations of Cd and Ni occur in the same areas of western Finland where copper is also high. The other extensive area of high nickel concentrations is in eastern Lapland, again coinciding with copper.

The broadest single area of high concentrations is achieved in the case of chromium, coinciding over part of its extent with areas of high cadmium and lead. Correspondingly, the areas of high aluminium and titanium content coincide in south-eastern Finland, while high lead concentrations are recorded in the south of the country.

Bearing in mind these areas of high concentrations together with the occurrence of high sulphur and nitrogen deposition values over wide areas of southern Finland, it may be said that it is difficult to find a place anywhere in the south of the country that does not have a higher loading than other parts of the country with respect to some element or other. The areas with the lowest loadings in general would seem to be the northern margins of central Finland, Kainuu and the northern parts of western Lapland.

The present results serve to indicate what elements form the main factors in deposition from the air in different parts of the country, but they do not, of course, allow any conclusions to be reached on the absolute volumes of deposition, nor is any attempt made here to explain the effects of this deposition on the natural environment. They should, however, provide an excellent starting point for the targeting of research of this kind to the appropriate geographical areas and the identification of sites on which investigations of the effects of such air pollution should be focused.

Conclusion

Analyses are made of Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, N, Na, Ni, Pb, S, Ti and Zn concentrations in a total of 2385 samples of the lichen *Hypogymnia physodes* collected from monitoring sites set up by the Finnish Forest Research Institute in 1985–86. The material represents 908 clusters of sites distributed evenly over the whole country, and the results are presented on maps on which the mean values for these clusters are plotted.

The results point to certain larger areas of high and low concentrations of these elements carried in the air in the form of metal dusts or gaseous compounds. In some cases, e.g. copper and chromium, high concentrations can be linked directly with sources of emissions.

The results confirm earlier observations on the suitability of *Hypogymnia physodes* as an indicator of air quality and the proportions of different substances in local airborne deposition.

The results also indicate that the forests practically throughout the country are subject to some degree of airborne pollution, often with deposition of several substances coinciding in the same area. It is impossible from the present results to ascertain the effects of these substances, however, or to obtain absolute figures for the amounts deposited.

Since airborne pollution includes components which have a major effect on soil and water acidity, and components which are not among the nutrients normally taken up by plants, increased emphasis should be placed on the necessity for plans and actions aimed at reducing anthropogenic emissions into the atmosphere to the lowest levels possible.

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Air Pollution Levels and Abundance of Forest Insects

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Summary

This chapter investigates and reviews the effects of industrial air pollution on forest damage through insect pests. A spatial pollution gradient (SO_2, heavy metals) was utilized in southwestern Finland around a factory complex producing copper, nickel, sulphuric acid and fertilizers. Several insects associated with the Scots pine, including bark bugs, aphids, diprionids and tortricids, abounded in the moderately polluted pine stands, but were scarce (excluding aphids) in the immediate vicinity of the industrial plants probably due to the toxic effects of heavy metals. Preliminary results showed no clear patterns for parasitization of pests in relation to the pollution level. Chemical analyses of the needles showed that the concentrations of heavy metals decreased exponentially with increasing distance from the emission source. Also the concentrations of potassium, sodium as well as ash weight and air-dry weight decreased, while those of magnesium, manganese and calcium increased with increasing distance. The peaked abundance patterns in the gradient found in many species could not be completely explained by findings in the laboratory. The pupal/cocoon weight of defoliator species reared was the smaller, the nearer to the emission source their larval food originated from. A considerable amount of variation in the weight could be explained by the heavy metal concentrations in the needles. In the European pine sawfly, the number of eggs laid was positively correlated with the cocoon weight. However, smaller females produced more viable eggs, which masked the effect of female size on the number of offspring produced. Contaminated food increased the pupal mortality and decreased the developmental rate of the large pine sawfly. Although air pollution affected several essential population parameters of insect pests, the available results cannot be generalized uncritically, since causal relationships are still insufficiently known. All signs suggest that the adverse effects of forest pests increase with pollutant load, which may lead to unexpected problems in forest management.

Introduction

The significance of insect pests in forests in relation to air pollution has been an overlooked field of study. Consequently, insects have received only little attention

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in the public discussion concerning the forest decline syndrome ("Waldsterben"). The reasons for this negligence are certain complexities in the object of study: unpredictable natural fluctuations in population sizes, areal restraint of serious insect damage, small size and fast development of individuals, often combined with cryptic habits. Insects are an extremely diverse group of animals; and their identification requires an experienced specialist. Such a group cannot be treated as a simple and compact variable in administration or debate of everyday occurrence. Mathematical modelling of such complex things is very problematic.

However, air pollution may drastically increase the virulence of insect pests, although damage caused by insects has previously been considered fairly moderate in northern Europe (Heliövaara and Väisänen 1984). The frequency of insect outbreaks may essentially increase. Formerly innocuous insects feeding on pine, spruce or birch may surprisingly be turned into pests (Baltensweiler 1985).

Air pollution may decrease tree vigour and forest growth and, in extreme cases, may cause the death of trees and entire forests. The way in which the forest damage process develops is the matter under dispute. The process has been suggested to be primarily a direct consequence of abiotic factors, the pollutants themselves affecting the condition of the trees. Alternatively, the catalytic role of biotic factors, such as insects and diseases, may be decisive. Trees stressed by pollutants are inevitably more susceptible to insect attacks and some diseases; and trees with an even more decreased resistance can in turn be more sensitive to new insect attacks and the effects of severe climatic conditions (Braun and Flückiger 1984; White 1984; Dohmen 1985; Führer 1985; Hain 1987; Heliövaara and Väisänen 1988d). A positive feedback cycle of declining tree vigour may arise (Loehle 1988). If this scenario is of relevance to the forest decline syndrome, biotic factors may multiply the magnitude of forest damage caused by chemicals alone. On the other hand, some insects may be more sensitive to pollutants than trees; this may counteract the damaging process (Alstad et al. 1982; Führer 1985). Air pollution is a considerable threat to several forest insects as well (Väisänen 1988).

In their review of the effects of pollutants on insect populations, Alstad et al. (1982) and Hain (1987) have pointed out that the literature has been largely retrospective, and has sought to find causal relations between observations that are merely correlated. Yet, it is important to reveal correlations between pollutant depositions and pest abundance, and to identify field patterns that may explain changes in the population dynamics of insect species. It is even more essential to obtain detailed information on actual causalities between pollution and responses in individual insect species. Thus, complementary experimental and laboratory studies are needed to grasp the meaning of field observations.

The purpose of the present investigation is to clarify how the intensity of air pollution possibly causes forest damage through insect pests. The spatial pollution gradient can be compared to a temporal gradient due to long-term changes in pollutant load. This can make it possible to prognosticate, monitor or even control insect outbreaks, although different pollutants affect ecosystems in different ways (Alstad et al. 1982). The separate branches of the present investigation cover the alterations in the abundance of single species, community structure, between-species interactions, and especially effects of changed food quality on central factors affecting population dynamics of insects. These factors include distribution, insect size, reproductive potential, fecundity, egg viability, larval and pupal developmental rate and mortality as well as predation.

The present chapter is based on several published papers (cited below), where more detailed information is available. To make the chapter more convenient for the reader, we have not considered it necessary to repeat all data and statistical tests in this context. Attention has been focused on young pine stands and their insect species. The Scots pine (*Pinus sylvestris* L.) is the most important tree species from the economic point of view in Finland. Disturbances in the regeneration, growth and yield of the pine essentially affect the foundations of the commercial and industrial life. The results of the present investigation are discussed in relation to previous results from mature forest, other tree species and other areas.

Material and Methods

Field Studies

Study Area

The field investigation was carried out around a distinctive emission source in the town of Harjavalta (61°20′N, 22°10′E), southwestern Finland, during 1987–1989. The town is surrounded by wide areas without local emissions. In the study area, the deposition of pollutants forms a decreasing gradient which was utilized in the present investigation. This gradient makes it possible to compare several stages of forest decline simultaneously in a small area. Five 9-km-long radial transects extending from the emission source were delimited in the pine stand. All of the transects contained nine sample plots at approximately logarithmic distances (Fig. 1).

The study area lies on a wide ridge running in a northwest-southeast direction. The vegetation of the area consists of plant species typical of eskers and dry upland forest sites (*Calluna vulgaris, Empetrum nigrum, Vaccinium vitis-idaea, Arctostaphylos uva-ursi* etc). The most abundant tree species is Scots pine. Industrial activities in the area date back to the early 1940's. The heavy pollution load is mainly caused by two factories: a metallurgical plant producing copper and nickel, and a chemical one producing sulphuric acid, aluminium sulphate and fertilizers. Air pollution has had a dramatic effect on the flora in the area since the mid-1940's. Coniferous trees have suffered most, and in the parks they have been largely replaced by poplars. Lichens have been observed to be absent within an area of 8.8 km^2 around the factory complex. In addition to the floristic studies, there is much background information available as to the deposition and effects of air pollutants in the study area (Laaksovirta 1973; Laaksovirta and Silvola 1975; Karhu 1982;

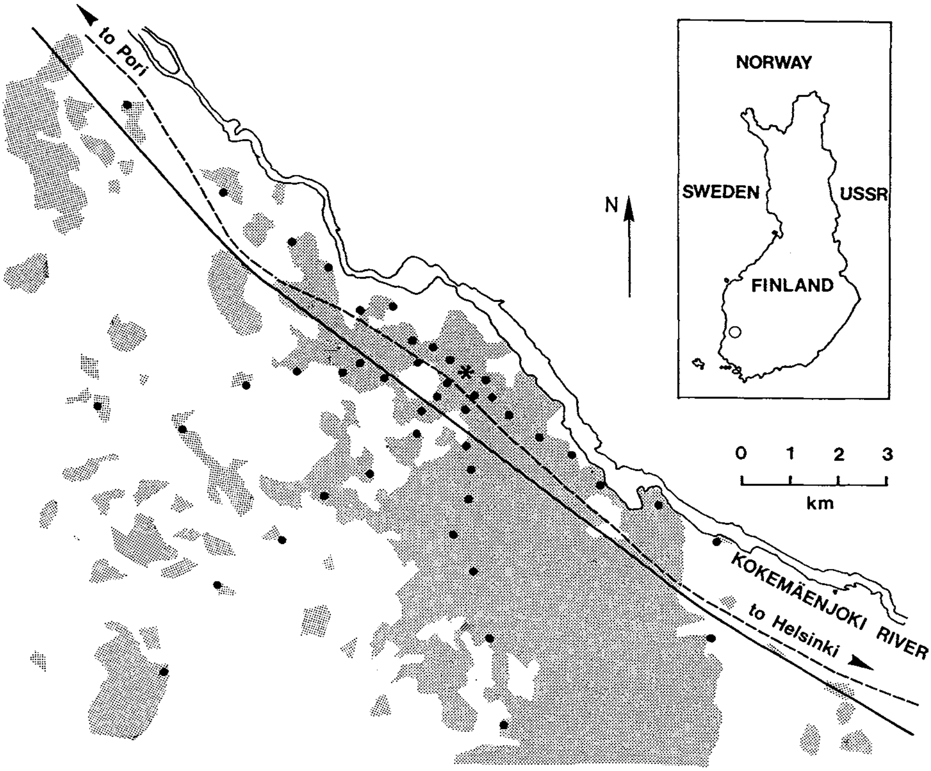

Fig. 1. The study area in Harjavalta, southern Finland. *Black dots* indicate the sampling sites along five transects running in NW, W, SW, S and SE directions. *Shaded area* indicates major pine stands, but scattered pines are present everywhere

Hynninen 1983, 1986; Arstila et al. 1986; Hynninen and Lodenius 1986; Kuokkanen 1986; Sippola and Erviö 1986). The annual mean of sulphur dioxide emission varied from 30 to 53 $\mu g\ m^{-3}$ during 1978–1985 (Kuokkanen 1986). A small amount of pollutants is derived from traffic and energy production. The amounts of copper, nickel and cadmium emitted in 1986 were ca. 305,000, 73,000 and 2000 kg.

Species Examined

The abundance of individual insects species or taxa along the pollutant gradient was studied in the field. Special attention was paid to the following groups associated with the Scots pine: the pine bark bug *Aradus cinnamomeus* Panzer (Heteroptera, Aradidae), the pine resin gall moth *Retinia resinella* (L.) and other pine tortricids (Lepidoptera, Tortricidae), aphids (Homoptera), pine sawflies (Hymenoptera, Diprionidae), bark beetles (Coleoptera, Scolytidae), and parasitoids and predators of various species. In addition, the abundance of hysterothecia of *Lophodermium* fungi (Ascomycetes) was recorded. The methods used in these studies have been described in the original papers (cited below).

The pine bark bugs were sampled at seventy-one sample plots along eight transects (Fig. 1, and similar transects pointing to N, NE and E). In every plot, 20 young pines were sampled for the bugs at the point of the trunk where the bug density was highest. The galls caused by the gall resin moth were sampled on the sample plots along the five transects shown in Fig. 1. The emerged parasitoids were recorded along two transects. In order to study the between-species interactions, the occurrence of pest species was examined in three pine stands. These otherwise similar young pine stands were located at different distances from the factory complex (100 m, 1 km, 3 km), and were selected to represent different stages in the forest damage process (Fig. 2). One hundred randomly selected pine saplings were examined in 1987 at each site.

Larval colonies of *N. sertifer* were reared at the sample plots along the S and SW transects (Fig. 1). The colonies originated from southern Finland. Small

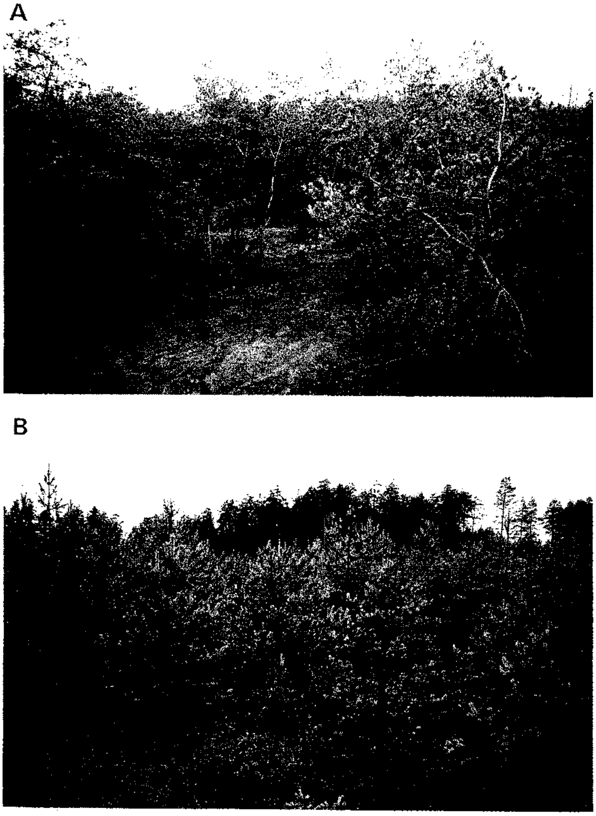

Fig. 2A, B. General views of the study stands in Harjavalta. **A** the badly damaged pine stands in the immediate vicinity of the pollutant sources. **B** The moderately polluted pine stand heavily infested by several insect pests branches, each bearing about 40 first instar larvae, were cut in early June from pines and transferred to the study area. Fifteen branches were attached with steel wire on the shoots at every sample plot. The total number of larvae in the beginning of the field experiment was ca. 10,800. As the original branches dried, the larvae moved on the previous year's needles of their new host tree. The larvae were let to grow for 30 days in the field until they reached their fifth instar. During this period, parasitoids could lay eggs in the larvae. After this, the lateral shoots bearing larvae were cut and transferred to the laboratory. The cocoons obtained from the rearings were kept for 2–3 months under laboratory conditions. During this period, emerging parasitoids were daily collected and identified.

Composition of bark and needle fauna was also studied in the field. Five pines at each plot were sampled along four transects (Fig. 1) by striking with a hoop net. Bark samples were taken by removing 100×500 mm^2 of loose bark at a height of 0.5–1.5 m. All the invertebrates present in the bark slices were removed and preserved in alcohol. The material was identified and counted except for very small (<0.5 mm) animals.

Bark beetle and associated fauna from 20 dead pines and ten spruces collected from the vicinity (less than 1 km) of the emission source were analysed in detail. The length of maternal galleries and the number of exit holes were recorded.

Laboratory Studies

Needle Analyses

Secondary pine shoots bearing the previous year's needles were collected from ten pines on the sample plots along the S and SW transects. The needles had been collected in June to obtain a realistic picture of the mineral nutrient and metal composition of them from a herbivore's point of view. These needles were used as larval food in the laboratory rearings. About 3 g of the needles were removed from branches around the lower part of the crown and placed in paper envelopes and transported to the laboratory. After determining the dry weight (105°C) and ash weight (muffle furnace at 550°C), the concentrations of total P, K, Mg, Mn, Fe, Al, Cu, Zn, Na and Ca were determined according to methods described by Halonen et al. (1983) on an ARL ICP 3580 Spectrometer. C, H and N were analysed on a LECO CHN analysor. Each sample was analysed in duplicate, and the mean value was used. The mean length and dry weight of ten needles from five pines at each sampling site (50 needles per site) were also determined.

Rearing of Insects

In the laboratory rearings the following pine insect species were used: moths (Lepidoptera): *Panolis flammea* (Denis and Schiffermüller), *Bupalus piniarius* (L.); sawflies (Hymenoptera): *Neodiprion sertifer* (Geoffroy), *Diprion pini* (L.), *Gilpinia socia* (Klug), *G. virens* (Klug), *G. frutetorum* (Fabricius), *Microdiprion pallipes* (Fallén) (Figs. 3, 4). The two moths have a long history as severe pests of Scots

Fig. 3. Larva of the pine looper moth, *Bupalus piniarius*, on the needles of Scots pine

Fig. 4. Larval colony of the large pine sawfly, *Diprion pini*

pine in Europe (Kudler 1978; Schwenke 1978). Two of the sawfly species (*N. sertifer, D. pini*) are also considered as pests of pine having extensive outbreaks at irregular intervals. The other species are of minor forest economic importance (Kangas 1963; Pschorn-Walcher 1982; Viitasaari and Varama 1987).

Adult insects collected from southern and central Finland were transferred to the laboratory for egg-laying. They were placed on small pine plants surrounded by nylon netting. In the moths and the gregarious sawflies (*D. pini, G. socia*), one female and one male were placed on each plant. In the solitary sawflies (*G. virens, G. frutetorum, M. pallipes*), male larvae were produced parthenogenetically from eggs oviposited by unfertilized females.

After the insect larvae had reached the first/second instar, they were transferred to the rearing pots. The moths and solitary sawflies were reared with one larva per pot, while gregarious sawflies (including *N. sertifer*) were reared in colonies of

20 or 60 larvae. Any genetic effects of parental insects were decreased by evenly distributing the broods of each female between the rearing pots, so that the offspring of each female were reared on needles collected from all the sample sites. Each larva always received its food from the same pine. Altogether about 3000 larvae were reared. The weight of the moth pupae and sawfly cocoons were measured after the larval development using a Mettler PE 360 balance.

Viability Analysis of *Neodiprion sertifer* Eggs

Female *N. sertifer* sawflies (n = 226) were induced to lay eggs on the needles in the field in August. One virgin female was released inside each bag made of nylon netting tightly fastened around the branch with steel wire. One half of these females was reared as larvae on pollutant-stressed pines (Harjavalta) and the other half on relatively unpolluted ones (Tuusula). In order to obtain a more precise picture about how pollutants affect this species, special attention was paid to the female size, fecundity, egg viability and embryonal development. The material yielded 15,568 eggs. Every egg pocket was opened with a fine pin under a stereomicroscope, and the contents of the egg examined. The eggs were divided into eight categories as follows: I. empty egg pocket; II. egg dried, no visible embryonal development; III. egg not dried, no visible post-development of an embryo; IV. abnormal embryo, its development disturbed and interrupted; V. needle and embryo withered; VI. development of the embryo stopped or prolonged; VII. fully developed and formed larva, unsuccessful hatching; VIII. normal larva hatched.

Measuring the Developmental Rate of *Diprion pini*

The effects of food quality on the mortality and developmental rate of larvae and pupae of the large pine sawfly *Diprion pini* were analysed. In the rearing experiment, the larvae were fed Scots pine needles originating either from a heavily polluted sample plot (Harjavalta) or from a relatively uncontaminated site (Tuusula). After larval development, the cocoon weight was determined. The cocoon material from both of the rearings was stored in identical semi-natural conditions over the winter. The hatching dates for females were recorded during June-July, after the cocoons had been brought into the laboratory. The material yielded 243 female cocoons.

Results and Discussion

Abundance of Insects Along a Pollution Gradient

Outbreaks and Declines

There are indisputable examples of insect outbreaks associated with pollutants (Alstad et al. 1982; Führer 1985; Braun and Flückiger 1984, 1985; Heliövaara and

Väisänen 1986a). Causalities are often unclear and difficult to understand, and the ultimate reasons for mass occurrences are not usually known. Air pollutants, depending on their quality and dose, certainly influence insect species in one way or other. Some species may increase in numbers, thus making them pests, and some may drastically decline (Charles and Villemant 1977; Smith 1981, 1984; Alstad et al. 1982; Katayev et al. 1983; Führer 1983, 1985, 1988; Morrison 1984; Baltensweiler 1985; Sierpinski 1985; Gunnarsson 1988).

The total numbers of aphids (mainly *Cinara pini* L.), pine bark bugs (*Aradus cinnamomeus* Panzer), diprionids (*Diprion pini* L.) and tortricid moths (*Blastesthia turionella* L., *B. posticana* Zetterstedt, *Rhyacionia pinicolana* Doubleday and *Retinia resinella* L.), were highest in the moderately polluted pine stands (Table 1; for details, see Heliövaara and Väisänen 1988c). These herbivores, excluding aphids, were scarce in the immediate vicinity of the industrial plants, probably due to toxic effects of heavy metals and other pollutants as well as the very poor condition of their host plants. A detailed study on *A. cinnamomeus* showed a peaked pattern (Heliövaara and Väisänen 1986a, 1987). Factors affecting outbreaks of *A. cinnamomeus* are presented in Fig. 5 (Heliövaara and Väisänen 1986a). A respective study on *R. resinella* showed a similar but less distinctive pattern (Heliövaara 1986; Heliövaara and Väisänen 1987). Air pollution may also affect fundamental life-history traits of *R. resinella* (Heliövaara and Väisänen 1988a, b). Pines growing near to pollutant sources were heavily infested by aphids and bark beetles (studies in progress) which were also abundant in areas with a moderate pollution load. It has often been observed that the number and biomass of sucking insects increase towards the source of contaminants (e.g. Katayev et al. 1983; Braun and Flückiger 1984).

The number of mites in the bark was positively correlated with increasing distance from the pollutant source (Heliövaara and Väisänen 1989c). The decreased number of individuals near the factories may be an indication of their sensitivity to air pollutants, or an indirect response to changes in their food quality

Table 1. Abundance of some pine herbivores per tree ($n = 100$) at study sites situated at a distance of 100 m, 1 km and 3 km from the pollutant source

Species	Measurement	100 m		1 km		3 km	
		$\bar{x}$	s.d.	$\bar{x}$	s.d.	$\bar{x}$	s.d.
Aphids	Ind./tree	13.1	24.6	15.9	20.6	1.9	3.7
Aphids	Ind./unit height	2.7	4.4	1.0	1.5	0.1	0.2
Coccinellids	Ind./tree	0.9	1.3	1.6	2.0	0.3	0.7
Aradus	Ind./1dm^2 of bark	0.1	0.4	1.5	1.5	0.1	0.2
Diprion	Colonies/tree	0.0	0.0	0.2	0.5	0.0	0.1
Retinia	1984 galls/tree	0.1	0.4	0.2	0.6	0.1	0.2
Retinia	1986 galls/tree	0.1	0.3	0.3	0.5	0.2	0.4
Rhyacionia	Larvae/tree	0.0	0.0	0.3	0.6	0.1	0.4
Blastesthia	Larvae/tree	0.0	0.0	0.1	0.4	0.0	0.1

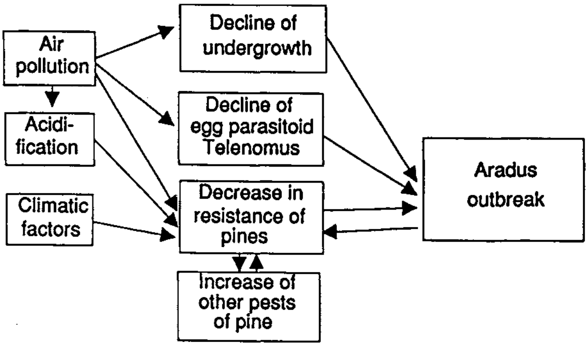

Fig. 5. The role of air pollution in the development of the outbreaks of the pine bark bug, *Aradus cinnamomeus*

(see Alstad et al. 1982). Similar decreasing patterns have been obtained, for instance, from studies on *Lophodermium* fungi on pine (Kowalski 1981; Heliövaara et al. 1989b). The loss of needles has been shown to affect conifer fauna indirectly. For instance, Gunnarsson (1988) has demonstrated a decline of large spiders due to more efficient predation on sparse-needled spruces. Species associated with lichens sensitive to air pollution are declining. Among moths, the best-known Finnish example is *Alcis jubatus* (Geometridae) which lives on *Usnea* species.

Biotic Relationships

Entomophagous species can be assumed to be more susceptible to air pollutants than phytophagous, if a parallel is drawn with pesticides (Führer 1985). However, our preliminary results do not support this assumption. Parasitoids, especially tiny wasps, are suggested to be sensitive to dust because of its desiccative function (Finney and Fisher 1964). The great number of aphids observed near highways (Flückiger and Oertli 1978; Braun and Flückiger 1984) may be partly due to detrimental accumulation of lead in the parasitoids of aphids.

The proportion of parasitized sawflies varied between 23 and 55% in *N. sertifer* along the transects. The number of cocoons at the end of the rearing period increased with increasing distance from the emission source. Nuclear polyhedrosis disease increased mortality of *N. sertifer* near the pollutant source. This study is still in progress. *Macrocentrus* spp. (Hymenoptera, Braconidae) and *Liotryphon* spp. (Ichneumonidae) were the most abundant among the emerged parasitic wasps in the *Retinia resinella* gall material (Heliövaara and Väisänen 1986b). Unidentified species belonging to Chalcididae and Tachinidae (Diptera) were also recorded. Although the proportion of the emerged moths varied between 13 and 37%, the value did not appear to depend on the distance from the emission source along the transects. The proportion of parasitized galls varied statistically nonsignificantly (43–57%) as a function of distance. Although the result naturally depends on the slope of the gradient and the absolute amount of pollutants, it suggests that parasitoids are not necessarily more sensitive to environmental pollutants than their hosts are. Precise conclusions require further studies on parasitoids with large materials, but the huge amount of predators, parasitoids and hyperparasitoids of eggs and small larvae makes this topic a laborious one.

There is reasonable evidence of herbivory inducing chemical changes in plants (e.g. Haukioja and Niemelä 1979; Baldwin and Schultz 1983; Leather et al. 1987). These changes may affect other phytophagous insects that later feed on the plant (Strong et al. 1984; Faeth 1986). Although these between-species interactions are usually negative (i.e. competitive, exclusive), it seems quite probable that, under certain circumstances, they may be positive as well (e.g. Hunter 1987). However, these biotic relationships being complex and the interactions between pest species in polluted areas poorly known, their role in the forest decline syndrome has remained obscure (Hain 1987; Lechowicz 1987).

A few positive but no negative interactions were found between herbivores (Heliövaara and Väisänen 1988c). The interactions between different insect species appeared to be weak even in a moderately polluted site with the highest abundance of insect pests. One herbivore is not very likely to have a direct positive effect on another, but an intensive herbivore attack may upset the metabolism of the plants which, in turn, could favour other herbivores. Insect outbreaks may cause serious local damage along the fringes of pollutant sources, and this may be partially due to the indirect interactions between herbivores.

Detrended correspondence analysis ordination was calculated on the basis of the bark invertebrate data. The DCA-axes 1 and 2 grouped the sampling sites of the zones near the emission source relatively widely apart, while the less polluted sites farthest away from the factories formed a distinct group (Fig. 6). The species assemblage in pine bark appeared to be rather similar at an extended distance, even though the distances between sampling sites were long. Near the factories, on the

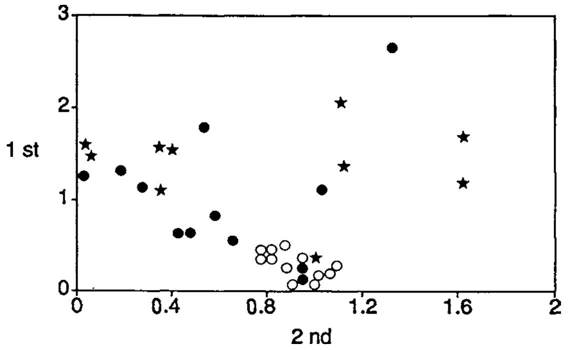

Fig. 6. The sampling sites plotted on the 1st and 2nd axes (eigenvalues 0.41 and 0.16) of detrended correspondence analysis ordination according to their bark invertebrates. *Black stars* 500–1400 m; *black dots* 1800–3900 m; *open circles* 4800–7700 m from the pollution source. (After Heliövaara and Väisänen 1989c)

other hand, there was much more variation among the more closely sited sampling sites (Heliövaara and Väisänen 1989c).

Effects of Polluted Food

Larval Nutrition

The abundance and population dynamics of insects are affected, for example, by the number of their offspring (which, in turn, is related to insect size and number of eggs), developmental rate and mortality in different developmental stages. Plant palatability, nutritional quality, fungal and bacterial epifloras or the attractiveness of the plant as an oviposition site may be altered as a result of pollution stress (e.g. Dohmen 1988; Bolsinger and Flückiger 1989; Braun and Flückiger 1989). Sulphur dioxide and ozone cause major injury to plants. However, near to distinctive sources of pollution, such as smelters, much damage is caused by fluorides, dust, and – as in the present case – heavy metals, which are generally considered to be of minor importance (Kozlowski 1980).

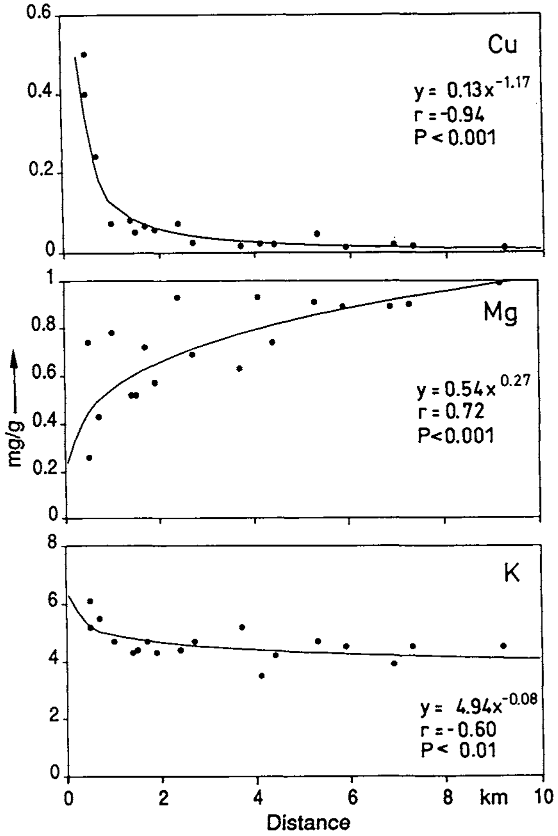

Fig. 7. The concentrations of copper, magnesium and potassium in the pine needles in relation to the distance from the pollutant source

The concentrations of copper, magnesium and potassium in the pine needles in relation to the distance from the pollutant source are described in Fig. 7. The heavy metals studied (Cu, Fe, Zn) followed a clear pattern: exponentially decreasing concentrations with increasing distance from the emission source (Heliövaara and Väisänen 1989b). The concentrations of potassium as well as sodium tended to decrease. A similar pattern was also observed as to ash weight and air-dry weight. The concentrations of magnesium as well as manganese and calcium increased with increasing distance from the factories. The other elements studied show varying and/or statistically non-significant patterns (Heliövaara and Väisänen 1989b).

Insect Size

A distinct tendency emerged from the measuring of pupal or cocoon size of the studied species in relation to the levels of pollution in the pine needles. The weight (as well as width and length) of the pupae/cocoons was the smaller, the nearer to the emission source their larval food originated from (Table 2; Heliövaara and Väisänen 1989a; Heliövaara et al. 1989a,c). The smallest pupae/cocoons occurred almost invariably in the rearing experiments using needles derived from the immediate vicinity of the factory complex. For instance, in the case of *B. piniarius*, the weight of females reared on needles originating from the sample plots nearest to the factories was only 51% of that of females reared on needles from the farthest plots along the two transects. However, the loss of weight was small in all species along the pollution gradient except for the sample plots nearest to the emission source. At moderately polluted areas the detrimental effects of pollution through decreased food quality were so small on the pest species examined that they can hardly counteract evoking outbreaks.

When the concentrations of elements in the needles were used as predictor variables in stepwise regression models, a considerable amount of variation in the weight of pupae/cocoons could be explained by them (Heliövaara and Väisänen 1989a; Heliövaara et al. 1989a). For instance, the elemental composition of the pine needles explained 24–54% of the variation in pupal weight of the two moths (Table 3). The first element to be entered into the regression equation in nearly all

Table 2. Regression equations for pupal/cocoon weight (mean values per plot) in relation to the distance from the emission source

Species	Sex	Equation	R	p<
Bupalus piniarius	Female	$y=0.088x^{0.195}$	0.61	NS
Panolis flammea	Female	$y=0.255x^{0.084}$	0.81	0.01
Gilpinia virens	Male	$y=0.067x^{0.053}$	0.65	NS
Gilpinia frutetorum	Male	$y=0.041x^{0.017}$	0.37	NS
Microdiprion pallipes	Male	$y=0.022x^{0.047}$	0.91	0.001
Neodiprion sertifer	Female	$y=0.055x^{0.072}$	0.94	0.001

Table 3. Total amount of variation (R^2) in pupal/cocoon weight of moths and sawflies covered by stepwise regression models, and elements with best explanatory potential as indicated by their partial correlation coefficients (r^2)

Species	Sex	R^2 (%)	Element	r^2 (%)
Bupalus piniarius	Male	29.3	Fe	23.0
	Female	53.7	Cu	47.2
Panolis flammea	Male	47.1	Cu	39.2
	Female	24.7	Cu	24.7
Gilpinia frutetorum	Male	–	–	
Gilpinia virens	Male	24.5	P	15.6
Microdiprion pallipes	Male	15.5	Fe	10.6
Neodiprion sertifer	Male	9.7	Fe	5.0
	Female	24.6	Fe	13.1

the analyses was either copper or iron. Copper could have been replaced by iron or zinc without any significant loss in the explanatory potential. The size of pupae/cocons was always negatively correlated with the concentrations of these metals.

Fecundity and Reproductive Potential

The insect size is often considered to be directly associated with fecundity. Larger and heavier individuals are often able to oviposit more eggs (Bevan and Paramonov 1956; Popo 1968; Dixon and Wratten 1971; Danthanarayana 1975; Marks 1976; Leather and Wellings 1981; Dixon et al. 1982; Jones et al. 1982; Miller et al. 1982). However, the potential fecundity or reproductive potential is not the same as the actual total fecundity (Leather 1988). For instance, the fecundity/weight ratio is often masked by other factors, such as adult longevity, temperature conditions and availability of an adult food source. This therefore poses the question of whether air pollutants can affect actual fecundity and offspring survival in insects.

The actual fecundity, when measured as the total number of eggs oviposited by the *N. sertifer* female, differed significantly between the study groups. The sawfly females reared as larvae on polluted needles oviposited an average of 69 eggs, and those reared on unpolluted ones 80 eggs per female (Heliövaara et al. in press). The proportions of the eggs in different viability categories are given in Fig. 8. A distinctly higher proportion of eggs resulted in a normally developed larva (VIII) in the polluted group, while the proportions of the different failure classes (II, V, VI, VII) were higher in the unpolluted group. The number of eggs laid in both study groups was positively correlated with the cocoon weight of the female (Fig. 9). The number of eggs with normal early embryonal development (categories VI–VIII) correlated with the cocoon weight, but the final number of normally developed first instar larvae (VIII) did not (Heliövaara et al. in press).

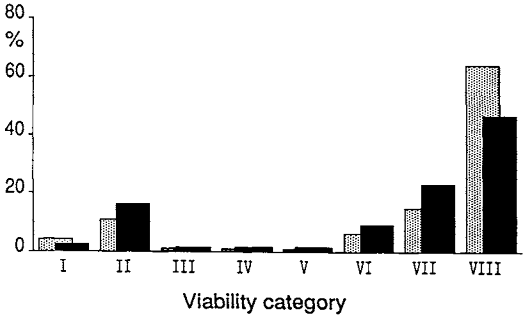

Fig. 8. The proportions of *Neodiprion sertifer* eggs in different viability categories. The eggs oviposited by females reared on unpolluted needles are indicated by *dark columns*, those by females reared on polluted needles by *light columns*

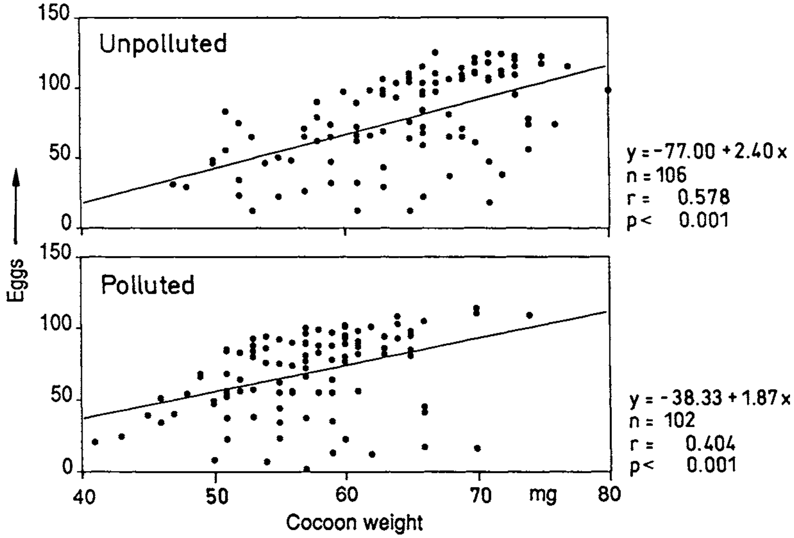

Fig. 9. The number of *Neodiprion sertifer* eggs laid in relation to the cocoon weight of the female. Results on females reared on unpolluted needles are shown in the *upper diagram*, and those on females reared on polluted needles in the *lower one*

The results suggest that female size would affect the survival and embryonal development of the eggs. A high level of pollutants in larval food would not increase the egg quality, but instead would be a specific feedback mechanism in *N. sertifer* that compensates in the next generation for the decrease in the female size. Smaller females may tend to produce better, i.e. more viable, eggs. Somewhat similar results are available on *Cydia pomonella* (Lepidoptera, Tortricidae), whose adult weight is also positively correlated with fecundity and heavier females tend to produce more infertile eggs (Deseo 1971). In some other Lepidoptera, fecundity is not correlated with pupal weight or adult weight (Karlsson and Wiklund 1984; Boggs 1986).

Developmental Rate

The developmental rate of the *Diprion pini* larvae was slightly slower in the group reared on polluted needles than in the control group (Heliövaara and Väisänen 1990). Larvae feeding on polluted needles showed a slightly lower mortality during the first days of their larval development. The cocoon mortality (excluding mould contamination) was statistically significantly higher in this group. Females fed with polluted needles tended to hatch later than those fed with unpolluted needles (Fig. 10). Although the observed prolongation of development was on an average no more than 4 days in the laboratory, it may affect population dynamics and outbreak patterns of *D. pini* in the field. The changed hatching times influence cocoon predation, mating, adult predation and early development of the next generation. No relationship was found between the cocoon weight and hatching time within the groups, but later-hatching individuals fed as larvae with polluted needles were smaller than early hatching ones fed with unpolluted needles (Heliövaara and Väisänen 1990).

In the laboratory conditions, pupal mortality may be attributed to the food quality or to the laboratory set-up. However, the length of the pupal period in the field affects the risk of being predated. A short delay in the hatching time at room temperature was demonstrated between the two groups. This may imply a more pronounced difference in cooler field conditions. Cocoon predators have been suggested to have a strong regulating effect on sawfly populations under a wide range of conditions (Hanski 1987). In *Neodiprion sertifer*, recent studies have shown that the rate of cocoon predation by arthropod and especially small mammal predators often exceeds 50% (Hanski and Parviainen 1985). Cocoon predation was the key mortality factor in a lifetable study of this species in Sweden (Olofsson 1987). A long ovipositing period in nature and the habit of larvae to eat both old and new needles indicate that the slightly increased age of needles, when the pupal period is longer, does not have much influence on the early larval development of *D. pini*. The changed timing of mating and the egg stage may have

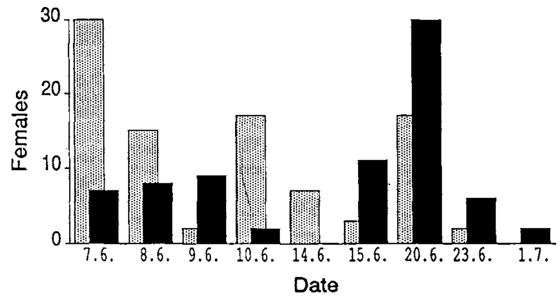

Fig. 10. Hatching dates of *Diprion pini* females. Individuals reared on unpolluted needles are indicated by *light columns*, and those reared on polluted needles by *dark ones*

an ambivalent effect on egg parasitization. The prolonged development may have the most significant impact on the population dynamics of sawflies through increased cocoon predation.

Consequences for Forest Management

The most serious forest decline has occurred in old forests in Central Europe. This may be related to decreased tree vigour and pest resistance in old trees (Loehle 1988). In Finland, damage in mature forests has so far been visible mainly as a loss of needle biomass (Jukola-Sulonen 1987). Insects and mites may contribute to this process. However, no serious insect outbreaks due to air pollution in mature forests have been recorded in Finland, though it is evident that forests are becoming more susceptible to insect attack.

The present investigation was restricted to the Scots pine, and little is so far known about the pests of other trees in Finland in relation to pollution. *Zeiraphera diniana* Guénee (Lepidoptera, Tortricidae) and *Cephalcia falleni* Dalm. (Hymenoptera, Pamphilidae) are pests of spruce which are known to be favoured by air pollution in Central Europe (Baltensweiler 1983; Sierpinski 1984). No outbreaks of spruce defoliators have been recorded in Finland so far, but bark beetles, especially *Ips typographus* (L.) (Scolytidae), living in dead or dying trees are a potential threat to spruce stands if pollution still decreases tree vigour. The number of aphids tend to increase in deciduous trees, such as birch, when the tree vigour decreases due to air pollution (Braun and Flückiger 1984, 1985). Simulated acid rain had similar effects on *Euceraphis betulae* (Koch) in experiments carried out in Finnish Lapland (Neuvonen and Lindgren 1987).

The results of the present investigation show that air pollution affects insects in many different ways. Causal relationships are still poorly documented; and the available results cannot be generalized uncritically. However, the complexity of the relationships does not mean that insects would be of minor importance. The present investigation shows that several essential population parameters have been affected by pollutants. Many forest pests are favoured by air pollution and the subsequent decrease in tree vigour, but laboratory experiments also show that high doses of pollutants have toxic effects.

Simple forecasting of pollutant-induced insect outbreaks in Finnish forests is impossible today. Consequently, it is necessary to continuously monitor the situation and reveal and control the changes in pest abundances at an early stage of damage. All signs suggest that the adverse effects of forest pests increase with the pollution load. And vice versa, recent findings suggest that various forms of insect damage make the food plants more susceptible to atmospheric pollutants than healthy food plants would be (Berge 1973; Rosen and Runeckles 1976; Warrington et al. 1989). The significance of forest pathogens has recently been generally recognized, but the seriousness and economic importance of damage caused by insects has often been ignored. This may lead to unexpected problems in forest management.

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Effects of Simulated Acid Rain on the Susceptibility to Scleroderris Canker [*Ascocalyx Abietina* (Lagerb.) Schläpher-Bernhard] and on Assimilation and Transpiration of Scots Pine Seedlings

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Summary

Scots pine (*Pinus sylvestris* L.) seedlings growing in plastic pots were exposed to addition of artificial rain of pH 5.6 (control), 4.5, 4.0 and 3.0. Inoculation with spores of *Ascocalyx abietina* (Lagerb.) Schläpher-Bernhard was carried out twice during the growing season. Exposure to acid rain did not affect the growth of the seedlings. The infection rate of *A. abietina* was high, probably mainly due to weather conditions unfavourable to pine seedlings. The dead part of the shoot was significantly shorter in the seedlings which were treated with both acid and natural rain at pH level of 5.6 and 4.0. Acid rain did not significantly change assimilation or transpiration.

Introduction

Air pollution may have various effects on Scleroderris canker caused by *Ascocalyx abietina* (Lagerberg) Schläpher-Bernhard. A low pH, which may have negative effects on the host plant, may also reduce the fungal growth itself (Shriner 1978). Bragg and Manion (1984) suggested that acid rain is not a major environmental factor affecting Scleroderris canker disease; it would appear that the various interacting factors of acid rain on the system generate a neutral minor impact on Scleroderris disease problem in New York State. In Sweden, Barklund et al. (1984) have shown that in spruce *A. abietina* is promoted by acid rain treatments in growth chambers.

In Finland, *A. abietina* has caused the most serious problems on Scots pine (*Pinus sylvestris* L.) over the last 15 years (Kurkela 1981). The Finnish conclusion has been that the major factor has been unfavourable climatic conditions. There was a serious *A. abietina* epidemic in the southern part of Finland during the 1970's, and another epidemic in the early 1980's; a new epidemic appeared in 1988. Because the frequency of new epidemics seems to increase and the disease is more serious than previously, it has been postulated that air pollution may affect the occurrence and development of *A. abietina*.

Acid deposition can have two types of effect on terrestrial ecosystems: (1) direct effects: vegetation may be injured directly and (2) indirect effects: vegetation may

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be affected indirectly by a changed supply of plant nutrients or by production of toxic compounds in the soil. Morrison (1984) tabulated the threshold pH levels of 2.0 to 3.2 for the production of visible symptoms on tree foliage. In coniferous trees acid rain may penetrate into coniferous needles in places, where the cuticular wax is thin, e.g. around stomata. Important physiological processes, photosynthesis, respiration, carbon allocation and stomatal function are known to be affected by air pollutants. The aim of the study was to find out the direct effects of simulated acid rain on the development of pine seedlings inoculated with *A. abietina* and on assimilation and transpiration.

Material and Methods

Material

A total of 320 2-year-old Scots pine seedlings, growing in plastic pots in a mixture of peat and sand, were used in this study.

In the experimental design, the following factorial combinations were examined:

Main plots	addition of artificial rain at pH 5.6, 4.5, 4.0 or 3.0.
Split plot	plus or minus natural rain.
Split split plot	addition of artificial rain sprayed to whole plant or applied to soil.

A major consideration was the comparison of inoculated versus uninoculated seedlings in these different treatment groups.

The seedlings were divided into four groups of 80 seedlings according to the pH level of addition of artificial rain as follows: group 1 (control pH 5.6), group 2 (pH 4.5), group 3 (pH 4.0) and group 4 (pH 3.0). In each group, seedlings were divided into subgroups of 40 seedlings, so that in subgroups A seedlings were exposed to natural rainfall and addition of artificial rain, subgroups B receiving only addition of artificial rain. Further, each subgroup was then divided into two groups of 20 seedlings according to whether the seedlings were treated with the artificial rain at the roots only or on the whole plant as well. The length of the seedlings was measured at the beginning (in May) and at the end of summer 1987 (late August).

Acid Rain Treatments

The acidity of the solutions was adjusted by adding sulphuric acid and nitric acid in a molar ratio of 3:1. The seedlings were exposed to the simulated acid rainfall two to three times per week for 3 months starting in the middle of June 1987. The total amounts of simulated acid rain deposited for the whole growing season was about 300 mm of water and about 25 $g\,m^{-2}$ sulfur and about 8 $g\,m^{-2}$ nitrogen at pH level of 3.0. At pH level 4.0 these figures were about 3.0 $g\,m^{-2}$ sulfur and

1 $\mathrm{g\,m^{-2}}$ nitrogen and at pH level 4.5 about 1.0 $\mathrm{g\,m^{-2}}$ sulfur and 0.3 $\mathrm{g\,m^{-2}}$ nitrogen. Pure deionized water was used as control (pH 5.4 to 5.8). The seedlings were fertilized by giving nutrients together with acid rain solution so that nutrient deficiency was minimized. The total amounts of nutrients addition to $\mathrm{m^{-2}}$ were: 9 g N, 2 g P, 8.2 g K, 0.1 g Mg, 0.02 g Fe, 0.01 g Mn, 0.004 g B, 0.002 g Cu and 0.003 g Zn. The used water was always deionized before adding acid solution.

Inoculation Treatments

Inoculation with *A. abietina* was carried out by spraying 1 ml of a suspension of conidial spores on top of every second seedling corresponding to 3 million spores. The pine seedlings were inoculated twice during the growing season: at the end of July and at the beginning of August.

Observations

Photosynthesis/transpiration

Assimilation and transpiration were measured in the autumn during October and in the beginning of November in the laboratory using an open flow infrared gas analysis (IRGA) system (URAS 3G, Hartman & Braun). Temperature was regulated and the partial pressures of CO_2 and H_2O vapour were controlled in the assimilation chamber with the help of mass flow controllers (Brooks Instrument B.V., The Netherlands). The climate in the assimilation chamber was constant during the measurement period: temperature 293 K, H_2O concentration 0.66 mol $\mathrm{mol^{-1}}$ and CO_2 concentration 340 $\mu\mathrm{mol\,mol^{-1}}$.

From a total of 14 seedlings, six seedlings at pH 5.6, six at a pH level of 3.0 and two at a pH level of 4.0, all inoculated with the spores of *A. abietina* and acid treatments sprayed to whole plant, a light response curve was measured in nearly parallel beam radiation provided by a profile spot projector (model HMV 1200, Ludwig Pani Ltd, Austria) equipped with a 1200 W metallogen lamp (Radium RSI). Light intensitity was varied stepwise with grey filters inserted between the lamp and the assimilation chamber and the photosynthetically active radiation (PAR) was measured in the chamber with a quantum sensor (Li-Cor, Lincoln, Nebraska, U.S.A.). The PAR levels were 0, 65, 125, 250, 500, 1000, and 2000 μmol quanta $\mathrm{m^{-2}\,s^{-1}}$. The photosynthetic capacity was expressed as a total projected area of measured shoot.

Incidence of Disease

All the seedlings overwintered in natural conditions with no shelter in the field. The number of seedlings infected by *A. abietina* was counted in spring 1988 (early May); the length of the dead part of the infected shoot was measured in middle of June, when the spread of infection seemed to have stopped.

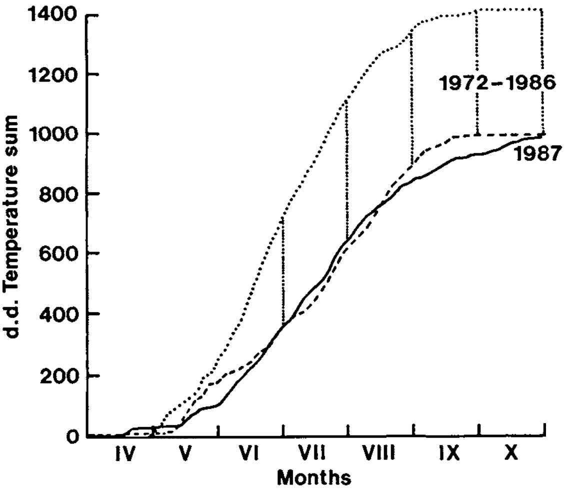

Fig. 1. Development of the temperature sum in 1987 and variation in 1972–1986

Weather observations were made in an experimental station at about 200-m distance from the acid rain experiment and the pH of natural rain was measured daily after rainfall. The total rainfall in 1987 was 510.7 mm, compared to 441.5 mm, which has been the average for the previous 14 years (this does not include rain which fell as snow). The pH of the natural rainfall varied between 3.7 and 5.1, with an average pH of 4.4. The summer of 1987 was the coldest summer in Finland within the last 15 years (Fig. 1).

Results

The simulated acid rain treatments had no significant effects on the growth of the seedlings. All inoculated seedlings contracted an *A. abietina* infection. Uninoculated seedlings were not infected, which proved all infection to be artificial. The average length of the dead part of the shoot (Table 1) differed between seedlings from different pH groups. The length was significantly shorter when whole plant had been treated with artificial rain plus ambient rain at pH of 5.6 and 4.0. Differences were not found at pH level of 4.5 and 3.0.

No significant differences were found between the mean light response curves of assimilation and transpiration measurements but results were more variable at pH level of 3.0 than 5.6 (Figs. 2 and 3), with transpiration data showing most variation. The dark respiration, on the other hand, varied more at pH level of 5.6 (sd = 1.05) than at pH level of 3.0 (sd = 0.58).

Discussion

Occurrence of *A. abietina* on Scots pine varies from year to year, primarily due to climatic conditions (Donaubauer 1972). Most of the time the host is resistant, and

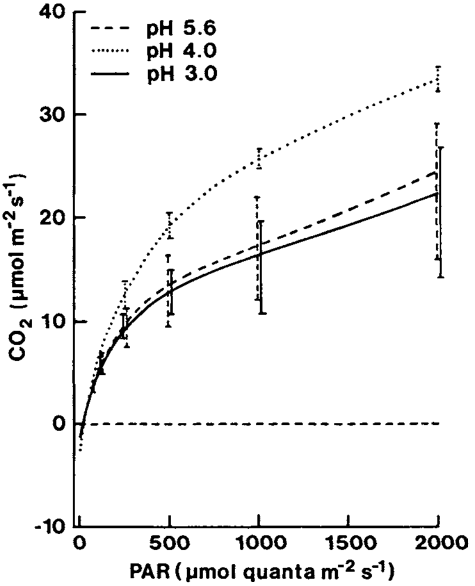

Fig. 2. Mean rate and variation of assimilation versus radiation. The numbers of measured seedlings were: n = 6 at pH 5.6 and at pH 3 and n = 2 at pH 4

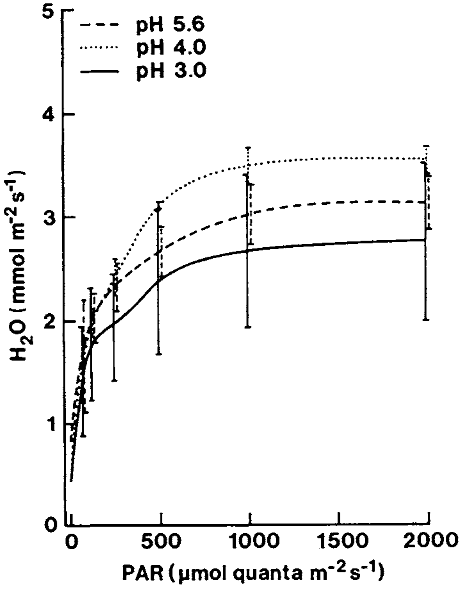

Fig. 3. Mean rate and variation of transpiration versus radiation are measured from the same shoots as assimilation in Fig. 2

the pathogen survives in damaged trees. Serious epidemics may break out during cold vegetative periods, when the resistance of the host may be reduced or fail to develop (Kurkela 1984). The vegetative period in 1987 was cold (Fig. 1) and rainy, and probably for this reason pine seedlings were susceptible to *A. abietina* infection.

Table 1. Mean and standard deviation (SD) of the length of the dead part of shoots

	Acidity (pH) of simulated rain				
	5.6 control	4.5	4.0	3.0	Mean
Ambient rain + artificial rain					
Artificial rain applied to whole plant	124.7	100.5	128.5	131.0	121.2
Artificial rain applied to soil	147.9	130.8	153.3	124.1	139.0
Mean	136.3	115.6	140.9	127.5	
Only artificial rain					
Artificial rain applied to whole plant	47.2	103.1	51.7	131.5	83.4
Artificial rain applied to soil	101.4	74.9	65.3	102.3	85.9
Mean	74.3	89.0	58.5	116.9	
Overall mean	107.4				
Overall SD	57.6				
LSD ($p = 0.05$) = 99.4					

If only the buds of pine seedlings are inoculated, usually the shoots show dieback starting in the top. Sometimes the fungus kills only the buds while the shoots remain alive. In this study, artificial inoculation was done by spraying conidiospores of fungus onto the tops of the seedlings. It was possible that the fungus infected only either the bud or the shoot. There were some differences between treatment groups in the length of the dead shoots. The ambient rainfall probably neutralized to an appreciable extent the effects of the simulated acid rainfall at pH 4.0, but was not enough at pH 3.0. Perhaps the effects of acid rain did reduce the natural resistance of pine to *A. abietina*. It is also possible that the extra volume of ambient rainfall washed away the conodiospores before they had a chance to infect the shoots.

The measurements of photosynthetic capacity is used in air pollution studies because it is a sensitive indicator of injuries to trees. In this study, there was no increase either in growth or in the photosynthesis of pine seedlings, in contrast to the findings of Seiler et al. (1987), who observed an increase in photosynthesis of red spruce after adding acid rain of pH 3.0. This increase may, however, have resulted from the addition of NO_3- to a system deficient in N. In this experiment N was not the limiting factor. These results suggest that simulated acid rain caused no obvious injuries in the photosynthetic system of pine seedlings.

Transpiration is affected by the water uptake and movement from roots to needles or by the function of stomata. The large variation between the individual seedlings at pH level 3.0 indicates that there were some injuries to the transpiration system in some individual seedlings. Because the treatments were continued, it was not possible to study roots separately, which may have become injured by the increasing acidity.

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Ecological Effects of Simulated Acid Rain in a Subarctic Area with Low Ambient Sulphur Deposition

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Summary

We review the results of the first 3 years of an experiment aimed at studying the effects on the resistance of trees against insects and on litter decomposition in a subarctic area with low ambient pollution level. The experimental set-up followed randomized blocks design with 20 replicate plots (5 × 5 m) of four different treatments. The treatments included dry controls, irrigated controls and two acid rain treatments (pH 4 and pH 3; both with H_2SO_4 and HNO_3). The mass loss of pine and birch litter was significantly lower on acid-treated than on irrigated control plots, especially on drier vegetation types. The quality of foliage for some insect species was enhanced by the acid rain treatments but most of the species tested did not show a significant response. Acid rain treatment affected the interaction between *Neodiprion sertifer* and its viral disease: the proportion of larvae surviving 16 days after virus application was significantly higher than on control foliage when the larvae were fed with needles from acid (pH 3)-treated trees.

Introduction

In spite of large research efforts, the effects of "acid rain" on different components of the ecosystem are poorly known. Changes in plants or in ecological processes have often been reported for sites close to sulphuric emission sources or in combination with rather drastic experimental acidification. The interpretation of the first type of studies is complicated by the possibility that the changes may be explained by the effects of pollutants other than sulphuric emissions or even by factors not related to pollution (cf. Leith and Fowler 1987; Westman 1981). Controlled and well-replicated field experiments are thus necessary for revealing causal links between supposed pollutants and ecological processes. Furthermore, it is important that the experiments last several years, because changes associated with acid rain are often slow and their direction may even change in different phases of acidification (Abrahamsen 1984).

In many experiments on the effects of acid rain in forest ecosystems, extremely heavy loads of sulphuric acid compared with the acidity of natural rain have been

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applied. These heavy loads may cause artefacts that bear little relevance to field situations with acid rain. Furthermore, the effects of nitrogen in acid rain have received less attention than those of sulphur, and most studies have been done in temperate areas where background levels of acidification are quite high. Consequently, it is not certain whether the control plots used are very realistic.

Effects of specific treatments to a tree or an insect pest are commonly studied by excluding their interactions with biotic environment (pests, diseases). Results of such studies cannot be directly extrapolated to a field situation where interactions between the treatments and the biotic environment of target organisms produce results which may differ from those with biotic interactions excluded (MacLeod 1988). One possibility to avoid problems of this type is to include biotic interactions of target organism(s) explicitly in the experimental set-up.

This chapter reviews the first results from a long-term study with the aim of investigating the effects of artificial acid rain (with acid loads close to those observed in nature, and including both H_2SO_4 and HNO_3) in a subarctic area with low ambient pollutant loads but with otherwise harsh environmental conditions. Also the effects of irrigation per se and of vegetation type have been considered. This paper concentrates on the effects of simulated acid rain on interactions between trees (Scots pine and mountain birch) and their insect herbivores (cf. Alstad et al. 1982; Morrison 1984; Führer 1985), on ground layer arthropods and on litter decomposition, while some other effects are reported elsewhere (Helander and Rantio-Lehtimäki 1989; Lodenius and Malm this Vol.).

Materials and Methods

Study Area

The study was conducted near the Kevo Subarctic Research Station (69° 45′ N, 27° 00′ E), in northern Finland. Kevo is situated about 60 km north of the continuous Scots pine forests, but in the river valleys around Kevo there is one of the northernmost pine stands in the world. The mean annual temperature is −2.0°C and the mean annual precipitation is about 390 mm (30–40% falling as snow). Minimum winter temperatures fall often below −40°C. Monthly precipitation and mean temperatures during the study period are shown in Fig. 1, together with long-term averages.

The study area is a mixed pine–mountain birch woodland, situated close to the river Kevojoki, about 1 km SW from the Kevo Subarctic Research Station. In 1985, 80 study plots of about 5 × 5 m (each having at least one pine and one birch bush) were selected from an area of about 3 ha. The height of the pines varied from 2.5 to 5.5 m and that of the mountain birches from 1.5 to 6 m.

Treatments

To guarantee a good interspersion of treatment replicates (Hurlbert 1984) the study area was divided into 20 blocks (designated subsequently as BS) of four plots

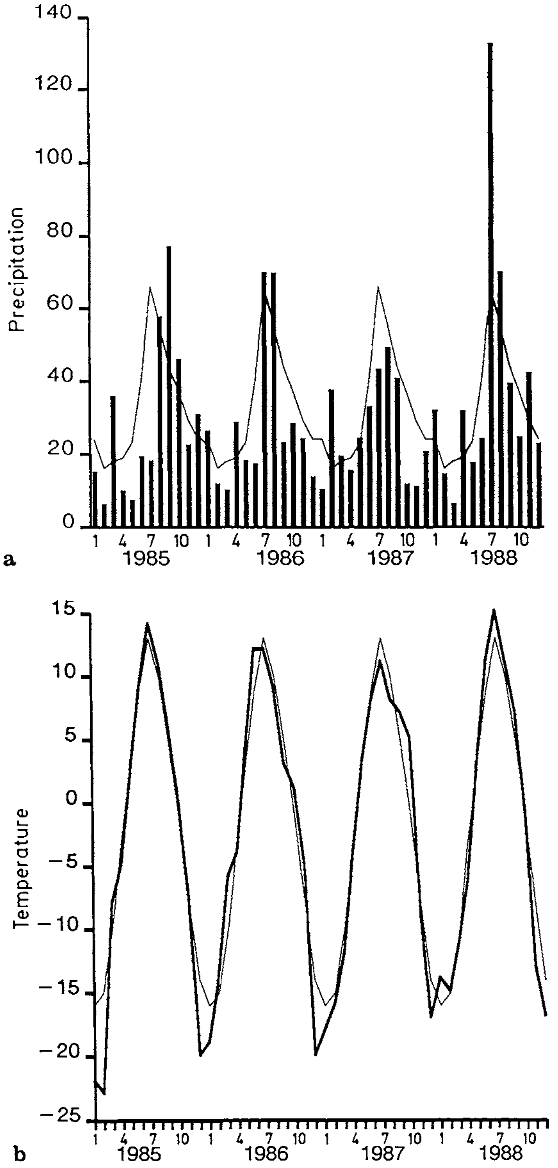

Fig. 1a,b. Monthly precipitation and mean temperatures at Kevo Meteorological Station during the study period (1985–1988). Long term averages are also shown (*thin lines*)

(Fig. 2), and within each block each plot was given randomly one of four treatments: dry controls (DC) with no additional irrigation; irrigated controls (IC), which were treated with spring water of pH 6; pH 4 treatment (A4); and pH 3 treatment (A3).

The water for the A4 and A3 treatments was prepared by adding both sulphuric acid and nitric acid [with a sulphate ($SO_4^=$) to nitrate (NO_3^-) ratio of 1.9:1 on a mass basis] to the control water. The pH of the water was checked at each treatment, and the amounts of acids added were adjusted when necessary.

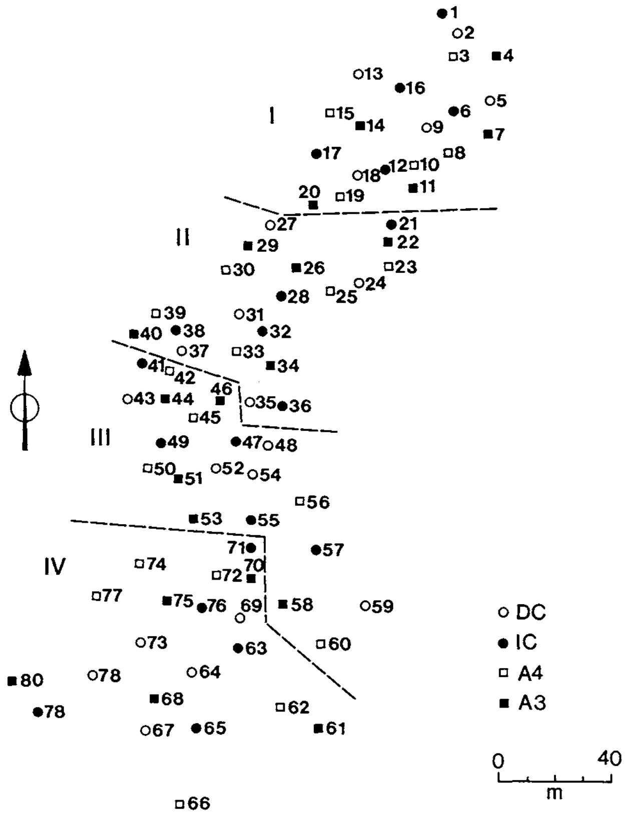

Fig. 2. Experimental design of the acidification experiment at Kevo in northern Finland. The four different treatments were randomly allocated within blocks of four plots (1–4, 5–8, etc). The irrigation was applied simultaneously to all treatments within the four subareas (*dashed lines*). *DC* plots receiving only ambient rain; *IC* plots irrigated with spring water (pH 6); A4 plots irrigated with simulated acid rain of pH 4; A3 plots irrigated with simulated acid rain of pH 3. See text for details

Treatments IC, A4 and A3 received similar amounts of artificial rain, applied with sprinklers over the canopy, three times (about 5 mm per occasion) per week during the periods shown in Table 1. Limitations of the sprinkling system did not allow a simultaneous application of treatments on all plots. The plots were divided into four subareas [plots 1–20 (I), 21–40 (II), 41–60 (III) and 61–80 (IV); named subsequently SA; see Fig. 2] within which the treatments were applied at the same time.

The amounts of sulphur and nitrogen applied during the first 4 years are shown in Table 1.

The ambient levels of sulphur and nitrogen deposition at Kevo Station in 1985 to 1987 were as follows: 152 mg (m^2 year)$^{-1}$ SO_4–S, 32 mg (m^2 year)$^{-1}$ NH_4–N, and 40 mg (m^2 year)$^{-1}$ NO_3–N (compiled from Anonymous 1985–1988). Our A4 treatment thus added about 300% to the annual sulphur load and about 200% to

Table 1. Amounts of sulphur (S) and nitrogen (N) added by spring water irrigation (IC) and simulated acid rain treatments (A4 and A3) in 1985–1988

	Amounts of S and N added by treatments					
	S mg m^{-2}			N mg m^{-2}		
	IC	A4	A3	IC	A4	A3
A[a]						
21 Aug–12 Sept-85	25	155	505	5	50	175
17 June–12 Sept–86	120	490	2400	20	150	820
19 June–28 Aug–87	100	450	2300	15	135	785
16 June–2 Sept–88	115	495	2635	20	155	900
B[b]						
After–85	25	155	505	5	50	175
After–86	145	645	2905	25	200	995
After–87	245	1095	5205	40	335	1780
After–88	360	1590	7840	60	490	2680

[a] Irrigation periods and amounts of sulphur and nitrogen added during different field seasons. [b]Cumulative amounts of sulphur and nitrogen added after each field season.

the annual nitrogen load (the sulphur deposition on IC plots was about 70% higher than on DC plots and the nitrogen deposition about 25% higher). The A3 treatment was about 15-fold to the ambient sulphur load and about 11-fold to the ambient nitrogen load, but was still within the range of deposition over wide areas in Europe (Kulmala 1985).

Vegetation

The study area ranged from open, dry plots with a mosaic of dwarf shrubs and lichens to more mesic ones covered by mosses and dwarf shrubs. The plots were divided on the basis of their vegetation into three classes which were used in analysing the data. This classification was a crude one, but a more detailed classification would not have yielded all combinations of treatments and vegetation types necessary for a two-way analysis of variance.

The vegetation type classes were as follows: (D) the driest plots with *Empetrum hermaphroditum* and *Vaccinium vitis-idea* dominating under the trees, lichens were abundant on open areas between trees (also *Arctostaphylos uva-ursi* or *Polytrichum* spp. were abundant on some plots); (M) a medium type with respect to the moisture conditions, with less lichens and more grasses (*Calamagrostis lapponica*, *Festuca ovina*) than on the previous type; *E. hermaphroditum* and *V. vitis-idaea* dominating (*Vaccinium uliginosum* and *Ledum palustre* may also occur); (W) the moistest vegetation types, with *Pleurozium* dominating in the ground layer; *V. vitis-idaea* and *E. hermaphroditum* dominated in the field layer, sometimes together with *V. uliginosum* and *L. palustre*.

Measurement of Responses

Our aim has been to study the effects of simulated acid rain on the quality of foliage for herbivorous insects and on the rate of mass loss of leaf or needle litter. It is possible to measure the responses either by following changes in the concentrations of some chemical constituents or by using bioassays to reveal changes in the relevant parameters. We have chosen the latter alternative, since it is often difficult or impossible to conclude how relevant a specific chemical change is for the process we are interested in. Accordingly, in our terminology good foliage quality means that an insect species has high growth and/or reproduction rates on that foliage.

It is probable that different insect species do not respond similarly to the chemical and/or physical changes in foliage quality caused by simulated acid rain. Thus we have used several insect species in bioassays to obtain a picture of the variation in responses among different insect groups. The specific names of experimental animals are shown in Table 2.

The details of experimental procedures used in bioassays are explained elsewhere (Neuvonen and Lindgren 1987; Neuvonen et al. 1990, MS), but in general we have used two basically different methods: (1) rearing insects in the laboratory on leaves/needles detached from the experimental trees; (2) rearing insects in mesh bags on the experimental trees.

Chewing insects have been reared on detached leaf/needle material because rearing in mesh bags may induce changes in foliage quality (Haukioja and Neuvonen 1985, 1988; Neuvonen and Haukioja 1985), which complicates the interpretation of results in a multiyear study. The duration of bioassays with detached leaves or needles varied from 24 h to the complete larval period. In short bioassays the amount of foliage needed is low and the same experimental trees can be used for several years. The disadvantage of short-term bioassays is that they measure the quality of foliage only at a specific time of the season, which does not have to be representative for foliage quality during the complete larval period. Bioassays covering the whole larval period are problematic due to the large amounts of foliage consumed. Thus only a limited number of long-term bioassays can be done if the experiment lasts several years.

Table 2. Insect species used in bioassaying the effects of simulated acid rain on foliage quality

	On *Pinus sylvestris*	On *Betula pubescens* ssp. *tortuosa*
Chewing insects:		
Lepidoptera:	*Panolis flammea*	*Epirrita autumnata* *Erannis defoliaria*
Hym., Symphyta:	*Neodiprion sertifer* *Diprion pini*	*Dineura virididorsata* *Arge fuscinervis*
Sucking insects (aphids):	*Schizolachnus pineti* *Cinara pinea*	*Euceraphis punctipennis* *Betulaphis quadrituberculata*

Performance of chewing insects (lepidopterans and sawflies) was measured as the relative growth rate of larvae, final (pupal or prepupal) weight and length of the larval period (with long larval periods indicating low foliage quality). The relative growth rates were calculated as $RGR = \ln(W_f/W_i)/T$ (T = duration of bioassay in days; W_f and W_i are the final and initial weight of the larva, respectively). Since RGR is often negatively correlated with W_i, we removed the variation due to the heterogeneity in initial size by using W_i as a covariate.

Aphids were kept in mesh bags (starting with one to four aphids of a specific developmental stage per bag) on the experimental trees. The duration of the bioassay varied from 2 to 4 weeks. Performance of the aphids was measured as the number of progeny produced per aphid.

In laboratory bioassays, two to five replicates were started with foliage of each tree, in field (mesh bag) bioassays there were one or two replicates per tree. The insects used in the bioassays were allocated randomly to the experimental trees, in laboratory bioassays also the position of larvae in rearing trays was randomized with respect to the treatments.

Statistical Analyses

The effects of treatments were generally assessed by analysis of variance (SAS Institute 1985). When there was more than one measurement from each experimental plot, either plot-specific means were used in the analyses, or the variation among replicate plots was used as the error term in statistical analyses (see Hurlbert 1984; Neuvonen and Haukioja 1985). With some insect species we used bioassays to measure the quality of host foliage in 1985 (before the treatments were begun), and this value was used as a covariate when analysing data from subsequent bioassays.

In some analyses the effects of the vegetation types were included. Also the two levels of blocking in the experimental design (see Fig. 2) were accounted for: the division of the study area to four subareas within which the treatments were applied simultaneously (blocking factor SA), and the groups of four plots within which the random allocation to treatments was done (blocking factor BS). The treatment effects were further decomposed to orthogonal (i.e. statistically independent) contrasts (see Sokal and Rohlf 1981).

The Effects of Simulated Acid Rain on Herbivorous Insects

Leaf and Needle Chewers

During the three experimental years there were no consistent differences in the foliage quality for chewing insects between control trees and trees receiving acid treatment (Figs. 3 and 4). In spite of significant treatment effects in some bioassays, the magnitude of the differences among treatments was generally modest (less than

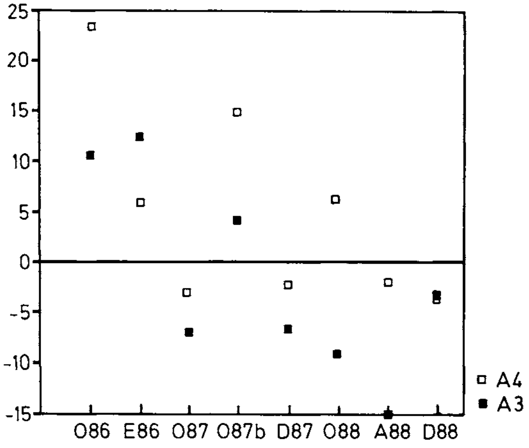

Fig. 3. The performance of moth and sawfly larvae on the foliage of birches treated with simulated acid rain in relation to that on control birches (average of DC and IC trees). Y-axis shows the % difference in the growth rate or final weight of larvae between acid treated and control trees. The code along the horizontal axis shows the insect species (O = *Epirrita autumnata*; E = *Erannis defoliaria*; A = *Arge fuscinervis*; D = *Dineura virididorsata*) and the experimental year

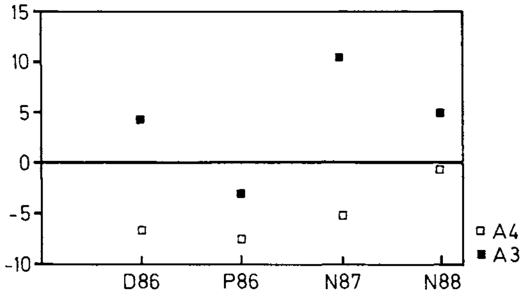

Fig. 4. The performance of moth and sawfly larvae on the foliage of pines treated with simulated acid rain in relation to that on control pines (average of DC and IC trees). Insect species: N = *Neodiprion sertifer*; P = *Panolis flammea*; D = *Diprion pini*. Other explanations as in Fig. 3

25%), and smaller, for example, than the delayed effects of partial defoliation on birch-feeding herbivores (see Haukioja and Neuvonen 1988; Neuvonen and Haukioja 1990). However, experiments of this type do not exclude the possibility that acid irrigation may affect foliage quality in a way that is important for the population dynamics of leaf-chewing herbivores.

Our bioassays with leaf-chewing insects did not consider survival and/or growth of young larvae, which may be the developmental stage most susceptible to changes in foliage quality (White 1984). Experiments made in 1987 suggested different effects on larvae of different age: IV-instar *Epirrita autumnata* larvae grew significantly faster on pH 4-treated foliage than on control trees, while growth of V-instar larvae showed no significant differences (Neuvonen et al. MS). It was not clear whether the variation in results was due to the difference in experimental conditions or due to a real difference in the responses of larvae at IV- vs. V-instars. An additional factorial experiment on the interactions between larval instar and acid treatments in 1988 confirmed the differential response of IV- and V-instar larvae to the treatments. In this case, however, the difference was mainly due to the relatively poorer performance of IV-instar larvae on pH 3-treated foliage (Neuvonen et al. MS).

Two series of experiments were designed to reveal the effects of simulated acid rain on the interactions between different trophic levels. The first deals with the damage-induced decrease in the quality of birch foliage, and the second with the interaction between the European pine sawfly and its virus disease.

Damage-induced changes in foliage quality may be important for the population dynamics of forest insects, since they may act as density-dependent feedbacks (with or without time lags) and may thus regulate insect population densities (Haukioja 1980; Berryman et al. 1987). Especially the delayed damage-induced increase in the resistance of host tree foliage (i.e. the lower quality of leaves in the year(s) following partial defoliation) seems to play an important role in the population dynamics of the autumnal moth, *Epirrita autumnata* (Haukioja 1980; Haukioja et al. 1988), and also of some other forest defoliators (like *Zeiraphera diniana* on larch in the Alps; Benz 1974). This delayed induced resistance introduces a time-lag to the negative feedbacks regulating the population dynamics of insects and is one of the factors generating cyclic density fluctuations in *E. autumnata.* It is also possible that environmental changes (e.g. acidification) alter the intensity and relaxation times of delayed induced resistance, and consequently, have important consequences for the population dynamics of cyclic insect pests (Neuvonen 1990).

We have started an experiment studying the interactive effects of the acid rain treatments and partial defoliation of mountain birch foliage on the expression of delayed induced resistance against *E. autumnata.* In this experiment we used additional birches in the experimental plots (11 replicates per treatment in this study). In 1987 we partially defoliated (about 25% of leaf area removed in early season) five to six randomly chosen birches from each of the acid rain treatments (including controls). In the following summer we reared *E. autumnata* larvae in mesh bags through the whole larval period both on defoliated and undefoliated trees. Defoliation had a significant ($p<0.01$) negative main effect on the pupal weights of *E. autumnata.* Moreover, the results suggested an interaction betwen defoliation and acid rain treatments ($p<0.10$): the negative effects of defoliation on the quality of birch foliage in the subsequent year were stronger with acid-treated than with control birches (Neuvonen et al. MS). Further experiments are necessary to reveal whether this kind of interaction affects the frequency or amplitude of cyclic fluctuations in the density of *E. autumnata.*

The effects of simulated acid rain on the susceptibility of the European pine sawfly (*Neodiprion sertifer*) to its nuclear polyhedrosis virus were studied in a bioassay having a factorial design with virus treatments (four levels), treatments of the host trees (four levels), and spraying detached needles with pure or acidified water (three levels: pH 6, pH 4, and pH 3). For this experiment we used ten blocks of the acid rain study area (i.e. ten replicates for each host tree treatment) and 480 groups of ten *N. sertifer* larvae in 1987, i.e. 2 years after the start of the acid rain treatments (details are published elsewhere: Neuvonen et al. 1990). As the two strongest dilutions of the virus treatment caused a rapid and almost total mortality of *N. sertifer* larvae, we discuss only the results of the most diluted virus treatment.

Of the virus-treated larvae 31% were alive 16 days after the virus application when fed with needles from pH 3-treated trees, while only 10–15% of the larvae reared on the needles from control or pH 4-treated trees were alive at this stage. This difference was significant, but there were no significant effects due to the spraying of needles (Neuvonen et al. 1990). Six weeks after the virus application, the disease had killed almost all larvae in the larval groups which had been treated with virus, and there was no longer any significant difference in mortality between larvae fed with needles from pH 3-treated trees and from trees of other treatments. However, our results showed that the interaction between *N. sertifer* larvae and the nucleopolyhedrosis virus depended on the quality of the host foliage and, furthermore, that simulated acid rain may delay the mortality of *Neodiprion* larvae with the viral disease.

This study did not answer the question of what was the mechanism of the reduced susceptibility to viral disease on the pH 3-treated foliage. We are continuing experiments based on the following hypotheses: (1) the larvae fed with foliage from pH 3-treated trees have a better nutritional condition (the acid rain contained also HNO_3) and the development of the disease was retarded for that reason (cf. Bauer and Nordin 1988); (2) the acid rain treatment changed the pH of pine needles and this affected the progress of disease (Keating et al. 1988).

In addition to the questions addressed above, the anthropogenic environmental changes raise several other questions which are important for the population dynamics of forest pests. For example: How does acid deposition affect the long-term persistence of viruses (cf. Anderson and May 1980; Mohamed et al. 1982; Olofsson 1988) in the ecosystem? What effects do changing climatic conditions ("greenhouse effect"; possible changes in the intensity of UV-radiation; see e.g. Ignoffo et al. 1977) have on the interactions between insects and their diseases?

Aphids

In the bioassays with aphids, mainly additional trees growing on the study plots (not the actual study trees used in other experiments) and also seedlings grown in plastic pots on the study plots were used. In many bioassays the performance of aphids was higher on dry control trees than on irrigated controls. Drought stress may predispose trees to aphid attack (e.g. White 1984; Mattson and Haack 1987). Therefore we compare the acid treatments to irrigated controls (IC).

Although the reproduction of birch-feeding aphids was 18–44% higher on pH 3-treated trees than on IC trees, there were only few significant treatment effects. This was mainly due to high variation in the quality of trees within the treatment and to the small number of replicates (we used only the additional trees) resulting in a low power of tests. In general, our results with birch-feeding aphids show that their performance on pH 3-treated trees was consistently higher than on IC trees, but the same was not true with pH 4-treated trees (Lindgren et al. MS).

Our previous experiments in southern Finland showed that simulated acid rain of pH 3.5 (only H_2SO_4) enhanced the performance of *Euceraphis betulae*, especially during periods which were drier than average (Neuvonen and Lindgren 1987).

Four of the bioassays with pine-feeding aphids were made with large trees, and in three of them the reproduction of aphids was higher on acid-treated (pH 3 and/or pH 4) than on irrigated control pines. In both experiments with pine seedlings the performance of aphids was higher on pH 4 and pH 3 treatments than on IC (Lindgren et al. MS)

The Effects of Simulated Acid Rain on Arthropods Living on the Ground Layer

Small insects and spiders living in and on the ground layer may play important roles as predators of other invertebrates in the ecosystem and also as food for insectivorous birds and mammals. Acidification may affect either the abundance or behaviour of arthropods living on the ground layer. We tested whether simulated acid rain affected the numbers of arthropods caught from the experimental plots. We used pitfall traps (one trap/plot) during three summers (1985–87), and the catch can be considered as a combined index of abundance and activity. In statistical analyses we used the combined numbers in certain taxonomic groups (see Table 3) since the analyses at species or genus level were not reasonable due to very low numbers of individuals.

The data were analysed with a two-way analysis of variance (after appropriate transformations), having the treatments and vegetation types as main effects. Analyses were run separately for each year and arthropod group. The main effect of acid treatments or the treatment × vegetation-type interaction was not significant in any of the analyses. There seemed to be higher numbers of Staphylinidae on irrigated plots (IC, A4 and A3) than on dry control plots. It is probable that many

Table 3. The mean number of animals in eight groups of ground layer arthropods caught by pitfall traps on experimental plots (20 replicates/treatment) during summer 1987 (3 months)

Treatment	Carabidae		Staphylin.		Other Col.		Col. larvae	
	x	SE	x	SE	x	SE	x	SE
DC	2.3	0.6	4.7	0.9	2.1	0.4	1.1	0.3
IC	2.9	0.6	7.8	1.3	1.4	0.3	1.3	0.3
A4	2.4	0.6	10.1	1.7	1.9	0.6	1.6	0.3
A3	2.7	0.6	7.7	1.0	1.7	0.4	1.8	0.4

Treatment	Formicinae		Lycosidae		Linyphiidae		Other spiders	
	x	SE	x	SE	x	SE	x	SE
DC	20.7	8.8	8.5	1.9	9.5	1.1	2.6	0.5
IC	29.9	13.5	5.1	1.1	7.5	0.8	1.9	0.4
A4	37.8	23.2	6.6	1.3	11.0	2.1	2.5	0.5
A3	18.9	6.3	7.4	1.9	10.1	2.1	3.3	0.5

of the arthropod groups in our study (e.g. Carabidae, Formicinae, Lycosidae) are so mobile that the range of individual movements spans several experimental plots which are small ($<100\ m^2$). Thus it is not likely that our treatments could have measurable effects on the population dynamics of these animals, but this does not exclude the possibility of behavioral responses to localized environmental changes (e.g. pH of the substrate, changes in vegetation structure).

The Effects of Simulated Acid Rain on the Decomposition of Pine and Birch Litter

Three kinds of experiments were done with pine needle litter and birch leaf litter. The first type (A) was done with mixed pine needle litter which had decomposed on the ground over winter, the second (B) with brown leaves/needles collected from trees on study plots, and the third type (C) with brown litter collected from trees on study plots. In this last experiment the samples were exchanged among plots to separate changes in litter decomposition caused by differences in litter quality (as modified by simulated acid rain) from those caused by changes in the decomposition processes in soil. The litter incubations had the following time schedule (S = start; R = retrieval of samples):

		June 1985	Sept 1985	Sept 1986	Aug 1987	July 1988
Exp A.	Pine	S-------	----------	R-------	R----------	
	Birch	S-------	R-------	R-------	R-------	R
Exp B.	Pine		S-------	R-------	R	
	Birch		S-------	R-------	R	
Exp C.	Birch			S-------	R-------	R

Experiment A. Scots pine needle litter and mountain birch leaf litter was collected in June 1985 from the ground (1 km from the study site), thoroughly mixed, and air dried at room temperature. Samples of approximately 2 g (pine) or 0.5 g (birch) were placed into 1-mm mesh Terylene net bags. The litter bags were fixed on the forest floor by metal pins in late June 1985. The bags with pine needle litter were put on open areas between trees, and those with birch leaf litter below birch canopies. In some cases with birch litter, dwarf shrubs had to be removed before placing the litter bags. Sampling of pine needle litter was made after 442, 775 and 1135 days, and that of birch litter after 92, 444, 777 and 1135 days. Notice that the experimental treatments did not begin until 21 August 1985 (2 months after the beginning of the incubation). The litter bags were transported to the laboratory and carefully cleaned of mosses and dwarf shrubs that had grown through the bags. The dry weight of remaining litter was determined after 2 days in +80°C.

Experiment B. Attached dead (brown) pine needles or yellow birch leaves (which were about to be shed) were collected from the trees on the experimental plots in September 1985. Note that the acid rain treatments had been started about

1 month before the collection of litter. The litter incubated on each plot originated from the trees of the same plot. The incubation was started in late September 1985 by placing two mesh bags with pine litter and two with birch litter on experimental plots. The first samples from each plot were retrieved in September 1986 (after 348 days incubation) and the second samples in August 1987 (after 680 days).

Experiment C. Yellow birch leaves were collected as in experiment B, but in August 1986, when the trees had been treated for about one growing season. The litter was incubated in the same plot from which it was collected, but in addition litter collected from IC plots was incubated on the plots receiving other treatments [but belonging to the same block (BS)]. Litter collected from DC, A4 and A3 plots was also incubated on the IC plot of the same block. This experimental set-up allowed us to separate possible differences caused by changes in the litter quality (= the effect of litter origin) from those in decomposition processes in the soil (= the effect of incubation site). The data were analysed by two-way analyses of variance (separately with each combination: IC/DC, IC/A4, IC/A3), having the treatment of litter origin and the treatment of incubation site as main effects.

In experiments A and B the comparison of different treatments was done with a decomposition to orthogonal contrasts as follows: the dry controls were compared to other treatments (IC, A4 and A3), the irrigated controls were compared to acid treatments (A4 and A3) and finally, the two levels of acid treatment (A4 vs. A3) were compared. This is not the only way of testing orthogonal contrasts with these four treatment levels, but it was selected due to the probable importance of moisture conditions for decomposition (see Meentemeyer 1978).

Our results give direct experimental evidence on the role of precipitation in regulating the mass loss of pine needle litter at Kevo. The mass loss was significantly higher on plots supplied with artificial irrigation than on control plots receiving only ambient rain in two experiments. The effects of acid rain treatments on pine litter decomposition were more subtle than those of irrigation per se. On the moistest vegetation type (W) there was no decrease in decomposition rates due to acid treatments (Fig. 5). However, 2 years after needle fall the decomposition rates were significantly reduced by acid treatments on the drier plots (Fig. 5). In experiment A the weight loss rates on the driest vegetation type were 7 to 14% lower on our A3 treatment than on IC plots. In experiment B the respective values were 3 to 5% lower than on IC.

In experiment B with birch litter the treatments differed significantly after 1 year of incubation. This was due to smaller mass loss in dry controls than in the other treatments. After 2 years the total mass loss was smallest in dry controls, but was smaller also in acid treatments compared to the irrigated controls. The mass loss during the second year of incubation differed significantly among treatments, because of differences between irrigated controls and acid treatments (Fig. 5; Neuvonen and Suomela 1990). After 2 years of incubation mass loss on A4 and A3 plots was 3 and 2% units smaller, respectively, than on the irrigated control plots. Experiment A with birch litter showed also a tendency of reduced mass loss on

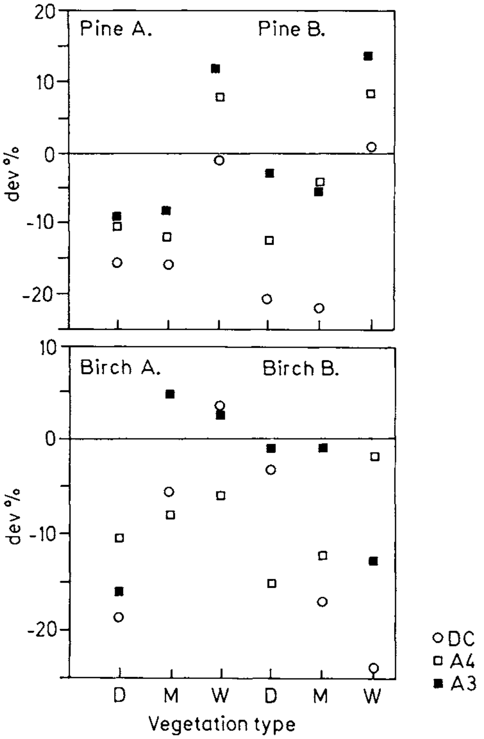

Fig. 5. The difference in mass loss of pine needle and birch leaf litter on plots treated with simulated acid rain in relation to that on irrigated control plots. The plots are divided into groups on the basis of their vegetation type (*D* dry; *M* medium; *W* wet). Y-axis shows the % difference in the mass loss at the end of each experiment when compared to the mass loss on IC plots

acid-treated plots compared to IC plots after 3 years (49–50% vs. 54%), although the difference was not significant (Neuvonen and Suomela 1990).

The third experiment (C) with birch litter revealed that the reduction in decomposition due to acid treatments was caused by changes in the incubation sites and not by changes in litter quality (Neuvonen and Suomela 1990). After the second year of incubation the mass loss on A3 plots was significantly lower than on IC plots, but there were no significant differences in the mass loss of litter collected from A3 vs. IC plots. The effects of A4 treatment on decomposition were not significant in this experiment.

Further studies are necessary to reveal the mechanisms of reduced decomposition rates due to acid treatments. Studies on soil microbiology in the experimental plots suggest that a reduction in the amounts of bacteria in different physiological groups (e.g. those utilizing cellulose, starch, pectin, xylan and protein; Kytöviita et al. 1990) may be at least a partial explanation.

Earlier studies on the effects of acid rain or sulphur deposition on the decomposition of litter yielded variable results. Reduced rates of litter decomposition have been reported close to sulphuric emission sources (Killham and Wainwright 1981, Prescott and Parkinson 1985). The interpretation is complicated by the possibility that the change in decomposition rate may be explained by the effects of other than sulphuric emissions (e.g. heavy metals).

In experiments, both negative and positive effects of simulated acid rain on litter decomposition have been found. There seem to be more reports of negative effects, but it is difficult to reach final conclusion as many of these studies (e.g. Bååth et al. 1980, Berg 1986) applied extremely heavy loads of sulphuric acid compared with the acidity of natural rain (1.6–9.6 g $S\,m^{-2}$ in one to three applications). It is not surprising that field experiments with high loads of H_2SO_4 have resulted in significant reductions in decomposition rate. Furthermore, the effects of nitrogen in acid rain have received less attention than those of sulphur, and most studies have been done in temperate areas where background levels of acidification (i.e. those on "control" plots) are quite high.

Our experiments indicate that at least in some environments even small additions in acid deposition may retard the decomposition rate of both coniferous (pine) needle and deciduous (birch) leaf litter. A differentiation between the impacts of sulphuric and nitric acids cannot be made in our experiments, but according to the literature, especially the effects of nitrogen on decomposition rate are controversial (Fog 1988).

Concluding Remarks

It is obvious that the effects of mild "acid rain" in nature are often subtle and have a long lag phase. Consequently, it is not surprising that the results discussed here (concerning only the first 3 years of the experiment) show only few statistically significant effects of acid treatment. However, in spite of the high level of natural variation among the plots, we found some interesting and statistically significant acid treatment effects. Furthermore, other research groups have used this experiment in their studies and found significant negative effects of acid irrigation on, e.g. epiphytic microflora on birch leaves and on pine needles, on mycorrhizas, and on soil bacteria. These results are reported elsewhere (Helander and Rantio-Lehtimäki 1990; Ranta MS; Kytöviita et al. 1990).

The results obtained until now make continuation of the experiment worthwhile. Some modifications in the experimental system will be made, starting from summer 1989. The most important modification concerns the composition of the simulated "acid rain". From 1985 to 1988 we used a mixture of both sulphuric and nitric acids. In the future we shall divide the experiment in three parts: in half of the plots (ten replicates/pH level) the experiment will be continued unchanged; in five replicates/pH-level only sulphuric acid, and in five plots/pH-level only nitric acid will be applied.

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Influence of Acidification on Metal Uptake in Plants

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Summary

An experiment using artificial acidification has been carried out under subarctic conditions in northern Finland. Vegetation samples from plots treated with simulated acid rain (pH 4 and pH 3) were analysed for their contents of aluminium, cadmium, manganese, mercury and zinc and compared with wet and dry control plots. No or only small differences in metal contents were detected between the plots. The acidification experiment is going to be continued and the contents of metals should be followed up for a longer period of time.

Introduction

The uptake of metals from the soil into plants is influenced by several soil quality factors including soil type, pH, organic matter and ion exchange capacity. A decrease in soil pH increases the solubility of most metals. Some metals in soil solution may be phytotoxic even in small concentrations (Godbold and Hüttermann 1985). However, the amounts of microelements – like mercury and cadmium – in solution are very small and difficult to measure. It is not known in detail how the transfer of metals from soil to vascular plants is affected by acidification.

Acid atmospheric deposition has been assumed to increase the solubility of several metals and also increase the uptake of these elements into plants. Simulated acidification has resulted in significantly increased concentrations and fluxes of Mg, Ca, Mn, Zn and Cd in soil (Bergkvist 1986). Also an increased amount of precipitation may affect the solubility. The soluble metals may either leach to deeper soil layers or to the ground or surface water or move into vascular plants through the roots. Mayer and Schulz (1987) found that acidification resulted in increased fluxes through both these routes. The most mobile metals in this respect were Mn, Zn, Cd and Co. Consequently, mobilization of metals in the soil does not necessarily result in increased metal concentrations of the vegetation. Acidification of the soil may even cause a decrease in metal content of vascular plants as has been shown for manganese, calcium and magnesium near a pollution source in northern Norway (Løbersli and Steinnes 1988).

Kauppi et al. (Eds).
Acidification in Finland

Carlson and Ragsdale (1988) treated soils with and without seedlings of *Pinus strobus* with artificial acid rain. They found significant changes in soil parameters and contents of cadmium and zinc at pH 2 but not at higher pH values (3, 4 and 5.3 respectively). At pH 2 the metal contents of pine stems and roots increased while the concentrations decreased in the roots.

For aluminium a clear correlation has been found between plant tissues and metal content of a south Swedish soil rich in clay. For manganese this correlation was highly significant for the NH_4-acetate extractable fraction but insignificant for the total content in soil. For this metal a negative correlation was found between content in leaves and pH of soil. For zinc and cadmium there were no or only insignificant correlations. The effects of soil pH on metal contents of plants were partly contradictory and different for different elements (Nordisk Ministerråd 1986).

The purpose of this investigation was to study the effects of simulated acid deposition on the uptake of certain metals into different plant species in barren, subarctic conditions, where it would be expected to see effects of acidification in an early stage.

Material and Methods

Study Area

The acidification treatments were carried out in field conditions in northern Finland, near the Kevo subarctic research station (Grid E 49:773). The mean annual temperature is −2.0°C and the mean annual precipitation 390 mm.

The area is situated approximately 60 km north of the line of continuous pine forest. The vegetation consists of mosses, lichens, dwarf shrubs and small trees. Samples were collected in September 1986 from the following species: *Betula pubescens* (leaves), *Empetrum hermaphroditum* (leaves), *Pinus silvestris* (needles of year classes 1986, 1985, 1983–84 and 1981–82), and *Vaccinium vitis-idaea* (leaves). In order to study possible treatment-related contamination also mosses (*Pleurozium Schreberi*; green parts) and lichens (*Cladonia* spp.; mainly *C. rangiferina*) were included in the sampling.

The vegetation on different plots was rather variable ranging from dry plots with *Cladonia* lichens dominating the ground layer to more moist plots with *Pleurozium* moss. Samples of all species were collected from seven parallel plots with the same treatment.

Treatments

Twenty blocks of four plots of the size 5 × 5 m have been established in the study area by the University of Turku. Four different treatments were randomized to four nearby plots forming one block. The following treatments were performed on the plots:

1. Dry control (no irrigation);
2. Wet control (irrigation with spring water, pH 6);
3. pH 4 (irrigation with artificial acid rain, pH 4);
4. pH 3 (irrigation with artificial acid rain, pH 3).

Artificial acid precipitation was prepared by adjusting the pH of the spring water with H_2SO_4 and HNO_3 (sulphate : nitrate = 1.9 : 1) to pH 4.0 and 3.0 respectively. The artificial precipitation was applied with sprinklers three times a week (approximately 5 mm per occasion) from August 21 to September 12 1985 and from June 17 to September 12 1986. Consequently, the irrigation in treatments 2–4 contributed 225 mm of precipitation in addition to the natural precipitation. The pH 4 treatment increased the annual ambient sulphur load 2.6 times and the pH 3 treatment 10 times (as compared to the normal deposition during the 2-year period 1985–86). For nitrogen the increment was 3.4 and 14 times respectively. The treatments and the study area are described in more detail by Neuvonen and Suomela, this volume.

Certain amounts of copper and iron were leached out from the irrigation pump and tubings. The contents of these metals in mosses and lichens revealed a contamination of the water used for irrigation. Consequently, results for these two metals are omitted.

Chemical Analyses

The samples were dried in +40°C (Hg) or +105°C (other metals). The metal contents were determined with flame (Al, Mn, Zn, Fe, Cu) or graphite tube (Cd) AAS (Varian SpectrAA 40) after digestion in concentrated HNO_3. The Hg content was determined by cold vapour AAS (Perkin Elmer Coleman MAS 50) after digestion in H_2SO_4 and HNO_3 (4:1). Mercury and cadmium contents of pine needles were not analyzed. The accuracy of the method was tested using parallel determinations and standard samples (NBS Pine Needles No. 1575 and Bovine Liver No. 1577A).

Statistical Methods

The statistical differences between treatments (Dry/Wet/pH 4/pH 3) were analysed by using one-way ANOVA and Tukey's test. To study the possible effect of plot location in the study area on metal contents of the plants a two-way ANOVA was performed with treatment and plot site as grouping factors.

Results and Discussion

There were almost no significant differences in the Al, Mn and Zn contents between different treatments (Tables 1, 3 and 5). For Cd a slight loss of metal could

Table 1. Aluminium concentrations ($\mu g\ g^{-1}$ dry wt) of plant samples after different treatments.

	Dry	Wet	pH 4	pH 3
Betula	20± 5.5	22± 6.8	22± 4.5	17± 4.9
Empetrum	31± 3.5	30± 3.6	28± 6.1	33± 10
Vaccinium	94± 16	96±27	91±11	100± 15
Pinus 86	170± 38	190±78	180±30	190± 40
Pinus 85	210± 31	220±72	210±33	220± 51
Pinus 83–84	270± 42	300±76	270±43	310±100
Pinus 81–82	290± 80	340±72	310±59	360±140
Cladonia	150± 28	190±37	150±40	180± 45
Pleurozium	270±110	240±39	260±41	380±190

Mean±S.D., N=7. Differences between treatments according to Tukey's test denoted (as—) only if significant. **: $p<0.01$; *: $p<0.5$; °: $p<0.1$.

Table 2. Cadmium concentrations ($ng\ g^{-1}$ dry wt) of plant samples after different treatments.

	Dry	Wet	pH 4	pH 3
Betula	180±35	190±68	180±45	200±34
Empetrum	19± 3.3	19± 7.0	19± 9.4	15± 5.8
Vaccinium	12± 7.7	11± 8.4	6.6± 3.3	11± 6.4
Cladonia	83±19	73± 4.2	73±4.0	58± 7.4
Pleurozium	180±32	150±16	160±17	140±26

Mean±S.D., N=7. Differences between treatments according to Tukey's test denoted only if significant. **: $p<0.01$; **: $p<0.5$; °: $p<0.1$.
Differences between treatments:
Cladonia: Dry>pH 3**, Wet>pH 3*, pH 4>pH 3°
Pleurozium: Dry>pH 3*, Dry>Wet°.

Table 3. Manganese concentrations ($\mu g\ g^{-1}$ dry wt) of plant samples after different treatments.

	Dry	Wet	pH 4	pH 3
Betula	1500±500	1600±490	1400±420	1900±650
Empetrum	650±130	650±180	660±130	610±150
Vaccinium	1700±250	1800±230	1700±260	1900±370
Pinus 86	480±110	470± 71	380± 89	440± 56
Pinus 85	760±200	710±140	550± 83	740±160
Pinus 83–84	720±180	700±120	530±100	700±190
Pinus 81–82	750±200	760±160	570±180	780±300
Cladonia	140± 61	140± 46	110± 18	79± 20
Pleurozium	490± 80	460±170	520± 67	400±160

Mean±S.D., N=7. Differences between treatments according to Tukey's test denoted only if significant (**: $p<0.01$; *: $p<0.5$; °: $p<0.1$).
Differences between treatments: Pinus 85: pH 4>Dry°; Cladonia: Dry>pH 3*, Wet>pH 3*.

Table 4. Mercury concentrations (ng g^{-1} dry weight) of plant samples after different treatments.

	Dry	Wet	pH 4	pH 3
Betula	34±11	36±16	34± 8	33± 7
Empetrum	21± 4	22± 4	19± 3	26± 6
Vaccinium	30±12	23± 6	19± 7	38±10
Cladonia	36±10	49±13	40± 6	41± 7
Pleurozium	53±13	52± 8	51±10	53±11

Mean±S.D., N=7. Differences between treatments according to Tukey's test denoted only if significant. **: $p<0.01$; *: $p<0.5$; °: $p<0.1$.
Differences between treatments:
Vaccinium: pH 3>pH 4**, pH 3>wet*
Empetrum: pH 3>pH 4*.

Table 5. Zinc concentrations (μg g^{-1} dry weight) of plant samples after different treatments.

	Dry	Wet	pH 4	pH 3
Betula	200±74	210±72	210±63	270±51
Empetrum	14± 2.9	15± 1.1	16± 2.8	15± 2.3
Vaccinium	31± 3.5	30± 3.3	31± 4.5	31± 4.9
Pinus 86	36± 6.9	40± 4.4	34± 5.6	36± 5.0
Pinus 85	43±19	47± 8.6	45±12	46± 7.7
Pinus 83–84	37±12	42±15	42±13	43±13
Pinus 81–82	44±12	49±20	50±16	53±21
Cladonia	20± 3.7	21± 4.1	22± 3.8	20± 2.2
Pleurozium	39± 4.7	40± 9.1	44± 9.9	39± 2.1

Mean±S.D., N=7. Differences between treatments (as—) according to Tukey's test denoted only if significant. **: $p<0.01$; *: $p<0.5$; °: $p<0.1$.

be detected in mosses and lichens when comparing the acid treatments with the dry control. This could possibly be due to a leaching of Cd from the plant tissues. In other species no significant differences occurred (Table 2). For mercury the highest contents were recorded from the pH 3 treatments in both *Vaccinium vitis-idaea* and *Empetrum hermaphroditum*, but not in *Betula pubescens*. In the lichens the content was higher in the wet control compared to the acid treatments (Table 4). The differences in metal content in relation to the wet control are shown in Figs. 1–4.

There were considerable differences in topography and vegetation within the study area. However, the two-way ANOVA of the significance of the plot location, showed no significant differences between the metal concentrations of plants in different blocks.

Mosses and lichens absorb most of the elements from the air and reflect atmospheric deposition rather than metal status of the soil. The metal contents of mosses and lichens in Kevo were at a level found in other parts of Finland and north Sweden (Lodenius and Tulisalo 1984; Rühling et al. 1987; Rantataro 1989).

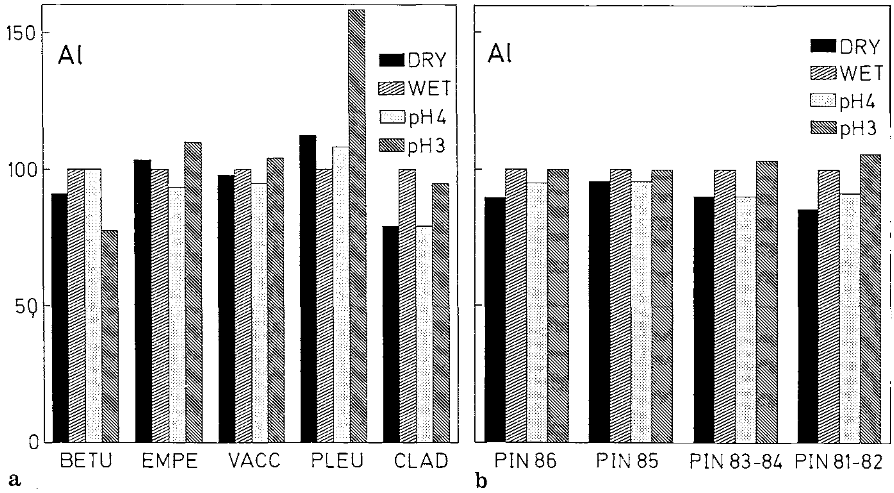

Fig. 1a,b. Relative content of aluminium in plant samples (Wet = 100; N = 7). BETU = *Betula pubescens*; EMPE = *Empetrum hermaphroditum*; VACC = *Vaccinium vitis-idaea*; PLEU = *Pleurozium schreberi*; CLAD = *Cladonia* spp.; PIN = *Pinus silvestris*

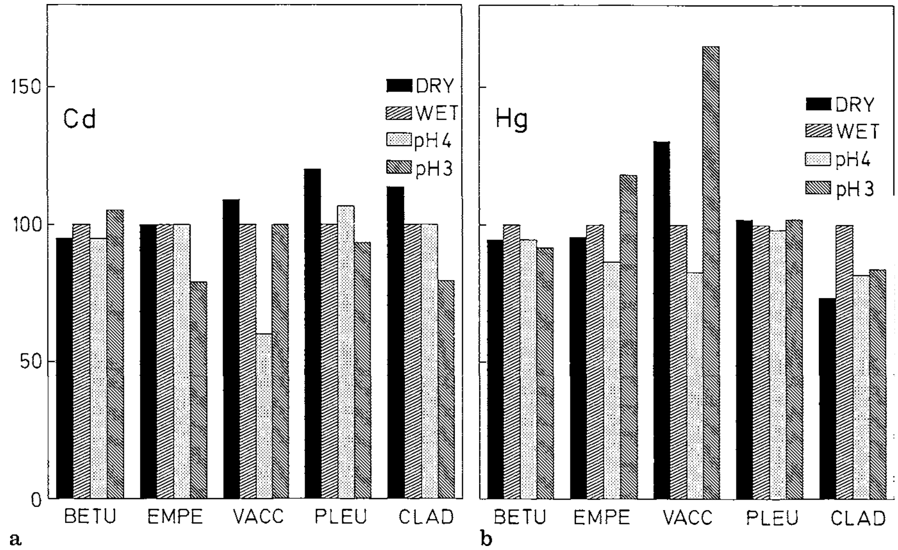

Fig. 2a,b. Relative content of cadmium and mercury in plant samples (Wet = 100; N = 7). BETU = *Betula pubescens*; EMPE = *Empetrum hermaphroditum*; VACC = *Vaccinium vitis-idaea*; PLEU = *Pleurozium schreberi*; CLAD = *Cladonia* spp.; PIN = *Pinus silvestris*

The metal contents of pine needles increased with increasing age (Fig. 5). There were surprisingly few significant correlations between the metal contents of different species. A highly significant positive correlation was found between the mercury contents of *Empetrum* and *Vaccinium* but also a highly significant negative correlation between the mercury contents of *Empetrum* and *Pleurozium* (Table 6).

Table 6. Correlation matrix for metal contents of different species; only correlations with significances $p<0.01$ (**) or <0.001 (***) denoted (correlations between different age classes of pine needles omitted).

	Betula	*Empetrum*	*Vaccinium*	*Pleurozium*	*Cladonia*
Betula	*Cd*–Mn** *Zn*–Mn*** *Zn*–Cd** *Zn*–Al^{-}***			*Hg*–Mn***	
Empetrum		*Al*–Cd**	*Hg*–Hg***	*Mn*–Cd**	*Mn*–Cd** *Al*–Al**
Vaccinium	*Cd*–Al^{-}**	*Hg*–Mn^{-}**		*Al*–Mn^{-}**	
Pleurozium	*Zn*–Mn^{-}**	*Hg*–Hg^{-}***	*Zn*–Mn^{-}**		*Al*–Cd^{-}**
Pinus 86	*Al*–Al***	*Mn*–Mn*** *Zn*–Cd^{-}**		*Al*–Al**	
Pinus 85	*Al*–Al*** *Al*–Hg**			*Zn*–Zn***	*Zn*–Zn**
Pinus 83–84	*Al*–Al**	*Mn*–Mn**	*Al*–Mn**	*Zn*–Zn***	
Pinus 81–82	*Al*–Al*** *Mn*–Mn**	*Mn*–Mn**	*Al*–Mn**	*Zn*–Zn***	

Elements marked with italics refer to plants in the left column.

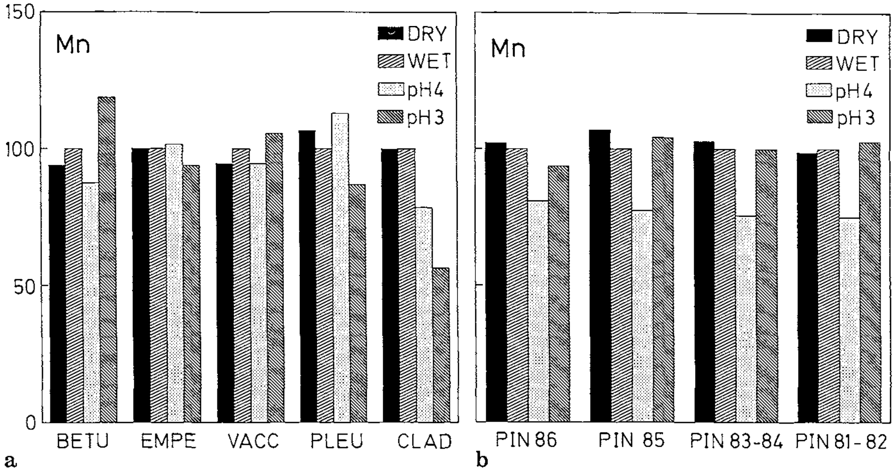

Fig. 3a,b. Relative content of manganese in plant samples (Wet = 100; N = 7). BETU = *Betula pubescens*; EMPE = *Empetrum hermaphroditum*; VACC = *Vaccinium vitis-idaea*; PLEU = *Pleurozium schreberi*; CLAD = *Cladonia* spp.; PIN = *Pinus silvestris*

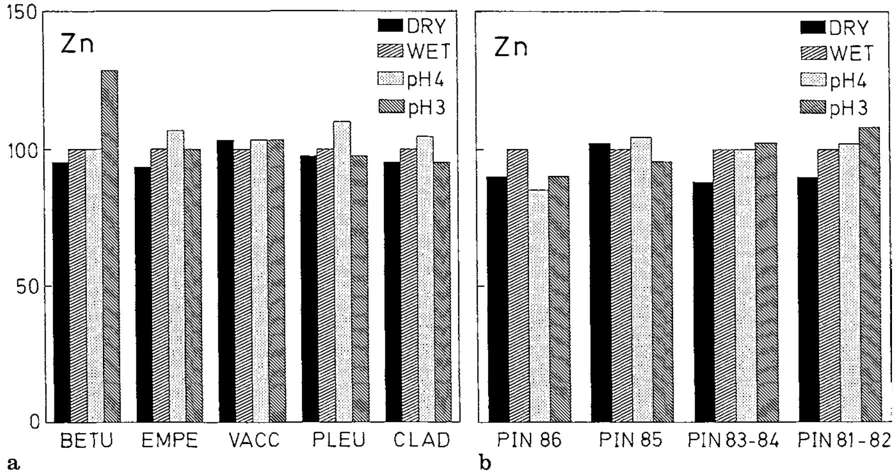

Fig. 4a,b. Relative content of zinc in plant samples (Wet = 100; N = 7). BETU = *Betula pubescens*; EMPE = *Empetrum hermaphroditum*; VACC = *Vaccinium vitis-idaea*; PLEU = *Pleurozium schreberi*; CLAD = *Cladonia* spp.; PIN = *Pinus silvestris*

No or only small changes in the metal contents of plants could be detected during this short period of acid precipitation treatment. The small effects may also be explained by the fact that the treatments were performed in addition to the natural precipitation, which means that the actual effects of acidification were "diluted". The experiment is going to be continued and the contents of metals should be measured again after a longer exposure.

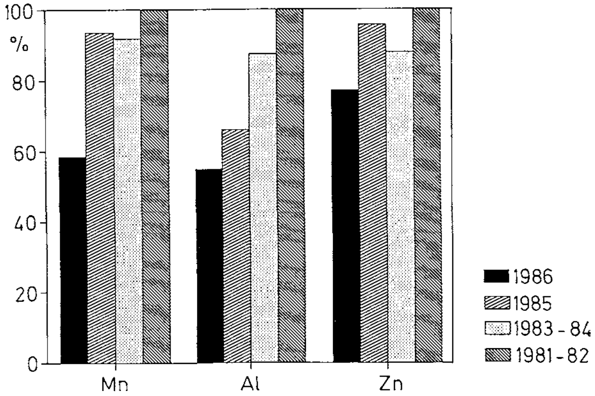

Fig. 5. Relative contents of Mn, Al and Zn (as means of different treatments; N = 28) in pine needles of different age classes (1981–82 = 100)

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2.4 Trees

Detecting Forest Growth Responses to Environmental Changes – a Review of Finnish Studies

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Summary

The growth of the Finnish forest has increased considerably during the last few decades. Several attempts have been made to analyse whether the increase can be attributed to improved silviculture and changes in forest structure. Alternatively, changes in the CO_2 concentration of the air and the fertilising effect of acidic deposition could partly explain the phenomenon. According to most of the studies reviewed, the increase in growth seems to be too large to be caused solely by silvicultural measures. Methodological problems connected with studies of this type are also discussed.

Introduction

New types of forest damage have recently been reported in different parts of Europe. "Novel forest damage" has received considerable publicity in the mass media. During the past decade, research connected with this phenomenon has increased greatly. A vast number of relevant details about changing environmental factors and their effects on forest ecosystems have been generated, ranging from atmospheric reactions to soil processes and tree physiology.

Although quite a lot is known about the details, it has proved difficult to combine the available information into a convincing theory concerning the reactions of entire forest ecosystems to environmental changes. Without such a strong theoretical understanding it is difficult to make predictions about the future development of forest impacts. This is especially true in the case of predicting forest growth, which is a typical complex process, involving several tree-specific processes, interactions between trees, soil processes and the different effects of the environment.

Forest growth can be studied by simulating the functioning of forest ecosystems. Models for this purpose have developed tremendously in recent years. In Finland the methodology of system analysis was used by Hari et al. (1987) for predicting changes of forest growth due to environmental changes. In the first versions of their model only a very few basic factors (toxic compounds in the air, CO_2 content and some others) were applied.

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The obvious alternative is to study empirical data in order to obtain basic knowledge about the effects of environmental changes on tree growth.

Experimental studies are the most straightforward example of this approach. However, forest trees are not ideal subjects for studies under laboratory conditions. Experiments with small plants can produce valuable results about biological processes, but it is not easy to generalize the results to cover varying natural ecosystems. Another drawback is that the time scale of the reactions of plants to different toxic substances varies greatly. Acute damage, caused by high doses of pollutants, can be studied relatively easily. The more gradual sort of damage, caused by subtle changes in soil processes, that may develop during several decades, are rather more difficult to reproduce.

Studying increment data from field measurements permits analysis of the actual development of forests.

It is relatively simple to measure the increment of a stand with reasonable accuracy. Assessing the causal factors behind the measured growth development is a rather more demanding task. There are a number of natural factors including climatic changes, competition and the ageing of the tree, which cause fluctuation as well as trend-like changes in the growth pattern. Human influence, especially silvicultural measures, also have an effect.

The effects of a changing environment may also take several forms. Changes in the composition of the atmosphere do not exclusively cause decline in the increment pattern. The constant increase in the CO_2 content of the atmosphere stimulates tree growth (LaMarche et al. 1984). Increased nitrogen deposition will have a similar effect under Finnish conditions, where forest soils are generally nitrogen-deficient (Viro 1967). Acidic deposition is known to cause a release of base cations in the soil (see e.g. Ulrich 1983). In theory this would, in the first phase, improve the nutrient status of trees, and bring about a growth increase. In the long run the effect of this process would be negative, increased leaching of cations would cause nutrient deficiencies and a subsequent decline in growth. Still another factor, which could have a positive effect on forest growth in most climatic zones, is the possible increase in average temperatures, caused mainly by the use of fossil fuel. It is not easy to assess the effects of temperature changes, since they might be associated with severe changes in annual rainfall, and the structure of ecosystems could be completely altered.

On the other hand, most hypotheses emphasize the role of different air pollutants as growth-reducing factors. Many of these hypotheses have strong experimental support. Most attention has been focussed on studying the effects of sulphur, nitrogen, ozone and heavy metals deposition. The levels of pollutants prevailing in many industrial regions have produced reductions in the growth of small plants under laboratory conditions. The combined effect of two or more pollutants have proved especially harmful. Increment studies near pollution sources have also clearly shown the possibility of severe growth reductions (see e.g. Wilhelmsson 1983).

The task of the forest growth researcher is to separate the possible effects of environmental changes – positive or negative – from the total variation in growth, which is the combined effect of a multitude of factors. This is not made any easier by the fact that the exact causal factors behind "the novel forest damage" are not understood very well. It is therefore hardly surprising that it has proved difficult to demonstrate direct relations between pollutant deposition levels of and growth changes over large forest areas. The analytical techniques available for this purpose have improved considerably during recent years.

This chapter is a review of recent Finnish studies concerned with analysing the growth development of Finnish forests. Special attention is focussed on the component of growth variation, which is unaffected by changes in forest structure.

Growth Results from National Forest Inventories

An exceptionally long time series exists concerning Finnish forest resource development. The first national forest inventory (NFI) was started as early as 1922 and completed in 1924. The inventory was repeated during 1936–1938. As the land area of Finland diminished after the Second World War it is difficult to compare the results of these first two inventories with later ones. In the main they have been omitted from the following figures. The result of the third inventory (1951–1953) is more comparable with subsequent ones. Line plot sampling was used in the first three as well as in the fourth inventory (1960–1963). Visual estimations were made along the lines between plots. In the fifth and subsequent inventories systematic cluster sampling was used. The field work rotated from Southern Finland towards the north, between one and four districts being inventoried each summer. It has taken 7–8 years to cover the whole country. The latest inventory to be completed was the 7th NFI (1977–1984).

In the present inventory (the 8th NFI), the sampling unit is a tract which consists of 21 sample plots. In Southern Finland the distance between tracts is 7 × 8 km. In the northern part of the country, where the conditions are not so favourable for forestry, a less intensive sampling design utilizing aerial photographs is used.

The total area of forestry land is 26.4 million hectares, representing 86.6% of the total land area of Finland. (Kuusela et al. 1986).

As can be seen from Figs. 1 and 2, there has been a considerable increase in the growing stock as well in the annual growth of Finnish forests during the last few decades (Yearbook 1987).

The most recent results are from southern Finland. The 8th NFI was started in 1986. The results for the area, which was covered by 1988 are presented in Fig. 3, together with respective results from earlier inventories. The differences in growth between mid the 1960's and early 1970's were fairly small. Since then there has been a considerable increase, the most rapid increase being in spruce growth

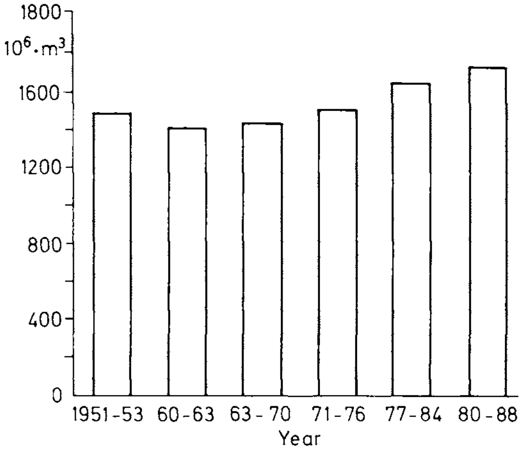

Fig. 1. Total volume of growing stock in Finland in 1951–1984. (Yearbook 1987)

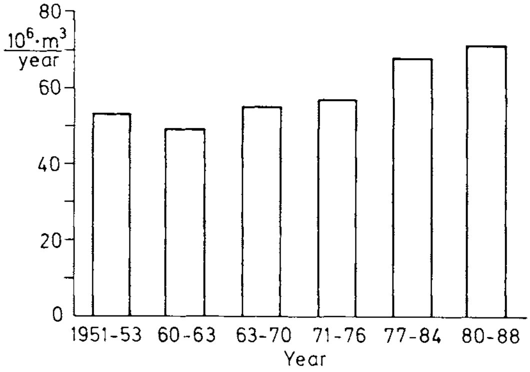

Fig. 2. Total annual growth in Finland in 1951–1984. (Yearbook 1987)

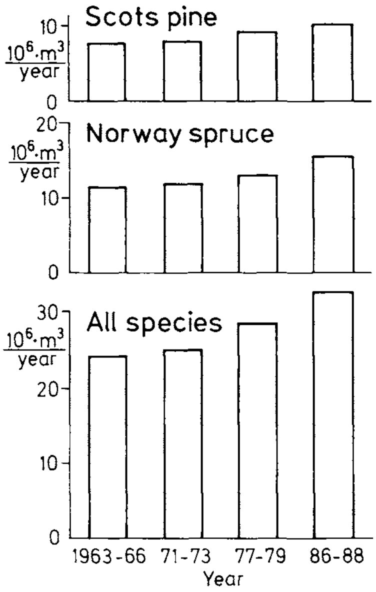

Fig. 3. Total annual growth in the nine southernmost forestry districts of Finland in 1963–1988

between 1977 and 1979 and 1986 and 1988 (Kuusela and Salminen 1980; Kuusela et al. 1983; Kuusela and Salminen 1986).

Many obvious factors have contributed to this development. During this century 4.5 million hectares of peatland (17% of the forestry area of Finland) have been drained. This has, according to Paavilainen and Tiihonen (1988), increased the annual growth by as much as 6–7 million m^3 a^{-1}. In the early 1970's 1–1.5% of the forest land was fertilized annually (Yearbook). Silvicultural methods have also developed greatly, changes in cutting methods being the most obvious improvement.

The age structures from four different inventories (Fig. 4) show a clear increase in the proportions of newly regenerated stands and stands older than 80 years (Yli-Kojola 1985). As the growth of over-aged stands is relatively low, the present age structure is hardly ideal for maximum growth. At first glance it seems that the age structure would have been favourable for growth at the beginning of the century. These age figures can be rather misleading, however. During the first half of the century selective cuttings were very common, which resulted in uneven age structures. Thus a stand in age class 40–60 years may actually include a mixture of trees from all age classes.

Studies Based on Extensive, Representative Data

The question arises whether the considerable increase in the growth of Finnish forests can be totally attributed to improved silviculture. The alternative hypo-

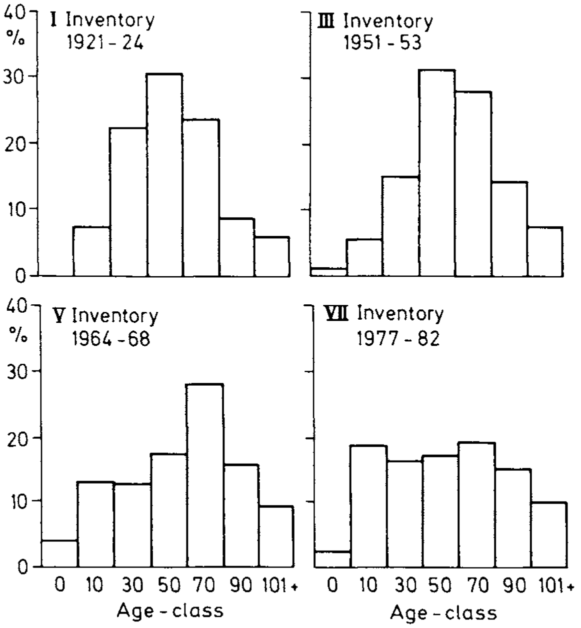

Fig. 4. Age structure in four different national forest inventories. (Yli-Kojola 1985)

thesis is that changes in atmospheric composition have significantly affected the growth.

As pointed out previously, there are many difficulties involved in studying such questions. However, some interesting research with the aim of enlightening this question has been carried out in Finland in recent years.

One basic problem associated with many growth and yield studies is that the data lack representativeness. If the study material is selected subjectively, the results describe the chosen trees or stands, but cannot be generalised to cover large areas. On the other hand, it is usually very laborious to collect an objectively selected sample of increment data.

The sample tree data from Finnish national forest inventories is an example of such study material. Three out of the 21 plots on each inventory tract are selected as sample tree plots. The trees are selected using a relascope. The basic dimensions, age and yearly increments for the preceding 5-year period are measured on each tree. The total number of sample trees in the 7th NFI was 66.113 (Kuusela and Salminen 1983; Kuusela et al. 1986). Also basic stand characteristics like site class and basal area are measured on each plot.

Arovaara et al. (1984) used sample tree data from three national forest inventories for analyzing the growth development of pine on subdry mineral soil sites. Their aim was to determine whether the growth of these subsamples differs significantly from one to another. If such differences were to be found, it would support the theory that increased atmospheric CO_2 levels would have affected forest productivity. Sample tree data from the third (1951–1953), sixth (1971–1976) and seventh (1977–1984) NFI's were used. In order to achieve maximum comparability, the most important stand characteristics causing variation in increment, including site quality, age class and stand quality, were selected. Stands belonging to certain characteristic classes were selected for the analyses. Following this procedure, the subsamples from these three inventories proved to be rather similar with respect to different stand characteristics.

The increment figures compared were under-bark volume increment percentage and under-bark volume increment, both for a 5-year period. The average 5-year increments for the third and sixth inventories were on a similar level (19.0–19.5 $m^3\ ha^{-1} \times 5$ yr), whereas the results of the seventh inventory indicated a considerably higher increment level (22.0 $m^3\ ha^{-1} \times 5$ yr).

These studies were supplemented by determining a function (Fig.5), based on the material from the 7th NFI, which predicts 5-year increment percentage without bark:

$I_v - \% = 5.287 - 0.048 \ln(A) - 0.027 \ln(V)$, where $I_v - \%$ = 5-year volume increment percentage, A = stand age, V = stand volume without bark.

The function was used for predicting the growth level for the material from the third and fifth inventories. The results of this comparison (Fig. 5) also showed that the growth results from the 7th NFI were on a significantly higher level than those in the previous ones.

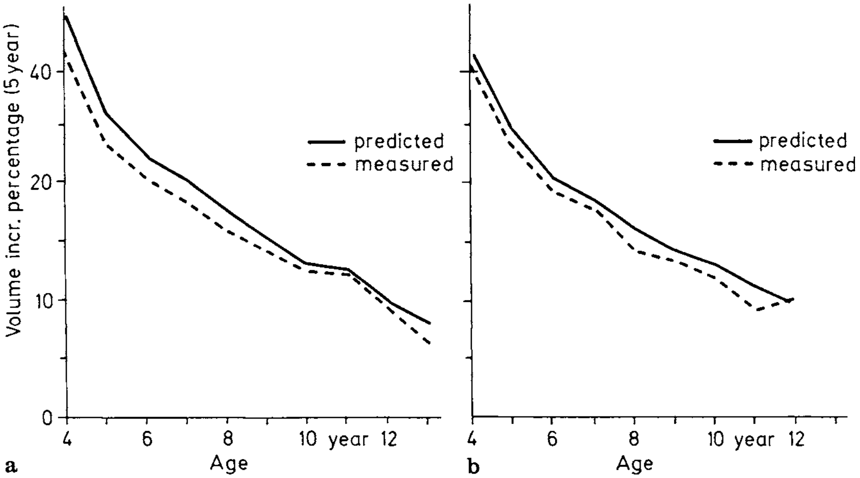

Fig. 5a, b. Mean of the volume weighted increment percentage in different age-classes, (e.g. 6 = 60–69 yr). *Solid lines* according to the function which was created using data from the 7th NFI. *Dashed lines* estimated from the material sampled from the third (**a**) and sixth (**b**) inventory data. (Arovaara et al. 1984)

The sensitivity analyses carried out showed that the result was fairly sensitive to possible systematic errors in determining stand age. Climatic conditions were also studied by calculating temperature sums for the increment calculation periods using a method presented by Ojansuu and Henttonen (1983). No significant differences between time periods of the inventories were found. A study carried out on two series of growth indices (Thammincha 1981; Tiihonen 1983) suggested that the period of the 7th NFI had perhaps been slightly more favourable for tree growth. However, the authors concluded that the observed difference in growth was too large to be attributed solely to climatic variation.

The sample tree material from the national forest inventories has also been used for analysing diameter growth variation of Scots pine and Norway spruce for the period 1960–1988 (Ilman epäpuhtauksien 1990; Henttonen Helena interview with author). Data from the area in southern Finland, which was covered by 1988 in the 8th NFI, were used. In the preliminary phase of the study the growth variation was analysed using a mixed linear model that predicts the annual increment of the average diameter of a stand:

$$y_{ik} = x_{ik} + v_k,$$

where y_{ik} = the mean diameter increment of sample plot i in year k; x_{ik} = a vector of the fixed explanatory variables on sample plot i in the year k; v_k = the random residual term.

The fixed explanatory variables include the average diameter, the basal area and the age of a stand. In addition, 29 dummy variables are used to specify at which year the tree ring has developed. The coefficients of the dummy variables are then estimates of the annual ring indices.

Some sources of growth variation were partly eliminated by selection of the study material. For example stands growing on peatlands, two-storied stands and stands with intermediate cuttings during the last 10 years were omitted from the material.

The results of the study illustrate the yearly fluctuations in diameter growth, but also provide interesting information about possible trend-like changes. As the explanatory variables included some basic stand characteristics, changes in forest structure (age distribution, average density) should not affect the results.

As can be seen from Fig. 6, the growth indices for Norway spruce (*Picea abies* K.) have been increasing throughout the study period. The indices for Scots pine (*Pinus silvestris*) follow a similar pattern up until the mid-1970's, since when there has been a rather clear decline (Fig. 7).

As the time period of 28 years is rather short, it is obviously quite impossible to deduct whether the decline marks the start of a falling trend or merely temporary

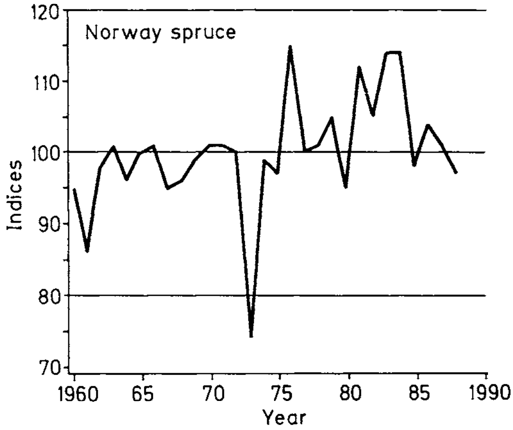

Fig. 6. Growth indices Norway spruce (*Picea abies K.*) for south Finland, calculated from the sample tree material from national forest inventories. (Ilman epäpuhtauksien 1990)

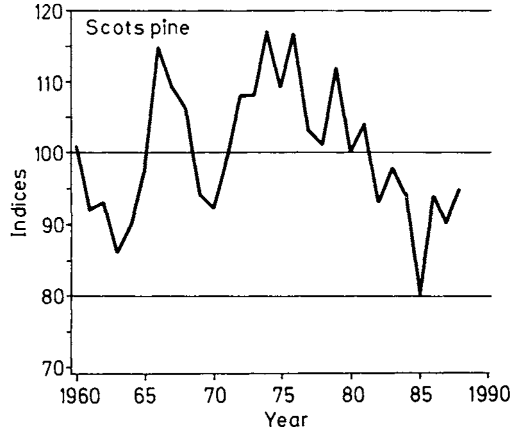

Fig. 7. Growth indices Scots pine (Pinus silvestris) for South Finland, calculated from the sample tree material from national forest inventories. (Ilman epäpuhtauksien 1990)

variation. A longer time series would be essential for making such conclusions. Sample tree data from earlier national forest inventories are unfortunately not very useful for studies of this type. The measurement techniques as well as data storage and processing capacity were very primitive compared with the situation today.

Climatic variables are not included in the model used in the preliminary phase of the study. Temperature sums for the period which is roughly equal to the average growing season and rainfall in June-July during the course of the study period are presented in Figs. 8 and 9. Both seem to have been at a low level at the beginning of the 1960's, which was also a period of low growth for both Norway spruce and Scots pine. At first glance it could appear that neither variable can explain the fairly rapid decline in the increment of Scots pine that started in the

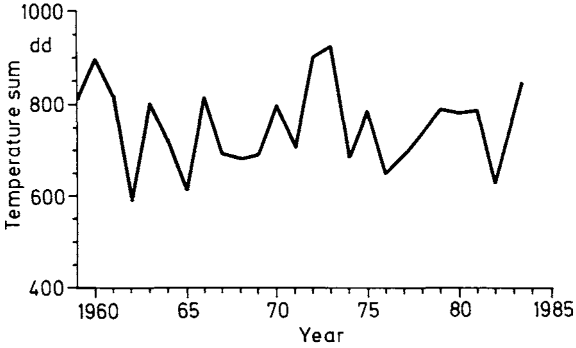

Fig. 8. Average temperature sums for south Finland for the period from January to August in 1959–1984. (Ilman epäpuhtauksien 1990)

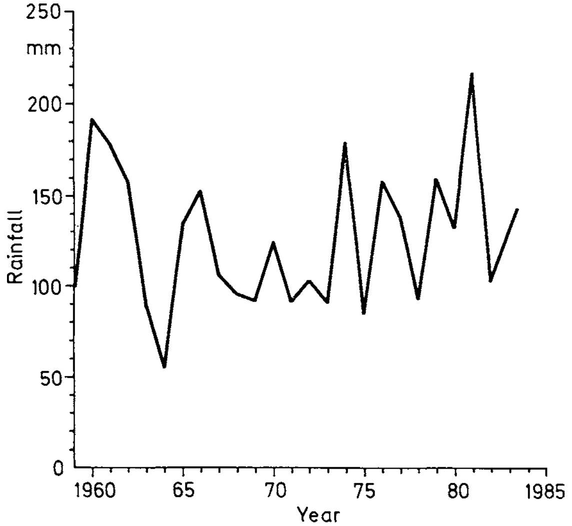

Fig. 9. Average rainfall in June–July for south Finland in 1959–1984. (Ilman epäpuhtauksien 1990)

mid-1970's. Compared with the mid-1970's, temperature sums have been somewhat lower in the 1980's, but rainfall in June-July has generally been at a higher level. It should also be pointed out that according to Henttonen (1984), the proportion of the variance of the growth indices that is explained by climatic factors using the existing models has been fairly low under the conditions prevailing in southern Finland. In the northern part of the country the situation is different, temperature being a major growth-regulating factor.

One likely reason behind the decline in pine growth is an extensive epidemic of *Ascocalyx abietina.* This fungal pathogen has increased rapidly during the 1980's. According to preliminary results from the 8th NFI, it has affected some 10% of the pine stands in southern Finland. The effects of the pathogen on pine growth have not been studied adequately. It strongly reduces the amount of needle biomass, also damaging the young shoots, which have very effective net photosynthesis. It is therefore likely to cause a considerable decline in growth in a severely affected stand.

It is interesting to note, however, that pine growth reached a peak around the mid-1970's, the period for the increment results of the 7th NFI. It therefore seems likely that if a study were to be repeated using the methods of Arovaara et al. (1984), then the growth results for the 1980's would be significantly lower than those for the 1970's.

A seemingly plausible means of studying the effects of environmental changes on tree growth is to relate the growth development of the tree to some measure of its state of health. During the 1980's most European countries joined the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests, coordinated by the United Nations Economic Commission for Europe. The main method recommended for studying tree vigour is ocular estimation of needle loss on individual trees. Considerable effort has been made in studying the possibilities of utilizing these results for growth trend studies (see e.g. Athari and Kramer 1983; Kramer 1986). The correlation between the estimated needle loss and the radial growth of a single tree has been studied by Nöjd (1989). The material consisted of sample tree data from the 8th National Forest Inventory, collected from southern Finland in 1986–1987. The aim was to eliminate – as well as possible – the variation in increment caused by other factors using a mixed linear model. The diameter and the age of the tree were used as fixed explanatory variables. The random variation in increment was partitioned into variation between stands and variation within stands. The needle loss classes were represented by dummy variables. The results (Fig. 10) showed a clear correlation. It is interesting to note that trees with needle loss of 41–50% (very easily visible damage) had lost, on the average, only about 20% of their diameter increment.

It may, however, be rather difficult to utilise this information in estimating possible growth reductions at the stand level. If the increment of a single tree declines due to a reduction in its needle mass, the neighbouring trees will have more growing space and nutrients available, and their growth will be increased. Such interactions are not easy to evaluate. The fact that environmental changes

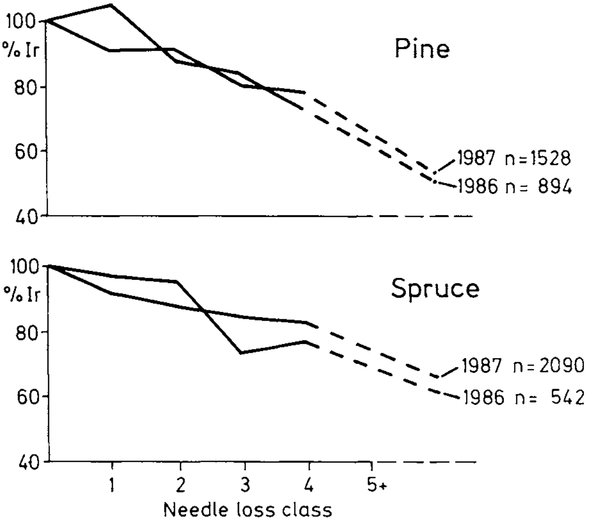

Fig. 10. The growth of trees in different needle loss classes (e.g. class 2=11–20%) compared to the growth of trees with needle loss of 0–10%. (Nöjd 1989)

may also have a positive effect on forest growth also has to be taken into consideration. It would thus appear that there is no simple way of utilising the results of forest damage surveys for growth trend analyses. Of course, if the vitality of most of the trees in a stand, measured by the needle loss method, declines really drastically, the stand growth is also likely to decline. However, such conclusions are not very accurate. Results about the dependence between the amount of needle mass and the diameter growth will be of interest to ecosystem modellers, but they are of dubious value for the forest inventory expert.

Studies Based on Subjectively Selected Material

Studies carried out using subjectively selected data also have certain advantages. It is possible to concentrate on those study objects which are most likely to produce informative results for the study in question. In growth studies it is possible to eliminate to a certain extent some sources of increment variation, like site and competition between trees. It is often possible to reduce the size of the study material. Against this, the results are of dubious general value. However, a lot of basic knowledge can be generated with the help of studies of this kind.

Hari et al. (1984) studied the growth development of dominant Scots pines (*Pinus silvestris*) in conservation areas in southern Finland. Regression analysis was used to estimate the dependence between the increment and the age of the tree. The parameters for the equation were calculated using increment ring data from old pines; only trees older than 200 years were used. A group of younger dominant trees from the same sites was then studied. Deviations from the established dependence between tree age and growth were assumed to be due to either climatic or trend-like changes in tree growth. The results (Fig. 11a) indicated that the

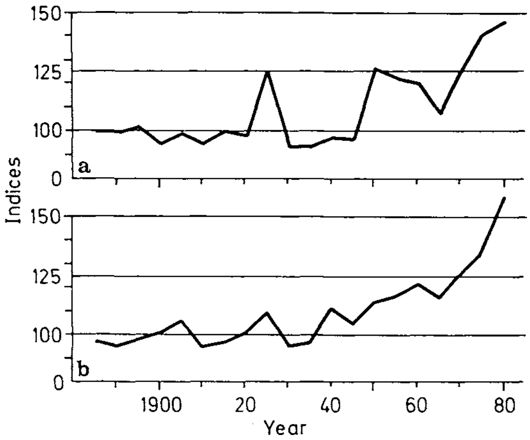

Fig. 11a,b. Mean joint effect of weather and trend on the pine growth. Uncorrected data (**a**) and data corrected with growth indices (**b**) (5-year averages). (Hari et al. 1984)

growth of the younger group had followed the pattern generated by the equation at the beginning of the century. A suprisingly large increase in ring width seems to have subsequently taken place over the last decades. The possible effect of climate on the result was studied by correcting the annual figures with growth indices (Thammincha 1981). The final, weather-corrected curve is presented in Fig. 11b.

Obviously, the results describe trend-like changes in tree growth only if the two groups of trees have been growing in fairly similar conditions. The effects of silviculture have been minimized by selecting the material from unmanaged stands on conservation areas. Nevertheless, it is impossible to totally eliminate the uncertainty concerning the growing conditions of the two groups, as the length of the study period is almost 300 years.

Ilvesniemi (1985) studied growth development of Scots pine on infertile sites. The starting hypothesis was that sites with a low nutrient status would be most sensitive to acidic deposition. Increases in aluminium concentrations, as well as the leaching of nutrients, would cause changes in growth development. The basic idea was to use the earlier development of the sample trees in order to predict their growth during the period 1962–1981. The measured annual ring widths were then compared with the predicted values. The results, however, did not show very clear changes in growth level. In 12 stands out of 17 the growth was somewhat lower than predicted. The study also included soil samples from each forest stand. Correlations between growth development and some basic soil characteristics like pH, the exchangeable aluminium concentration and the Ca/Al ratio were studied. Only the aluminium concentration appeared to be correlated with growth, albeit weakly.

Forests close to the arctic tree line are interesting subjects for growth trend studies. It is relatively easy to find very old trees, which have long ago passed the culmination point of radial growth. Their radial growth therefore shows very little decrease in ring width due to ageing. On the other hand, trees growing in such harsh climatic conditions react strongly to external changes, which is shown by the great short-term fluctuations in increment (Mikola 1952).

Hari and Arovaara (1988) studied 300- to 400-year-old pines growing at high elevations (300–350 above sea level) in northern Finland. In these conditions the natural density of the stands is very low, and competition between trees has probably had little effect on the growth of individual trees. As no silvicultural measures are allowed at such high elevations, only climatic and possibly environmental changes are likely to have major effects on tree growth.

Using the methods developed in an earlier study an equation describing the dependence between daily maximum temperature and daily radial increment was constructed (Hari and Siren 1972). The parameters for the equation were estimated using data from the period 1906–1940. (Daily meteorological data from northern Finland are not available prior to 1906). Estimates of daily radial increments were then calculated for the period 1906–1983 using the model and daily weather data. Annual increments were calculated using the model:

$$I_j = (R_j + a(I_{j-1} - 100))D_j,$$

where I_j = the radial growth index of year j; R_j = the radial growth in mm in year j calculated as a sum of daily increments; D_j = cone correction (no correction $D_j = 1$); $a(I_{j-1} - 100)$ = an autoregressive term.

As can be seen from Fig. 12, the measured increments for the period 1941–1983 are on the average much higher than the predicted values. This appears to support the theory of growth enhancement due to an increase in the CO_2 level of the atmosphere.

Interpretation of this result is somewhat problematic. The weather conditions in northern Finland were unusually cold at the beginning of the century. Also forest productivity was at a low level. If there is a direct causal link between these two phenomena, the model of Hari and Arovaara is likely to predict the increment for the period 1941–1983 reasonably well. If, however, the most important reason for the low growth at the beginning of the century was some other factor, then the model will overemphasise the effect of daily maximum temperatures on growth. Mikola (1952) suggests that sudden frosts early in the autumn of 1902 may have

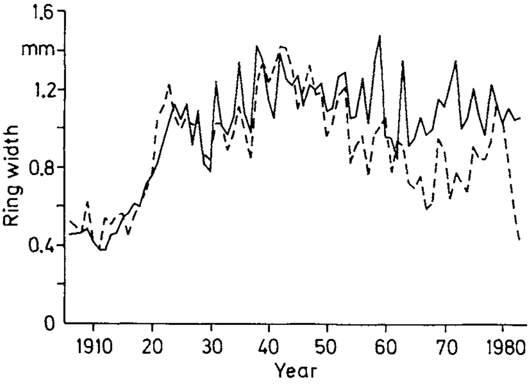

Fig. 12. Measured (*solid line*) and calculated (*dashed line*) ring widths from 1906 to 1983. (Hari and Arovaara 1988)

damaged forest trees severely, which could partly explain the unusually low forest growth in northern Finland during the first years of the century.

If daily meteorological data prior to 1906 had been available, it would have been interesting to use calibration periods of different lengths to study the sensitivity of the model.

Discussion

The studies reviewed here do not give a completely unambiguous view of the effects of environmental changes on forest growth in Finland.

The results of the national forest inventories show a quite rapid and continuing increase in increment, starting from the 1960's. The standard error for these figures is very low.

The sample tree material from National Forest Inventories was used for analysing the growth development in two studies (Arovaara et al. 1984; Ilman epäpuhtauksien 1990). The results from both studies suggest that, despite many obvious causes for the growth increase, changes in the structure of forests cannot exclusively explain the phenomenon. The study period of both studies is rather short, which makes it difficult to draw definite conclusions, but environmental changes can hardly be excluded as a possible contributing factor.

The studies by Arovaara and Hari for South Finland (1984) and the northern part of the country (1988) gave similar results, namely a significant growth increase for Scots pine. These studies describe a longer period, suggesting that the increase in the growth indices during the period 1960–1975 (Ilman epäpuhtauksien 1990), may indeed be part of a long-term trend. According to both studies by Arovaara and Hari, the rising trend started already in the 1940's. In the latter study (Arovaara and Hari 1988) the calibration period selected (1906–1940) for the model perhaps decreases the significance of this finding.

The possible effect of climatic variation on these results is not easy to analyse. The use of growth indices for "correcting" the results is especially problematic, since they may (depending on the calculation method) actually be affected by the same trend-like change that is being analysed. The approach used for analysing the growth data from national forest inventories (Ilman epäpuhtauksien 1990) offers possibilities for using climatic factors as explanatory variables for the model.

The results of Ilvesniemi (1985) suggest that the growth of Scots pine stands on infertile mineral soils did not exhibit any growth increase during the 1960's and 1970's. In most cases it had actually slightly diminished. The result clearly differs from that of other studies, which demonstrate a significant increase in pine growth during the 1960's and 1970's. As the data for the other studies were generally collected on better site types or from different geographical locations, these results are not necessarily contradictory. According to Tamminen and Mälkönen (1986), coarse, infertile soils are the most susceptible to the effects of acidification. This could be one possible explanation for the differences.

It is interesting that the most recent results (Ilman epäpuhtauksien 1990) suggest that the increase in the growth of Scots pine did not continue during the 1980's. On the contrary, there has been a considerable decline.

Only one of the studies (Ilman epäpuhtauksien 1990) includes also results about Norway spruce. The difference between the growth results for Scots pine and Norway spruce after the mid-1970's is quite suprising (Figs. 6 and 7). Although the two species obviously do not have a similar reaction to climatic variations, one would not expect such a different development.

As results about the years prior to 1959 are completely lacking, it is impossible to draw conclusions about the length of period of enhancement in spruce growth. It would be rather problematic to study the growth development of Norway spruce using the methods of Arovaara and Hari (1984). As a shade-tolerant species, it may grow very slowly under other species. The growth may later increase rapidly due to an increase in growing space. Because of the differences in early development, it may be quite misleading to make conclusions about the growth of Norway spruce, based on the dependence between age and increment.

The uncertainty connected with the interpretation of these study results reflects the general problems with analysing time series. The conclusions should be based on sufficiently long study periods. Frequently, however, such data do not exist. When the time unit of the series is 1 year, additional data, although of great interest, will also not provide a "final" answer within reasonable time.

It would be interesting to study the sample tree material from the Finnish national forest inventories by stratifying the material according to site class and tree species. The results should be of great help in evaluating the hypotheses concerning the different suspectibility of different site types to the effects of acidic deposition.

A highly interesting subject for further studies is the eastern part of northern Finland. Northern Fennoscandia is not densely populated, and the local pollutant sources in North Finland are rather insignificant. The only large industrial centres are situated on the Kola peninsula close to the border of the U.S.S.R. and Finland. According to the latest model calculations, an unusually steep gradient in sulphur deposition can be found in the region (Tuovinen et al. this Vol.). The forests of the area should therefore provide excellent possibilities for studying the spatial relationships between tree growth and pollutant deposition.

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The Vitality of Conifers in Finland, 1986–88

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Summary

Regional distribution in the vitality of Scots pine and Norway spruce was assessed in Finland in three consecutive years, 1986–1988. The condition of a total of 3600 trees on systematically selected 450 permanent, mineral soil sample plots was surveyed using needle loss and the number of needle age classes as vitality indicators. Abundance of branch damage and secondary branches were also recorded in 1988.

The methodological studies showed that defoliation was covariated with many other vitality variables. According to confidence tests, different observers made consistent estimations of defoliation class on the same trees with a deviation of one class in 80% of the cases. Long-term observations indicated large annual variation in the needle litterfall in a pine stand.

The most defoliated coniferous forests were located in Lapland and in western Finland. The regional distribution of defoliated forests did not correlate with the known deposition distribution. The number of needle age classes increased with both species to the north. During the monitoring period there was an increase in the defoliation degree. Altogether 1.3% of the surveyed trees died during the study period.

Introduction

The vitality of trees is affected by both internal (genetic makeup) and external factors such as the site, climate, competition for resources, herbivores, pathogens and various types of abiotic damage. During the past few decades air pollutants have become a new, serious threat to the health of forest ecosystems (Pitelka and Raynal 1989). The response of trees to external stress factors varies according to tree species, development stage and site (Loehle 1988). The survival, growth and reproduction of trees are interrelated and dependent on environmental factors and the internal state of the tree (Fig. 1).

Crown vitality, as well as healthy roots, is a prerequisite for functioning of trees. Changes in the phytomass are reflected in stem growth (Dong and Kramer

Kauppi et al. (Eds).
Acidification in Finland

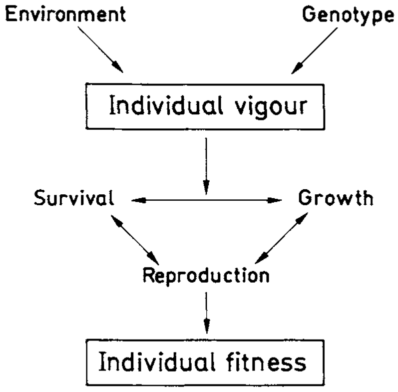

Fig. 1. Components of individual fitness and the factors affecting plant vigour. (After Sarukhan et al. 1984)

1987), root functioning (Eichhorn et al. 1988), and nutrient allocation (Lechowicz 1987). The amount of phytomass and changes in it are considered to be one of the most important indicators of tree condition and growth potential. Both direct (gaseous) and indirect (via the soil) effects of air pollutants can be seen in the properties of the foliage: initially as histopathological changes, and later as discoloration and crown thinning.

Many other factors in addition to air pollution also cause defoliation. Needles are shed as a result of normal ageing of the tree and the properties of the site type. Climatic and weather factors regulate the amount of needle biomass. On the other hand, little is known about the physiological processes of trees which are responsible for the production of new needles and the shedding of older ones. Neither is it known what is the normal variation in the amount of needle biomass (McKay 1988).

The results of monitoring coniferous tree vitality in Finland during 1986–88 are presented in this report. The aims of the study were to determine:

1. The regional distributions in the vitality of conifers in Finland;
2. The magnitude of three-year variation in the vitality variables;
3. Methodological problems in visual estimation of tree vitality.

Material and Methods

The Sample Plot Network and Sampling

The sampling network of 450 mineral soil plots (Fig. 2) is a subset of the 3009 permanent sample plots of the 8th National Forest Inventory (NFI) (Jukola-Sulonen et al. 1987). The first sample plot in each NFI tract was systematically selected for an annual survey. Of these plots every tenth, as well as all peatland and treeless plots, were excluded. The material during the 3-year monitoring period (1986–88) consists of a total of 2152 Scots pine (*Pinus sylvestris* L.) and 1420 Norway spruce [*Picea abies* (L.) Karst.] trees. The geographical distribution in the

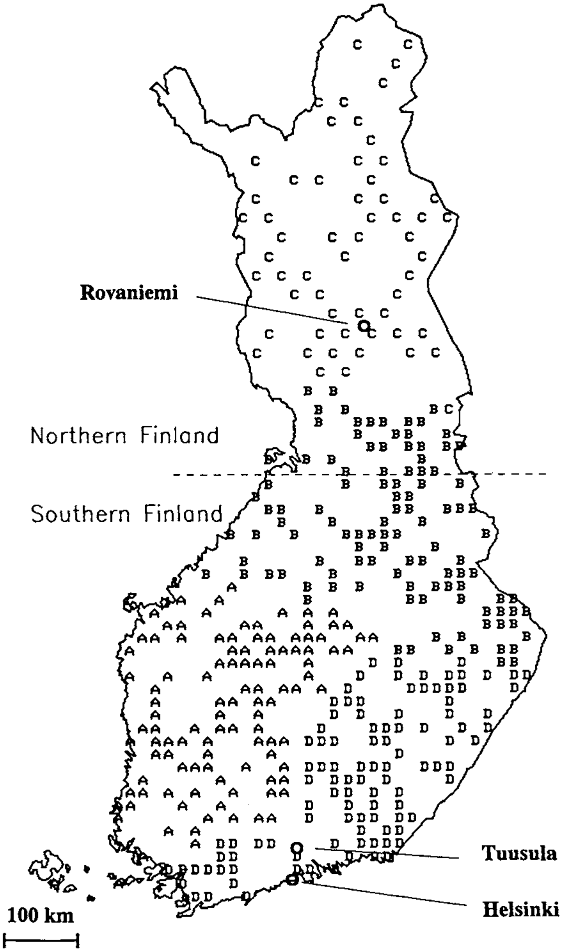

Fig. 2. Sample plot network on mineral soils (n = 450). The areas surveyed by the four observers are marked with the letters *A–D*. The boundary between southern and northern Finland is shown with the *dashed line*. The reference stands for the defoliation confidence test were situated in Tuusula and Rovaniemi

number of trees is not even, there being more sample plots and trees per unit surface area in southern Finland than in northern Finland. The same observers estimated the same trees at the same time of year during 1986–88. Field work was carried out in July-October.

Variables Describing Tree Vitality

The variables used to describe tree vitality were defoliation, number of needle age classes, abundance of branch damage and amount of secondary branches. Stand and site parameters, as well as stem diameter, were measured during 1985–86 in connection with establishment of the permanent sample plots of the 8th NFI (Table 1).

Defoliation of Norway spruce and Scots pine was estimated using binoculars. The sample trees represented the dominant crown layer with a diameter ($d_{1.3}$) of at least 4.5 cm. Defoliation in the upper half of the living crown of spruce and the upper two-thirds of pine was assessed. Defoliation was recorded using 10% classes as follows:

Class	Degree of defoliation	Needle loss %
0	No defoliation	0–10
1	Slightly defoliated	11–20
2	Moderately defoliated	21–30
3	Moderately defoliated	31–40
4	Moderately defoliated	41–50
5	Moderately defoliated	51–60
6	Severely defoliated	61–70
7	Severely defoliated	71–80
8	Severely defoliated	81–90
9	Severely defoliated	91–100

An imaginary or real, similar-aged tree with full foliation growing on the same site was used as reference. The defoliation type of both conifers and crown type in the case of spruce were noted (Westman and Lesiński 1986). Whipping by neighbouring trees, male flowering and resin top (*Peridermium*) of pine have no effect on the defoliation estimation. The assessment was done each year from the same point in the stand. In 1987 the observers were provided with the previous year's defoliation results. This was not the case in 1988.

The number of needle age classes was estimated on the upper and lower crown for pine, and on the lower crown for spruce. Binoculars were used if the branches were too high for direct counting. An annual shoot, with at least half of the needles still attached, was recorded as a full needle age class.

Branch damage (Table 1) describes the extent of openings in the crown and the amount of dead branches. The abundance of branch damage is one component of the defoliation degree.

Secondary (adventitious) branching in spruce (Table 1) indicates an attempt by the tree to compensate for the effect of needle loss (Westman and Lesiński 1986).

The abundance of the fungal pathogen *Ascocalyx abietina* was noted when moving from plot to plot using a coarse scale (Table 1).

The abundance of epiphytic lichens on the stems of the sample trees was estimated as a variable indirectly indicating air pollution. The lichen groups were: sensitive fruticose lichens (*Alectoria, Bryoria* and *Usnea* species), fairly pollution-tolerant foliose lichens (mainly *Hypogymnia physodes, Parmelia ambigua* and *Cetraria pinastri*), and pollution-tolerant *Scoliciosporum chlorococcum* and green algae (Table 1).

Table 1. Variables used in the present forest monitoring study in Finland. The survey concerns years 1986–88 and both pines and spruces if not otherwise stated

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Phytomass

1. Defoliation
   Estimated in 10% needle loss classes.
2. Needle age (yrs)
   Estimated from the upper crown (pine), and estimated or measured from the lower crown (pine and spruce).

Degeneration symptoms

3. Abundance of branch damage
   Estimated from the primary branches using the following codes: 1 = no damage, 2 = a few dead branches, 3 = many dead branches, 4 = small openings, 5 = clear openings in the crown, 6 = lateral branches heavily damaged.
4. Amount of secondary branches in spruce
   Codes: 1 = no sec. branches, 2 = a few sec. branches, 3 = proportion of sec. branches < prim. branches, 4 = sec. = prim. branches, 5 = sec. > prim. branches, 6 = only sec. branches.

Other variables

5. Diameter ($d_{1.3}$) (1985–86)
6. Abundance of the fungal pathogen *Ascocalyx abietina* (1988, assessment when moving from plot to plot)
   Codes: 0 = no infections, 1 = slight infections on individual trees, 2 = slight infections common, 3 = severe damage in individual stands, 4 = severe damage common.

Epiphytic lichens (on tree stems between 0.5–2 m, 1988)

7. Abundance of fruticose lichens
   Codes: 0 = no lichens, 1 = scanty, 2 = a few, 3 = abundant, 4 = highly abundant, 5 = abundant above 2 m (only in reindeer grazing areas).
8. Abundance of foliose lichens
   Estimated percent coverages. Codes: 0 = < 1%, 1 = 1–10%, 2 = 11–40%, 3 = 41–70%, 4 = 71–100%, 5 = abundant above 2 m.
9. Abundance of *Scoliciosporum chlorococcum* and green algae
   Percent coverages as above.

Stand factors (1985–86)

10. Effective temperature sum (degree days)
11. Altitude (m) above the sea level
12. Site type
13. Stand age (yrs)
14. Stand basal area (m^2/ha)
15. Exposition

Methodological Considerations

Studying the condition of forests at a national level requires the use of a rapid and rather inexpensive method. The purpose is to identify problem areas and to demonstrate clear changes in the condition of the trees. Visual estimation of defoliation and needle discoloration of individual trees has been applied in a number of European countries for surveying the vitality of forests (Anon. 1986). These methods have also been used in Finland in accordance with UN-ECE recommendations. The used variables describe the general health of the trees and not only the effects of air pollution. Demonstrating causality requires more precise research and the use of more specific diagnostic indicators (Huttunen 1988).

There are many problems in applying visual methods, the most serious being the subjectivity of the estimation. In addition, there is large natural variation in all of the vitality parameters which causes problems in unambiguously defining a "healthy" tree.

Estimated Defoliation vs. Measured Needle Mass

The relationship between the defoliation class, branch-specific needle loss, and the measured needle biomass scaled by crown height from the same trees was investigated using a sample of ten spruces (age 52 to 94 years) (Fig. 3). The study was carried out in 1985 in southern Finland (Tuusula). Following visual estimation of defoliation, the trees were felled and one sample branch selected from every second branch whorl. The branch-specific needle loss was assessed as the proportion of

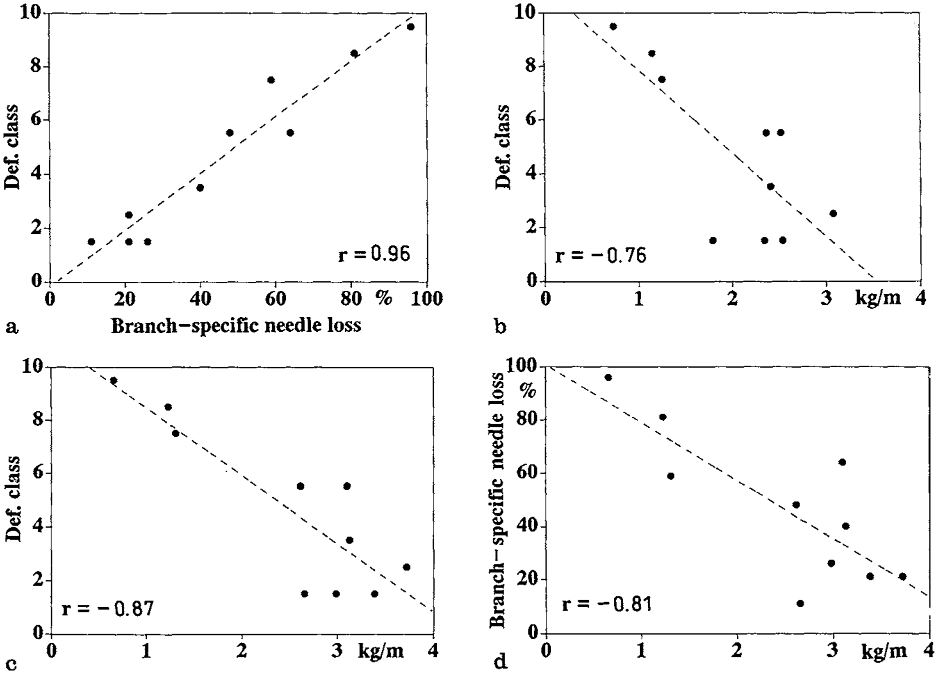


Fig. 3a–d. Relationship between visually estimated defoliation class (upper half of the crown of standing spruces) and **a** branch-specific needle loss % (upper half of the crown) determined from felled trees (n = 10); **b** needle biomass of the whole living crown (kg dry weight) divided by the crown height (m) from felled trees; **c** needle biomass of the upper half of the crown (kg dry weight) divided by the height of the upper crown (m) from felled trees; **d** Needle biomass of the upper half of the crown (kg dry weight) divided by the height of the upper crown (m) vs. branch-specific needle loss %. (**a**) Korhonen et al. 1989, **b**–**d** Tuominen and Jukola-Sulonen 1989)

lost needles compared to a branch with full needle density. The needle dry weight was determined and the needle biomass of the crowns was then estimated.

The relationship between the defoliation class of the standing trees and the branch-specific needle loss was remarkably clear (Fig. 3a). The correlation of defoliation class with the scaled needle biomass of the whole crown (Fig. 3b) was weaker than with the biomass of the upper crown (Fig. 3c). This result was as expected because defoliation was estimated on the upper half of the crown only. The needle biomass of the upper half of the crown correlated as strongly with defoliation class as with branch-specific needle loss (Figs. 3c and 3d).

Defoliation and Other Vitality Indices

The relationship between defoliation and other vitality variables was investigated using 50 even-aged spruces (70 years) at Tuusula. Defoliation varied in accordance with a number of other vitality parameters – amount of branch damage, abundance of secondary branches, under-bark electrical impedance, and growth of individual trees (Table 2). These results show that a carefully made estimation of the defoliation class represents an integrated measure of the vitality of spruces.

Time Series of Pine Needle Litterfall

Time series and historical records are valuable in analysing environmental changes. It is possible to draw a distinction between a trend and short-term fluctuation or irregular variation with the help of long-term data. A 24-year time series (1962–1986) of annual needle litterfall in a pine stand is shown in Fig. 4. The stand is situated in SW Finland and was 111 years old at the time monitoring was

Table 2. Spearman rank correlations between the defoliation class and growth variables, branch damage, amount of secondary branches and impedance values. (Salemaa and Jukola-Sulonen 1990)

	Stand 1 (n=27)	Stand 2 (n=23)	Pooled data (n=50)
Growth variables			
5-yr height increment	−0.712***	−0.388*	−0.850***
5-yr radial increment	−0.573**	−0.627***	−0.708***
5-yr volume increment	−0.526**	−0.630***	−0.810***
5-yr volume increment/ crown surface area	−0.691***	−0.572**	−0.796***
Other vitality variables			
Branch damage	0.514**	0.748***	0.838***
Secondary branches	0.284°	0.447*	0.566***
Impedance values	0.537**	0.476*	0.763***

*** = $P < 0.001$, ** = $P < 0.01$, * = $P < 0.05$, ° = $P < 0.10$.

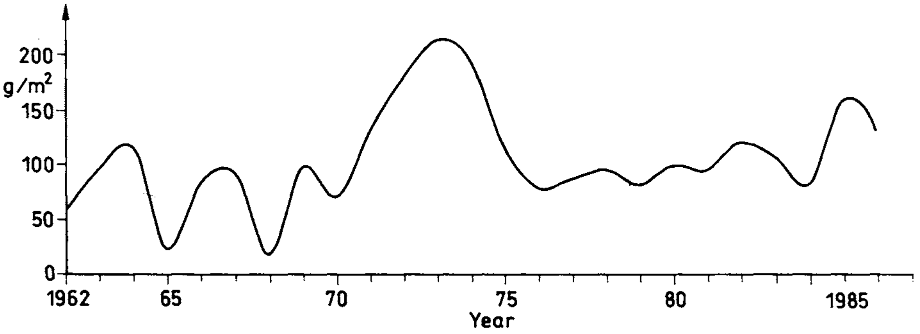


Fig. 4. Time series (1962–86) of needle litterfall (g/m^2) in a pine stand (SE Finland). (Kouki and Hokkanen 1989)

started. The annual amount of litterfall varied greatly and no clear trends can be found. The measured litter accumulation is dependent on the needle shedding and size of the crowns and thus reflects variation in the needle biomass.

Confidence of Visual Defoliation Assessment

The visual estimation of tree condition is a subjective process, and subject to a number of sources of error. There can be considerable variation between the value obtained by different observers for defoliation of the same tree, and even the number of needle age classes. Innes (1988) has classified the sources of error affecting defoliation estimation as follows: (1) the learning factor, which is dependent on the experience of the estimators, (2) the variation associated with species, tree condition and state of the environment, (3) the bias attributable to the observer, and (4) random variation. Weather conditions, illumination and stand density all have an effect on the result. Error variation also arises in defining the part of the crown to be assessed.

Differences Between the Observers

The differences between the observers in estimating defoliation of conifers was studied in August 1988 in both northern (Rovaniemi) and southern (Tuusula) Finland (Fig. 2). A sample of 100 pines and 100 spruces representing all defoliation classes were selected subjectively at both locations. The test spruces at Tuusula (age 70 years) were growing in four stands. The pines (age 50 to 155 years) were growing in five stands. The test spruces at Rovaniemi were growing in two stands (ages 125 and 200 years) and pines in one stand (age 115 years).

Estimation of the test-trees demonstrated that there were systematic differences between the observers (Table 3). However, the defoliation frequency distributions did not differ statistically from each other when comparing three of the four observers (spruce: observers A, B, D and pine: A, C, D). The greatest differences in

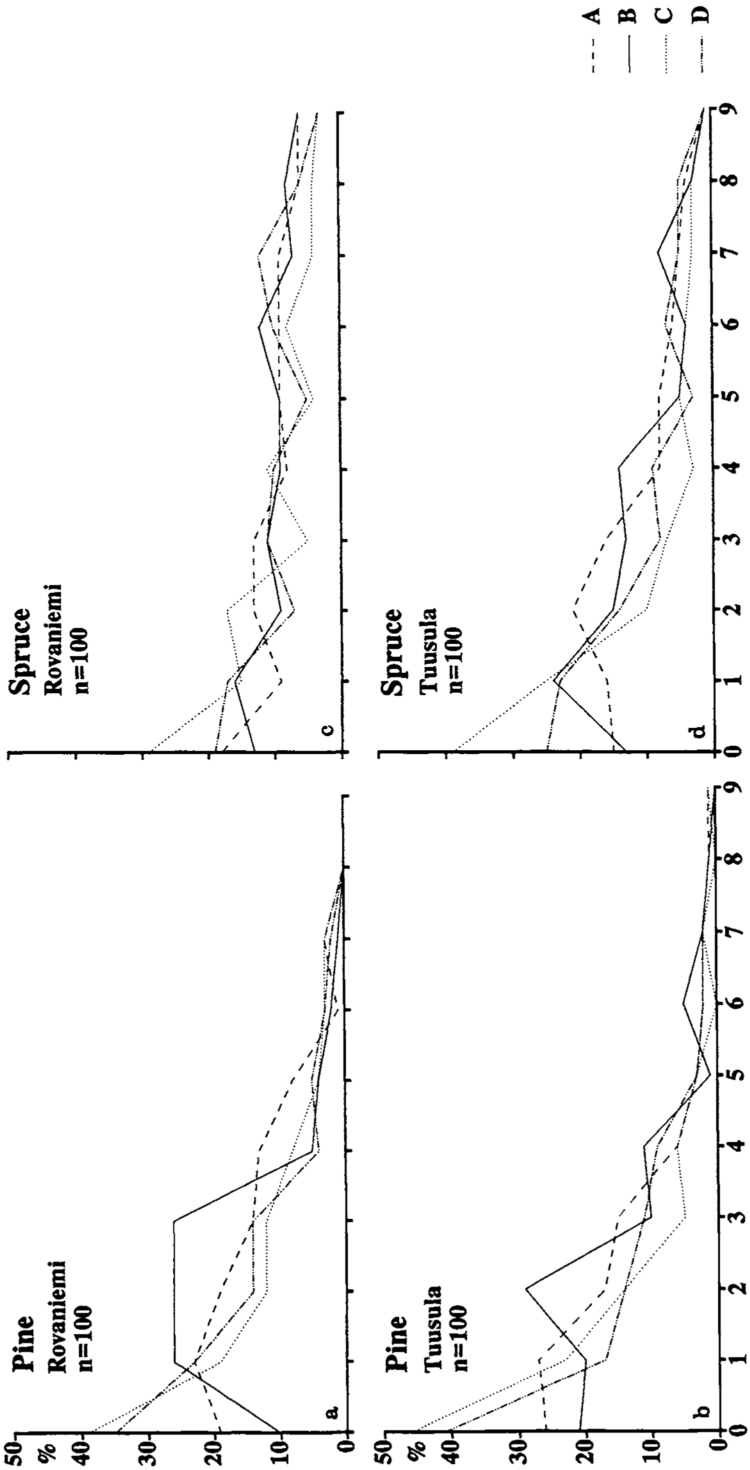
Table 3. Means (x̄) and medians (Md) of the test-tree defoliation distributions of the four observers (A-D). Number of test trees is 100 for both species and both areas

		Pine x̄	Md	Spruce x̄	Md
Rovaniemi	A	2.2	2	3.7	3
	B	2.2	2	3.9	4
	C	1.7	1	2.6	2
	D	1.7	1	3.5	3
Tuusula	A	1.9	1	2.9	2
	B	2.1	2	2.9	2
	C	1.3	1	1.8	1
	D	1.6	1	2.5	2
Areas combined	A	2.1	2	3.3	3
	B	2.1	2	3.4	3
	C	1.5	1	2.2	1
	D	1.6	1	3.0	2

the frequency distributions were in class 0 for both pine and spruce (Fig. 5). In pine there were no statistical differences between the observers in determining the number of trees with over 30% needle loss. When the results by observer C were omitted the same result was found also for spruce.

No interactions were found between the observer and the geographical area in estimating the test-trees. The estimation level of observers A and B is very similar with respect to both pine and spruce in both areas, as well as in the combined material (Table 3). The proportion of conifers estimated by these two persons out of the whole national material is 58%, and their estimation level will be taken as a reference in further studies. Estimations by observers C and D are problematic, C's level is about one class lower for spruce, and about 0.5 class lower for pine compared to observers A and B (Table 3). Interpretation of the reliability of the results obtained by observer D is still more difficult. The level difference compared to A and B is 0.3 to 0.4 classes for spruce in the combined material. The level difference for pine is half a class (Table 3).

In addition to comparing the frequency distributions (Fig. 5), the correspondence between the estimates made by different observers on the same trees was studied, i.e. the reliability of the estimates (Fig. 6). The results obtained by the four observers were examined for this purpose as six paired combinations (AB, AC, AD, BC, BD, CD). The number of trees which both observers classified in the same class, and those having a difference of the order of 1, 2 etc. classes, were calculated for each of the combinations. The mean of the six paired comparisons was calculated. The test trees at Rovaniemi and Tuusula were combined. On the average 41% of the test spruces and 44% of the test pines were estimated to be in the same defoliation class; 81% of the spruces and 86% of the pines were classified to the same or to the nearest class. Estimation differences of more than one class occurred in about 20% of the spruces and about 14% of the pines (Fig. 6). The


Pine
Rovaniemi
n=100
a
Pine
Tuusula
n=100
b
Spruce
Rovaniemi
n=100
c
Spruce
Tuusula
n=100
d
50
%
40
30
20
10
0
0
1
2
3
4
5
6
7
8
9
Defoliation class
A
B
C
D

consistency of the defoliation estimations of different observers was not dependent on the defoliation degree of the trees.

Maintaining the Individual Estimation Level

The consistency of the estimation level over time (1986–88) was studied using a small group of test-trees selected from the Tuusula material. The reference stand used for year-to-year monitoring consists of 39 spruces and 13 pines. The condition of the test-trees has remained almost unchanged throughout the course of the study.

The combined distributions of four observers for the same test-trees on four estimation occasions did not differ statistically from each other (Fig. 7). The individual distributions for spruce, according to the X^2 test, also remained consistent over time. The individual distributions were also tested by the Kolmogorov-Smirnov test by comparing paired chronologically successive estimation results. None of the observers had any statistical differences.

The result for pine was not as good as that for spruce, although there were no differences between the combined distributions based on different estimation times (Fig. 7). The distributions of observer C did not remain constant over time. However, the pine material is too small ($n = 13$) for any conclusions to be drawn concerning the consistency of the estimation level over time.

◁ **Fig. 5a–d.** Comparison of the defoliation frequency distributions by the four observers (**A–D**) in the confidence test. Pine and spruce test-trees were studied at Rovaniemi and Tuusula (see Fig. 2 for the areas surveyed by each observer). The consistency of the distributions is analysed using the X^2 test. If the number of trees in the highest defoliation classes were less than three, classes were pooled.

Pinus

a) Rovaniemi
Classes 0–7 (>4 pooled): $X^2 = 44.50$, $P < 0.001$, df = 15
" 1–7 " : $X^2 = 14.25$, $P = 0.285$, df = 12
" 0–7 " without observer B:
$X^2 = 14.78$, $P = 0.140$, df = 10

b) Tuusula
Classes 0–9 (>4 pooled): $X^2 = 31.43$, $P = 0.008$, df = 15
" 1–9 " : $X^2 = 11.98$, $P = 0.447$, df = 12
" 0–9 " without observer B:
$X^2 = 14.79$, $P = 0.140$, df = 10

Picea

c) Rovaniemi
Classes 0–9: $X^2 = 30.35$, $P = 0.299$, df = 27
" 1–9: $X^2 = 22.64$, $P = 0.541$, df = 24

d) Tuusula
Classes 0–9 (>7 pooled): $X^2 = 43.65$, $P = 0.008$, df = 24
" 1–9 " : $X^2 = 19.93$, $P = 0.526$, df = 21
" 0–9 " without observer C:
$X^2 = 17.46$, $P = 0.357$, df = 16

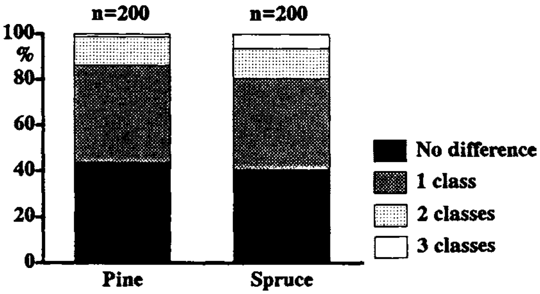


Fig. 6. The reliability of the defoliation class estimates of individual test-trees. The four observers were compared in pairs. The result averages all possible pairwise combinations among the four observers. The test-trees from Rovaniemi and Tuusula were pooled. (Key: *No difference* = observers are consistent; *1 class* = deviation of judgement is 1 class, etc.). See text for further information

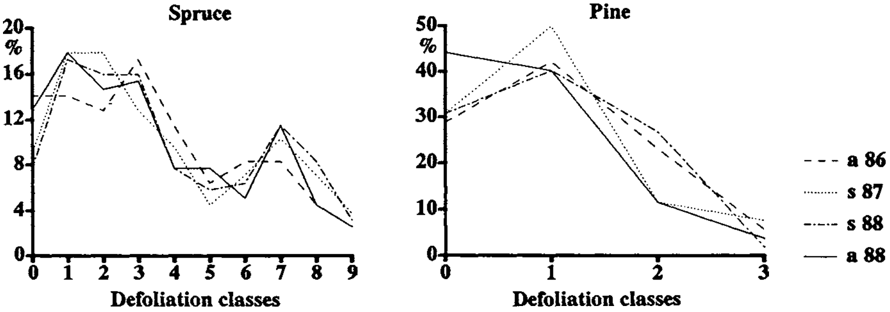


Fig. 7. Temporal consistency between the defoliation frequency distributions of the test-trees in Tuusula. The results of the four observers are pooled for each time period. *a* autumn; *s* spring. Spruce (n = 39): $X^2 = 16.24$, P = 0.948, df = 27, pine (n = 13): $X^2 = 10.47$, P = 0.314, df = 9

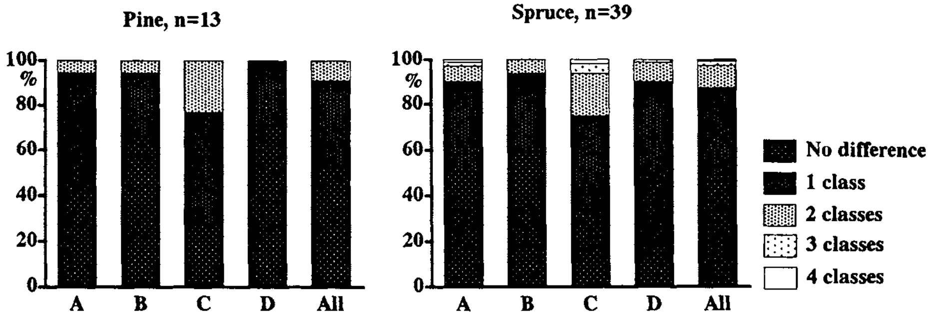


Fig. 8. Consistency of defoliation estimates of the individual test-trees in different time periods for four observers (*A–D*) and for pooled data (ALL). Pine: n = 13, spruce: n = 39. *Raster descriptions* as in Fig. 6. See text for further information

The reliability of the tree-specific estimations was studied by comparing the results of chronologically successive estimation rounds pairwise for each observer (Fig. 8) in the same way as the differences between the observers had been examined (Fig. 6). On the average, 47% of the spruces were estimated to be in the same class over the course of time. When an estimation error of one class is permitted, 88% of the spruces were estimated in the same way. An average of 53.2% of the estimates for pine remain unchanged, and with a variation interval of one class, the result is 92% (Fig. 8).

It was not possible to calibrate the estimation levels during the survey period because it would make it impossible to monitor the changes. The level differences thus have to be accepted, but are taken into account when interpreting the results.

Results

Cuttings and Mortality Rate

During the survey period (1986–88) 4.1% of the 3600 conifers being monitored were cut. The felled trees were more defoliated than the remaining trees ($X^2 = 14.29$, $p < 0.001$, $df = 1$).

1.3% of the conifers died during the three-year period: 1.5% of the pines and 1% of the spruces (Table 4). The highest mortality was recorded in 1986 and lowest mortality in 1987. The mean annual mortality rate was 0.5% for pine and 0.4% for spruce.

46% of the dead conifers were still standing, while 54% were thrown or broken. 64% of the dead standing trees had suffered from only slight defoliation (<10%) the previous year, and the other 36% from severe defoliation (>90%).

Table 4. Number of dead and living trees during 1986–88.

Year	Dead				Total		Living	Total
	Standing		Thrown or snapped					
Pine	n	%	n	%	n	%	n	n
1986	7	0.3	15	0.7	22	1.0	2130	2152
1987	0	0	3	0.1	3	0.1	2095	2098
1988	6	0.3	2	0.1	8	0.4	2060	2068
Total	13	0.6	20	0.9	33	1.5		
Spruce								
1986	5	0.4	2	0.1	7	0.5	1413	1420
1987	0	0	4	0.3	4	0.3	1401	1405
1988	4	0.3	0	0	4	0.3	1358	1362
Total	9	0.6	6	0.4	15	1.1		

Table 5. Defoliation frequency distributions of the same trees during 1986–88 in the whole country. Pine n = 2046, spruce n = 1353

	Defoliation % 0–10	11–20	21–30	31–40	41–50	51–60	61–70	71–80	81–90	91–100
Pine										
1986	81.4	12.4	4.2	1.2	0.6	0.2	0.0	0.0	0.0	0.0
1987	77.5	15.1	5.0	1.4	0.6	0.1	0.1	0.1	0.0	0.1
1988	72.0	16.9	7.3	2.5	0.7	0.3	0.1	0.1	0.0	0.1
Spruce										
1986	52.4	21.7	12.0	7.2	3.2	1.8	0.8	0.4	0.3	0.1
1987	43.9	22.3	16.4	7.2	5.2	1.9	1.7	0.4	0.7	0.1
1988	43.2	18.6	14.8	10.5	5.3	3.6	2.0	1.0	0.8	0.2

Defoliation on the thrown or broken conifers the previous year had been 0–10%. The causes of death of the dead standing trees were unknown, but the thrown or broken trees were the result of storm damage.

Defoliation During 1986–1988

The Whole Country

The defoliation distributions of the trees in 10% needle loss classes were strongly positively skewed in all 3 years. The majority of the trees were concentrated in low defoliation classes (0 and 1). Spruce was more defoliated than pine (Table 5).

The defoliation distributions of pines and spruces differed significantly in 1988 from the distributions for 1986 and 1987 (X^2 test). Between the distributions for 1986 and 1987 there was a significant difference ($P < 0.001$) only in the case of spruce. Significance of the difference for pine was 0.068. The changes in the distributions were caused by an increase in defoliation during the 3-year monitoring period. The number of defoliated trees was highest in 1988, and lowest in 1986.

The number of trees with defoliation of over 10% increased overall by 10%-units during 1986–1988. The number of trees with defoliation of over 20% increased by 8%-units in 3 years. The corresponding values for pine were 9 and 5, and for spruce 9 and 12.

The defoliation class of the majority of the trees remained unchanged during the 3-year period. Altogether 87% of the spruces and 95% of the pines were recorded to the same defoliation class with a deviation of one class in 1986 and 1988. An increase in defoliation was more common than recovery from defoliation. Defoliation increased by at least two classes in 12.5% of the spruces and 4.6% of the pines. A reduction in defoliation of at least two classes was recorded for about 1% of both species (Table 6).

Table 6. Proportion of individual trees (%) classified in the same defoliation class in different years, and those classified in either a worse (more defoliated, +) or better (less defoliated, −) direction

	Change in defoliation degree						
	+30%	+20%	+10%	Same	−10%	−20%	−30%
Pine (n = 2046)							
1986–87	0.0	0.6	8.7	86.9	3.7	0.1	0.0
1987–88	0.2	2.2	13.6	77.5	5.8	0.6	0.1
1986–88	0.6	4.0	14.2	75.6	4.8	0.7	0.1
Spruce (n = 1353)							
1986–87	0.4	3.6	22.3	70.5	2.9	0.3	0.0
1987–88	0.9	3.5	21.4	62.9	9.9	1.3	0.1
1986–88	2.7	9.7	24.7	56.4	5.5	1.0	0.0

Regional and Temporal Variation in Defoliation

Scots pine. The most severely defoliated pine forests were located in NE and SW Lapland, in Kuusamo, and in the western part of southern Finland (Fig. 9). The means have been calculated from the midpoint classes (0 = 5%, 1 = 15%, 2 = 25% etc.). The regional pattern was similar during all 3 years (Fig. 10). A similar

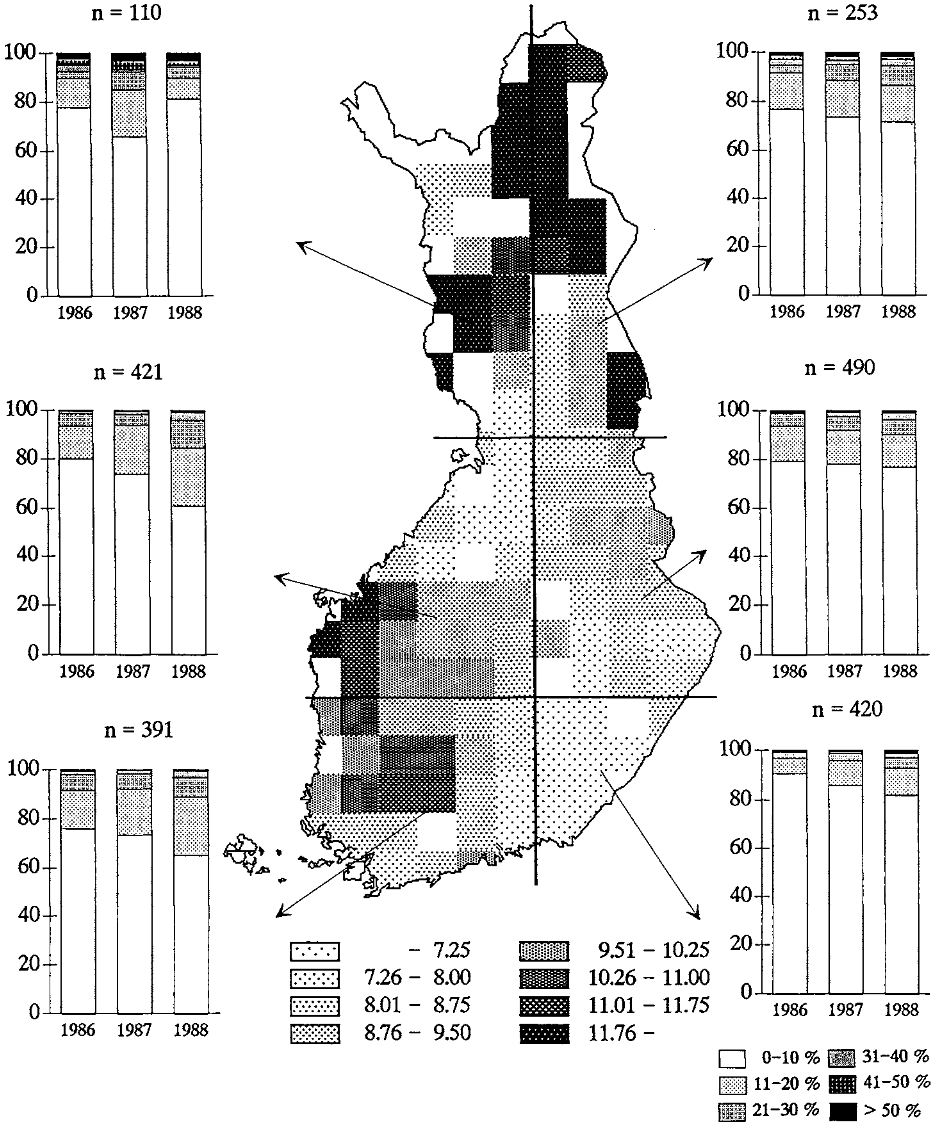


Fig. 9. Three-year averages (1986–88) of defoliation in pine forests in Finland. Size of the grid in the map is 50 × 50 km². *White areas* lack observations. Annual defoliation distributions in different parts of the country are presented by the *bar diagrams.* The map legend is given *under* the map and the bar legend *lower right*

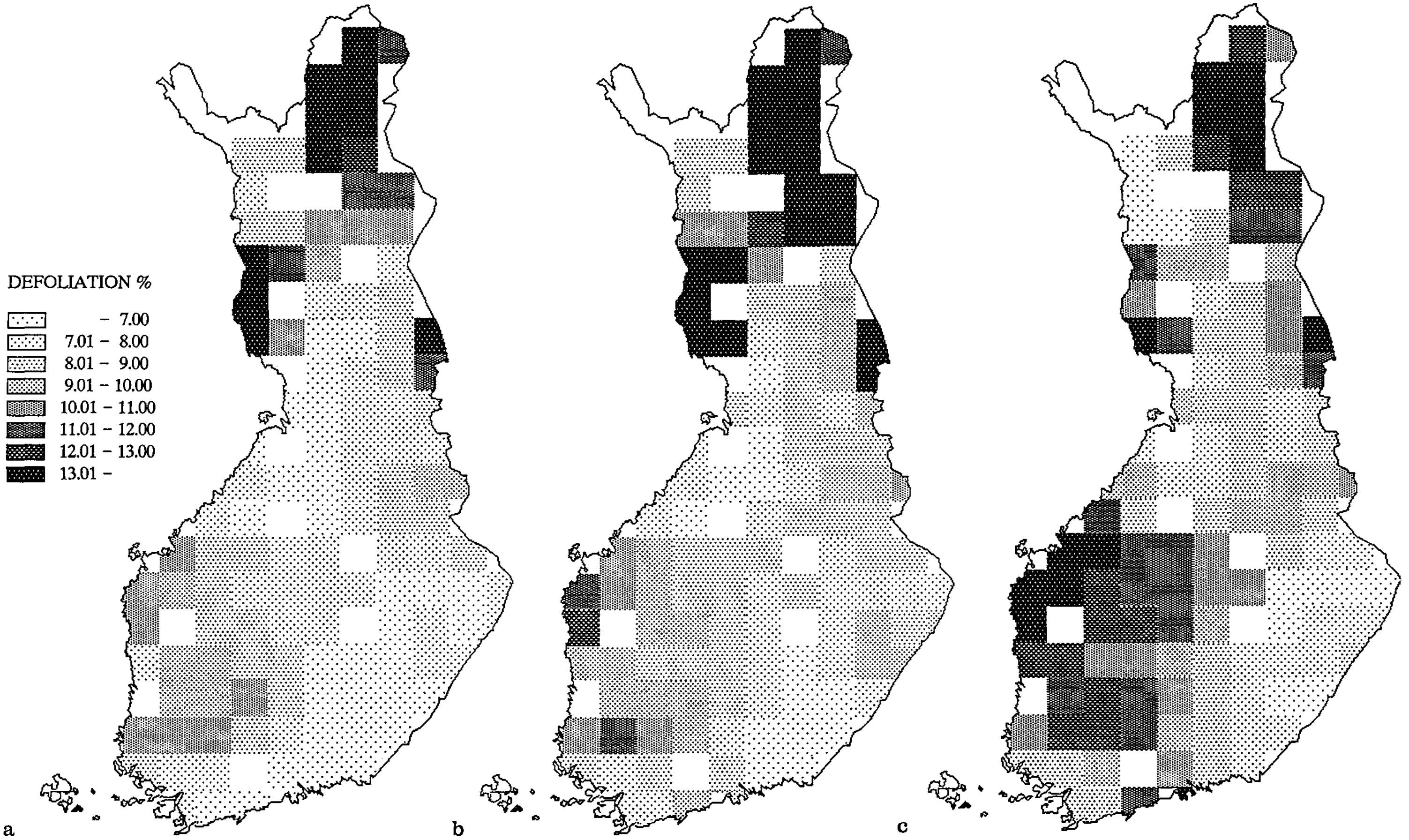


Fig. 10a–c. Defoliation of pine in **a** 1986, **b** 1987, and **c** 1988. 50 × 50 km^2 grid averages are given

regional pattern is also obtained when the result for 1988 is depicted as the proportion of trees with defoliation of at least 20 or 30% out of all sample trees in the area (Fig. 11). The regional differences in the means between the southern and northern parts of the country, and between the eastern and western parts, were less than one class. There were no differences between defoliation of pines growing on different site types.

Defoliation increased the most in SW Finland during the 3-year period (Fig. 9). The greatest increase in defoliation in 1987 compared to 1986 occurred in western Lapland. Defoliation decreased in 1988 compared to 1987 in western Lapland, but increased in the western part of southern Finland (Fig. 9).

Norway spruce. The 3-year defoliation means for spruce were highest in the northernmost Lapland, Kainuu and Pohjanmaa (Fig. 12). The same regional pattern is evident in all 3 years when defoliation is compared as grid means (Fig. 13). A similar regionality can also be seen when the results for 1988 are presented as the proportions of trees with at least 20 and 30% defoliation out of all sample trees in each grid (Fig. 14). The regional means in southern Finland vary by less than 0.4 class, i.e. the regional differences are rather small. The difference between Lapland and southern Finland is about 1.5 classes. The most defoliated spruces were growing on mesic site types.

The proportion of spruces defoliated by more than 20% increased during the 3-year period throughout the whole country (Fig. 12). The highest defoliation increase was observed in central parts in Finland. The amount of severely defoliated spruces increased in Lapland (Fig. 12).

Stand Age

Defoliation correlated positively with stand age (Fig. 15). The trend was stronger for spruce than for pine (Spearman rank correlations: pine $r_s = 0.300$, $n = 2156$; spruce $r_s = 0.621$, $n = 1440$, both $P < 0.001$).

The focal point of defoliation in growing, less than 80-year-old pine forests was in western Finland (Fig. 16a). Defoliation in young spruce forests was centred in the southern half of the country (Fig. 16b).

Needle Age Classes During 1986–1988

The number of needle age classes on pine and spruce (i.e. the ages of the oldest needles) were distributed normally in southern and northern Finland (Fig. 17). The range in the number of needle age classes on pine in northern Finland was 1–7 on the upper branches and 2–9 on the lower branches. The corresponding values in southern Finland were 2–5 and 2–6. The number of needle age classes on the lower branches of spruce varied in northern Finland from 6 to 20, and in southern Finland from 2 to 13. The mean number of needle age classes for each year and for the 3-year period are presented in Table 7.

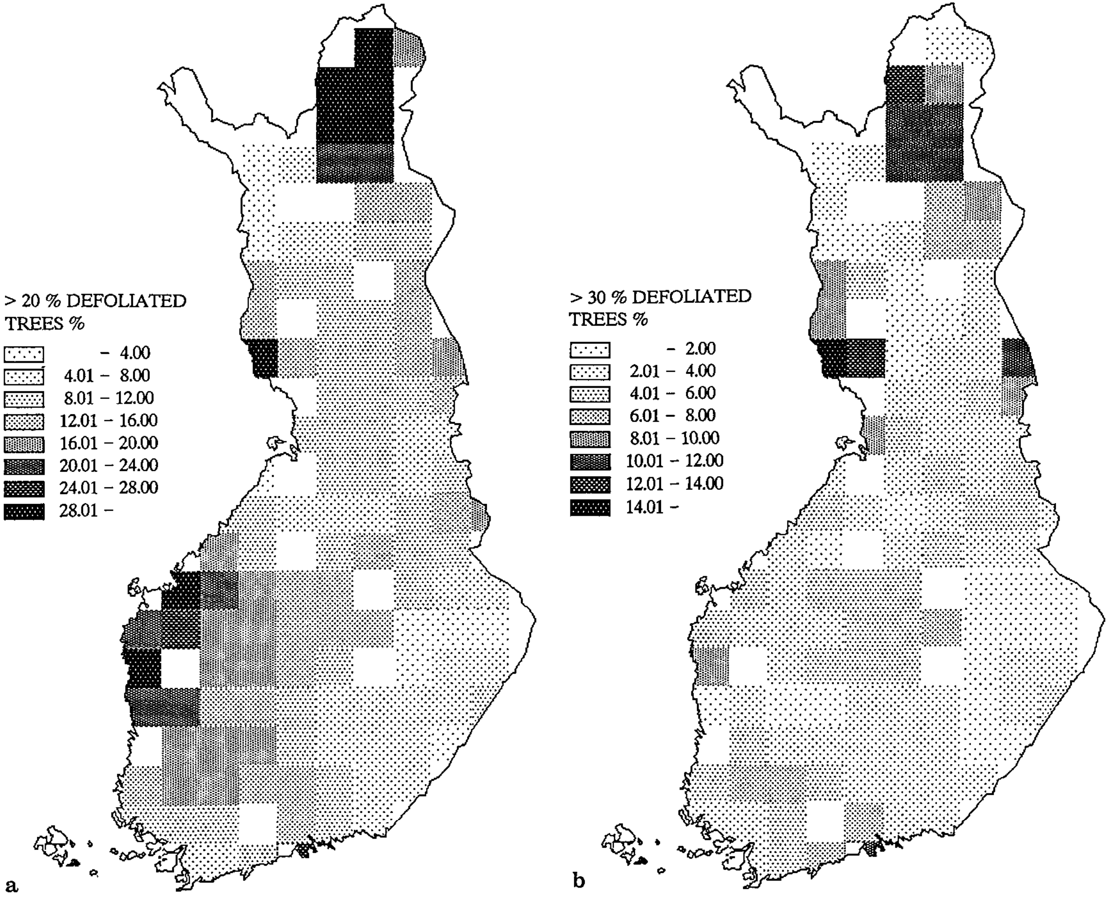


Fig. 11a,b. Defoliation of pine as a proportion of **a**>20% and, **b**>30% defoliated trees out of all sample pines in 50 × 50 km^2 grids. Data from 1988

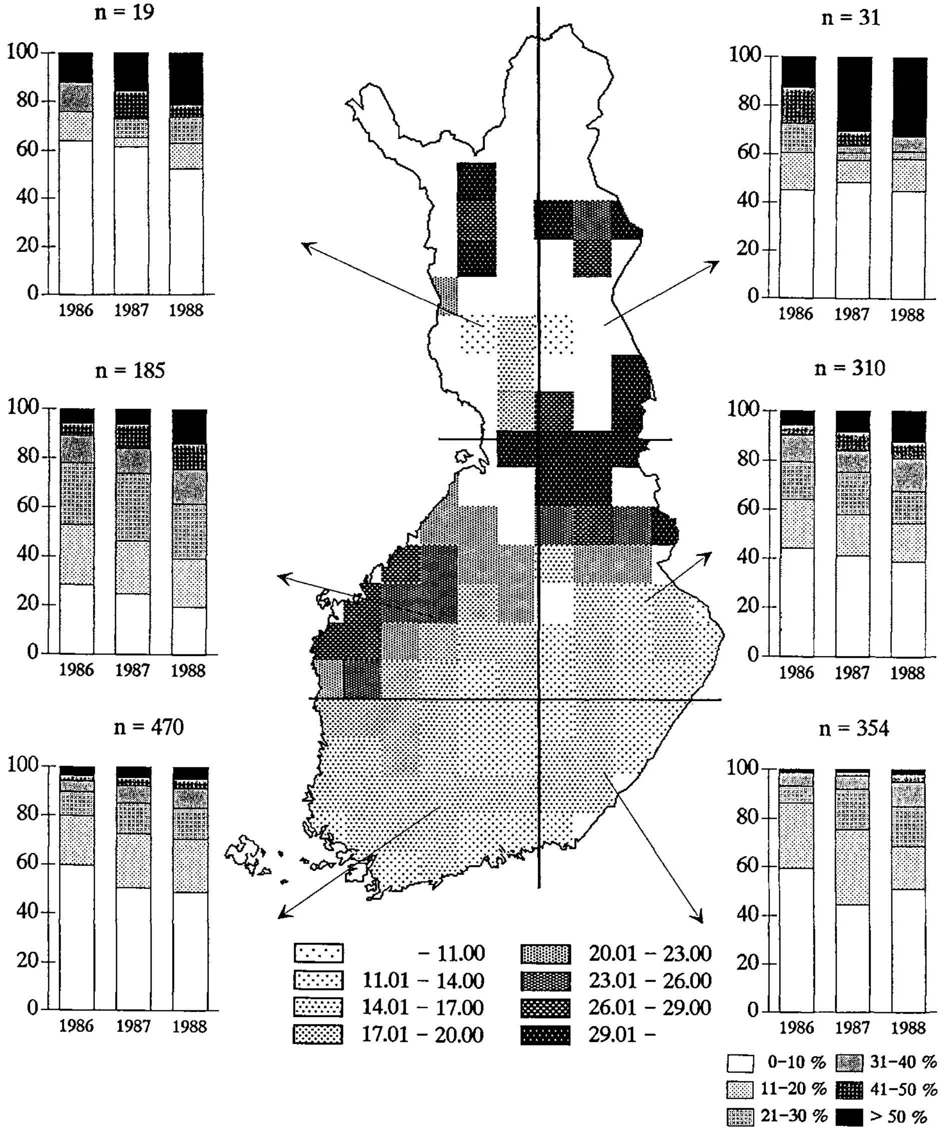


Fig. 12. Three-year averages (1986–88) for defoliation of spruce forests in Finland. Annual defoliation distributions in different parts of the country are presented by *bar diagrams*. See details in Fig. 9

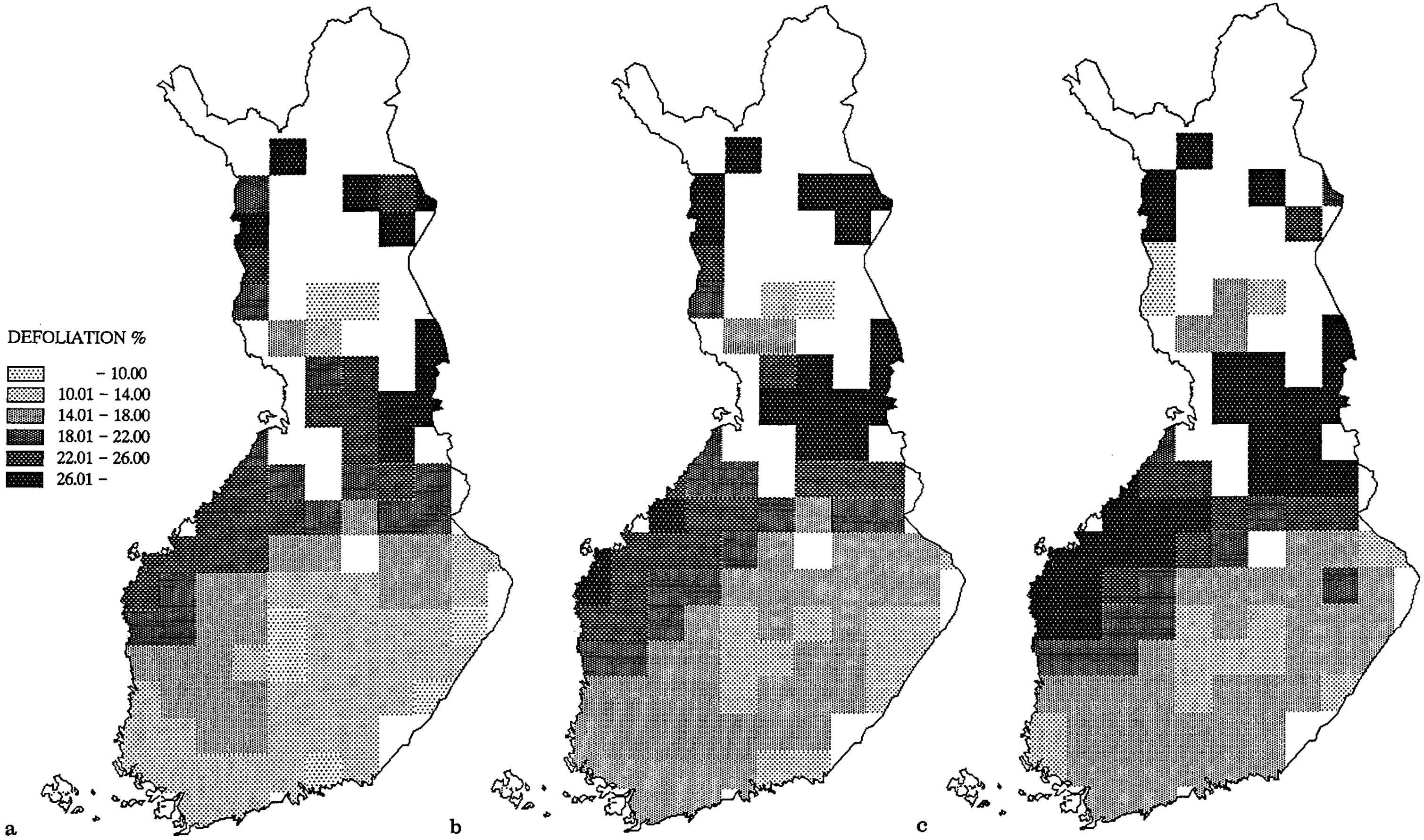


Fig. 13a–c. Defoliation of spruce in **a** 1986, **b** 1987, and **c** 1988. 50 × 50 km^2 grid averages are given

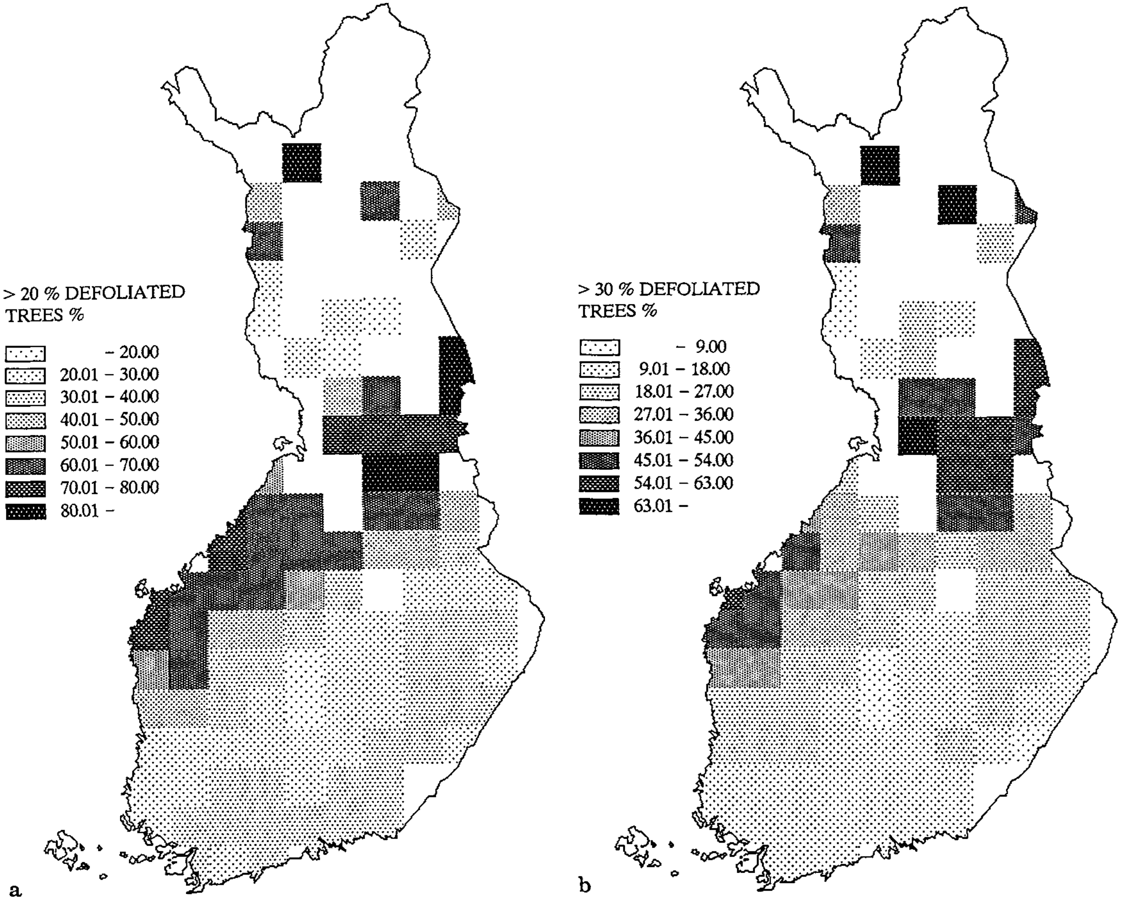


Fig. 14a, b. Defoliation of spruce as a proportion of **a** >20% and, **b** >30% defoliated trees out of all sample spruces in 50 × 50 km^2 grids. Data from 1988

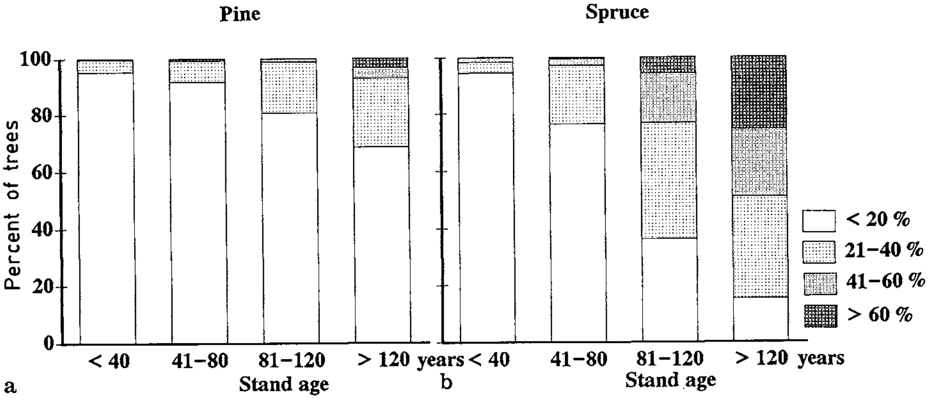


Fig. 15a, b. Frequency distributions of **a** pine and **b** spruce defoliation in stands of different age. Whole country, year 1988

A number of different factors affect the variation in the retention time of needles. The most important are the variation caused by geographical location, site type and stand age. The age differences between the years were statistically significant at the 5% risk level in all cases apart from spruce in northern Finland (Table 7). The direction of the changes in pine varied from year to year, and in different parts of the crown, in northern Finland. The number of needle age classes decreased for spruce but increased slightly for pine in southern Finland over time.

The geographical variation running from south to north was considerably greater than the year-to-year variation. On the average, the oldest needles on spruce in northern Finland were 3 years older than those in southern Finland. The corresponding value for pine was 1 year (Table 7).

Changes in the number of needle age classes also occur as the stand ages (Fig. 18). The age of the needles on pine initially increases slightly, reaches a maximum in southern Finland at the age of 41–60 years and in northern Finland at 61–80, and then starts to decrease slightly. A decreasing trend in the number of needle age classes on spruce as the stand age increases can be seen in both the southern and northern parts of the country. Both tree species had the greatest number of needle age classes on poor (xeric) sites, and the lowest number on fertile (mesic) ones (Fig. 19).

The variation in the number of needle age classes followed a similar trend as defoliation estimated for the same trees (Fig. 20). The dependence in pine was stronger than for spruce. (Pine: northern Finland $r_s = -0.375$, $n = 104$, southern Finland $r_s = -0.399$, $n = 1621$, spruce: northern Finland $r_s = -0.361$, $n = 99$, southern Finland $r_s = -0.169$, $n = 1098$, all: $P < 0.001$).

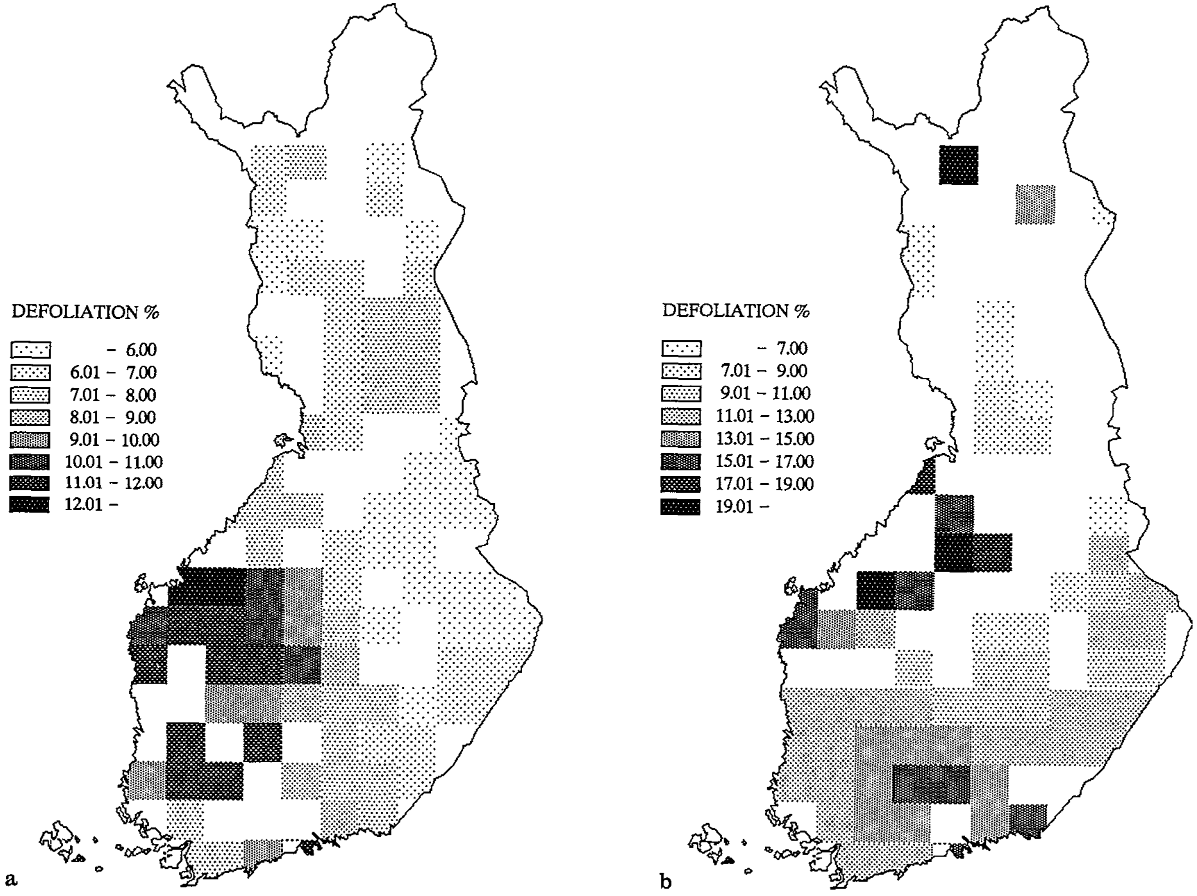


Fig. 16a, b. Defoliation of **a** pine and **b** spruce in stands younger than 80 years. $50 \times 50\ \mathrm{km}^2$ grid averages are given

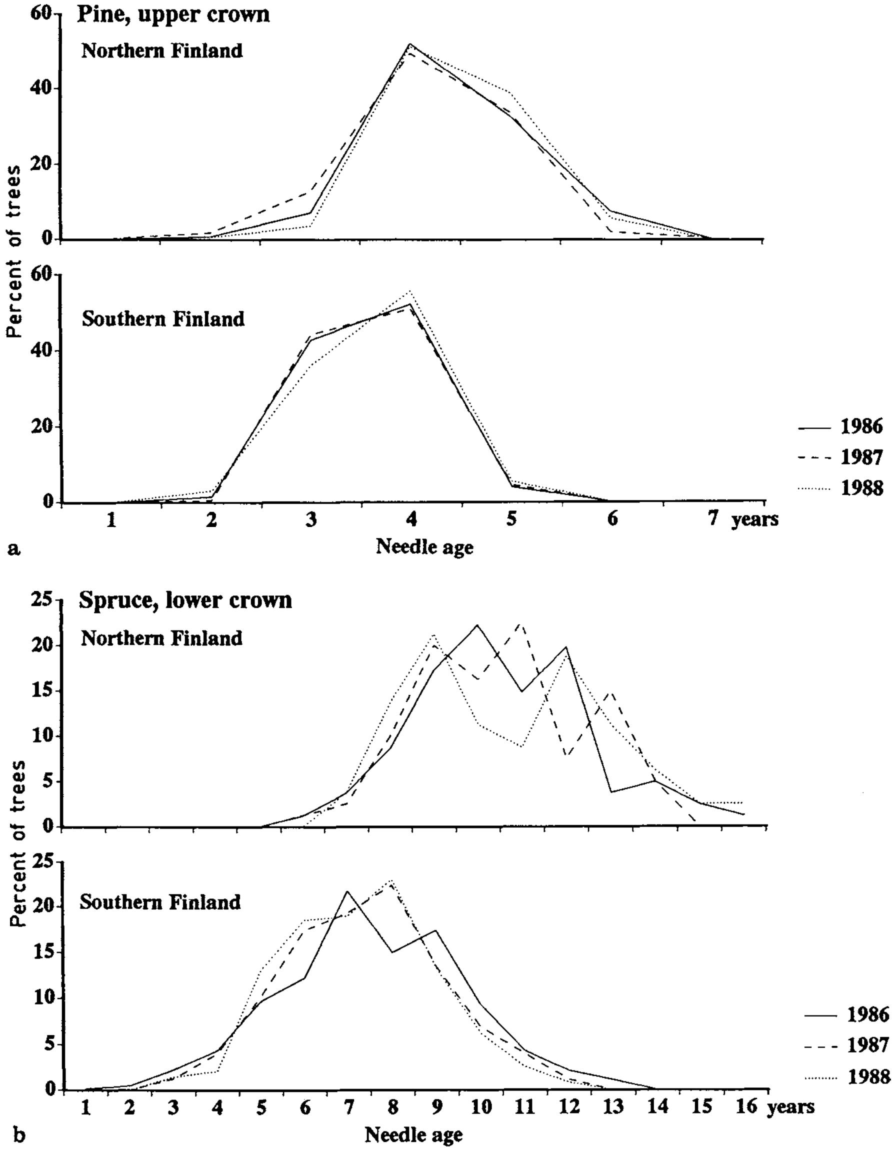


Fig. 17a, b. Needle age class distributions of **a** pine and **b** spruce during 1986–88. Number of trees as in Table 7

Regional and Temporal Variation in Needle Age Classes

Scots Pine. Pine has the greatest number of needle age classes (4.5–5) in NW and northern Lapland. There are less than four needle age classes in most parts of southern Finland. The lowest number (2–3) occurs along the SW coast (Fig. 21a).

The number of needle age classes decreased slightly in 1986–87 in Lapland and eastern parts of Finland, but returned to the previous level in 1987–88. In the latter

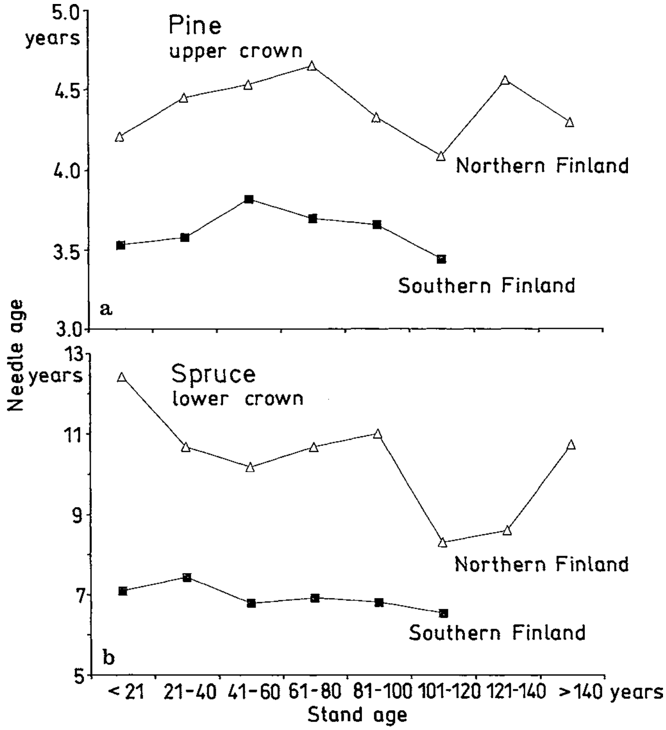


Fig. 18a,b. Relationship between needle age and stand age in **a** pine and **b** spruce in 1988. Northern and southern Finland are presented separately. Number of trees as in Fig. 20

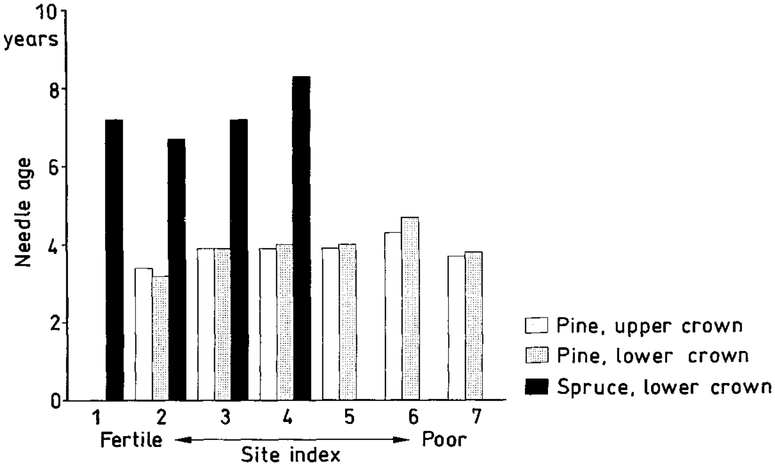


Fig. 19. Average needle age of pine and spruce growing on different site types. The site indexes form a nutrient and moisture gradient ranging from mesic (*fertile*) (*level 1*) to xeric (*poor*) (*level 7*) types. Number of trees as in Fig. 20 (whole country, 1988)

period the number of needle generations decreased along the western coast (Fig. 21a).

The number of needle age classes varied from year to year in the same way as defoliation in western Lapland (Figs. 9 and 21a). No synchronised variation between these variables was found in the other parts of the country.

Norway spruce. Spruce had the greatest number of needle age classes (10–11) in southern and western Lapland (Fig. 21b). The number of needle age classes was 6–9 in the other parts of northern Finland. In most parts of southern Finland the number was less than 6, the lowest number (4) being in southern Pohjanmaa.

The number of needle age classes slightly decreased during the 3-year period in all other regions except Lapland and SE Finland (Fig. 21b).

Table 7. Needle age classes (means and standard deviations) of pine and spruce in 1986–88 in northern and southern Finland (boundary 65° latitude). Years differing from each other at the risk level P = 0.05 (matched t-test) at least are connected with a line

Pine: lower crown

	Southern Finland n = 1524		Northern Finland n = 501	
	$\bar{x}$	SD	$\bar{x}$	SD
1986	3.40	0.68	4.55	0.85
1987	3.51	0.62	5.16	1.06
1988	3.59	0.78	4.80	0.77
3-yr mean	3.50	0.58	4.84	0.70

Pine: upper crown

	Southern Finland n = 1519		Northern Finland n = 514	
	$\bar{x}$	SD	$\bar{x}$	SD
1986	3.58	0.59	4.39	0.77
1987	3.59	0.59	4.20	0.83
1988	3.63	0.63	4.45	0.70
3-yr mean	3.60	0.47	4.35	0.58

Spruce: lower crown

	Southern Finland n = 619		Northern Finland n = 81	
	$\bar{x}$	SD	$\bar{x}$	SD
1986	7.57	2.09	10.54	1.98
1987	7.39	1.80	10.59	2.04
1988	7.28	1.71	10.84	2.45
3-yr mean	7.42	1.66	10.66	1.75

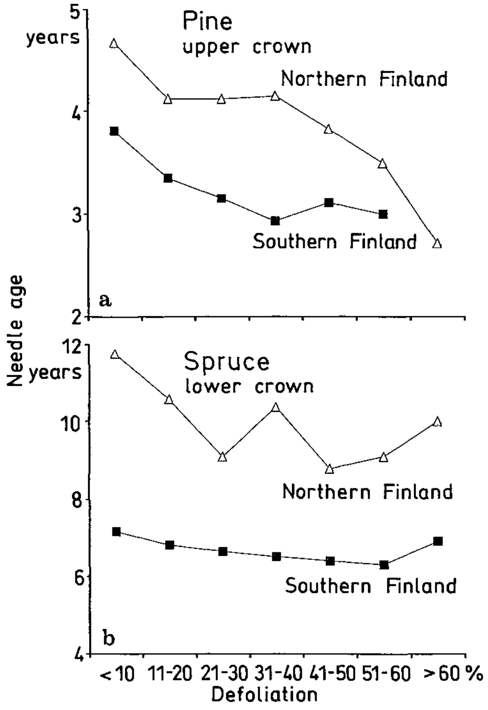


Fig. 20a, b. Relationship between needle age and defoliation of the same trees in **a** pine and **b** spruce in 1988. Northern and southern Finland are presented separately

The changes in defoliation (Fig. 12) and in needle age (Fig. 21b) are synchronised in southern and central Finland, apart from SE parts of the country. The increase in the amount of severely defoliated spruces in Lapland is not reflected in a change in the number of needle age classes.

Degeneration Symptoms

Branch Damage

Branch damage was recorded on about 40% of the pines and about 75% of the spruces in 1988. There was clear correlation between branch damage severity and defoliation (Fig. 22a). When defoliation exceeds 20%, dead branches and small openings in the crown, formed as the dead branches break off, were observed. When defoliation reached 41–50%, large openings were seen in the crown, and in trees suffering from over 50% defoliation many of the lateral branches were damaged. An increase in the severity of branch damage as defoliation increases was also shown in the age class 60 to 80-year-old forests (pine: $r_s = 0.667$, $n = 486$, spruce: $r_s = 0.815$, $n = 326$, both: $P < 0.001$).

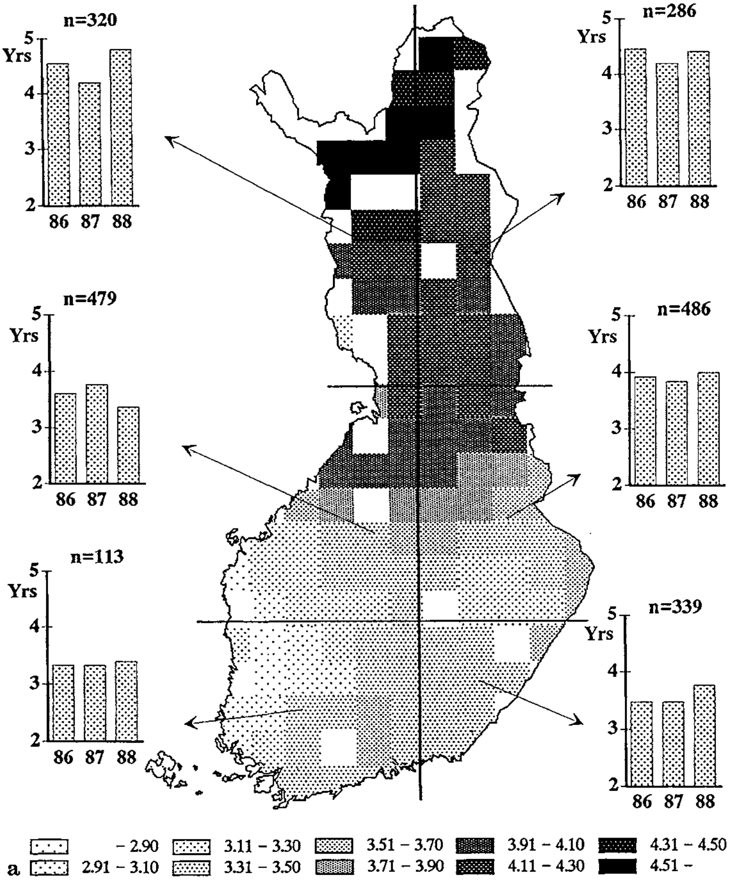


Fig. 21a,b. a Three-year averages (1986–88) for needle ages (years) of pine in Finland (50×50 km^2 grid averages). Annual means of needle ages are shown in bar diagrams in different parts of the country.

Secondary Branches in Spruce

The abundance of secondary shoots was positively correlated with defoliation (Fig. 22b). The proportion of secondary shoots was clearly smaller than that of primary shoots when defoliation was below 50%. However, the proportion of secondary shoots increased when defoliation exceeded 50%. The effect of stand age on the results was minimized by examining the relationship between the abundance of secondary branches and defoliation in the age class 60–80 years. A positive correlation was also found in this age ($r_s = 0.515$, $P < 0.001$, $n = 326$).

Pine Canker Fungus, *Ascocalyx abietina*

Ascocalyx abietina infection was found on pines in all parts of southern and central Finland in summer 1988. In Lapland it only occurred close to the eastern border (Fig. 23). Complete stands were marked with a brown shade in the most affected

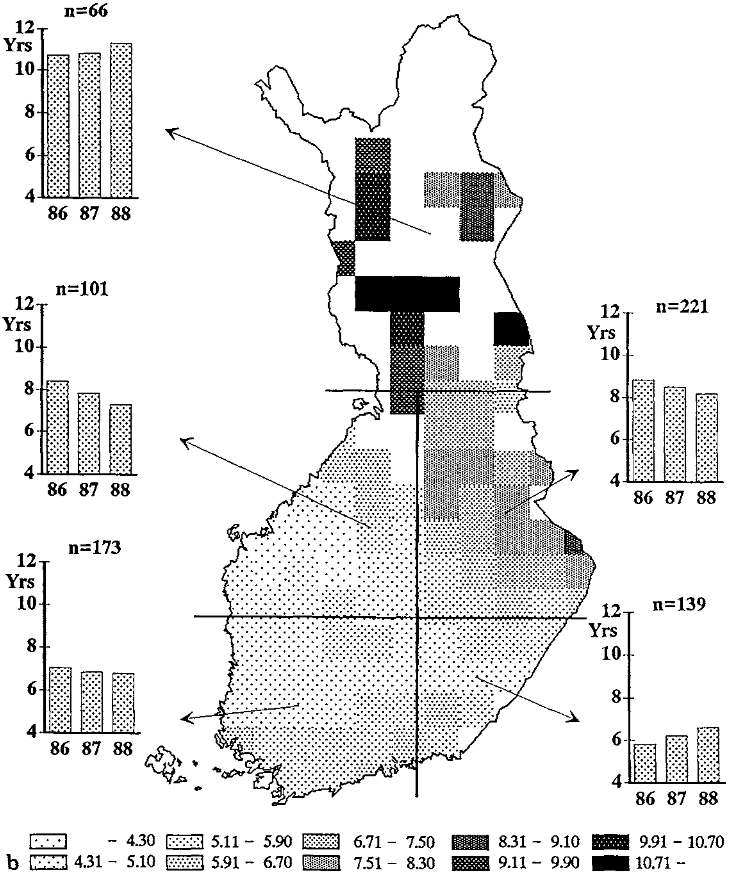


Fig. 21b. As **a** but for spruce

areas in western Finland, and needles killed by this pathogen were to be found throughout the crown.

Relationships Between Tree Variables and Other Ecological Parameters

Principal Component Analysis

The covariation between the environmental and tree variables was investigated using principal component analysis based on the correlation matrix (Table 8). The principal components are the numeric vectors explaining the most important variation gradients, and are independent of each other. They condense the multidimensional data into a form which is easier to analyse. This facilitates the formulation of research hypotheses.

Scots pine. The north-south variation in the variables is clearly condensed in the first principal component. This is most clearly shown by the high loading values for

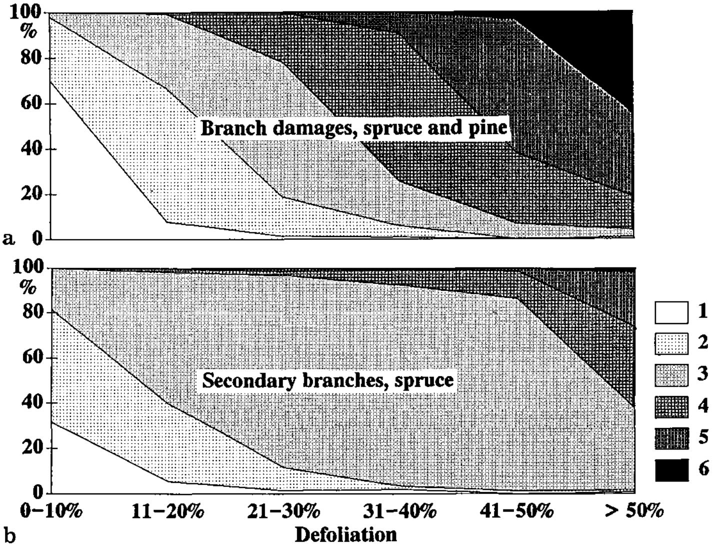


Fig. 22a, b. Defoliation in relation to some degeneration symptoms in 1988: **a** branch damages (pine and spruce) and **b** secondary branches (spruce). Y-axis: percent of trees. See explanation for legend codes in Table 1

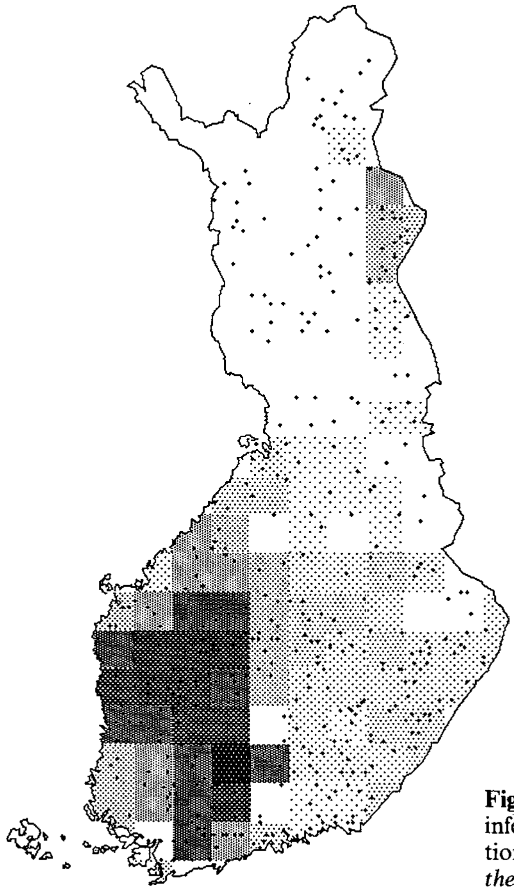


Fig. 23. Regional distribution of pine forests infected with *Ascocalyx abietina*. Observation points are marked with *dots*. The *darker the raster*, the more severe the epidemic

Table 8. Principal component analysis of the tree and stand variables. Loadings (absolute values > 0.250) are given for the first four components

a) Pine (n = 2030)	Principal components			
	I Latitude and age	II Site quality	III Needle loss	IV Exposition
Degree days	−0.848			
Stand age	0.679	0.391	0.319	
Fruticose lichens	0.708			
Altitude	0.738			
Needle age (upp. cr.)	0.531		−0.314	
Site type		0.585		−0.367
Scoliciosp. and algae	−0.440			−0.317
Diameter		0.690		
Defoliation (1988)		0.394	0.857	
3-yr change in defol.			0.673	
Foliose lichens		0.348		0.488
Exposition				0.751
Basal area		0.641		0.243
Variance explained (%)	22.4	15.4	11.8	8.8

b) Spruce (n = 1115)	Principal components			
	I Latitude and age	II Site quality	III Needle loss	IV Exposition
Degree days	−0.898			
Altitude	0.756	0.309		
Needle age (lower.cr.)	0.640		−0.427	
Stand age	0.722		0.255	
Diameter		0.742		
Stand basal area	−0.285	0.475	0.268	0.398
Scoliciosp. and algae	−0.516	0.408		
Site type	−0.443	0.455		
Defoliation (1988)	0.470		0.689	
3-yr change in defol.			0.680	−0.396
Exposition				0.706
Fruticose lichens	0.502			0.437
Foliose lichens		−0.580	0.281	0.283
Variance explained (%)	26.0	13.4	11.6	8.7

the temperature sum and latitude on this component. Fruticose lichens, needle and stand age also receive high positive loadings. The southern nature of green algae is also seen in this component.

The second principal component is strongly associated with site factors. The more fertile the site, the taller, older and more defoliated are the trees. Foliose lichens also benefit from sites of this sort.

The third principal component reflects the covariation of needle age and defoliation. The increase in defoliation in the 3-year monitoring period appears to be centred on old and defoliated trees.

Exposition (effect of a southern slope) and foliose stem lichens have the highest positive loadings on the fourth principal component. Southern slopes have been classified as being less fertile than northern ones, and the trees growing there have less green algae on stems.

Norway spruce. The first principal component for the spruce data is almost identical to that of pine, i.e. describing the north-south gradient. Defoliation of spruce increases more clearly than that of pine to the north. The site types have been classified as being less fertile in the north than in the south.

The second principal component describes the fertility of the site. The more fertile the site, the larger are the trees, the more green algae to be found growing on stems, and the less foliose lichens.

The third principal component is associated with the variation in needle biomass which is independent of latitude and site. Defoliation and changes in defoliation have the highest positive loadings. Needle age receives a negative loading.

The fourth principal component depicts the exposition of the site. In spruce this variation is also associated with a more abundant occurrence of fruticose lichens on southern slopes than on northern slopes. The negative loading of the change in defoliation demonstrates the deterioration in tree condition especially on northern slopes.

Discussion

Confidence of the Defoliation Results

Most of the conifers sampled have been classified into defoliation class 0. However, there is error variation in the number of trees in class 0, as demonstrated by the frequency distributions of the test trees. According to the confidence test, the proportion of trees with over 30% defoliation was estimated consistently for pine and, omitting observer C (Lapland), also for spruce. We can thus assume that the most severely defoliated forests have therefore been located rather reliably.

According to the results for the test-trees, the regional distributions of defoliation for spruce are independent of the observers, when Lapland is excluded. The most severely defoliated trees are located in Lapland in the present survey. The spruces growing in Lapland have narrow, tapering crowns (ssp. *obovata*) being adapted to ice and snow accumulation. This makes their defoliation assessment difficult. The results of the confidence tests indicate that their defoliation degree could be classified as being even higher. If the results for Lapland are made compatible with those for the rest of the country, then the mean defoliation degree for Lapland should be one class higher than the presented figure. According to the confidence test, temporal change in defoliation can be demonstrated rather reliably for spruce.

Since the regional defoliation results for pine, as well as the temporal differences, also contain an unknown amount of error variation, care has to be taken in drawing conclusions. Especially the reliability of the temporal changes for pine cannot be verified with any certainty because the test material was too restricted. The situation in Lapland is the same as for spruce: compatible regional means are about half a class higher than the presented figures. There is also uncertainty in the interpretation of the regional differences in southern Finland in the east-west direction. The confidence test reveals that there would be slightly more defoliated pines in the area surveyed by observer D (southern and SE Finland) than the results indicate.

According to the tree-specific analyses, over 80% of the observations are reliable, with a variation interval of one class (±10%). In the extreme, the margin of error of this sort could be as much as 20% needle loss, e.g. defoliation of 11 and 30% could be coded in classes 1 and 2.

The amount of needle biomass can be estimated by means of the tree's allometric ratios or using, for example, the cross-sectional area of the sapwood (Kaipiainen and Hari 1985). In the future, an attempt will be made to change from subjective defoliation estimation to indirect measurement of needle biomass. Changes in the amount of needle biomass would then be used as an indicator of tree vitality.

According to McKay (1988), maximum needle age is not a good measure of their retention time because it does not take into account the loss of younger needle classes. This is especially the case with spruce, which bears rather a large number of age classes and sheds needles from different age classes at the same time. It would be better to count the number of needle age classes on the branches in the upper crown. The number of needle age classes on the lower branches is affected by many of the factors that are related to stand density.

Factors Affecting Forest Vitality

Tree condition, estimated on the basis of needle loss and number of needle age classes, deteriorated in Finland during the 3-year monitoring period. However, interfering factors were different in different years and in different parts of the country.

Most of the environmental factors which affect the tree variables are strongly intercorrelated (PCA, Table 8). A particular variable measured on a tree can include considerable covariation with a single environmental factor. There may also be other, unmeasured factors or interaction of different factors affecting tree vitality. It is thus difficult to elucidate the underlying causal structure.

Age and Latitude

The most severely defoliated pine and spruce forests are located in Lapland. The northern aspect, which in this study is indicated by temperature sum and altitude

(PCA), has an effect similar to that of age since the age of forests in Finland increases on moving northwards. According to Swedish inventories, defoliation of conifers is also greatest in the old stands in the north and at high altitudes (Bengtson and Wulff 1987; Andersson 1988). The severe climate especially affects defoliation in the north. Trees growing at the extremes of their distribution range are, however, sensitive to even small increases in stress factors such as air pollutants (Huttunen et al. this Vol.). Air pollution can also speed up tree degeneration, which normally increases with age, but it is difficult to distinguish the effect of air pollution from other factors.

Tree ageing does not explain all the variation in vitality. A deterioration in tree condition was also found in young forests in southern Finland.

Weather Factors

The weather conditions during the monitoring period (1986–1988) and preceding period (1984–1985) have been rather untypical (Anon. 1984–1988).

The first summer of the survey (1986) was exceptionally warm and dry. Deciduous trees growing on dry, rocky sites turned yellow and shed their leaves as early as July. Winter 1986–87 was the coldest of the century and, especially in northern Finland, there was very little snow in early winter. The following summer 1987 was cool and wet. Early summer 1988 was the warmest and driest of the century (Anon. 1984–1988). In 1988 deciduous trees growing on dry sites again shed their leaves in the middle of the growing season. The exceptionally severe weather conditions have undoubtedly stressed trees throughout Finland.

Ascocalyx abietina

Condition of pines decreased in all three years in western Finland. This was expressed as both an increase in defoliation and a reduction in the number of needle age classes in the 1988 survey in the area, where an epidemic of *Ascocalyx abietina* was the severest. The epidemic broke out in western Finland in 1982 (Uotila 1986), and again in 1988 as a result of the unfavourable weather conditions (cool, wet summer). A more detailed evaluation of this epidemic is given by Nevalainen and Yli-Kojola (this Vol.). Air pollution is known to lower the resistance of trees against disease, but it is extremely difficult to separate its effect from that of other factors (Vuorinen this Vol.).

Air Pollution

The deposition of sulphur and nitrogen is unevenly distributed in Finland (see this Vol.). The greatest loads are in southern and SE Finland, where most of the industry is situated, and which is subject to the highest long-range transboundary air pollutants. It was not possible to demonstrate any clear relationship between the regional distribution of defoliation and deposition levels. However, the susceptibility of the soil to acidification may have an effect on the defoliation degree. Young, defoliated pine stands are growing on nutrient-poor soils in western Finland that contain high levels of weatherable aluminium (Raitio this Vol.). Defoliation of pine increased in this area the most during the survey. The NE parts of Finland have a moderately high levels of sulphur deposition (Tuovinen et al., this Vol.), which may exceed the low resistance of ecosystems in the north.

Defoliation on spruce increased in the fell district of Kainuu and in Pohjanmaa, where there were also young trees suffering from defoliation. The forests in these areas are exposed to emissions from the industrial centres of Oulu and Raahe in the west, and sulphur emissions coming from the district of Kostamus (U.S.S.R.) in the east. The southern parts of Finland are subjected to the highest air pollution loads. Defoliation of young spruce forests were the greatest in this area.

Defoliation on both spruce and pine increased the most in southern Pohjanmaa. Needle age was also lower in this area. Most of Finland's 5600 fur farms are to be found in southern Pohjanmaa. Volatilization of ammonia from the urine and faeces of the animals has been shown to cause nutrient disturbances in trees on a local scale (Ferm et al. this Vol.). There is reason to believe that emissions from fur farms may have an effect on the condition of forests also over a more extensive area. The coastal location may also be expected to result in the poor condition of spruce along the Gulf of Bothnia.

Conclusions

Defoliation of conifers increased during the 3-year monitoring period (1986–88). The defoliated trees also had other degeneration symptoms. The deterioration in the condition of spruce was greatest in central parts of Finland and in Lapland. Defoliation on pine increased the most in western Finland. The areas with the greatest changes varied from year to year. The results of the 3-year survey do not justify drawing conclusions about whether the deterioration in tree condition is due to long-term changes or represents merely fluctuations in the forest ecosystem. For example, a long-term monitoring study has indicated that there are considerable year-to-year fluctuations in the amount of the annual needle litterfall of pine (Fig. 4).

Defoliation expresses the overall vitality of the tree, and can be caused by many different factors. It can be considered to be a multi-stress symptom. Of the single stand parameters, age correlated the highest with defoliation. The effects of air pollutants on tree condition are being investigated in experiments carried out under controlled conditions. The results of such experiments should be related to the distributions and time series observed in the field. The study of causality should be intensified using a wide range of diagnostic studies.

Although the regional distribution of forests suffering from defoliation did not correlate with the modelled deposition distribution, there are associations between air pollution levels and the defoliation of young forests in southern Finland. Some consistency was found between the areas where defoliation increased and areas hypothetically sensitive to soil acidification. The proposed critical levels for nitrogen and sulphur deposition (Anon. 1988) are being exceeded over almost the whole country, the first symptoms of acidification have been observed in the surface waters (Forsius et al. this Vol.), and the most sensitive bioindicators (epiphytic lichens; Kuusinen et al. this Vol.) have reacted, demonstrating that changes are taking place in the condition of forest ecosystems. Unless a reduction in emissions is achieved, the risk of damage to forests from air pollution will definitely increase over time.

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The Occurrence of Abiotic and Biotic Damage and its Relation to Defoliation (Needle Loss) of Conifers in Finland (1985–1988)

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Summary

The data from permanent and temporary plots of the 8th National Forest Inventory were used in this study. Some form of abiotic or biotic damage was registered in roughly one third of the stands or sample trees. The proportion of damage that greatly reduced the stand quality or was likely to cause the death of trees was considerably low, in the range of 1–3%. In Lapland the frequency of damage (broken stems, crown injuries etc.) was higher than in southern Finland. Damage caused by abiotic factors and fungi, especially *Ascocalyx abietina* were the most important types of identified damage. Damage frequencies were higher in defoliated than non-defoliated conifers, but most of the observed defoliation could not be directly attributed to specific biotic or abiotic causes. *Ascocalyx* caused some increase in defoliation in western Finland. Other biotic/abiotic damage was only locally important in this respect.

Introduction

In Europe the overall vitality of forests on a large scale is monitored mainly on the basis of relative loss of needle biomass (needle loss, defoliation, crown thinning, Kronenverlichtung) and discoloration. Most of the published regional or nationwide results concerning forest damage are based on the needle loss symptom, the definition between a "damaged" or "healthy" tree varying from 10 to 20%. Relatively little attention has been paid to the occurrence of biotic or abiotic damage. This situation might have been influenced by the general assumption that air pollution effects predispose the trees to insect, fungal or frost attack and these classical types of damage are therefore of secondary nature. However, such damage has two kinds of interactions with different measures of forest vitality: firstly, the positive feed-back mechanisms, leading to repeated attacks of pests or pathogens to more and more weakened hosts, or to increased susceptibility, e.g. to frost. Secondly, these may cause mimicking symptoms that are incorrectly attributed to aerial pollutants. Defoliation (needle loss) itself, although a usable variable for monitoring the overall vitality of forests, is a very unspecific indicator, being greatly influenced by tree age, genetic factors, shading and many abiotic

Kauppi et al. (Eds).
Acidification in Finland

factors, e.g. wind (Westman and Lesinski 1986). The rapid changes in forest condition have in some cases been attributed to biotic or abiotic damage (Strelezki 1985; Roloff 1985; Hütte 1986; Innes et al. 1986). Therefore results concerning forest damage should be analyzed very thoroughly. Under relatively low pollution levels this kind of "differential analysis" is extremely important.

Some types of pathogens are, mostly indirectly, favoured by host predisposition caused by stress agents, including anthropogenic influences. Rot fungi, e.g. *Heterobasidion annosum* Bref. (Domanski 1978; James et al. 1980a, 1980b) and some needle pathogens, e.g. *Rhizosphaera kalkhoffii* Bubak (Tanaka 1980) are among these. Pathogenic species of needle infecting fungi may also be inhibited by high pollution levels. On the other hand, the damage caused by biotrophic pathogens, such as rust fungi, e.g. *Cronartium* species (Linzon 1971; Grzywacz and Wazny 1973) or mildews (Hibben and Walker 1966) are reported to be negatively influenced by, at least, high average concentrations of pollutants. Review articles on the influence of air pollutants on pathogenic fungi have been made e.g. by Heagle (1973); Horn (1985); Smith (1981); Nevalainen and Liukkonen (1988).

Pest outbreaks which were attributed to the influence of pollutants (smoke) were recorded in Europe more than 100 years ago, as reviewed by Flückiger et al. (1987). Bark beetles and some bugs, aphids, sawflies and tortricid species may be favoured, mostly because of the altered metabolism of their hosts (Wenzel and Ohnesorge 1961; Ranft 1968; Cobb et al. 1968; Stark et al. 1968; Charles and Willemant 1977; Baltensweiler 1983; Braun and Flückiger 1984; Führer 1985; Heliövaara and Väisänen 1986; Heliövaara and Väisänen this Vol.).

There is also increasing evidence that resistance of trees to winter-time desiccation or to frost is decreased by air pollution (Huttunen et al. 1981a,b; Feiler 1985; Davidson et al. 1987).

On the other hand, there is no direct evidence of increasing susceptibility to wind or snow damage. Routine applications of fertilizers may increase the risk of windfall (e.g. Laiho 1987), but effects of increased nitrogen inputs by air pollution have not been studied in this respect. Frühwald et al. (1988) were unable to detect differences in wood density and elastomechanical properties of "healthy looking" and "declining" Norway spruces in Sweden.

Most of the results presented above have been obtained in industrial regions with relatively large concentrations of pollutants. There is very little field evidence under low pollution levels to support most of the presented predisposition hypotheses. It is very difficult to prove direct cause-effect relationships, since pests and pathogens are greatly influenced by climate, topography and forestry practices (see e.g. Roloff 1985; Baltensweiler 1985).

Using the information from broad surveys of forest condition – an epidemiological approach – it is possible to uncover large spatial or temporal patterns. In Finland, some forms of damage were recorded nationwide for the first time in the 7th National Forest Inventory during 1977–84. At the stand level, wind, snow, elk and pine-twisting rust (*Melampsora pinitorqua* Rostr.) damage, as well as the occurrence of decay and some other forms of damage were registered. At the tree level decay in its various forms, dry or broken tops and resin tops of pine caused by *Cronartium* sp. were recorded.

Different types of damage are recorded at stand, and tree, level in national forest inventories e.g. in Sweden (Instruktion 1984) and Austria (Jahresberichte 1987). In the ECE Manual (Manual on Methodologies 1988) it was proposed that different forms of abiotic and biotic damages should be recorded. Special inventories on forest damage usually do record biotic damage (Schöpfer 1985).

The aim of the present study was to describe the extent, and possible spatial and temporal fluctuations in the occurrence of different forms of biotic or abiotic damage. Further, their associations with analyses of forest vitality based on "needle loss", an in itself very inexact indicator of forest condition, were analysed.

Material and Methods

Damage Assessments on the Permanent Sample Plots of the 8th National Forest Inventory

During the years 1985–86, a network of 3009 permanent sample plots was established, covering the whole of Finland systematically. Permanent plots were used in order to obtain an overall picture of the vitality of forests of the country and to produce information especially about the changes in forests, that cannot be obtained from traditional inventories using temporary plots.

Sampling units are four-plot clusters in a 16 × 16 km grid with a 400-m distance between circle plots (0.1–0.3 ha each) in southern Finland, and tree-plot clusters in a 32 × 24 km grid in northern Finland (plots 600 m apart). This network will be measured at 5-year intervals and the next results will be available in 1990.

This report describes the occurrence of abiotic and biotic damage on forest land. Forest land is defined as land where the mean annual production of timber is at least 1 m^3 ha^{-1}. A total of 2506 plots and 7283 sample trees with diameter at breast height (dbh) over 10.5 cm were assessed on forest land during 1985–86.

Injuries (symptom and cause) and their apparent severity (degree of damage) were registered for individual sample trees and at the level of a stand. The codes for registering damages in permanent sample plots are presented in Appendix 1. In addition, defoliation was also registered for coniferous sample trees (Norway spruce and Scots pine) in 10%-classes. For stands, defoliation was coded according to the mean defoliation class and the percentage of affected trees. Defoliation is not treated in detail in this chapter, since the results from the first inventory of permanent plots have already been published (Jukola-Sulonen et al. 1987).

From the complete network about 600 plots, referred to as extensive plots, were systematically subsampled. The first plot of each tract was selected, excluding every tenth plot and treeless plots. For biotic and abiotic damage assessments, the data from 389 mineral soil plots comprising 4037 trees (2096 Scots pines, 1333

Norway spruces and 608 deciduous trees) was used in this study. On these plots, studies of the variables which describe the overall vitality of forests (defoliation, number of needle years, the amount of branch damage and secondary branches etc.) were carried out in 1986–1988. The damage recording was principally the same as on all 2506 forest land plots, although more than one type of damage was recorded for each tree and some additional causal agents were registered. In addition, damage coding systems were slightly different in successive years, e.g. male flowering was coded as a damage symptom in 1986–87, but not in 1988. Damage assessments were made from dominant and co-dominant sample and tally trees. Defoliation was assessed for conifers and deciduous trees, but in the present study we used only the defoliation data for conifers (Norway spruce and Scots pine), because defoliation of deciduous trees was not assessed in all the permanent plots during 1985–86. The network of sample plots and details of different measurements on forest vitality as well as the defoliation results from the extensive level are presented by Jukola-Sulonen et al. this Volume.

In addition, a number of plots were checked by specialists in forest pathology and entomology. The chosen plots were those showing signs of defoliation or severe damage, or those with damage caused by unidentified factors. Also all the extensive level plots in southern Finland were surveyed in 1987. Altogether 4715 trees (4016 conifers) and 588 plots were inspected during 1987–1988 in Southern Finland. Special variables assessed on these plots were, for example the degree of defoliation caused by abiotic factors, fungi or insects, the identification of wood-rotting fungi, if present, and a detailed analysis of the causal agents of different symptoms.

Survey of the Temporary Sample Plots Used in the 8th National Forest Inventory

The 8th National Forest Inventory with temporary sample plots is being carried out in South Finland. Sampling units are 21-plot clusters in a 8 × 7 km grid, with a 200-m distance between plots. Three of the plots in each cluster are sample tree plots, while on the rest of the plots only standwise damage assessments are made. During 1986–88 about 20,500 sample plots and some 19,000 sample trees, dbh more than 10.5 cm, were measured on forest land. The area covered by temporary plots by 1988 is nearly 5.5 million hectares (27% of the total forest land). It is possible to classify this large data set into various classes, for example according to land (soil use) classes, forest types, development classes, tree species, age classes etc. The damage on these plots has been described in the same way as on permanent sample plots. Together the permanent and temporary plots enable two separate estimates of damage to be made and compared in southern Finland. The inventory areas, as well as the separation between the northern and southern parts of the country in the permanent plots, are presented in Fig. 1. Comparable results from permanent and temporary plots are available from areas 0–9 of Fig. 1.

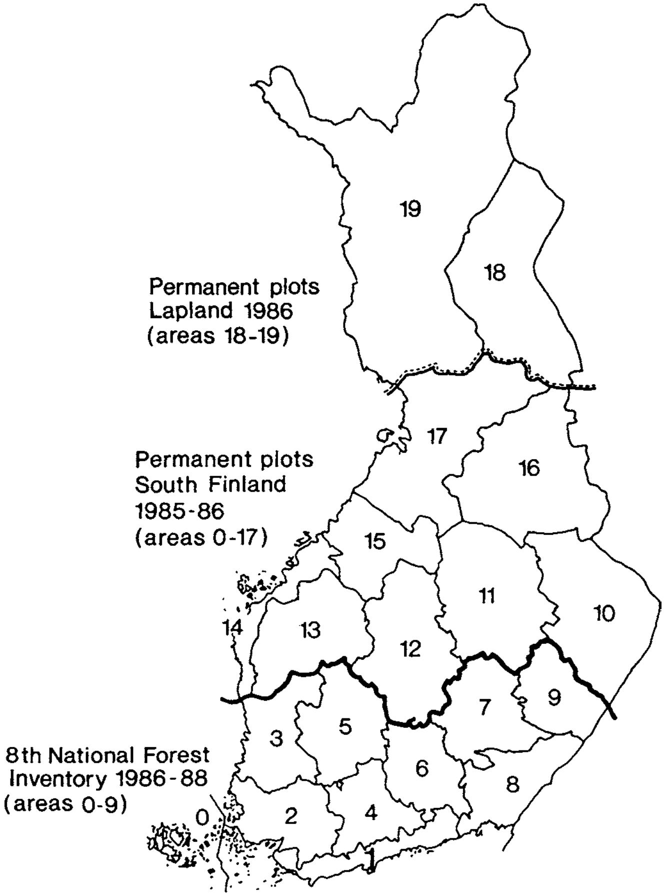

Fig. 1. Inventory areas of the 8th National Forest Inventory. Permanent plots cover the whole country systematically. Areas 0–17 (south Finland) had a different network than areas 18–19 (Lapland). Temporary plots were measured in areas 0–9 in southern Finland during 1986–88

Results and Discussion

Occurrence of Biotic and Abiotic Damage

On permanent sample plots during 1985–86 in the whole country, damage occurred on 50.6% of the total forest land area (Fig. 2). In Lapland (areas 18–19 of Fig. 1) some form of damage was registered on 74.2% and in south Finland on 41.1% of the forest land. Most of the damage expressed in Fig. 2. is areas with slight damage, where the signs of injury observed were unlikely to have effects on stand quality. In the rest of the cases, stand quality or the health status of the stand were more or less decreased. In south Finland, the frequency of damage that

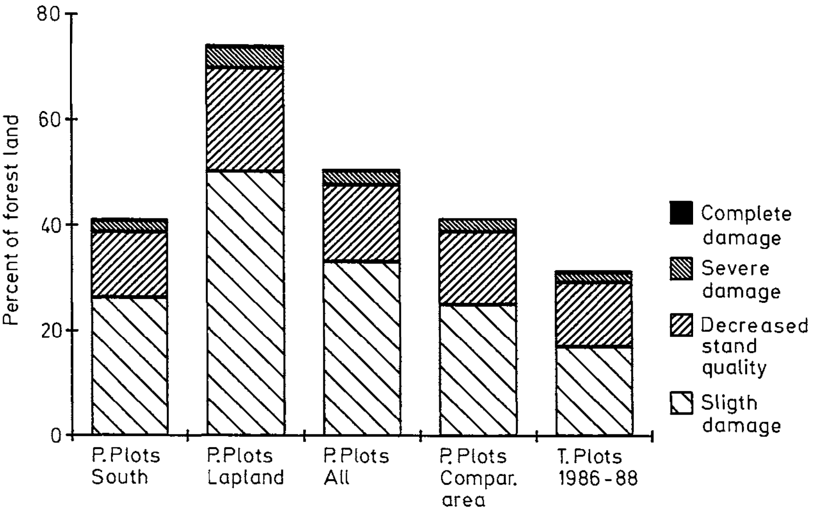

Fig. 2. Proportion of plots with some degree of damage in the permanent and temporary plots of the 8th National Forest Inventory. Standwise estimations. Source of data: *P.plots* permanent plots; *south* southern Finland; *T.plots* temporary plots; *P.plots compar. area* permanent plots on the area comparable to the area of temporary plots (areas 0–9 of Fig. 1). For degrees of damage, see Appendix 1

decreases stand quality or tree vigour was 14.8% and in Lapland 24.0%, respectively. The area of severely damaged forest land was 2.6% (stand quality decreased more, or the development class of the stand was changed). The proportion of completely damaged stands (stands requiring immediate artificial regeneration) was 0.1–0.3% of the total forest land area. In the so far inventoried temporary plots the damaged area has decreased from 41.5% to 31.5%, compared to the result from the permanent plots of the same area. Of these, significant damages occurred on 16.4% and 14.5% of the forest area, respectively.

While damage to individual trees may be severe, its impact on a population or a stand of trees may be less. Separate assessments on these two levels are therefore necessary. Figure 3 presents the occurrence and degree of damage to trees on forest land. The results cover dominant, co-dominant and dominated trees with diameter at breast height (dbh) over 10.5 cm. Nationwide, 36.9% of sample trees showed some damage, 30.5% in south Finland and 60.6% in Lapland. 1–3% of trees showed severe damage (damage class 3). Comparison in the same area between permanent and temporary sample plots shows a reduction of 6.7% in the number of damaged trees from 1985 till 1986–88, which has happened mainly in the share of slight damages.

Figures 4 and 5 illustrate the distributions of different symptom classes on forest land on the stand and sample tree level. Needle damage and different crown and stem injuries were the most commonly observed types of damage, at least at the tree level. The occurrence of dead, broken and fallen trees and the occurrence of crown injuries was greater in Lapland, as well as the decay frequency at the

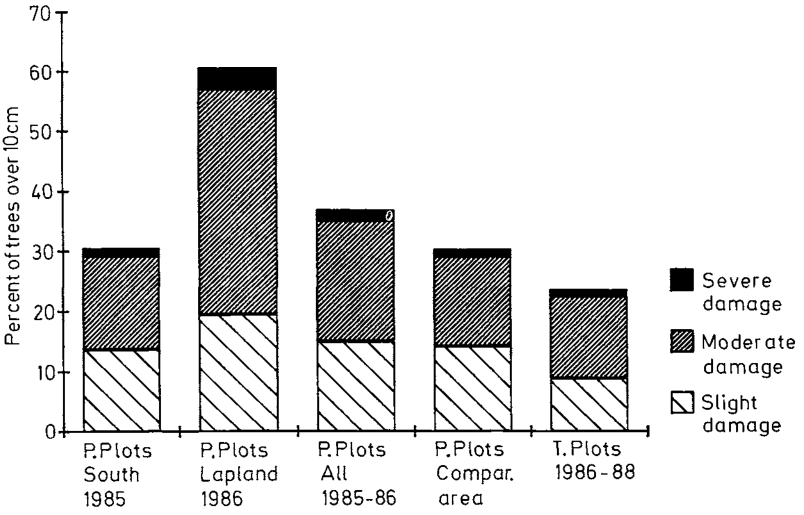

Fig. 3. Distribution of degrees of damage in the sample trees (dbh over 10.5 cm) in the permanent and temporary plots of the 8th National Forest Inventory. For explanations of different inventories see Fig. 2

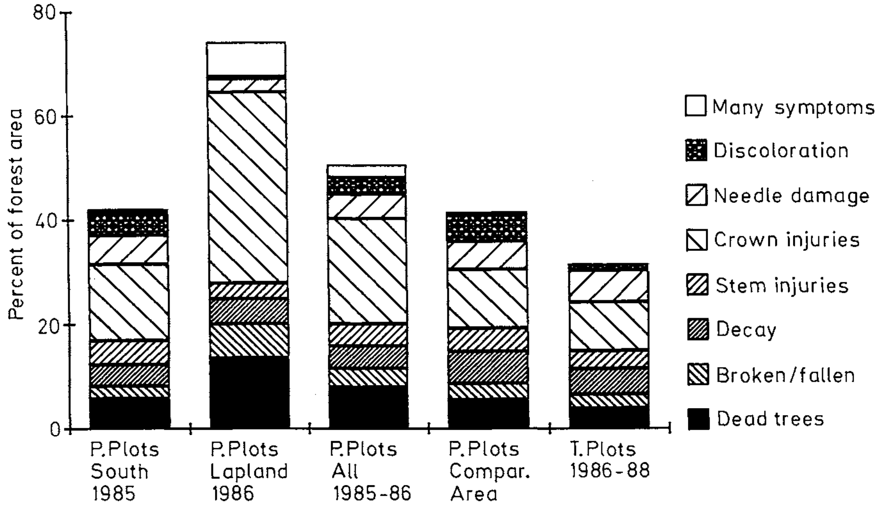

Fig. 4. Occurrence of damage symptoms in the permanent and temporary plots of the 8th National Forest Inventory. Standwise estimations. For explanations of different inventories see Fig. 2

sample tree level. The frequency of stands with many different symptoms due to age, excessive competition and so on, was also greater there. Discoloration, on the other hand, was more common in southern Finland in 1985. At the tree level, the frequency of dead trees was 0.5, 2.2 and 0.4% (on the permanent plots in southern Finland, in Lapland and on the so far inventoried temporary plots, respectively).

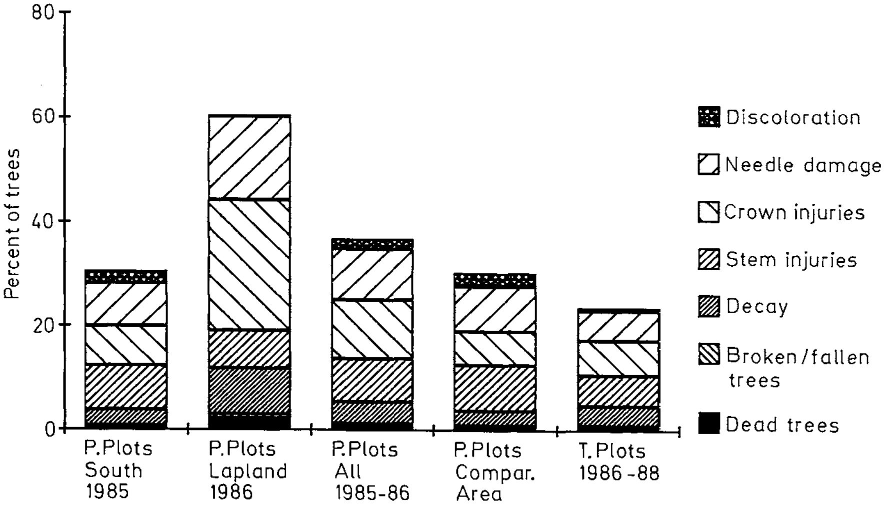

Fig. 5. Occurrence of damage symptoms in the permanent and temporary plots of the 8th National Forest Inventory. Sample trees with dbh over 10.5 cm. For explanations of different inventories see Fig. 2

For decay, the corresponding values were 3.0, 8.8 and 3.9%. The reduction in the amount of damages from permanent plots 1985–86 compared to temporary plots 1986–88 has mainly happened in the occurrence of crown injuries, needle damage and discoloration.

Fungi and abiotic factors were the most important of the identified causal agents on permanent and temporary plots (Figs. 6 and 7). On permanent plots, *Cronartium* damage was present in 3.3 to 7.0% of the stands (South Finland and Lapland, respectively). *Ascocalyx abietina* and other fungi were present in 8.4 and 9.2% of the plots. Signs of injury caused by wind were noted on 1.3/6.6%, damage by snow in 1.0/12.2% and by other abiotic factors in 6.7/4.4% of plots. Insect damage was present only in 1.7 and 1.3% of the stands (southern Finland and Lapland). At the tree level the presence of all these causal agents was somewhat lower.

Of the nearly 5.5 million ha covered by temporary plots during 1986–88, 1.7 million ha (31.5% of inventoried forest land) showed signs of damage – 925,000 ha of this was slight damage, in 670,000 ha stand quality was decreased, 98,000 ha had severe damage and 22,000 ha complete damage. The distribution of different causal agents in hectares in the 1986–88 surveyed area in south Finland is presented in Table 1.

Due to the slightly different coding systems at the extensive level plots, one must be cautious when comparing damage results obtained in 1986–1988 in these plots. As a mean, the proportions of different groups of causal agents at this level were as follows: not identified 37.7%, abiotic factors 1.3%, competition between trees 3.6%, damage caused by man 0.2%, mammals 0.1%, insects 5.0% and fungi

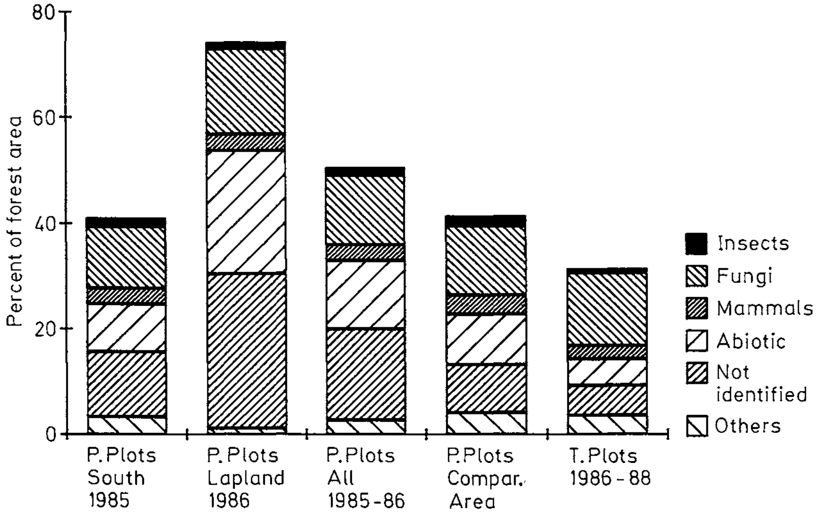

Fig. 6. Occurrence of different groups of causal agents in the permanent and temporary plots of the 8th National Forest Inventory. Standwise estimations. For explanations of different inventories see Fig. 2 and Appendix 1

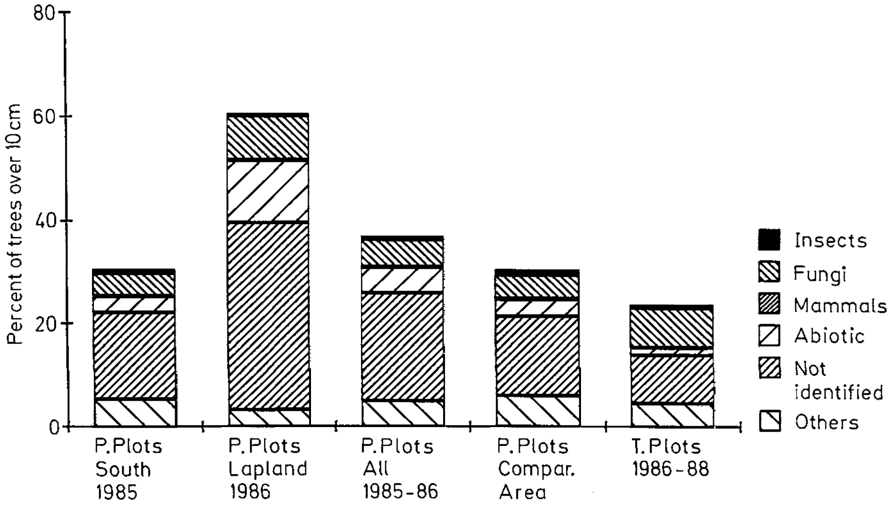

Fig. 7. Occurrence of different groups of causal agents in the permanent and temporary plots of the 8th National Forest Inventory. Sample trees with dbh over 10.5 cm. For explanations of different inventories see Fig. 2 and Appendix 1

7.3% of trees. The proportion of damaged trees has increased from 44.4% in 1986 to 62.8% in 1988. At least moderate damage (classes 2–3) was recorded for 11.8, 19.3 and 18.3% of trees in 1986, 1987 and 1988, respectively, and severe damage (class 3) in 1.6 to 2.1% of the trees. When changes in individual trees were inspected, the damage degree had increased in 32.5% of trees from 1986 to 1987

Table 1. Occurrence of causal agents in the stands (on forest land) at the temporary plots in 1986–1988 in southern Finland (areas 0–9 of Fig. 1)

Causal agent		Hectares
Abiotic:	Wind	103,000
	Snow	33,000
	Other abiotic (frost, soil factors)	136,000
Fungi:	*Cronartium* sp.	109,000
	Ascocalyx abietina	299,000
	Other fungi	343,000
Insects:	*Tomicus* spp.	22,000
	Other insects	22,000
Mammals:	Voles	11,000
	Elk	125,000
Others:	Competition	98,000
	Harvesting	54,000
	Other man-made injuries	49,000
Not identified		311,000
Occurrence of damage total		1 715 000
Stands without signs of damage		3 728 000
Total forest land		5 443 000

and in 21.3% during 1987–1988. The increase can partly be explained by the fact that male flowering was coded as a damage symptom during 1986–87 but not in 1988. In calculation, these trees were considered as "healthy" in 1986–87. The other explanation is the increase in fungal damage, from 2.4% of trees (1986) to 13.6% (1988). *Ascocalyx abietina* was the main causal agent in this group in 1988. *Ascocalyx* was registered in 378 trees in 1988 at the extensive level, at about the same frequency than in the temporary plots. Of these cases, 24 were classified as moderate or severe injury.

Abiotic factors and fungi were the most important of the identified causal agents in this study. No mass outbreaks of insects, e.g. bark beetles were observed. The insect damage observed were mainly *Tomicus* damage, although in some regions in southeastern Finland also sawflies (*Diprion/Neodiprion*) caused local damage and defoliation. Insect and fungal damage reported, e.g. from Germany (Waldschäden 1986; Waldschadenserhebung 1987) were less in 1985 but greater in 1986–1987 than was observed in this study. Direct comparisons are, however, impossible, because most of the fungal and insect attacks in Germany occurred on deciduous trees. On conifers, only 2–8% of spruce and pine trees were attacked by fungi and insects there.

The results show that damage by *Ascocalyx abietina* is by far the biggest problem in our forests in some areas. The disease may even play a role in the growth reduction of Scots pine observed in Finland (Nöjd this Vol.). In more than

600 publications in the world literature (Stephan and Schulze 1987), there are many in which the possibility of a greater predisposition of trees to this disease by air pollution is discussed, but only a few reports, in which it has been studied (Bragg and Manion 1984; Laurence et al. 1984; Donaubauer 1984; Vuorinen and Kurkela this Vol.). Studies have been short-termed artificial treatments with acid rain and/or sulphur dioxide and no statistically valid evidence has been obtained. Barklund and Unestam (1988) suggest that air pollution may enhance infections by this fungus through its harmful effects on epi- and endophytic microflora on pine buds and needles, while Bragg and Manion (1984) discuss the possible effects of soil acidity. Soil acidification processes can be reflected, e.g. in the reduced availability of nutrients. So far hypotheses concerning increased predisposition of trees to *Ascocalyx* infection lack field evidence.

The greater occurrence of damage in Lapland at all levels is probably related to the greater average age of forests than in the south, and to a greater degree of abiotic damage due to wind and snow, plus the appearance of trees in a cold climate. Different types of crown injuries have earlier been reported to occur about four times more frequently in Lapland than in the other parts of the country, in trees subjected to defoliation assessments (Jukola-Sulonen et al. 1987). The cold winter of 1985 caused considerable browning of needles of conifers in south Finland, especially of spruce needles, the next summer (Kubin and Raitio 1985). In successive years the trees had at least temporarily recovered from the sudden loss of the youngest needles, which was reflected in the inventory result.

The numbers of injuries where the causal agent remained unknown were fairly high, partly because the inventory groups had had insufficient training and partly because of the rate at which the inventory work was done. The amount of unidentified damage was highest in Lapland as were the proportions of abiotic damage. In Lapland snow and wind have caused most of the abiotic damage and to some extent also other weather factors.

When comparing different inventories, it is necessary to take into account random errors related to the different densities of the sampling grids. The temporary plots are expected to give a much more realistic picture of the occurrence of different causal agents.

Interaction Between the Defoliation of Conifers and Biotic or Abiotic Damage in the Permanent Plots

The proportion of trees affected by biotic or abiotic damage increases as defoliation increases. Inventories at the extensive level in 1986–88 showed that while 68% of all the defoliated (defoliation more than 20%) Scots pines and Norway spruces also showed signs of other form of damage, the number was 78% in the trees which were defoliated more than 60%. The corresponding values in the inventory made on all of the permanent plots during 1985–86 was 72% (defoliation more than 20%) and 92.9% (defoliation more than 60%).

However, the most important phenomenon is the increase in the proportions of trees showing "moderate" or "severe" damage (degrees 2 or 3). This proportion increases rigidly as the defoliation increases. This phenomenon can be found in all of the four nationwide inventories made on permanent plots (Figs. 8–11). While 8 to 12% of the non-defoliated conifers (defoliation 0–20%) had moderate or severe damage of biotic or abiotic origin in different inventories, 31–35% of the defoliated conifers had similar damage. Of all the conifers showing more defoliation than 60%, 47 to 85% had biotic or abiotic damage with a degree of 2 or 3. The proportion of severe damage (class 3) in these trees was 30 to 40%.

The proportion of unidentified damage was rather high in all the cases where the degree of damage was rated as "moderate" or "severe". The most common symptoms for non-identifiable causes (Figs. 8–11) were needle damage (36%), other top damage (crown malformations etc.) (35%) and stem injury (17%). Abiotic factors and fungi are the two most important groups among identified causal agents in the inventory made at all permanent plots in 1985–86. The result from extensive level plots during the successive years 1986–1988 shows considerable variation between inventories. In 1986, fungi were the most important of the identified causes of injury. During 1987–88 abiotic factors and fungi were the most important, but insect damage and damage due to excessive competition were also present to some degree. Fungi and abiotic factors were identified as causal agents more often in all permanent plots (the 2506 plot level) than at the extensive level.

The proportion of moderate or severe damage caused by factors that are not likely to be influenced by air pollution (wind, snow, competition, man, mammals and rust fungi) ranged from 4 to 20% of the defoliated trees.

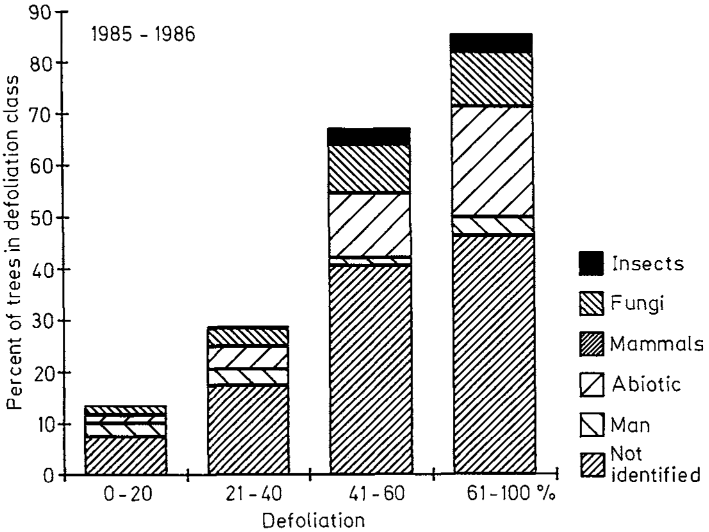

Fig. 8. Proportion of trees showing "moderate" or "severe" damage (see Appendix 1) and the groups of causal agents in defoliation classes in all permanent plots 1985–86. Dominant or co-dominant pines and spruces

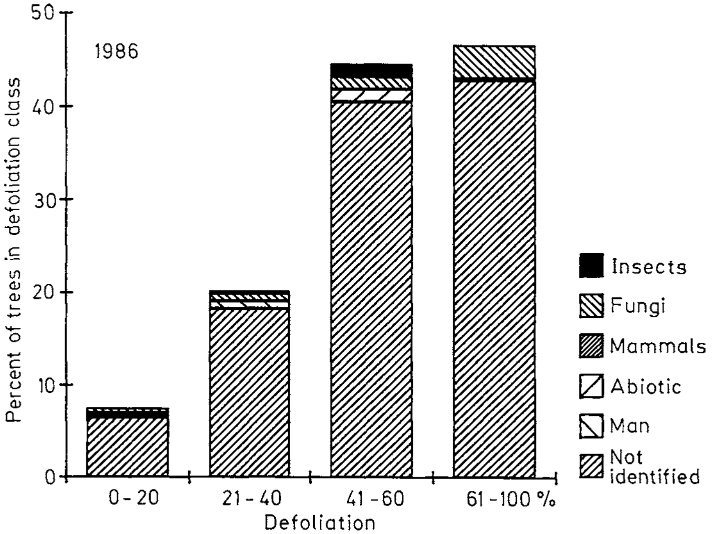

Fig. 9. Proportion of trees showing "moderate" or "severe" damage (see Appendix 1) and the groups of causal agents in defoliation classes in permanent plots, extensive level 1986. Dominant or co-dominant pines and spruces

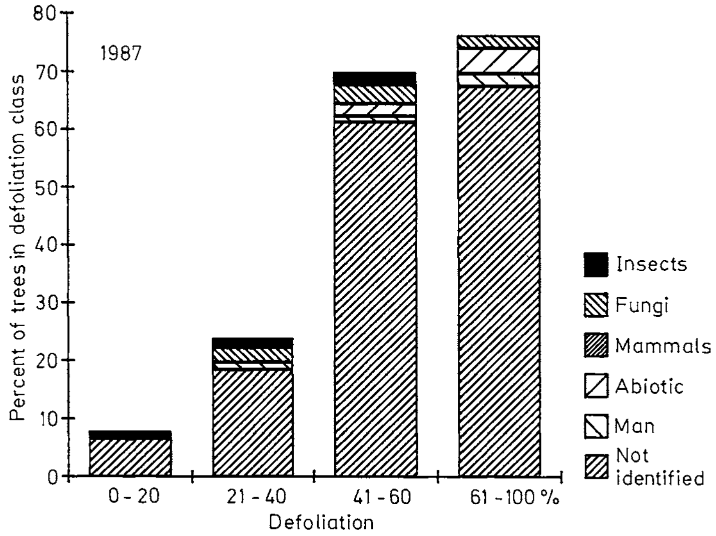

Fig. 10. Proportion of trees showing "moderate" or "severe" damage (see Appendix 1) and the groups of causal agents in defoliation classes in permanent plots, extensive level 1987. Dominant or co-dominant pines and spruces

An increased occurrence of any specific causal agent could not be detected in the defoliated trees in the whole country, because the distributions of damage types in non-defoliated (0–20%) and defoliated (21–100%) trees were not statistically significantly different. Largely this is due to the great number of trees in the

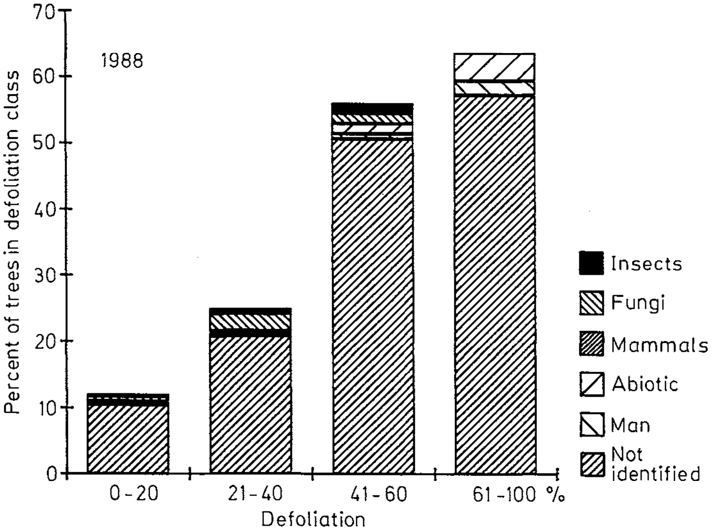

Fig. 11. Proportion of trees showing "moderate" or "severe" damage (see Appendix 1) and the groups of causal agents in defoliation classes in permanent plots, extensive level 1988. Dominant or co-dominant pines and spruces

defoliation classes 0–10% and 11–20%, as compared to the rest of the classes and to the great proportion of non-identified causal agents.

According to Kendall nonparametric correlation analysis, there was a significant correlation between the increase of degree of damage and the increase in defoliation in the extensive level plots during 1986–87 (tau=0,792, N=2099, p=0,000) and also 1987–88 (tau=0,102, N=2060, p=0,000). The degrees of damage in previous years did not, however, correlate with the increase in defoliation in the successive years. When the trees were divided into groups which were either (1) free of damage during 1986 and 1987 or (2) had slight damage during one of the years or (3) had at least moderate damage in one or both years or (4) had at least moderate damage in both years, there were no differences in the change in defoliation between these groups (population medians) using the box plot technique (McGill et al. 1978).

To directly attribute some observed damage types to the local changes in defoliation, pairwise comparisons were made between trees which had some sort of injury, and healthy trees from the same plots. Table 2 presents the statistically significant differences observed at all the permanent plots 1985–86 and Table 3 the corresponding values for the extensive level surveys. Tables 2 and 3 show that different damage types can be attributed to defoliation in different years, which leads to quite different "vitality" patterns.

The location of some of the plots in which defoliation could be attributed to biotic or abiotic damage in this way is presented in Fig. 12. The figures reveal that in southwestern Finland *Ascocalyx abietina* had at least partly caused the observed increase in defoliation in 1988. Defoliation most likely attributable to other types

Table 2. Statistically significant differences in defoliation between trees with biotic or abiotic damage, compared to trees from the same plots without injuries. All permanent plots 1985–86

	Pine 1985–86					Spruce 1985–86				
	Defoliation % Mean	Incr.	T	Plots	Prob.	Defoliation % Mean	Incr.	T	Plots	Prob.
Fungi						11.8	6.6	−3.04	17	0.008
Insects	16.3	7.0	−2.28	19	0.035					
Frost, soil	14.7	6.7	−2.52	16	0.024	13.7	5.8	−2.15	25	0.041
Crown injuries	7.8	1.4	−3.18	173	0.002					
Stem injuries	10.3	1.9	−2.47	145	0.015	10.9	2.6	−3.12	81	0.003
Needle damage	19.6	12.8	−13.32	101	0.000	20.0	13.2	−6.13	60	0.000

Mean = mean defoliation % in affected trees, incr. = increase of mean defoliation compared to unaffected trees

Table 3. Statistically significant differences in defoliation between trees with biotic or abiotic damage, compared to trees from the same plots without injuries. Extensive level

	Pine 1987					Pine 1988				
	Defoliation %					Defoliation %				
	Mean	Incr.	T	Plots	Prob.	Mean	Incr.	T	Plots	Prob.
Ascocalyx						12.6	3.4	−2.51	42	0.016
Cronartium	27.0	13.6	−2.69	10	0.025					
Other fungi	9.5	3.2	−2.43	19	0.026					
Insects	11.8	3.7	−3.07	34	0.004	11.9	3.9	−2.45	53	0.018
Competition	16.7	8.6	−2.94	13	0.012					
Crown injuries	10.0	2.1	−2.53	76	0.014	11.0	3.8	−3.71	77	0.000
Needle damage	19.1	9.1	−3.63	43	0.001	15.8	8.0	−5.40	82	0.000
Discoloration	9.8	3.1	−2.40	30	0.023	11.1	3.1	−3.17	62	0.002

	Spruce 1987					Spruce 1988				
	Defoliation %					Defoliation %				
	Mean	Incr.	T	Plots	Prob.	Mean	Incr.	T	Plots	Prob.
Other fungi						15.4	3.8	−2.59	36	0.014
Needle damage	38.4	26.3	−10.02	33	0.000	25.7	13.8	−7.42	74	0.000
Discoloration						18.3	6.0	−5.28	58	0.000

Mean = mean defoliation % in affected trees, incr. = increase of mean defoliation compared to unaffected trees.

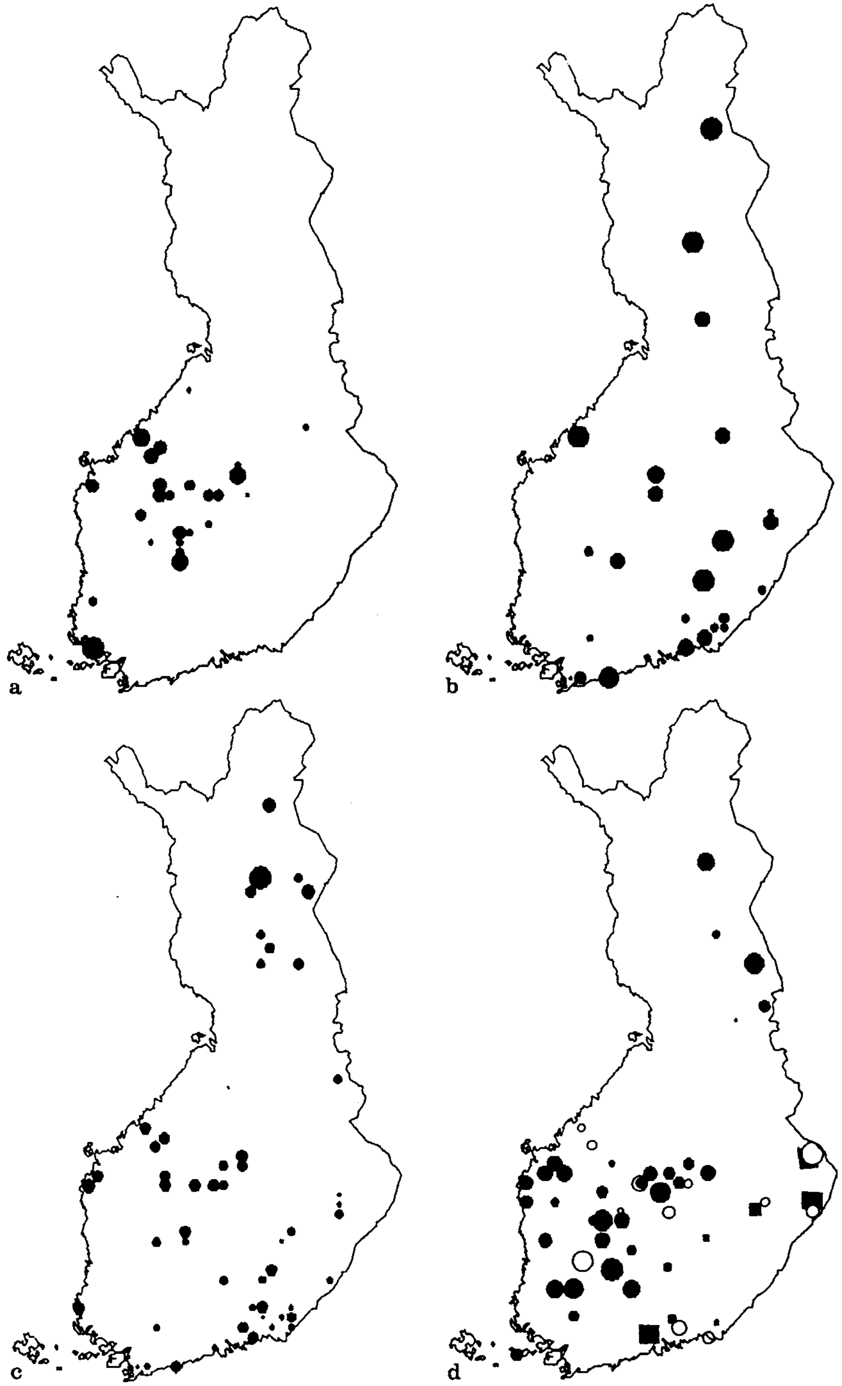

Fig. 12a–d. Location of the plots, where, by comparing affected trees within the plots, it was possible to associate defoliation with biotic or abiotic damage. Extensive level 1988. **a** Pine: *Ascocalyx abietina*. **b** Pine: insect damage. **c** Pine: needle damage. **d** Spruce: *closed circles* needle damage; *open circles* other fungi; *closed squares* discoloration

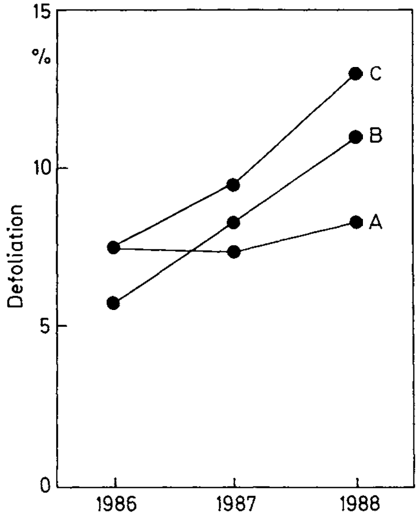

Fig. 13. Schematic presentation of changes in defoliation in areas 12–15 (see Fig. 1) *A* trees without damage as compared to *B* trees with *Ascocalyx* damage in 1988 and to *C* trees with *Ascocalyx* damage 1988 and other damage 1987 or 1986

of damage showed a more or less scattered picture in all the inventories, although in 1985–86 "needle damage" and "crown injuries" of pine were most pronounced in the central and northern parts of the country and "stem injury" of spruce in the southern parts.

Figure 13 presents schematically the mean defoliation during 1986–1988 in the plots with *Ascocalyx* damage in 1988, as compared to defoliation of the trees without this specific damage in the areas 12–15 shown in Fig. 1. The defoliation had slightly increased also in the trees without damage, but more rapidly in the trees with the specific damage. As a mean, *Ascocalyx* seem to have caused a 5% increase in defoliation in southwestern Finland.

The degree to which defoliation could directly be attributed to biotic or abiotic factors in the three samples of plots surveyed by forest pathologists or entomologists in southern Finland showed again that in a large area these are of minimal importance. While some form of damage was registered in 54.1% out of the 4016 conifers inspected in 1987–1988, biotic or abiotic factors were directly responsible for the increase in defoliation in 8.0% of the cases. The proportions of abiotic factors (snow, wind, frost etc.), damage caused directly by man, insects and fungi were 2.2, 0.8, 2.6 and 2.4% of the trees, respectively.

Conclusions

According to the results of the National Forest Inventory, some form of abiotic or biotic damage was registered in about one-third of the stands or sample trees. The proportion of damage that greatly reduced the stand quality or was likely to cause the death of trees was considerably lower, in the range of 1–3%. In Lapland the frequency of damage was roughly two times higher than if calculated nationwide.

This was especially the case in different mechanical types of damage (broken stems, crown injuries etc.). Needle damage and different mechanical injuries were the most common damage symptoms also nationwide. Fungi and abiotic factors were the most common of the identified causal agents. *Ascocalyx abietina* was the most important of these. The canker and die-back disease caused by this pathogen was having a new epidemic in Finland during the study period. The connection of the occurrence of the disease with air pollution warrants further research. The complex interactions of soil factors, topography, silvicultural factors and the possible role of air pollution/soil acidification will be analysed in a special study using the data from the temporary plots. Also other forms of damage and their possible spatial and temporal patterns should be studied more closely. This should mean intensified research in small-scaled areas by many specialists. Damage inventories presented in this study proved useful in providing the primary data for such cause-effect-orientated studies.

According to the results, there was an important co-occurrence of biotic and abiotic damage and defoliation. A major portion of damage in defoliated trees was caused by abiotic factors. Biotic pests and pathogens occurred on scattered plots around the country and had only local importance. The important exception was *Ascocalyx abietina*, which caused a regional increase of defoliation in western Finland. Damage that decreases the growth potential of trees was found in about one-third of the defoliated conifers and in most of the trees defoliated more than 40%. About one-quarter of this damage was caused by factors which cannot be favoured by air pollution-related stresses. In many defoliated individual trees, abiotic and biotic damage can play a crucial role, even as a cause of defoliation. If results are calculated for a very large area, their importance can be greatly reduced due to the large number of slightly defoliated or non-defoliated trees. It can be concluded that in most cases of this study the defoliation symptom was not directly attributable to known abiotic or biotic causal agents. A maximum of about 20% of the defoliated conifers were severely injured by agents which can be considered independent of air pollution-related stresses. However, when studying acute regional changes in forest condition, the possible role of abiotic factors, fungi and insects should be carefully analysed.

Appendix

Codes for registering stand- and tree damage on permanent sample plots

Occurrence of damage on stand level

Symptom of injury
0. Healthy tree
1. Dead trees
2. Broken and fallen trees
3. Decayed trees
4. Stem injury

Cause of injury
0. Not identified
1. Wind
2. Snow
3. Other abiotic
4. Competition

5. Dead tops
6. Other top injury
7. Defoliation
8. Discoloration
M. Many symptoms (due to age, overdensity etc.)

5. Harvesting
6. Other man-made injury
7. Voles
8. Elk
9. *Tomicus* spp.
A. Other insects
B. *Cronartium* spp.
C. *Ascocalyx abietina*
D. Other fungi

Defoliation
0. No defoliation
Slight defoliation, an average of 20–40%
1. Defoliated trees 6–20%
2. Defoliated trees 21–50%
3. Defoliated trees 51–100%
Moderate defoliation, an average more than 40%
4. Defoliated trees 6–20%
5. Defoliated trees 21–50%
6. Defoliated trees 51–100%

Degree of injury
0. Slight occurrence of damage
1. Damage decreases the quality of the stand
2. Severe damage
3. Complete damage

Damage on tree level

Symptom of injury
Same as on the stand level, except that code 'M' is not used

Cause of injury
Same as on the stand level

Defoliation
Dominant and co-dominant pines and spruces in older development classes
0. Defoliation 0–10%
1. Defoliation trees 11–20%
2. Defoliation trees 21–30%

. . . .

9. Defoliation trees 91–100%

Degree of damage
0. Recovered from damage = slight
1. Recovering from damage = slight
2. Decreased tree quality = moderate
3. Dead or dying tree = severe

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An Approach to Analyse the Dynamics of Environmental Change and its Effects on Forest Growth

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Summary

The anthropogenic emissions into the atmosphere have changed the material flows in the system formed by the atmosphere, vegetation, soil, ground and surface waters. The concentrations of several nutrients and toxic compounds are changing. These concentrations are environmental factors and forests are reacting to the changes in the environment.

The material flows are analysed and basic structures to describe the changing concentrations are outlined. Soil acidification is used as an example of changing environmental factors. The photosynthetic and nutritional response of trees is modelled. Aggregated variables are introduced to describe annual effects of environmental change on metabolism of trees. A stand growth model is described in a static environment and necessary modifications in a changing environment are introduced. A more aggregated model to account for the effects on changing environmental factors on forest growth is described.

Introduction

This chapter outlines a theoretical framework for the analysis of forest decline. The framework links the functioning of a forest stand with environmental factors, thus enabling the stand's response to changing environmental factors to be predicted. The framework, which is expressed in the form of a hierarchical family of dynamic models, is demonstrated with examples from Finland.

According to current understanding, the novel forest decline in Europe is caused by an interaction of natural and anthropogenic stress (Krause 1988; Schulze 1988). Zoettl and Huettl (1986) found that insufficient nutrient supply of the soil is a predisposing stress factor, while photooxidants and intensive insolation are inciting stress factors.

Leaching of nutrients from the needles, enhanced by the interaction with photooxidants, leads to nutrient depletion and reduced assimilate production. Together with changes in soil chemistry, this impacts the root system, disturbs nutrient uptake and incites a spiral of steadily decreasing vitality. The weakened trees provide favorable conditions for pathogens (Krause et al. 1986).

Kauppi et al. (Eds).
Acidification in Finland

Grossmann (1988) reports that products of photooxidants such as aldehydes, organic acids, peroxides and radicals together with ozone explain the extent and form of the new forest decline in Austria. Needles may be damaged by gaseous and dissolved oxidants. Mycorrhiza and roots may be injured by photooxidation products deposited by precipitation. The vitality of the tree is thus reduced both through the direct impact on the needles and through a reduced uptake of calcium and magnesium by the damaged root system (Grossmann 1988). Hauhs and Wright (1986) put forward a multiple-cause hypothesis which relates needle loss and yellowing of needles to reduced fine root biomass and weakened root functioning in response to changes in soil chemistry. They also show that their hypothesis is sufficient to account for the distribution of different forest damage symptoms on the local and the regional scale and along a cross-section from South Germany to Central Scandinavia.

Schulze (1988) summarises the responses to acid deposition into the soil. According to his review, whole plant growth reduction is caused by cation deficit of needles, needle loss and long-term effects on photosynthesis. Growth stimulation due to deposition of nitrate and ammonium leads to a nutrient imbalance in the needles, which in turn makes the needles fall off prematurely and hampers photosynthesis on the long term. Reduced photosynthetic activity is reflected in reduced root growth and nutrient uptake and thus contributes to the cation deficit of needles (Schulze 1988). The long-term phenomenon of acidification has altered the stability of forest ecosystems. The addition of nitrogen has accelerated this process, and it has increased the demand for macronutrients in a situation of reduced supply. Short-term events of dry years have made matters worse (Schulze 1988).

Plants respond primarily to their micro-environment, i.e. the properties of the immediately surrounding atmosphere and soil. The micro-environment is a part of the local environment of the stand, which in turn interacts with the larger environment of the region. This division into micro-, local and regional environment is artificial, but serves to stress that the temporal features of the environment are associated with the spatial features. The temporal scale of the micro-environment is in the range of seconds to days, that of the local environment of hours to years, whereas the regional environment changes over to centuries. The dissipation of energy in the atmosphere of the earth follows the same pattern; large-scale motion is much more predictable than the final dissipation due to small scale turbulence. Air dispersion modelling is one reflection of this phenomenon.

The paper is divided into five sections. The second section describes the environmental characteristics that we consider important for forest growth. Special emphasis is given to a quantitative definition of the environmental factors and to a method for analysing their dynamics. A strong relationship exists between the immediate state of the environment and the functioning of trees. A forest stand forms a functional unit, which is normally characterized by an area of several hectares and a time span of about a century.

A forest region comprises stands of different age, type, structure etc. and may extend to hundreds of hectares. The use of knowledge about plant function in the analysis of stand development and regional forest growth forms a methodological problem of aggregation, or scaling-up. The third section considers the stand development. The focus is on functionally based aggregation of environmental factors and on the use of stand models. The question of aggregation is also addressed. The fourth section enlarges the scope to regional level. The paper is closed with concluding remarks in the fifth section. The report is a direct continuation of our previous work reported by Raunemaa et al. (1982, 1987) and Hari et al. (1986, 1987).

Environmental Factors

General

Environmental factors are the properties of the environment that influence the metabolic processes of plants. They include irradiance, temperature and concentrations of those elements and compounds which trees utilize in their metabolism or which are toxic to trees. These environmental factors have to be described by a vector consisting of several components. For example, the number of macronutrients is nearly ten, and also the number of potentially toxic compounds is numerous.

Environmental factors vary within both space and time. While the spatial properties of the light climate (e.g. Ross 1981; Oker-Blom 1986) and the seasonal and diurnal changes in temperature are well known, the ecological implications of these variations are problematic. Concentrations of nutrients and toxic substances vary strongly with space and time, introducing large variation. Thus the environment, u, should ideally be determined at each point in space, x, and time, t. For practical measurements the environment is treated in a small spatial and temporal volume element.

Matter is transferred among the following components of the ecosystem: atmosphere, vegetation, soil, groundwater and surface waters (Fig. 1). The system includes sources and sinks. Matter is introduced into circulation by e.g. weathering processes and it leaves the cycle by leaching and sedimentation. Sedimentation occurs to subsoil and to the bottom of surface waters. Weathering of minerals and volcanic activity constitute the most important sources of matter. It is important to note that the concentrations of the circulating species are determined by the flow rates of the dispersion media, by the rates of weathering and sedimentation, and by the rates of internal biogeochemical transformation processes.

In the following, a method for quantitative description of the dynamics of the plants' micro-environment is outlined. Space and time are subdivided into volumes and intervals so small that each subvolume during each time interval can be considered homogeneous with respect to the compound of interest. The amount of the compound in the subvolume can change due to in- and outflow and by internal processes that produce or consume the compound.

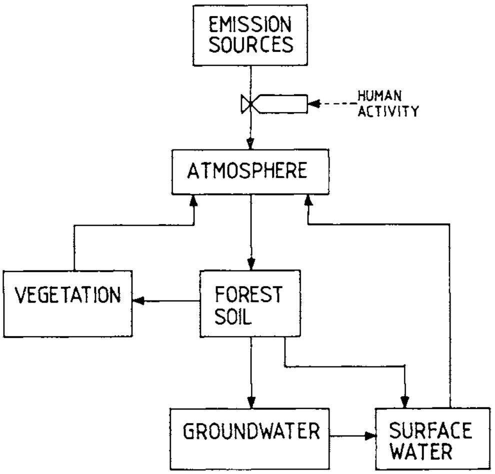

Fig. 1. Massfluxes in the ecosystem Chemical compounds (CO_2, SO_2, NO_x, O_3, H^+, Ca^{++}, Mg^{++}, K^+) are transported with air and water and participate in biogeochemical processes within the ecosystem. The arrows represent massfluxes of air, water and chemical species. The direction of the arrows represent the predominant direction of water flow.

Let $M_i(\Delta V,t)$ denote the amount of compound i in the subvolume ΔV at the moment t. The spatial coordinate is x and Δx is the increment in the direction of the predominant flow. Let $Q_i(x,t)$ denote the inflow of the compound i into the subvolume and $Q_i(x + \Delta x,t)$ denote the outflow of the same compound. Furthermore, let $R_i(\Delta V,\Delta t)$ denote the internal production and $S_i(\Delta V,\Delta t)$ the internal consumption of the compound i in the subvolume ΔV during the time interval Δt. The volume increment ΔV is chosen so that one of its sides is perpendicular to Δx. The law of mass conservation applies to all environmental factors except irradiance and temperature. Thus, the change in amount of some compound in the subvolume ΔV during the time Δt equals inflow minus outflow plus internal production minus internal consumption.

$$M_i(\Delta V,t + \Delta t) - M_i(\Delta V,t) = Q_i(x,t) - Q_i(x + \Delta x,t) + R_i(\Delta V,\Delta t) - S_i(\Delta V,\Delta t). \tag{1}$$

If the transport processes in the air or water are modelled in addition, then the amounts in each subvolume and at each moment can be determined using Eq. (1). The spatial and temporal behaviour can be calculated by, for example, numerical approximation. If the transport system is well known, Eq. (1) takes the form of a partial differential equation. When the transport medium can be assumed homogeneous, the parameters of this partial differential equation can be lumped, resulting in an ordinary differential equation.

As far as is known from historical data, climate and matter fluxes have been changing at least within the time span of a few thousand years. In shorter intervals there are random fluctuations around a constant mean value. The atmospheric CO_2 concentration has been rather stable since the ice age until the last century. Since the ice-age the podzolization process has been taking place in the Finnish forest soils. However, this process is rather slow.

During the last century the flow of several compounds from the surface of the earth into the atmosphere has been increasing with the use of fossil fuels. The chemical and physical properties of the atmosphere have been changing because the composition of the atmosphere has changed due to increased inputs and these changes have generated changes in the flow from the atmosphere to forests and forest soils. Thus, also the soil processes are accelerating and changing.

Atmospheric Environment

Plants assimilate carbon dioxide from the atmosphere in the process of photosynthesis. At prevailing ambient concentrations, 350 ppm (430 $mg\,m^{-3}$), the CO_2 concentration strongly limits photosynthesis, especially at high irradiance. Thus any increase in the availability of CO_2 will have a considerable effect on plant production. Among the anthropogenic emissions to the atmosphere, CO_2 is dominating. CO_2 is very inert and reacts only with few substances in the atmosphere. Spatial variations in CO_2 concentrations are small and thus its time development can be studied on a global scale.

Sulphur dioxide is one of the most abundant toxic compounds in anthropogenic emissions. It is reactive in the atmosphere transforming readily to particle compounds, especially with water vapour. Its transformation time in the atmosphere is in the order of days. Due to its reactivity, sulphur is removed from the atmosphere differently than CO_2. The main mecahnisms are wet and dry deposition.

The spatial variation of SO_2 emissions and partly also sulphur deposition is pronounced, especially at the regional scale. Thus a rather small volume element is needed in the analysis. It is possible to model the time development and spatial variation of SO_2 using the volume-element approach. The result, however, covers generally only an episode and a restricted area. High concentrations of SO_2 are found only close to the major emission sources, for instance in Central Europe. The levels of SO_2 in remote areas such as northern Scandinavia are low, although increasing. Concentrations of sulphate and nitrate in Greenland ice-cores have doubled from 1895 to 1978 (Neftel et al. 1985).

Nitrogen oxides are emitted in combustion of fossil fuels in energy production and traffic and ammonium is produced in large amounts in agriculture and in natural bacterial action. NO_x are transformed to nitric acid in the atmosphere, thus contributing to the acidity of rain. NO_x are also precursors of ozone. The chemistry of NO_x in the atmosphere is complicated, as a large number of formation and decomposition reactions are involved. The residence time of NO_x is short. The atmospheric distribution of NO_x is non-uniform. Calculations of spatial and temporal variations in ambient NO_x concentrations are therefore cumbersome and prediction of long-range transport of nitrogen is still a subject for discussion (Grennfelt et al. 1987). The behaviour of NO_x and SO_2 is summarized in Table 1.

Ozone is formed in the atmosphere in reactions of nitrogen oxides and carbon species, especially hydrocarbons, carbon monoxide and aldehydes under the effect of solar energy. The key role is played by the hydroxyl radical. Ozone is very active and consequently its concentration varies considerably. The volume element must

Table 1. Dispersion and transformation of chemical species in terms of spatial and temporal scales. (After Grennfelt et al. 1987 and Seinfeld 1986)

Species	Space (Grennfelt)	Time (Grennfelt)	Residence time (Seinfeld)
NO	1 km	< 1 h	
NO_2	Some 100 km	2 d	
$NO + NO_2$			1 d
HNO_3			1 d
SO_2	Some 100 km	2 d	40 d
SO_4^{2-}	1000 km	5 d	

be chosen so that no considerable variation of hydrocarbons, nitrogen oxides or O_3 appears. The spatial requirement now becomes very strict because of the high variability of the hydrocarbon substances. Because vegetation emits hydrocarbons, greater amounts of ozone than expected may be formed (Atkinson et al. 1984) and cycled very close to the leaf surface. Ozone is toxic to plants. Because of complex ozone chemistry in the air, the effects of ozone on trees are difficult to quantify at the moment.

Soil Environment

A forest soil develops through processes of chemical, physical and biological weathering of the parent material, dissolution and precipitation of minerals, and formation of organic complexes. The rate of soil formation and the characteristics of the end-product depend on the geochemical properties of the parent material, the climatic conditions, the vegetation and the topography of the site.

Soil is a multi-phase system consisting of a solid (ca. 50 % by volume), a gaseous (10–40 % by volume) and an aqueous phase. The solid phase consists of colloids and larger particles of minerals and dead organic material. The reactive surface of the solid phase is very large, ranging from a few square meters to some 500 $m^2 g^{-1}$ (Scheffer et al. 1982). The higher the clay and organic matter content, the larger is the specific surface of the soil. The gaseous phase consists of atmospheric constituents and volatile organic compounds. The main substance in the aqueous phase is water, with ionic species. The rate of cycling of elements in the different phases in the soil depends on the ionic concentrations of acids and bases in soil.

The method for describing the micro-environment of plants outlined in the previous section was implemented for the soil environment. A dynamic model of transport and local processes in forest soil was developed in order to study the effect of ionic deposition and hydrology on the vertical distribution of ions in the soil profile (Holmberg et al. 1985b). The vertical transport of water in forest soil takes place through gravitational flow in micro- and macropores and capillary rise of water. Ions are transported vertically in soil by convective flow, i.e. mass flow with water, and by diffusive flow that arises from concentration gradients in soil.

Assuming a homogeneous soil, the diffusivity equation (e.g. Hillel 1971) can be used. It takes the form of partial differential equations (Appendix 1), which are solved numerically. This distributed model of the transport processes in soil may be simplified by lumping, or aggregating, the spatial characteristics.

The uptake of water by the roots is calculated from the evapotranspiration rate and the vertical distribution of roots. The weathering rate of minerals is assumed to increase with the distance from topsoil such that a total annual weathering of around 1 meq m^{-2} is obtained in the uppermost 0.5 m of mineral soil (Nilsson 1986).

The exchange of ions between soil solution and soil particles is a dynamic process, the rate of which was assumed to be determined by the equivalent concentrations of ions in solution and on soil particles. The rates of the exchange reactions are calculated from differential equations (Appendix 2). These equations are combined with the transport equations (Appendix 1) to give the vertical distributions of ions in soil.

The distribution model was used to study the impact of water uptake on the ionic concentrations in the profile. Drying out of topsoil as a consequence of water uptake by the roots with a mass peak at 0.05 m below the surface of the soil was simulated. Transpiration results in an increase in the ion concentrations in the soil solution and intensifies the ion exchange between soil solution and soil particles. Figure 2a and 2b shows the vertical distributions of acid and base cations after 100 h of drought. The initial distributions of ions were uniform.

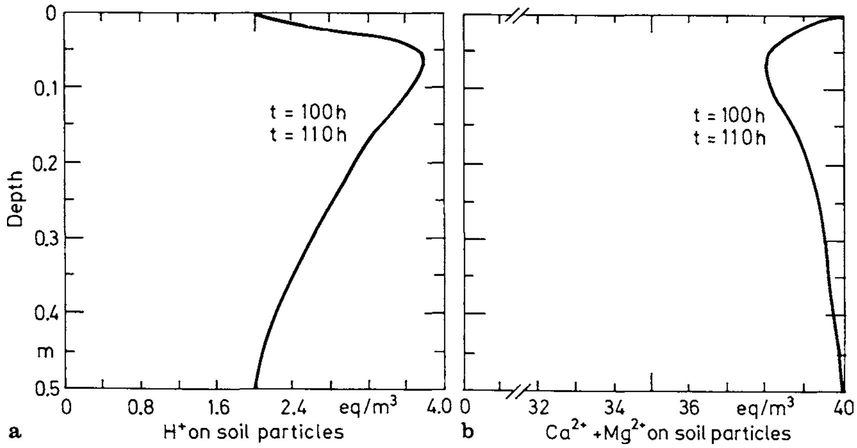

Fig. 2. Simulated vertical profiles of hydrogen ions (**a**) and base cations (**b**) adsorbed to soil particles following a period of 100 h of high transpiration (1.5 mm h^{-1}) (Holmberg *et al.* 1985b).

Functional Basis of Stand Development

Plants extract material from the environment and process it through metabolic processes. Carbon dioxide, water and nutrients (e.g. N, K, Mg, Ca, P) are the most important compounds in the flows to the plants. In addition, plants transpire large amounts of water. For each main metabolic process there exists a specialized tissue; leaves account for photosynthesis, fine roots for uptake of water and nutrients, and coarse roots, stem and branches for water transport. The flows within a plant are thus diverse.

All functioning requires energy. The energy for metabolism is converted for usable form in photosynthesis when carbohydrates are formed from carbon dioxide and water using light as the primary source of energy. The energy from solar radiation, more specifically irradiance, is the dominant environmental factor affecting photosynthesis in field conditions (Hari et al. 1981). The low level of CO_2 available in the atmosphere limits photosynthesis, especially at high irradiance. The structure of leaves is such that the intake of CO_2 is associated with the transpiration of water. The amount of transpired water is usually about 100-fold greater than the amount of photosynthetic products.

Large amount of water taken up by fine roots during transpiration transports dissolved nutrients from the soil to the trees. This source is not sufficient, however. Additional nutrients are carried to the plant by diffusion down the electrochemical gradients forming around the fine roots as a result of nutrient uptake. The ion flows close to roots (or hyphaes) may enhance the availability of additional nutrients from the surfaces of soil particles. Carbohydrates are used for root growth and for the functioning of ion pumps.

In relatively nutrient poor soils, as in Finland, the roots are practically always infected by mychorizal fungae. They greatly extend the surface area of root systems, thus facilitating especially the nutrient uptake of rather immobile species such as phosphorus. The energy captured in photosynthesis as carbohydrates is used in roots for the growth of roots and hyphae and the active uptake of nutrients.

Acclimation of whole plant functions to short-term, environmental changes can take place through changes in the input-output processes, such as photosynthesis or nutrient uptake, and changes in the amount of stored substances. However, in case of long-term changes, also structural acclimation takes place. Over a longer time period the capacity of roots to supply water and nutrients is balanced with the need of other organs, and parts of the water transport system are balanced with each other and with the need of the leaves. It is evident that evolutionary pressure has been strong to develop effective allocation in trees.

Aggregation

Field measurements have shown that the dependence of photosynthetic rate on environmental factors is simple and strong (Hari et al. 1981). Let p denote photosynthetic rate [g g(needle)$^{-1}$ s^{-1}] and T_n leaf mass distribution [g(needle) m^{-3}]. The annual amount of photosynthetic production $P(t_k)$ during the kth year is obtained by integration as follows:

$$P(t_k) = \int_V \int_{t_k}^{t_k+1} \rho_n(x)\, p(x,t)\, dt\, dV, \tag{2}$$

where V is the volume of the tree under consideration. A multiplicative model has proved applicable in the analysis of photosynthetic rate, i.e.

$$p(x,t) = p_0 f_1 [u_1(x,t)]\, f_2 [u_2(x,t)]\, f_n [u_n(x,t)], \tag{3}$$

where the function f_i, $i = 1, 2, \ldots, 9$, is the impact of the environmental factor i on photosynthetic rate. These functions can be quantified with measurements of photosynthesis and environmental factors. The parameter p_0 describes the value of maximal photosynthetic rate ($p_0 = 6$ g dry matter (g needles* h)$^{-1}$. The functions f_i, $i = 3, \ldots 9$ are normalized in such a way that they equal unity in the conditions before apparent anthropogenic influence on the environment.

We define the relative annual effect of environmental factors on photosynthesis during the kth year, $U^P(t_k)$, as the ratio of the amount of photosynthesis during the year k to that amount the same needle system would have been able to form in conditions before anthropogenic influence on environmental factors.

The relative annual effect of the environment on the photosynthesis $U^P(t_k)$ can now be determined using Eqs. (2) and (3).

$$U^P(t_k) = \frac{\int_V \int_{t_k}^{t_k+1} \rho_n(x)\, f_1 [u_1(x,t)] \ldots f_n [u_n(x,t)]\, dt\, dV}{\int_V \int_{t_0}^{t_1} \rho_n(x)\, f_1 [u_1(x,t)] \ldots f_n [u_n(x,t)]\, dt\, dV}. \tag{4}$$

Although the above equation is operational in principle, it is rather complicated to use in practice. The following approximation is, however, sufficiently accurate. We define the annual impact, $U_i^P(t_k)$, of the ith environmental factor on the photosynthetic rate as follows

$$U_i^P(t_k) = \frac{\int_V \int_{t_k}^{t_k+1} \rho_n(x)\, f_i [u_i(x,t)]\, dt\, dV}{\int_V \rho_n(x)\, dV}. \tag{5}$$

Multiplication of the effects of each component of the environmental vector gives a sufficient estimate of the relative annual impact of the environment on the photosynthetic rate

$$U^P(t_k) = \Pi\, U_i^P(t_k). \tag{6}$$

We can now consider the different factors in some detail. The increase in atmospheric CO_2 concentrations is the most important change in environmental factors

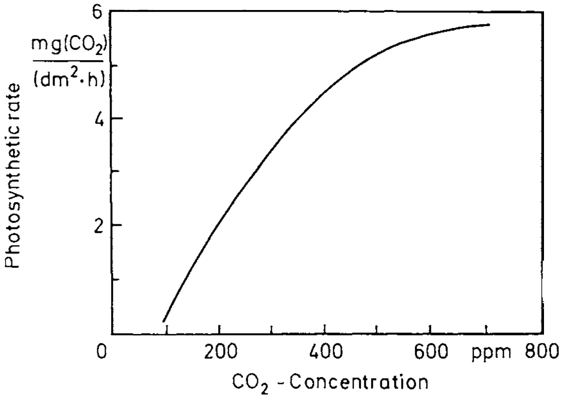

Fig. 3. Dependence of photosynthetic rate on atmospheric CO_2-concentration. Measured in Hyytiälä, Central Finland in 1982. Light intensity 630 μE m^{-2} s^{-1}, temperature 17.5°C.

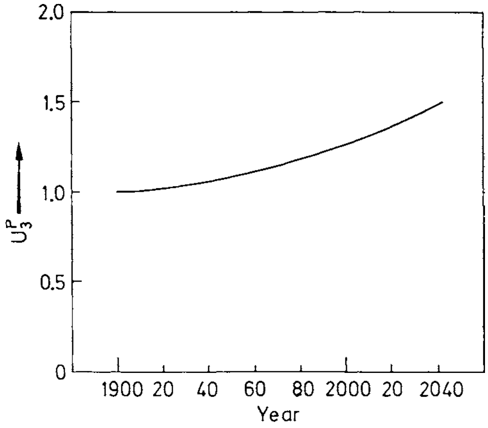

Fig. 4. Annual impact of CO_2 on photosynthetic rate, assuming a conservative prediction of a linear increase in atmospheric CO_2 concentrations.

on a global scale. We denote the atmospheric concentration of CO_2 by u_3. The dependence of the photosynthetic rate on the CO_2 concentration is linear at concentrations below 400 ppm. The response saturates at high CO_2 concentrations. When the dependence of photosynthetic rate on u_3 depicted in Fig. 3 is applied in determining U_3^P, the time development of Fig. 4 is obtained. Consequently, increasing the concentration of CO_2 causes a major change in the global photosynthetic production.

The other atmospheric compounds cause principally only local effects on photosynthetic production, since these compounds are chemically very reactive. Ozone may be produced in toxic amounts near some leaves, when the ratio of concentrations of nitrogen oxides to hydrocarbons is at right level. This happens mainly in the vicinity of emission sources.

The relative annual effect of environmental factors on nutrient uptake in the k^{th} year, $U^N(t_k)$, is defined as the ratio of the amount of nutrient uptake during that year to the amount that could have been taken up by same root system under conditions of no anthropogenic emissions. The process of nutrient uptake is less well understood in quantitative terms than photosynthesis. However, the same approach in quantifying U^N can be applied but the results are more uncertain.

Let r denote nutrient uptake rate and ρ_r the root density in the soil. The relative annual effect on nutrient uptake can be quantified as follows

$$U^N(t_k) = \frac{\int_V \int_{t_k}^{t_{k+1}} \rho_r(x)\, r[u(x,t)]\, dt\, dV}{\int_V \int_{t_0}^{t_1} \rho_r(x)\, r[u(x,t)]\, dt\, dV}. \tag{7}$$

The nutrients can be either in the soil solution or on soil particles. Assume that the nutrient uptake rate is a saturating function of concentrations in the soil solution and on soil particles:

$$r[u_8(x,t), u_9(x,t)] = \frac{r_{max}(a\, u_8 + b\, u_9)}{(a\, u_8 + b\, u_9 + c)}. \tag{8}$$

The weights a and b are determined in such a way that trees utilize the nutrients carried by the flow of water from the soil to the roots and then satisfy their remaining need for nutrients by uptake from the surfaces of soil particles.

The analysis of nutrient concentrations as functions of space is too detailed for this purpose. The soil model in the preceding section can be simplified by aggregating with respect to the spatial variability. The resulting lumped model is delineated in the following. Denote the acid and base cations in the soil solution as $u_6(t)$ and $u_8(t)$, and hydrogen and base cations adsorbed on soil particles as $u_7(t)$ and $u_9(t)$. Since spatial variability is not considered, the concentrations are only functions of time $[u_6(x,t) = u_6(t)$, etc.$]$. The fluxes $q_6(t) = q_6(0,t)$ and $q_8(t) = q_8(0,t)$ represent the total external input by dry and wet deposition of hydrogen ions and base cations K, Mg and Ca.

The water fluxes in the soil are denoted by q_{10}. Here $q_{10}(0,t)$ is the rate of rainfall, or the flow of water to the surface of the soil, and $q_{10}(L,t)$ is the rate of leaching to groundwater, or the flow of water at depth L. Assuming no surface run-off, the change in water content $u_{10}(t)$ in the profile can be expressed by the equation

$$\frac{d\, u_{10}(t)}{dt} = q_{10}(0,t) - q_{10}(L,t) - s_{10}, \tag{9}$$

where s_{10} represents the rate of evapotranspiration. We make the simplifying assumption that the water content does not change, i.e.

$$\frac{d\, u_{10}(t)}{dt} = 0. \tag{10}$$

This gives an approximation for the rate of leaching

$$q_{10}(L,t) = q_{10}(0,t) - s_{10}, \tag{11}$$

i.e. the rate of leaching equals precipitation minus evapotranspiration.

The changes in the amount of acid and base cations in the uppermost mineral soil layer of thickness L can be formulated using expressions for the transport and the exchange reactions and weathering.

$$\frac{d\,u_6(t)}{dt} = q_6(t) - \frac{q_{10}(L,t)\,u_6(t)}{u_{10}(t)\,L} + s_6 \tag{12}$$

$$\frac{d\,u_7(t)}{dt} = s_7 \tag{13}$$

$$\frac{d\,u_8(t)}{dt} = q_8(t) - \frac{q_{10}(L,t)\,u_8(t)}{u_{10}(t)\,L} + s_8 \tag{14}$$

$$\frac{d\,u_9(t)}{dt} = s_9, \tag{15}$$

where the rates of ion exchange s_6, s_7, s_8 and s_9 are calculated as in Appendix 2.

In the soil model it is assumed that the rate of cation exchange depends on the equivalent concentrations of ions in soil solution and on the exchange sites and that the rate of weathering is independent of these concentrations. Furthermore, surface run-off is assumed not to take place, i.e. the rate of water percolating through soil equals precipitation minus evapotranspiration.

The lumped soil model was used to simulate the impact of changing atmospheric deposition of hydrogen ions. Starting from the year 1900 with a deposition of hydrogen ions and base cations below 5 meq m^{-2}, the deposition was assumed to peak in 1970 (25 meq m^{-2} H^+ and 5 meq m^{-2} $Ca^{2+} + Mg^{2+} + K^+$) and thereafter to decrease by 30% by the year 1995. The deposition peak in the 1970 is reflected in the concentrations of hydrogen ions and base cations in soil solution (Fig. 5a). This input of H^+ results in a depletion of base cations from the exchange sites on the surface of the soil particles (Fig. 5b).

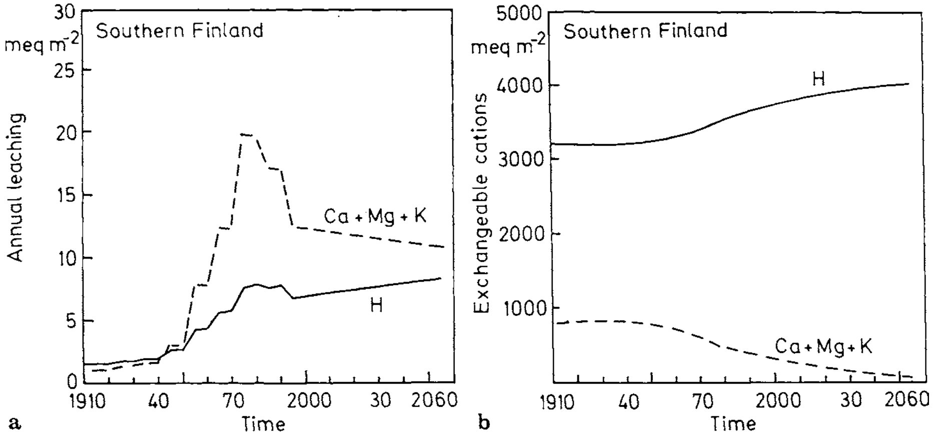

Fig. 5. Simulation of the impact of acid deposition on forest soil. **a** Leaching of base cations to groundwater. **b** Depletion of base cations on exchange sites (Holmberg *et al.* 1985a).

Toxic compounds may also cause direct damage to leaves and roots or to mycorhizal fungae. Let $U_n^D(t_k)$ denote the degree of damage of the leaves of $U_r^D(t_k)$ that below the soil in the kth year. Let h denote the rate of damage. The degree of damage is obtained analogously to $U^P(t_k)$ and $U^N(t_k)$ by integration

$$U_n^D(t_k) = \int_V \int_{t_k}^{t_k+1} \rho_n(x)\, h_n[u(x,t)]\, dt\, dV \tag{16}$$

$$U_r^D(t_k) = \int_V \int_{t_k}^{t_k+1} \rho_r(x)\, h_r[u(x,t)]\, dt\, dV. \tag{17}$$

The rates of damage h_n and h_r and their dependence on environmental factors are not well known.

Stand Development

Process-based, causal stand-growth models constitute an operational framework for assessing the effects of changing environmental factors on forest growth. This type of modelling is gaining increasing attention (cf. McMutrie and Wolf 1983; Mäkelä and Hari 1986; Mohren 1987). Our stand model (Mäkelä and Hari 1986) considers several size classes in the stand. The size classes interact with each other through shading, which reduces photosynthetic production. Annual amounts of photosynthetic production are allocated to needles, branches, stem and roots. In the latest version of the stand model (Hari et al. 1985; Mäkelä 1986; Nikinmaa and Hari in press), the dynamics of carbohydrate allocation are formulated on the basis of regularities in the structure of a tree.

Let $M_n(t_k)$ denote the needle mass in a tree during the kth year, $P(t_k)$ the amount of photosynthesis and A_n the coefficient of allocation of photosynthesis to needles. Let $M_r(t_k)$ denote the root biomass and A_r the allocation of photosynthates to roots. It is noted that the amount of nutrients supplied by roots should fulfill the foliage's need of nutrients. The stand model links consequent years as follows:

$$M_n(t_k) = F[P(t_k - 1), M_n(t_k - 1), A_n(t_k - 1)] \tag{18}$$

$$M_r(t_k) = G[P(t_k - 1), M_r(t_k - 1), A_r(t_k - 1)] \tag{19}$$

$$M_r(t_k) = \gamma M_n(t_k). \tag{20}$$

The effects of environmental factors, such as CO_2 and soil fertility, are not treated in the above stand model; it is implicitly assumed that they do not change with time. This implicit assumption has no justification any more. The stand model should be developed, however, to include the effect of such changes.

Changes in the environmental factors generate changes in the metabolic rates and in the amounts of metabolites produced during a summer. The annual relative effect on photosynthesis $U^P(t_k)$, annual relative effect on nutrient uptake $U^N(t_k)$, degree of needle damage $U_n^D(t_k)$ and degree of root damage $U_r^D(t_k)$ are defined for use in the stand model. If we assume that the functioning principles of the stand do not change due to changes in environmental factors, but that metabolic rates do change, then the model structure remains the same. Consequently, the functions in Eqs. (18) and (19) do not change but the amounts of metabolites have to be replaced as follows:

$$M_n(t_k) = F[U^p(t_k - 1)\,P(t_k - 1), (1 - U_n^D(t_k - 1))\,M_n(t_k - 1), A_n(t_k - 1)] \tag{21}$$

$$M_r(t_k) = G[U^p(t_k - 1)\,P(t_k - 1), (1 - U_r^D(t_k - 1))\,M_r(t_k - 1), A_r(t_k - 1)] \tag{22}$$

$$M_r(t_k) = \gamma M_n(t_k)/U^N(t_k). \tag{23}$$

The model outlined above includes several details which are rather poorly known, and many parameter values used are inaccurate. The behaviour of the stand model in its two forms has been demonstrated using the parameter values in the simulations corresponding to a moderately poor site in southern Finland (in Mäkelä and Hari 1986) (Figs. 6 and 7). In the simulations the dynamic environment is derived from the predictions made earlier (see Figs. 4 and 5). It is assumed that the amout of toxic compounds are not changing the nutrient uptake efficiency of root system but that it is only affected by the amount of exchangeable nutrients available. The effect of increasing CO_2 is derived as presented in Fig. 4.

The stand development in a static environment is characterized by a rapid increase in needle mass in early stand age. Later the needle mass begins to decline due to increasing allocation to the water transport system and respirational losses. The development of fine root mass follows the pattern of needle mass. On the other hand, in a dynamic environment the decreasing availability of cations causes an increasing allocation to the roots, which is reflected in a decrease of needle mass, stem volume and number of trees. The effect of CO_2 fertilization can be seen as a temporary increase in needle mass and stem volume in the early phase of stand development. The changes in the soil seem to be dominating in the present simulation example (Figs. 6 and 7).

Regional Forest Growth

Our knowledge of stand development is considerable, but too detailed for strategic decision making. Analysis and scenarios of forest growth on a national scale are needed for emission control. One way to produce information on the national scale is to base it on simulations at the level of the stand. This would, however, take too long a time in the present situation in which decisions about the reduction of emissions are urgently needed.

The scaling-up from a forest stand to a regional or national scale of forest growth is a problem of aggregation. Description of the environment and structure of forests at a national level has to be done in less detailed terms in order to facilitate the analysis. The spatial aggregation of environmental factors can be done either by using spatial mean values of environmental factors or by using the

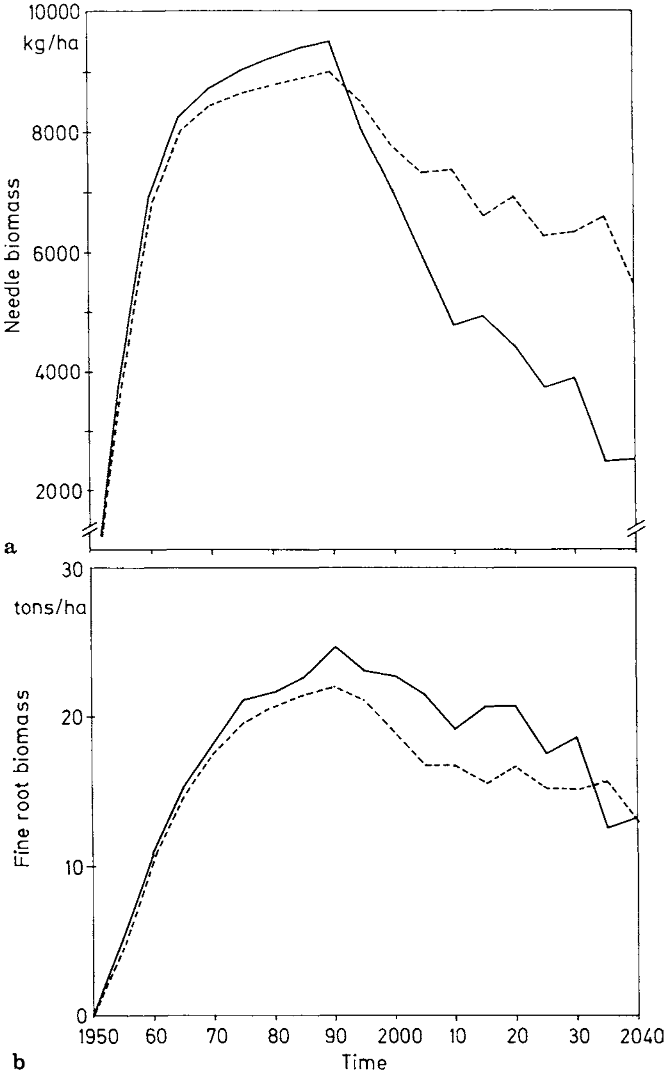

Fig. 6. Simulated stand development assuming a static (broken line) and a dynamic (thick line) environment. Temporal development of needle biomass (**a**) and root biomass (**b**).

distributions of environmental factors within the area. Forest production then is obtained by integration over the distribution. The use of spatial distributions evidently results in more reliable estimates than the use of mean values.

Aggregation of the structure of forests is possible if the age structure of the forests in a region does not change. This requirement is fulfilled in forests that are treated on the basis of sustained yield or if they are climax communities. The principle of sustained yield is largely accepted as the basis of forestry in industrialized countries. Assuming that the age structure of forests does not change on

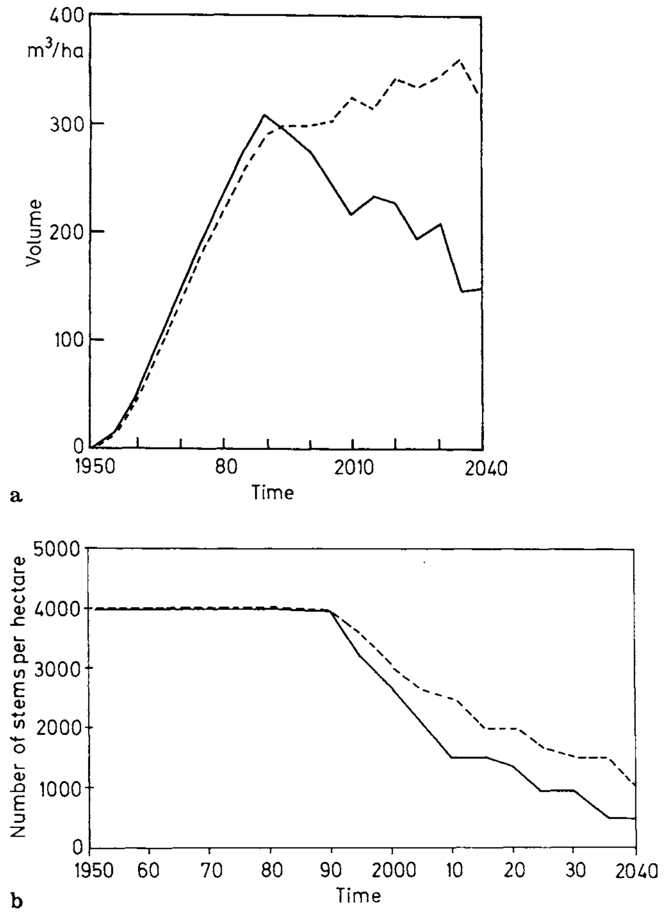

Fig. 7. Simulated stand development assuming a static (broken line) and a dynamic (thick line) environment. Temporal development of total stem volume (**a**) and number of trees (**b**).

a regional or national scale, the relative analysis of the changes of forest growth per unit area is sufficient.

Let Y denote the time development of forest growth in the region under consideration. Divide the area into N classes according to the environmental factors. Let $g_j[u(t)]$ denote the time development of relative forest growth in the j^{th} subarea, A_j the area and V_j mean volume growth and u^j the state of the environment in the j^{th} subarea.

$$Y = \sum A_j V_j g_j [u^j(t)]. \tag{24}$$

Forest growth in the subareas differs since the time development of the environmental factors differs. Analysis of the changes in the flows of compounds in the system formed by the atmosphere, forest soil, trees and groundwater gives the time development of the environmental factors for each subarea.

The determination of the growth g_j is problematic. In the long run it can be based on the behaviour of the stand models. Rather rough estimates have to be applied at the present level of understanding of the dynamics of the change in environmental factors and its consequences for forest growth. A multiplicative model for linking the different components of the environment seems justified.

The nutrient concentrations on soil particles and in the soil solution can be treated together since from these two sources nutrients are supplied to trees. Let u_8 denote the base cation concentration of the soil solution and u_9 that on soil particles. We assume that these two sources of nutrients are equally important for the forest in the pre-industrialized situation. Let v denote the availability of base cations for trees. Assume that v can be obtained as a weighted mean of the concentrations in soil solution and on soil particles, i.e.

$$v = \alpha u_8 + \beta u_9. \tag{25}$$

The weights α and β are determined in such a way that trees utilize the nutrients carried by the flow of water the soil to the roots and then satisfy their remaining need of nutrients by uptake from the surface of soil particles.

Let u_3, u_4 and u_5 represent the atmospheric concentrations of CO_2, SO_2 and O_3, u_6 and u_7 the concentration of acid ions in soil solution and on soil particles, and u_8 and u_9 the concentrations of base cations in soil solution and on soil particles.

The multiplicative approximation leads to the following model

$$g_j(t) = \Pi g^i[u_i^j(x,t)], \tag{26}$$

where g^i is the effect of the i^{th} environmental factor on the growth. The determination of the functions has to be done with rather limited information, and only rough estimates can be obtained. A natural way is to estimate the effect of a change in a component of the environment on the metabolism of trees and then convert this change to growth. The metabolic processes considered are photosynthesis, nutrient uptake and allocation of carbohydrates.

The concentration of carbon dioxide affects photosynthesis, since CO_2 is the source of carbon for carbohydrates. The present low level strongly limits photosynthetic production. The dependence of photosynthetic rate on CO_2-concentration is easy to measure in the laboratory. We assume that the dependence of growth, g_3, on carbon-dioxide concentration is the same as that of the photosynthetic rate.

The effects of SO_2 and O_3 on growth are so weakly known at present that it is impossible to estimate the functions g_4 and g_5. Until more information is available, we assume that they equal 1.

The amount of cations in soil solution and on soil particles combine to describe availability, v. In fertilization experiments in the 1960's it was observed that cation fertilization does not affect growth (e.g. Kukkola and Saramäki 1983). On the other hand, a severe potassium deficit is lethal for trees. We assume that a saturation function of the Michaelis-Menten type is a good approximation for the growth response to variable cation availability.

$$g_8(t_k) = \frac{v(t_k)}{v(t_k) + \gamma v(t_0)}. \tag{27}$$

The parameter $v(t_0)$ is the availability of cation without anthropogenic emissions and gamma is a scaling parameter.

The time development of deposition can be constructed using statistical information and scenarios of energy use, and measurements of deposition (Fig. 8). When deposition is input into the models, the development of the environmental factors is obtained in each subarea and the time development of environmental factors can be converted into forest growth (Fig. 9). The estimates of regional forest growth are obtained using Eq. (22).

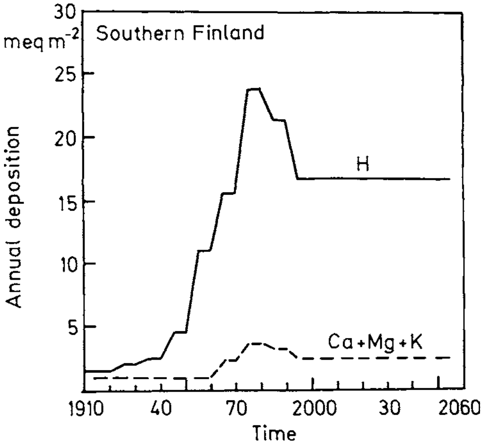

Fig. 8. Temporal development of the deposition of hydrogen ions and base cations (Ca, Mg and K) in southern Finland. The peak of the 1970's is approximated from measurements by the Finnish Board of Waters (Järvinen and Haapala 1980). The deposition is assumed to follow the sulfur emissions in the period of 1900–1980. Furthermore, the present reductions of sulfur emissions are assumed to decrease the deposition by 30% of the 1980 value by the year 1995.

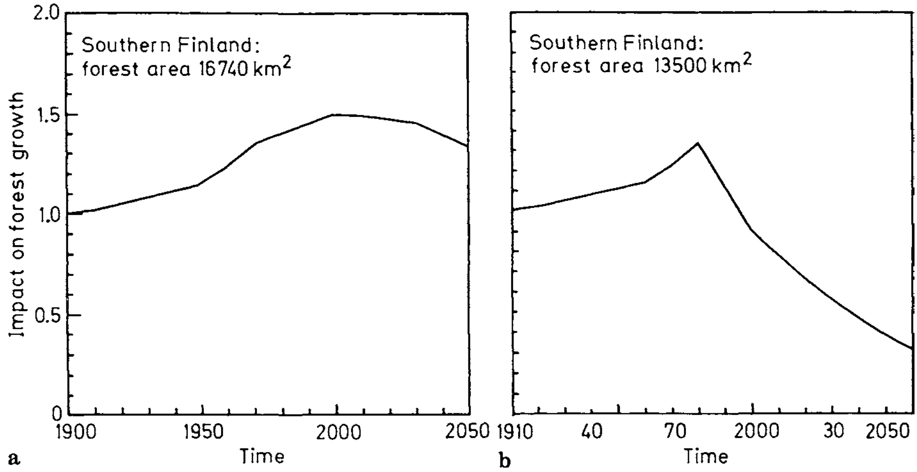

Fig. 9. Temporal development of the impact on forest growth on two forest sites: (**a**) fertile soil with slow percolation; (**b**) poor soil with high percolation.

Concluding Remarks

The present formulation of the impact of environmental change on forest growth has a modular structure, which is easily expandable to include environmental variables others than those accounted for in the model runs presented here. The functions that relate the changes in the environment to forest growth may also easily be modified as more knowledge about the mechanisms becomes available.

The direct damaging impact of toxic substances on needles and mycorrhiza may be incorporated in the functions h_n and h_r that describe the rate of damage of needles and roots. The triggering effect of drought or frost lies in the shortening of the life time of roots and needles and may also be introduced through the damage rates h_n and h_r. The impact of a deficient soil nutrient supply is taken into account in the nutrient uptake rate r, which decreases with the supply. A low nutrient uptake rate again decreases forest growth. Tree growth is in the model stimulated by increases in carbondioxide and nitrogen. The aspect of nutrient imbalance caused by nitrogen-stimulated growth coupled to low nutrient supply in the soil cannot be accounted for by the present formulation.

The analysis above is based on the flow of material in the system formed by the atmosphere, the forest soil, vegetation, groundwater and surface waters. This starting point is very operational in the analysis, and a coherent set of models was constructed on the basis of the flows.

From an ecological point of view, the change in environmental factors is the most important result. The analysis shows that several concentrations of nutrients and toxic compounds are changing. Plants respond to this change of environmental factors. Forest growth is changing on a global scale. The assumption of an environment in a steady state in which the environmental factors vary more or less randomly around a constant mean value, is implicit in many ecological studies. It appears to be no longer justified and calls for a revision of ecological research.

Aggregation or scaling-up is the most important methodological question in assessing the effects of changing environmental factors on the functioning of regional vegetation systems. It can be done either on a mathematical or on an ecological basis. When mathematical aggregation is applied, statistical mean values are usually used. This is the prevailing methodology used nowadays. Most measuring results are published only as mean values, monthly or daily. The plants do not, however, respond to mean values, but to the prevailing environment. The dependence of plant response to environmental factors is mostly non-linear. The use of mean values leads to biased results if the response is non-linear. This difficulty can be avoided if the aggregation is based on the analysis of the dependence of plant response as has been demonstrated in Eqs. (4)–(8), (25) and (26).

There are several details in the analysis presented which are not sufficiently well known. Uncertainty about the deposition in forests, concerning especially base cations, the formation and levels of ozone near trees, the dependence of tree and mycorhiza response on nutrient deficiency and toxic compounds in soils limit the analysis at present. However, the approach can be used as a tool to focus research on the relevant questions.

Forest decline is usually considered a phenomenon in heavily polluted areas in Central Europe or in North America. However, we prefer to view forest decline as a symptom of a process in which the trees are responding to changes in their environment. It is remarkable that these changes and the consequent responses are no longer restricted to areas close to industrial activity. Such global and rapid environmental change as that which vegetation is presently experiencing has hardly ever occurred before.

Appendix 1

Transport Processes in Soil. Flow Equations

The processes of diffusive and convective flow of water and ions are formulated on the basis of the diffusivity equation (Hillel 1971). The parameters of the flow processes in soil are the hydraulic diffusivity ($D = 0.0012\,m^2\,h^{-1}$), the hydraulic conductivity ($K = 0.005\,m\,h^{-1}$), the ion diffusivity ($C = 0.0012\,m^2\,h^{-1}$) and the porosity of the soil ($P = 0.6\,m^3\,m^{-3}$). Assuming a homogeneous soil, the Darcy flow equation can be used and the vertical distributions of the ionic concentrations can be calculated from the following partial differential equations, where $u_{10}(x,t)$ denotes water content of the soil, $u_6(x,t)$ and $u_8(x,t)$ denote the concentrations of acid and base cations in soil solution, $u_7(x,t)$ and $u_9(x,t)$ are the concentrations of hydrogen and base cations absorbed to the exchanger. The mass fluxes are denoted by $q_{10}(x,t)$ for the flow of water, $q_6(x,t)$ for the flow of acid and base cations in the liquid phase.

$$\frac{d\,u_{10}(x,t)}{dt} = \frac{d\,q_{10}(x,t)}{dx} + s_{10} \tag{A1}$$

$$q_{10}(x,t) = -\frac{d\,u_{10}(x,t)}{dx} + Ku_{10} \tag{A2}$$

$$\frac{d\,u_6(x,t)}{dt} = -\frac{d\,q_6(x,t)}{dx} + s_6 \tag{A3}$$

$$q_6(x,t) = -\frac{C\,d\,u_6(x,t)}{dx} + \frac{q_{10}(x,t)\,u_6(x,t)}{P\,u_{10}(x,t)} \tag{A4}$$

$$\frac{d\,u_8(x,t)}{dt} = -\frac{d\,q_8(x,t)}{dx} + s_8 \tag{A5}$$

$$q_8(x,t) = -\frac{C\,d\,u_8(x,t)}{dx} + \frac{q_{10}(x,t)\,u_8(x,t)}{P\,u_8(x,t)} \tag{A6}$$

$$\frac{d\,u_7(x,t)}{dt} = s_7 - r_9 \tag{A7}$$

$$\frac{d\,u_9(x,t)}{dt} = s_9 + r_9. \tag{A8}$$

The function s_{10} stands for water uptake by the roots, and s_6, s_7, s_8 and s_9 for ion exchange between soil solution and soil particles and r_9 for the weathering of minerals.

Appendix 2

Cation Exchange Between Soil Solution and Soil Particles

The exchange of ions between soil solution and soil particles is a dynamic process, the rate of which was assumed to be determined by the equivalent concentrations of ions in solution and on soil particles. The rates of the exchange reactions are calculated in the following equations, where cec stands for the total cation exchange capacity of the mineral soil and L for the depth. The selectivity coefficient of the Gaines-Thomas ion exchange equation is here split into the rate parameters v_1 and v_2.

$$s_6 = -\frac{v_1\,u_9(x,t)}{cec}\left(\frac{u_6(x,t)}{u_{10}(x,t)\,L}\right)^2 + \frac{v_2\,u_8(x,t)}{u_{10}(x,t)\,L}\left(\frac{u_7(x,t)}{cec}\right)^2 \tag{A9}$$

$$s_7 = -\,s_6 \tag{A10}$$

$$s_8 = -\,s_6 \tag{A11}$$

$$s_9 = s_6. \tag{A12}$$

List of Symbols

Symbol	Unit	State variable
Environmental variables		
$u_1(x,t)$	$W\,m^{-2}$	irradiance
$u_2(x,t)$	°C	temperature
$u_3(x,t)$	$g\,m^{-3}$	concentration of CO_2
$u_4(x,t)$	$g\,m^{-3}$	concentration of SO_2
$u_5(x,t)$	$g\,m^{-3}$	concentration of O_3
$u_6(x,t)$	$eq\,m^{-3}$	acid cations in soil solution
$u_7(x,t)$	$eq\,m^{-3}$	acid cations on exchanging surfaces
$u_8(x,t)$	$eq\,m^{-3}$	base cations in soil solution
$u_9(x,t)$	$eq\,m^{-3}$	base cations on exchanging surfaces
$u_{10}(x,t)$	$m^3\,m^{-3}$	water content of soil

Flux variables

$q_3(x,t)$	$g\,m^{-2}\,h^{-1}$	flux of CO_2
$q_4(x,t)$	$g\,m^{-2}\,h^{-1}$	flux of SO_2
$q_5(x,t)$	$g\,m^{-2}\,h^{-1}$	flux of O_3
$q_6(x,t)$	$g\,m^{-2}\,h^{-1}$	flux of hydrogen ions
$q_8(x,t)$	$g\,m^{-2}\,a^{-1}$	flux of base cations
$q_{10}(x,t)$	$g\,m^{-2}\,a^{-1}$	water flux

Stand variables

Mn	$g\,ha^{-1}$	needle mass
Mr	$kg\,ha^{-1}$	root mass
ρ_n	$kg\,m^{-3}$	needle mass distribution
ρ_r	$kg\,m^{-3}$	root mass distribution
U^P	—	relative effect of environment on photosynthesis
U^N	—	relative effect of environment on nutrient uptake
U^D_n	—	degree of damage of leaves
U^D_r	—	degree of damage of roots
P	$g\,yr^{-1}$	annual amount of photosynthesis
p	$g\,g(needle)^{-1}s^{-1}$	photosynthesis rate
n	$g\,g(root)^{-1}s^{-1}$	nutrient uptake rate

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Wintering Response of Conifers to Acid Rain Treatment Under Northern Conditions

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Summary

The wintering response of conifer seedlings and adult trees, and injuries inflicted by cold and acid rain on their needles and buds, were studied experimentally. The results reveal the greater susceptibility of seedlings of Norway spruce to cold and indirect acid rain effects (e.g. in terms of growth and viability of seedlings) than those of Scots pine, whereas adult Scots pine suffer significant cellular damage and disturbances in the surface wax layers following the acid rain treatment and also exhibit significantly reduced needle length after treatment at pH 4 and stomatal size after pH 3. Scattered $CaSO_4$ crystallites were observed on the needle surfaces of the seedlings treated at pH 3. The southern provenances of spruce seemed to derive a slight advantage from the acid rain treatment, whereas deterioration effects were clearly observable in the northern provenances after the pH 3 treatment in the form of poor seedling condition.

Introduction

In order to survive, plants growing in cold environments must resist the fatal strain caused by lowering of the temperature. Climatic demands have evolved species with narrow genetic material which are highly specialized in adapting to a cold climate. Thus by developing a high degree of hardiness the tree genera lose a lot of their genetic flexibility. Considering the extent of the variation in climate from year to year, a flexible regulation system would be most desirable for conifer species with a long life span.

It has been demonstrated experimentally that frost resistance begins to increase gradually towards the end of the growing season (Kandler et al. 1979; Öquist 1982). The gradual changes in the physiology and anatomy of conifers cause hardening, which enables them to endure the frosts in autumn without severe damage. The beginning of the hardening period, its rate of progression and the reactions taking place are genetically regulated (Menzies and Holden 1981; Tigerstedt 1985), and vary greatly between plant species and according to the time of year. Sakai (1982) observed the cold tolerance of the Abietoidae to be as low as −70°C (*Picea glauca,* (Moench) Voss. *Abies balsamea* Mill., *Larix sibirica*

Kauppi et al. (Eds).
Acidification in Finland

Ledeb.), whereas the frost resistance point of the needles of *Picea abies* (L.) Karst. has been found to be −44°C at its maximum (Pümpel et al. 1975), and the cambium and cortex cells will tolerate −50°C. Christersson and Krasavtsev (1972) observed *Picea abies* branches to have a frost resistance of −40 to −60°C, depending on the rate of freezing. The cold tolerance limit for *Pinus sylvestris* L. branches was about −50°C. Frost resistance in forest trees has recently been reviewed by Skre (1988).

The relationships between the effects of air pollution and low temperature tolerance have been extensively studied in recent years (Davison and Barnes 1986; Freer-Smith and Mansfield 1987; Lucas et al. 1988; Reinikainen and Huttunen 1989). These effects may be related to the delayed development of wintering organs or changes in the hardening and dehardening processes. It has been suggested that the increased susceptibility of forest trees to wintertime drought stress may be a consequence of eroded cuticular structures, resulting in a disturbance in the water balance (Mäkelä and Huttunen 1987).

The direct effects of acid rain on forest trees have been observed experimentally (Evans and Curry 1979; Evans 1984; Haines et al. 1985; Percy 1987; Mengel et al. 1987), while Percy (1986) observed seedling survival to be the most sensitive parameter in an acid rain experiment. Differences between tree species in their responses to acid rain were reported by Abouguendia and Baschak (1987), who found the white spruce [*Picea glauca* (Moench) Voss.] to be more sensitive to sulphur accumulation and more likely to develop visible injuries than the jack pine (*Pinus banksiana* Lamb.). Haines et al. (1980) found the threshold for acute visible damage in *Pinus strobus* L. to be pH 1.0, while the broad-leaved species examined exhibited damage at pH 2.0.

The present work was aimed at determining the direct effects of acid rain on needle ultrastructure and surface structures together with the morphological and biochemical changes occurring in needles in the course of the hardening and dehardening processes during and after acid rain treatment. The cold tolerance of seedlings of *Picea abies* (L.) Karst. and *Pinus sylvestris* L. was tested during the autumn, winter and spring of each year.

Materials and Methods

Experimental Design and Procedures

Two experiments were performed, one at Oulu (65°00′N, 25°30′E), using transplanted seedlings of *Picea abies* and *Pinus sylvestris* 10–30 cm in height, and the other with adult pines at Kevo (69°45′N, 27°01′E), where 80 test plots were designated in a natural mixed stand of *Pinus sylvestris* (2–3 m tall) and *Betula tortuosa* Ledeb. The experiments included four acid treatments (unsprayed control, clean water control and water acidified to either pH 3 or pH 4 with sulphuric and nitric acids).

The test area with seedlings in Oulu is located about 5 km north of the city centre, near the university, in a 40- to 50-year-old pine forest stand, in which some spruces and birches are also found. The plots were established in summer 1986.

The experiment with adult pines was located at the Kevo Subarctic Research Station, where the University of Turku had designed an acid rain experiment with 50- to 70-year-old Scots pines and mountain birches (Neuvonen et al. this Vol.). A large experimental field was established in summer 1985 on a west-facing slope of a fell, at 100 m above sea level.

The acid solutions for the Oulu experiment were made by adding sulphuric acid and nitric acid (vol:vol 2:1, pH adjusted to 3 or 4) to tap water (drinking water, chemical analyses by the Oulu City Council). The clean water was chlorinated tap water, with an average pH of 7. In summer 1988, this was replaced with distilled water, pH 5.6 (other analyses performed by the University of Oulu), and the acids were diluted in solution at w:w 2:1. The springwater used at Kevo (for the information about chemical analyses, see Neuvonen et al. this Vol.) was acidified with sulphuric acid and nitric acid (w:w 2:1), the additional rainfall was 50 mm month^{-1}, and the dose of experimental rain was sprayed from a height of 1.5–2 m.

The calculated additional sulphur and nitrogen deposition values for both the Oulu and Kevo experiments are given in Table 1. An average of five to ten times more sulphur was administered in the Oulu experiment than is received by the trees in a normal year (pH 3 treatment), while the sulphur load at Kevo was more than tenfold (pH 3). Wet deposition of nitrogen was increased by a factor of between two and five times over that occurring in an average year (pH 3).

Table 1. Additional amounts of sulphur and nitrogen (g m^{-2}) added by spraying the seedlings (at Oulu) and 50–70-year-old trees (at Kevo) with a simulated acid rain (pH 4 or 3) containing sulphuric and nitric acids

	Kevo		Oulu	
1985	pH 4	pH 3	pH 4	pH 3
Sulphur	0.130	0.485	–	–
Nitrogen	0.046	0.170	–	–
1986	pH 4	pH 3	pH 4	pH 3
Sulphur	0.368	2.283	0.233	1.825
Nitrogen	0.128	0.968	0.040	0.317
1987	pH 4	pH 3	pH 4	pH 3
Sulphur	0.347	2.195	0.898	9.870
Nitrogen	0.121	0.767	0.156	1.713
1988	pH 4	pH 3	pH 4	pH 3
Sulphur	0.384	2.517	0.623	5.862
Nitrogen	0.135	0.880	0.188	1.770
Total 1985–88	pH 4	pH 3	pH 4	pH 3
Sulphur	1.229	7.480	1.732	17.515
Nitrogen	0.430	2.615	0.381	3.790

Table 2. Monthly mean atmospheric concentrations of SO_2 and NO_2, annual deposition of sulphate and nitrate ions and monthly mean pH of the ambient rain at Oulu and Kevo in 1985–1988

	1985	1986	1987	1988
Oulu				(1.1–30.9)
Atmospheric concentrations of				
SO_2 ($\mu g\,m^{-3}$)	14	11	11	
NO_2 ($\mu g\,m^{-3}$)	12	18	22	
Annual wet deposition				
SO_4^{2-} ($g\,m^{-2}a^{-1}$)	1.3	1.2	1.0	
NO_3^- ($g\,m^{-2}a^{-1}$)	0.3	0.3	–	
Rainfall pH	5.9	6.1	5.6	
Kevo				
Atmospheric concentrations of				
SO_2 ($\mu g\,m^{-3}$)	3	3	5	4
Annual wet deposition				
SO_4^{2-} ($g\,m^{-2}a^{-1}$)	0.17	0.15	0.13	0.14
NO_3^- ($g\,m^{-2}a^{-1}$)	0.03	0.05	0.04	0.05
Rainfall pH	4.6	4.7	4.7	4.6

The ambient pollutant concentrations in Oulu and Kevo are given in Table 2 (Air Quality in Oulu in 1983–1986; Air Quality in Oulu, measurements in 1987; Finnish Meteorological Institute 1985–88a). The main gaseous pollutants in Oulu are sulphur dioxide and nitrogen oxides, and considerable amounts of fertilizer dust and ammonium are also emitted from a fertilizer factory in the vicinity of the city. The weekly mean pH of the ambient rain at the test field in Oulu in summer 1988 was 6.9, which is high, due to alkaline dust from the urban area and the fertilizer factory. Both the sulphur dioxide and deposited sulphate and nitrate values at Kevo are close to the background levels.

The climatic conditions in Oulu and Kevo during the experiments are illustrated in Fig. 1 (Finnish Meteorological Institute 1985–88b). The climate of the Kevo area is strongly influenced by the nearby Arctic Ocean, which makes the winter relatively warm and increases precipitation. One extremely cold winter and one cool summer were experienced during that time, especially in Oulu, namely in 1986–87. Mean annual rainfall is 479 mm in Oulu and 361 mm at Kevo.

The seedling material in Oulu was obtained from the nurseries of the Finnish Forest Research Institute and the National Board of Forestry. 540 one-year-old seedlings of Norway spruce [*Picea abies* (L.) Karst.] and Scots pine (*Pinus sylvestris* L.), representing 14 provenances were planted in summer 1986, 1518 new one and 2-year-old seedlings of 17 provenances in summer 1987 and 238 new 2-year-old seedlings of 7 provenances in summer 1988. Thus the total material comprised 2296 seedlings of 29 Finnish provenances (Fig. 2a: northern provenances 1–14, southern provenances 15–29). The seedlings were planted in 20 litres or 11 litres plastic boxes, four in each box. The soil was standardized to consist of acidic unfertilized peat, sand and composted soil (2.5:0.5:1.0), and was steam sterilized to minimize the development of weeds and pathogens. The boxes were

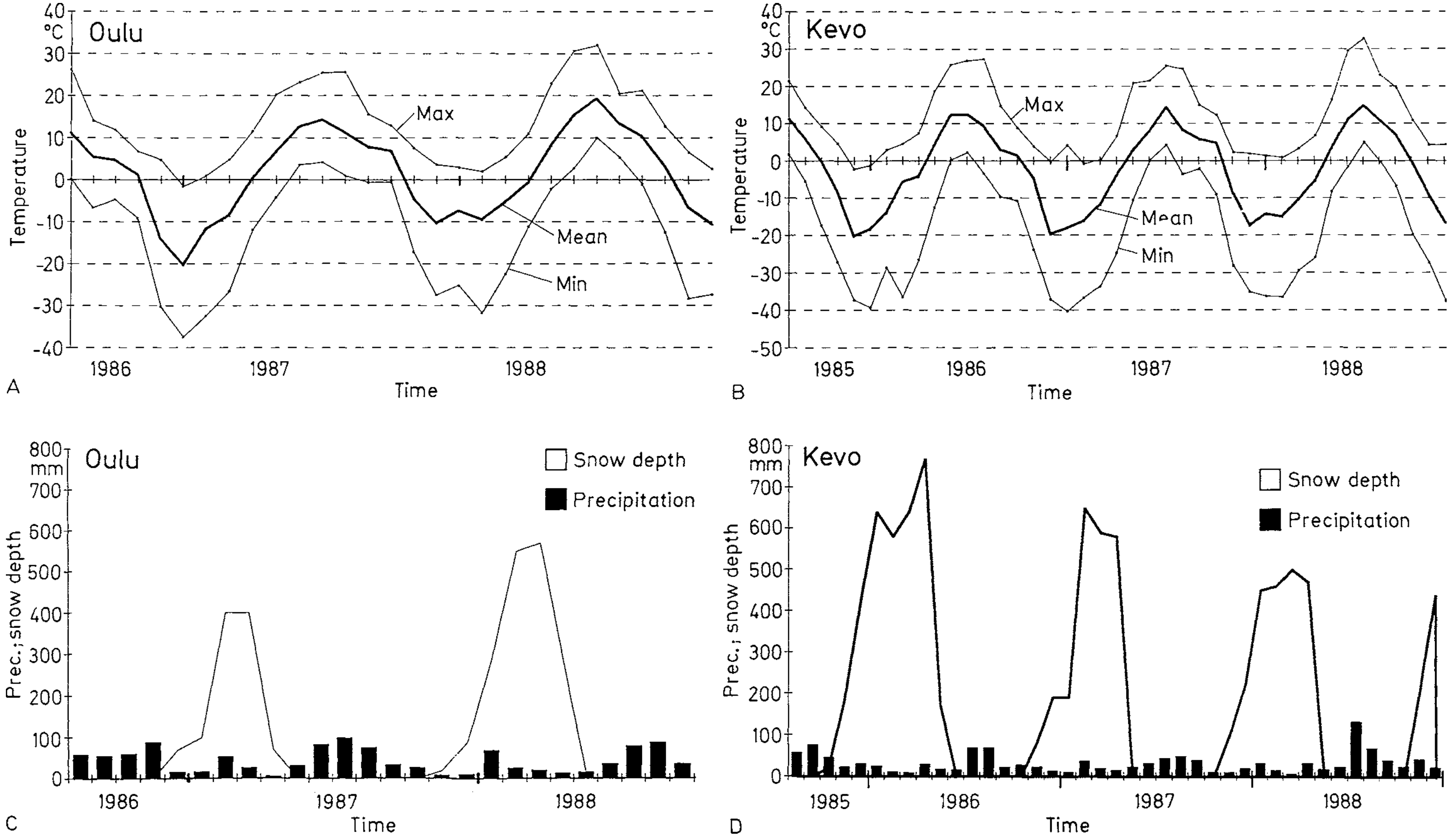
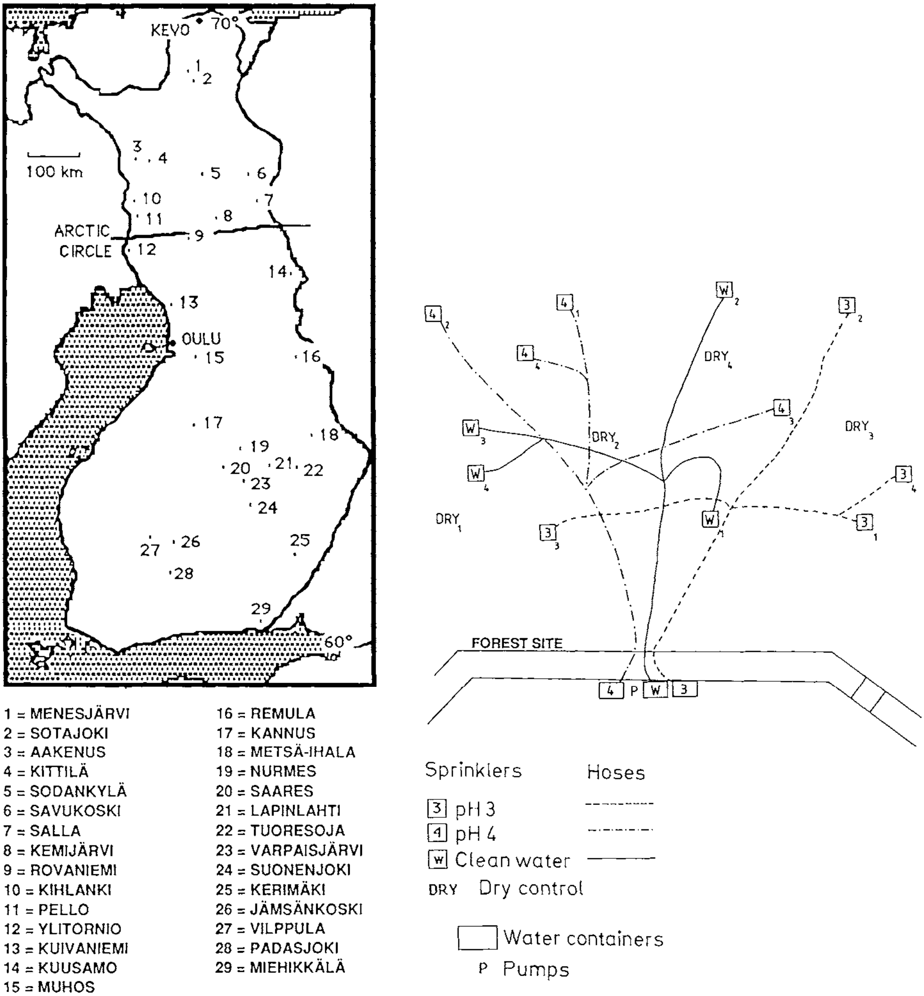


Fig. 1A–D. Monthly minimum, maximum and mean temperatures (°C), and precipitation and snow depth (mm) in Oulu (**A**, **C**) and at Kevo Subarctic Research Station (**B**, **D**) perforated from the bottom, in order to facilitate the passage of water through the soil. There were 560 boxes altogether providing 140 replicates for each treatment.

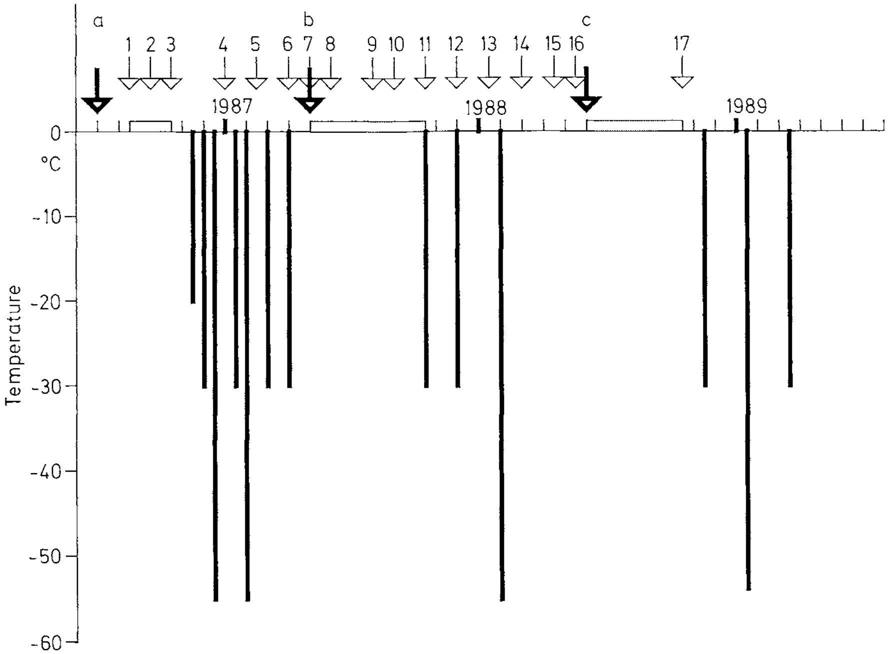
For the exposure experiments, the boxes were randomly divided into four treatment groups: pH 3, pH 4, tap or distilled water, unsprayed controls (Fig. 2b). The boxes were placed at a standardized distance from the sprinklers (Uniflex Violetta) and sprayed three times a week with an amount corresponding to 5 mm of rain each time. This was allowed to permeate through the soil to the roots, thus



A Material

B Acid rain treatment

Fig. 2A–C. Location of the sites of the experiments and origins of the seedlings used in Oulu (**A**), arrangement of the experimental area in Oulu (**B**), and sampling and exposure schedule in Oulu (**C**). **A** 1–14 northern provenances, **B** 15–29 southern provenances. **C** 1–17 = sampling dates. **a**, **b**, **c** seedling planting dates; □ = acid rain exposure; *bars downwards* cold tolerance testing, date and temperature



C Treatment and sampling schedule

Fig. 2. (continued)

giving a total of 60 mm month^{-1} in addition to the "natural" rain (60 mm month^{-1} in an average summer month; Finnish Meteorological Institute 1985–88b), which was not prevented from reaching the seedlings.

Observations and Measurements

Samples were taken from the Oulu experiment about once a month (16 plots, Fig. 2b,c) in order to investigate the direct effects of acid rain by scanning and transmission electron microscopy and measurements of the pH of the needle surfaces. These methods were also used to indicate the changes in the hardening process (indirect effect of acid rain). Growth, viability and alterations in cold tolerance of the seedlings were also studied for indirect effects of acid rain. In the Kevo experiment samples for scanning (20 plots) and transmission (4 plots) electron microscopy of the pine needles were taken twice a year (spring or summer and autumn). Needle length from the adult pines was measured in autumn 1988 as an indirect indicator of the effect of acid rain.

Growth and Overall Condition

The measurements of seedling viability and growth in height in the Oulu experiment were made in spring, before the growing season, and in autumn, after the end of the growing season. The condition of the seedlings was estimated on a five-point scale which took in account damage to the needles, seedling growth and condition of the buds. Seedling viability was classified as follows: class 5 = perfectly healthy seedlings, 2 needle years at least, stem growth straight, growth vigorous, buds healthy; class 4 = good condition, a few damaged needles, growth at least average; class 3 = fair condition, 30% of needles damaged, stem tortuous, growth average; class 2 = poor condition, over 30% of needles damaged, stem broken, bud dead, slow growth; class 1 = dead seedlings. In the Kevo experiment, the lengths of needles from each needle year (n_{tot} 3365), stored in a freezer, were measured after the end of growing period in 1988.

Microscopy

Transmission electron microscopy (TEM) (n_{tot} 564): 0.5 mm sections of needles were fixed with glutaraldehyde and OsO_4 in 0.05 or 0.1 M phosphate buffer and then dehydrated in an alcohol series and embedded in Ladd's epon (Reinikainen and Huttunen 1989b).

Scanning electron microscopy (SEM) (n_{tot} 1318): Surface erosion was monitored by collecting needle samples from the middle part of each annual growth of the conifers and storing these in a freezer. Other samples for SEM were air-dried at room temperature. The needles were covered with gold-palladium (45 nm) with sputter equipment (Polaron E5100), and micrographed under a scanning electron microscope (JEOL JSM-35) at 15 kV with an exposure of 45 or 90 s. Microanalysis of the particulate deposits on the needle surfaces was performed by EDS (Energy Dispersive X-ray Spectrometer) (LINK AN 10000) (Turunen and Huttunen 1988, 1990).

pH of Needle Surfaces

The pH of the needle surfaces (n_{tot} 650) was measured with a special surface pH electrode (Ingold electrode, LOT 403-M2) linked to a pH meter (PHM 29b, Radiometer). pH was measured on both sides of five needles from each seedling, which had been subjected to a humid microclimate on the moistened base of a Petri dish (Turunen and Huttunen 1988).

Frost Tolerance

Seedlings treated with acid rain were exposed to cold in automatically regulated low temperature cabinets (dry, dark conditions at − 30 or − 55°C, Fig. 2c). This was carried out only with seedling material from the Oulu experiment (for more details, see Reinikainen and Huttunen 1989b; Reinikainen et al. 1989).

Potassium output test: Whole needles (weight about 50 mg = 3 pine needles or 12 spruce needles) were carefully placed into clean test tubes with tweezers without damaging them and 10 ml double-distilled water was added. The samples were shaken for 1 h at room temperature, after which they were lifted out with a spatula. Two controls, without needles, were included. K^+ concentrations were analysed by AAS (Atomic Absorption Spectrophotometer) (Perkin Elmer 380), with a Na-K lamp, using 1 ppm and 2 ppm KCl standards. K^+ output samples were taken upon commencement of the cold treatment and 7 days later. Total K^+ output was measured from needles killed in liquid nitrogen and kept in a freezer for 1 to 4 days. Relative K^+ output values (RK) were calculated as follows:

$$\mathrm{RK}\ (\%) = \frac{\mathrm{K^+\ output\ (treated\ sample)}}{\mathrm{total\ K^+\ output\ (liquid\ nitrogen)}} \times 100.$$

A low RK value indicates that the plant sustained little or no damage at all during freezing, whereas high values indicate severe damage.

TTC test for bud viability: Halved buds (2–3 buds of spruce, 1–2 buds of pine) were placed in 0.1% TTC (2,3,5-triphenyltetrazoliumchloride) in a Petri dish for 30 min at room temperature. Colour changes in the bud tissues were observed by light microscopy, and the percentage of injured buds was calculated.

Statistical Analyses

The results were tested statistically with one-way and two-way Analyses of Variance, Tukey's studentized range (HSD) test, Spearman correlation coefficients and the Kruskall-Wallis test (SAS Institute Inc., Cary, NC, U.S.A.).

Results

Success of the Seedlings

Some of the results concerning seedling survival are presented in Fig. 3. The southern spruce seedlings were in poor condition in May 1987 after the cold winter of 1986–87, at which time the differences between the southern and northern spruce provenances were highly significant ($p = 0.0001^{***}$). Significant differences were also found in August 1987 ($p = 0.0018^{**}$) and August 1988 ($p = 0.0136^{*}$) between the exposure groups of the southern spruces planted in 1986, when the pH 3-treated seedlings were found to have survived better than the dry controls. On the other hand, the northern pH 3 spruce seedlings planted in 1987 were in a highly significantly poorer condition ($p = 0.0001^{***}$) than the water and dry control seedlings of the same provenance and age. The pH 3-treated seedlings of the northern pine provenances had a fairly high level of success from August 1986 to August 1988 compared with the dry controls, while the situation in the northern spruces was the reverse.

The viability of the seedlings was reduced by fungal and insect attacks and freezing injuries. Some of the pine seedlings were already infected with *Ascocalyx* sp. in the nurseries, which spread to several seedlings at the test field as a result of

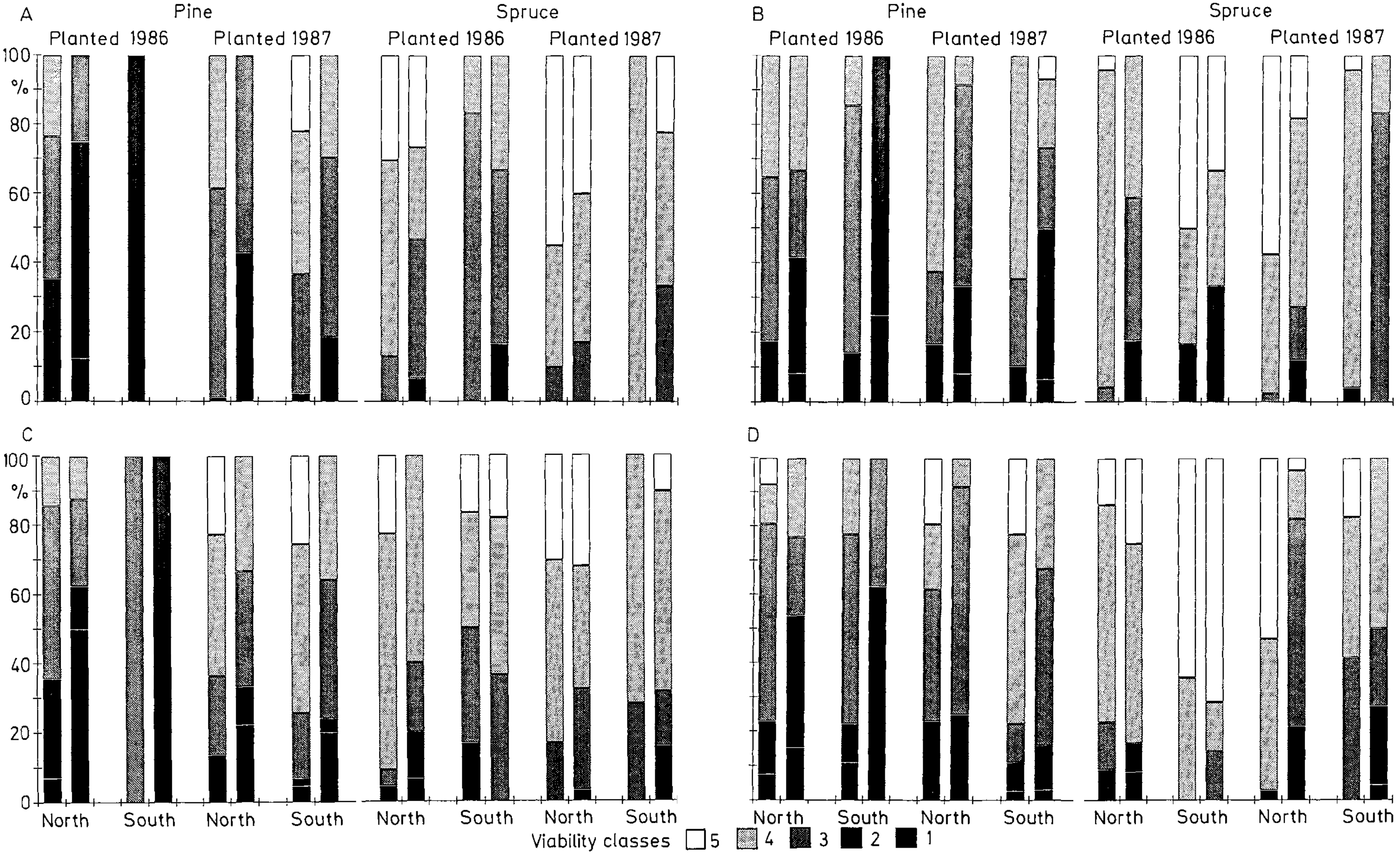

A
Pine
Spruce
Planted 1986
Planted 1987
Planted 1986
Planted 1987
B
Pine
Spruce
Planted 1986
Planted 1987
Planted 1986
Planted 1987
C
D
100
%
80
60
40
20
0
North
South
North
South
North
South
North
South
North
South
North
South
North
South
North
South
Viability classes
5
4
3
2
1

Table 3. Mean height growth from August 1987 to August 1988 in cm (± standard deviation) of different provenances of conifer seedlings in an acid rain experiment in Oulu

	Dry control	Clean water	pH 4	pH 3
Spruce				
Northern	5.48 ± 3.04 n = 65	5.73 ± 0.94 n = 68	6.23 ± 1.46 n = 66	5.18 ± 3.11 n = 60
Southern	6.03 ± 1.52 n = 20	4.04 ± 0.93 n = 36	5.79 ± 1.41 n = 25	4.67 ± 0.38 n = 36
All proven.	5.68 ± 2.45 n = 85	5.09 ± 1.23 n = 104	6.04 ± 1.34 n = 91	4.98 ± 2.37 n = 96
Pine				
Northern	4.33 ± 3.02 n = 19	5.07 ± 2.38 n = 16	4.30 ± 2.97 n = 18	6.39 ± 1.56 n = 25
Southern	7.16 ± 2.01 n = 25	5.09 ± 1.61 n = 35	5.36 ± 2.17 n = 28	5.91 ± 2.64 n = 26
All proven.	5.74 ± 2.82 n = 44	5.08 ± 1.97 n = 51	4.83 ± 2.54 n = 46	6.19 ± 1.93 n = 51

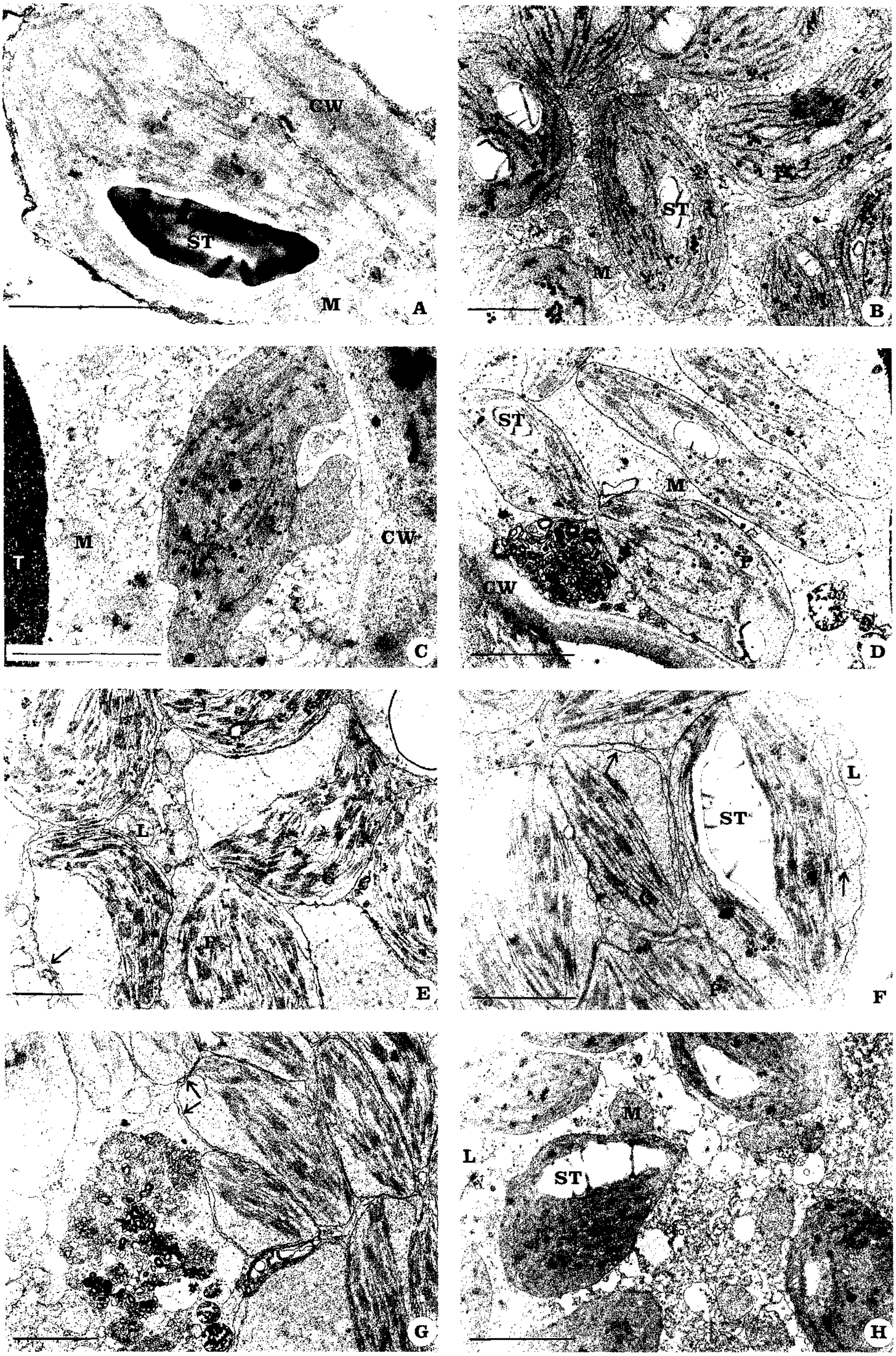
the wet growing conditions and cold winters and reduced their viability in many cases. The differences in the viability between the conifer provenances were already somewhat significant at the beginning of the experiment, but those between the exposure groups of the spruce provenances increased in significance during the exposure period.

Provenance was the main determining factor in both the spruce and the pine seedlings, as regards growth in height (Table 3). The differences were highly significant, especially among the spruce seedlings ($F = 51.73$, $p = 0.0001$***, $df = 1$), the southern provenances growing faster than the northern ones. The critical time seemed to be the first summer after planting, when the differences in growth rate among the spruces were significant in respect of both provenance and exposure group regardless of the weather conditions. The pH 3 and clean water-treated spruce seedlings generally had lower growth rates than the pH 4 and dry control seedlings.

The Hardening of Conifers from Different Provenances

The timing of the hardening period is genetically controlled, as was observed at the beginning of the period. The northern conifer seedlings, from Salla and Kemijärvi, began their hardening in mid-August, whereas the southern seedlings, from Lapinlahti and Muhos, remained in a metabolically active state for about 1 month longer (Fig. 4). The spruce seedlings started their hardening earlier than the pine

◁ **Fig. 3A–D.** Effects of acid rain treatments and provenance on the viability of conifer seedlings in August 1987 (*left bars*) and August 1988 (*right bars*). **A** Dry controls; **B** clean water controls; **C** pH 4 and **D** pH 3. The classification of viability is explained in detail in the text (class 5 = healthy, class 1 = dead). The August 1988 dry control bar from pine seedlings is missing due to the absence of seedlings in this group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seedlings. Changes in the hardening state were noted from the reduction in the size and numbers of the starch grains in the mesophyll cells, which began from the outer mesophyll and continued towards the endodermis later on. Almost all cells lacked starch grains by October, and showed a normally hardened ultrastructure with reticular cytoplasm, abundant lipid droplets and small vacuoles. The chloroplasts moved towards their winter-time position near the cell edges in September to October, but this took place even later in the southern seedlings.

No significant changes in the timing of hardening were observed in the pine and spruce seedlings at the light microscopy level during the 2 year exposure period 1986–88, but the number of disintegrated mesophyll cells containing starch was somewhat greater in the pH 3-treated pine needles than in the dry controls in late October 1988.

The pH of the needle surfaces of the seedlings of both northern (Kemijärvi, Salla) and southern provenances (Muhos, Lapinlahti) was found to rise gradually during the hardening time. The rise in pH values was at its highest from August to October in 1986 ($p = 0.0000$***), being 0.7 units for current pine needles and 0.6 units for current spruce needles. The rise in surface pH in the needles of the pH 3- and pH 4-treated seedlings was lower than following the other treatments, but the differences were not statistically significant (Table 4) (Turunen and Huttunen 1988).

Altered development of cuticular structures could be observed in needles from the pine seedlings and adult trees. Exceptionally short wax tubes were sparsely distributed in the stomatal area, and this led to an unoccluded epistomatal chamber. After three growing seasons with pH 3 treatment, the number of stomata with retarded and eroded waxes of adult pines was increased when compared to the

◁ **Fig. 4A–H.** Ultrastructure of the mesophyll of hardening and dehardening needles of pine and spruce seedlings. **A** was published earlier in Reinikainen and Huttunen (1989a). **A** August 1986, a spruce needle of southern provenance, from Lapinlahti (treatment: clean water). The medium-sized starch grain and the position of the chloroplast indicate a metabolically active period. **B** October 1986, a spruce needle of southern provenance, from Lapinlahti (treatment: clean water). Starch grains are still observable, although the chloroplasts have moved into a clump near the cell edge. **C** October 1986, a pine needle of northern provenance, from Kemijärvi (treatment: dry control). The chloroplast is deformed and no starch is visible. **D** October 1986, a pine needle of southern provenance, from Muhos (treatment: dry control). Dense membrane packing is seen beside the dividing chloroplast, where starch is still observable. **E** February 1987, a spruce needle of northern provenance, from Salla (treatment: clean water). Lipid droplets are typically situated between the chloroplasts, the envelopes of which are curled and doubled over (*arrow*). Note the position of the grana on only one side of the chloroplast. **F** April 1987, a spruce needle of northern provenance, from Salla (treatment: dry control). The envelopes are doubling over (*arrow*) and forming vesicles in the chloroplast stroma. Starch has again been assimilated into the chloroplasts. **G** April 1987, a pine needle of northern provenance, from Rovaniemi (treatment: clean water). Note the lack of starch, doubling of the membranes (*arrow*) and the large, curly form of the accumulated membrane. **H** May 1987, a pine needle of southern provenance, from Muhos (treatment: pH 4). The chloroplasts have again started to assimilate starch. Symbols: *ST* starch; *L* lipid; *M* mitochondria; *P* plastoglobuli; *CW* cell wall; *G* grana. *Bar* 2 μm

Table 4. Surface pH values (± standard deviation) during August–October in 1986 and 1987 of the current needles of pine and spruce seedlings as means for given provenances (n = 2, measured from ten needles in each treatment)

	Pine (Kemijärvi, Muhos)			Spruce (Salla, Lapinlahti)		
1986	Aug	Oct	Change	Aug	Oct	Change
Dry Control	3.87 ± 0.17	4.67 ± 0.16	0.80 ± 0.19	4.02 ± 0.20	4.72 ± 0.20	0.70 ± 0.23
Clean Water	3.80 ± 0.22	4.57 ± 0.25	0.77 ± 0.27	3.96 ± 0.04	4.64 ± 0.36	0.68 ± 0.30
pH 4	4.02 ± 0.05	4.58 ± 0.14	0.56 ± 0.12	4.06 ± 0.04	4.70 ± 0.16	0.64 ± 0.13
pH 3	4.02 ± 0.16	4.62 ± 0.21	0.60 ± 0.22	4.05 ± 0.26	4.52 ± 0.10	0.47 ± 0.23
Mean	3.93 ± 0.16	4.61 ± 0.16	0.68 ± 0.22	4.02 ± 0.13	4.65 ± 0.19	0.63 ± 0.22
	Pine			Spruce		
1987	Aug	Oct	Change	Aug	Oct	Change
Dry Control	4.58 ± 0.19	4.68 ± 0.04	0.10 ± 0.16	4.48 ± 0.02	4.70 ± 0.21	0.22 ± 0.17
Clean Water	4.60 ± 0.14	4.76 ± 0.13	0.16 ± 0.16	4.46 ± 0.17	4.35 ± 0.04	−0.11 ± 0.14
pH 4	4.69 ± 0.07	4.85 ± 0.04	0.16 ± 0.06	4.25 ± 0.18	4.43 ± 0.01	0.18 ± 0.15
pH 3	4.62 ± 0.18	4.68 ± 0.01	0.06 ± 0.15	4.28 ± 0.22	4.50 ± 0.02	0.22 ± 0.18
Mean	4.62 ± 0.13	4.74 ± 0.09	0.12 ± 0.13	4.37 ± 0.17	4.50 ± 0.16	0.13 ± 0.20

other treatments (F = 7.64, p = 0.0066**, df = 3). The cuticles and epicuticular waxes of nursery-produced seedlings of all provenances were markedly retarded as compared with naturally grown seedlings in a forest ecosystem. Figure 5 illustrates the delayed and altered development and erosion of the epicuticular wax structure of the seedlings of northern provenance from October 1986 to October 1988 in Oulu.

The retarded epistomatal waxes, morphologically deformed stomata and strong erosion in the adult pine trees (Fig. 6) were related to the unfavourable growing seasons of 1985 and 1987, with reduced effective temperature sums. There was a significant variation in the number of stomata with a retarded edge towards the epistomatal chamber (F = 7.91, p = 0.0001***, df = 3) and stomata with completely occluded epistomatal chambers (F = 15.80, p = 0.0001***, df = 3) in needles of different ages. In needle year 1987, the number of stomata with completely occluded epistomatal chambers was greater in needles of pH 3-treated pines when compared to the other treatments (F = 4.34, p = 0.059**, df = 3).

Dehardening of the needles of the conifer seedlings began in March, when the first small starch grains were seen in the inner mesophyll chloroplasts of the spruce seedlings of southern provenance, from Lapinlahti. Marked starch accumulation

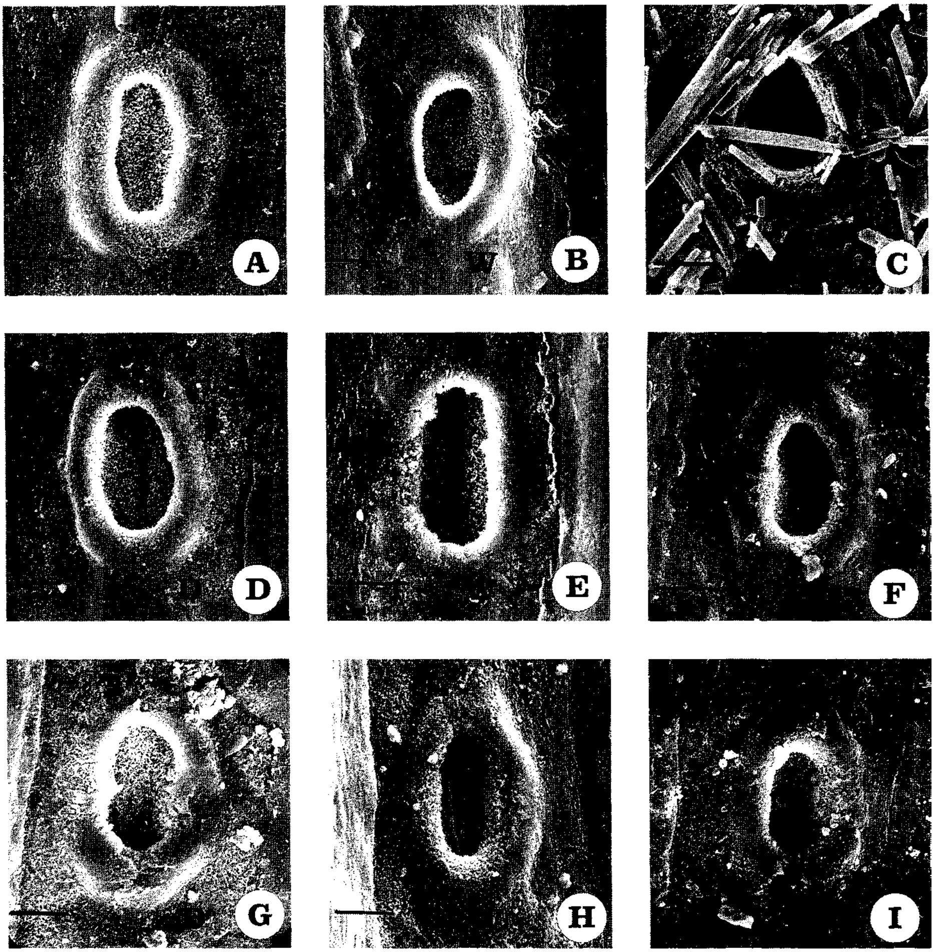

Fig. 5A–R. Delayed and altered development and erosion of epistomatal waxes of pine needless from October 1986 to October 1988 in Oulu. Compare the well-developed wax structure in Fig. 6A. *D* dry control; *W* water control; *pH 3* = pH 3 treatment. Bar 10 μm Wax structure of 1986 needles in October 1986, northern provenance (Kemijärvi) (**A**–**C**); June 1987, northern provenance (Kemijärvi) (**D**–**F**) and May 1988, northern provenance (Pello) (**G**), (Kemijärvi) (**H**, **I**). Wax structure of 1987 needles in October 1987, northern provenance (Sotajoki) (**J**–**L**) and May 1988, northern provenance (Aakenus) (**M**–**O**). Wax structure of 1988 needles in October 1988, northern provenance (Pello) (**P**), (Kemijärvi) (**Q**–**R**). Significant amounts of scattered $CaSO_4$ crystallites (**C**) were found on the needle surfaces of the pH 3-treated seedlings, after forming characteristic bows (L)

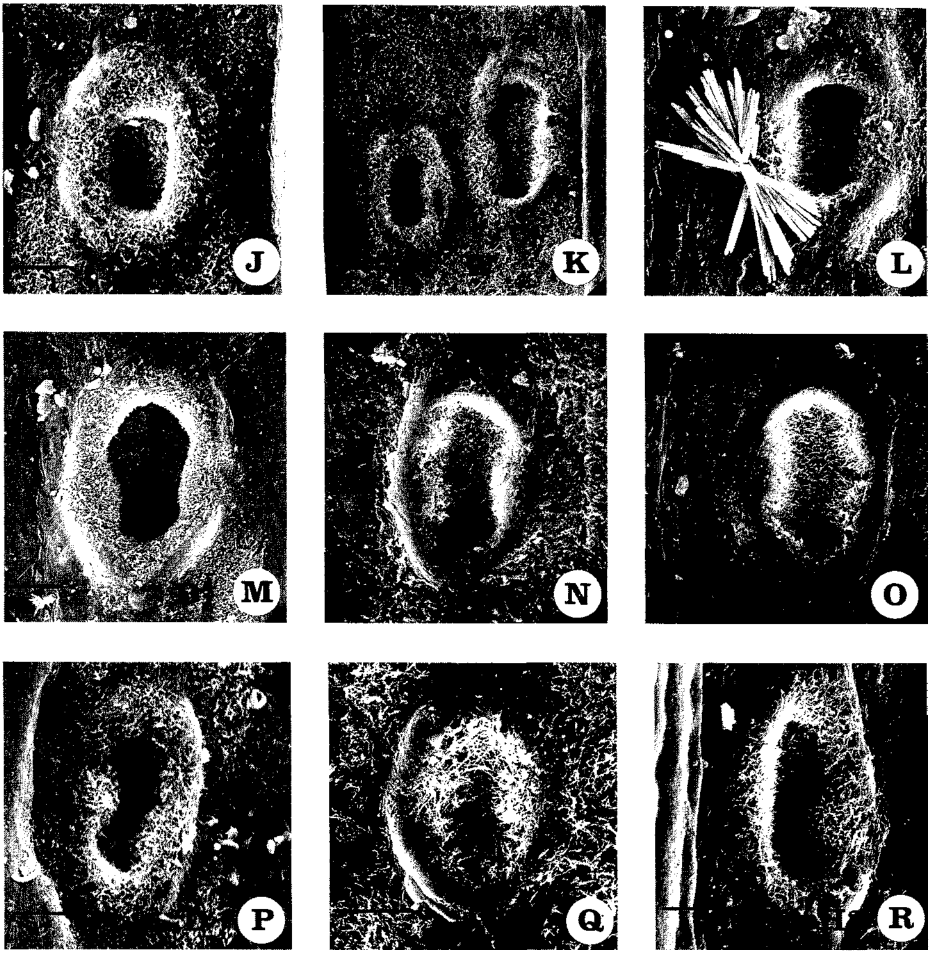

Fig. 5. (continued)

was seen in April in all the spruce provenances and in May in all the pine provenances, when the chloroplasts had again scattered around the cell. Abundant membraneous formations had already been seen in the cytoplasm and chloroplasts in mid-winter, and these tended to reach their maximum during the early phase of the dehardening period (Fig. 4).

The shape and size of the mesophyll chloroplasts in the needles of the pine and spruce seedlings depended greatly upon the season. During the high photosynthetic activity which prevailed in summer the chloroplasts were filled with starch and their shape was roundish, whereas in the hardened state they were rather flat and lenticular in appearance. During the winter time they normally showed irregularities in both the shape and the number and compartmentalization of the membranes (Reinikainen and Huttunen 1989a). The change in the shape of the

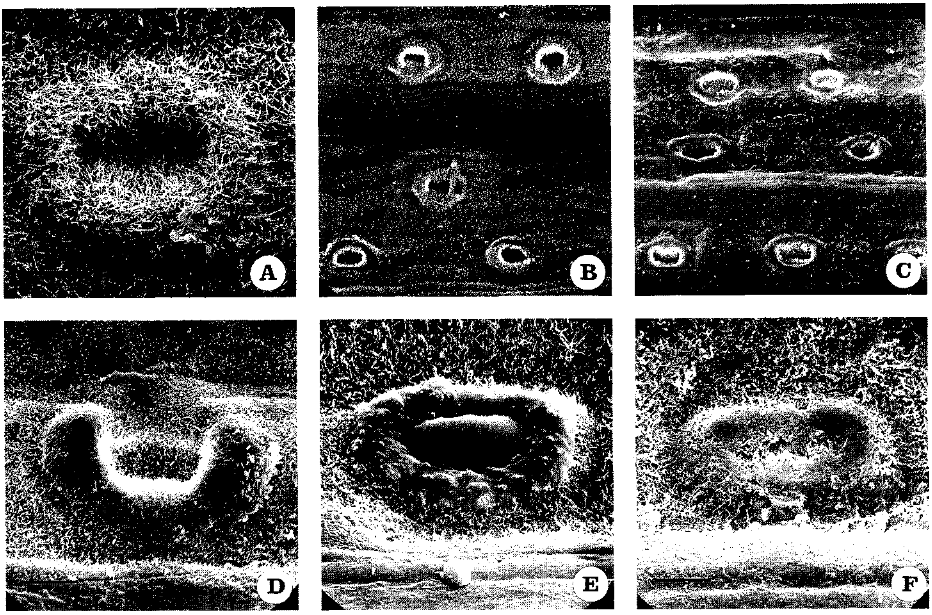

Fig. 6A–F. Epistomatal wax structures of needles of adult pines in the Kevo experiment. **A** Well-developed epistomatal wax structure with long wax tubes in a current needle from a dry control pine in July 1986. *Bar* 10 μm. **B** Retarded epistomatal wax structures with short wax tubes and an unoccluded epistomatal chamber in a current needle from a dry control pine in August 1985. *Bar* 50 μm. **C** Retarded, eroded epistomatal wax structures in a 2-year-old dry control needle in October 1987. *Bar* 50 μm. **D** Deformed stoma with a retarded edge of its epistomatal chamber in a 2-year-old needle from a pH 4-treated pine in July 1987. *Bar* 10 μm. **E** Stoma with a fully occluded epistomatal chamber in a current needle from a water-treated pine in September 1988. *Bar* 10 μm. **F** Stoma with a narrow epistomatal chamber in a 2-year-old needle from a pH 3-treated pine in July 1987. *Bar* 10 μm

chloroplasts at the light microscopy level occurred later in the acid rain-treated needles of pine and spruce seedlings than in the control chloroplasts, and a number of mesophyll cells with roundish chloroplasts could be seen in late October in the pH 3-treated spruce and pine needles.

Injuries Inflicted by Cold

The most prominent visual sign of freezing injury to the seedlings was needle discoloration, which gradually advanced from tip-burn towards grey or violet belts and total greyness of the needles. The damage at the tissue level seen before any visible damage occurred was highly localized, being concentrated on the central part of the mesophyll tissue (Fig. 7). Few signs of freezing injury could be seen on the cuticle, epidermis, hypodermis or endodermis.

The damage to the acid rain-treated 2-year-old needles spread to include the whole mesophyll, and the epidermis and endodermis of the most seriously injured areas were also damaged. The vascular tissue exhibited some alterations, probably

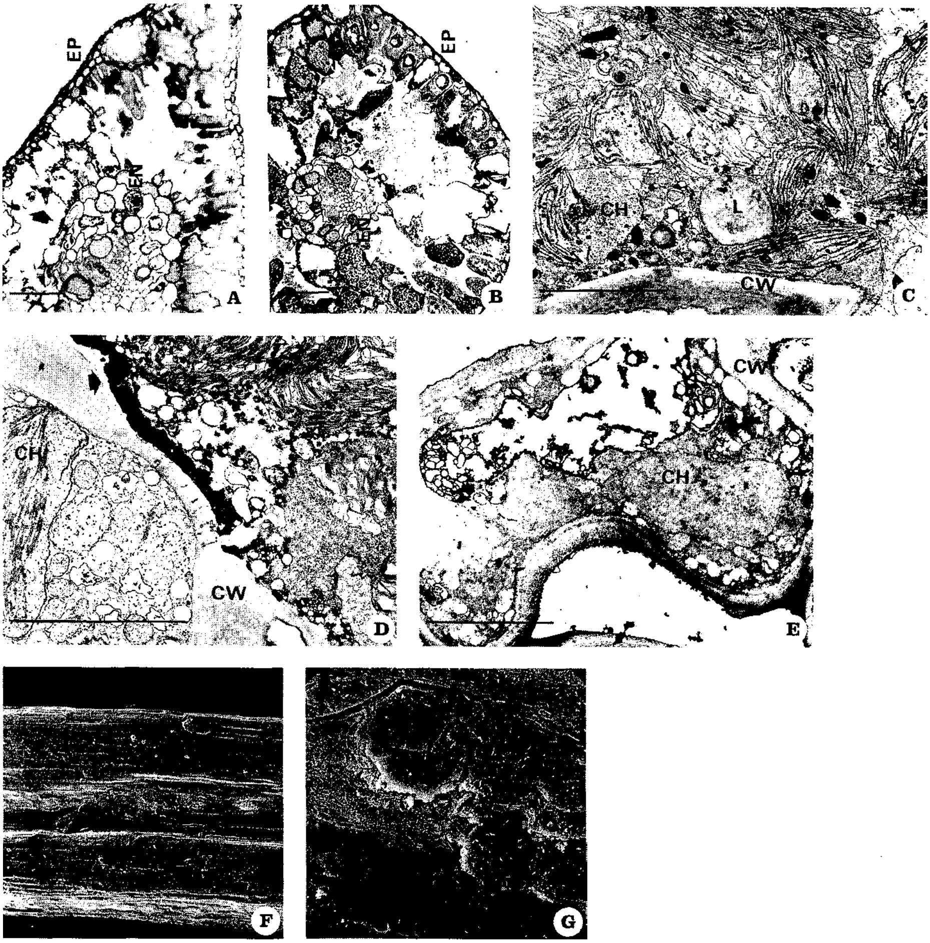

Fig. 7A–G. Freezing-induced damage to hardened pine and spruce needles. The seedlings were kept at −55°C for 3 days. **A, B** light micrographs (*bar* 100 µm); **C–E** transmission electron micrographs from mesophyll cells (*bar* 5 µm); **F, G** scanning electron micrographs (*bars* 100 µm, 20 µm). **A, B, E** were published earlier in Reinikainen and Huttunen 1989b. **A** A pine needle of southern provenance, from Padasjoki (treatment: pH 4). The freezing damage is highly local. Perfectly healthy cells (*) can be seen on the adaxial side of the mesophyll cells, whereas those on the abaxial side have collapsed (*arrow*). **B** A spruce needle of a southern provenance, from Padasjoki (treatment: pH 4). Totally disorganized and collapsed cells in the mesophyll (*). The outermost cell layer in the mesophyll is in good condition. **C** A spruce needle of a southern provenance, from Padasjoki (treatment: pH 3). The cytoplasm and chloroplast stromata show thinning and dark accumulations (*arrow*), and the net-like cytoplasmic structure typical of normally hardened cells has disappeared. **D** A spruce needle of southern provenance, from Padasjoki (treatment: clean water). Adjacent cells show different conditions: the lower cell is perfectly healthy, whereas the upper cell has disintegrated badly and has abundant dark accumulations between the plasmalemma and the cell wall (*arrow*). **E** A pine needle of southern provenance, from Padasjoki (treatment: pH 4). A shrunken protoplast in which the cell structures are difficult to discern. **F** A spruce needle of northern provenance, from Salla (treatment: pH 3). Mechanically broken epicuticular waxes of current needles surrounding the buds. **G** The same symptom at a higher magnification. Symbols: *EN* endodermis, *EP* epidermis; *CH* chloroplast; *CW* cell wall; *L* lipid caused by an interaction between the acid rain and cold treatment. Thus the acid rain treatment led to a greater susceptibility of tissues to damage by freezing, even though the type of injury at the cellular level viewed under a TEM was similar with all treatments.

The frost-damaged mesophyll cells with no visible signs exhibited characteristic ultrastructural features (Fig. 7). The first indications of an injury were a reduction in the numbers of cytoplasmic membraneous structures, thinning of the cytoplasm and accumulation of dark-stained particles in the cytoplasm and chloroplast stromata. Later, the chloroplast thylakoids became reduced in number and the stromata became thinner. Swelling of the thylakoids was observed at the final stage of the injury, together with folding and eventual total disappearance of the plasmalemma.

The epicuticular wax of the youngest needles surrounding the buds of the spruce seedlings was fractured to form upward-projecting, ultra-thin wax splinters. Mechanically broken waxes caused by freezing injury could occasionally be seen in interstomatal areas in the needles of spruce and pine seedlings (Fig. 7). The snow cover and particulate deposition from meltwater was observed to have a principally mechanical effect on epicuticular waxes in April and May.

Effects of Acid Rain on the Needles

No visible injuries related directly to the acid rain treatment could be observed after 3 years of the experiment, but microscopic examination revealed significant changes in the structure and morphology of the needles of adult pine.

Significant differences could be observed in the growth of the pine needles between the growing seasons ($F = 124.0$, $p = 0.0001$***, $df = 3$) and the treatment groups ($F = 39.53$, $p = 0.0001$***, $df = 3$) in the Kevo experiment. The pH 3-treated and dry control pines had shorter needles than the water and pH 4-treated ones during the first three growing seasons but after four years it was the pH 4-treated group that had the shortest needle length when compared to the other treatments (Fig. 8) (Turunen and Huttunen 1990).

The retarded wax structure in the needles of the pine seedlings in Oulu was found to have deteriorated, and the number of exceptionally short, sparsely distributed wax tubes had also decreased in response to moisture (Fig. 5). The conifer seedlings treated at pH 3 had significant amounts of scattered $CaSO_4$ crystallites and characteristic piles and bows on the needle surfaces, as detected by EDS (Figs. 5 and 9). $CaSO_4$ crystallites occasionally formed spherical areas on the needle surfaces as a result of the evaporation of acid rain droplets. The number of $CaSO_4$ crystallites on the needle surfaces was observed to change with the season, the maximum occurring in October-November. The number of $CaSO_4$ crystallites was higher on the surfaces of the spruce needles than on those of the pine needles. The current needles had more crystallites than the previous year's needles.

The length and the width of the stomata and the width of the epistomatal chamber in the needles of adult pines, as observed under a SEM, were generally

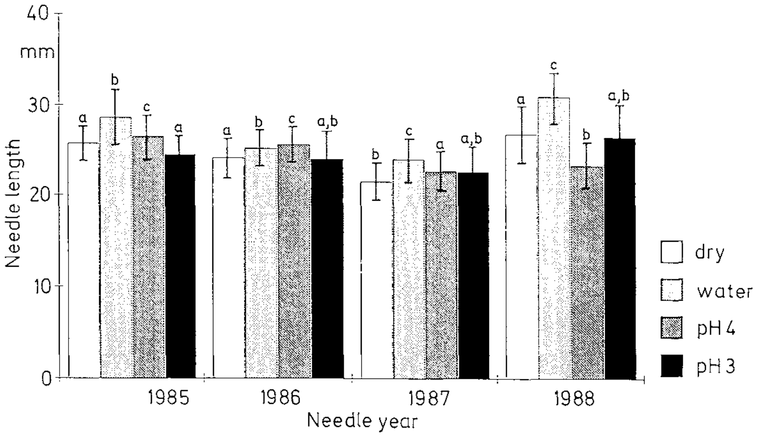

Fig. 8. Lengths (mm) (± standard deviations) of pine needles from 4 needle years in the Kevo experiment after the growing season of 1988. Columns marked with different letters are significantly different at the 0.05 level. (Turunen and Huttunen 1990)

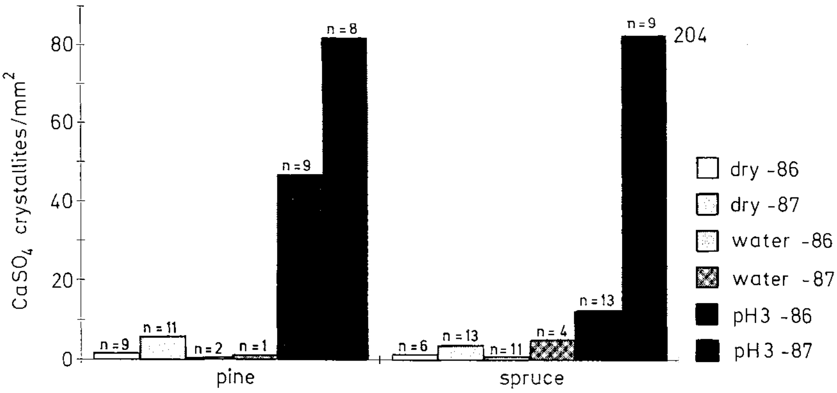

Fig. 9. Numbers of $CaSO_4$ crystallites mm^{-2} on current and previous year's needles from dry control, water and pH 3-treated pine and spruce seedlings in Oulu in October

reduced ($p = 0.0001^{***}$) after pH 3 treatment as compared with the other treatments, while the number of stomata with a narrow epistomatal chamber (1–2 nm) had increased in the needles of pH 3- and pH 4-treated trees. The difference between the acid rain treatments and controls was most pronounced in the needles from 1985 and 1987.

Light microscopy showed the most seriously injured mesophyll cells in the needles to be located close to the hypoderm. The injuries took the form of broken cell structures and collapsed and plasmolysed cells. In addition the cells of the vascular bundle, especially the phloem cells, were seen to be fused, perhaps as a result of nutritional disturbances.

Although the mesophyll chloroplasts of the needles of the adult pines changed in size from one season to another (Fig. 10), the dry control needles and pH

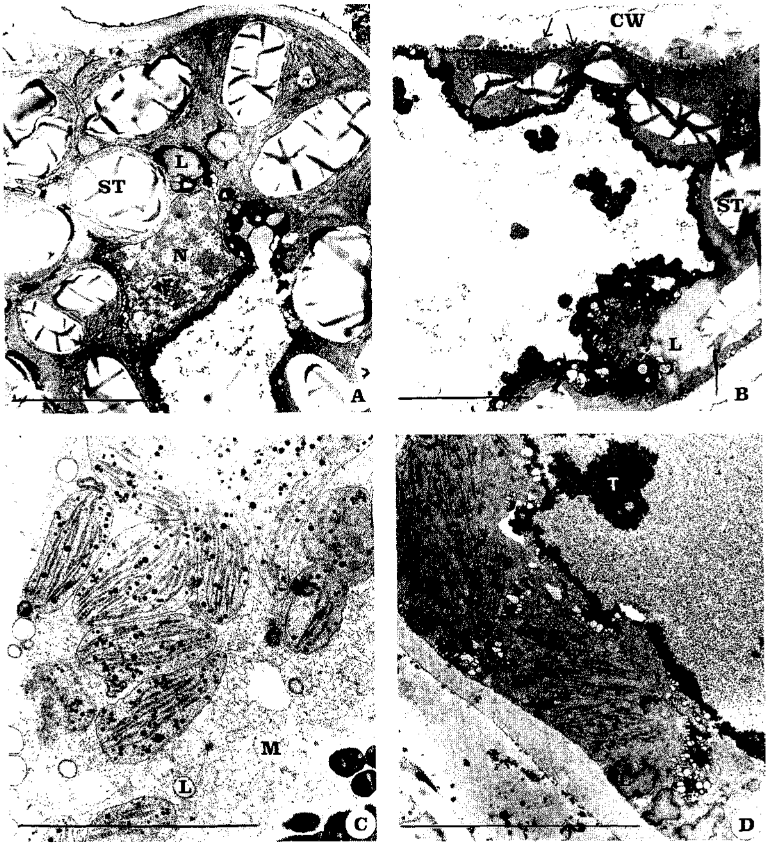

Fig. 10A–D. The ultrastructure of needles of adult Scots pines exposed to acid rain (published earlier in Reinikainen and Huttunen 1988). **A** Dry control, 2-year-old needle in July 1987. **B** pH 3, 2-year-old needle in July 1987. **C** Dry control, 3-year-old needle in October 1987. **D** pH 3, 3-year-old needle in October 1987. Lipid material is seen to be accumulating in the cytoplasm of the pH 3-treated needles, and between the plasmalemma and cell wall (*arrow*) (**B**). The chloroplasts are dark stained and appear to be fused, and the cytoplasm shows a tendency to vacuolization (**D**). Symbols: *N* nucleus; *CH* chloroplast; *ST* starch; *L* lipid; *M* mitochondria; *P* plastoglobuli; *CW* cell wall; *G* grana; *T* tannin; *V* vacuoles. *Bar* 5 μm

3-treated needles had the smallest chloroplasts. The differences in chloroplast size between the summer and autumn were smaller in the young current needles. The most prominent change in the needle ultrastructure was the accumulation of lipid material (Fig. 10), the amount of which was least in the needles from the beginning of the experiment, after which accumulation increased continuously, especially in the pH 3 and pH 4-treated needles. Accumulated lipid material could be observed on both the inside and the outside of the chloroplasts in July. The greatest amount of the accumulated lipid material was situated in the mesophyll cells of the older needles. In the pH 3 and pH 4-treated needles, lipid droplets were also observed between the tonoplast and cell wall, and some dark stained material was observed to have accumulated in the cytoplasm.

Cold Tolerance of the Seedlings

Terminal bud injury, which can be classed as a visible symptom, was observed after the cold treatment in 1986–88. Terminal and lateral bud injuries were studied by means of a TTC test in winter 1988–89. There were no statistical differences between the treatments, but the most seriously injured buds were quite often found in the seedlings treated with clean water. There was a significant difference in the incidence of injury between the spruce and pine buds, the spruce buds always showing a lower cold tolerance than the pine buds and being injured in most of the experiments. The terminal buds of the pine seedlings were injured in December 1986 (– 55°C) in all except the pH 4-treated samples, those in the water-treated group were injured in January 1987 (– 55°C), those in water- and pH 4-treated groups in February 1987 (– 55°C) and those of the dry controls in March 1987 (– 30°C).

The cold tolerance of the seedlings was tested with several cold exposure periods during the winters of 1986–87, 1987–88 and 1988–89. The temperatures used during winter-time (– 55°C) caused significant damage measured as the potassium leakage to the spruce seedlings in all the treatment groups, including the dry control group, whereas exposure to – 30°C in autumn and spring had an elevating effect on the potassium leakage only in the watered spruce seedlings (pH 3, pH 4, clean water). In many cases, the seedlings were already damaged before the testing of cold tolerance, and some recovery could be observed during the incubation time of 7 days. The previous year's needles of pines treated at pH 3 and those of the clean water group were more susceptible to freezing injury than the current needles, whereas in spruce it was the current year's needles of the pH 3 and dry control groups that were the most damaged. The southern provenances of spruces were more easily affected by the cold than northern provenances. The cold tolerance results are discussed in more detail in Reinikainen et al. (1989).

Discussion

The threshold pH value for precipitation to cause visual damage to conifer needles (*Pinus strobus, Picea abies*) has been noted to lie between 2.3 and 2.75 (Wood and Bormann 1977; Mengel et al. 1987). Thus, visible symptoms directly caused by acid rain were not seen at the present pH levels of 3 and 4, but the incidence of other types of injury, e.g. fungal diseases, freezing injuries, can be attributed to the indirect effects of acid rain, which predisposes needles to such injuries. The seedlings suffered from natural freezing injuries especially badly during the winter of 1986–87, and this was reflected in the generally poor condition of the southern spruce seedlings in particular in the following spring. The origins and course of development of the artificially cold-induced injuries are discussed in detail in Reinikainen and Huttunen (1989b).

Where Maurice and Crang (1986) observed a significant increase in total and component cross-sectioned needle areas after acid misting, our experiment showed needle length to be reduced after 4 years' exposure to pH 4. The most pronounced effect of pH 3 treatment was observed in the stomatal morphology of the needles, where the length and width of the stomata and the width of the epistomatal chamber were reduced. Rinallo et al. (1987) observed erosion of epicuticular waxes in *Pinus pinaster* Ait. after simulated acid rain treatment at pH 3.4 and 2.4, and Schmitt et al. (1987) similarly observed erosion of needles in *Picea abies*. Acid mist and fog (Magel and Ziegler 1986; Mengel et al. 1987) have also been reported to cause epicuticular wax erosion. Retarded wax development with short and sparse wax tubes and deterioration of undeveloped wax structures were the main effects observed here.

A large number of $CaSO_4$ crystallites were detected on the needle surfaces of pH 3-treated seedlings as compared with the dry and water control seedlings, there being more $CaSO_4$ crystallites on the young needle surfaces than on the older needles. This observation of $CaSO_4$ crystallites is in agreement with the experimental results of Adams and Hutchinson (1984), who found crystallites of the same kind on cabbage leaves after spraying them with acid water of pH 3.0 for 30 min in an enclosed rain chamber in a greenhouse. Mengel et al. (1987) observed significant leaching of K, Ca, Mg, Mn, Zn and carbohydrates out of spruce seedlings in response to 7 weeks' treatment with acidic fog of pH 2.75 as compared with a control fog of pH 5.

Experiments with short-term acid rain or fog have revealed a collapse of epidermal cells as the first symptom, followed by abnormal cell division, growth and finally cell collapse, in the mesophyll tissue of *Artemisia, Tradescantia* and *Phaseolus* (Adams et al. 1984; Evans and Curry 1979; Evans et al. 1977). These effects on the ultrastructure of plant tissues are thought to be mediated by the dysfunctions in ion regulating systems (Evans 1984), which cause irregularities in the tonoplast, plasmalemma and chloroplasts (Swiecki et al. 1982; Holopainen and Nygren 1988). The alterations in pine needles caused by acid treatment were seen here to consist of disintegration, collapse and plasmolysis of the mesophyll cells, whereas the epidermal tissue was not markedly affected. The finding of abundant lipid accumulations in the 3-year-old needles treated with acid rain is in agreement with Holopainen and Nygren (1988), but the chloroplasts were highly variable in shape and size and the effect was dependent on the season. Thus abnormality in the shape of the chloroplasts as an indicator of acid rain damage has to be considered with caution (Sutinen 1987).

The changes in starch appearance during the acid rain treatments are probably signs of some dysfunction in carbohydrate metabolism. Carbohydrate metabolism dysfunctions also affect hardening, as the energy reserves stored to meet the needs of the rest period and for the cryoprotection of cell membranes are reduced

(Aronsson et al. 1976). The effect of the depletion in energy reserves reaches its maximum on sunny, cold spring days, when respiration and transpiration rates are high but no great amounts of starch can be assimilated (Havas 1971). The effect may additionally be increased by wintertime water stress caused by enhanced cuticular transpiration as a consequence of the retardation of the cuticle and the erosion of epicuticular waxes. Another consequence of the disturbances in the carbohydrate balance is the decreased needle growth in the pH-treated pines.

The onset of the hardening period is regulated by light and temperature conditions (Heide 1974; Senser et al. 1975; Christersson 1978), which vary considerably between different parts of Finland. A difference in the timing of hardening between conifer provenances and species was established by light and electron microscopy. The maximum hardiness level, estimated in terms of the level of cold tolerance, was reached in December to February. The cold tolerance of the spruce seedlings was lower than that of the pine seedlings throughout the winter in spite of the earlier onset of hardening. This shows clearly that the critical factor determining the advance of spruce towards the north under northerly climatic conditions is temperature.

Deposited nitrogen causes a prolongation of the growing period, thus leading to a later onset of hardening. This can cause the plants to suffer exposure to early autumn frosts (Soikkeli and Kärenlampi 1984; Skre 1988). The significance of excess nitrogen has been stressed in the context of the Central European Forest Decline phenomenon, which is thought to be a consequence of heavy loads of air impurities and years of cold and dry climatic conditions (Prinz et al. 1985).

The growth response data on conifer seedling exposure to acid rain are somewhat contradictory. Abrahamsen (1984) observed an initial stimulation of the growth of Scots pine seedlings at pH 3.0 over the first 2 years, followed by significant reductions over the succeeding 5 years when exposed to pH 2.5. Growth was not affected in a short-term experiment with white pines (Wood and Bormann 1977), but Percy (1983, 1986) showed significant growth reductions and alterations in seedling morphology in a number of conifer species. The present pine and spruce seedling experiments revealed a great difference between these species. Differences in condition and height growth between seedlings treated with acid rain were more prominent in the spruces than in the pines, and the different provenances also varied in their response to acid rain treatment. The southern spruces seemed to derive a slight advantage from the acid rain treatment, whereas in the northern spruces the deleterious effects of the pH 3 treatment became clearly observable in the poor condition of the seedlings.

The effects of acid rain on the mycorrhiza, roots and soil are not discussed here, but these will also be examined at the next stage in the research. The effects of acid rain on the decomposition of pine needle litter have been studied by Neuvonen and Suomela (1989).

What do these findings mean to Finnish forests subjected to air pollution stress? The increasing duration of acid rain affecting the Finnish forests and accentuated damage in northernmost Finland will mean an increasing possibility of tree damage in the future, and the cumulative effect of time and the harsh climate will expose the forests of Lapland to an especial risk.

A combination of two simulated acid rain experiments, one with adult pines and the other with pine and spruce seedlings revealed a variable response of both species to acid rain. The morphology and ultrastructure of the needles were affected at both the cellular level and the level of surface wax structure. The effects of acid rain on pine needles were clearly accentuated from the central part of Finland, 65°00′N to the northernmost area 69°00′N as a consequence of the harsher climate.

The seedlings varied significantly in growth and condition after the 3 years of the experiment. Mean height growth was poorest in the spruces treated at pH 3 and the pines treated at pH 4, about 84–88% of the control value. The southern provenances of spruce seemed to derive a slight advantage in the overall success, whereas deterioration effects after pH 3 treatment were observable in the northern provenances of this species. The variable wintering response of seedlings can be related to interactions between acid rain and cold climate.

Abbreviations: TEM, Transmission Electron Microscopy; SEM, Scanning Electron Microscopy; EDS, Energy Dispersive X-ray Spectometer; AAS, Atomic Absorption Spectrophotometer; RK, relative K^+ output from needles; TTC, 2,3,5-triphenyltetrazoliumchloride; n_{tot}, total number of the examined needles

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Effects of High Nitrogen Deposition on Forests: Case Studies Close to Fur Animal Farms

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Summary

Amount and effects of nitrogen depositions near fur animal farms in the major mink and fox growing area of Finland were investigated in Scots pine (*Pinus sylvestris*) forests along gradients. Distance from the farm and presence of forest canopy had a strong effect on ammonium depositions measured as bulk deposition from May to October. The highest deposition values were recorded in the stand near a large mink farm, where 50 m from the farm the ammonium deposition was 33 kg N ha^{-1} yr^{-1} under the canopy and 7 kg N ha^{-1} yr^{-1} in the open field. The macroscopic symptoms of forest damages resembled growth disturbances of nutritional origin. The observed tree damage and growth disturbances were in correlation with the high foliar total N and ammonium N contents and high contents of soluble nitrogen in the humus. High amounts of ammonia led to a decrease in the K, Ca and particularly Mg and B contents in the needles and to an increase in total nitrogen, amides and amino acids. Excessive nitrogen was stored mainly in the form of arginine.

Introduction

There are over 5000 fur farms in Finland, mainly in Ostrobothnia, the western coast (Fig. 1). The largest number of fur farms in any single commune can be as high as 700, as in Uusikaarlepyy. Fur animals such as mink and fox are grown in shade houses throughout the year. One by-product of these farms is a large quantity of nitrogen-rich dung, which at first falls onto the ground beneath the cages and can sometimes remain there for a considerable time before it is removed.

The amount of nitrogen annually produced in dung is now nearly 8 million kg (see Helin 1982). As a comparison, other farm animals in Finland annually produce about 62.8 million kg of nitrogen in dung (Keränen and Niskanen 1987). The nitrogen content of mink dung is higher than that of cow or pig dung, but lower than chicken dung (Kjellerup and Lindhard 1977). Nearly 40% of the nitrogen of mink dung is ammonium nitrogen, whereas the corresponding proportion in cow, pig and chicken dung is 20–25%. The number of fur animals is largest

Kauppi et al. (Eds).
Acidification in Finland

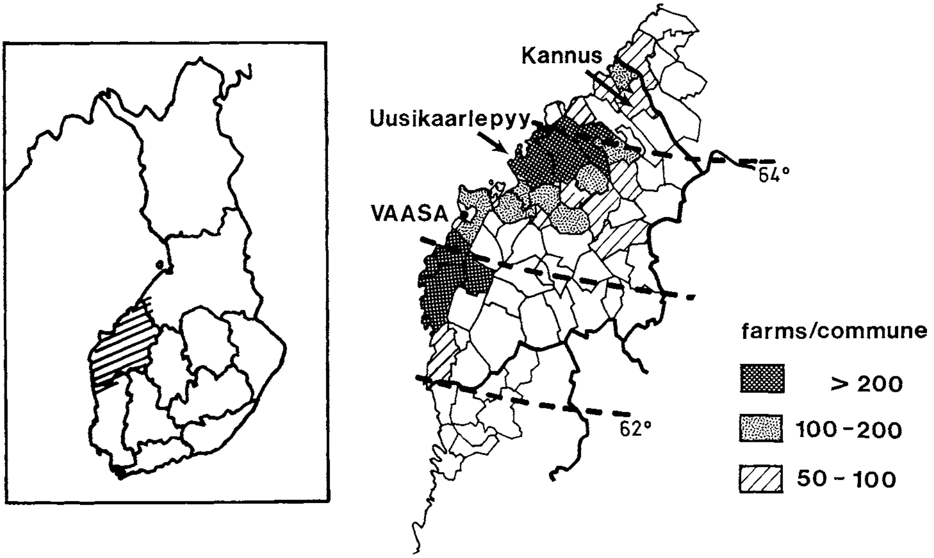

Fig. 1. The principal fur farming region of Finland

in July–September, when the amount of ammonia evaporating from dung is also at its maximum.

Particularly large amounts of ammonia evaporate from dung and agricultural farmland in countries with vigorous animal husbandry. The situation in the Netherlands is possibly the worst. The total annual ammonia emission is 130–150 million kg, which means 64 kg NH_3 ha^{-1} a^{-1} (Buijsman 1984). In Finland the nitrogen loss of animal husbandry and field fertilization has been estimated to be 38 million kg (Keränen and Niskanen 1987), or 16 kg per hectare of agricultural land per annum.

A large fraction of dung nitrogen evaporates in a short time. From a field spread with sludge, 41% of the ammonia evaporated in a day (Ferm and Christensen 1987). The ammonia content in the air decreases when the distance from the emission point grows. Ammonia reacts with sulphur (SO_2 and sulphuric acid) and nitric acid in the atmosphere, forming ammonium salts. Ammonium salt particles may be transported over large distances. Ammonia and ammonium are deposited on the ground both as dry and wet deposition. There is very little quantitative knowledge of what happens to ammonia and ammonium in the atmosphere. For example, the dry deposition velocity of ammonia has not been measured in forest or agricultural areas (Asman and Diederen 1987).

Atmospheric deposition of ammonium N is as high as nitrate N in Finland. The total nitrogen deposition is 5–10 kg h^{-1} a^{-1} in south Finland (Kauppi et al. 1987). According to Van Aalst (1983) the total deposition of ammonia and ammonium alone was about 30 kg ha^{-1} a^{-1} in the Netherlands. Also in southern Scandinavia high N loads up to 20 kg N ha^{-1} a^{-1} are found (Grennfelt and

Hultberg 1986). Varying estimations and results, ranging between 50 and 500 kg ha^{-1}, have been given of the depositions near the emission sources (see Asman and Diederen 1987).

About 60% of the total deposition of reduced nitrogen (NH_3^+/NH_4^+) occur as dry deposition (Van Aalst 1983). The proportion of dry deposition can be as high as 90% , close to the emission points (Draaijers et al. 1987). High vegetation, such as trees, intercepts more ammonia than low vegetation. Dry deposited ammonia intercepted by canopy is leached and may reach the ground during rainfall (Ferm and Grennfelt 1986). After dry periods the ammonium contents of canopy throughfall water may be exceptionally high.

Harmful effects of ammonia emissions caused by animal husbandry on tree stands and forests have been investigated in West and East Germany, Austria and particularly in the Netherlands, where forest damages caused by ammonia emissions are perhaps more devastating than elsewhere in Europe (Kühne 1966; Hunger 1978; Tesche and Schmidtchen 1978; Rudolph 1981; den Boer and Van den Tweel 1985; Roelofs et al. 1985, 1987; Asman and Diederen 1987). In the early 1980's, investigations on ammonia emissions and their effects on tree stands and the forest ecosystem were carried out also in Sweden (Rodhe 1982; Nihlgård 1985; Nilsson 1986). It has been shown that high NH_4–N deposition as ammonium sulphate results in increased leaching of basic cations from leaves and from the soil, which may cause severe nutritional imbalances (Van Breemen et al. 1982; Roelofs et al. 1985).

The physiological effects of ammonia emissions on forest trees have been investigated to some extent (Kühne 1966; Tesche and Schmidtchen 1978; Rudolph 1981). In the last few years, research on the topic has been increased (Van der Eerden 1982; Villanueva et al. 1986; Zedler et al. 1986; Roelofs et al. 1987; Hällgren and Näsholm 1988; Van Dijk and Roelofs 1988). In general, conifers are sensitive to ammonia. Even a content in dry plant material of 150 µg/g can inhibit photosynthetic phosphorylation (Van der Eerden 1982). Increasing frost sensitivity may result from the effects of ammonia on the cell membranes by increasing permeability and decreasing cellular flexibility. Zedler et al. (1986) reported elevated levels of amino acids in damaged spruce trees in polluted areas in south-western Germany and attributed this to increased ammonium and ammonia uptake. Similar results have been obtained in the Netherlands (Van Dijk and Roelofs 1988) and Sweden (Hällgren and Näsholm 1988). Diseased trees have suffered from severe excess nitrogen. The resulting imbalance between nitrogen and other nutrients caused an accumulation of amino acids, e.g. free arginine.

The reasons for launching this study were growth disturbances and other forest damages observed by foresters in the fur farming areas. The primary aim was to describe and explain growth disturbances of trees in the close vicinity of fur farms. Forest stands were monitored to determine the degree of damage at varying distances from the farms and the extent of the most severe damages (see Ferm et al. 1988). Later the annual cycle of the foliar nutrients and especially that of the organic and inorganic nitrogen reserves as a function of the distance to the fur farms were investigated. Precipitation and throughfall chemistry in the vicinity of the fur farms were monitored to estimate nitrogen deposition.

Deposition of Major Ions in Bulk Precipitation

Material and Methods

Scots pine (*Pinus sylvestris* L.) forests close to three fur animal farms were chosen for the study. One of the farms can be considered as a large fox farm, the second as a large mink farm and the third as a small mink farm. Also a pine stand for control measurements was chosen (> 850 m from fur farms). Fixed sample plots were marked along gradients. The gradient by the large mink farm ran north and the sample plots were 50, 100, 150 and 250 m from the farm. The gradient by the large fox farm ran east and the sample plots were situated 50, 150 and 700 m from the farm. The gradient by the small mink farm ran southwest and the sample plots were 50, 150, 300 and 700 m from the farm. Some characteristics of the pine stands are presented in Table 1.

The bulk deposition values inside the forests were compared with those in the open field approximately at the same distance from the emission source. Every station consisted of three to five collectors (a polyethylene funnel and a 1-l bottle) in a group in the open field and beneath the canopy of pine stands. The collector groups were placed at least 10 m from the forest edge. Collectors were emptied after each rain event and combined to give a single sample per collector group. Samples were deep-frozen upon arrival at the laboratory. Contaminated samples (e.g. with bird faeces) were discarded. Deposition samples were collected from 18 May to 8 November 1988.

Table 1. Stand characteristics of the pine forests under study

Stand near	Distance from the farm m	Stem number n ha^{-1}	DBH cm	V m^3 ha^{-1}
Large mink farm	50	1000	14	78
	100	2100	11	61
	150	1700	11	68
	250	2700	11	75
Large fox farm	50	2000	11	114
	150	800	14	56
	700	800	13	48
Small mink farm	50	1500	12	87
	150	800	16	46
	300	800	19	67
	700	600	11	23
Control	> 850	1400	12	83

Bulk deposition samples were analysed for pH, conductivity, NH_4–N by FIA using the ammonia gas diffusion principle and NO_3–N by FIA using the cadmium reduction method. Other elements (Ca, Mg, K, P, S, Fe, Mn) were measured by ICP (ARL 3580).

Results

It rained 25–30 times during the study period, with a total of 363–404 mm in the open field and 234–373 mm under the canopy (Fig. 2). Differences between the stations were small for total rainfall in the open field but somewhat greater under the canopy. The average interception loss due to canopy in the stand near the large mink farm was 122 mm, near the small mink farm 69 mm, near the large fox farm 52 mm and in the control stand 92 mm.

The distance from the farm had a strong effect on ammonium nitrogen levels in water collected in the open field, as well as under the canopy (Fig. 2). In throughfall NH_4–N deposition was several times higher than in the open field in all areas. The highest deposition values were recorded in the stand near the large mink farm, where ammonium deposition 50 m from the farm was 32.5 kg ha^{-1} under the canopy and 6.6 kg ha^{-1} in the open field. In this area high ammonium nitrogen deposition values (16.7 kg ha^{-1} in throughfall and 4.2 kg ha^{-1} in the open field) were found still 250 m from the farm. Deposition values of NH_4–N in the other areas were 13–14 kg ha^{-1} in throughfall at the stations closest to the farms. However, a great difference between the furthest stations under the canopy (700 m from the farm) was seen in areas of the small mink farm (0.8 kg NH_4–N ha^{-1}) and the large fox farm (7.0 kg NH_4–N ha^{-1}). This difference could be explained by the different set-up of stations relative to the prevailing wind direction, by differences in forest cover pattern or in farm size. In the control area NH_4–N deposition values were 2.3 kg ha^{-1} under the canopy and 0.9 kg ha^{-1} in the open field, indicating slightly elevated ammonium levels as far away as about 1 km from the farms.

The nitrate nitrogen deposition in throughfall was 2 to 3 kg ha^{-1} near the large mink and fox farms and 1 to 2 kg ha^{-1} near the small mink farm. In the open field NO_3–N deposition was about 1 kg ha^{-1} in most cases (Fig. 2).

The deposition of potassium, phosphorus and sulphur in throughfall was high in the stands with the highest NH_4–N values (Fig. 2). Maximum values, 13.4 kg K ha^{-1}, 1.5 kg P ha^{-1} and 13.7 kg S ha^{-1} were found in the pine forest at 50 m from the large mink farm. Also in other stations these three elements correlated fairly well with ammonium.

No distinct relationships between calcium or magnesium deposition and distance to the farm were found (Fig. 2). In general Ca and Mg deposition was two to five times higher under the canopy compared to that in the open field. However, near the large mink farm, deposition of calcium and magnesium under the canopy was nearly the same or even lower than in the open field. This may indicate that the

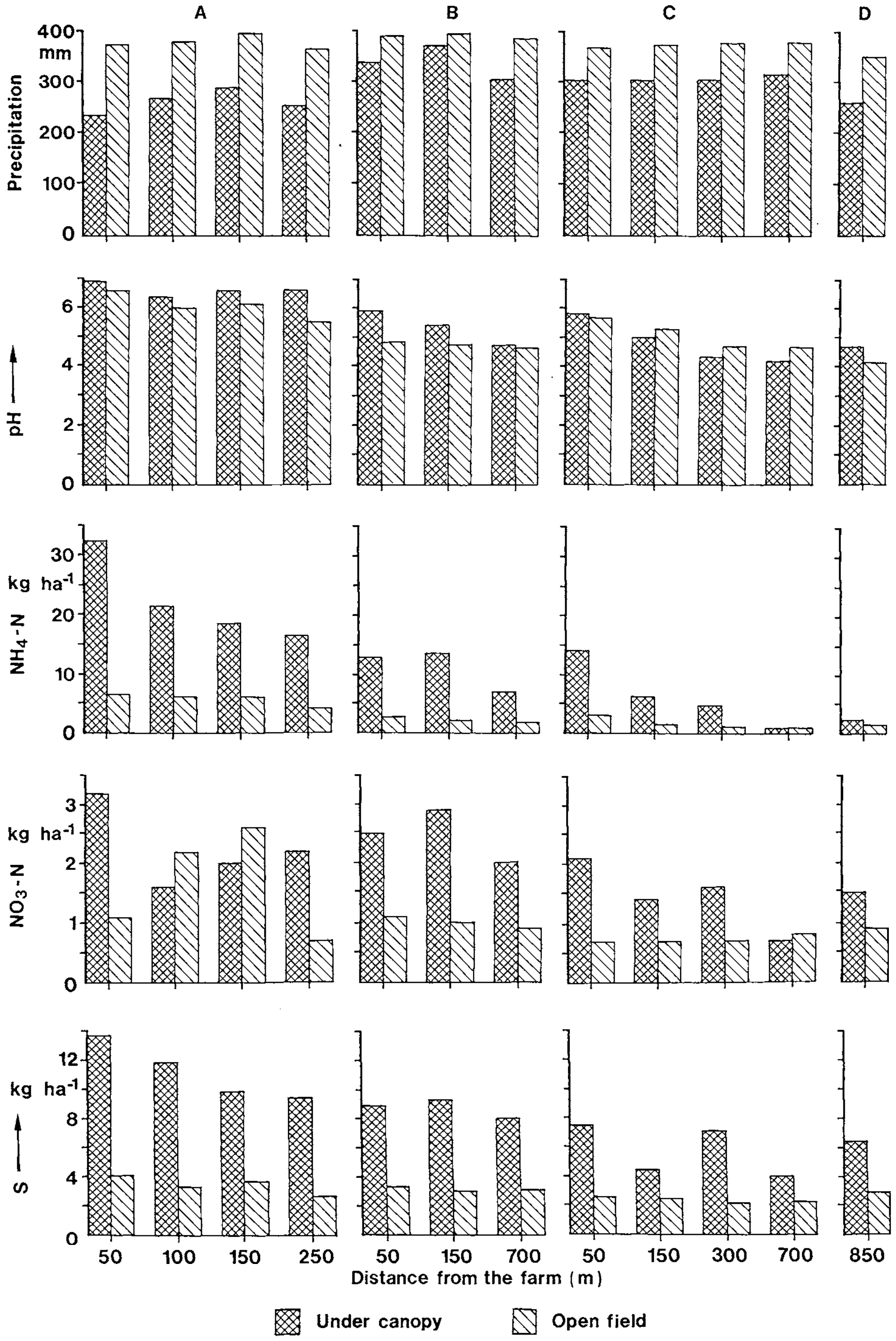

Fig. 2. Deposition of major ions in bulk precipitation along the investigated gradients. *A* large mink farm; *B* large fox farm; *C* small mink farm; *D* control

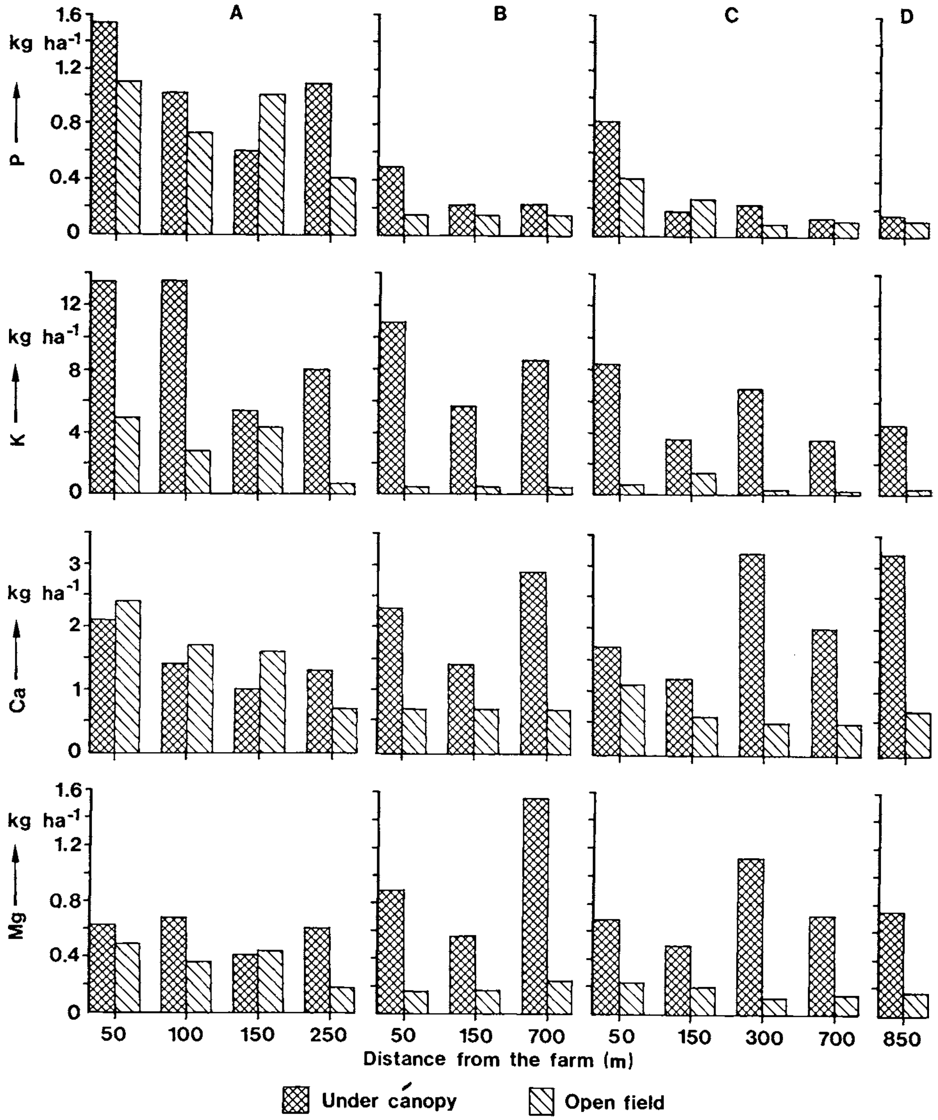

Fig. 2. (continued)

base cation reserve of needles had decreased in this area where the NH_4-N deposition was highest and had lasted for a rather long time.

The highest mean pH values were found in the large mink farm area where values under the canopy were about 0.4 units higher than in the open field (Fig. 2).

Discussion

The measured values of throughfall compared to deposition in the open field differ from those obtained from the areas of lower nitrogen deposition. Normally nitrogen compounds (NH_4, NO_3) are adsorbed from rainwater by tree crowns by active or passive uptake of leaves (Ulrich 1983). This interception loss in pine and spruce stands might be up to 40–60% for nitrate and 30–60% for ammonium compared to deposition in the open field (Pätilä 1987).

The high sulphur deposition values indicate that ammonium is to a great extent deposited as ammonium sulphate at least in throughfall. Although sulphur deposition in throughfall is normally greater than in the open due to adsorption of dry deposited sulphur by foliage (e.g. Hyvärinen this Vol.), sulphur values under the canopy near the large mink farm were rather high. For instance, Pätilä (unpubl.) has measured a sulphur deposition of 3.0 kg ha^{-1} in the open field and 4.5 kg ha^{-1} under the canopy in western Finland during a growing season (precipitation ca. 400 mm) in similar pine stands as in this study.

Abundant leaching of potassium from tree crowns is well documented (Horntvedt et al. 1980), but the values measured in this study were exceptionally high. This may be due to ammonium uptake and corresponding potassium release of needles as described by Roelofs et al. (1985). Calcium and magnesium, which could also be excreted from needles due to high ammonium sulphate deposition, were, on the contrary, normal in the throughfall and in good coordination with those published by Helmisaari and Mälkönen (1989) from healthy Scots pine stands in Finland. The only exception were the pine stands near the large mink farm, where the throughfall deposition of Mg and Ca were lower than in the other areas.

The high deposition values of ammonium and sulphate indicate that similar adverse effects of deposited ammonium sulphate on the needle and soil base cation balance may occur as described by Roelofs et al. (1985). Results of calcium and magnesium in throughfall from the most seriously affected area (large mink farm) suggest that this has already taken place.

Symptoms and Interpretation of Growth Disturbances in Trees

Material and Methods

Sample plots were established close to fur farms in young Scots pine stands which were as similar as possible in terms of growing site and growing stock (Ferm et al. 1988). The plots were arranged on lines each setting out from a fur farm or group of fur farms, the first being as close to the farm as possible and the subsequent points at intervals of approx. 50 m.

The radius of the sample plots was selected so as to include at least 30 trees. Diameter at breast height, and the height, annual height increment and number of needle year classes of certain sample trees were evaluated. Observations were made on the occurrence of green algae on the trunks, the crown forms and any damage suffered by the trees. A total of 59 plots was set up in 22 forests, together with eight control plots located further away from the fur farms (Table 2).

Table 2. Characteristics of trees in the investigated stands

Tree characteristic	Distance from the farm									
	0–100 m			101–400 m			Control > 400 m			
	x̄	min	max	x̄	min	max	x̄	min	max	F
Age, a	23	13	35	20	11	47	20	5	40	0.50
Height, m	8	2	13	7	2	14	7	2	14	0.59
Diameter at breast height, cm	10	2	18	7	1	17	8	2	15	1.40
Number of sample plots		26			25			8		

Needle samples, collected from each plot in winter 1986–87, were analysed for total nitrogen, ammonium, nitrate, phosphorus, potassium, calcium, magnesium, boron, iron, zinc, manganese, copper, sodium and aluminium. Humus samples were collected in connection with measurement of the trees in spring and summer 1987 for the analysis of pH (water), conductivity, total nitrogen, phosphorus, potassium, magnesium, iron, manganese, zinc, copper and boron and exchangeable potassium, magnesium, iron, manganese, zinc and copper. The proportion of soluble phosphorus was also determined, and ammonium and nitrate nitrogen separately.

The relationships between the foliar nutrient contents, nutrient contents in humus and stand characteristics were investigated as a function of the distance to the fur farm. The material was divided into three distance classes, whose differences were tested by the analysis of variance (Table 2).

Results and Discussion

Macroscopic Symptoms of Growth Disturbance in Trees and Other Symptoms of High Nitrogen Deposition

Forest damage close to the fur farms resembled the growth disturbances of nutritional origin, described chiefly in pine forests growing on peat soils (cf. Veijalainen et al. 1984). The principal macroscopic findings were weakened apical dominance, with little apical shoot growth compared to growth of the upper side branches (Fig. 3), and dieback of the leading shoots year after year. Growth disturbances also resembled the disorders appearing after excessive nitrogen fertilization (Möller 1983) when not only the terminal buds of the leader but also those of the upper branches die.

Other common disturbances include increased number of branches in the annual whorls, the occurrence of vertical branches and pronounced radial growth of the branches. Where these disturbances had continued for a number of years the outcome was thick-butted stems, multiple crowns and a bushy growth form

Fig. 3. Dieback of the apical shoot resulting in bushy growth form

Fig. 4. Continuous poor growth for a number of years in a pine stand close to a fur farm has led to the development of a flat crown canopy

Fig. 5. Abnormal growth of branches, stem changes and crooks close to a fur farm

(Fig. 4). Changes in the leading shoot may affect the technical quality of the timber with sharp crooks in the stem common (Fig. 5). Although the appearance of such disturbances may be preceded by an exceptional lushness of growth and dark green colour in the needles, the eventual outcome is a pronounced needle loss (Fig. 6) and a change in needle colour to a yellowish brown. In the forests near pig and poultry farms tips of pine needles have turned yellow or brown in two of the latest needle year classes and also the tips of spruce needles have turned reddish brown (Tesche and Schmidtchen 1978; Rudolph 1981). Premature loss of old needle year classes has also been observed.

Symptoms of nutrient deficiency were detectable at some sites close to the fur farms (Fig. 7). Indications of more profound changes in the ecosystem are root damages and the consequent susceptibility to wind damage (Fig. 8). The susceptibility of young vigorously growing pine stands to wind and snow damages has been attributed to tall, thin and bent shoots (Rudolph 1981).

Green algae are found on the trunks of trees close to the fur farms (Table 3, Fig. 9). Also elsewhere in the vicinity of the emission sources plenty of green algae has accumulated on trees (Rudolph 1981; Nihlgård 1986). The ground layer vegetation is characterized by a decline in the proportion of dwarf shrubs and an increase in grasses (Figs. 10 and 11).

Stand damages clearly decreased with the distance from the fur farms (Table 3, Fig. 12). In the forests near the fur farms the most severe damages were observed at a distance of less than 100 m from farms. In Central and Western Europe stand damages were observed to 700–1000 m from the emission source (Kühne 1966; Rudolph 1981; Roelofs et al. 1985, 1987) and they were also proportional to the distance from the source (Rudolph 1981).

Fig. 6. Needle loss in a pine close to a fur farm

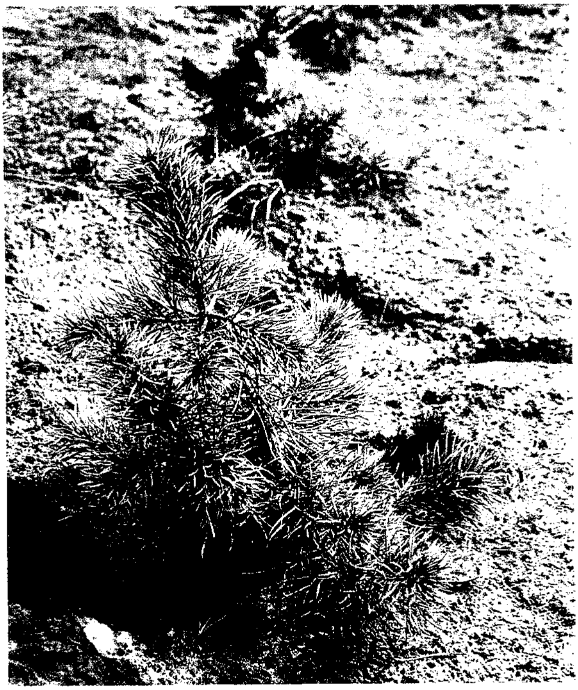

Fig. 7. Magnesium deficiency (foliar Mg content $<0.5\,\mathrm{mg\,g^{-1}}$) symptoms in a young pine growing on open ground close to a fur farm

Fig. 8. Root damages and susceptibility to wind damage

Fig. 9. An accumulation of green algae on the trunk of a spruce growing close to a fur farm

Fig. 10. Field layer vegetation of a control plot. The dominant element is *Vaccinium vitis-idaea*

Fig. 11. Field layer vegetation of a plot of 70 m from a fur farm. The dominant element is *Deschampsia flexuosa*

Growth Disturbances of Trees Related to Soil Humus Properties and Foliar Nutrient Contents

Of the soil properties studied, only the ammonium and nitrate nitrogen content in the humus was significantly changed with distance from the source (Table 4, Fig. 13). Also unlike the other soil properties, ammonium and nitrate contents

Table 3. Mean and range of some damage characteristics at different distances from the farms

Measured quantity	Distance from the farm									
	0–100 m			101–400 m			Control > 400 m			
	$\bar{x}$	min	max	$\bar{x}$	min	max	$\bar{x}$	min	max	F
Mean number of leader changes/tree	1.5	0.0	1.8	1.3	1.0	2.1	1.6	1.0	2.0	3.48*
Number of needle year classes	2.1	1.2	2.7	2.3	1.3	3.1	2.3	2.0	2.8	1.54
Share of damaged trees, %	35.6	2.8	70.3	21.6	0.0	36.7	4.5	0.0	11.6	10.04***
Share of the trees with green algae accumulated on the trunks, %	22.7	0.0	95.9	0.9	0.0	22.6	0.0	0.0	0.0	5.33**

* = $p < 0.05$
** = $p < 0.01$
*** = $p < 0.001$.

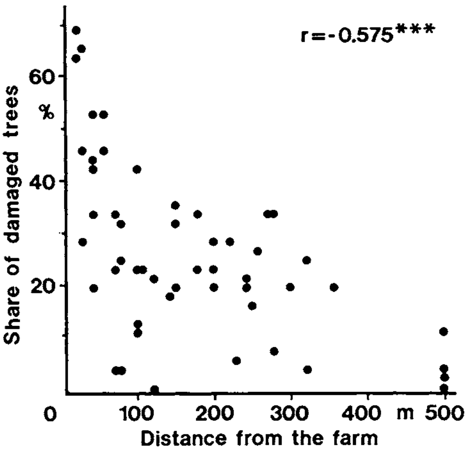

Fig. 12. Dependence of the share of damaged trees on the distance from the farm

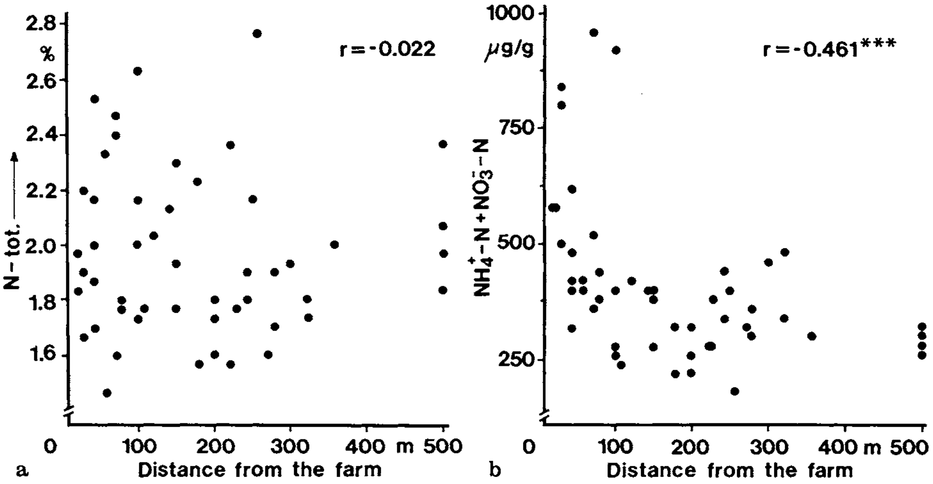

Fig. 13. Dependence of total nitrogen, ammonium and nitrate content of the humus on the distance from the farm. Contents calculated out of organic matter

correlated closely with the relative number of trees with leader and crown damages (Fig. 14). However, there were no such correlation with total nitrogen content in soil humus. Ammonium contents were about 30 times higher than those of nitrate. The humus was acid, the mean pH 3.75, in the whole material. No changes in pH as affected by the distance from the fur farms could be found.

The nitrogen content of pine needles was very high near the farms (< 100 m), the highest contents being over 2.5% (Table 5, Fig. 15). At a 100–150 m distance the foliar nitrogen content was still slightly higher than in the control material. Foliar ammonium nitrogen contents showed a pattern similar to that of the total nitrogen (Table 5), whereas the foliar nitrate nitrogen content did not change with the distance of the source.

Table 4. Properties of the humus layer at different distances from the farms

Measured property	Distance from the farm						Control			
	0–100 m			101–400 m			> 400 m			
	x̄	min	max	x̄	min	max	x̄	min	max	F
pH	3.78	3.53	4.30	3.73	3.44	4.12	3.65	3.63	3.68	0.83
Conductivity, µS cm^{-1}	233	134	305	214	146	258	242	217	256	2.28
N-tot, OM[a], %	2.01	1.46	2.63	1.92	1.55	2.78	2.06	1.84	2.37	0.77
NH_4-N, OM, µg g^{-1}	501	252	920	327	169	469	278	250	310	10.31***
NO_3-N, OM, µg g^{-1}	15.0	3.2	37.2	4.9	1.9	8.9	9.0	3.7	21.6	11.11***
P tot. mg g^{-1}	1.09	0.72	1.90	1.13	0.69	2.35	0.96	0.85	1.16	0.39
P soluble, mg g^{-1}	0.12	0.02	0.24	0.92	0.01	0.20	0.13	0.08	0.16	1.49
K tot., mg g^{-1}	0.54	0.36	1.14	0.52	0.33	0.96	0.50	0.43	0.59	0.28
K extractable, mg g^{-1}	0.47	0.22	1.14	0.45	0.23	0.78	0.48	0.42	0.58	0.10
Ca tot., mg g^{-1}	3.47	0.58	6.18	3.01	0.46	5.43	4.80	3.96	6.55	2.47
Ca extractable, mg g^{-1}	2.19	0.34	3.89	1.86	0.26	3.49	3.05	2.68	3.94	2.75
Mg tot., mg g^{-1}	0.43	0.08	0.80	0.41	0.11	0.70	0.60	0.40	0.81	2.16
Mg extractable mg g^{-1}	0.31	0.04	0.63	0.30	0.04	0.57	0.45	0.28	0.63	1.99
Na extractable, ppm	26.7	12.5	58.3	34.0	16.6	86.4	23.0	18.5	27.7	1.93
Fe tot., ppm	2273	585	7089	2263	802	6284	2775	1590	5737	0.38
Fe extractable, ppm	25.1	1.0	116.1	42.6	1.0	137.5	25.8	5.7	84.3	1.32
Mn tot., ppm	158	7	507	128	7	629	147	64	191	0.23
Mn extractable, ppm	118	0	388	89	0	521	99	36	128	0.30
Zn tot., ppm	58.9	5.3	109.1	49.2	4.2	107.1	64.3	40.4	76.9	0.95
Zn extractable, ppm	23.0	10.1	41.8	22.1	10.5	40.8	23.3	16.3	29.9	0.08
Cu tot., ppm	6.6	3.4	10.1	6.7	3.8	10.5	7.2	6.0	8.2	0.16
Cu extractable, ppm	0.15	0.00	0.65	0.05	0.00	1.27	0.08	0.00	0.32	0.87
Al tot., ppm	1.98	0.79	6.15	2.60	0.95	10.64	1.21	0.96	1.52	0.89
B tot., ppm	1.72	0.07	3.86	1.65	0.16	3.70	2.22	1.61	2.98	0.93

[a] OM = out of organic matter.

*** = $p < 0.001$.

Table 5. Foliar nutrient contents and nutrient ratios of Scots pine at different distances from the farms

Nutrient or nutrient ratio	Distance from the farm									
	0–100 m			101–400 m			Control > 400 m			
	x̄	min	max	x̄	min	max	x̄	min	max	F
N, %	2.00	1.56	2.52	1.56	1.30	1.76	1.43	1.34	1.53	36.42***
Nitr-N, ppm	875.5	510.0	1050.0	867.3	640.0	1060.0	–	–	–	0.08
Amm-N, ppm	229.2	30.0	551.0	94.1	20.0	208.0	–	–	–	19.45***
P, mg g^{-1}	1.79	1.23	2.08	1.75	1.43	2.12	1.78	1.58	2.17	0.37
K, mg g^{-1}	4.82	3.68	6.04	5.16	4.18	6.46	5.44	4.77	6.31	4.35
Na, ppm	46.4	21.0	83.0	63.9	33.0	119.0	166.0	97.0	255.0	86.00***
Ca, mg g^{-1}	1.88	1.34	2.84	2.11	1.48	2.80	1.88	1.36	2.18	3.72*
Mg, mg g^{-1}	0.91	0.48	1.25	1.02	0.78	1.31	1.08	0.87	1.49	4.27*
Fe, mg g^{-1}	51.5	32.0	102.0	50.0	37.0	87.0	50.4	42.0	67.0	0.12
B, ppm	7.02	2.90	11.80	9.85	3.90	14.90	11.81	7.70	16.90	15.26***
Mn, ppm	321.4	116.0	558.0	304.8	141.0	512.0	304.0	226.0	410.0	0.15
Zn, ppm	45.5	16.0	66.0	47.0	28.0	62.0	47.8	41.0	53.0	0.22
Cu, ppm	3.8	2.0	5.3	4.4	3.7	5.3	3.3	2.6	4.1	12.03***
Al, ppm	186.1	51.0	305.0	213.9	131.0	314.0	187.9	104.0	282.0	1.51
N/K	4.21	2.65	5.74	3.06	2.50	3.74	2.65	2.33	2.91	32.29
N/P	11.34	8.21	19.67	8.97	7.83	10.19	8.14	6.68	9.96	15.77***
K/P	2.71	1.81	3.45	2.96	2.21	3.54	3.09	2.30	3.50	4.79*
N/Ca	11.09	6.02	17.31	7.57	5.29	11.17	7.81	6.27	11.10	17.84***
N/Mg	23.50	12.56	50.42	15.86	11.07	22.56	13.54	9.73	17.59	13.91***
N/B	3320	1380	7450	1710	1100	4410	1280	800	1840	18.54***
N/Cu	5670	3300	12600	3630	3000	4700	4500	3460	5770	12.44***
N/Al	140	50	470	80	50	130	80	50	130	5.15*
N/Zn	520	250	1510	350	240	580	300	250	370	5.85*
P/B	293	145	576	192	116	469	59	104	238	10.73*
P/Mg	2.03	1.74	2.71	1.77	1.24	2.62	1.67	1.42	2.23	5.57*
Amm-N/Nitr-N	0.28	0.03	0.68	0.11	0.02	0.22	–	–	–	16.94***

*, ** and *** see Table 3.

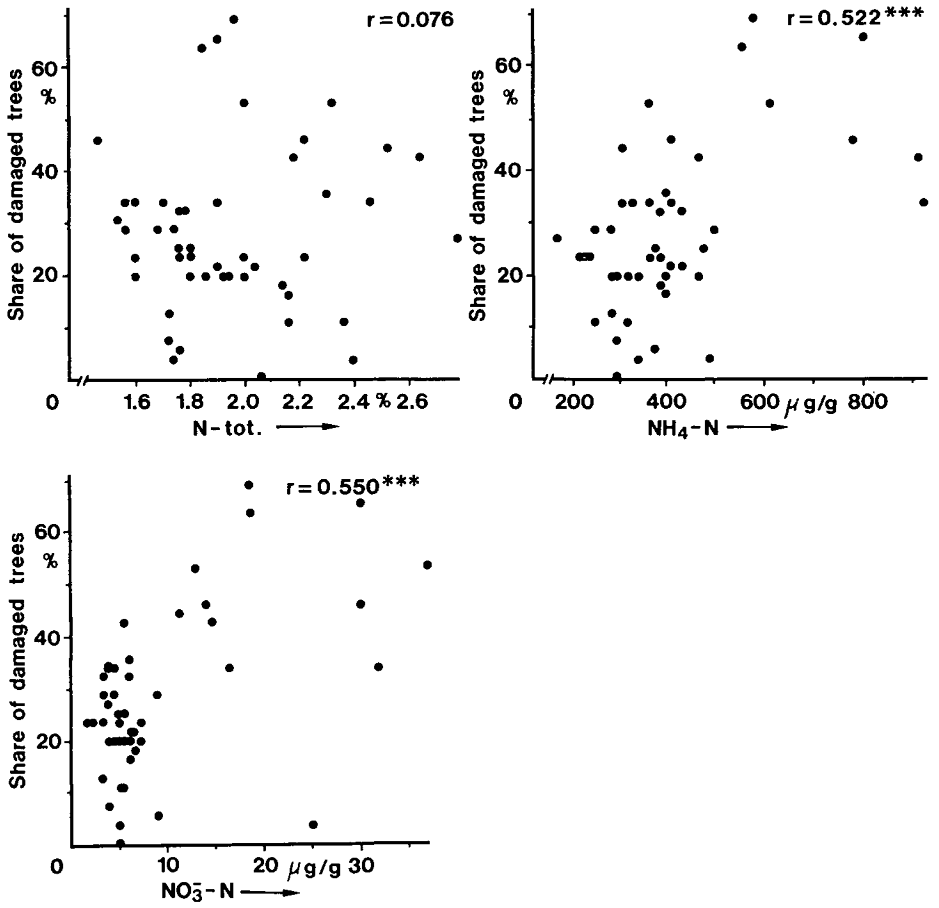

Fig. 14. Dependence of the relative number of damaged trees on the total nitrogen, ammonium and nitrate content of the humus. Contents calculated out of organic matter

In addition to nitrogen, magnesium, sodium and boron contents in needles changed with the distance from the fur farms. Contrary to the foliar nitrogen contents, however, the contents of these nutrients increased with the distance to the fur farms (Table 5, Fig. 15). Foliar potassium contents slightly decreased near the farms, but did not fall below the recommended values (Metsänterveysopas 1988). The lowest magnesium content near the farm was 0.48 mg g^{-1}. A limit value of under 1 mg g^{-1} has been suggested for the suspiciously low foliar magnesium content in Scots pine stands (Metsänterveysopas 1988). A rise in the sodium content can be explained by the fact that control pine stands were closest to the sea.

Boron contents of 5–10 ppm are considered to imply deficiencies in Scots pine (see Kolari 1979) and contents below 5 ppm are usually associated with growth disturbances in trees on peat soils (Veijalainen et al. 1984). On dry mineral soils contents of less than 8 ppm point to a deficiency (Metsänterveysopas 1988). The mean foliar boron content was 7.0 ppm at less than 100 m from the fur farms

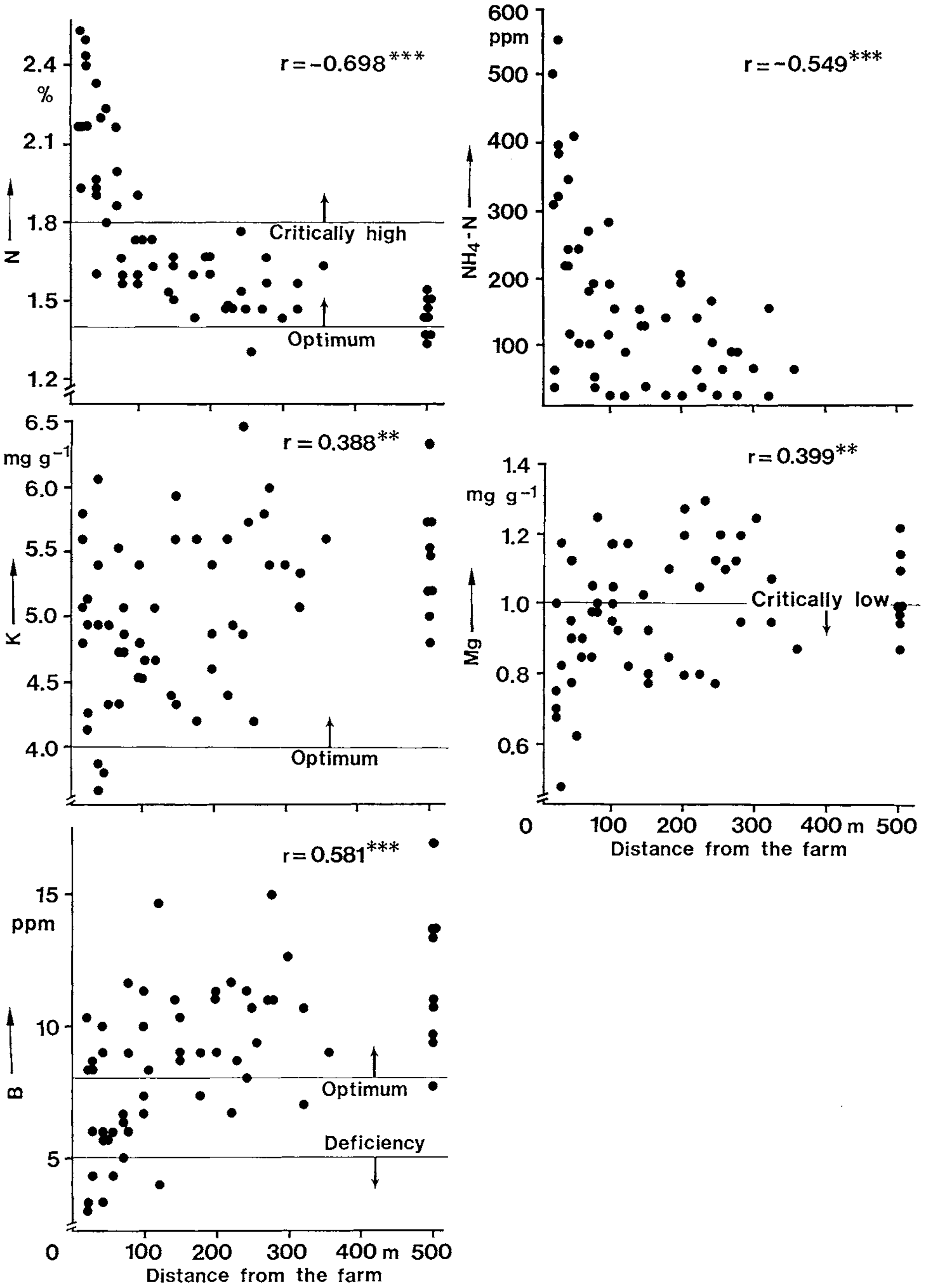

Fig. 15. Dependence of foliar total nitrogen, ammonium, potassium, magnesium and boron contents on the distance from the farm

(Table 5, Fig. 15). Boron contents of less than 5 ppm were found on 23% of the sample plots near the fur farms. The lowest boron content was 2.9 ppm. Boron contents of less than 10 ppm were found on 92% of sample plots near the fur farms and on 53% at distance of 100–400 m from the farms.

No differences were found in foliar phosphorus, manganese, zinc, aluminium and iron contents near fur farms and control areas (Table 5). The mean phosphorus content was 1.8 mg g^{-1}.

The negative correlation between foliar N and other nutrients was most clearly visible in the foliar magnesium and boron contents (Fig. 16). On the other hand, the foliar potassium content correlated only slightly and phosphorus content did not correlate at all with the foliar nitrogen content. Near the fur farms the ratios between nitrogen and the other nutrients were highest and decreased with the distance from the fur farms (Table 5).

The percentage of trees with leader damages correlated better with the total foliar nitrogen and magnesium contents than with the distance (cf. Figs. 12 and 17). Similarly, the correlations between the ratio of the foliar nitrogen and some other nutrients and leader damages emphasized the important role of nitrogen in the occurrence of growth disturbances and crown damages in trees (Fig. 17). In the stepwise regression analysis the share of damaged trees was best explained with the ratio of the foliar nitrogen and magnesium content ($R^2 = 31.2\%$).

The total nitrogen content of the humus had no significant correlation with the total foliar nitrogen content. However, the soluble nitrogen (NH_4 and NO_3) of the humus and the total foliar nitrogen content displayed a significantly positive correlation ($p < 0.001$) (Fig. 18). The soluble nitrogen of the humus also had a positive correlation with the foliar ammonium nitrogen, but not with the foliar

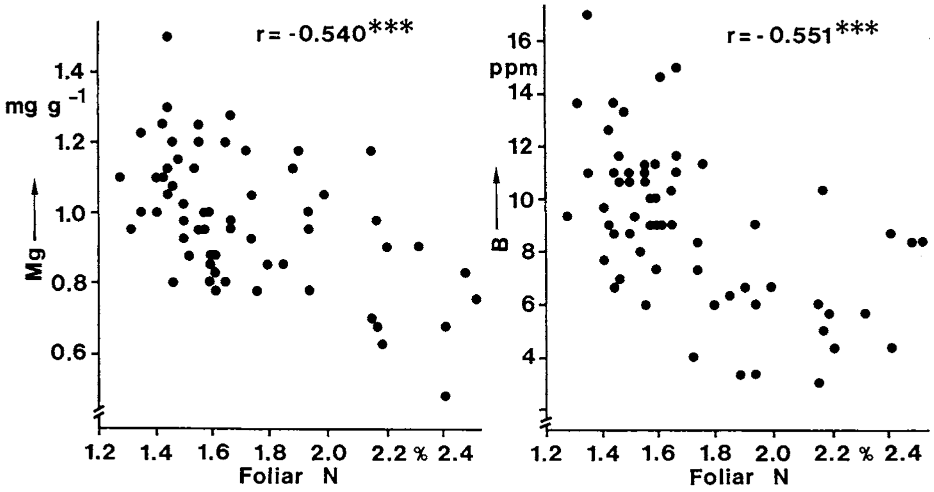

Fig. 16. Dependence of foliar magnesium and boron content on the foliar total nitrogen content

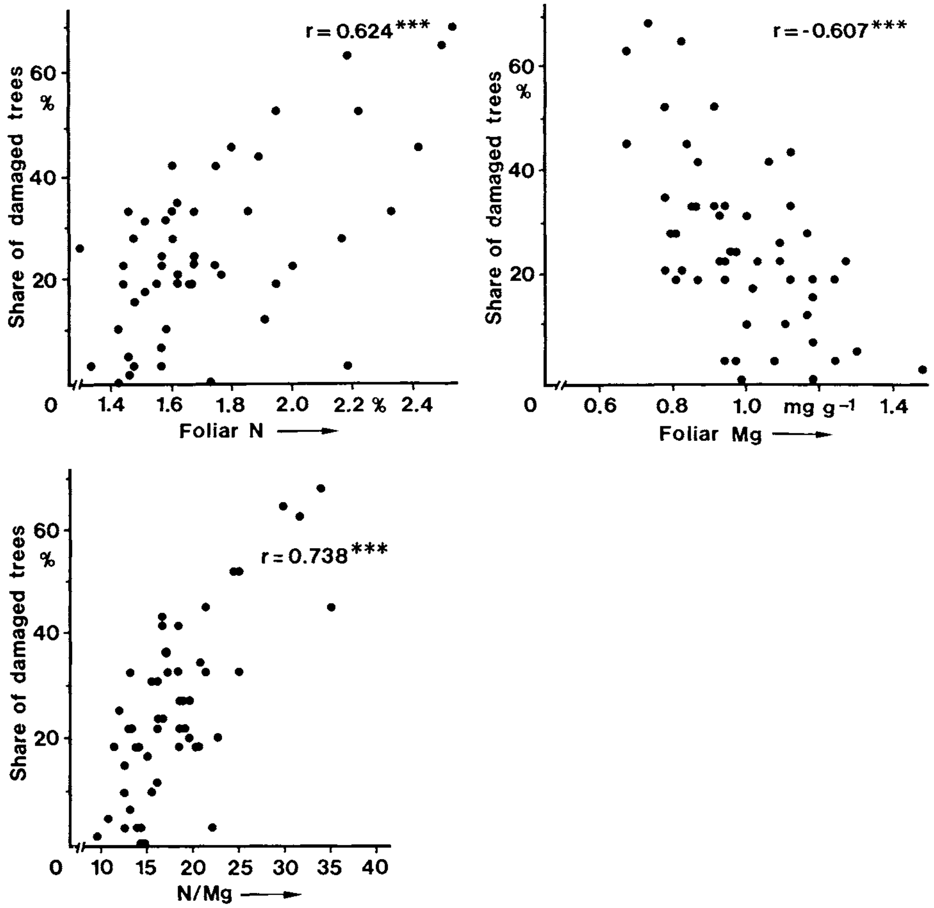

Fig. 17. Dependence of the relative number of damaged trees on the foliar nitrogen and magnesium contents and on the foliar N/Mg ratio

nitrate nitrogen. Moreover, there was a significantly negative correlation between the soluble nitrogen in the soil and foliar magnesium and calcium (Fig. 18).

As the foliar nitrogen content and the total nitrogen, ammonium and nitrate nitrogen of the humus increased, the percentage of trees with green algae on their trunks rose. Tree stands with the foliar nitrogen content of less than 1.8% had hardly any green algae at all. Similarly, no green algae were present if the foliar magnesium content exceeded 1.1 mg g^{-1} or that of boron exceeded 10 ppm.

Seasonal Variation of Foliar Nutrient Contents

Material and Methods

The pine stands as presented in Table 1 were used in this study. Twelve trees were marked in each plot. Needle samples were taken from the upper third of the crown

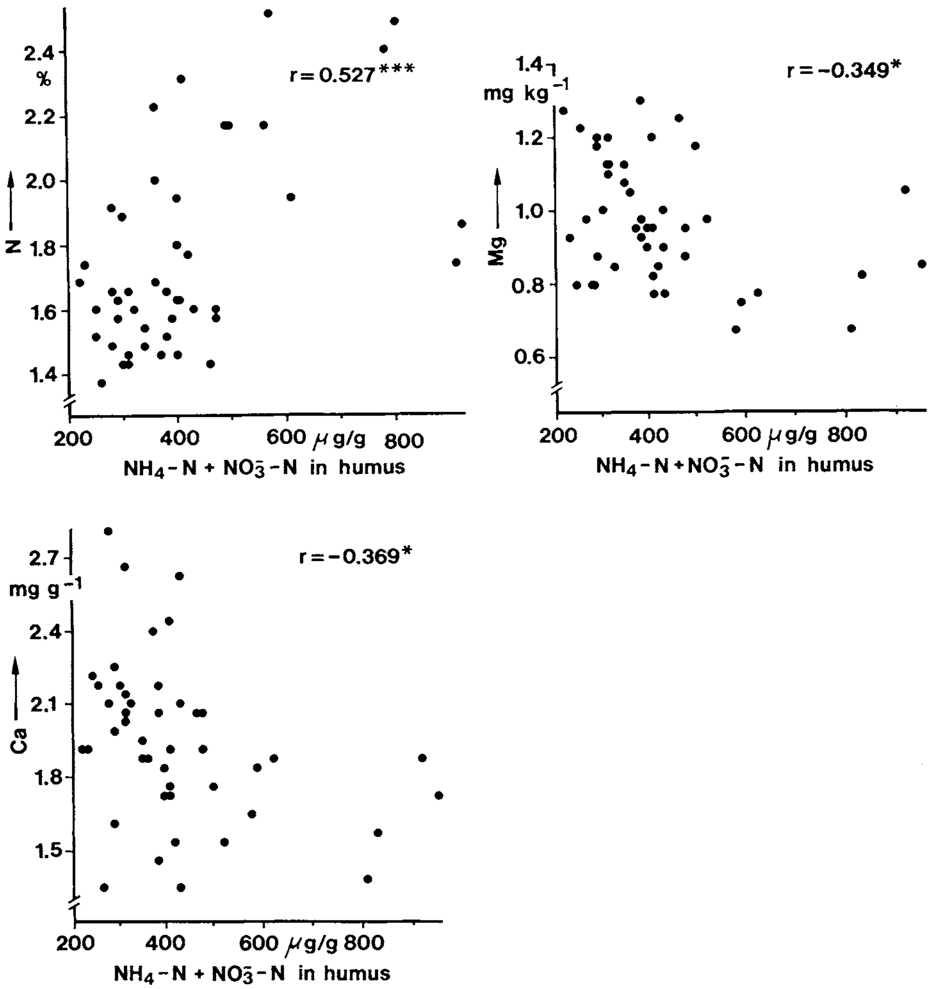

Fig. 18. Dependence of foliar nitrogen, magnesium and calcium content on the amount of soluble nitrogen in the humus

from four randomly chosen pines of the twelve sample trees on each plot. Samples were taken each month from July 1988 to December 1988. The foliar nutrients (N, P, K, Ca, Mg, Fe, Zn, Cu and B) were analysed according to the outlines of Halonen et al. (1983) to see if any nutrient concentration exceeds the known critical level at any phase of the annual growing cycle.

Results and Discussion

The foliar phosphorus and potassium contents did not differ to any appreciable level from the control for the whole study period and the potassium contents in general were rather high (Fig. 19). The foliar nitrogen levels were higher, exceeding

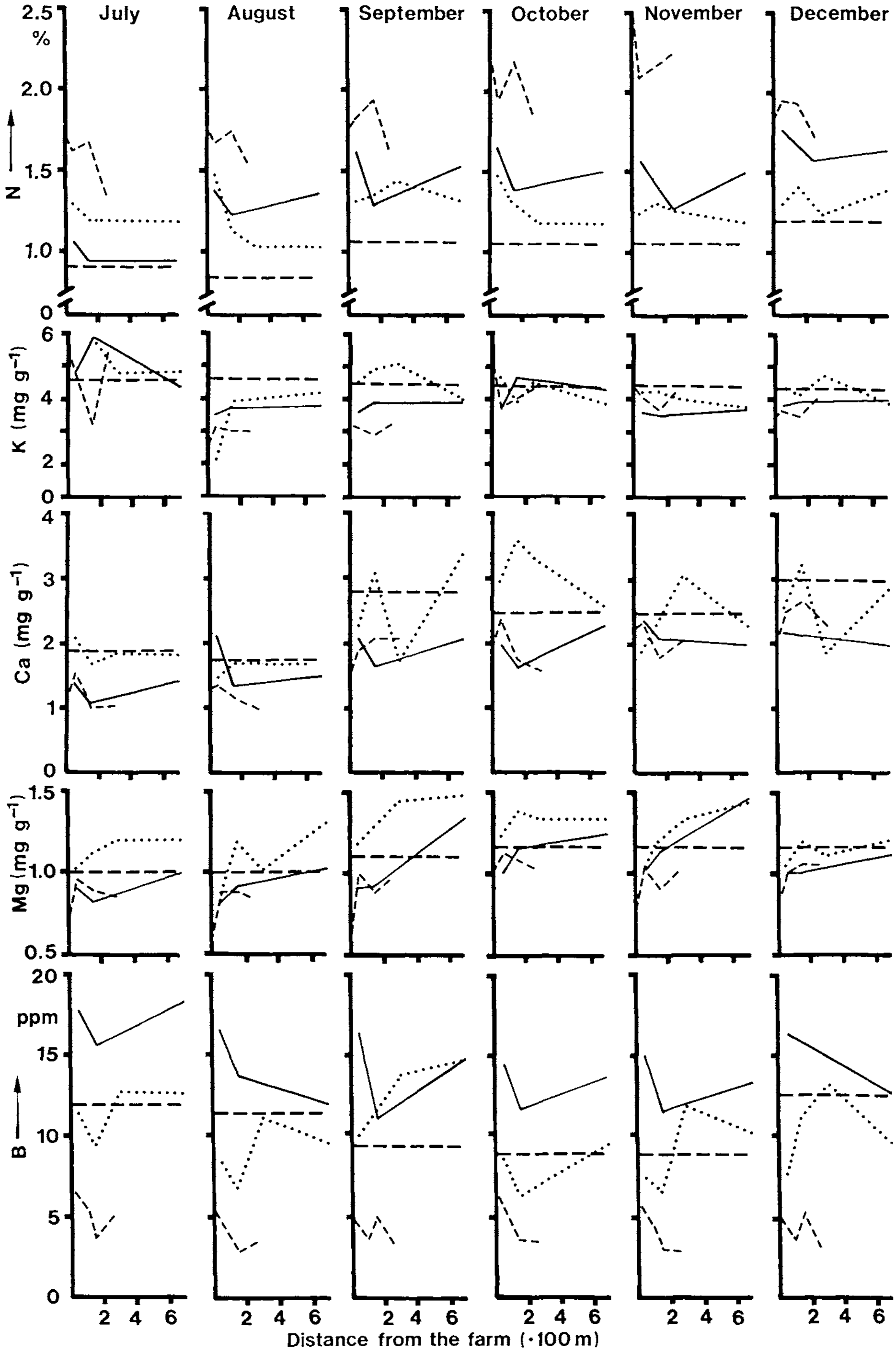

Fig. 19. Foliar total N, K, Ca, Mg and B contents along gradients near fur farms from July to December 1988. *Straight lines* large fox farm; *dashed lines* large mink farm; *dotted lines* small mink farm; *heavy dashed line* control level

1.8% in several cases, in all of the sample plots along the gradients compared to the control (Fig. 19). This was consistent throughout the sampling period. The contents increased towards the autumn and were exceptionally high at the onset of winter dormancy of the trees, especially near the large mink farm.

High nitrogen contents in pine needles coupled with low boron contents can, according to Aronsson (1980), decrease the frost hardiness of Scots pine. The foliar boron contents were distinctly in different levels in the different areas and the deficiency of boron was obvious in the pine forests close to the large mink farm (Fig. 19).

Near the large farms the foliar calcium contents were lower than in the control area during the study period (Fig. 19). A distinct decrease was observed in the foliar magnesium contents very near the large fur farms. The foliar manganese contents were lower in the study areas than in the control stand.

The pH, Buffer Capacity and Nitrogen Metabolism of Pine Needles

Material and Methods

It was tested whether ammonia as base either increases the pH value of the needles or exhausts the buffering capacity. To study the effect of high ammonia deposition on pine needles, individual amino acids and total amino acid pool were studied (since ammonia is a precursor in amino acid synthesis). In addition, the total and soluble proteins were determined to see how changes in amino acids are reflected in the protein pool.

The pine stands as presented in Table 1 were investigated in this study, too. The needle material was collected from the same sample trees as described above. The pH of the needle homogenate was measured after homogenizing 1 kg needles in 1-l distilled water and centrifuging. The pH of the remaining supernatant was measured using Orion 601 I electrode. The buffer capacity of the above supernatant was measured by titrating with 0.1 mol l^{-1} HCl and following pH changes with the above electrode. Buffer capacity = 1 when 1-l solution requires 1 eq (mol) acid or base to change the pH by one pH unit.

The total proteins and proteins soluble in 0.1 ml l^{-1} Tris-HCl (pH 9.0) were determined using the method of Bramhall et al. (1969). After solubilization the homogenates were centrifuged, proteins precipitated with 10% (w/v) trichloroacetic acid and washed with ethanol and diethyl ether. Proteins and amino acids were always extracted from fresh needles, but the concentrations were calculated per dry weight, which was obtained after overnight drying at 80°C.

Free amino acids were extracted by homogenizing the needles in 5% trichloroacetic acid which was then removed after centrifugation by shaking with diethyl ether. The remaining supernatants were then treated three to four times with hot diethyl ether and benzene to remove the waxes and resins. The extracts were then lyophilized and the residues dissolved in lithium citrate buffer (pH 2.2) for analysis in an automatic amino acid analyzer (Kontron Liquimat III). For further details, see Pietiläinen and Lähdesmäki (1986).

Results and Discussion

The pH of the Scots pine needles varied around 5 in the samples collected in April and May 1988, but was significantly lower (3.5) in the needles collected in August 1988. No pH variation as affected by the distances from the fur farms was observed (Fig. 20). The cardinal point location of the sampling area was reflected in the pH values, however, the pH value being somewhat lower in the area situated southwest than in that situated northwest from the fur farm. The negative correlation between pH and the buffer capacity (Fig. 20) was evident: the lower the pH value, the higher the buffer capacity was. Thus the basic NH_3 pollutants seem to consume the buffer capacity, which shows that the pine tissues are more poorly buffered against bases than against acids. The difference between the samples taken in April-May and August 1988 was particularly clear. However, after the growing season in August many more buffering substances may exist in pine tissues than after the winter rest in April-May when the production of new material is just

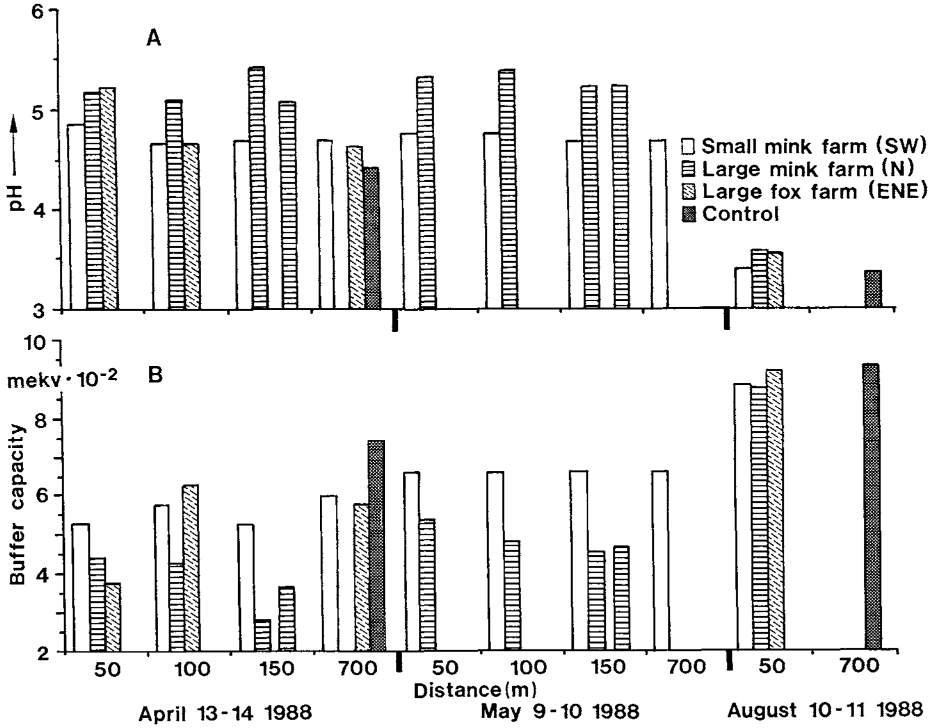

Fig. 20A, B. pH (**A**) and buffer capacity (**B**) of the pine needle extracts as a function of the distance from the fur farms starting. Again no differences in the buffer capacity as the function of the distance from the fur farms were, however, observed.

The total protein concentration of the needles slightly decreased with the distance to the fur farms (Fig. 21). The concentration in the needles taken in April was about twice as high as in those taken in August (20–30 g kg^{-1} dry weight vs. 12 g kg^{-1}). Thus the proteins do not seem to be in the most important role as buffering substances, since the buffer capacity was the greatest in August. The soluble proteins of the needles comprised only 10^{-4} of those of the total proteins, but they showed more variability, depending on the distance of the sampling area from the fur farms and on the cardinal point location of the sampling area (Fig. 21). Thus it appears that the extra exogenous nitrogen supply in the near vicinity of the fur farms increases soluble proteins in the pine needles.

Free amino compounds (amino acids, amides, some peptides, NH_4^+) showed also a decreasing tendency as a function of the distance from the fur farms (Fig. 22). The trees near the larger farms had very high contents of amino acids, particularly in October. About half of the amino N appeared in arginine, the behaviour of which was almost identical with that of the total amino compounds (Fig. 22). The highest arginine content was above 400 mmol per kg dry weight,

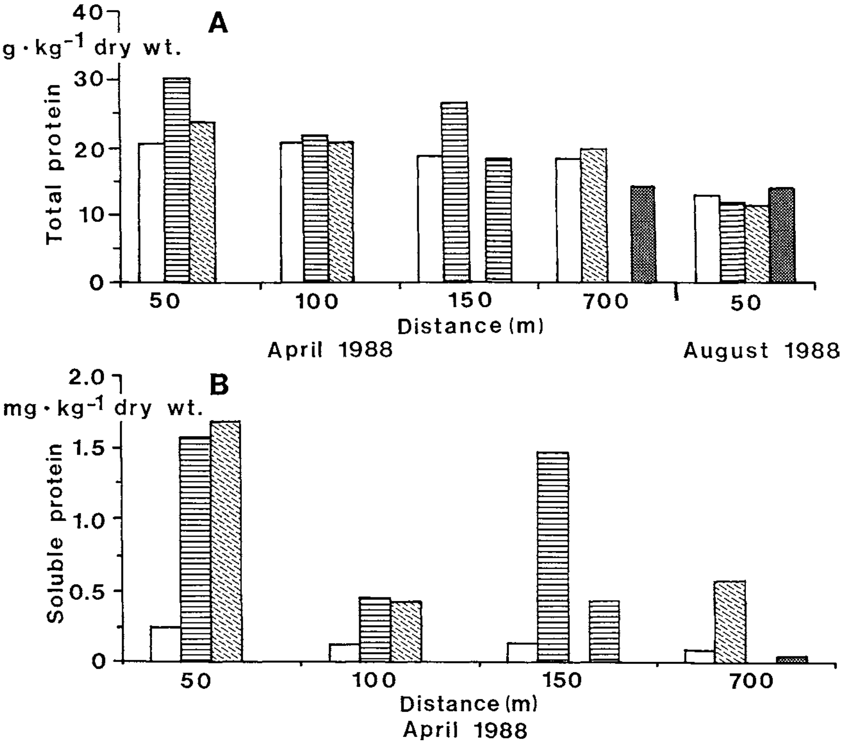

Fig. 21A, B. Concentration of total (**A**) and soluble (**B**) proteins in pine needles (legends in Fig. 20)

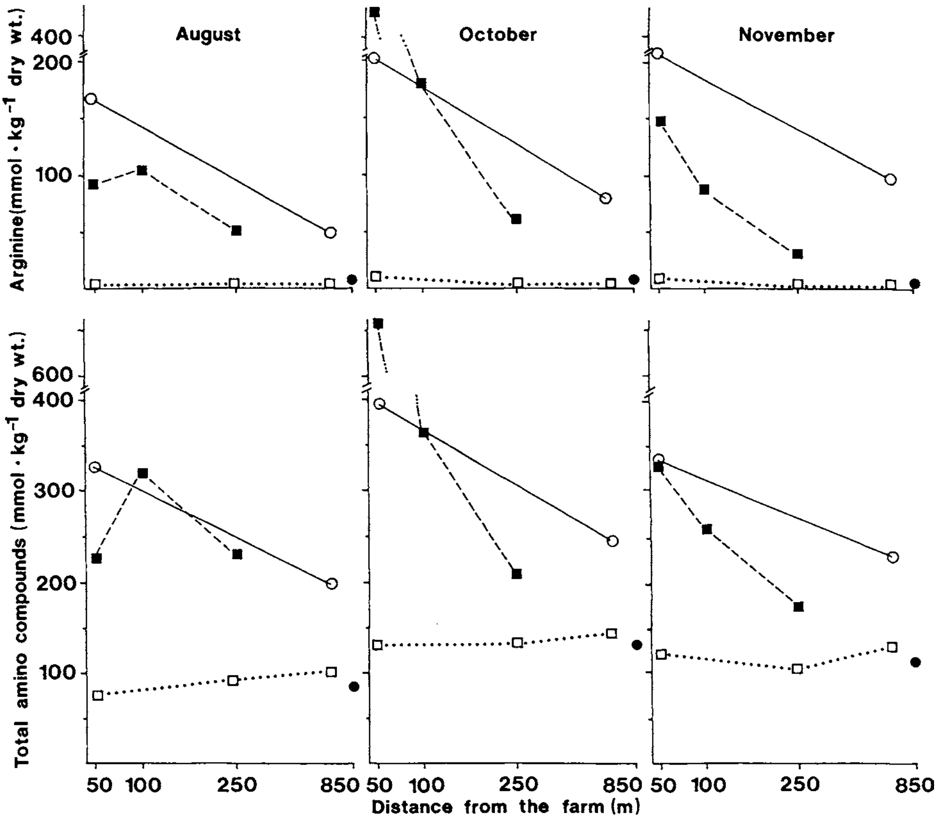

Fig. 22. Concentration of total free amino compounds and arginine in pine needles. *Straight line* large fox farm; *dashed line* large mink farm; *dotted line* small mink farm; *black circle, right* control

which is a very large amount compared to other investigations (cf. Van Dijk and Roelofs 1988; Hällgren and Näsholm 1988). The results also show that even quite far (700 m) from the large fur farm the foliar amino acid contents, especially arginine contents, had increased. The concentration of glutamine also showed a dependence on the location of the fur farms to some extent, while the concentrations of most other amino compounds were quite even in all the samples. Even the concentration of NH_4^+ compounds was relatively stabile in all the samples. Thus the extra NH_3 supply seems to be bound in arginine rather than appearing as free NH_4^+.

For the high level of basic amino acids (first of all arginine plus lysine, histidine and its derivatives) the ratio of the acidic amino acids (aspartic and glutamic acids) to these was very low near the fur farms, but increased with the distance from the fur farms (Fig. 23). The cationic amino acids certainly gives an extra cationic charge to the cytoplasm allowing thus the binding of a high amount of negative ions (NO_3^-, HCO_3^-, $H_2PO_4^-$).

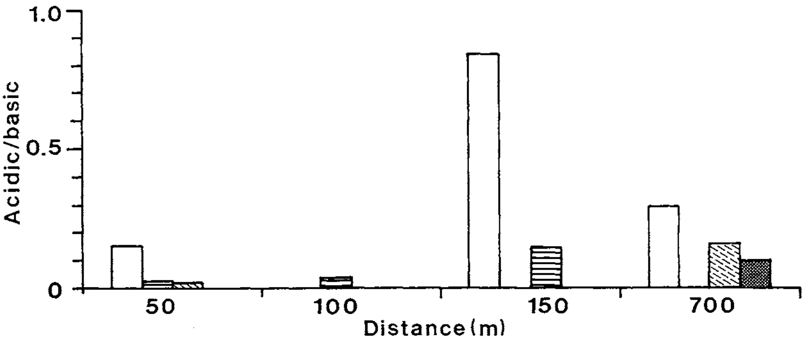

Fig. 23. Ratio of acidic (aspartic and glutamic acids) to basic amino acids (arginine, lysine, histidine plus ist derivatives) in pine needles in August 1988 (legends in Fig. 20)

Conclusions

The main problem near the fur farms is abundant ammonium nitrogen deposition. In throughfall measurements even 32.5 kg ha^{-1} ammonium N and over 3 kg ha^{-1} nitrate N reached the forest floor in May–October. These values exceed 15 times for ammonium and two times for nitrate the normal deposition in open areas in this part of the country (Järvinen 1986). The share of nitrate was only one-tenth of the amount of ammonium. The investigation of Tietema and Verstraten (1989) indicates that the total atmospheric nitrogen deposition will be even larger (maybe 15%) and thus the foliar uptake in the form of NH_4^+ by the canopy would have been rather high.

In Dutch conditions the nitrogen output from forest soil can be high (Tietema and Verstraten 1989). In the conditions of the fur farming area, however, only a slight increase in nitrification (and possibly in leaching) was observable. Also denitrification can be assumed minor because of the acid soil (cf. Nömmik 1956).

Besides nitrogen also some other elements showed increased throughfall depositions. Deposition of acid gases, e.g. SO_2, might be higher due to the alkaline surfaces from ammonia deposition. Internal circulation of ions may also have increased due to the NH_3 deposition and thus increase leaching from the needles. The phosphorus deposition in throughfall was at its highest more than ten times greater than normally in forest stands (Pätilä unpbl.). Leaching of the bird faeces – fur farms allure enormous amounts of birds – from the tree canopies is one possible factor contributing to the elevated depositions.

The observed tree damages and growth disturbances were in correlation with the high total N and ammonium N contents in needles and high contents of soluble nitrogen in the humus. In the vicinity of piggeries and poultry farms the effect of ammonia emissions is seen as risen total N and ammonium N contents in pine and spruce needles (Tesche and Schmidtchen 1978; Rudolph 1981; Roelofs et al. 1985). Deviations from the control figures were 50–250% and thus of the same magnitude as in this investigation. Suspiciously high nitrogen contents were discovered in pine needles on sample plots near the fur farms. Even the lowest nitrogen content at less than 100-m distance was 1.56%, which would be an exceptionally high value even on lusher forest site types (Metsänterveysopas 1988). No nitrogen shortage was found on the control plots.

Plants are able to take gaseous ammonia through their stomata (Lemon and Van Houtte 1980). Direct ammonia is more dangerous for plants than ammonium (Mengel and Kirkby 1982), but also excess ammonium may have serious consequences for plants and trees. High ammonium contents are toxic to plants (Haynes and Goh 1978). Plants are able to synthesise fast the absorbed ammonium into organic molecules thus trying to detoxify it. This procedure consumes the carbohydrate reserves of the plant (Givan 1979), since they are more important for the uptake of ammonium than nitrate.

High amounts of ammonium in the soil or solution lead to a decrease in the Ca, Mg and K contents of plants (e.g. Cox and Reisenauer 1973) and, on the other hand, an increase in the total nitrogen (Kirkby 1968; Ferguson and Bollard 1969), free ammonium nitrogen, amides and free amino acids (Harada et al. 1968; Ikeda et al. 1974) and a decrease in organic acids such as malic acid (Kirkby 1968; Harada et al. 1968). Excessive ammonium is stored in the form of glutamine, asparaginine and arginine. A sharp rise in amino acid content of the plant tissue has been attributed to the inhibition of the protein synthesis (Zedler et al. 1986; Van Dijk and Roelofs 1987). In this investigation near the fur farms extremely high foliar concentrations of total amino acids and especially arginine were observed. It seems evident that arginine is a good indicator of detrimentally high ammonium deposition.

Abundant ammonium may prevent plants from taking water (Quebedeaux and Ozbun 1973), checks the respiration (Vines and Wedding 1960) and photosynthesis (Gibbs and Calo 1959; Barker et al. 1970). An excess of ammonium destroys the lamel constructions of chloroplasts (Puritch and Barker 1967). Ammonium has been found to inhibit the activity of IAA oxidase, thus causing an exceptional increase in IAA (Varga and Zsoldos 1963). Excessive ammonium is particularly harmful to the growth of roots (Varga and Zsoldos 1963; Bennett et al. 1964; Haynes and Goh 1977) and also to the growth and occurrence of mycorrhizae (Arnolds and Jansen 1987).

In the stands near the fur farms, observations were made of a decrease in the foliar potassium, calcium and particularly magnesium and boron contents, related to high foliar and humus ammonia N and total N contents. A reduction of the foliar potassium and magnesium contents has also been observed in the stands near poultry farms, resulting in a deficiency of these nutrients (Roelofs et al. 1985). The foliar magnesium content of the forests near the fur farms has a closely negative correlation with stand damages. The lowest contents indicated a magnesium shortage (Baule and Fricker 1967; Metsänterveysopas 1988).

There was a high probability of frost damage in the forests near the fur farms (< 100 m), for there is a close correlation between the frost resistance and the nitrogen content of pine needles (Aronsson 1980). The best frost resistance is achieved if the nitrogen content of pine needles is about 1.5%. The occurrence of frost damage increases considerably when the foliar nitrogen content is over 1.8–2.0% (Aronsson 1980). Besides a high nitrogen content, the reduced contents of other nutrients may weaken winter dormancy, which essentially decreases frost resistance. In some cases, with rather high nitrogen contents, no frost damage occurs. If there are small amounts of boron, besides abundant nitrogen, risk of frost damage rises. The high foliar nitrogen content and low boron content have made plants vulnerably to frost damage (Aronsson 1980) and growth disturbances (e.g. Veijalainen et al. 1984). In fact, we are dealing with the same phenomenon which proceeds step by step from nutritional disturbances via a fault in the physiological function of trees to poor winter dormancy, which may result in visible damage triggered by frost, spring wind, light, etc.

Due to high ammonium nitrogen deposition, ammonium is accumulated, resulting in a disturbed nutrient balance and decreased vitality of trees. Further research into this problem should be carried out and these investigations could contribute to the national and international research on the mechanisms of forest decline. It has been shown that it is essential to adopt an approach which takes into account the whole forest ecosystem. Ammonium nitrogen deposition may affect wood production of the forests – unfavourable near the farms, but also favourable further away from the farms – within a wide range on the western coast of Finland. One of the most urgent tasks is to determine the extent of the nitrogen emissions from fur farms at different stages in the raising of the animals, the effect of the farm size and the prevailing wind directions on the emissions, and naturally to discover and examine methods for reducing these emissions. Peat, for instance, has proved to be an efficient material for binding nitrogen.

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Causes of Conifer Injuries in Some Industrial Environments

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Summary

Effects and relative importances of individual air pollutants and their combinations were studied. Half-open chambers were used near industrial sources and exposures of trees in open-field experiment. Effects on needle injuries were followed by visual and microscopic observations and chemical and physiological analyses. Dry deposition and winter conditions appeared to be significant factors near industrial sources. Direct effects of wet deposition seemed to be of minor importance. The importance of fluoride to injury development was emphasised; whenever fluoride was involved the damages were more pronounced. Interaction between fluoride and other pollutants could be seen so that exposure to SO_2 or nitrogen compounds increased fluoride accumulation of needles. Sulphate applied as wet deposition did not increase sulphur content of needles. Accumulated sulphur and fluoride content was two or five to ten times, respectively, higher in spruce than pine needles.

Introduction

In spite of the fact that forest injuries around industrial point-sources have been studied for quite some time in Finland (e.g. Havas 1971; Huttunen 1973; Laaksovirta and Silvola 1975; Kärenlampi et al. 1979; Soikkeli 1981), the factors and processes causing these injuries have as yet not been exactly specified. Only through a better understanding of the factors and their role will it be possible to suggest which emissions should be restricted and what investments for emmission control equipment should be made in order to obtain the best possible benefits. This study was divided into two main parts: (a) exclusion experiments by using half-open chambers in industrial environments (mainly SO_2, NO_2 and F emissions) and (b) exposures of trees in open-field experiment. The aim was to estimate the role of individual pollutants and their combinations on the development of conifer needle injuries in industrial areas.

Acute high SO_2 exposures have been observed to result in a water-soaked appearance of the needle tips; this soon turns to a red-brown to light-brown tip necrosis that may extend to the base of the needle. Often, a well-defined dividing

Kauppi et al. (Eds).
Acidification in Finland

line between the necrotic tip and the unaffected green tissue occurs. In chronic injury the needles remain short and chlorosis is frequently observed. Pale green or yellow-green areas appear at the tip of the needle followed by a colour change to brown (Knabe 1976: Manning and Feder 1980; Halbwachs 1984).

Fluoride injury appears as chlorosis of needle tips. With progress of the injury, the needle tip becomes necrotic and turns brown. A distinct dark brown, band separates dead and healthy tissue (Weinstein 1977; Manning and Feder 1980). Fluorides have been reported to be very phytotoxic in their effects, e.g. to membranes, enzymes, lipid composition and translocation of photoassimilates (e.g. Weinstein 1977; Zwiazek and Shay 1987; Giannini et al. 1987; Madkour and Weinstein 1988).

For NO_x there are no typical diagnostic symptoms. Acute NO_2 injury may resemble acute SO_2 injury. At low concentrations, growth simulation may occur and the plant may be a darker green in colour. Chlorosis may occur, which is followed by premature leaf fall. Apparently very high concentrations are required to produce visible plant injury symptoms (Reinert et al. 1975; Manning and Feder 1980).

Acid rain has been observed experimentally to cause tissue injury in the form of small necrotic lesions and premature abscission. The threshold for the occurrence of these visible injuries is usually reported as being between pH 3.0 and 3.6 and for growth effects between pH 3.5 and 4.0 (Neufeld et al. 1985; Shriner 1986).

Combination of SO_2 and NO_x has usually been found to cause more injuries than either of the two alone (Reinert et al. 1975; Manning and Feder 1980; Mansfield and Freer-Smith 1981). Effects of SO_2 and HF combinations vary, being less than or greater than additive (Reinert et al. 1975; McCune 1986).

The above descriptions of needle symptom development do not fit the northern industrial environments, where the symptoms mostly appear after year-long chronic exposure and after winter stress. Therefore there still is need to analyse the causes of both needle and whole tree symptoms.

Material and Methods

The Half-Open Chambers

Two types of half-open chambers were used throughout the year for excluding air pollutants around selected trees. Elimination of the critical component or combination of components was assumed to prevent the development of injuries to the needles. In one experiment the half-open chambers protected the lower parts of the tree from dry deposition by exposure to filtered air (Fig. 1). This chamber is a simplified and inexpensive modification of the commonly used open-top chambers (e.g. Mandl et al. 1973; Heagle et al. 1979; Kats et al. 1985). The filtering system consisted of an activated charcoal filter, two particulate filters and fan with an air flow of $0.22\,m^3\,s^{-1}$. Filters were changed once a year. Filtered air was

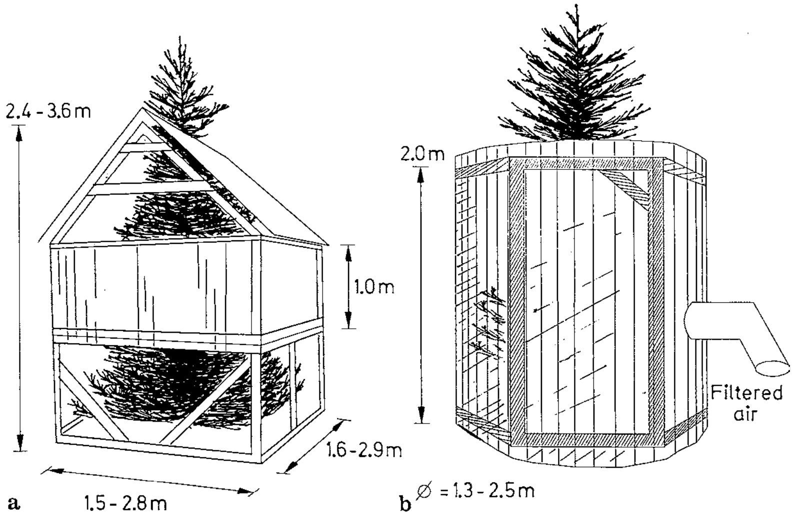

Fig. 1a, b. Construction and dimensions of the half-open chambers. **a** Exclusion of wet deposition. **b** Exclusion of dry deposition.

passed around the trees through a perforated air duct that encircled the chamber at a height of 1 m.

Half-open chambers were also used to exclude wet deposition by covering lower parts of the tree with a transparent shelter (Fig. 1). The covering shelters were as open as possible to maximise natural ventilation around the trees; this simultaneously prevented an absolute exclusion of wet deposition. Under covering shelters, temperature did not much differ from the ambient, but in open-top chambers 1.5–2°C higher values were recorded. The material for the chambers was polycarbonate.

The efficiency of air filtration was tested by using biological material. Lichens (*Hypogymnia physodes*) from a clean rural site were transplanted onto the inner and outer sides of the filtered air chambers and accumulated fluoride and sulphur were analyzed after 3 months. The reduction of accumulated fluoride and sulphur inside the chambers was about 75% at the site near the fertilizer factory. Near the pulp mill the reduction was small (30%). This may have been due to incursion of the polluted air through the open top.

The half-open chambers were situated in two differently polluted industrial and one background site in central Finland. The industrial sites surrounded a pulp mill which mainly emitted SO_2 (12,000 t SO_2/yr) and some ammonia, and also a phosphate fertilizer plant with SO_2, NO_2 and F emissions (5000, 800, 22 t/yr, respectively, in 1986). Experiments were performed in naturally grown Norway spruce (*Picea abies*) stands which were located 500 m and 1.8 km to the NW from pulp mill and fertilizer plant, respectively. The background site was situated in a rural environment more than 50 km away from the industrial sites. The studied spruce trees were about 20 years old and had 1–10 living needle classes. In all of three experimental sites there were three covered, two filtered-air and three reference ("unbuilt") trees under study. Only trees with clearly visible symptoms were selected for this study, while the approach taken was to observe if individual trees showed any improvement when dry or wet deposition was, at least partially, excluded.

The Open-Field Experiment

Young Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) trees were exposed in the open field to gaseous SO_2 and to sprayings of solutions (pH 5) containing nitrogen, fluoride and sulphate compounds. Pollutants were given both individually and in combinations. More detailed information about the exposures is shown in Table 1. Trees were growing in the ground as circular groups. Each exposure group consisted of about 20 spruce and 20 pine trees. The control group received only an artificial rain solution. The exposure lasted for about 5 months during the summer.

The open-field SO_2 exposure was resulted in a gradient around one release point (9000 µg SO_2 m^{-3}) which was situated in the center of the plot. Because of the strong and rapid dilution of the gas the concentrations among the trees fluctuated from about 100 to 400 µg SO_2 m^{-3} at levels dependent on velocity and direction of the wind. The SO_2 levels were measured occasionally using an SO_2 analyser. Exact knowledge of concentration was not required as the aim was not to quantitate the dose/response relation but to search characteristic symptoms caused by SO_2.

Methods for Observation of the Needle Symptoms

The Visible Symptoms

Visible symptoms of needles were carefully recorded throughout the year. Development of different kinds of colour changes were followed and the effects of insects and fungi were also studied. The length and the proportion of remaining needles and the number of living needle classes were counted.

Table 1. Pollutants and concentrations used in open-field exposures of 5-year-old pine (*Pinus sylvestris*) and spruce (*Picea abies*) trees during summers 1987 and 1988.

Pollutant	Concentration	Exposure time	Number of exp. days 1987	1988
SO_2	100–400 µg SO_2 m^{-3}	8 h/day (08.00–16.00 h)	119	120
F^- (NaF)	50 mg F l^{-1}	Once a day	84	33
N (NH_4NO_3)	200 mg N l^{-1}	Once a day	84	33
SO_4^{2-} (H_2SO_4)	200 mg SO_4 l^{-1}	Once a day	84	0

Chemical Analyses

The assembled needle samples were dried (60°C, 24 h) and ground for sulphur and fluoride analyses. Before drying the needles were washed with distilled water (2 × 20 s) to remove possible contamination from the surface of the needles. Two analyses of each sample were always made.

Levels of sulphur in the needles were assayed by ion chromatography after combustion in calorimetric bomb where all sulphur was oxidised to sulphate (e.g. Small 1975). The micro-diffusion method (Kari et al. 1976) was used to release the fluoride from organic matter. Finally, fluoride was measured by fluoride selective electrode (e.g. Cooke et al. 1976).

The Conductivity Test and Water Content of Needles

Membrane damages were assessed by measuring the conductivity of water extracts from the needle material (e.g. Dexter 1932; Green and Warrington 1978; Aronsson 1980; Beckerson and Hofstra 1980; Smit-Pinks et al. 1983; Feiler 1985; Zwiazek and Shay 1987). Relative conductivity was high when the tissues were badly damaged.

Two needle samples were collected from each individual tree and kept in an ice box (+4°C) until sample preparation. The needles (about 0.05 g) were cut into 1–2-mm pieces with razor blade and incubated in 2 ml distilled water for 4 h in 20°C. After this the conductivity (C_1) of extract was measured using a conductivity meter (Philips PW 9505). For calculating a relative conductivity (RC) value the needles were boiled after the first measurement for 10 min followed by 4 h incubation and second measurement (C_2) of the extract. The RC value was calculated as follows:

$$C_1/C_2 \times 100 = \mathrm{RC}\ (\%)$$

The water content of needles was measured simply by weighing the needles before and after drying (60°C, 24 h) (e.g. Slavik 1974).

Light and Electron Microscopy

Changes at the cellular level in the needles were studied by using both light and transmission electron microscopy. Selected needles were cut into 0.5-mm pieces with a razor blade, prefixed in 2% glutaraldehyde in 0.1 M phosphate buffer (in summertime 0.05 M) and postfixed in 1% OsO_4 in the same buffer. The dehydration was done in graded ethanol series followed by propylene oxide and embedding in Ladd's epon (e.g. Soikkeli 1980). Thick sections for light microscopy were stained with toluidine blue. Thin sections were mounted on copper grids and stained with uranyl acetate and lead citrate. Both JEOL JEM 100B and JEOL 1200 EX transmission electron microscopes were used for ultrastructural observations.

Air Quality and Deposition Observations

The bulk deposition collectors were situated in the open and analysed monthly for liquid volume, pH, conductivity, sulphate, fluoride and ammonium.

The atmospheric fluoride concentrations were measured at varying intervals for few days periods using a dual tape sampler (Mandl et al. 1971). The sampler draws air through the filters at a rate of 17 l min^{-1}. The volume of each 6 h air sample was thus 7 m^3. The filter papers for gaseous and particulate fluoride were soaked in Orion Total Strength Buffer (TISAB) and the fluoride concentrations were determined as $\mu\mathrm{g\,F\,m}^{-3}$ using an Orion fluoride-ion-specific electrode.

Results: Experimental Sites with Half-Open Chambers

Results from the Monitoring of the Air Quality and Deposition

Results of precipitation analyses are shown in Table 2. The mean pH was 4.8 (min 3.8, max 6.2, $n = 57$); 74 % of pH values were below 5.

The atmospheric gaseous fluoride concentrations varied during the sampling periods (from August 1987 to November 1988) from 0.06 to 1.46 $\mu\mathrm{g\,F\,m}^{-3}$ (mean 0.35 $\mu\mathrm{g\,m}^{-3}$, $n = 71$) near the fertilizer plant and in the background area the mean was 0.1 $\mu\mathrm{g\,F\,m}^{-3}$ ($n = 26$). Concentrations of particulate fluoride rarely exceeded the detection level.

Visible Needle Symptoms

Visible Symptoms Before the Experiments

In the summer of 1986, prior to the construction of the half-open chambers around the trees, the visible symptoms of the selected trees were studied. The most prominent colour changes detected in the needles were chlorotic and brown tips but also light and brown flecks and entirely brown needles were found especially in the older year-classes. The length of first-year needles of the studied trees was significantly ($p < 0.01$) shorter at industrial sites and annual growth (1986 growth) of shoots was significantly ($p < 0.001$) shorter at the site near fertilizer plant compared to the background site.

In the background area trees were healthy-looking and had about 10 living needle classes. In all needle classes younger than 6 years over 90% of needles remained on the branch. Brown tips were found in 0–5 % of the young needles and occasionally more in needles older than 4 years.

At the site near the pulp mill the decreased amount of remaining needles and increased occurrence of brown tips and entirely brown needles was already detected in second-year needles. In the branches near to the ground this occurred from the fourth needle class. There were 2–5 needle classes left in the upper part (in height more than 1 m from the ground) of the tree and 5–9 in lower part (less than 0.5 m from the ground).

Table 2. Mean monthly pH, conductivity and concentration of SO_4, NH_4 and F in open-field precipitation at the exclusion experiment sites during June 1987 to December 1988

	pH	SD	Cond. (µg S/cm^{-1})	SD	SO_4-conc.	SD	NH_4-conc.	SD	F-conc.	SD
Backgr.	4.9	0.6	16.9	8.2	2.3 mg l^{-1} 85.7 mg m^{-2}	1.6	0.7 mg l^{-1} 39.8 mg m^{-2}	0.6	0 mg l^{-1} 0 mg m^{-2}	
Pulp mill	4.7	0.6	29.0	20.2	5.6 mg l^{-1} 275.5 mg m^{-2}	4.4	1.5 mg l^{-1} 102.6 mg m^{-2}	0.9	0 mg l^{-2} 0 mg m^{-2}	
Fert. plant	4.9	0.5	21.5	13.9	3.9 mg l^{-1} 157.0 mg m^{-2}	3.2	1.0 mg l^{-1} 65.4 mg m^{-2}	0.6	0.2 mg l^{-1} 7.8 mg m^{-2}	0.2

Near the fertilizer plant the proportion of remaining needles rapidly decreased in third-year and older needle-classes and simultaneously the proportion of needles with brown tips increased. In the lower part of the trees needle loss began from about the fifth-year needles and brown tips were found in the fourth-year and older needles. Number of remaining needle classes was 4–6 in upper part of the trees and 7–9 in lower parts.

Visible Symptoms After the Experiments

By the end of this study (winter 1989) the overall situation at the industrial sites had worsened based on the observed needle losses as at best only 1–4 and most usually only 2 or 3 needle classes remained. At the background site the needles of chamber trees remained healthy-looking, which indicates that the chambers themselves had no harmful effects on the trees. As only the two youngest needle classes had entirely developed inside the chambers the observations are concentrated on those needles. First-year needles showed mainly a green coloration at all the sites.

Near the fertilizer plant the second-year needles in the filtered air chambers had only a few brown tips, which was less than observed on the other study trees at the site, indicating a weak recovery. The covered trees had chlorotic and brown tips in 10–50% of the second-year needles and reference trees in 10–100% of needles.

At the site near the pulp mill certain mites (*Oligonychus ununguis* Jac.) invaded the chamber trees (especially the filtered air trees) and caused severe visible symptoms (small yellow-green flecks followed by a colour change to brown). The second-year needles of covered trees had more visible symptoms (an average 30% of the needles had brown tips or necrosis of the entire needle) than in the reference trees (in 10% of the needles). Brown tips on the reference trees were often found in the needles facing the ground.

The visible symptoms (chlorotic and brown needles and needle tips) were usually first seen in late winter. These symptoms obviously caused by air pollutants could be mainly seen in second-year and older needles (in the first-year class these symptoms were expressed in less than 5% of the needles). In addition, after the unusually hard winter 1986/1987, a different kind of symptom caused by winter stress could be seen in first-year needles at all sites. Needles started to turn irregularly greyish in late February and gradually continued to a brown coloration before needle loss in June. The amounts of these winter injuries varied greatly between individual trees. In the most sensitive trees the needle loss in first-year needles was 100% and occasionally injuries to the buds were also seen. The highest proportion of winter injuries was observed at the site near the fertilizer plant.

Chemical Analyses of Needles

The sulphur and fluoride contents of needles were analyzed to reveal whether the chambers had affected the accumulation of air pollutants (Tables 3 and 4). Only the latest results are shown, while samples collected in the preceding autumn had an exactly similar trend of concentrations.

Table 3. Mean sulphur content of Norway spruce needles in the exclusion experiment. Sampling date 4.10.1988.

	Sulphur concentrations, $\mu g\, S\, g^{-1}$											
Site	Reference trees				Covered trees				Filtered air trees			
	1st	SD	2nd	SD	1st	SD	2nd	SD	1st	SD	2nd	SD
Background	1143	137	1228	25	1197	50	ND		1122	18	1173	27
Pulp mill	1800	60	2070	67	1926	4	2568	332	1616	29	1698	70
Fert. plant	1230	54	1166	15	1063	48	1134	53	1154	42	1256	30

1st = 1st-year needles, 2nd = 2nd-year needles, ND = not determined.

Table 4. Mean fluoride content of Norway spruce needles in the exclusion experiment. Sampling date 4.10.1988.

	Fluoride concentrations, $\mu g\, F\, g^{-1}$											
Site	Reference trees				Covered trees				Filtered air trees			
	1st	SD	2nd	SD	1st	SD	2nd	SD	1st	SD	2nd	SD
Background	2.5	0.7	3.2	1.9	9.9	1.0	ND		2.5	0.4	5.0	1.6
Pulp mill	2.7	0.7	11.4	11.1	ND		ND		8.9	3.1	7.7	3.3
Fert. plant	21.0	2.1	30.7	0.6	26.6	0.8	59.1	8.8	20.1	0.1	31.7	2.4

1st = 1st-year needles, 2nd = 2nd-year needles, ND = not determined.

Table 5. Mean content of sulphur and fluoride in Norway spruce needles depending on age of the needles and sampling height in the exclusion experiment. Sampling date 4.11.1986. SD < 10%.

Needle class (years)	Background HB	Background LB	Pulp mill HB	Pulp mill LB	Fertilizer plant HB	Fertilizer plant LB
	Sulphur, μg S g^{-1}					
1st	730	1005	2028	1543	1199	1133
2nd	913	987	1689	1619	1216	1129
3rd	960	934	2055	1626	1525	1197
4th	996	852	1994	1349	1266	994
	Fluoride, μg F g^{-1}					
1st	4.8	4.7	5.2	4.8	16.4	14.5
2nd	5.7	5.7	4.3	4.3	30.4	32.2
3rd	5.6	5.2	8.9	4.4	47.7	46.7
4th	5.9	5.6	8.1	4.2	47.6	52.4

HB = branch higher than 1.5 m above the ground; LW = branch lower than 0.5 m from the ground.

High SO_2 emissions at the site near the pulp mill and fluoride emissions at the site near the fertilizer plant were reflected in the vegetation as significantly ($p < 0.05$, t-test) increased sulphur and fluoride contents in needles. Based on the S-content of needles near the pulp mill, the reduction caused by filtering was about 44% ($p < 0.05$, t-test). Needles of the covered trees had the highest fluoride ($p < 0.05$, t-test) and sulphur concentrations. Unlike sulphur, clear fluoride accumulation during ageing was observed, as also differences in sulphur but not in fluoride contents of needles relating to the sampling height (Table 5).

Conductivity Test and Water Content of Needles

Membrane damages measured by the conductivity test showed remarkable differences between individual trees. Although relative conductivity (RC) values varied greatly between trees, similar seasonal trends in all the trees could be seen. RC values were always quite low in the autumn and spring but in the winter showed higher peaks.

Differences between trees at the background and industrial sites could thus best be found only in early winter (December-January) or late spring (April-May) when interfering frost-injured needles were not sampled. For example, in the early winter 1987 there were in green needles significantly higher RC values at the industrial sites than at the background site (Fig. 2). After the hard winter of 1986/1987, RC values were elevated at all the sites in the following spring. The very mild winter 1988/1989 decreased the amount of membrane damages at industrial sites and in the spring of 1989 the RC values were very low at all sites. No significant difference

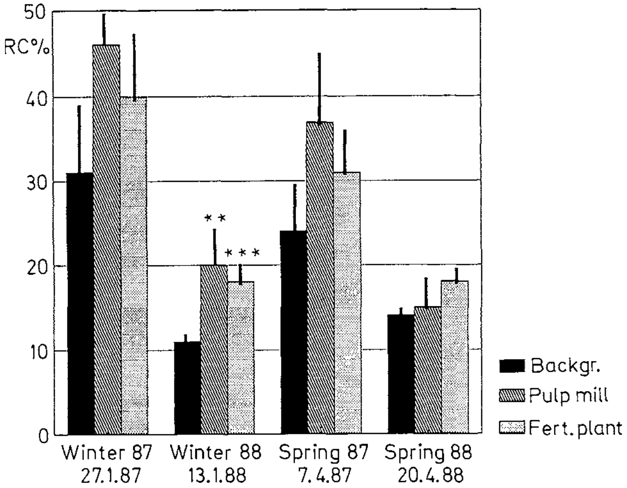

Fig. 2. Mean relative conductivity values +/− SE at the exclusion experiment sites. Significance of difference from background, ** $p<0.01$, *** $p<0.001$ (t-test)

in RC values between two industrial sites could be found. The appearance of individual trees correlated well with RC values so that poor-looking trees showed higher RC values (higher proportion of damaged membranes) than trees in better condition.

The constant water content of needles at the background site indicated that half-open chambers themselves had no harmful effect on the water economy of the

Table 6. Mean water content (% of fr.wt.) of needles at the exclusion experiment sites in three study winters.

	Winter 86/87 6.1.1987			Winter 87/88 13.1.1988			Winter 88/89 12.12.1988		
	BG	PM	FP	BG	PM	FP	BG	PM	FP
Reference									
1st	57.4	59.8	59.7	58.4	59.4	57.8	59.5	59.7	57.1
2nd	57.7	59.1	55.4	55.8	57.4	55.2	58.8	56.3	55.0
Covered									
1st	59.8	55.7	56.5	58.7	56.9	57.4	57.2	55.6	57.2
2nd	57.1	55.4	56.9	57.0	55.3	53.7	54.6	53.9	54.8
Filt. air									
1st	58.5	54.8	56.8	59.0	55.6	56.9	60.5	57.5	56.3
2nd	56.5	53.4	54.5	55.7	52.1	53.4	55.4	49.9	55.0
Means of all									
1st	58.6	56.8	57.7	58.7	57.3	57.4	59.0	57.6	56.9
2nd	57.1	56.0	55.6	56.2	54.9	54.1	56.3	53.4	54.9

BG = background, PM = pulp mill, FP = fertilizer plant,
1st = 1st-year needles, 2nd = 2nd-year needles

needles (Table 6). The lower water contents frequently found at the industrial sites have thus to be explained by other factors.

Ultrastructural Changes in Mesophyll Cells of Needles

In the autumn of 1986, the ultrastructure of mesophyll cells of needles was normal (e.g. Soikkeli 1980) at the background site. At the industrial sites the most frequent ultrastructural changes were increases of the lipid material and in the number of plastoglobuli and swelling of chloroplast thylakoids. In addition, lighter plastoglobuli and irregular-shaped lipid bodies were often found near the pulp mill. At the site near the fertilizer plant, curling of thylakoids could occassionally be seen. The changes and effects of chambers on needle ultrastructure will be analysed later.

Results: The Open-Field Experiment

Visible Symptoms of Needles

There were only few visible symptoms after exposures to nitrogen or sulphate compounds. Exposures to SO_2, and particularly to fluoride, caused more symptoms. The most frequent visible symptoms were brown and chlorotic needles or needle tips. The amount of symptoms was, however, quite small and varied greatly between individual trees. The proportion of strongly symptomatic trees represented less than 50% of the exposed trees. The strongest visible symptoms were observed after combination exposure ($F + SO_2 + N$) in both spruce and pine trees. The first summer exposure resulted in the detection of visible symptoms in mainly first-year needles. Following the second summer, the symptoms observed were similar but the amounts of visible symptoms, especially the number of chlorotic tips, had increased in the second-year needles of exposed trees.

In autumn 1987, after fluoride exposures, the most prominent symptoms in first-year spruce needles were the presence of entirely brown needles, chlorotic tips and chlorosis.- These brown needles were observed (not necessarily in great amounts) in about 30% of trees when fluoride alone or in combination with sulphate was applied and in 70% of trees when fluoride was combined with nitrogen or SO_2 or both. In pine needles brown tips were the most frequently observed symptoms besides chlorosis, chlorotic tips and entirely brown needles. Brown tips were observed in about 65% of trees after fluoride exposure, in 35% if fluoride was combined with SO_2, in 80% if combined to nitrogen and in 100% of trees after exposure to combination of nitrogen, fluoride and SO_2. A dark band at the interface of necrotic tip and healthy tissue was frequently found in pine needles.

The trees seemed to be quite resistant to SO_2 and produced only a small amount of visible symptoms after SO_2 exposure, mainly chlorosis, chlorotic and brown tips (abundantly in 37, 37 and 13% of the trees, respectively) and a few entirely brown first-year needles in the spruce needles. In pine trees brown tips and entirely brown needles (abundantly in 6 and 17% of trees, respectively) in addition to a few chlorotic needles were observed.

Chemical Analyses

Fluoride and sulphur contents of needles after exposures during the summers of 1987 and 1988 are shown in Tables 7 and 8. Accumulated pollutant concentrations were always lower in pine than in spruce needles.

The fluoride content of needles clearly increased after fluoride exposures. In spruce needles combined exposure to SO_2 and fluoride increased the fluoride accumulation compared to pure fluoride exposure but to a lesser extent than combination exposures of F + N or F + SO_2 + N. Sulphate exposure did not affect the fluoride accumulation. In pine SO_2 + F exposure resulted in the greatest increase in fluoride accumulation.

Sulphate exposure did not increase, but SO_2 exposure resulted in an elevated sulphur content of the needles. No clear specific effect of different combinations on sulphur accumulation (neither on visible symptoms) could be seen.

Conductivity Test and Water Content of Needles

No differences in relative conductivity values between control and exposed trees were observed in the autumn following the exposure. Slight increases in the relative conductivity values of the needles of spruce trees exposed to fluoride or SO_2 or combination of fluoride and SO_2 and nitrogen were detected in the following winter. In pine needles no increase could be measured.

Exposures did not have any drying effect on the water economy of needles. Water content of first-year spruce needles (mean 60.3%) was always somewhat higher than of pine needles (mean 57.7%) (measurements in December 1988).

Table 7. Mean fluoride content (μg F g^{-1} d.w.) of needles after exposures (cf. Table 1) in open field in summers 1987 and 1988. Sampling dates 29.9.1987 and 5.10.1988.

Exposure	Norway spruce 1987		1988				Scots pine 1987		1988			
	1st	SD	1st	SD	2nd	SD	1st	SD	1st	SD	2nd	SD
Control	1	1	3	1	5	2	2	1	4	1	4	1
F	84	6	121	12	183	32	9	1	14	0	14	2
F + N	157	0	146	4	422	68	13	0	11	1	17	3
F + N + SO_2	149	5	145	5	342	28	18	2	22	3	33	2
F + SO_2	119	5	128	14	189	1	32	5	19	4	33	4
F + SO_4	88	5	–		–		10	0	–		–	
F + SO_4 + N	124	1	–		–		24	2	–		–	
F + SO_4 + N + SO_2	156	6	–		–		20	2	–		–	

1st = first-year needles, 2nd = second-year needles.

Table 8. Mean sulphur content (μg S g^{-1} d.w.) of needles after exposures (cf. Table 1) in open field in summers 1987 and 1988. Sampling dates 29.9.1987 and 5.10.1988.

	Norway spruce						Scots pine					
	1987		1988				1987		1988			
Exposure	1st	SD	1st	SD	2nd	SD	1st	SD	1st	SD	2nd	SD
Control	1048	7	1216	52	1336	243	865	112	1218	57	1300	13
SO_2	3815	220	–		–		1286	14	–		–	
SO_2 + F	2338	9	3055	4	3256	6	1635	0	1362	47	1382	29
SO_2 + N	2620	14	3127	5	3689	117	1540	187	1560	14	1602	84
SO_2 + F + N	2909	8	3542	53	2949	53	1336	25	1632	17	1708	7
SO_2 + SO_4	3213	186	–		–		1529	110	–		–	
SO_2 + SO_4 + F + N	2817	58	–		–		1759	28	–		–	
SO_4	1126	78	–		–		868	119	–		–	

1st = first-year needles, 2nd = second-year needles

Structural Changes in Mesophyll Cells of Needles

Preliminary results of the light microscopy study showed only slight changes after exposures in autumn 1987. Enlarged intercellular spaces, changes in appearance of tannin and collapse of mesophyll cells were occasionally seen. Observations made by electron microscopy revealed the increase of cytoplasmic lipid material and enlargement and lightening of plastoglobuli in exposed trees. Ultrastructural changes were most pronounced in trees exposed to fluoride alone or in combination. Final results of structural changes will be published later.

Discussion

Visible Symptoms

Only a slight recovery at the industrial sites could be seen based on visible symptoms in the filtered air trees. This may be explained by the only partial exclusion of gaseous pollutants and the original poor condition of trees, which prevented recovery. The observed increased needle loss during the study was obviously caused by the unusually hard winter 86/87. The better condition of needles in the lower part of trees at industrial sites may have been due to protection by snow during the winter. This refers to the direct effects of air pollutants or importance of winter conditions rather than indirect effects via soil. Havas (1971) also observed that pine branches covered by snow remained healthier than the exposed branches near the fertilizer plant.

The observed increased number of mites could have resulted from the originally weakened condition of these trees or from the exclusion of precipitation. In addition, there is reasonable evidence that air pollutants influence the outbreak patterns of forest insect species (Hain 1987). Brown tips in the needles facing the ground could have resulted from long-term exposure of these needles to rain drops with harmful compounds.

Visible symptoms after SO_2 or fluoride exposures in the open-field experiment were similar to the symptoms observed at the industrial sites and reported in the literature (e.g. Manning and Feder 1980; Halbwachs 1984) to be typical for SO_2 or fluoride. At the industrial sites, visible symptoms usually did not appear until late winter. The appearance of visible symptoms in winter may be explained as resulting from the triggering effect of winter conditions. In the open-field experiment, exposure to fluoride combined with SO_2 or nitrogen compounds always resulted in more injuries than when fluoride was applied individually. This kind of additive effect of simultaneously existing air pollutants has often been reported (e.g. Reinert et al. 1975; McCune 1986). Only few visible symptoms observed after exposures to nitrogen or sulphate compounds give support to the suggestions of Chevone et al. (1986) that ambient wet and dry sulphate concentrations are insufficient to have a direct impact on the vegetation.

Chemical Analyses

The sulphur content of the needles was clearly elevated at the site near pulp mill. Knabe (1984) has classified sulphur contents in relation to injuries of spruce needles; contents below 1600 μg S g^{-1} are recorded for relatively green and healthy trees, 1600–1999 μg S g^{-1} indicates possible injury, 2000–2399 μg S g^{-1} emerging injury, 2400–2799 μg S g^{-1} manifest injury and more than that very serious injury. Compared to this classification, the sulphur contents in reference trees near the pulp mill were high enough to possibly cause injuries. On the other hand, Lehtiö et al. (1980) found that the sulphur content of the needles relative to the visible injuries were different at each study area, thus indicating the influence of injurious factors other than SO_2.

The filtering effect could be especially seen in second-year needles of the filtered air trees as lower sulphur contents were recorded than in reference trees at the pulp mill site. However, these concentrations were higher than in the background area, which indicates either that filtering was not highly effective, incursion of ambient air occurred or there was translocation of sulphur from soil or other parts of tree.

Normal fluoride concentrations in the needles were recorded at the background site (below 10 μg F g^{-1}) (e.g. Treshow 1970; Havas 1971; Weinstein 1977). At the site near the fertilizer plant, fluoride concentrations were clearly increased, being equal in needles of both filtered air and reference trees. This probably results from the strong and rapid accumulative property of fluoride. While fluoride exclusion was not absolute and via the precipitation deposited some fluoride, needles rapidly reached the saturation level.

According to results of the open-field experiment it seems that nitrogen compounds and SO_2 may worsen the condition of conifer trees in fluoride-polluted areas via increased accumulation of fluoride to needles. Consequently, the clearly lower fluoride content of needles measured during this study than earlier at distances closer to the same fertilizer plant may reflect the fact that both the nitrogen and SO_2 emissions of this plant have been reduced since an earlier study of this site (Kärenlampi et al. 1979). Brown tips observed may result from accumulation of fluoride at the tips of the needles (e.g. Jacobson et al. 1966; Garrec et al. 1973; Kärenlampi et al. 1979). Havas (1971) found that the accumulation of fluoride was not concentrated in the tips during the winter, which he suggested was a result of the low transpiration flow under winter conditions.

Plants have a wide variation in tolerances to foliar injury by accumulated fluoride. Most sensitive plants develop foliar injury at a concentration of 20 μg F g^{-1} and tolerant species may survive at concentrations exceeding 4000 μg F g^{-1} (Jacobson et al. 1966). According to results obtained from the industrial sites and the open-field experiment a concentration of more than 20 μg F g^{-1} is needed in pine needles and more than 30 μg F g^{-1} in spruce needles to cause visible symptoms.

In the exclusion experiment, the higher pollutant concentrations in covered trees may be explained both by the absence of a protective snow cover and by the lack of a leaching effect caused by smelting snow in the winter and rain in the summer. Conifers in SO_2 and HF exposures have been observed to accumulate sulphur and fluoride at reduced rate during dormancy (Keller 1982; McLean et al. 1986). This indicates that lack of leaching of pollutants may be a more important factor increasing pollutant accumulation than the lack of protective snow cover during the winter period.

Consequently, low annual precipitation may result in a decrease in the loss of pollutants by leaching and thus lead to relative increase of pollutants inside the needles. It has been observed that rainfall constitutes a natural protection against excessive accumulation of pollutants in plants (e.g. Havas 1971; Craggs and Davison 1985; Samujlo and Machoy 1986; Huttunen et al. 1985). Higher pollutant concentrations in trees without wet deposition also indicate that pollutant uptake from dry deposition is very significant at industrial sites. The drier surfaces of the needles in the covered trees may have facilitated direct penetration of gaseous pollutants through the stomata. The abundance of visible symptoms in covered trees can also be explained by higher pollutant concentrations.

Unlike sulphur, clear fluoride accumulation in the needles during ageing was observed. The proportion of visible symptoms also clearly increased in older needles in the F-pollutant area, which at least partially indicates the importance of fluoride in the development of injuries. Correspondingly, Garrec and Audigier (1980) observed in conifer forests subjected to fluoride pollution a logarithmic correlation between the F-content of needles and the decrease in wood production.

Clearly lower concentrations of sulphur observed in the lowest branches account for fewer visible symptoms observed. Lower concentrations may result from protective and leaching effect of snow cover and the reduced air flow (less ventilation, smaller flux of pollutants) near ground. A lack of difference regarding the F-concentrations may be explained by rapid and strong accumulation of fluoride. Fewer visible symptoms on low branches can thus not be explained by lower fluoride concentrations near the fertilizer plant. This suggests that in addition to high pollutant concentrations, winter stress is needed for injury development. This does not mean that possible mild winters caused by the greenhouse effect would be a beneficial change in the long term, as a milder climate may result in disturbances of the annual rhythm of conifers.

Nitrogen content of needles (1.6% N) was slightly increased near the industrial areas as compared to the control area (1.1% N) (Saarelainen 1989) but is far from the 4% level which has been shown to cause direct damage (Treshow 1970).

In the open-field experiment, interactions between fluoride and other pollutants were seen such that SO_2, and especially nitrogen compounds, increased fluoride accumulation. This indicates that decrease of SO_2 and nitrogen emissions in fluoride-polluted areas would also diminish the harmful effects of fluoride. It is surprising that the high concentrations as measured in spruce needles (about $3000\ \mu g\ S\ g^{-1}$) after SO_2 exposures did not cause really severe visible symptoms (cf. Knabe 1984). This may be explained by the good basic condition of trees and the absence of other gaseous air pollutants.

After exposures in the open field there were clear differences in the needle fluoride and sulphur contents of spruce and pine, fluoride was found in five to ten times and sulphur twice higher concentrations in spruce needles. Surprisingly, Lehtiö et al. (1980) did not find any large difference in the suplhur content between spruce and pine needles of adult trees. We do not yet have any explanation for this.

Conductivity Test and Water Content of Needles

The conductivity test revealed a high variation in amount of membrane damages between individual trees. This supposedly reflects the great genetic variation among trees (e.g. Maronek and Flint 1974; DeHayes 1978; Kolb et al. 1985). High RC values at the background site in late winter may be explained by the obvious frost sensitivity of the trees at this site (cf. Green and Warrington 1978).

High RC values measured in green needles in early winter 1987 indicate that latent damages inside the needles already exist in early winter at the industrial sites. In the open-field experiment only in late winter were slight increases in RC values of exposed spruce trees detected. This may indicate that membrane injuries caused by pollutants do not develop until the winter, which supports the observations that visible symptoms at industrial sites usually appear in late winter. In pine needles no increase in RC values could be measured, which may be explained by lower pollutant contents in pine than in spruce needles or better resistance.

There were clear disturbances in the water economy of trees at the industrial sites, based on observed decreases of water content of needles. It has earlier been shown that there is a more intense winter water stress in polluted areas (e.g. Huttunen et al. 1981). The very low water content (49%) in the needles of the filtered air trees at the site near the pulp mill was likely to be the result of damages caused by the mites. At the site near the fertilizer plant, the water content of second-year needles in the covered trees decreased during the study. The increased fluoride content of needles observed in these same trees gives support to Zwiazek and Shay's (1988) suggestions that changes observed in jack pine (*Pinus banksiana*) after fluoride treatment may be the result of water stress following the initial fluoride injury.

Ultrastructural Changes in Mesophyll Cells of Needles

Preliminary results of the microscopy study agree with the earlier observations made in SO_2- and F-polluted areas (e.g. Soikkeli 1981; Soikkeli and Tuovinen 1979). When the effects of needle ageing on ultrastructure were studied (Wulff et al. 1988) it was clear that changes occurring during normal ageing were stronger and could be observed in younger needles at the industrial sites. This, together with observed premature needle loss, supports the idea that the effect of air pollution can partly be interpreted as accelerated ageing.

Monitoring the Air Quality and Deposition

There were no large differences in pH and conductivity of precipitation between the study areas. The pH was not low enough to cause visible symptoms (Shriner 1986). The sulphate and ammonium concentrations at the industrial sites were clearly higher than the average monthly concentrations measured at background stations during the years 1971–1977 in Finland at this latitude (Järvinen and Haapala 1980), but based on the results of the open-field experiment they alone are unlikely to directly damage trees. Ammonium deposition may alternatively exert an acidification of soil (Nihlgård 1985).

Mean atmospheric fluoride concentrations in coal-burning areas in the U.K. were found to be 0.05 μg F m^{-3} at the rural sites and 0.28 μg F m^{-3} at the urban sites (Davison et al. 1973). The authors presumed that the concentrations of fluoride measured in some of the urban sites would be sufficient to cause visible damage to certain conifers. Sidhu (1979) found that boreal vegetation in Newfoundland, Canada, did not exhibit any serious foliage damage in areas where the fluoride concentrations were 0.17 to 0.23 μg F m^{-3} but higher concentrations resulted to visible symptoms. Our measurements showed slightly higher atmospheric fluoride concentrations (mean 0.35 μg F m^{-3}), which suggests that there is a strong possibility of vegetation damage caused by fluoride at the site near the fertilizer plant.

Conclusions

High pollutant concentrations in the needles of the covered trees (without wet deposition) highlight the minor direct importance of wet deposition. This also indicates that pollutant uptake from dry deposition is very significant in these industrial areas. These results suggest that low annual precipitation may lead to relatively higher pollutant contents of needles and thus increase harmful effects of air pollutants. Premature needle loss and ultrastructural observations support the idea that air pollutants accelerate senescence. The conductivity test appeared to be useful in assessing membrane damages in the polluted areas.

Combination exposures resulted in more injuries than when pollutants were applied individually. The importance of fluoride to injury development was emphasized. Whenever fluoride was added the damages were more pronounced. Results indicate that decrease of SO_2 and nitrogen emissions in fluoride-polluted areas would also diminish the harmful effects of fluoride via decreased accumulation of fluoride. According to our results a concentration of more than 20 μg F g^{-1} is needed in pine needles and more than 30 μg F g^{-1} in spruce needles to cause visible symptoms. Accumulation of pollutants was always lower in pine than in spruce needles which may affect the sensitivity of these trees to air pollutants.

Air pollutants are obviously the main reason for needle injuries, but winter stress is the other important factor which triggers the appearance of the symptoms. Without winter stress the final damage would come later.

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Needle Retention, Age, Shedding and Budget, and Growth of Scots Pine Between 1865 and 1988

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Summary

Four northern Finnish Scots pines (*Pinus sylvestris* L.) were felled, sectioned into 1-year bolts and planed with an electric planing machine in order to examine the needle history of the trees. By using the vascular bundle method, the retention, age and shedding of the needles as well as the needle budget in the main stem of pines were defined for the period of 1865–1988. No descending change in needle retention was found from 1868 to 1988. The number of needle sets varied between 1.2 and 4.2, being mostly between 2.0 and 3.5. Needles had been over three growing seasons in the shoots on the average. The whole set of needles were shed very seldom during the same year. Annual shedding of needles varied from nil to two needle sets. Needle factors were compared with the annual radial increments of the same trees. The use of the vascular bundle method for forest health studies is discussed.

Introduction

In surveys of forest defoliation, or conversely needle retention, assessments are mainly based on numbers of needle sets reflecting the age and longevity of living needles. Until recently, data have usually been acquired from annual investigations of the same trees and/or sample plots. In Finland, attempts have also been made from the 1960's onwards to estimate annual needle biomass from litter samples, but as yet data about long-term fluctuations are not available. It is thought that data of this sort might be valuable for the estimation of forest health in the past, as well as the present.

To be able to make more correct conclusions about the effect of needle retention for the health of pines, Kurkela and Jalkanen (1990) described a new method to determine annual needle retention in a pine tree during its life. This method – the vascular bundle method (VBM) – has now been used to study the history of the foliage of 60–130-year-old specimens of Scots pine, and its relation to stem annual radial increment. This could be of significance in investigations of forest decline.

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Material and Methods

Four northern Finnish Scots pines (*Pinus sylvestris* L.) were felled, and their stems cut into the bolts of each annual shoot. These trees, nos. 12, 13, 16 and 17, the age of which varied from 60 to 130 years, with breast height diameters ranging from 15 to 20 cm. They were located on a dry pine heath in the Kivalo research area at Hietaperänkangas, Rovaniemi (66°22'N, 26°43'E). When felled, all the trees were retaining needles in three year classes. After being cut, the bolts were planed carefully year-ring by year-ring in the laboratory. From each of the ten oldest year-rings, numbers of vascular bundle scars were counted and the numbers of needle sets (needle retention) were calculated (see Kurkela and Jalkanen 1990).

Vascular bundle data were further used in calculations of average needle age, amounts of annual needle loss (needle shedding) and needle budgets from 1875 to 1912 (tree no. 13), and from 1933 to 1987 (tree no. 16). From trees nos. 12 (1865–1906) and 17 (1915–1988) only needle retention was presented. Although all four trees were alive prior to felling, year-rings were examined only in basal sections of the oldest trees, as they were too narrow in upper sections of the stem (Kurkela and Jalkanen 1990).

In needle age calculations, it was postulated that most needles die at the end of the growing season (e.g. Jalkanen 1986). If shedding occurred in the first year, an age of 3 months (0.25 years) was used. Shedding at the end of second, third, fourth, fifth etc. growing seasons would give ages of 1.25, 2.25, 3.25, 4.25 years and so on. Because dwarf shoots within one set of needles do not shed in the same year, the average needle age was balanced by the number of annually shed needles. Needle retention refers to numbers of over-wintering needle sets. The amount of annual needle shedding, which should be one needle set per year if needle retention were the same from year to year, was obtained by substracting the estimates of needle retention in two consecutive years and then adding 1 to the difference. In shedding calculations and figures, the number of needle set is a relative value and in most cases consists of needles of different ages. Comparisons of annual values of needle retention and the mean of all the values within a tree gave needle budgets for each years.

Annual stem increments were measured on discs taken at breast height.

Variations in Needle Biomass Between 1865 and 1988

Needle Retention

Needle retention varied from year to year but the evidence restricted to two trees between 1865 and 1912 and another two between 1915 and 1988, does not suggest long-term changes (Fig. 1). The greatest difference between minimum and maximum numbers of retained needle classes was 3.0 in tree no. 13, but only 1.7 in tree 12 recorded over a similar period. This difference may reflect genotype differences.

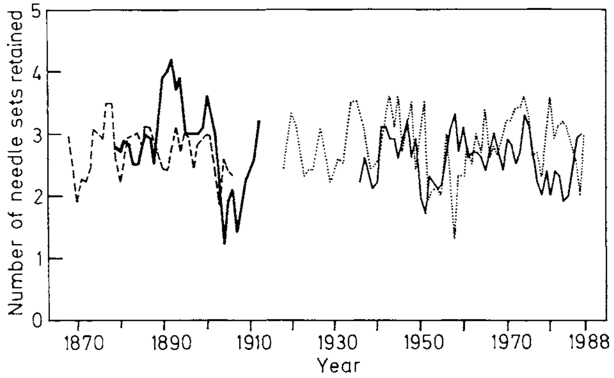

Fig. 1. Annual needle retention of Scots pine at Hietaperänkangas in northern Finland (lat. 66°N) in 1868–1988. Trees nos. 12 (*dashed line*), 13 (*thick solid line*), 16 (*continuous line*) and 17 (*dotted line*) (Kurkela and Jalkanen 1990)

Average needle retention of main stem of single trees was 2.6–2.8. Needle retention between 1865 and 1988 was at its lowest in early 20th century, when it dropped to below 2.0 for years. Number of needle set was also low in the 1950's (Table 1).

Table 1. Needle retention on the main stems of four specimens of Scots pines growing at Hietaperänkangas, Rovaniemi in northern Finland (lat. 66°N)

Numbers of needle year classes retained

	Minimum Year	Value	Maximum Year	Value	Average	Range between max. and min.
Observation between 1865 and 1912						
Tree no. 12						
	1870	1.9	1877	3.5	2.7	1.7
	1903	1.8	1878	3.5		
Tree no. 13						
	1904	1.2	1891	4.0	2.8	3.0
	1905	1.9	1892	4.2		
	1907	1.4	1894	3.9		
	1908	1.7				
Observation between 1915 and 1988						
Tree no. 16						
	1950	2.0	1958	3.3	2.6	1.6
	1951	1.7	1974	3.3		
Tree no. 17						
			1934	3.5	2.8	2.3
	1952	1.9	1943	3.6		
	1955	2.0	1945	3.6		
	1958	1.3	1974	3.6		
			1980	3.6		

Needle Age

Average age of main stem needles between 1933 and 1984 (tree no. 16) was 2.8 years, and in 1875–1912 (tree no. 13) 3.1 years, indicating that short shoots usually remained intact for three growing seasons. In these trees needle age varied from 1.9 to 3.8 and from 0.4 to 4.8 years, respectively.

On studying the history of tree no. 13, it was found that the needles of an age class were usually shed over 2 or more years, maximum being six years in 1912 (Fig. 2a). However, in 1889 when the average needle age was 4.3, all the needles born in that year shed during the same (fifth) summer. In most years, short shoots started to be shed at the end of second growing season. Their longevity was least in 1902–1903, only 0.5–0.4 years, implying that most needles died in the first season and only a few short shoots survived to the second season. In the longer period of 1875–1912, average needle age was nearer to maximum than minimum age.

There was a close relationship between average needle age and needle retention. With a time lag of about 3 years, curves of needle age and retention fitted closely

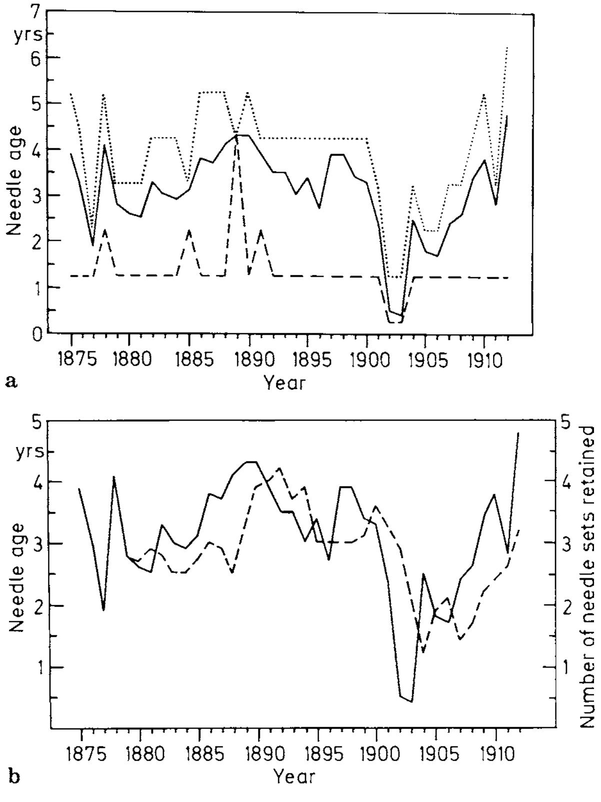

Fig. 2a,b. Needle age and relationship between age and retention of needles in tree no. 13. **a** Needle age and its variation. Min. age (*dashed line*), aver. age (*continuous line*) and max. age (*dotted line*). **b** Age (*continuous line*) and retention (*dashed line*) of needles in Scots pine

(Fig. 2b). Thus in tree no. 13, the deepest depression of needle age was met in 1902–1903, as compared to 1904 of needle retention.

Needle Shedding and Budget

Annual amounts of needle shedding varied from 0.1 to 2.0 in trees nos. 13 and 16 with averages of 0.99 and 0.97 respectively (Fig. 3a, b). Thus in the year of low shedding value, short shoots stayed for a longer period in trees, which in turn increased needle retention.

Needle budget varied between −1.7 and +1.3 sets of needles in tree no. 13 (Fig. 4a) being much greater than in tree no. 16, with a variation of −0.9– +0.7 (Fig. 4b).

Radial Increment Versus Needle Properties

In tree no 16, annual radial growth tended to reflect needle age and needle retention, the former, however with a 3-year lag (Fig. 5). However, in the 1940's

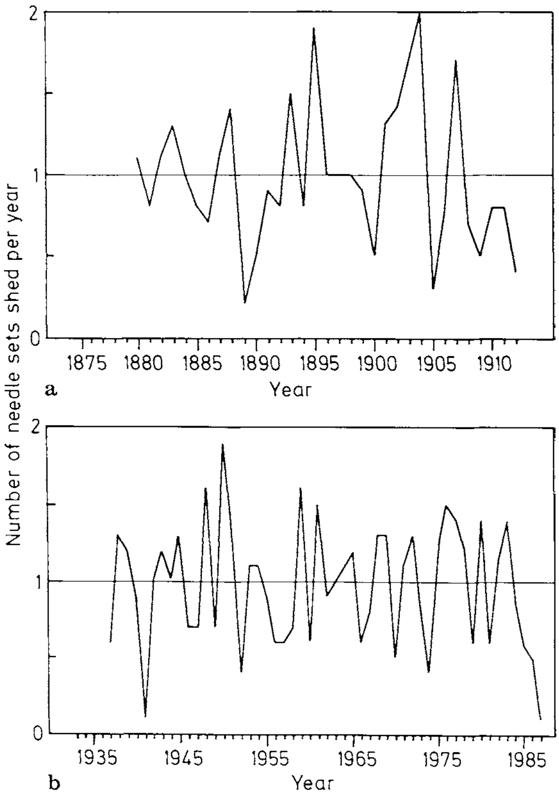

Fig. 3a,b. Annual shedding of needles of Scots pine. **a** In 1880–1912, tree no. 13. **b** In 1937–1987, tree no. 16

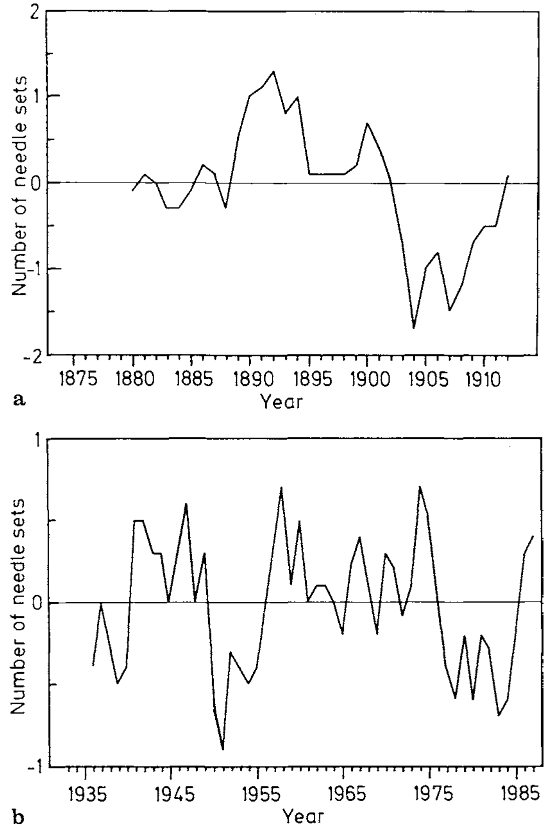

Fig. 4a,b. Needle budget of Scots pine. **a** In 1880–1912, tree no. 13. **b** In 1935–1987, tree no. 16

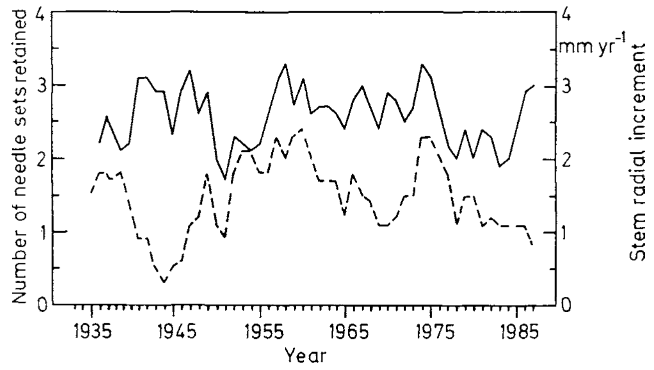

Fig. 5. The relationship between needle retention (*continuous line*) and stem annual radial increments (*dashed line*) in specimen no. 16 of Scots pine grown at Hietaperänkangas in northern Finland (lat. 66°N)

and again in the 1960's, there were conspicuous divergencies with slowing of growth while needles were retained. The same seems to be happening in the 1980's. Radial increment of tree no. 13 had slowed down from over 2 mm level in 1881 to less than 1.0 in 1912.

Discussion

The vascular bundle method (VBM) seems to be a useful method for needle history studies. The method is more objective as compared to annual defoliation surveys in shedding calculations in which accurate definition of annual needle retention is difficult. It is especially difficult if needle sets are partially shed. Although VBM is destructive, it makes it possible to examine the whole life of a pine. On spruce, the vascular bundle connecting the needle to the xylem of the stem is formed differently and is much less visible.

Results show that needle retention and needle age vary from year to year, as does radial increment. Variation is also obvious between the trees in the same stand. However, strong changes, e.g. in needle ages, are connected with radical changes in the environment of trees. In the northern hemisphere, the climate has been such a factor. So the deep depression in the needle age in 1902–1903 fits well with the growth depression at the same period in northern Fennoscandia (e.g. Mikola 1952).

Within these few data, needle retention and needle age seem to stay stable so that there is no descending trend towards present years. One would assume this to have occurred due to the effects of acid rain on forests. It should be mentioned also that the area from which the sample trees for this study were collected has not been loaded much with acid precipitation (see Tuovinen et al. this Vol.). For this kind of comparison, needle retention of branches which carry needles 1–1.5 sets more than the main stem might be more suitable. Although the needle retention in branches may give higher correlation with the growth or is principally more closely connected with the condition of a tree, its use will be very laborious because annual rings cannot be distinguished without a microscope. The relative position of a branch is also changing annually while the trees are growing.

The material of this study was too limited to obtain reliable correlation between the annual needle retention and radial growth of pines. Especially this aspect needs more investigation.

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The Foliar Chemical Composition of Young Pines (*Pinus sylvestris* L.) with or without Decline

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Summary

Tree decline and death have been observed recently among 20–30-year-old pine stands in dry heath forests in the Hämeenkangas and Pohjankangas areas of southwestern Finland. Typical symptoms of affected trees include dieback of leading shoots and bright yellow colour in needles in the upper parts of the crowns in spring.

The results supported the assumption that poor soil nutrition with many interacting factors, including frost and the pine bark bug *Aradus cinnamomeus*, are responsible for the dieback of young pines.

The high aluminium and low nitrogen, calcium and magnesium concentrations in the soil are related to the acidic, nutrient-poor bedrock, the shallow and poor quality of the humus and the low cation exchange capacity. Also the leaching of nutrients, acid deposition and the removal of nutrients by tree harvesting may have affected the soil nutrition.

Introduction

Tree decline and death have been observed recently among 20–30-year-old pine stands in *Cladina*- and *Calluna*-type heath forests (Cajander 1949) in the Hämeenkangas and Pohjankangas areas of southwestern Finland. Most trees grew more or less normally for the first 15 years with increased growth for the following 7 or 8 years. During the years 1982–1984, however, they displayed a sudden decline in height growth increment. In June 1984, many trees suffered from dieback and others from complete crown death due to severe night frosts (Raitio 1987). It is obvious that some trees had already been damaged previously. Since 1985, healthy trees have grown quite normally but most of the affected trees have not grown new leading shoots. Both healthy and affected trees retain only 1 to 3 years' needles. The most typical needle symptom of the affected trees is the bright yellow colour in spring in the upper part of the crown. In winter 1985, however, all needles of the trees were yellowish or brownish. Other typical symptoms were basal stem girdles, especially on the ground level, and rents in the bark. In addition, the trees were frequently infested with insects, including the *Aradus* bug. Trees with this abnor-

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mal growth pattern were found most commonly in depressions, where some of the trees were more severely affected. In addition, in some areas none of the young trees had survived.

Similar losses of young pines in dry heath forests have been noted earlier in Finland (Kangas 1931, 1937, 1940), in Germany (Rebel 1921) and in Sweden (Eiche 1966; Brammanis 1975). From his observations, Kangas (1931, 1937, 1940) eventually concluded that insect pests were the major cause of this syndrome. The same conclusion was made by Brammanis (1975). On the other hand, Rebel (1921), after mentioning both insects and diseases as possible causes, also emphasised the role of drought, soil quality and the importance of the root systems of the saplings. He claimed that sapling mortality was typically experienced on dry, sandy sites with little Ca or exchange capacity and where the underlying rocks were acidic and nutrient-deficient. Eiche for one (1966) has been examining the importance of frost as the main cause of this kind of syndrome.

During the last 10 years there has been an increasing interest in the "new type" of forest decline. The most common decline symptoms are unspecific foliage losses, foliar discoloration and dieback. According to symptomatic findings, acute nutritional disturbances, especially the calcium and magnesium nutrition are discussed (Rehfuess 1983; Zech and Popp 1983; Buchner 1985; Hüttl 1989). To explain the sudden and widespread appearance of the damages, a remarkable number of hypotheses have been suggested (Hüttl 1989). Besides natural stress factors, the effects of various air pollutants have been suggested as causes of this phenomenon. The location and topography of Hämeenkangas and Pohjankangas are such that these areas receive more rain and therefore also more pollution than the surrounding areas. The symptoms of tree decline in that area resemble also the symptoms of the "new type" of forest decline. It is therefore possible that air pollutants, especially acid rain, are one of the stress factors in the tree decline of the Hämeenkangas and Pohjankangas areas.

According to the symptoms of the tree decline in the Hämeenkangas and Pohjankangas areas trees are suffering from nutritional disturbances. This chapter examines the role of a number of factors affecting tree nutrition at Hämeenkangas and Pohjankangas. The study mainly relies on nutrient analyses done on both the affected and healthy trees and the soil in which they were growing.

Material and Methods

Foliar samples were collected altogether from seven different areas in 1985 and 1988 and soil samples from four areas in 1985. Test sites (T) displayed symptoms of decline, while at control sites (C), although nearby, the young pines appeared healthy (Table 1).

Needle samples were collected from randomly selected young pines growing within a 1-ha area at each of the five sites on 25–28 March 1985 and the four sites on 18–20 January 1989 (Table 1). In each case, 15 in 1985 and 20 in 1989 of the

Table 1. Description of sample areas and collected samples

Site	Code	Position			Description	Samples		
						Needle		Soil
		Lat.	Long.	Elev. m. a.s.l.		1985	1989	1985
Control site 1	C1	61°47′50″	22°30′30″	130	Gentle slope	x		x
Control site 2	C2	61°46′05″	22°33′40″	115	Flat ground	x		x
Test site 1	T1	61°45′50″	22°40′30″	125	Hills and depressions	x	x	x
Test site 2	T2	61°47′50″	22°30′30″	130	Depression	x		x
Test site 3	T3	61°46′50″	22°44′45″	125	Flat ground	x	x	
Test site 4	T4	61°43′30″	22°54′30″	135	Flat ground		x	
Test site 5	T5	62°04′27″	22°14′12″	125	Flat ground		x	

dominant healthy and/or affected young trees were selected. In 1985, the samples for each tree were taken from among the youngest needles on the first and third whorls of branches down from the growing tip. A total of 105 needle samples was obtained in this way. In 1989 composite samples of 20 trees were produced separately from among different needle year classes on the first, third, fourth and eighth whorls of branches of healthy trees and on the fourth and eighth whorls of branches of affected trees, except at T 3. At that site samples were produced only from among the youngest needles on the first whorls of branches down from the growing tip. At T 3 all trees were healthy in 1989. At the test sites there were no needles in the first and third branch whorls of branches in 1989. A total of 68 needle samples were obtained in 1989. In addition, the height of the sample trees was measured in each year.

Determinations of the dry weight of 1000 needles and the lengths of 50 needles were made together with analyses of N, P, K, Ca, Mg, Fe, B, Cu, Zn, Mn and Al concentrations after Halonen et al. (1983). In addition, sulphur was analysed by LECO S-132 sulphur analysator from the samples of 1989 using a high temperature combustion method with infrared absorption procedure (ASTM Standard D4239–85). These results made it possible to calculate the $N\ P^{-1}$ and $Ca\ Al^{-1}$ ratios.

The soil samples were taken from the four sites on 12–13 July 1985 (Table 1). About 1 l of soil was taken from each of ten randomly chosen spots at each site. Each soil stratum was removed separately and its thickness measured before sampling. A subsoil sample was taken from a mean depth of 40–50 cm. Because the surface topography at test site 1 was more variable, with clearly defined humps and hollows, samples were taken separately from these two site types in the same manner as elsewhere.

Soil pH was determined from distilled water and 1-N KCl extracts (1:2.5) and conductivity from distilled water extracts. Soluble aluminium (Al^{3+}) was determined from a 1-N potassium chloride extract from fresh soil samples (Halonen et al. 1983). The remaining soil was air-dried and passed through a 2-mm sieve and the humus samples were ground to a powder. The total nitrogen was determined by the Kjeldahl method, and extractable P, K, Ca, Mg, Fe, Cu, Zn, Mn and Al from an acid (pH 4.65) ammonium acetate extract (Halonen et al. 1983). Amorphous Mn, Fe and Al were measured from a 0.05 M ammonium oxalate extract (Hartikainen 1981). Organic carbon was determined after Heanes (1984). The texture of the soil samples was also evaluated (Elonen 1971), as was their loss on ignition, this latter in order to calculate total nitrogen as a percentage of the organic material present. Loss on ignition was not determined for the subsoil samples, nor was total nitrogen or organic carbon concentration.

The results of the nutrient analyses from the needles and soil samples were compared using the analysis of both variance and Tukey's test.

Results

Pine Trees

The age of the pines at all the studied sites was about 25 years. Among those at the control sites, the trees found at site C 1 were on average 1.8 m shorter than those at C 2 (Table 2). Trees at the test sites, on the other hand, were shorter than those at the control sites in 1985. The height of the pines at T 1 varied greatly. On the hills at T 1 the pines were taller than the trees in the hollows. The height of the healthy and affected trees did not differ in 1985 and 1989 (Table 2). Both the needle length and the dry weight of 1000 needles were greater at the control sites than at the test sites in 1985. Similarly, the needles from the healthy trees at the test sites were longer on average than those from the affected trees, and their dry weight for 1000 needles was greater both in 1985 and 1989 (Table 2). The mean needle length and the dry weight of 1000 needles were highest in the first branch whorl and lowest in the eighth branch whorl of the healthy trees (Table 3). There were no needles in the first and third branch whorls of the affected trees. The trees at all sites had retained either 2 or 3 years' needles in 1985.

The N, Ca, Mg, Zn, Mn and Al concentrations, $N P^{-1}$ and $Ca Al^{-1}$ ratio of the needles from the affected trees were lower than for the healthy trees at T 1 and T 3 in 1985 (Table 2), whereas P, K and Fe concentrations were higher. The differences between the healthy and affected trees were statistically highly significant. The B and Cu concentrations between the tree groups did not differ statistically.

The Mg and Mn concentrations ($p < 0.001$) and $Ca Al^{-1}$ ratio ($p < 0.01$) of the needles from the trees of the control sites (C 1 and C 2) were higher and the Al ($p < 0.001$), K ($p < 0.01$), Fe and Cu ($p < 0.05$) concentrations were lower than for the healthy trees of the test sites (T 1 and T 3) in 1985 (Table 2).

The average N, Ca, Mg, S, B, Cu, Zn and Mn concentrations of the needles were higher and the P, K, Fe and Al concentrations were lower in 1985 than in 1989. The Ca ($p < 0.001$), Zn ($p < 0.01$) and Mn ($p < 0.01$) concentrations of the needles from the affected trees were lower and the Al ($p < 0.01$) concentration was higher than for the healthy trees at T 1, T 4 and T 5 in 1989. The concentrations of the other elements between the tree groups did not differ statistically (Table 2).

The results of the needle analyses made on material collected in various branch whorls of the crown are presented in Table 3. The N ($p < 0.01$) and K ($p < 0.05$) concentrations of the current needles from the healthy trees were the lowest and the B ($p < 0.05$), Zn ($p < 0.01$) and Mn ($p < 0.01$) concentrations were the highest in the first branch whorl. The differences in the element concentrations of the current needles from the affected trees were not statistical between the fourth and eighth branch whorl.

Table 2. Analysis results of young pines and the current needles

Site	Health of trees	Year	Height of trees	Dry weight of 1000 needles	Mean needle length	Element concentration												Element ratio	
						N	P	K	Ca	Mg	Fe	S	B	Cu	Zn	Mn	Al	NP^{-1}	$Ca\ Al^{-1}$
			m	g	mm	%	‰				ppm								
C1	Healthy	1985	4.8	14.0	42	1.22	1.28	3.97	1.31	0.86	52		12.9	2.69	43	330	302	9.5	4.3
C2	Healthy	1985	6.6	15.2	45	1.22	1.30	3.83	1.37	0.90	48		12.0	2.74	42	378	361	9.4	3.8
T1	Healthy	1985	3.5	13.5	38	1.24	1.38	4.74	1.27	0.68	55		12.4	2.98	42	250	467	9.0	2.7
		1989	3.7	17.4	43	1.35	1.31	4.40	1.87	0.86	48	920	13.0	3.57	42	357	255	10.3	7.3
	Affected	1985	3.6	7.9	25	0.77	1.51	7.69	0.40	0.44	61		11.5	3.33	31	111	309	5.1	1.3
		1989	3.1	7.4	27	1.35	1.27	4.20	0.91	0.54	43	970	6.4	3.60	28	199	258	10.6	3.5
T2	Affected	1985	3.8	8.5	28	0.83	1.49	6.84	0.34	0.38	64		10.5	4.33	28	118	249	5.6	1.4
T3	Healthy	1985	4.5	14.0	40	1.26	1.30	4.45	1.30	0.86	54	903	11.3	3.52	45	374	378	9.7	3.4
		1989	5.9	26.7	59	1.39	1.43	4.15	1.59	0.97	37	1036	15.9	4.18	54	321	110	9.7	14.5
	Affected	1985	4.5	7.1	26	0.93	1.57	7.12	0.48	0.54	72	648	11.3	3.99	32	148	322	5.9	1.5
T4	Healthy	1989	3.2	15.6	43	1.35	1.39	4.32	1.73	0.91	34	970	14.7	3.74	43	461	200	9.7	8.7
	Affected	1989	3.6	7.8	30	1.30	1.41	4.07	1.20	0.80	36	930	12.0	3.11	39	398	261	9.2	4.6
T5	Healthy	1989	3.7	21.4	53	1.43	1.32	4.19	2.36	0.88	32	960	15.2	2.03	49	559	175	10.8	13.5
	Affected	1989	3.3	7.8	29	1.43	1.37	4.11	1.55	0.88	35	960	9.0	3.10	42	460	181	10.4	8.6

Table 3. Analysis results of current needles in the different part of tree crown in 1989

Health of trees	No. of branch whorls	Dry weight of 1000 needles	Mean needle length	Element concentration N	P	K	Ca	Mg	Fe	S	B	Cu	Zn	Mn	Al
		g	mm	%	‰				ppm						
Healthy	1	17.2	45	1.31	1.29	3.76	1.72	0.95	44	957	16.2	3.59	46	448	238
	3	12.2	36	1.35	1.38	4.09	1.88	0.92	41	987	14.7	3.26	44	438	207
	4	9.8	34	1.38	1.34	4.30	1.99	0.88	38	950	14.3	3.38	45	459	210
	8	7.0	29	1.32	1.27	3.91	1.65	0.77	33	940	11.6	3.06	38	419	177
Affected	4	7.6	30	1.36	1.35	4.13	1.22	0.74	38	930	9.1	3.27	36	352	233
	8	8.0	32	1.36	1.38	4.07	1.55	0.80	33	970	12.1	3.10	37	368	196

Soil

Each of the control sites had an uninterrupted humus layer (Oh) about 2 cm thick (Table 4), whereas elsewhere this layer was patchy, mixed with sand and barely 1 cm thick. The presence of sand indicated that the organic carbon content of this humus was low, especially in the hollows at T 1. The eluvial horizon (Eh) of the podzol profile was relatively thin everywhere, about 5–6 cm, but was pronouncedly darker in colour in those places where the affected trees were growing. As expected, the illuvial horizon (Bs) was correspondingly a darker brown there. The mean thickness of the illuvial horizon varied between 10 cm and 19 cm. Because the humus layer and the eluvial horizon were exceptionally thin, the roots of the trees were mainly in the illuvial horizon. The soil texture was sand at C 2, coarse sand at C 1 and T 2, and fine sand at T 1.

Both test sites were similar in their soil chemistry, as were the control sites (Table 4). When the humus at the control sites was compared to that at the test sites, higher concentrations of Ca and Mg were most pronounced, but N, P, Mn and in some cases K were also higher. Similarly, the eluvial horizon at the control sites contained more Ca, Mg and Mn but less Al than at the test sites. All differences were statistically significant. However, the illuvial horizon and subsoil nutrients did not vary in any consistent way from one site to another. pH was very low at all sites in the humus and in the eluvial horizon (Table 4).

Amorphous Fe and Al and soluble Al were present in the greatest quantities in the humus and eluvial horizons from the test sites, whereas amorphous Mn was highest in the corresponding horizons of the control sites (Table 5). The ratio of Ca to soluble Al in the humus and eluvial horizons was highest at the control sites and lowest in the depressions at T 1, but the differences in the Ca Al^{-1} ratio between the sites were negligible in the other horizons.

Discussion

When the foliar analyses were compared for the affected trees and the healthy ones, it was found that the affected trees were suffering from a severe nutritional disorder. The nutrient concentrations in the needles suggest that the trees were suffering from a lack of Ca and Mg and also N in 1985. On the other hand, P and especially K concentration was higher than normal (Baule and Fricker 1967; Paarlahti et al. 1971; Bosch et al. 1983; Reigber and Braun 1985; Schulze and Küppers 1985). Although the Zn and Mn concentrations in the needles in the affected trees were also lower than in the healthy ones at the test sites in 1985, they were not yet below the critical levels (Ahrens 1964; Stone 1968).

According to the needle analysis results of the year 1989, the nutrition of the trees was better than in 1985. The affected trees were suffering only from a lack of Ca (Reigber and Braun 1985). Wehrmann (1959) and Huphreys et al. (1972) also found that there were significant differences between the foliar nutrient concentrations obtained in different years and that these were in most cases related to the

Table 4. Thickness of soil horizon, soil pH, conductivity and concentrations of organic carbon, total nitrogen, total nitrogen in organic matter (in brackets) and nutrients extracted by acid ammonium acetate

Site and horizon	Depth cm	pH (H_2O)	pH (KCl)	Conductivity µs cm^{-1}	C	N		P	K	Ca	Mg	Fe	Cu	Zn	Mn	Al
					%	%		mg kg^{-1}								
C 1																
Oh	2	4.1	2.9	32	26.1	0.82	(1.94)	42	168	1044	112	4	0.30	17.1	81.8	33
Eh	5	4.5	3.4	18	2.9	0.10	(2.01)	3	25	74	9	52	0.10	1.8	5.0	159
Bs	12	5.0	4.4	16	2.3	0.11	(2.09)	5	21	11	4	66	0.15	1.0	2.5	898
C		5.2	4.5	9	–	–	–	4	5	2	1	4	0.10	0.1	0.3	134
C 2																
Oh	2	4.1	3.0	31	25.8	0.80	(1.67)	55	258	927	117	7	0.33	17.1	76.4	60
Eh	5	4.4	3.3	20	1.6	0.06	(1.64)	3	23	53	8	30	0.08	1.1	4.0	88
Bs	16	4.9	4.4	14	0.8	0.04	(1.73)	4	10	6	2	48	0.11	0.6	3.0	358
C		5.4	4.6	8	–	–	–	4	5	4	1	4	0.08	0.1	1.0	102
T 1 Depression																
Oh	1	4.3	3.0	27	11.8	0.49	(2.32)	13	83	329	31	10	0.30	8.8	15.1	96
Eh	6	4.6	3.7	14	2.5	0.10	(2.30)	2	21	33	4	51	0.10	1.2	1.9	203
Bs	19	5.0	4.7	13	0.8	0.04	(2.44)	3	9	6	1	11	0.12	0.5	1.7	406
C		5.4	4.7	11	–	–	–	1	6	7	1	3	0.10	0.1	0.8	98
Hill																
Oh	1	4.3	2.9	34	23.9	0.77	(1.98)	37	168	688	75	8	0.30	13.2	34.4	72
Eh	5	4.6	3.6	15	1.7	0.06	(2.10)	3	16	40	5	50	0.10	1.2	1.4	137
Bs	10	5.0	4.5	13	0.8	0.04	(2.14)	4	9	9	1	43	0.14	0.7	2.3	435
C		5.4	4.5	7	–	–	–	3	5	9	1	3	0.09	0.1	0.7	79
T 2																
Oh	1	4.2	2.9	28	22.0	0.66	(2.17)	29	145	600	61	7	0.30	16.7	31.1	63
Eh	6	4.6	3.7	13	2.9	0.10	(2.18)	2	23	33	5	57	0.09	1.3	1.5	276
Bs	13	5.0	4.6	15	1.7	0.07	(2.22)	3	14	4	2	25	0.11	0.8	1.6	720
C		5.2	4.5	8	–	–	–	5	5	2	1	3	0.10	0.1	0.3	119

Table 5. Amorphous manganese, iron and aluminium, soluble aluminium (Al^{3+}_{KCl}) concentrations and $Ca_{mol.eq.}\ Al^{-1}_{mol.eq.(KCl)}$ ratio in the soil horizons

Site and horizon	Mn	Fe	Al	$Al^{3+}_{(KCl)}$	Ca Al^{-1}
	mg kg^{-1}				
C 1					
Oh	57	460	616	85	5.51
Eh	6	730	864	172	0.19
Bs	5	1176	6080	75	0.07
C	2	136	1112	16	0.06
C 2					
Oh	54	738	798	115	3.62
Eh	5	366	416	145	0.16
Bs	6	992	2840	56	0.05
C	4	164	974	17	0.11
T 1					
Depression					
Oh	12	504	646	182	0.81
Eh	6	658	938	177	0.08
Bs	6	722	3780	23	0.12
C	6	108	896	18	0.18
Hill					
Oh	24	602	826	132	2.34
Eh	3	472	576	147	0.12
Bs	5	946	3020	41	0.10
C	7	820	580	12	0.34
T 2					
Oh	23	556	714	150	1.79
Eh	4	950	1484	194	0.08
Bs	6	1076	5920	39	0.05
C	2	128	1008	13	0.07

weather conditions of the growing season. The results of this study indicated that summer frosts especially affect the foliar nutrient concentrations. In the summer 1984 the severe, successive night frosts, which occurred after the warmest May on record, badly damaged the plants, even pines, during their most intense growth period (Raitio 1987). The winter 1984–1985 was exceptionally cold. The summer 1988 was normal and the winter 1988–1989 exceptionally mild as compared with that of the normal period 1931–1960 (Meteorological Institute 1984, 1985, 1988, 1989).

It is known that trees suffering from a deficiency in N, P, K or Mg attempt to ensure adequate nutrient levels in their younger, photosynthesizing needles by transferring a larger percentage of these elements than normal from their older needles before they are shed (Commerford 1981; Ryan and Bormann 1982). Since both the healthy and affected trees retained 2 to 3 years of needles in 1985, this transfer mechanism was not being effectively utilized by the affected trees. One reason for this may well be the frost damages of trees in the summer 1984 (Raitio 1987). This agrees with the occurrence of the affected trees at depressions of the test sites. The high K and P concentrations in the needles of the affected trees may be due to the small size of needles and the effect of the Ca deficiency or frost on the permeability of cell membranes. The low Ca concentration increases especially K translocation in plants (Mengel and Kirkby 1982).

Generally it has been observed that in coniferous species the concentration of individual elements in the needles increases up the crown. On the other hand, the calcium concentration in the needles tends to increase down the crown (Leyton 1948; Wehrmann 1959; Fornes 1969; Morrison 1972). Fober (1976) has, however, suggested that the N, P, K, Na and Ca concentrations in the needles of 30-year-old Scots pines increases towards the inside of the crown and down the crown. According to him the lower concentrations in the upper and outside parts of the crown could be explained by the greater vegetative growth in these crown region, which could result in a greater dilution of the elements. The results of this study supported those of Fober (1976). It is obvious that, due to nutritional differences, the upper part of the crown in Scots pines is more susceptible to cold than the lower part during the growing season. One reason for the dieback of young Scots pines in the area of Hämeenkangas and Pohjankangas is probably frost damages. The cause of this type of cold damage is quite often radiation frost (cf. Eiche 1966).

In the area of Hämeenkangas and Pohjankangas young pines were frequently infested with pine bark bugs, especially at the test sites. Heliövaara (1984) suggested that the pine bark bugs are primarily responsible for tree damages studied in this case. The results of this study did not support this assumption. It is obvious that this kind of sucking insect easily causes disturbances in the nutrition of young pines at the nutrient-poor growing sites, causing injuries in the phloem and xylem.

The nutrient requirements of trees vary with age and are greatest at the time when the crown of the tree is developing. One exception is the need for Ca, which is necessary for stemwood production (Mälkönen 1974; Gosz 1984; Miller 1984). Ilvessalo (1920) suggested that in young pine forests of the *Calluna* and *Cladina* types the stemwood production increases from the age of 20–30 years onwards. Thus it is understandable that the young pines at the sites studied here should have a high calcium requirement.

The N, Ca and Mg concentrations in the soils, in particular, differed between the control and test sites. Only at the control sites was the total N and Ca in the humus and eluvial horizons consistent with the average values recorded for forests of the *Calluna* and *Cladina* types, while the Ca concentration of the illuvial horizon and subsoil was lower than the average for the corresponding forest types even at the control sites (Urvas and Erviö 1974). No reference values for Mg concentrations are available for individual forest types, but it is significant that all the sites where the young pines had been affected had markedly lower Ca and Mg concentrations in their humus and eluvial horizons than at the control sites. The carbon concentration of the humus was lower at all sites studied than the mean values quoted for the corresponding forest types by Urvas and Erviö (1974).

The low levels of N, Ca and Mg noted in the soils of Hämeenkangas and Pohjankangas may be attributed to a number of factors. One is undoubtedly the nutrient-poor, acid bedrock (Matisto 1961). Another is the low cation exchange capacity of sorted sands, which readily permits leaching of nutrients. The numerous forest fires and fellings have left the area with only a thin layer of poor-quality humus which is incapable of supplying an adequate amount of nutrients. Also, K may release in the forest fires and can promote the leaching of Ca and Mg by displacing them from the surfaces of the soil particles (Viro 1969). Further, Ca has been removed with the bark and stemwood during felling (Mälkönen 1974).

The soil was found to be acid at all the studied sites. Many plants are able to grow normally in such soils, however, if they can obtain adequate amounts of nutrients, particular Ca, and if the concentrations of harmful elements such as Mn and Al in the soil water remain sufficiently low (Bergmann 1983). Once the soil pH (KCl or $CaCl_2$) falls below 4.2, Al occurs as a trivalent ion, which can be toxic to plants (Foy 1974; Ulrich 1983; Matzner and Ulrich 1985). The toxicity depends on the Ca level of soils. Al toxicity is visible mainly as a disturbance in the nutrient balance; Al binds anions in a virtually insoluble form and hampers the uptake and transport of cations, which initially cause damage to root systems (Clarkson and Sanderson 1971; Foy 1974; Bergmann 1983; Evers 1983; Rost-Siebert 1983; Gomes et al. 1985; Hüttermann 1985). Soil Ca and Mg concentrations were lowest and soluble Al highest in humus and eluvial horizons of the growing sites of the affected pines where the pH was below 4.2. One reason for the nutritional disturbances of trees at the test sites may be the low Ca Al^{-1} ratio in the soil (cf. Rost-Siebert 1985).

Air pollution has been assumed to cause changes detrimental to tree growth, in the low soil Ca Al^{-1} ratio (Ulrich 1981; Abrahamsen 1983; Hüttermann 1985; Matzner and Ulrich 1985; Rechcigl and Sparks 1985). In this regard, the location and topography of Hämeenkangas and Pohjankangas are such that these areas receive more rain and therefore also more pollution than the surrounding areas. Although the Ca Al^{-1} ratio in the humus and eluvial horizons of the test sites was low, it is difficult to demonstrate what role air pollution may have in the injury displayed by the trees, especially because the same kind of damages were described about 50 years ago in the same area (Kangas 1940). The air sulphur dioxide content is known to affect the foliar sulphur concentration (e.g. Materna 1981, 1985; Hällgren et al. 1982; Norby and Kozlowski 1982; Huttunen et al. 1983). The mean foliar sulphur concentrations were relatively low in the Hämeenkangas and Pohjankangas areas as compared to the needles analysed in industrial areas (e.g. Linzon et al. 1979; Materna 1981; Kowalkowski et al. 1984; Reigber and Braun 1985). It is probable, however, that the detrimental effects of air pollution will manifest themselves first at sites such as Hämeenkangas and Pohjankangas, which are already poor in nutrients (cf. Tamminen and Mälkönen 1986).

The results of this study supported the assumption that the poor soil nutrition with many interacting factors, including the frost and the pine bark bug *Aradus cinnamomeus*, is responsible for the needle discoloration and the dieback of young pines at the area of Hämeenkangas and Pohjankangas.

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The Effects of Soluble Inorganic Aluminium and Nutrient Imbalances on *Pinus sylvestris* and *Picea abies* Seedlings

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Summary

Tests were made of the response of *Pinus sylvestris* L. and *Picea abies* (L.) Karst. seedlings to a range of soluble inorganic aluminium and nutrient concentrations during 12–15-week cultivation periods in 1986 and 1987. The seedlings were grown in quartz sand under field conditions. Nutrients were given via irrigation water (pH 3.7–3.8).

Partly depending on the nutrition, the growth of spruce seedlings was inhibited at Al concentrations varying between 10–50 mg l^{-1}. For pine seedlings the corresponding concentrations were 20–50 mg Al l^{-1}. With poorer cation and phosphorus nutrition the seedlings were smaller, the proportion of needle and stem biomass decreased and the proportion of root respiration and root biomass increased. Aluminium and poorer nutrition also affected needle nutrient concentrations.

Introduction

Anthropogenic atmospheric acid deposition has been observed to bring about changes in soil properties. Such changes include a decline in the soil solution pH, a decrease in base saturation, increased nitrogen availability, and increases in soluble aluminium concentrations (Ulrich 1981; Bergkvist 1986). In southern Sweden a drop of 0.4–0.7 pH units in some podzolic soils has been found over the periods 1927 to 1984 and 1945 to 1983 which cannot totally be accounted for biological processes (Tamm and Hallbäcken 1986; Tyler et al. 1987). In deeper layers of podzolic soils (pH 4.5), even a minor increase in acidity may considerably increase the solubility of aluminium (Tyler et al. 1987).

These changes in soil properties may affect tree growth differently. Several investigations dealing with soluble inorganic aluminium toxicity have revealed great variation in Al tolerances among tree seedlings. (McCormick and Steiner 1978; Abrahamsen 1984; Hutchinson et al. 1986; Ryan et al. 1986; Göransson and Eldhuset 1987; Arovaara and Ilvesniemi 1990). Toxicity from Al is often reduced in the presence of Ca ions and therefore the Ca/Al ratio of the soil solution might be more meaningful than aluminium concentrations alone (Rost-Siebert 1983).

Kauppi et al. (Eds).
Acidification in Finland

The deposition of nitrogen which is about 10 kg ha^{-1} per year in southern Finland, may actually serve as a fertilizer and thus promote tree growth (Arovaara et al. 1984). On the other hand, increased leaching of potassium, calcium and magnesium may reduce the availability of these nutrients.

In this chapter we present results from a series of laboratory experiments aimed at determining the effects of soil solution inorganic aluminium concentrations and changes in the nutrition of K, Ca, Mg and P on the growth, carbon allocation and nutrition of Scots pine and Norway spruce seedlings.

Material and Methods

Four irrigation experiments were established during 1986–1987 using draining plastic pots and deionised water-washed quartz sand as the growth medium.

Aluminium and/or nutrients were supplied with irrigation water in soluble form in concentration ratios described by Ingestad (1979). Stock solutions were made from NH_4NO_3, $CaNO_3$, K_2SO_4, $NaHPO_3$, $NH_4H_2PO_4$, $MgSO_4$, and $Al_2(SO_4)_3$. The ratio between NO_3^- and NH_4^+ nitrogen was around 1. The pH of the irrigation water was maintained at 3.7–3.8 by the addition of H_2SO_4 or NaOH. At each application time irrigation was maintained until throughflow occurred so as to achieve fairly constant Al/nutrient contents in each pot. In experiments 3 and 4 the cation and phosphorus concentrations of throughflow were monitored.

At the end of each experiment, the seedlings were lifted, washed free from sand, and separated into stem, roots and needles. The needles were further divided into age and the roots into fine (diameter < 1mm) and coarse (diameter > 1mm) roots. The different plant parts were then oven dried at 105°C for 24 h after which their dry weights were determined.

Two samples from both the youngest needle age class and fine roots of each seedling were prepared except in experiment 1, where the plants were pooled. The tissue N concentration was determined by the Kjeldahl method. For the analyses of Al, K, Ca, Mg and P, the needle and root samples were digested in 17 ml of conc. HNO_3 H_2SO_4 mixture (10:1 by volume). The following day 3.5 ml of $HClO_3$ solution was added. After 24 h the samples were stepwise heated up to 250°C. Al, Ca and Mg were determined by AAS. P was measured colorimetrically and K using flame spectrometry.

The data were analysed with ANOVA. Treatment means were compared with the controls within each species in each experiment with Dunnett's t-test.

Experiment 1

Scots pine and Norway spruce seeds from south, central and north Finland (Arovaara and Ilvesniemi 1990) were sown on 23 May 1986 in 18 pots. In each pot 60–100 seeds of pine and spruce from the same geographical origin were sown. After 2 weeks the germinated seedlings were thinned so as to give 20 evenly distributed seedlings of both pine and spruce in each pot. The seedlings were grown for 17 weeks under a glass cover to prevent precipitation from falling on the seedlings. In all other respects the seedlings were grown in field conditions.

The concentrations of N, K, P, Ca and Mg in the irrigation water were 100, 45, 14, 6 and 6 mg l^{-1} respectively. Six different Al concentrations 0, 10, 20, 50, 75 and 100 mg Al l^{-1} were applied. Aluminium was added to the irrigation water from 26 June onwards. The seedlings were harvested after 12 weeks at the end of September.

In order to facilitate the comparison of the effects of Al on different species and different provenances, all the biomass values are presented relative to the 0 Al treatment. The seedling of the northern spruce provenance stopped growing in height already in mid July, so it was impossible to evaluate the effect of the Al treatment on the growth of these seedlings.

Experiment 2

Three-year-old Scots pine and Norway spruce seedlings were lifted from nursery on 15 May 1986 and planted into 7-l plastic pots, each equipped with a tight wooden cover to prevent evaporation from the sand and precipitation of Al and nutrient salts on the surface of the sand and for the measurement of root respiration. For both species there were three nutrient levels (Table 1) and 5 Al levels (0, 20, 50, 100 and 150 mg l^{-1}) in a factorial design. There were three replicates of each treatment, giving a total of 45 pots for both species. The seedlings were watered three times a week with 250 ml of fresh nutrient solution. Al was added to the nutrient solution from 14 June onwards. The seedlings were harvested at 21 September.

The seedlings were allowed to synthetisize $^{14}CO_2$ on six occasions during the experiment (Arovaara and Ilvesniemi 1987). On each occasion the seedlings were

Table 1. Nutrient levels applied in Experiment 2 in 1986 and Experiment 3 in 1987

Exp. 2. in 1986					
Pine and spruce					
Nutrient level	N mg l^{-1}	K	P	Ca	Mg
1/1	100.0	45.0	14.0	6.0	6.0
1/3	100.0	15.0	4.7	2.0	2.0
1/10	100.0	4.5	1.4	0.6	0.6
Exp. 3. in 1987					
Pine and spruce					
1/1	50.0	22.0	7.0	3.0	3.0
1/10	50.0	2.2	0.7	0.3	0.3
Spruce					
1/3	50.0	7.3	2.3	1.0	1.0

enclosed in a plastic cuvette and the tracer brought into the cuvette as NaH $^{14}CO_3$ from which $^{14}CO_2$ was released by addition of H_2SO_4. The seedlings were enclosed in the cuvette for 1/2 h. $^{14}CO_2$ respiration of the roots was measured after this for 4–6 days. The evolved $^{14}CO_2$ was trapped by sucking air from the pot through a Lumasorb II solution. Before entering the trap the air was forced through silica gel. The disintegration of the ^{14}C was determined from the trap solution using a scintillation counter (1215 Rackbeta).

For the determination of ^{14}C assimilated into the biomass, two subsamples were prepared from the different plant parts after the seedlings were lifted and dried. The samples were oxidized in a sample oxidizer (Junitek) and the released carbon was trapped in a solution, the activity of which was then determined. From these measurements the total activities of different plant parts were calculated.

Before potting the seedlings, their root and stem biomasses were determined as follows: After gently rinsing the roots the fresh weight of the seedlings was recorded. The root system was then immersed in a water-filled container of known weight. The weight of the container was then reweighed to determine the weight (volume) of water displaced equivalent to the volume of the roots. The volume dry weight of the roots had been previously determined from independent material following the same procedure to determine root volume. The dry weight of the experimental seedlings root biomass was then calculated using the recorded water displacement weight (vol) and volume dry weight value. Shoot dry weight was calculated by subtraction and corresponding correction for moisture.

Experiment 3

Two-year-old Scots pine and Norway spruce seedlings were used in this experiment. There were two levels of nutrient concentrations used on the pine and three on the spruce (Table 1) which were combined with five Al concentrations 0, 5, 10, 20 and 50 mg l^{-1}. The experiment started on 19 May. Al was added to the nutrient solution from 6 June onwards. The seedlings were harvested at 15 September. The experimental design and the growing methods were in other respects similar to experiment 2 in 1986, except labelling with ^{14}C. In experiments 3 and 4 the root to shoot ratio of a large number of seedlings was determined among which a homogenous group was chosen.

Experiment 4

This experiment was aimed at determining the effect of different nutrition on carbon allocation in Scots pine seedlings. The seedlings of treatments 0 and 20 mg Al l^{-1} from experiment 2 in 1986 were used. In 1987 2-year-old seedlings were used (Table 2). In group 1 K concentrations, in group 2 P, in group 3 K and P, in group 4 Ca and Mg and in group 5 K, P, Ca and Mg concentrations were reduced to 1/2, 1/5 and 1/10 of the control. In the control treatment there were five seedlings. In each treatment there were three seedlings. Shoot and root dry weight at the start of the experiment were determined and the seedlings were exposed to $^{14}CO_2$ as

Table 2. Composition of irrigation solutions used in Experiment 4, 1987 material

Group	Nutrient level	N	K	P	Ca	Mg
		mg l^{-1} of irrigation water				
Control		50.0	22.5	7.0	3.0	3.0
	1/2	50.0	11.3	7.0	3.0	3.0
1 (K)	1/5	50.0	4.5	7.0	3.0	3.0
	1/10	50.0	2.2	7.0	3.0	3.0
	1/2	50.0	22.5	3.5	3.0	3.0
2 (P)	1/5	50.0	22.5	1.4	3.0	3.0
	1/10	50.0	22.5	0.7	3.0	3.0
	1/2	50.0	11.3	3.5	3.0	3.0
3 (K+P)	1/5	50.0	4.5	1.4	3.0	3.0
	1/10	50.0	2.2	0.7	3.0	3.0
	1/2	50.0	22.5	7.0	1.5	1.5
4 (Ca+Mg)	1/5	50.0	22.5	7.0	0.6	0.6
	1/10	50.0	22.5	7.0	0.3	0.3
	1/2	50.0	11.3	3.5	1.5	1.5
5 (All)	1/5	50.0	4.5	1.4	0.6	0.6
	1/10	50.0	2.2	0.7	0.3	0.3

described for experiment 2. The experiment was started on 20 May with nutrient treatments being given from 1 June and the seedlings were harvested 17 September.

Results

Effects of Al on Seedling Growth

Experiment 1

Soluble inorganic Al in the irrigation water affected the dry matter production of all origins. Growth inhibition in Scots pine seedlings started when the Al concentration in the irrigation water was 50 mg l^{-1} (Ca/Al molar ratio = 0.08). The difference in the dry matter production, compared to control, was statistically significant when the Al concentration was 75 mg l^{-1} (Ca/Al molar ratio = 0.05). There were no differences between the three Scots pine provenances as regards their response to aluminium (Table 3).

The growth reduction of the Norway spruce seedlings originating from southern Finland started when the Al concentration in the irrigation water was 10 mg l^{-1} (Ca/Al molar ratio = 0.41). The growth reduction compared to control was statistically significant from 50 mg l^{-1} (Ca/Al molar ratio = 0.08) upwards. The corresponding Al concentrations for the seedlings originating from central Finland were 50 and 75 mg Al l^{-1} (Ca/Al molar ratios were 0.08 and 0.05). When the results of both origins of spruce are combined the differences in the means are statistically significant from concentration 50 mg l^{-1} upwards (Table 3).

Table 3. Effect of Al on the total dry matter production of seedlings as a percentage of control, which is presented in mg. Values followed by a letter are significantly different compared to the control at 5% level using Dunnett's t-test. S, C and N refer to seedlings from southern, central and northern provenances

	Al conc. mg l^{-1}					
	0	10	20	50	75	100
		Ca/Al molar ratio				
		0.41	0.20	0.08	0.05	0.04
Pine	Total dry matter production					
S	1258.3	93	100	86	80a	64a
C	782.4	101	109	94	84a	64a
N	744.7	103	109	88	87	70a
Mean	928.5	99	106	89	84a	66a
Spruce						
S	346.3	85	87	66a	42a	36a
C	143.9	106	100	87	63a	49a
Mean	245.1	96	94	77a	53a	43a

Experiment 2

The dry weight of the Scots pine seedlings grown at the 1/1 nutrient level was significantly reduced at 100 and 150 mg Al l^{-1} (Ca/Al = 0.04 and 0.03 respectively). At 50 mg Al l^{-1} (Ca/Al = 0.08), growth was reduced by about 20%, but because of the small number of seedlings this difference was not statistically significant. At the 1/3 nutrient level, the dry-weight of the seedlings was 20% less compared to control when the Al concentration was 20 mg l^{-1} (Ca/Al = 0.07) but the difference was significant when the aluminium concentration was 50 mg l^{-1} (Ca/Al = 0.03). At the 1/10 nutrient level the Al concentration where significant growth reduction started was 20 mg l^{-1} (Ca/Al = 0.02).

At the 1/1 nutrient level the dry weight of the spruce seedlings was significantly lower, about 35%, when the Al concentration of the irrigation water was only 20 mg l^{-1} (Ca/Al = 0.2). With the two other nutrient treatments, the dry weights were 20–30% lower compared to the control in all Al treatments except 100 mg Al l^{-1}. None of the differences was statistically significant (Table 4).

In spite of the growth reductions induced by Al, the ^{14}C allocation between shoot and roots was not affected by Al, except in Norway spruce at 150 mg Al l^{-1} (Fig. 1).

Experiment 3

At the 1/1 nutrient level, Scots pine seedling dry weight was significantly lower at 50 mg Al l^{-1} (Ca/Al = 0.04) compared to 0 mg Al l^{-1}. With the 1/10 nutrient level

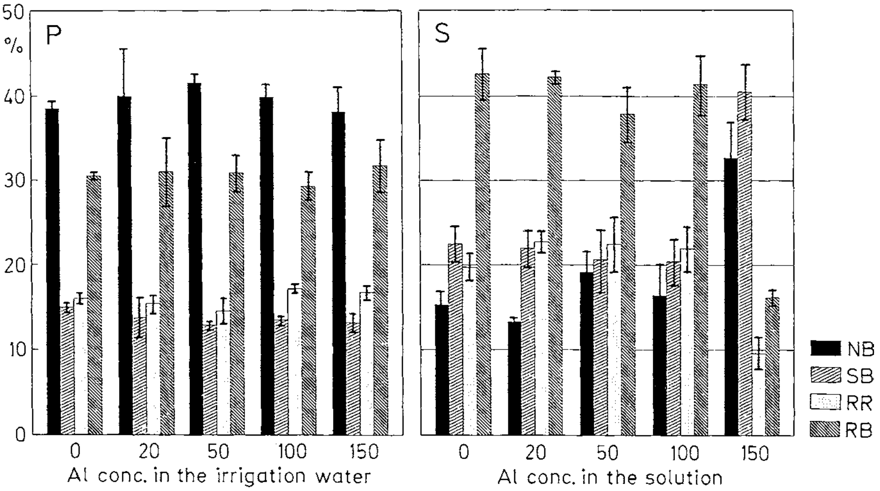

Fig. 1. The effect of aluminium concentration of the irrigation solution (mg l^{-1}) on ^{14}C allocation (with SEM) in Scots pine (*P*) and Norway spruce (*S*) seedlings for 1/1 nutrient level of experiment 2. activity in *NB* needle biomass; *SB* stem biomass; *RR* root respiration; *RB* root biomass

Table 4. The effect of soluble inorganic aluminium on the dry-weight of Scots pine and Norway spruce seedlings in 2 years, 1986 and 1987. For 0 mg Al l^{-1} treatment values given are grams; for all other treatments values are given as percentages of the 0 treatment value. Letters indicate a significant difference compared to 0 Al treatment ($p < 0.05$).

Exp. 2.

Tree species	Nutrient level	Al mg l^{-1} of the irrigation solution 0	20	50	100	150
	1/1	36.6	102	81	70a	50a
Pine	1/3	34.9	79	73a	61a	53a
	1/10	29.0	80a	79a	59a	55a
	1/1	26.8	63a	66a	49a	73a
Spruce	1/3	17.7	82	73	101	69
	1/10	18.5	81	92	99	78

Exp. 3.

		Al mg l^{-1} of the irrigation solution 0	5	10	20	50
	1/1	8.19	95	93	93	71a
Pine	1/10	7.24	93	77	74	82
	1/1	6.88	98	111	98	102
Spruce	1/3	7.19	102	92	102	79
	1/10	6.56	109	125	108	77

seedling dry weights were about 25% lower from 10 mg Al l^{-1} (Ca/Al = 0.02) upwards, but the differences were not significant at 5% risk level when compared to 0 mg Al l^{-1} (Table 4).

The dry weight of Norway spruce seedlings grown at the 1/1 nutrient treatment appeared not to be affected by Al concentrations. With both 1/3 and 1/10 nutrient treatments dry weight at 50 mg Al l^{-1} (Ca/Al = 0.013 and 0.004, respectively) was more than 20% lower compared to 0 mg Al l^{-1}, but difference was not significant.

Effects of Aluminium on Seedling Nutrient Concentrations

Experiment 1

For both species, needle concentrations of Ca and Mg decreased with increasing Al given in the irrigation water (Fig. 2). For seedlings receiving the highest Al level, needle Ca concentrations were only half those of the control seedlings and Mg concentrations were even less. The results have been presented in more detail previously (Arovaara and Ilvesniemi 1990).

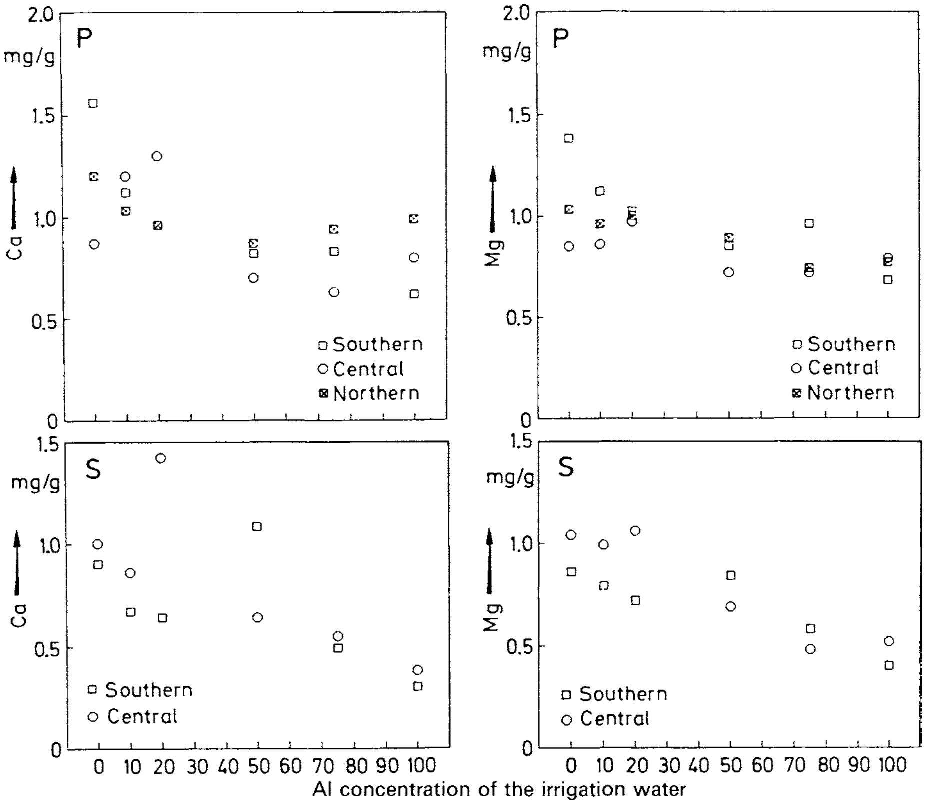

Fig. 2. The effect of aluminium concentration of the irrigation solution (mg l^{-1}) on needle Ca and Mg concentrations of Scots pine (*P*) and Norway spruce (*S*) seedlings according to seed origin (Experiment 1)

Experiment 2

Ca concentrations in the youngest needles of Scots pine seedlings grown at the 1/1 nutrient level were reduced by increasing aluminium concentrations. Unexpectedly, the two highest Al levels at 1/3 and 1/10 nutrient level resulted in Ca concentrations that were higher than those at the 1/1 nutrient level (Fig. 3). Mg, K and P concentrations were not markedly affected by different Al treatments. It may be of importance that at the lowest nutrient level, needle K concentration slightly increased with increasing Al level of the treatment (Fig. 3). Needle Al concentration increased with increasing Al concentration (Fig. 3).

For spruce seedlings, needle Ca, Mg and K concentrations were not affected by Al treatment. P concentrations were reduced by Al treatment, but significantly only at the 1/1 nutrient level (Fig. 3). Needle Al concentrations increased with increasing Al treatment (Fig. 3).

Experiment 3

The Ca concentrations of Scots pine needles were fairly strongly affected by aluminium at both 1/1 and 1/10 nutrient levels while Mg and K concentrations were not. Phosphorus concentrations were slightly reduced by aluminium treatment at the 1/1 nutrient level. Needle Al concentration increased somewhat with increasing Al concentration (Fig. 4).

Norway spruce seedling needle Ca and Mg concentrations were affected by Al treatment while K and P concentrations were not. Needle Al increased with increasing Al treatment (Fig. 4).

Effects of Nutrient Imbalances on Seedling Growth

The results from experiments 2 and 3 showed that seedling growth was affected by nutrient treatment. The poorer the cation and phosphorus nutrition, the smaller the seedling biomass (Table 4). When the different nutrient levels in experiment 4 are compared with control, no differences in the seedling biomass could be observed (Table 5).

The effect of reduced cation and phosphorus nutrition on carbon allocation within the seedlings is evident in the material from 1986 (Fig. 5, Table 6). The proportion of needles and stem biomasses reduced while root respiration and root biomass increased with reducing nutrient concentration treatment. In 1987 the shoot to root ratio based on activities of treatment groups 2, 4 and 5 was reduced more than for the two other treatment groups. The differences were not, however, statistically significant at 5% risk level (Table 6).

The amount of ^{14}C activity in the root respiration of Scots pine increased proportionally to the amount of activity bound in the root biomass. The proportion of carbohydrates consumed in respiration in relation to the amount transported to the roots was smaller in 1986 than in 1987 (Fig. 6).

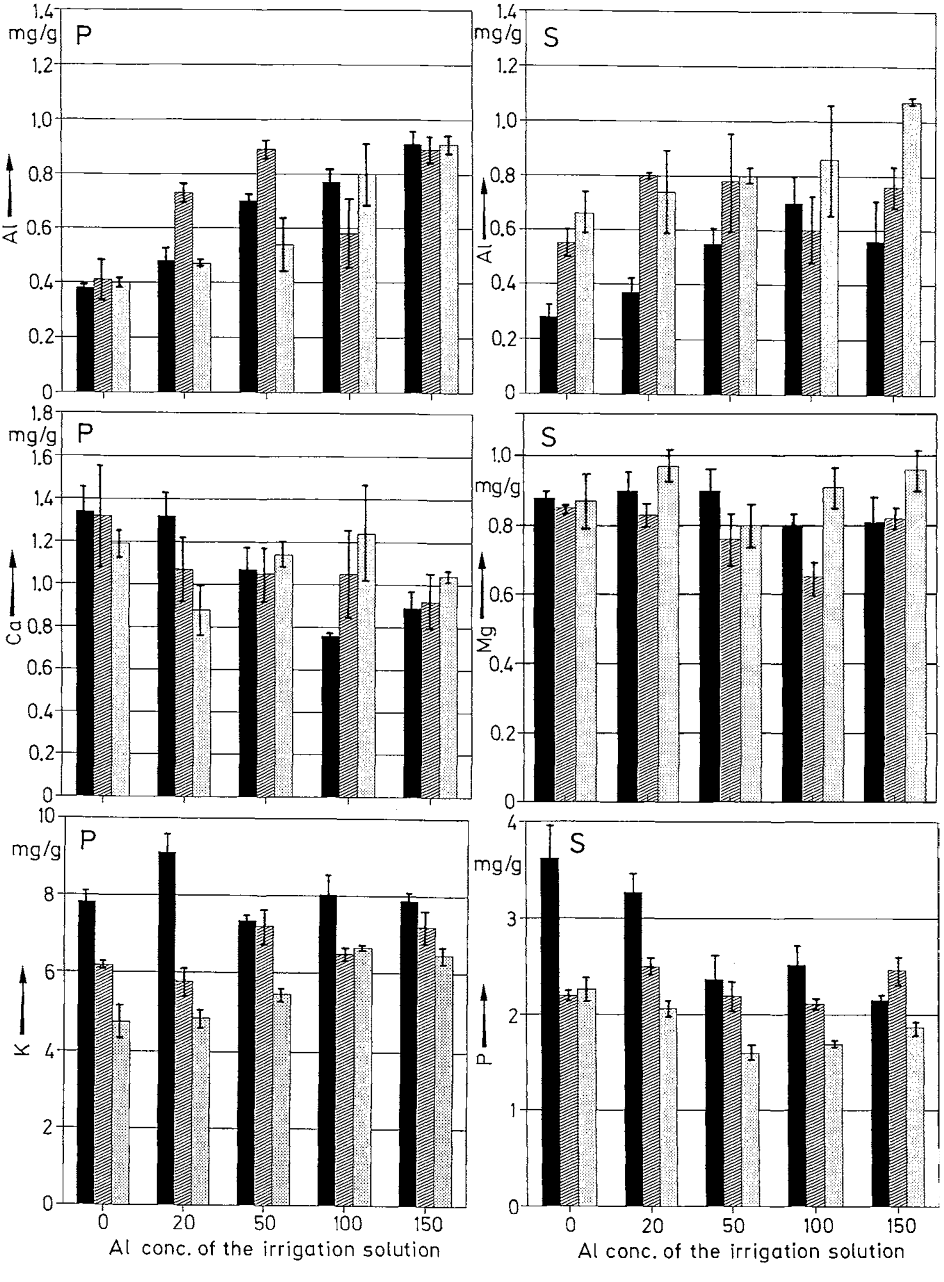

Fig. 3. The effect of aluminium concentration of the irrigation water (mg l^{-1}) on Scots pine (*P*) and Norway spruce (*S*) needle concentrations of different elements (with SEM) (Experiment 2). 1/1, 1/3 and 1/10 are the nutrient levels as described in Table 1

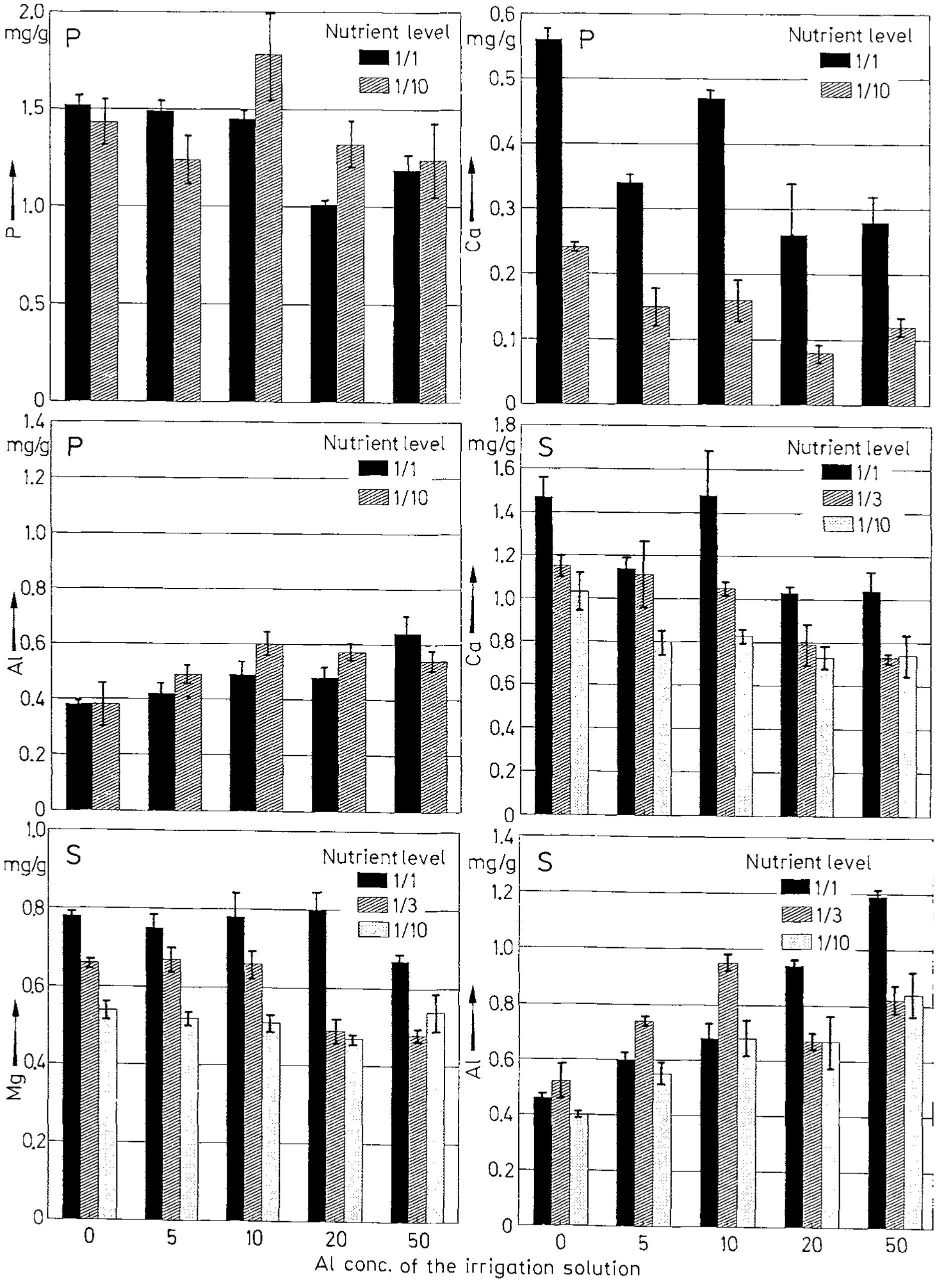

Fig. 4. The effect of aluminium concentration of the irrigation water (mg l^{-1}) on Scots pine (*P*) and Norway spruce (*S*) needle concentrations of different elements (with SEM) (Experiment 3). 1/1, 1/3 and 1/10 are the nutrient levels as described in Table 1

Table 5. The effect of decreasing nutrients (nutrient in question is given in brackets) on the dry weight of Scots pine seedlings. Groups and nutrient levels are presented in Table 2

Group	Nutrient level Control Dry-weight, g	1/2	1/5	1/10
1 (K)	8.20	7.95	8.66	8.41
2 (P)	8.20	9.65	8.36	9.86
3 (K+P)	8.20	9.36	8.89	8.03
4 (Ca+Mg)	8.20	8.92	8.68	8.84
5 (All)	8.20	8.73	8.92	8.09

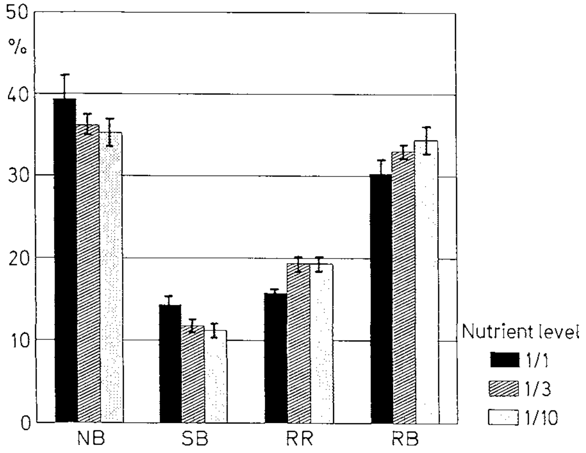

Fig. 5. The effect of different nutrition of Scots pine seedlings on ^{14}C allocation (with SEM). (Exp. 4, 1986 material). Nutrient levels as in Table 1 and abbreviations as in Fig. 1.

Nutrient concentration treatment had a clear effect on needle nutrient concentrations (Fig. 7, Table 7). A tenfold decrease in treatment nutrient concentration resulted in a near halving of the tissue concentrations, but varying somewhat between experiments and elements.

Discussion

The Effect of Aluminium on the Seedlings

According to many studies, Scots pine and Norway spruce seedlings seem to be fairly tolerant to soluble inorganic aluminium. McCormick and Steiner (1978)

Table 6. The effect of decreasing various nutrients on shoot to root ratio of Scots pine seedlings based on growth (upper line) and ^{14}C activities (lower line). Root respiration is included in root activity. The different groups are presented in Table 2. In 1986 material each value is a mean of six and in 1987 a mean of three seedlings

1986 Material

	Nutrient level 1/1	 1/3	 1/10
	Shoot to root ratio		
	0.31	0.15	0.11
	2.31	1.83	1.71

1987 Material

Group	Nutrient level Control (1/1) Shoot to root ratio	1/2	1/5	1/10
1 (K)	0.33	0.23	0.26	0.32
	0.97	0.94	0.97	0.92
2 (P)	0.33	0.42	0.35	0.33
	0.97	1.19	0.81	0.88
3 (K+P)	0.33	0.33	0.35	0.32
	0.97	1.06	0.90	0.92
4 (Ca+Mg)	0.33	0.34	0.31	0.30
	0.97	0.98	0.87	0.84
5 (All)	0.33	0.34	0.30	0.29
	0.97	1.02	0.85	0.85

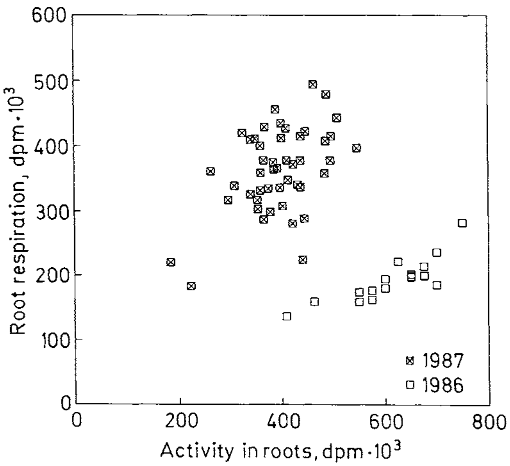

Fig. 6. The relation between the amount of ^{14}C activity in root biomass and in root respiration of Scots pine seedlings. (Experiment 4). *Dpm*, disintegration per minute

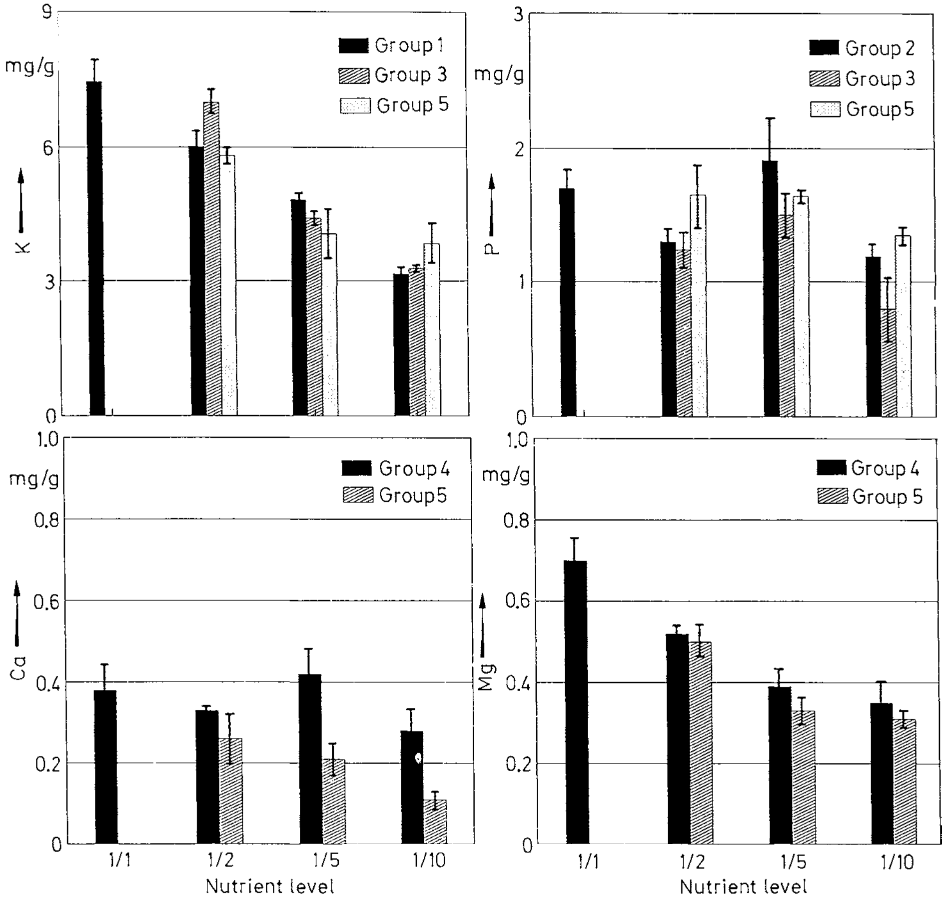

Fig. 7. The effect of different nutrition of Scots pine seedlings on needle nutrient concentrations (with SEM). 1/1, 1/2, 1/5 and 1/10 and groups as in Table 2

obtained reduction in growth of three *Pinus* species at 80 mg Al l^{-1}. In the study of Eldhuset et al. (1987), Scots pine and Norway spruce seedlings suffered permanent growth reduction when the Al concentration of the irrigation water exceeded 80–135 and 13.5–27 mg Al l^{-1} respectively. Godbold et al. (1988a and 1988b) found severe inhibition of root growth of Norway spruce seedlings at levels of 13.5–22 mg Al l^{-1}. In the results of Abrahamsen (1984), growth reductions of Norway spruce seedlings occurred when the Al concentration was 20 mg l^{-1} or higher. Makkonen-Spiecker (1984) has presented much higher tolerances, up to 80 mg Al l^{-1}, for Norway spruce.

In this study, negative effects for Scots pine began at 50 mg Al l^{-1} in all experiments when the nutrient ratios in the irrigation water were optimal (1/1 nutrient level). If the amount of cations and phosphorus in the irrigation water were reduced, the negative effects appeared at 10–20 mg Al l^{-1}. The results thus show that the nutrient concentrations of the irrigation water influences the Al

Table 7. The effect of different nutrition on the corresponding nutrient concentration of Scots pine and Norway spruce seedling needles in 1986 and 1987. At each nutrient treatment level the results of nutrient analyses of the seedlings growing on different Al treatments (5) are pooled

Nutrient	Species	Nutrient level 1/1	1/3	1/10
Exp. 2. in 1986				
Ca	Pine	1.08	1.09	1.10
	Spruce	1.37	1.14	1.34
Mg	Pine	0.69	0.69	0.77
	Spruce	0.87	0.78	0.90
K	Pine	8.09	6.57a	5.64a
	Spruce	6.28	3.87a	3.11a
P	Pine	3.27	2.69a	2.08a
	Spruce	2.88	2.27a	1.90a
Exp. 3. in 1987				
Ca	Pine	0.38	–	0.15a
	Spruce	1.23	0.98a	0.83a
Mg	Pine	0.60	–	0.40a
	Spruce	0.76	0.60a	0.52a
K	Pine	8.39	–	4.61a
	Spruce	8.21	5.27a	4.50a
P	Pine	1.33	–	1.39
	Spruce	1.47	1.06a	0.82a

tolerance of seedlings. The seedlings irrigated with water having suboptimal nutrient ratios were, in general, also smaller.

When the nutrient relations in the irrigation water were optimal, the dry weight of Norway spruce seedlings started to decrease from 10 and 20 mg Al l^{-1} in experiments 1 and 2 respectively. At the two other nutrient levels of experiment 2, the growth reduction with increasing aluminium in the irrigation water was much smaller than that at the 1/1 nutrient level. It is thus possible that the poorer nutrition masked the effect of aluminium on the growth of the seedlings. In experiment 3 the dry weight had not decreased at all at the 1/1 nutrient level. In contrast, at the other two nutrient levels in experiment 3, the dry weight had decreased quite markedly at 50 mg Al l^{-1}.

Most studies dealing with Al toxicity to trees have been performed using small, recently germinated seedlings. The use of older seedlings, which would more resemble adult trees, is perhaps more relevant. However, seedlings are known to suffer from transplantation, especially Norway spruce, which may mask the effect of aluminium treatments in any experiments. It might be wiser in the case of Norway spruce therefore to use a longer experiment period. Old Scots pine seedlings recover quickly from the transplantation shock and thus they can be used for studying the effect of Al without major difficulties.

In many studies, a negative correlation between the aluminium concentration of the irrigation water and Ca and Mg concentration of different organs, most often needles, has been observed. This effect was also observed in experiment 1 and 3. In experiment 2 the calcium concentrations of Scots pine needles were reduced only at the 1/1 nutrient level and the magnesium concentrations were not at all affected.

In experiment 1, some of the lowest needle Ca and Mg concentrations were near or below the deficiency limits presented by Ingestad (1962). In experiment 2, which utilised the same concentration of Ca at the 1/1 nutrient level as experiment 1, needle Ca concentrations in all nutrient levels were above the deficiency limits. On the contrary, in experiment 3, with nutrient concentrations half those of the concentrations in experiment 2, Scots pine needle Ca and Mg concentrations were below deficiency limits even at the control level. According to Ingestad (1962), the concentrations in the irrigation water should have been adequate. Some of the Mg concentrations of Norway spruce needles were also below deficiency limits. Visual deficiency symptoms, however, were not observed.

The seedlings in experiment 2 were 3 years old. The effect of Al on needle Mg concentration may therefore have been masked by translocation from older plant parts. Translocation, however, should not have interfered with the effect of aluminium on needle Ca concentration.

With the present study it is not possible to fully analyse the effect of the irrigation Ca/Al molar ratio on the dry weight of the seedlings, claimed to be more relevant than Al concentrations alone (Rost-Siebert 1983). Different Ca concentrations were applied, but at the same time the concentrations of other nutrients were also lowered.

In experiment 2, the Ca/Al molar ratio at which the dry weight of the Scots pine seedlings started to decrease was 0.08 at the 1/1 nutrient level and 0.02 at 1/10 nutrient level. In experiment 3 the corresponding figures were 0.04 and 0.02, which are markedly lower than value of 1.0 mentioned by Rost-Siebert (1983).

The Effects of Nutrient Imbalances

An important factor controlling forest ecosystem productivity is the allocation of carbohydrates between the above- and belowground parts of the plants (Axelsson and Axelsson 1986, Mäkelä 1988). The ratio of above- to belowground carbohydrate consumption is, among other things, controlled by the amount of moisture and nutrition of the trees (Linder and Rook 1984).

Changes in soil nitrogen and cation concentrations have been of main interest in the soil acidification process. Cations are depleted from the soils by leaching and the amount of available N increased by deposition. The behaviour of phosphorus is not as well known in relation to the soil acidification. It has been supposed that reactions with aluminium might reduce availability of P. In any case, the increased input of nitrogen leads to a relative reduction of all other nutrients in relation.

Lower cation and phosphorus concentrations markedly reduced the growth of the seedlings in experiments 2 and 3, but not in the 1987 material of experiment 4. The growing season was very cloudy and chilly, which clearly affected the growth of the seedlings compared to 1986. Poor growth may have masked the effect of nutrients.

Carbon allocation measured as the amount of ^{14}C activity bound in biomass of the shoot and roots changed in favour of the roots in experiment 4 1986 material when the concentration of K, P, Ca and Mg in treatment solution diminished in relation to nitrogen. In 1987 material this effect was seen in groups 2, 4 and 5. These results indicate that of the nutrients studied, phosphorus and may be also Ca and/or Mg are most important in changing the carbon allocation, although the change was not as pronounced as in 1986.

In 1986 the nitrogen concentrations used in experiments was 100 mg l^{-1} whereas in 1987 it was 50 mg l^{-1}. The shoot to root ratio was not, however, markedly different between these years (Fig. 5, Table 6).

Nitrogen and phosphorous dificiencies result in decreases in the shoot/root ratio of plants (Asher and Lonegran 1966; Atkinson 1973; Ingestad 1962; Taylor and Goubran 1976). In the case of potassium, shoot to root ratios has been observed to be fairly constant over a wide range of concentrations (Asher and Ozanne 1966). Considering that the nitrogen affects carbon allocation only at lower nitrogen concentrations (e.g. Ingestad 1962), the results of this study are in good agreement with the results presented earlier.

In both 1986 and 1987 root respiration increased in proportion to root growth. The amount of ^{14}C activity in the root respiration in relation to the amount of activity in root biomass was smaller in 1986 than in 1987. One explanation for this is that respiration is related to the difference in the nitrogen nutrition of the seedlings. This conclusion is supported by the findings of Keller and Wehrmann (1963), who observed that the proportion of root respiration rose in N-deficient plants when compared to well N-fed plants.

In experiment 4 in Scots pine seedlings, the effect of change in the nutrition on needle nutrient concentrations can be clearly observed. Potassium and phosphorus concentrations of the needles were decreased, but they were never below deficiency limits. Mg concentrations were below deficiency limits except in the control seedlings. Ca concentrations were below these limits even in the control seedlings.

To estimate the importance of soluble inorganic aluminium as a growth-reducing factor in natural conditions, it would be necessary to have information about the variation in the concentrations of soluble inorganic aluminium in the soil. It is very difficult, however, to measure the properties of soil solution in the immediate vicinity of the roots and the ionic composition of the collected soil solutions can only be used as an approximation. In West Germany soil solution Al concentrations higher than 10 mg l^{-1} have been found in the upper soil horizons (Matzner and Ulrich 1987). In Sweden and Finland inorganic Al concentrations are generally low, below 1 mg Al l^{-1} (J Derome pers. commun; Cronan 1987; Abrahamsen et al. 1983). If the concentrations are as low as this in the vicinity of the roots, aluminium would be of little harm to the trees. If this is not the case, the possibility of aluminium toxicity remains.

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2.5 Materials

Effects of SO_2 on Construction Materials: Preliminary Results

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Summary

The effects in variations of air pollutant levels in Finland on several construction materials were investigated. This included observations of the degradation of painted metal surfaces and lime-washed or plastered surfaces in existing structures, laboratory studies of plaster samples from buildings, and field tests on metal specimens. The effects of air pollutants on the materials are recognizable, although no quantitative relationships applicable to an estimation of the practical consequences of changes in pollutant levels can be evaluated on the basis of the results.

Introduction

The study comprised three parts, the first of which evaluated the condition of painted steel surfaces and lime-washed or plastered facade surfaces, and monitored the maintenance frequency in order to establish whether air pollutants had any significant effects on the deterioration of surfaces and the need for service and repair. The second part comprised laboratory studies of lime plaster samples aimed at clarifying whether the condition of plastering had deteriorated more rapidly in regions with poor air quality. In the third part, further field studies at outdoor stations were initiated in connection with joint international programmes aimed at finding reliable relationships between air pollutants and the corrosion rates of materials.

Effects on Metals and Painted Surfaces

The concept of corrosion refers to the reaction of materials with the environment with undesirable consequences. The atmospheric corrosion of metals is electrochemical, that is it advances through water solutions. A small amount of electrolyte is typical of the atmospheric corrosion of metals. Surfaces are sometimes damp and wet and sometimes dry. The formation, properties and stability of the film of water depend on the humidity and temperature of the ambient air and the type and amount of its pollutants. Air pollutants increase the conductivity of water (solution) and thus accelerate the corrosion of most metals. At the metal surface, metal

Kauppi et al. (Eds).
Acidification in Finland

ions dissolve in the water and form a layer of corrosion products on the surface as they are oxidized. In outdoor conditions, some metals, such as aluminium and zinc, become covered with a protective layer of corrosion products, which prevents or at least slows down corrosion. The layer of corrosion products on steel, i.e. rust, is porous and easily detachable and poorly prevents the propagation of corrosion.

Active Atmospheric Factors

As the atmospheric corrosion of metals does not occur on dry surfaces, the probability of corrosion can be described in terms of the duration of the wet period of the surface. Surfaces are naturally wetted by rain and condensed humidity from the air.

Corrosion is possible even without visible moisture, if the relative humidity of the air exceeds a certain critical value, which varies with the metal and pollutants present on the surface; for most metals it is in the range 60–95%. Depending on the sulphur dioxide content of the air, the corrosion rate of steel accelerates radically at a relative humidity of 75–80% (Fyte 1976). With low humidity, corrosion is not significant even in air containing pollutants. Surfaces are usually considered wet when the relative humidity of the air exceeds 80% and the temperature is above 0°C (Barton 1976).

Once corrosion has started, the humidity of the air necessary for corrosion propagation may decrease due to corrosion products that bind moisture. Corrosion products containing chloride can cause corrosion, e.g. in steel, even though the relative humidity of the air is only 40% (Fyte 1976).

Rain is especially beneficial where air quality is low because it cleans surfaces of pollutants. Structures that are sheltered from rain and are only affected by air humidity and dry deposited pollutants can corrode much faster than those that are exposed (Fyte 1976).

The air temperature influences both the rate of corrosion and the length of the wet period. As the presence of a water film on the surface is a prerequisite for atmospheric corrosion, no corrosion takes place in clean rural conditions during the cold period. On polluted surfaces, however, corrosion may propagate even at temperatures just below zero, because many salts lower the freezing point of the electrolyte. Generally, a rise in temperature accelerates corrosion reactions. However, in warm weather surfaces dry out faster, i.e. the wet period of the surface is shortened (Barton 1976).

The corrosion rate of metals is usually lower if there are no pollutants on the surface. Air pollutants of natural origin include sea salts; their effect is only felt in the vicinity of the coast. Chlorides may also reach metal surfaces through deicing salts on roads. Chlorides cause a local rather than general type of corrosion, so that if a metal has become evenly thinner due to the effects of humidity and oxygen from the air, the presence of chlorides may cause pitting corrosion which can rapidly penetrate through a metal wall. Sulphur dioxide, present in air as combustion products of oil and coal, oxidizes to sulphur trioxide, and on a metal surface, produce sulphuric acid which, in turn, reacts with metal ions to form sulphates. The sulphates of several non-iron metals are water-soluble, and once the rain has washed them off the surface a corrosion layer again forms and the attack on the metal continues (Fyte 1976).

Different metals adsorb sulphur dioxide from the air in different ways. The corrosion products of copper and aluminium reduce the amount adsorbed, by whereas a rusty steel surface adsorbs almost all of the sulphur dioxide even in dry air at 0°C (Fyte 1976).

In winter, the sulphur dioxide content of air is high due to the heating of buildings. Structures exposed to the outdoor atmosphere in the autumn generally corrode more heavily than those taken into use in the spring. The initiation time of exposure affects the production of the corrosion product layer and may thus influence even the long-term resistance of some metals.

Steel

The joint effect of oxygen and humidity in the air forms a reddish-brown corrosion product, FeOOH, on the steel surface. The porous rust layer lets through the oxygen, humidity and pollutants of the air, and corrosion proceeds as long as the relative humidity of the air is adequate. For this reason, ordinary structural steels are not used unprotected in open air. Chlorides accelerate the rate of corrosion in steel by forming water-soluble compounds, and cause pitting corrosion in steel (Barton 1976).

The sulphur compounds in air radically accelerate the corrosion of steel. At the steel surface the ferrous sulphate produced by sulphur trioxide oxidizes further to ferric sulphate and ferric hydroxide (rust). As the ferric sulphate hydrolyzes, more rust is produced and sulphuric acid is liberated. In this way sulphuric compounds regenerate on the steel surface and one sulphur dioxide molecule can lead to as many as 15 to 40 rust molecules (Fyte 1976).

Zinc

Steel intended for outdoor use is often protected by hot galvanizing. The corrosion rate of zinc is only about one tenth (1/10) that of steel, and zinc affords cathodic protection. When the zinc layer is damaged and the steel becomes exposed, it is the zinc that starts to corrode instead of the more noble steel. The corrosion products of zinc cover smallish areas of damage, and the corrosion of steel is thus prevented or at least delayed. In outdoor conditions, an alkaline zinc carbonate layer is produced, which is dense and adherent. Owing to the effects of humidity, zinc dissolves at a steady rate. The service life of the zinc coating is directly proportional to the coat thickness.

The effect of chlorides, which accelerate corrosion, is smaller in zinc than in steel because the alkaline salts produced on the zinc surface are poorly soluble.

The corrosion of zinc accelerates on exposure to sulphur dioxide. Sulphuric acid makes the protective carbonate layer produced in pure air water-soluble and thus easily washed off with water. However, the acceleration rate of corrosion is not as high as in the case of steel (Barton 1976).

Copper

In outdoor conditions a layer of corrosion products forms on the surface of copper and copper compounds, making copper highly resistant to outdoor atmosphere. On exposure to sulphur dioxide, copper sulphate is formed which is at first water-soluble but gradually becomes insoluble and thus protective. The production of copper sulphate – the common green patina – is quickest in an industrial climate, but may be totally absent in the countryside (Fyte 1976).

Aluminium

A dense layer of oxide protects the surfaces of aluminium and aluminium alloys. Sulphur dioxide and chlorides can accelerate the corrosion rate of aluminium, particularly in humid conditions, but normally air pollutants only cause blackening of the surface. Pitting corrosion may occur, but the corrosion depth is usually less than 0.1–0.2 mm.

Painted steel

Structures of ordinary carbon steel are not normally used unprotected if exposed to the outdoor atmosphere. The most common method of protection is painting. Painting prevents steel corrosion in several ways: first by isolating the surface from the environment and thus impeding penetration of the metal surface by oxygen, humidity and chemicals. The paint mixture may also contain active anti-corrosion pigments which passivate the metal surface, and paints containing zinc pigments protect the steel cathodically.

The service life of paintwork on a steel surface depends on the paint combination, care of application, air pollutants and, for example, the amount of solar radiation. No reliable quantitative data are available about the effects of air pollutants on the service life of paints. The great number of paint mixtures makes research difficult. The effect of pre-treatment (cleaning of the surface, removal of rust and roughening) on the service life of the paint is probably greater than that of air pollutants.

Effects on Plaster and Natural Stone

Damage to construction materials such as marble, limestone and plaster – especially lime plaster – has clearly accelerated in recent decades in areas with high levels of acid air pollutants. Even buildings that had previously kept well for hundreds of years have started to weather at an increasing rate. Many studies have indicated that a significant reason for the damage, for instance in Europe, is sulphur oxides which act both in the form of gas and through acid rain.

Figure 1 shows the mechanism of interaction between carbon dioxide, sulphur dioxide, and a plaster containing dolomite (Hoffmann et al. 1977).

The hydration, carbonation, sulphatization and dissolution shown in Fig. 1 take place partly simultaneously, but have been plotted consecutively for better readability. During the first phase, when sulphur dioxide acts, only part of the calcium carbonate changes into gypsum, and part of the magnesium hydroxide converts to magnesium sulphite, which rapidly oxidizes to magnesium sulphate. Magnesium sulphate dissolves in water, as does part of the gypsum. During the second phase the above reactions with sulphur dioxide continue, as does dissolution. Magnesium and calcium carbonates are more resistant to sulphur dioxide than the corresponding hydroxides; as the mortar hardens, the weathering effect of the sulphur dioxide may be slowed (Hoffmann et al. 1977).

Gruber and Sternad (1981) studied the gypsum content at various depths in sandstone, pyroclastic tuff and quartz sandstone at Linz Cathedral in Austria. Over 70 samples were examined, and thin section analyses revealed the following:

- the gypsum contents were highest in dark-layered areas;
- they were also highest at the stone surface;
- at a depth of 10 mm there was usually no gypsum;
- clearly crystallized gypsum was found just below the surface;
- consequent to recurrent changes in humidity gypsum crystals grow in size due to recrystallization;
- if rainwater has direct access to the gypsum surface the gypsum dissolves and its contents at the surface are therefore low;
- the effect of high levels of sulphur dioxide in the air is most harmful on surfaces directly exposed to rain, unlike metal surfaces where rain is considered beneficial;
- no significant gypsum contents were found in quartz sandstone.

Weathering due to sulphur dioxide has been found in marble walls and statues (Cheng et al. 1987; Frediani et al. 1979; Gauri and Holdren 1981). The deteriorated layer is thick in porous marble because a sulphuric acid solution can more easily penetrate the inner layers of the stone (Gauri and Holdren 1981). Frediani et al. (1979) observed that the gypsum content usually increases if the material is not in contact with rain water. About $2.4\,\mathrm{g\,l^{-1}}$ of gypsum dissolve in water, and the gypsum contents on the surfaces of marble statues exposed to rain are usually low because the material is considerably weathered.

Experimental Methods

Maintenance Frequency

The original intention was to compare the actual maintenance frequencies of actual structures at locations with different levels of air pollutants. As it turned out

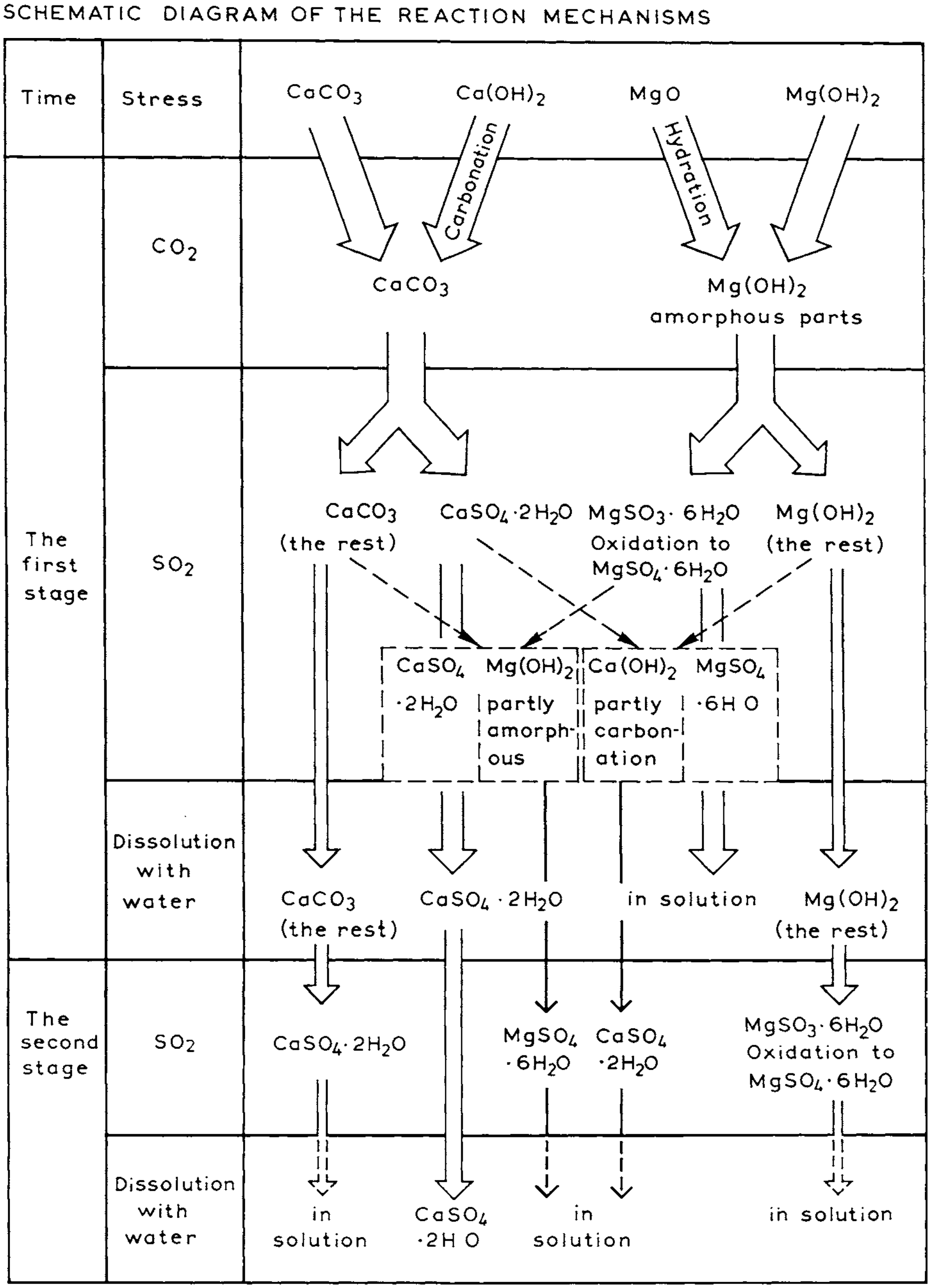

Fig. 1. The mechanism of interaction between sulphur and carbon dioxide and a plaster containing dolomite. (After Hoffmann et al. 1977)

that sufficient data for such a comparison were not available, this part of the study was performed by comparing the conditions of similarly treated surfaces at various locations. To eliminate, as far as possible, the effects of variables other than air pollutants, structures belonging to large organizations were chosen to be inspected.

Painted Steel Surfaces

The poor documentation of data on painting and changes in paint composition, resulting from variations in the quality of raw materials and product development of paints, made the acquisition of comparable data difficult. This study used data from the National Board of Public Roads and Waterways, and the Finnish companies Imatran Voima Oy and Neste Oy. For the evaluation of the sulphur dioxide contents of air, the data were obtained from the Meteorological Institute.

The condition of coats of paint was evaluated in accordance with Standard SFS 3762 (1981).

The degree of corrosion of the surfaces is given on a scale from Ri 0 to Ri 5 as shown in Table 1.

Power line pylons. The Naantali-Imatra power line runs in the east-west direction close to the 61st latitude. The examined pylons were painted in 1949 or 1950. The primer was red lead, the undercoat and paint finish alkyd paint. The condition of the paint coat was inspected in autumn 1985 along the line section Turku-Forssa. The location of the power line is shown in Fig. 2.

Bridges. In addition to atmospheric stresses, bridges are exposed to mechanical stress and dirt caused by traffic. In this study only bridges not exposed to deicing salts were included. Two paint systems were examined: the eight bridges painted with alkyd systems in 1976–1979, and the 21 bridges painted with zinc epoxy-polyurethane systems in 1978–1980. The condition of the paint on the bridges was classified according to data given by regional representatives of the National Board for public Roads and Waterways.

The corrosivity of the atmosphere was classified according to Finnish Standard SFS 4596 (1980) into groups M2 or M3. Group M2 represents the rural atmosphere and group M3 urban, industrial and marine atmospheres.

Table 1. Degree of corrosion according to SFS 3762 (ISO 4628)

Degree of corrosion	Area rusted, %
Ri 0	0
Ri 1	0.05
Ri 2	0.5
Ri 3	1
Ri 4	8
Ri 5	40/50

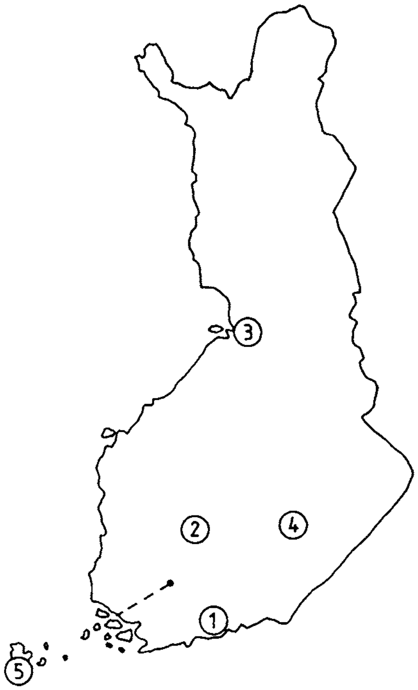

Fig. 2. Sample collection areas. 1. Helsinki; 2 Tampere; 3 Oulu; 4 Mikkeli; 5 Åland. The *dotted line* shows the power line

Oil tanks. Oil tanks painted with alkyd paint combinations are located at Naantali, Hamina and Kemi. The tanks, painted between 1963 and 1978, were inspected in autumn 1985.

Lime-Washed and Lime-Plastered Surfaces

Seven buildings in Helsinki, Turku, Tampere, Oulu and Mikkeli were chosen on the basis of information from archives for surveying the frequency of maintenance and repairing of facades painted with lime chalk or lime-wash (Table 2). The year of reparation of the facade, the measures taken, the cause of the reparation and the sources used were documented on a special form.

The information stored in the archives is based almost entirely on visual inspection. Only in the case of Helsinki Cathedral are there some of the results from laboratory experiments. Usually only the type of damage is mentioned and there are no comments as to the possible causes.

Study of Plaster in the Laboratory

The weathering of construction materials caused by acidifying air pollutants was examined on the basis of the literature, by collecting data on sulphur dioxide contents in Finland, and by gathering plaster samples which were chemically analysed for their sulphur content. The degree of weathering was established through thin section analysis.

Table 2. Frequency of maintenance and repairing of facades painted with lime chalk or lime-wash

Building	Year of maintenance or repair	Material/procedure
Helsinki Cathedral	1840	lime plaster
	1848	painted with lime-wash
	1857	painted with lime-wash, reparation
	1872	painted with lime-wash
	1886	plaster and lime-wash
	1912	painted with white lead
	1926	painted
	1950	painted
	1960–62	plastered and painted with latex paint
	1975, 76, 78	plastered and painted with lime-wash
	1981	a test coat of paint applied to the columns
Trinity Church, Helsinki	1827	painted with lime-wash
	1844	plastered and painted with lime-wash (partly)
	1876–78	plastered and painted with lime-wash
	1933	painted with lime-wash
	1951	painted with lime wash
	1956/61	plastered, painted with varnish paint
	1967	painted with alkyd paint
	1976–77	painted with acrylate paint
The Old Library in Tampere	1925	painted with lime-wash
	1967	painted with varnish paint
	1975–76	painted with acrylate paint
	1984–85	painted with alkyd paint
Secondary School for Girls, Tampere	1902	plastered and painted with lime-wash
	1950's	reparations in connection with the 50th anniversary, no information about the facades
	1960's	probably painted with latex paint
	1974–75	painted with alkyd paint
Oulu Cathedral	1832	painted with lime-wash
	1897	painted with lime-wash or whitewash
	1932	painted
	1977	painted
	1986	plans for painting the facades at the recommendation of the facade board
Oulu City Hall	1887	plastered and probably painted with lime-wash
	1920	plastered and painted with lime-wash
	1945	plastered and painted with lime-wash
	1920	plastered and painted with lime-wash
	1945	plastered and painted with lime-wash
	1968	painted with "Spread-Glide-On"
	1982	plastered and painted with lime-wash
Mikkeli County Hall	1843	plastered and painted with lime-wash (probably)
	1964	extensive reparations
	1982	reparations, painted

For the laboratory tests, two series of samples were collected from plastered and, in some cases, lime-washed buildings. The places of sampling are shown in Fig. 2.

A large series of samples was collected in Helsinki: the oldest samples date from the 1890's and the most recent ones from the 1950's. Some of the buildings had undergone repairs, e.g. lime-wash, in the 1960's. In addition to Helsinki, small series of samples were gathered in Tampere, Mikkeli and Oulu and from historical buildings on the Åland islands. A sample of at least $10 \times 10\,\text{cm}^2$ of plaster was taken each time if possible. Two separate samples were taken of each building whenever there were clear differences on the facade surfaces in terms of weathering and wear. The samples were classified in connection with field work as samples sheltered from rain and samples exposed to rain.

Determination of Sulphur Content

The sulphur content was determined at the surfaces of plaster and lime-wash samples with a LECO CS-044 automatic carbon-sulphur analyser. Since the analysed quantity of sample was only about 200 mg, at least two parallel determinations were made in order to improve the representativeness of the results.

Thin Section Analyses

Petrographical thin sections were prepared from most of the samples taken in the field for microscopic studies.

In each case a plaster sample about $30 \times 50\,\text{mm}^2$ in size, was sawn and dried at 38°C and impregnated in a vacuum with epoxy resin containing fluorescent colour. As the composition of the layers of plaster and possible changes at the outer plaster surface were the objects of study, the thin sections were cut perpendicular to outer plaster surface, and the sawn surface was ground and glued onto the sampling glass. The sample was thinned with a diamond saw down to a thickness of 0.5 mm. Thinning was continued by grinding to a final sample thickness of 25 μm. The thin section was finished by glueing a thin cover-slip on top to protect the sample.

Altogether 32 thin sections were prepared and studied under Leitz Ortholux II POL-BK polarizing and fluorescent microscopes. Two photographs were also taken of each sample with an automatic Wild Photoautomat MPS 45 Camera: one of the plaster surface and one of the inside of the plaster. The first picture documented the dirt and gypsum layers on the plaster surface or possible alluviation, the second the composition and structure of the plaster (mainly the binder type). The amounts of dirt and gypsum on the plaster surface were estimated with the score method.

Field Tests

Two international projects dealing with atmospheric corrosion are currently in progress at the Metallurgy Laboratory of the Technical Research Centre of

Finland (VTT). In 1987 a pilot programme was started at the initiative of the United Nations' Economic Commission for Europe, Executive Body for the Convention on Long-Range Transboundary Pollution (UN/ECE/EB) Task Force, which examines the effects of long-range emissions on metals and other construction materials. The tests take a long time and no results are available as yet. In 1986 a field test programme involving metal samples located at over 50 outdoor stations was started in 14 countries at the initiative of the International Organization for Standardization (ISO), Technical Committee TC 156 (Corrosion of metals and alloys), Working Group WG4. In order to determine the relations between the corrosivity of the atmosphere, namely atmospheric parameters and corrosion rates of different metals, WG4 has been preparing Standard ISO/DIS 9223 (1988). The standard includes tables for the corrosion rates of carbon steel, zinc, copper and aluminium in five environmental classes.

If the atmospheric parameters (the wet period of the surface and sulphur dioxide and chloride contents) are known, the corrosivity of the atmosphere in question for the given metals can be estimated from the tables. If atmospheric data are not known, the corrosivity of a certain atmosphere can be determined with 1-year field tests by comparing the obtained values for corrosion rates with those in the tables of the standard, which in addition to the steady state corrosion rate includes the corrosion rate during the first year. The corrosion rate is calculated on the basis of the weight loss of the samples. The field programme was launched in order to improve the reliability of the numerical of values of the standard.

Plate and wire samples (helix) of carbon steel, zinc, copper and aluminium have been located at Otaniemi in Espoo, at Vallila in Helsinki and at Ähtäri. Espoo and Helsinki have an urban atmosphere and Ähtäri a rural atmosphere. At these locations the temperature, relative humidity and sulphur dioxide and chloride contents of the air are measured regularly over test periods of 1, 2, 4 and 10 years. The corrosion rate is calculated from the weight loss per unit area of specimens, after removal of corrosion products from the specimens. There are several test periods of 1 year starting both in spring and autumn. The results from three 1-year and one 2-year test periods are reported here.

Results and Discussion

Maintenance Frequency

Painted Steel Structures

Power line pylons. The inspection of the paint condition indicated that the condition of paintwork is worse in the vicinity of built-up areas. The results of the inspection carried out in 1985 between Turku and Forssa are presented in Table 3.

The results indicate a weak correlation between the degree of corrosion and the sulphur content of the air. However, along the entire length of the power line the

Table 3. Degree of corrosion of powerline pylons between Turku and Forssa in autumn 1985. For scores of degree of corrosion see Table 1

Distance from Turku, km	Sulphur dioxide content of air, $\mu g\ (m^3)^{-1}$	Degree of corrosion SFS 3762
0	30–60	Ri 5
15	10–30	Ri 4–5
20	about 10	Ri 4
30	about 10	Ri 4
50	about 10	Ri 3–4
55	about 10	Ri 3
65	about 10	Ri 3
80	about 10	Ri 3–4

condition of the paintwork was poor owing to its age (35 years) and the differences were therefore small.

Bridges. The results of the evaluations of bridge paintwork are summarized in Tables 4 and 5. Differences in the corrosion degree of bridges were small. Slightly higher values in areas where the sulphur content of air is assumed to be greater may be due to the heavy traffic.

Oil tanks. The degree of corrosion of oil tanks according to inspections carried out in 1985 is shown in Table 6. On the basis of the results presented in the table, the sulphur dioxide content of air cannot be shown to have any relation to the degree of corrosion of oil tanks painted with alkyd paints. All the tanks examined were in very good condition considering their age.

Lime-Washed and Plastered Surfaces

The necessary data were collected during field inspections carried out when collecting samples for an ongoing investigation.

Damage to facades most probably caused by acid air pollutants was found only in Oulu. Several buildings in Oulu have facades that have been treated with

Table 4. Degree of corrosion of bridges painted with alkyd paint; the coat thickness is 140 μm

Place	Atmosphere SFS 4596	Year of painting	Degree of corrosion SFS 3762	Distance from Turku, km
Ylihärmä	M2	1976	Ri 1–2	
Alahärmä	M2	1976	Ri 1–2	
Nurmo	M2–3	1976	Ri 3–4	
Vammala	M2–3	1979	Ri 2	
Parainen	M3	1978	Ri 4	20
Mynämäki	M3	1977	Ri 3	30
Masku	M3	1977	Ri 4	15
Raisio	M3	1977	Ri 3	< 10

Table 5. Degree of corrosion of bridges painted with zinc epoxy base coat and polyurethane paint finish; total thickness of paint 130 μm

Place	Atmosphere SFS 4596	Year of painting	Degree of corrosion SFS 3762
Kärkölä	M2	1978	Ri 1
Hämeenlinna	M3	1978	Ri 1
Vilppula	M2	1978	Ri 1
Virrat	M2	1978	Ri 1
Lahti	M3	1979	Ri 1
Asikkala	M2	1979	Ri 0
Valkeakoski	M3	1979	Ri 1
Teisko	M2	1979	Ri 0
Asikkala	M2	1979	Ri 0
Hattula	M3	1980	Ri 1
Kangasala	M3	1980	Ri 1
Lammi	M2	1980	Ri 0
Lempäälä	M2–3	1980	Ri 0
Kortesjärvi	M2	1979	Ri 0
Muurla	M2–3	1980	Ri 1
Kisko	M2–3	1980	Ri 0
Kaarina	M3	1980	Ri 1
Hämeenkyrö	M3	1980	Ri 1
Muurla	M2–3	1979	Ri 1
Pertteli	M2–3	1979	Ri 1
Huittinen	M3	1977	Ri 4

Table 6. Degree of corrosion of oil tanks painted with alkyd paint. Year of inspection 1985

Place	Sulphur deposit mg $(m^2)^{-1}a^{-1}$	Sulphur dioxide content of air μg $(m^3)^{-1}$	Year of painting	Coat thickness μm	Degree of corrosion SFS 3762
Kemi	700	20–40	1971	130	Ri 1
	700		1972	130	Ri 1
	700		1974	130	Ri 1
	700		1977	130	Ri 1
	700		1978	130	Ri 1
Naantali	1700	30–60	1968	130	Ri 0–2
	1700		1977	130	Ri 0–2
	1700		1963	100	Ri 2–3
	1700		1970	150	Ri 0–1
	1700		1972	130	Ri 0–1
	1700		1971	130	Ri 0–1
	1700		1970	150	Ri 0–1
Hamina	1100	10–20	1972	140	Ri 2
	1100		1971	140	Ri 2
	1100		1974	140	Ri 2

lime-wash or lime plaster: corrosion was clearly visible in places where water had washed off the surface. The facades examined in Mikkeli were in excellent condition. In Helsinki and Tampere, the effects of air pollutants were evenly distributed over the facade and seemed to be related to the density of traffic.

Laboratory Studies on Plasters

Sulphur Dioxide Levels in Sampling Areas

Measured yearly average values of the sulphur dioxide concentrations in the sampling areas were available for Helsinki, Tampere and Oulu for periods starting in the 1970's. The samples were taken in 1984 or 1985; thus measurements after this time are not of interest.

In Helsinki the average SO_2 concentration decreased from about 40 $\mu g\,m^{-3}$ in 1976 to about 20 $\mu g\,m^{-3}$ in 1985, according to information obtained from the Helsinki Metropolitan Area Council (YTV). In Tampere the measured values exceeded 100 $\mu g\,m^{-3}$ during 1973–1976 and decreased to about 30 $\mu g\,m^{-3}$ by 1985. In Oulu values measured over the years 1979–1985 showed also a decreasing tendency: from about 30 $\mu g\,m^{-3}$ to about 10 $\mu g\,m^{-3}$. The values for Tampere and Oulu were obtained from the Environment Protection Bureaus of these cities.

For Mikkeli and Åland the sulphur dioxide concentrations can only be estimated. In both these areas the concentrations are expected to have been of the order of the background levels in Southern Finland, i.e. less than 10 $\mu g\,m^{-3}$ during the summer and at most in the range 10–20 $\mu g\,m^{-3}$ during the winter months.

Sulphur Contents of Samples

The sulphur contents of the samples are presented in Table 7. Samples which have been in direct contact with rain water are marked S. If it is assumed that the sulphur contents presented in Table 7 originate only from gypsum, the results can be converted into gypsum contents by multiplying them by 5.4.

Thin Section Studies

On thin sections, microscopic studies were carried out to determine the plaster type of each sample and paint type and number of paint layers on plasters. The amount of dirt and the formation of gypsum were also studied.

The plaster and paint types had to be determined, as background information on the field samples was so scarce. This is important because different materials, such as organic and lime paints, behave differently under the influence of air pollutants. The identified paint and plaster types are presented in Table 8.

Only two plaster surfaces had an organic paint. The other samples had a lime paint, or the surfaces were unpainted, or the paint layers had eroded away. Most of the samples were lime or hydraulic lime plasters. Six were lime cement plasters and

Table 7. Sulphur contents of samples from buildings. The results of LECO analyses are the mean values of at least two parallel samples

Place of sampling	Sample	Sulphur content, weight-%
Helsinki	1A	3.2
	1B s	2.3
	1C	3.8
	1D	1.6
	2A	1.0
	2B s	0.6
	3A	2.3
	3B s	<0.1
	4A	1.1
	4B s	0.3
	5A	3.2
	5B s	0.6
	6B s	1.7
	7A	3.1
	7B s	0.2
	8A	2.8
	8B	2.4
	8C s	0.4
	9A	5.2
Tampere	1B	0.9
	2A	1.4
	2B s	0.2
	3B	0.5
	4A	0.8
Mikkeli	4 samples	≤ 0.1
Oulu	6 samples	0.1 . . . 0.7
Åland	5 samples	≤ 0.1

five had at least two layers, the innermost of lime plaster and the outermost of lime cement plaster. The lime cement plasters were rich in lime.

Varying amounts of different dirt particles and gypsum formed at the plaster surface were found on the samples. In order to transform the qualitative information obtained into a more quantitative form, a method of evaluation was used, which scores the amount of dirt and gypsum on the plaster. The principle of the analysis was as follows: zero indicates very little dirt or gypsum on the plaster surface, and the maximum score 3 indicates a plaster with a high gypsum and dirt content. The quality classes and scores are shown in Table 9, and the results of the score analysis in Table 8.

The amounts of dirt and gypsum found at the plaster surfaces correlated very well with the results of the LECO analysis. Plasters sheltered from rain and with a high sulphur content had a thick layer of dirt on the surface and the outermost part of the binder had been transformed into gypsum. Plasters exposed to rain had

Table 8. Paint and plaster types, determined microscopically and results of the score analysis

		Paint		Plaster type			
Place of sampling	Sample	Number of layers	Type	L	H	LC	Score given in the analysis
Helsinki	1B	0	–	●			2
	1C	2	LW	●			3
	1D	0	–	●			2
	2A	1	LW			●	2
	2B	1	LW	●		●	0
	3A	1	LW	●			3
	3B	1	LW	●			0
	4A	0	–		●		0
	4B	0	–	●		●	0
	5A	0	–	●			3
	5B	0	–	●		●	2
	6B	1	LW			●	1
	7A	2	LW	●			3
	7B	0	–	●			0
	8A	1	LW	●			1
	8B	0	–	●			2
	8C	0	–	●			0
	9A	about 3	LW	●			2
Tampere	2A	2	LW	●		●	0
	2B	1	LW			●	0
	3B	1	LW	●			0
	4A	2	LW	●		●	0
Mikkeli	1A	1	OR			●	0
	1B	1	OR			●	0
	2B	1	LW	●		(●)	0
	3A	0	–			●	0
Åland	1A	1	LW	●			0
	2A	1	LW	●			0
	2B	1	LW		●		0
	3A	3	LW		●		0
	4A	2	LW		●		0

LW lime-wash
OR organic paint
L lime plaster
H hydraulic lime plaster
LC lime cement plaster

lower sulphur contents. Microscopy showed these samples to be weathered and to have very little dirt or gypsum on the surface. No differences were found between lime and lime cement plasters.

Field Tests

In addition to the results of the 2-year period the results of three 1-year periods are available also. Table 10 gives the corrosion rates and atmospheric data of the period in question.

Table 9. Quality classes and results of the score analysis

Quality classes	Analysis score
dirt and gypsum	
none	0
very little	0
a little	1
moderately	2
much	3

The environmental parameters of the testing stations differ mainly in terms of the sulphur dioxide content of the air. The annual mean value was about 5 $\mu g\,(m^3)^{-1}$ in Ähtäri but roughly 20 $\mu g\,(m^3)^{-1}$ in Helsinki and Espoo. The chloride contents corresponded to the background values at all stations. The periods of wetness deviated only slightly from each other and the effect on differences in corrosion rates could not be shown.

The corrosion of steel became clearly stronger the higher the sulphur dioxide content of the air. In rural atmosphere (Ähtäri), the corrosion rate of steel during the first year was less than half of that in the urban atmosphere (Helsinki). The results of the 2-year test indicate a decrease in the corrosion rate after the first year. In Ähtäri, the corrosion rate of steel in the 2-year results was about 10–15 $\mu m\ a^{-1}$ and in Helsinki 30–35 $\mu m\ a^{-1}$. The corrosion of steel was considerably less in tests initiated in spring than in those started in autumn, although the mean annual values of the atmospheric data did not differ much. The effect of the time of starting the tests on the estimation of long-term durability cannot be ascertained with the tests in question, as those started in spring were all 1-year tests. The corrosion rate of zinc is also faster in an urban atmosphere, that in Helsinki being twice as much as in Ähtäri.

The results obtained for steel and zinc corresponded well to those carried out earlier in Finland (Hakkarainen et al. 1982). Figure 3 compares the earlier results for steel with the present ones. Koski represents a rural atmosphere. The sulphur dioxide concentration in Koski is not measured, but, being in the southern part of Finland, the concentrations probably are somewhat higher than in Ähtäri.

The corrosion rate of steel in Helsinki has not changed when compared to the results from the 1970's. The progress of the corrosion seems to become slower in the course of exposure time. After Hakkarainen the total loss of material in the first 2 years was about 60 μm, being only 40 μm more in following 2 years.

The sulphur dioxide content had no effect on the corrosion of copper samples. The results of the aluminium test results were to some extent contradictory. The corrosion of aluminium was very slight and the numbers were so small that no conclusions can be drawn on the basis of them. The corrosion rates are based on average weight loss results, while the corrosion attack of aluminium is usually

Table 10. Corrosion rates and environmental parameters at the field stations.

	Corrosion rate µm a^{-1}								Environmental parameters			
Test site and period	Steel		Zinc		Copper		Aluminium		Temperature (annual average) (°C)	Relative humidity (annual average) (%)	SO_2 (annual average) µg $(m^3)^{-1}$	Period of wetness (h)
	Plate	Helix	Plate	Helix	Plate	Helix	Plate	Helix				
Ähtäri												
10/86–9/87	17	19	0.8	1.5	0.7	1.2	0.04		0.3	79	6	3300
10/87–9/88	16	20	0.9	1.5	0.9	1.3	0.04	0.1	3.4	77	5	2700
4/87–3/88	11	14	0.5	0.9	0.7	0.7	0.1	0.1	2.2	79	5	3000
10/86–9/88	12	16	0.6	0.9	0.6	0.9	0.02	0.04				
Espoo												
10/86–9/87	31	43	1.1	1.8	0.6	1.3	0.1	0.2	3.0	–	19	2600
10/87–9/88	35	48	0.9	2.3	0.9	1.6	0.1	0.3	5.4	74	19	3000
4/87–3/88	21	35	0.9	1.6	0.7	1.4	0.1	0.2	4.8	–	16	2800
10/86–9/88	22	32	0.8	1.2	0.6	1.2	0.1	0.2				
Helsinki												
10/86–9/87	37	49	1.6	3.2	0.6	1.3	0.2	0.5	3.3	76	21	3000
10/87–9/88	41	53	1.4	2.7	0.7	1.3	0.2	0.5	6.4	79	20	3400
4/87–3/88	33	44	1.3	2.4	0.7	1.2	0.3	0.3	5.1	76	21	3400
10/86–9/88	30	37	1.2	2.4	0.5	1.0	0.2	0.3				

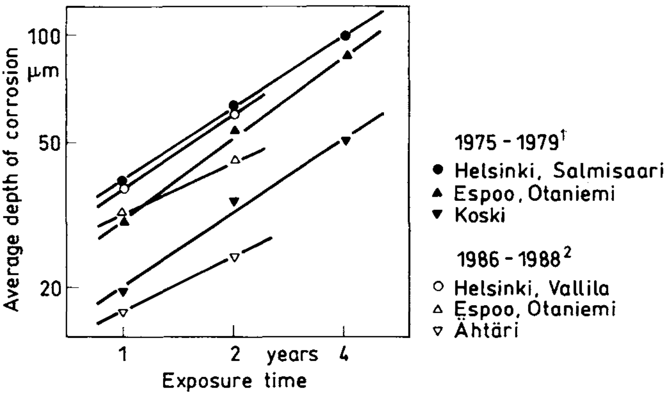

Fig. 3. Corrosion of steel plate specimens at the field stations. [1] After Hakkarainen et al. 1982; [2] This chapter

localized (pitting corrosion). Consequently, the rates measured do not correctly represent the rates of penetration.

The shape of the samples influenced the results. The mean corrosion rates of helix samples were up to double those of plate samples. The smallest differences were found in steel samples. Although the corrosion of the entire surface is calculated on the basis of weight loss, the upward and downward surfaces of the plate in the rack are not subjected to identical stress. Pollutants reach the lower surface only in the form of dry deposition and rain water has no access. Helix samples are better in this respect.

Conclusions

No clear quantitative relationship was observed between the maintenance-free service life of painted steel surfaces and the sulphur dioxide content of air: any possible correlation is hidden by other factors. Even in those cases where the existence of such a dependency seemed probable, no quantitative conclusions could be drawn on the basis of the available data.

No quantitative conclusions can be made about the effect of the sulphur dioxide content of air on surface deterioration from the monitoring of maintenance frequency of lime-washed or lime-plastered facade surfaces.

On the basis of laboratory studies of plaster samples and the results so-far of field studies with bare metal samples, it is clear that air pollutants – sulphur dioxide most of all – strongly lower the resistance of many construction materials in outdoor exposure.

Finding quantitative relationships requires carefully performed field tests. Such tests are currently being carried out for some materials within the framework of this study.

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PART 3 WATER

3.1 Aquatic Chemistry

Statistical Lake Survey in Finland: Regional Estimates of Lake Acidification

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Summary

The Finnish Lake Survey, conducted in 1987, was designed to quantify the present extent of lake acidification in Finland. The surveyed lakes were selected statistically (n = 987), allowing estimation of lake frequencies, as well as corresponding variances, for any predetermined criteria. The median pH of the lakes was 6.3, median acid neutralizing capacity (ANC) 75 μeq l^{-1}, and median sulphate concentration 71 μeq l^{-1}. The organic anion was estimated to be the most significant anion in Finnish lakes (median 89 μeq l^{-1}). Sulphate concentrations in lakes corresponded to the pattern of acidic deposition, being highest in southern Finland. The acidity of Finnish lakes reflects the interaction of the atmospheric loading of sulphate, the catchment sensitivity, and the amount of organic anions present. The estimated proportion of acidic lakes (ANC $\leq$ 0 μeq l^{-1}) in Finland was 12%, representing 4900 lakes. The proportion of the acidic lakes with pH < 5.3 estimated to be naturally acidic (original pH < 5.3), was 56–81%.

Introduction

Large areas of Finland are considered sensitive to acidification (see e.g. Kämäri 1986). Mineral soils in Finland are podzolic, having developed from till or glaciofluvial deposits mainly on granitic bedrock. Thin soil overlying granitic bedrock occurs quite commonly throughout the country. The topography is fairly flat and the climate is humid. Peatlands cover more than 30% of the land area, but today around half of the peatlands have been ditched for forestry.

The total deposition of sulphur in Finland is highest along the coastal area of southern Finland, generally above 65 keq km^{-2} yr^{-1}, and decreases to the north (Tuovinen et al. this Vol.). However, there are elevated levels of deposition also in eastern Lapland due to the extensive smelting industry in the Kola peninsula. The present total sulphur deposition is about 60 keq km^{-2} yr^{-1} at the deposition monitoring station in Svanvik in northeastern Norway (SFT 1988), and at the eastern border of Finland (Tuovinen et al. this Vol.). The loading of acidic deposition in this region is probably highly episodic, because western winds prevail. The present acidic deposition load over large areas of the country is thus

Kauppi et al. (Eds).
Acidification in Finland

clearly above the critical load for sensitive ecosystems, estimated to be in the range 15–30 keq km^{-2} yr^{-1} (Nilsson and Grennfelt 1988).

There are approximately 56,000 lakes larger than 0.01 km^2 in Finland, about 15,700 of them being larger than 0.1 km^2 (Raatikainen and Kuusisto in press). The lakes are very unevenly distributed throughout the country. Areas with a high number of lakes are found especially in central and eastern Finland, and in the northernmost regions. These regions have also generally been classified as the most sensitive to acidification (Kämäri 1986). The areas with the lowest number of lakes are located in the coastal areas of the Gulf of Finland and the Gulf of Bothnia, and in the central parts of Lapland.

The first signs of the effects of acidic deposition in Finnish waters were noticed in a few studies in the early 1970's. The acidification-oriented studies of larger unpolluted lakes revealed no statistically significant trends in pH, but decreasing alkalinity and increasing conductivity have been found to occur in many lakes (Kenttämies 1973, 1979). Haapala et al. (1975) have found snow melt to cause flushes of acidity to weakly buffered river waters of the Kiiminkijoki water course in central Finland. In the 1970's the acidification of surface waters was not considered as a widespread problem in Finland. There were, however, no studies conducted on the most sensitive ecosystems, small oligotrophic lakes. The first observations of acidification of such lakes were reported by Becker (1978), who observed low pH values in the studied lakes during the snowmelt period. Pätilä (1980, 1982) found drastic changes in the water chemistry and biology of 23 small forest lakes near Helsinki. Later several studies have shown that lake acidification is a common phenomenon in small lakes in many areas, especially in southern Finland (e.g. Tolonen and Jaakkola 1983; Kämäri 1985; Simola et al. 1985; Tolonen et al. 1986; Forsius et al. 1987; Kortelainen and Mannio 1988).

The monitoring results of large lakes (Laaksonen and Malin 1984a,b) show a general, significant trend of increasing conductivity. The concentrations of all measured cations and anions, except bicarbonate (estimated from alkalinity) have increased since the late 1960's to the early 1980's. Clear changes in ionic composition of the lake waters were detected when comparing observations from the years 1968–70 and 1981–83. Bicarbonate had decreased in about 75% of the stations. During the earlier period, sulphate was the most important anion in 52% of the observation stations, whereas in 1981–83 the corresponding number of stations had increased to 65%. During the period of observation water colour increased at the sites by an average of 8.2% (from 49 to 53 mg Pt l^{-1}), indicating also an increased load of humic matter from the drainage basins.

The comparison of old (1911–31) and recent (1962–79) monitoring data of large rivers has revealed a clear trend of decreasing alkalinity, especially in spring samples (Alasaarela and Heinonen 1984).

As a response to the increasing concern of the effects of acidic deposition the interdisciplinary Finnish Research Project on Acidification (HAPRO) was launched in 1985. As part of this project a nationwide survey of 1189 lakes, of which 987 lakes were randomly selected, was conducted in 1987. In this paper the chemical status of the randomly selected lakes is discussed, and population estimates of main variables related to acidification are presented.

Methods

Random Selection of Lakes

Although acidification of surface waters has been demonstrated for several parts of Finland, there has not been sufficient data available for assessing the number and distribution of acidified lakes. The Finnish Lake Survey was planned in order to provide such information. The statistically based survey design allows estimation of lake frequencies, as well as corresponding variances, for any predetermined criteria.

A detailed description of the methods of chemical analyses, data-base management procedures, and the statistical methods used in the lake selection procedures as well as in the calculations of statistics for the data set is given in Forsius et al. (1990). The first results of the survey, and point maps of the major chemical variables have been presented by Kämäri et al. (1990). Some results of the survey have previously been presented also by Forsius (1989) and Kortelainen et al. (1989).

The Finnish Lake Survey had four primary objectives: (1) to collect a representative chemical and physical limnology data base for estimating the number and spatial distribution of acidified lakes, (2) to assess the influence of major watershed and soil characteristics on lake water quality, (3) to evaluate the role of organic acidity in the lakes, and (4) to provide a data base for regional modelling of the aquatic impacts of acidic deposition with varying acid loadings.

A lake was defined as a water pool greater than 0.01 km^2. In northern Finland, however, only lakes larger than 0.1 km^2 were sampled. Moreover, the sampling intensity for northern Finland was lower than that for southern and central regions. The reasons for this are obvious. The whole region is sparsely populated and there are only few roads; thus access to the lakes is often difficult. There are areas in northern Finland with vast numbers of small lakes. A large proportion of these lakes are shallow, and often frozen down to the bottom during winter, and almost completely dried out during summer.

An upper limit for the lake size (10 km^2) was also adopted. The larger lakes are generally being monitored extensively, and reliable water quality information for these lakes was already available.

The lakes for the survey were selected from two separate subregions, 1 and 2, which together covered the country (Fig. 1). The statistical sampling "frame" in each subregion consisted of the previously described data set (Raatikainen and Kuusisto in press); i.e. of the set of surface area distributions of lakes in a grid net consisting of a series of 1:50,000-scale topographic maps (20 × 30 km^2). The lakes were originally counted on maps scaled 1:20,000 (10 × 10 km^2). In the lake counting procedure the size of the lakes was estimated by means of using transparent cutouts of different shapes.

Owing to the uncertainty of the size distributions included in the lake frame population and the large variations in lake density in the different regions, a two-stage cluster sampling was used. In this procedure the selection of lake areas to be investigated was weighted by lake density. This strategy, furthermore, makes the field sampling cheaper and more efficient. Because there are no large, uniform insensitive regions in Finland, no part of the country was disregarded beforehand when deciding on the area to be surveyed.

In the first sampling stage, 100 maps of scale 1:50,000 were selected from Subregion 1 using the "probability proportional to size" method (pps) (e.g. Cochran 1977), according to which the selection of the maps was weighted by lake density. Twenty-five maps were selected from Subregion 2 using the same statistical methods.

In the second sampling stage, the lakes were selected from each previously selected map by systematic random sampling. All basins considered as lakes, with a surface area within the determined size range were numbered, and eight lakes were randomly sampled from each map. If the number of lakes on the map was eight or less, all the lakes were sampled. The total number of selected lakes was 797 in Subregion 1 and 190 in Subregion 2.

Four of the statistically selected lakes were actually not visited. In addition, five lakes were eliminated after field sampling due to intensive urban or industrial influence. This introduces some additional uncertainty in the regional estimates of the variables. The final number of lakes in the data set was then 789 for Subregion 1, and 189 for Subregion 2.

The lake sample represents ca. 2% of the total number of lakes in the size range 0.01–10 km^2 in Subregion 1, and 5% of the lakes with surface areas 0.1–10 km^2 in Subregion 2. Within the uncertainty in the statistical lake frame population, the size distribution of the selected lakes can be considered as representative of the actual situation (see Forsius et al. 1990).

Water Sampling and Analyses

Water samples of the lakes were taken during fall overturn 1987. The period of field sampling was from August 25, to November 23, starting in the northernmost Finland. Most of the lakes were sampled by two-member field sampling teams. In northern Finland about 130 lakes were sampled by helicopter. Water samples were collected from a depth of 1 m at least 30 m from the lake shore using Ruttner-type water samplers. Heavy metal samples were collected directly in bottles, either by hand while wearing plastic gloves, or the bottle was attached to a stick.

A total of 23 chemical variables were measured on each lakewater sample (Table 1). Heavy metal analyses were carried out on a selected group of 300 headwater lakes. Twelve measurements which are affected by long storage times were

Table 1. Analytical methods

Variable(s)	Preservation	Analytical method
pH		Radiometer combination electrode GK 2401 C
Conductivity		Conductometric determination
ANC		Acid titration by the Gran-plot method
Chemical oxygen demand (COD_{Mn})	H_2SO_4, pH < 2	Titrimetric determination with $KMnO_4$
Colour		Comparative determination
Total organic carbon (TOC)	deep-frozen	ASTRO model 2850 TOC/TC Analyzer
NH_4		Colorimetric determination with hypochlorite and phenol, wavelength 630 nm
NO_3		Reduction to NO_2 (Hg-Cd or Cu-Cd) and colorimetric determination, wavelength 520 nm
Total N		Oxidation with $K_2S_2O_8$ and determination of NO_3 as above
PO_4 (filtered)		Filtration with 0.45 Gelman GA membrane and colorimetric determination (phosphomolybdate), wavelength 700 or 880 nm
Total P	H_2SO_4, pH < 2	Oxidation with $K_2S_2O_8$ and determination of PO_4
Total Fe	H_2SO_4, pH < 2	Oxidation with $K_2S_2O_8$ and colorimetric determination with TPTZ-reagent, wavelength 593 nm
Mn	H_2SO_4, pH < 2	Oxidation with $K_2S_2O_8$ and colorimetric determination with formaldoxine, wavelength 450 nm
SiO_2		Reduction of molybdosilicid acid to heteropolyblue and determination on FIA analyzer, wavelength 820 nm
Cl, SO_4		Dionex Serier 4000i Ionchromatograph
F		Ion selective electrode, Orion ionanalyzer 940
Na, K, Ca, Mg		Flame atomic absorption, Perkin-Elmer 603
Total monomeric Al		Autoanalyzer with pyrocatechol violet
Non-labile monomeric Al		Autoanalyzer after ionexchange
Cd, Cu, Ni, Pb	HNO_3, pH < 2	Atomic absorption in graphite furnace, Perkin Elmer 5000 and HGA 500
Zn	HNO_3, pH < 2	Flame atomic absorption, Perkin Elmer 5000

measured at the district laboratories of the National Board of Waters and the Environment on the next day after sampling. These measurements included pH, acid neutralizing capacity (ANC), and the main nutrients.

The main cation, fluoride, SiO_2, and heavy metal analyses were carried out at the Research Laboratory of the National Board of Waters and the Environment in Helsinki. Chloride and sulphate measurements were carried out by ion chromatography at the Water Conservation Laboratory of the City of Helsinki. The TOC and aluminum samples were analysed at the Norwegian Institute for Water Research in Oslo.

Labile aluminum (difference between total monomeric and non-labile monomeric Al) was included in charge balance calculations with a charge value of 3 to represent cationic aluminum species. ANC (Gran alkalinity) was used as an estimate of bicarbonate, although these measurements may include also some organic alkalinity (Thompson 1986). Non-marine sulphate and base cations (denoted by asteriks, SO_4^*, Ca*, Mg*, Na*, K*) were estimated as the differences between total concentrations and concentrations attributable to marine salts, the latter based on ratios to chloride in seawater.

Estimation of the Proportion of Naturally vs. Anthropogenically Acidic Lakes

The pH 5.3 was chosen as the reference value for estimating the proportions of naturally acidic (original pH < 5.3) vs. anthropogenically acidic (original pH ≥ 5.3) lakes. The surveyed lakes with pH < 5.3 were included in this estimation procedure. There was, however, some inconsistency between ANC and pH measurements in some of the surveyed acidic lakes, probably due to the difficulty in measuring pH in dilute systems. A few lakes had slightly negative ANC and still a pH above 5.3. These dilute acidic lakes were, however, not included in the estimation procedure.

An estimate of the proportion of naturally acidic lakes was obtained from ionic balance relationships. The lakes were assumed to be naturally acidic if the sum of estimated organic anion, non-marine background sulphate, and fluoride concentrations (assuming no contribution from nitrate, and no change in fluoride) exceeded estimated non-marine background base cation concentrations. In the case where the estimated anion concentration was less than the base cation concentration, the base cations would be balanced by bicarbonate and organic acids with higher proton dissociation constants (pK_a-values) and the pH therefore higher than 5.3.

The background (or "historic") non-marine base cation concentration, BC*b (all concentrations in $\mu eq\ l^{-1}$), can be estimated as follows (modified from Henriksen 1982):

$$[BC^*b] = [BC^*] - F([SO_4^*] - [SO_4^*b]), \qquad (1)$$

where: $[BC^*b]$ = estimated background base cation concentration, $[BC^*]$ = present base cation concentration, F = base cation change factor, $[SO_4^*]$ = present sulphate concentration, $[SO_4^*b]$ = estimated background sulphate concentration.

Two different estimates of the base cation change factor (F) were used in the calculations. It was assumed that the F-factor varied as a non-linear function of the base cation concentration, approaching 0 in the most dilute lakes, and being 1 at base cation concentrations exceeding alternatively 200 or 400 $\mu eq\ l^{-1}$ (Brakke et al. in press):

$$F = \sin\left(\frac{90[BC^*]}{S}\right), \tag{2}$$

where S was the point at which $F = 1$ (200 or 400 μeq l^{-1}).

The background sulphate concentration was estimated in two ways: Firstly, the background sulphate concentration was assumed to be dependent of the base cation concentration (Henriksen pers. commun.):

$$[SO_4^*b] = 15 + 0.16[BC^*], \tag{3}$$

Secondly, a constant background sulphate value of 15 μeq l^{-1} was used, which is the estimated non-marine background sulphate concentration for dilute lakes (Brakke et al. 1989).

The original "maximum" concentration of organic anions was calculated by the Oliver et al. (1983) model, assuming no change in TOC over time. However, the Oliver equation yielded higher values for the organic anion concentration than the values calculated from the charge balance, and thus seemed to overestimate the organic anion concentration also in the acidic lakes (see Kortelainen et al. 1989). Therefore, the value of carboxyl acid content per mg TOC used in the Oliver equation was changed by a trial and adjustment procedure, so that the best possible fit between the values from the Oliver model and the charge balance calculations was obtained for the presently acidic ($pH < 5.3$) lakes. This calibrated charge density value of 7.7 was then used in the Oliver equation, instead of the value 10 in the original model. When using this calibrated value there was a reasonable agreement between the estimates from the charge balance and the Oliver model ($r^2 = 0.86$ by linear regression).

After this initial calibration procedure, the original organic anion concentration was estimated by using a pH of 5.3 in the Oliver equation, in order to obtain an estimate of the maximum contribution of organic anions in lakes with no bicarbonate alkalinity (pCO_2 $10^{-3.5}$ atm).

Results

Physical Characteristics of the Lakes

The median lake surface area was 0.07 km^2 in Subregion 1, and 0.20 km^2 in Subregion 2 (Table 2). This difference in lake size has to be considered when comparing the chemical status of the lakes in the two subregions. The size range of all the surveyed lakes was 0.01–7.5 km^2. The watersheds of the lakes were also larger in Subregion 2. There was only a slight difference in the watershed/lake ratios between the two subregions.

Table 2. Physical characteristics of the lakes in the two subregions

	Subregion 1	Subregion 2
Median lake characteristics		
Lake area km^2	0.07	0.20
Watershed area km^2	1.6	4.2
Watershed/lake ratio	20	17
Hydrological lake type (%)		
Drainage	69	75
Headwater	18	12
Closed	3	3
Seepage	10	10

Drainage lakes are the most common lake type in both subregions (Table 2). The proportion is, however, somewhat larger in Subregion 2. The headwater lakes are the second most abundant hydrological lake type in both subregions. Closed lakes are not common.

Chemical Characteristics of the Lakes

The chemical status of the lakes in the two subregions and in the whole country is described by presenting median values of the chemical variables, and by calculating population estimates of lakes in relation to different reference values of four primary variables, separately for these different regions. Cumulative frequency distributions of the primary variables are also presented. The population estimates calculated for the whole country are based on results from 0.01–10 km^2 lakes in southern and central Finland, and on results from 0.1–10 km^2 lakes in the north.

Calcium is the main cation of the lakes in both subregions (Table 3). High concentrations of base cations ($Ca^* + Mg^* + Na^* + K^*$) are found in many different locations in Finland, but most of them are in southern Finland. Lowest base cation concentrations are found in central and northernmost regions (see Kämäri et al. 1990). The estimated proportion of lakes with base cations < 100 $\mu eq\ l^{-1}$ was 8% in Subregion 1, and 7% in Subregion 2 (Fig. 2, Table 4). An estimated number of 3200 lakes had a base cation concentration below this value in the whole country.

High concentrations of organic carbon are found in lakes throughout the country, but especially in lakes in southern and central Finland (Kortelainen et al., 1989; Kortelainen and Mannio, this Vol.). The median value for TOC was 14 $mg\ l^{-1}$ in Subregion 1, and 6.4 $mg\ l^{-1}$ in Subregion 2 (Table 3). The percentage of lakes with TOC > 5 $mg\ l^{-1}$ was 93 in Subregion 1, and 69 in Subregion 2 (Fig. 2, Table 4). Of all Finnish lakes, 65% were estimated to have TOC > 10 $mg\ l^{-1}$. The median colour was 120 mg Pt l^{-1} in Subregion 1 and 40 mg Pt l^{-1} in Subregion 2. Organic anions, estimated from the charge balance, were on average the most important anion in Subregion 1 (median 99 $\mu eq\ l^{-1}$), and the second most

Table 3. Median chemical characteristics of the lakes in the two subregions, and in the whole country

		Subregion 1	Subregion 2	Finland[a]
pH		6.1	6.8	6.3
ANC	µeq l^{-1}	69	90	75
Conductance	mS m^{-1}	3.4	2.2	3.1
Total N	µg l^{-1}	510	270	450
NO$_3$	µeq l^{-1}	1.5	0.2	1.1
NH$_4$	µeq l^{-1}	1.0	0.4	0.8
Total P	µg l^{-1}	18	8	15
PO$_4$	µg l^{-1}	1	2	1
TOC	mg l^{-1}	14	6.4	12
COD$_{Mn}$	mg O$_2$ l^{-1}	17	6.7	15
Colour	mg Pt l^{-1}	120	40	100
Fe	µg l^{-1}	560	120	460
Mn	µg l^{-1}	37	13	30
SiO$_2$	mg l^{-1}	4.6	2.5	4.2
Ca*	µeq l^{-1}	143	90	129
Mg*	µeq l^{-1}	68	47	63
Na*	µeq l^{-1}	35	35	35
K*	µeq l^{-1}	15	7.4	12
Labile Al[b]	µg l^{-1}	17	<10	14
SO$_4^*$	µeq l^{-1}	90	35	71
Cl	µeq l^{-1}	31	20	25
F	µeq l^{-1}	<5	<5	<5
Organic anions[c]	µeq l^{-1}	99	58	89

[a] Median value in the full data set.

[b] Inorganic, monomeric Al (Røgeberg and Henriksen 1985), assumed to have a charge value of 3 in ion balance calculations.

[c] Organic anions = $[Ca^{2+}+Mg^{2+}+Na^{+}+K^{+}+H^{+}+NH_4^{+}+Al^{3+}]-[SO_4^{2-}+Cl^{-}+NO_3^{-}+F^{-}+HCO_3^{-}]$, HCO_3^{-} estimated from ANC.

* Values corrected for marine contribution.

important in Subregion 2 (median 58 µeq l^{-1}). The lakes in which organic anions are the dominant anion are most common in central regions, on the western coast and in eastern Finland.

The median sulphate concentration was 90 µeq l^{-1} in Subregion 1. Lakes in southern Finland frequently had sulphate concentrations $>$ 100 µeq l^{-1} (Fig. 2). Sulphate is on average the second most important anion in this subregion. However, in the southernmost Finland the lakes are mainly dominated by sulphate (Kämäri et al. 1990). The median sulphate value for lakes in northern Finland was 35 µeq l^{-1}. Twenty-two % of the lakes had sulphate $>$ 50 µeq l^{-1} in this subregion (Table 4); most of these lakes are located in northern Lapland. The median sulphate concentration was lower than that of bicarbonate (90 µeq l^{-1}) and the organic anion (58 µeq l^{-1}). Seventy % of the lakes in Finland were estimated to have sulphate $>$ 50 µeq l^{-1}.

Fluoride concentrations are generally low (Table 3). However, in some lakes in rapakivi granite areas in southern Finland high concentrations were observed. In

Table 4. Population estimates of lakes in relation to two reference values of non-marine base cations ($Ca^* + Mg^* + Na^* + K^*$), TOC, non-marine sulphate, and ANC for lakes in Subregion 1, Subregion 2, and the whole country. The estimated percentage, number (N_c), and 90% upper confidence limit on the number (N_{cu}) of lakes below (base cations), below or equal to (ANC), or above (sulphate, TOC) each reference value (X_c) are presented

		Region								
		Subregion 1			Subregion 2			Finland[a]		
Variable	X_c	%	N_c	N_{cu}	%	N_c	N_{cu}	%	N_c	N_{cu}
Base cations	$(<)$ 100 μeq l^{-1}	8	3000	3700	7	270	430	8	3200	4100
	$(<)$ 150 μeq l^{-1}	15	5500	6600	26	1000	1280	16	6500	7900
TOC	$(>)$ 5 mg l^{-1}	93	34,300	35,100	69	2670	3090	91	37,000	38,200
	$(>)$ 10 mg l^{-1}	70	25,900	27,300	16	620	890	65	26,500	28,200
SO_4^*	$(>)$ 50 μeq l^{-1}	75	27,700	29,900	22	850	1160	70	28,500	31,100
	$(>)$ 100 μeq l^{-1}	44	16,200	18,800	4	150	270	40	16,400	19,100
ANC	$(\leq)$ 0 μeq l^{-1}	13	4800	5900	2	80	150	12	4900	6100
	$(\leq)$ 50 μeq l^{-1}	42	15,500	17,400	18	700	890	40	16,200	18,200

[a] Estimates based on results from 0.01–10 km^2 lakes in southern and central Finland (Subregion 1), and 0.1–10 km^2 lakes in northern Finland (Subregion 2).

Subregion 1 the fluoride concentration was > 10 μeq l^{-1} in 6% of the lakes, the highest value being 126 μeq l^{-1}.

Nutrient concentrations are low for most of the lakes (Table 3). Median concentrations for nitrate were only 1.5 (Subregion 1) and 0.2 μeq l^{-1} (Subregion 2), and for ammonium 1.0 and 0.4 μeq l^{-1}. The values for total phosphorus were 18 (Subregion 1) and 8 μg l^{-1} (Subregion 2).

The median values of ANC and pH were lower in Subregion 1 (ANC 69 μeq l^{-1} and pH 6.1) than in Subregion 2 (ANC 90 μeq l^{-1} and pH 6.8). There is a clear difference between the ANC distributions of the two subregions (Fig. 2, Table 4). The proportion of acidic lakes is much larger in Subregion 1. A total of 4800 lakes, representing 13% of the lakes, were estimated to have ANC ≤ 0 μeq l^{-1} in this subregion. The corresponding proportion in Subregion 2 was 2%, representing 80

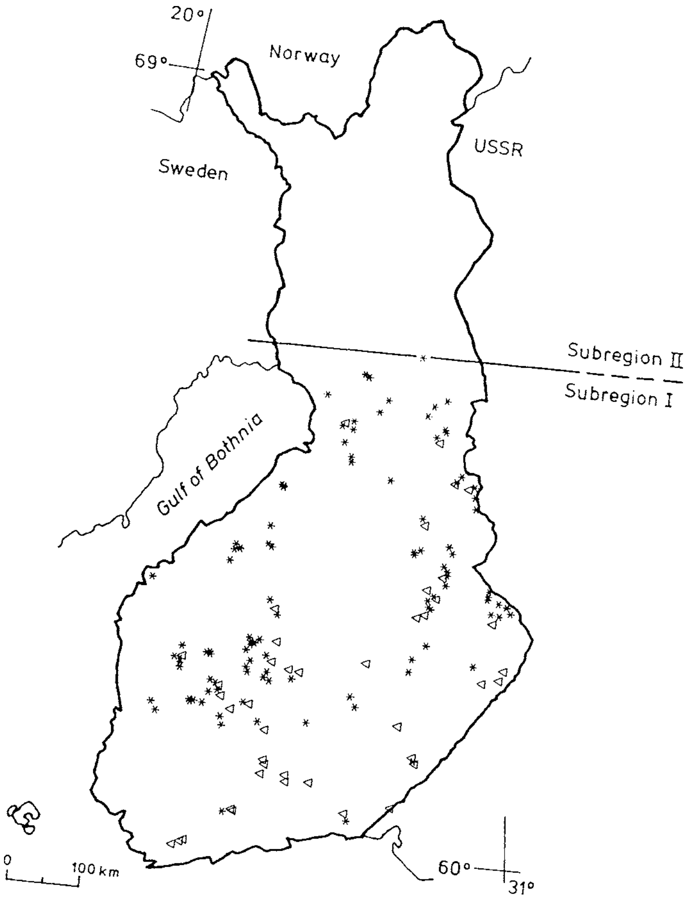

Fig. 1. Location of surveyed acidic (pH < 5.3) lakes, divided into lakes estimated to be naturally acidic (original pH < 5.3) (*), and (Δ) lakes estimated to be anthropogenically acidic (original pH ≥ 5.3). $SO_4^* b = 15 + 0.16$ [BC*] $S = 400$ (see text). The Subregions 1 and 2 are distinguished by the northern coordinate 7340 of the uniform coordinate system

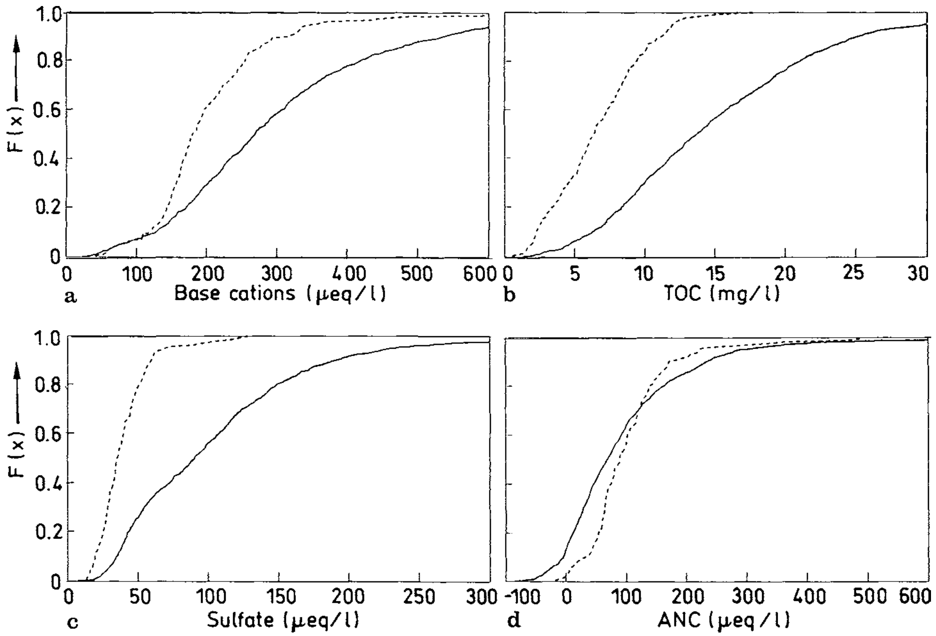

Fig. 2. Cumulative frequency distributions [F(x)] for non-marine base cations [Ca* + Mg* + Na* + K*], TOC, non-marine sulphate, and ANC in Subregion 1 (*continous line*), and Subregion 2 (*dashed line*)

lakes. On a 90% confidence level an estimated 3700–6100 acidic (ANC ≤ 0 µeq l^{-1}) lakes can be given for Finland. An estimated 15,500 lakes (42%) had ANC ≤ 50 µeq l^{-1} in Subregion 1, compared with 700 lakes (18%) in Subregion 2. The estimated number of lakes in Subregion 1 with pH < 5.0 was 4100, representing 11% of the lakes. In Subregion 2 no lakes with pH below this value were surveyed.

Acidic (ANC ≤ 0 µeq l^{-1}) lakes are found in many different places, throughout almost the whole country. However, the acidic lakes occur most commonly in southwestern and central regions, and in eastern Finland along the border Highest labile aluminum concentrations were observed in southernmost Finland, with concentrations decreasing to the north. Of all Finnish lakes a total of 16% were estimated to have labile aluminum concentrations > 50 µg l^{-1}. Most of these acidic lakes are highly humic, and they are located mainly in southern Finland (see Kämäri et al. 1990).

Naturally vs. Anthropogenically Acidic Lakes

The acidity of Finnish lakes is strongly affected by both the high concentrations of dissolved organic acids from peatland catchments, and the anthropogenic mineral acids from acidic deposition. In the southern parts of the country, where the acidic deposition is highest, the minerogenic acidity commonly exceeds the catchment derived acidity (Kortelainen et al. 1989; Kortelainen and Mannio this Vol.). In the surveyed acidic lakes (ANC ≤ 0 μeq l^{-1}) organic anions were, however, clearly the dominant anion (median 88 μeq l^{-1}) compared with sulphate (median 54 μeq l^{-1}). The contribution of nitrate to the acidity was very small (median 0.8 μeq l^{-1}). The acidic lakes have on average very high concentration of organic matter, the median TOC was 15 mg l^{-1}. One surveyed lake located in the coastal area of the Gulf of Bothnia had an extremely high sulphate concentration (833 μeq l^{-1}), and was clearly naturally acidic due to a local sulphate source from acidic marine sediments.

The concentration of mineral acid anions ($SO_4+Cl+F+NO_3$) exceeded the concentration of non-protolyte bases ($Ca+Mg+Na+K+NH_4$) in < 2% of the surveyed lakes in Subregion 1, and in no lakes in Subregion 2. This further emphasizes the importance of organic anions in regulating the acidity of Finnish lakes.

The estimated proportion of the lakes that presently had pH < 5.3 was 17% for the whole country, representing 7000 lakes. The proportion of these acidic lakes estimated to be naturally acidic was 56–81%, depending on the values used for background sulphate and base cation change factor (Table 5). In eastern and central regions most of the presently acidic lakes were estimated to be naturally acidic. The lakes estimated to be acidified below pH 5.3, were located mainly in high deposition areas in southern Finland (Fig. 1).

There is a clear difference in the water chemistry of the two lake groups. Lakes estimated to be naturally acidic (case 2 in Table 5) had much lower concentrations of sulphate (median 52 μeq l^{-1}), than the anthropogenically acidic lakes (median sulphate 94 μeq l^{-1}). About 25% of the naturally acidic lakes had TOC > 25 mg l^{-1}.

Discussion

General characteristics of the lakes

The chemistry of pristine clearwater lakes is usually dominated by the primary weathering products in the catchment, calcium, magnesium, and bicarbonate. Therefore, the sum of base cations normally shows a good relationship with ANC (alkalinity) in this type of lakes (Henriksen 1980). Concentrations of strong acid anions originating from acidic deposition, and naturally occurring organic acids with low pK_a-values decrease ANC relative to the base cation concentration, and acidic lakes will result if the concentrations of strong acid anions exceeds the supply of base cations (Henriksen and Brakke 1988a).

Naturally occurring organic acids can strongly affect the acidity of lakes. The organic functional groups in humic matter have a wide distribution of mean pK_a-values, ranging from 3.7–12.5 (Perdue et al. 1984). Estimates for the mean

Table 5. Percentage and numbers (N_c) of presently acidic (pH < 5.3) lakes estimated to be naturally acidic (original pH < 5.3) or anthropogenically acidic (original pH ≥ 5.3), with different assumptions of background sulphate (SO_4^*b), and base cation change factor [value of S in Eq. (2)]

		Naturally acidic		Anthropogenically acidic	
SO_4^*b (μeq l^{-1})	S	%	N_c	%	N_c
15	400	56	3900	44	3100
Eq. (3)[a]	400	72	5000	28	2000
15	200	77	5400	23	1600
Eq. (3)[a]	200	81	5700	19	1300

[a] $SO_4^*b = 15 + 0.16[BC^*]$

pK_a-value of carboxylic groups have varied between 3.5 and 4.2 (Perdue et al. 1984; Eshleman and Hemond 1985; Thurman 1985). Organic solutes thus exhibit a wide range of acid/base characteristics, and organic functional groups with higher pK_a-values can also act as buffers against strong mineral acids in the pH range found in natural waters (Wright et al. 1988). However, in humic lakes in regions receiving acidic deposition, the influence of strong mineral acids is superimposed on organic acid contributions to acidity. In the case of lakes with the same concentrations of base cations organic acids make humic lakes more sensitive to acidic inputs from the atmosphere than clearwater lakes (Brakke et al. 1987).

The main reason for the higher base cation concentrations in the surveyed lakes in southern Finland compared with more northern lakes is probably the thicker and more fertile soils. In addition, the higher level of acidic deposition in the south may have increased the leaching of base cations more than in northern regions. However, it is likely that the base cations originate also from anthropogenic sources, because the base cation deposition in southernmost parts of the country is higher than elsewhere in Finland (Järvinen and Vänni this Vol.). Recent increases in the concentration and accumulation rates of base cations in lake sediments of small headwater lakes in southernmost Finland suggest that these ions are partly of atmospheric origin (Verta et al. 1989).

The highest concentrations of organic matter in the lakes were observed on the peatland-dominated areas on the western coast, whereas the lowest concentrations were found in northernmost Lapland and on the south-coast where there is little peatland. The highest organic matter concentrations were observed in the smallest lakes having a relatively large catchment area. The high concentrations of organic matter decrease the pH values of the lakes throughout the country, and the humic lakes are on average more acidic than the clearwater lakes (Kortelainen et al. 1989; Kortelainen and Mannio this Vol.).

In areas not influenced by acidic deposition, dilute lakes normally have non-marine sulphate concentrations of 10–15 μeq l^{-1} (Brakke et al. 1989). In our survey only some 2% of the lakes had non-marine sulphate concentrations < 20 μeq l^{-1}. The pattern of lake water concentrations of sulphate was similar to the pattern of acidic deposition, i.e. with highest concentrations in southern Finland. Slightly elevated sulphate concentrations were found also in high deposition areas in northeastern Lapland. However, the sulphate concentrations in some lakes scattered throughout the country were higher than would be expected from anthropogenic deposition. These high concentrations are probably due to geological sources of sulphate in the watersheds of these lakes. It is clear that elevated sulphate concentrations in precipitation has caused increased concentrations of sulphate in the lakewaters in large areas in Finland, thus causing an acidic load to the system.

Nitrate does not at present contribute significantly to the acidity of Finnish lakes. Even in southernmost Finland, where the nitrogen deposition is highest, 73% of the lakes had nitrate concentrations $< 5\ \mu\text{eq}\ \text{l}^{-1}$ (Kämäri et al. 1990). Nearly all lakes in northern Finland had nitrate concentrations $< 1\ \mu\text{eq}\ \text{l}^{-1}$. Also in the acidic lakes the contribution was minimal. Despite the fact that nitrate is being added as fertilizers on both agricultural and forest land in some catchment areas of the surveyed lakes, concentrations in most lakes were low. However, increased leaching of nitrate has been observed in lakeless catchments in southernmost Finland (Lepistö and Seuna this Vol.), indicating increased saturation of nitrogen in high deposition areas. Increased concentrations of nitrate have been observed also in Norwegian surface waters (Henriksen and Brakke 1988b). The importance of nitrate to the acidity of surface waters in Finland is likely to be increasing, because no major reduction in the emissions of nitrogen compounds is expected. At present, nitrate is probably most important during the snowmelt period, when the vegetation uptake in the catchment is small.

The interaction between acidic loading and lake acidity is complicated, and depends on several partly interrelated factors, such as hydrological flow paths, base cation supply, and organic matter concentration (Henriksen and Brakke 1988a; Landers et al. 1988a). The frequency of acidic lakes in regions receiving similar amounts of acidic loading will thus vary, depending on the inherent sensitivity of these regions. Relatively few acidic lakes were found in high deposition areas in southernmost Finland, because the base cation concentrations were high (see Kämäri et al. 1990). Similarly, few acidic lakes were observed in northeastern Lapland. The original buffering capacity of the lakes in this region has generally been sufficient to keep them non-acidic at the present levels of acidic deposition. However, there is a large number of rather poorly buffered lakes in the northeastern region, and the potential for episodic effects on the biota, particularly during the intensive snowmelt period, cannot be excluded even under the present atmospheric loadings. Furthermore, in this region lakes $< 0.1\ \text{km}^2$ were not included in the survey. The smaller lakes would probably show a greater proportion of acidic lakes. Generally, the surveyed acidic lakes were located on areas estimated as sensitive to acidification on the relative sensitivity map of Finland presented by Kämäri (1986).

Natural vs. anthropogenic acidity

The acidic lakes in Finland are typically dominated by organic anions, implying that in those lakes a substantial fraction of the overall acidity is natural in origin.

This is further supported by the fact that the concentration of mineral acid anions exceeds the concentration of base cations in only a small proportion of the lakes. However, the acidic lakes in high deposition areas in southern Finland have higher contributions of strong acids to the acidity. Some of the acidic lakes also have fairly low concentrations of organic matter.

The approach used to estimate the proportion of naturally vs. anthropogenically acidic lakes includes many assumptions. The results obtained will depend on the base cation change factor (F) used. Within a region the F-factor varies spatially and temporally depending on the watershed characteristics and the pattern of acidic deposition loads. The value of F is a function of the base cation concentration and is 1 at base cation concentrations exceeding 200–400 μeq l^{-1} (Brakke et al. in press).

The empirical model by Oliver et al. (1983) has commonly been used to estimate the organic anion concentration in surface waters. However, this model appears to overestimate the contribution of organic anions when compared with the ion balance method (Brakke et al. 1988; Eilers et al. 1988a), which was observed also in this study. For the calculation of the proportion of naturally acidic lakes it was important to use a value of the carboxyl acid content in the Oliver equation that seemed to give the best agreement with measured anion deficit values. When using the calibrated acid content value a reasonable agreement between these two estimates was obtained. The estimations of the original organic anion concentration were made assuming no changes in the TOC concentrations in the lakes over time. This is a major source of uncertainty because of the extensive peatland ditching and forestry practices carried out in Finland. Such management measures may increase the leaching of organic matter to surface waters (e.g. Ahtiainen 1988). However, several mechanisms have also been proposed to decrease the concentrations of organic matter in lakes receiving acidic deposition (see review by Marmorek et al. 1987).

There is some difference between the estimated proportions of naturally acidic lakes with the different assumptions of background sulphate and the base cation change factor. However, all the different estimates predicted that a large proportion of the presently acidic lakes consists of naturally acidic, highly humic lakes. The lakes estimated to the anthropogenically acidic are located mainly in high deposition areas in southern Finland. These lakes have on average lower concentrations of organic matter and higher concentrations of sulphate than the lakes estimated to be naturally acidic. The proportion of lakes impacted by the acidic deposition is naturally much larger, and a decrease in pH in already acidic lakes has probably also occurred. Although the estimates of the proportions of naturally and anthropogenically acidic lakes are uncertain, they give an indication of the great importance of catchment-derived organic acidity in Finnish waters.

The summer of 1987 was exceptionally cold and rainy. The total precipitation for the summer season set new records for the 20th century over wide areas of southern and central Finland. In northern Finland the conditions were not as exceptional; the summer rainfall was higher than normal in June and August.

However, in July rainfall was less than normal in this region. October was dry throughout the whole country; precipitation was only 30 to 60% of the seasonal mean (National Board of Waters and the Environment 1987). The water quality of the lakes has certainly been affected by these very unusual conditions. Some of the headwater lakes ($n = 59$) surveyed in 1987 were sampled also during fall overturn in 1983 or 1986. Compared with the previous values, TOC concentrations in 1987 were slightly lower for lakes in Subregion 2, and somewhat higher for lakes in Subregion 1 (see Kortelainen and Mannio this Vol.).

Intercomparison between surveys

Results of this survey may be compared with results of other extensive lake surveys in Scandinavia and North America (Jeffries et al. 1986; Swedish Environmental Protection Board 1986; Eilers et al. 1988b; Henriksen et al. 1988a; Landers et al. 1988b). When making these comparisons, one has to keep in mind, however, that the lake selection in the Finnish Lake Survey was targeting not only the most sensitive areas, which was the case both in Norway and in the United States. Some of the distinct differences that are to be noted can be related to the catchment characteristics in these different countries. Some differences are clearly related to the different methodologies in lake selection.

Large numbers of acidic lakes were observed in the survey of 5700 randomly sampled lakes in Sweden in 1985. A total of 4600 lakes were estimated to have $pH < 5.0$, and about 15,000 lakes were estimated to be acidified (Table 6). The highest proportion of acidified lakes was found in southwestern parts of the country (Swedish Environmental Protection Board 1986). The number of lakes with $pH < 5.0$ is approximately equal to the one obtained in the Finnish Lake Survey. However, the chemical analyses of the Swedish lakes did not include all major cations and anions (e.g. sulphate), which makes the estimation of the sources of acidity highly uncertain, and comparison with results from other surveys difficult.

The median concentrations of base cations ($Ca^* + Mg^*$) in the Finnish lakes, 220 $\mu eg\ l^{-1}$ in Subregion 1 and 140 $\mu eg\ l^{-1}$ in Subregion 2, were relatively high compared with the lakes in the Norwegian 1000 lakes survey; over 75% of the Norwegian lakes had $Ca^* + Mg^* < 75\ \mu eq\ l^{-1}$. Large areas of Norway, roughly 45% of the surface area, are underlain by bedrock that is expected to yield runoff waters with low ionic strength. Nitrate concentrations were highest in lakes in southernmost Norway, 100–400 $\mu g\ l^{-1}$. Very large numbers of acidic lakes were observed, although almost all the lakes sampled were greater than 0.2 km^2 in surface area; 40% had $pH < 5.0$ (Table 6) and 60% had $pH < 5.5$. Ninety % of the lakes had $TOC < 6\ mg\ l^{-1}$, and more than 60% $< 2\ mg\ l^{-1}$ (Henriksen et al. 1988a, b), indicating much lower contribution of organic acidity than in Finnish lakes. The water quality of the Norwegian lakes in the northeastern Finnmark area shows close agreement with values from Finnish lakes along the eastern border. An east-west gradient in lake sulphate values can be observed, with clearly higher

Table 6. Population estimates of acidic lakes in Fennoscandia and North America. The median values of pH and ANC (μeq l^{-1}), and the estimated percentage and number (N_c) of lakes below or equal to two reference values (pH 5.0, ANC 0 μeq l^{-1}), are presented

Region	pH			ANC			Reference
	Median	% pH $\leq$ 5.0	N_c	Median	% ANC $\leq$ 0	N_c	
Finland	6.3	10[a]	4100	75	12	4900	1
Sweden		5.6[a]	4600				2
Norway		40[a]					3
Northeast Region, U.S.A.		3.4	240	137[b]	4.6	326	4, 5, 6
Upper Midwest, U.S.A.		1.5	130	287[b]	1.7	148	5, 6, 7
Florida, U.S.A.		12.4	259	76[b]	22	463	5, 6, 8
Southern Blue Ridge, U.S.A.		0	0	236[b]	0	0	5, 6, 8
NW Ontario, Canada	7.1	0		254	<1		9
Quebec, Canada	6.3	3		36	1		9
Nova Scotia, Canada	5.2	39		0	51		9

[a] % pH $<$ 5.0.

[b] Bicarbonate concentration computed from open-system pH and dissolved inorganic carbon.

1 This chapter; 2 Swedish Environmental Protection Board 1986; 3 Henriksen et al. 1988a; 4 Brakke et al. 1988; 5 Landers et al. 1988a; 6 Landers et al. 1988b; 7 Eilers et al. 1988a; 8 Eilers et al. 1988c; 9 Jeffries et al. 1986.

values on the Norwegian side closer to the point sources of air pollutants in the Soviet Union.

The base cation concentrations in several areas covered in the Eastern Lake Survey in the United States are rather comparable to Finnish values. Fairly high median values for dissolved organic carbon (DOC) were also observed, especially in the subregions of northeastern Minnesota, the upper Great Lakes area, and Florida (8.6–9.2 mg l^{-1}). Sulphate values were by far highest in the Northeast region, where 97.3 and 26% of the lakes were estimated to have sulphate ≥ 50 μeq l^{-1} and ≥ 150 μeq l^{-1} respectively. Generally more than 50% of the acidic lakes in these regions had DOC ≤ 3 mg l^{-1}. (Brakke et al. 1988; Eilers et al. 1988a; Eilers et al. 1988c; Landers et al. 1988a; Landers et al. 1988b). The estimated proportion of acidic lakes (ANC ≤ 0 μeq l^{-1}) in the different regions varied between 0–22% (Table 6).

Virtually no acidic lakes were observed in the Western Lake Survey conducted in the United States in 1985, and there was no evidence of chronic acidification in the lakes. The lakes typically had low sulphate concentrations (median 18.9 μeq l^{-1}), and low concentrations of organic matter (median DOC 1.21 mg l^{-1}) (Eilers et al. 1988b).

Compiled data of several extensive surveys conducted in eastern Canada (Jeffries et al. 1986) have shown that variations in the regional and subregional distributions of pH, ANC and sulphate in lakes could be explained by a combination of biogeochemical factors and atmospheric deposition. The Nova Scotia subregion contained the highest proportion of acidic and ultra-low ANC lakes, 51% of the lakes having ANC ≤ 0 μeq l^{-1} (Table 6). The lakes in northwestern Ontario had concentrations of organic anions similar to those in Finland (median 94 μeq l^{-1}). In other subregions median organic anion concentrations ranged from 38 to 56 μeq l^{-1}. The organic anions did not have a predominant influence in the acidic lakes.

Conclusions

Since the beginning of the 1980's it has been well known that acidified lakes occur in many different regions in Finland. However, the Finnish Lake Survey has provided information of the geographical extent of the problem, and regional estimates of the number of the acidic lakes in Finland within a specified level of confidence. The extensive chemical analyses have made it possible to evaluate the role of organic and anthropogenic acidity in the lakes. Furthermore, the statistically based survey design allows estimations of proportions of lakes fulfilling any other predetermined criterias that may be of interest in the future.

The anthropogenic deposition of sulphur is clearly reflected in the water quality of Finnish lakes; elevated sulphate concentrations in lake waters are found in high deposition areas. Nitrate does not presently contribute significantly to the acidity of the lakes. The acidity of Finnish lakes reflects the interaction of the atmospheric loading of sulphate, the catchment sensitivity, and the amount of organic anions present. The effect of the strong mineral acid deposition is superimposed on high natural organic acid contributions to acidity in the lakes.

The proportion of acidic or poorly buffered lakes in Finland is fairly large. The acidic lakes are spread almost around the whole country, however, concentrating in southwestern, central, and eastern regions. The acidic lakes are on average clearly dominated by organic anions, although some lakes have rather low concentrations of organic matter. Based on calculations using a few empirical equations, it can be estimated that 56–81% of the presently acidic lakes are naturally acidic (original pH < 5.3). The lakes that can be assumed to be acidified below pH 5.3 are located mainly in high deposition areas of southern Finland. These lakes have on average lower concentrations of organic matter and higher concentrations of sulphate than the lakes estimated to be naturally acidic.

Few acidic lakes are observed in northeastern parts of Lapland, even though this region receives considerable amounts of acidic deposition. The original buffering capacity of the larger lakes in this region has generally been so high that the present level of acidic deposition has not led to large numbers of acidic lakes. However, there is a fairly large proportion of poorly buffered lakes in the area, and the potential for episodic effects on the biota, particularly during the intensive snowmelt period, cannot be excluded even under the present atmospheric loadings.

Compared with similar lake acidification surveys conducted in Scandinavia and North America, the Finnish lakes show on average high concentrations of organic matter, and a high contribution of organic acidity also in the acidic lakes.

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Modelling Long-Term Development of Surface Water Acidification in Finland

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Summary

This chapter reviews recent applications of two acidification models to Finnish catchments and to Finnish lake regions. The two models, RLM and MAGIC, attempt to describe mathematically the key mechanisms governing surface water acidification. MAGIC is applied to stream water data of two small catchments in southern Finland. RLM is tested against palaeolimnological evidence on the historical time development of lake acidification in southern Finland. The two models are also compared, and differences in predicting the historical dynamics of lake acidification are pointed out. Finally, applications of the RLM model to synoptic survey data are presented. All above applications of the two process-oriented models demonstrate that deterioration of sensitive surface waters will proceed unless significant reductions in deposition are achieved.

Introduction

Air pollutants cause numerous changes in the biotic and abiotic environment. The best known and, perhaps, the most important of the chemical changes is the accelerated acidification of the environment. Acidification is a result of several factors, natural and man-made. The series of chemical reactions starting from the emissions of sulphur dioxide and nitrogen compounds to the depletion of the natural acid neutralizing capacity of freshwaters has been established in extensive research programmes of Europe and North America. This depletion of water acid neutralizing capacity is defined as water acidification.

Conceptualization of the acidification phenomenon has naturally been based on the recent findings on soil and water chemistry. Yet, because we are dealing with a new problem area and thus with a fairly poorly defined system, the modellers have not always chosen exactly the same processes for the key mechanisms that are thought to determine the system behaviour. Additionally, the approaches chosen to represent computationally these various processes and observed water quality patterns have varied. The different models used to date to describe the acidification process include representatives from practically all existing model types (see Kämäri 1987). They range from simple to complex,

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from dynamic to steady state, and from black box to highly deterministic models.

Although the acidifying effect of atmospheric acidic deposition was demonstrated already in the 1960's and the effect of individual catchment characteristics on sensitivity was known already in 1970's, the processes controlling acidification of surface waters have been described quantitatively only quite recently (see e.g. Reuss et al. 1987). These processes include: (1) anion retention by soils and lake sediments (e.g. soil sulphate adsorption and sulphate reduction in lakes), (2) cation desorption by catchment soils, (3) alkalinity generation by carbonic acid dissociation, (4) dissolution of aluminium minerals and mobilisation of aluminium, and (5) weathering of minerals as a source of base cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}).

Two factors appear necessary and sufficient to explain the distribution of acidified waters: the inherent sensitivity of the catchment to acidification and acidic atmospheric deposition. The above key soil processes coupled with inputs of strong acids from the atmosphere explain the observed trends in soil and water acidification in North America and Europe (Reuss et al. 1987). The simultaneous effects of inorganic carbon equilibria, cation exchange, inorganic aluminium equilibria and chemical weathering determine the quality of the runoff from the soil. In pristine areas not subjected to acidic deposition, their simultaneous interaction results in runoff with a high pH, typically above 6, even from naturally podzolized soils.

Acidic deposition increases the flow of strong acid anions, sulphate and nitrate, through the soil solutions. The cations associated with these anions are mainly hydrogen ions and ammonium ions. The hydrogen ion inputs from the atmosphere to the soil take part in two important processes – cation exchange and dissolution of soil minerals (Reuss and Johnson 1985). Aluminium released in the dissolution tends to replace base cations from the negatively charged soil particles and colloids. This phenomenon is referred to as the decrease of soil base saturation.

From these equilibrium reactions one should clearly distinguish the ion fluxes controlling the total amounts of elements in the soils and lakes. In the long run, the element fluxes can alter the equilibrium relationships in the soils. The mechanisms controlling the acidity of freshwaters can be classified on one hand to equilibrium relationships determining ion concentrations at a particular time, and on the other hand, to flux relationships that are dependent on capacity factors (see Reuss et al. 1987). Both types of mechanisms can be identified in both soils and surface waters.

The changes in ion concentrations due to equilibrium relationships are fast. Thus, increased strong acid anion concentrations lead quickly to new equilibrium conditions. The flux relationships cause a slow change in the overall total amounts of elements in the soil, and a significant decrease in base saturation may take decades.

Base cations are of crucial importance in determining the acidity of soils. The elevated sulphate concentrations in the soil solution necessarily lead to elevated cation concentrations, including base cations. The increased sulphate fluxes out of the soil thus lead to increased leaching of base cations. If this base cation leaching is not compensated by fluxes originating from base cation deposition or weathering, the equilibrium concentrations in the soil change accordingly: base saturation decreases, soil acidifies and the alkalinity of soil solution decreases. This changes the chemistry of the water discharging from the soil.

In sensitive areas the acidic deposition can mobilise hydrogen and aluminium ions in amounts that are toxic to fish. Where soils have naturally low base saturations, even low acidic deposition may increase the hydrogen and aluminium concentration to such an extent that the alkalinity drops below zero. As a consequence, acidic water is being drained from the soil without any change in the soil base saturation.

In acidification studies the focus is recently being moved from qualitative analysis to quantitative approaches. As a result of extensive research on mechanisms, the processes have been identified that can explain the long-term dynamics of surface water acidification. In the following, models are presented that attempt to describe some of these mechanisms mathematically and provide predictions on the long-term development of acidification. Recent applications of the two models, RLM and MAGIC, to Finnish catchments and regions are reviewed.

Models Describing Long-Term Surface Water Acidification

The MAGIC Model

As emphasized above, certain chemical processes are assumed to be likely keys to the responses of surface water quality to acidic deposition. The MAGIC model (Model of Acidification of Groundwater In Catchments) is based on mathematical representations of those processes (Cosby et al. 1985a). The model is conceptually simple with regards to spatial heterogeneity in the catchment. The model contains four compartments which are assumed to be internally homogenous. The objective is to estimate long-term (i.e. decades) changes in annual average water quality.

Atmospheric deposition, mineral weathering and cation exchange processes in the soil and soil water are assumed to be responsible for the observed surface water chemistry in a catchment. The model calculates the concentrations of base cations, three strong acid anions (SO_4^{2-}, Cl^-, NO_3^-) and organic anions in both soil and stream water. Alkalinity is generated in the soil water by the formation of bicarbonate from dissolved CO_2 and water. Sulphate is assumed to have an adsorbed phase in the catchment soils. The model assumes that Al^{3+} and four base cations are involved in cation exchange between soil and soil solution. The parameters describing the cation exchange process in the model are the selectivity coefficients, S_{AlBC} (one coefficient for each base cation) and the cation exchange capacity, CEC. Details of the equations and the model structure have been given by Cosby et al. (1985a,b).

The RLM Model

This model, termed the RAINS Lake Module (RLM), has been developed at the International Institute for Applied Systems Analysis (IIASA) as part of the integrated RAINS (Regional Acidification Information and Simulation) model system (see Alcamo et al. 1987). RLM provides a simple representation of those processes only that are believed to be most important in controlling the long-term acidification dynamics. For example, the sulphate adsorption is not included since the young podzolic soils of Finland, developed in post-glacial times on granitic bedrock have been considered as having low SO_4-adsorption capacities (cf. Johnson and Todd 1983). The model separates the catchment into three distinct water reservoirs (two soil layers and lake), between which it computes the fluxes of major ions contributing to acidity or alkalinity of surface waters. The processes incorporated into the model include (1) forest filtering effect, (2) weathering of base cations, (3) cation exchange, (4) aluminium equilibrium with gibbsite, (5) in-lake sulphate retention, and (6) in-lake carbonic acid dissociation.

The principal driving variables of the RLM model are the total deposition of sulphur and base cations. This input is supplied for the model by observations or transport/deposition models. The observed throughfall deposition generally exceeds the deposition predicted by the transport models. To overcome this problem, the modelled deposition to an area is allocated to forests and to open land by assigning the deposition on forested land to exceed that on open land by a specified factor (see Kämäri 1986).

To calculate lake water pH and alkalinity, the ion fluxes from both soil and atmosphere into the lake are considered; the flux of protons to the lake is the sum of the convective flow of ions from the two soil reservoirs and directly from the atmosphere. The fluxes of bicarbonates contributing to the alkalinity of the lake originate both from the terrestrial catchment and from the in-lake (internal) alkalinity generation (cf. Baker et al. 1986). The above ion fluxes mix with the lake water and cause a change in the bicarbonate and hydrogen ion concentrations until an equilibrium according to specified inorganic carbon species is reached.

Data Sources for Model Applications

The applications draw on data on soils (Nuotio et al. this Vol.), precipitation chemistry (Järvinen and Vänni this Vol.) and deposition estimates (Tuovinen et al. this Vol.) that all have been collected during the HAPRO project. The lakes and streams in this study are included in the research programme of the water and environment administration. Therefore, rather extensive chemical and biological data are available from these forest catchments (see Kenttämies et al. 1985; Lepistö and Seuna this Vol.). The palaeolimnological reconstruction of pH history are given by Tolonen and Jaakkola (1983) for Lake Orajärvi and by Simola et al. (1985) for Lake Siikajärvi.

The historical deposition patterns used to drive the model are constructed by assuming they are strictly proportional to European total sulphur emissions (e.g. Fjeld 1976). Based on this historical emission information, a relative deposition pattern is derived, which is then used to calculate the deposition patterns for each individual site. The deposition is scaled such that the presentday deposition agrees with present estimated values at each site.

Responses of Individual Catchments

Stream Waters

The Catchments Studied

A modelling exercise using the MAGIC model was undertaken for two contrasting conifer forest catchments in Finland. The Yli-Knuutila (0.07 km^2) catchment in southern Finland is characterized by well-buffered soils; annual average pH values in the stream water are over 6 with high concentrations of base cations and sulphate. Yli-Knuutila consists mainly of Norway spruce (*Picea abies*); the volume of growing stock is high, 162 m^3 ha^{-1}. The catchment is described by Lepistö and Seuna (this Vol.). The Liuhapuro (1.65 km^2) catchment of eastern Finland is characterized by peatlands and dilute, acid surface waters (annual average pH 4.2–4.4) with high quantities of dissolved humic substances. Coniferous forests dominate in the area; volume of growing stock is 105 m^3 ha^{-1}. The mineral soil consists of silty and sandy moraines. There is no arable land or lakes in the catchments and the only anthropogenic factor affecting stream water chemistry is atmospheric deposition. Modelling of these two catchments has recently been discussed by Lepistö et al. (1988) and comparison of Liuhapuro pH reconstruction to palaeolimnological data by Lepistö (1989).

Materials and Methods

Stream water samples were collected at the measuring weirs, concentrating sampling at spring and autumn periods of high flow. The number of water samples varied from 16 to 32 annually. Analysing methods have been described by Lepistö and Seuna (this Vol.).

Yli-Knuutila. Atmospheric deposition of base cations and strong acid anions was calculated using concentrations of each ion in precipitation (Table 1) and the precipitation volume. Annual precipitation at Yli-Knuutila in 1984 was 750 mm, of which 198 mm appeared as runoff in stream.

Sulphur deposition in excess of sea salt inputs was increased by a constant factor, 1.3, to account for dry deposition of anthropogenically derived sulphur. A basic assumption of the modelling exercise was that the catchment was in steady state with constant background levels of deposition prior to 1844. A 140-yr deposition history was estimated for southern Finland based on an estimate of changes in sulphur dioxide emissions in the whole of Europe and Finland (Ministry of the Environment 1984; Kulmala 1985). Observed soil data, values of the

Table 1. Chemical characteristics of bulk precipitation in 1984, model output of stream-water quality variables at different points in the simulation and a comparison with measured values in 1984 in Yli-Knuutila

$\mu eq\ l^{-1}$	Bulk precipit. 1984	Stream water model output 1844 background	Stream water model output 1984	Stream water measured 1984
H^+	68	0.3	0.6	0.8
Ca^{2+}	49	90	377	400
Mg^{2+}	14	72	281	301
Na^+	29	95	171	167
K^+	5	11	23	28
NH_4^+	76	0	6	7
SO_4^{2-}	122	13	603	585
NO_3^-	60	3	89	80
Cl^-	26	100	100	103[a]
HCO_3^-	–	152	65	74
Cations	241	268	858	904
Anions	208	268	857	841
pH	4.2	6.6	6.2	6.1

[a] Mean value of 1983 and 1985.

selectivity coefficients and estimated weathering rates for the Yli-Knuutila catchment have been published by Lepistö et al. (1988).

Two scenarios were used for projecting future water quality in Yli-Knuutila. The first scenario assumes continued deposition at current (1984) rates for the next 140 years. The second scenario assumes a 50% reduction of the deposition in excess of sea salts during the next 20 years.

Liuhapuro. The year 1983 was selected for calibration of the model because of the most frequent data for sulphate in stream water. Annual precipitation at Liuhapuro in 1983 was 766 mm, of which 480 mm was runoff. Sulphate deposition in excess of sea salt inputs was increased by a constant factor, 1.1, to account for dry deposition of anthropogenically derived sulphur. The same deposition curve was used for Liuhapuro as for Yli-Knuutila. The presentday (1983) concentrations of each ion in precipitation are given in Table 2. Background (1843) deposition inputs were calculated from the sea salt fraction of current deposition at Liuhapuro. Soil parameters, values of the selectivity coefficients and estimated weathering rates for the Liuhapuro catchment have been published by Lepistö et al. (1988). Estimates of weathering rates for calcium, magnesium and potassium are about the same for both catchments, for sodium the one for Liuhapuro is much higher.

Table 2. Chemical characteristics of bulk precipitation in 1983, model output of stream water quality variables at different points in the simulation, and a comparison with measured volume weighted mean values in 1983 at Liuhapuro

$\mu eq\ l^{-1}$	Bulk precipit. 1983	Stream water model output 1843 background	Stream water model output 1983	Stream water measured 1983
H^+	35	26	36	54
Ca^{2+}	18	38	65	67
Mg^{2+}	5	28	45	47
Na^+	10	37	47	48
K^+	3	4	5	7
NH_4^+	13[a]	0	0	0
Al^{3+}	–	4[b]	10[b]	13[b]
SO_4^{2-}	53	2	81	82
Cl^-	9	14	14	14[c]
NO_3^-	21	0	2	0
A^-	–	118	109	104[d]
Cations	84	137	208	236
Anions	83	134	206	200
pH	4.5	4.6	4.4	4.3

[a] Estimated.

[b] All the aluminium assumed as Al^{3+}.

[c] 1984.

[d] Estimated according to Oliver et al. (1983).

Characterization of the Stream Water and the Model Results

Yli-Knuutila. Bulk precipitation at the Yli-Knuutila catchment was acid (pH 4.17) and had high concentrations of sulphate, 122 $\mu eq\ l^{-1}$, and nitrate, 60 $\mu eq\ l^{-1}$ (Table 1). Average bulk deposition of sulphur in this station was 0.9 g S m^{-2} a^{-1} during the years 1971–82 (Järvinen and Vänni this Vol.). Table 1 shows the ion balance of stream water in 1984, which is almost the same as that calculated for 1985 (Lepistö and Seuna this Vol.), when the annual number of samples was over three times higher.

High concentrations of calcium, magnesium and sulphate dominate the stream water chemistry. Sodium, chloride and nitrate also are relatively important on an equivalent basis. There was 74 $\mu eq\ l^{-1}$ alkalinity in the stream in 1984. During high flow, alkalinity drops to zero. pH values as low as 5.5 occurred during the snowmelt peak in spring 1985. The volume weighted annual average pH was 5.9 in 1985 and 6.1 in 1984. Hydrochemical characteristics of the Yli-Knuutila stream during snowmelt of 1985 are discussed by Lepistö and Seuna (this Vol.).

Ammonium nitrogen deposited on the catchment was used very effectively by the vegetation; the concentration in the stream water was less than one-tenth of that of precipitation. Nitrate nitrogen behaved in a different way, however. Concentrations in the stream water were higher than in precipitation, the main reasons being probably effective nitrification of ammonium to nitrate and relatively high deposition of nitrogen. Increase in the nitrate-nitrogen concentrations of stream water during the last 20 years is discussed by Lepistö and Seuna (this Vol.).

Volume weighted annual concentrations of variables estimated by the model for 1984 can be compared with those measured at Yli-Knuutila in 1984 (Table 1). The historical reconstruction of water quality at Yli-Knuutila indicates that the catchment surface waters have lost 90 μeq l^{-1} of alkalinity, which is about 60% of their pre-acidification alkalinity in 140 yrs (Fig. 1a). This estimate is about the same as the average loss estimated for the small clearwater forest lakes of the southern coastal area in Finland (Kämäri 1985). During the same period the sum of base cations (SBC) has increased up to three times from the pre-acidification background value. The increase in SBC is due to increased leaching of base cations from the soil exchange sites mainly due to increased quantities of sulphate passing through the soil layers and also due to increased inputs of base cations in precipitation.

According to the model, the decline in pH of stream water at Yli-Knuutila has been 0.4 pH units, from 6.6 to 6.2 during the 140-yr period (Fig. 1a). The majority of the decline has occurred in the last 30 years. Continued deposition at current

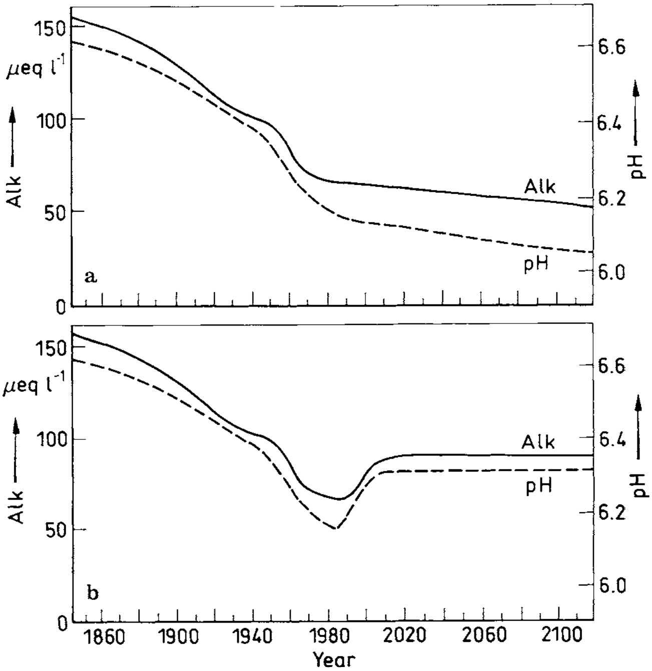

Fig. 1a,b. Simulation of alkalinity and pH at Yli-Knuutila in response to two scenarions of future atmospheric deposition; **a** no reduction, **b** 50% reduction in 1985–2005 levels will result in further decreasing of pH and alkalinity at Yli-Knuutila with constant conditions in the sum of base cations and strong acid anions. A reduction by 50% of deposition over a 20-yr period (1985–2005) results in an improvement of water quality with considerably smaller leaching of base cations from the forest soil. That is followed by reasonably steady conditions (Fig. 1b) but not a return of the buffer capacity to preacidification levels.

Liuhapuro. Chemical characteristics of bulk precipitation and streamwater in Liuhapuro are shown in Table 2. Bulk precipitation was moderately acidic with an average pH of 4.46 in 1983. Average bulk deposition of sulphur in 1971–82 was 0.56 g S m^{-2} a^{-1} (Järvinen and Vänni this Vol.), about 60% that of the deposition at Yli-Knuutila.

Streamwater of Liuhapuro is more acidic than precipitation and has high concentrations of humic substances. Organic anions, A^-, are the main factor causing the difference between the measured sums of cations and anions in stream water. An estimate of organic anion concentration, A^{-1}, that results from the dissociation of humic material, HA, was made from the measured pH and COD values of Liuhapuro, using the method presented by Oliver et al. (1983) yielding a value 103.6 μeq l^{-1} for A^- (see Lepistö et al. 1988). When adding organic acid concentration A^- to the sum of inorganic anions a good charge balance was observed (Table 2). Organic anions contribute about 50% of anions at Liuhapuro. Sulphate was clearly the dominant inorganic anion, 82 μeq l^{-1} in 1983. The range of pH was 4.0–5.8 with the lowest values occurring during high flow. Calcium was the dominant cation (67 μeq l^{-1}).

Concentrations of variables estimated by the model for 1983 can be compared with the volume weighted mean annual values of those variables measured at Liuhapuro (Table 2). The reconstructed trajectories of the pH, base cations except potassium, and sulphate in streamwater (Fig. 2) all show accelerating rates of change in response to the increased atmospheric deposition of sulphate. The increase in base cations is due to increased leaching from the soil exchange sites in response to increased quantities of sulphate passing through the soil layers. Calcium and magnesium concentrations have increased 60–70% from the preacidification values estimated by the model.

Aluminium species are likely to account for a considerable part of the buffer intensity not related to carbonate system and organic compounds. In addition to Al^{3+} and aluminium hydroxides, aluminium complexes with fluoride and with organic compounds are of importance (Driscoll et al. 1980). Unfortunately only total aluminium has been analysed. In 1983 volume weighted mean of total aluminium was 114 μg l^{-1} (13 μeq l^{-1}); the range was 50–280 μg l^{-1}. Total aluminium was simulated to have increased from 4 to 10 μeq l^{-1} during the period studied (Fig. 2). It seems that Al^{3+} and H^+ are increasing on the soil-exchange complex. The risk of an increasing leaching of aluminium to surface waters is obvious, and has already occurred to some extent.

The stream has been acid before atmospheric pollution because of the high load of organic acids. According to the model there has been a decline of 0.2 pH units.

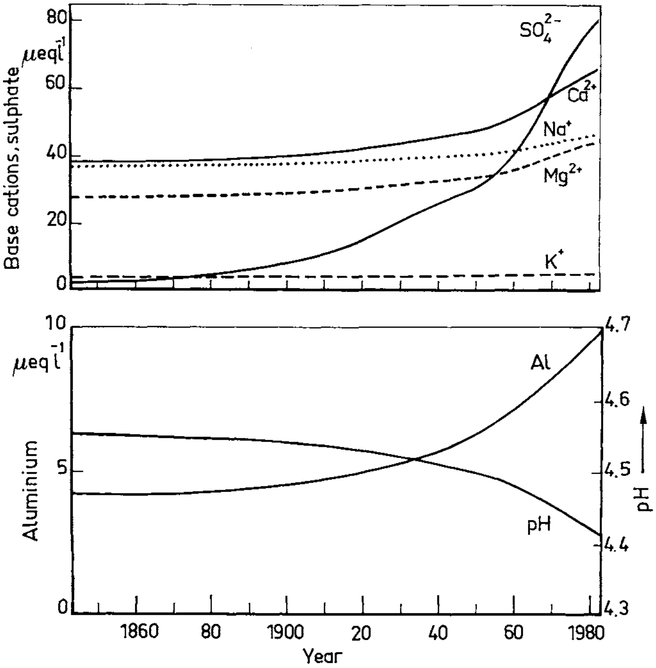

Fig. 2. Model reconstruction of base cations, sulfate, total aluminium and pH of stream water for the 140-year period at Liuhapuro

H^+ concentration is estimated to have increased 10 μeq l^{-1}, from 26 to 36 μeq l^{-1} by 1983. The simulated pH history is comparable to the results of diatom analysis from the small, humic Lake Matojärvi in the same region (Huttunen et al. this Vol.). The addition of H_2SO_4, of atmospheric origin, has increased the acidity of dilute, organic waters at Liuhapuro despite the buffering system of organic compounds. It is probable that, together with increasing acidity, the annual variation of the pH has become larger with more acid stream water during the melt period and the autumn rains.

Concluding Remarks on MAGIC Application

Application of the model to a peaty catchment with high concentrations of organic acids in stream water presented no difficulty. The model reconstructed stream water chemistry in two very different types of catchments and surface waters. Similar success has been obtained applying the model to catchments in Scotland receiving large amounts of neutral sea salts (Cosby et al. 1986) and in Wales (Whitehead et al. 1987).

There has been a significant change in the quality of the surface waters of Yli-Knuutila with declining alkalinity (90 μeq l^{-1}) and increasing sulphate; together with leaching of high quantities of base cations, mainly calcium and magnesium, from the soils. The response of the organic rich soils of Liuhapuro has been quite different. Liuhapuro was acidic even before the atmospheric pollution; a recent decline of 0.2 pH units was estimated with increased leaching of base cations and aluminium from the soils.

Lake Waters

Catchments Studied

The RLM model was applied to two individual catchments for which there were palaeolimnological diatom data (Table 3). Lake Orajärvi is a small clearwater, oligotrophic, acidified lake located in a sparsely populated forest area about 25 km north-west of the city of Helsinki. This region receives the highest acid deposition in Finland. The bedrock in this region is composed of Precambrian granites, with a large portion of exposed bedrock (Table 3). The soil is very thin, and the prevailing soil type is gravelly moraine. The lake catchment also contains some peatland. There are no roads or human settlements. Scots pine (*Pinus Sylvestris*) is the dominant tree species. *Sphagnum* carpets cover large areas of the bottom of the lake.

Lake Siikajärvi is a moderate size (0.90 km^2), oligotrophic, fairly acidic clearwater lake in the southern part of the country. It is the largest acidified lake detected by palaeolimnological research in Finland (Simola et al. 1985). This part of the country still receives fairly high levels of acid deposition (Table 3). Coarse moraine forms a major part of the catchment, with a rather high percentage of

Table 3. Characteristics of the lake catchments. Water quality based on fall samples

Catchment characteristics	Orajärvi	Siikajärvi
Total sulphur deposition (1980) (meq m^{-2} yr^{-1})	115	80
Lake area (km^2)	0.22	0.90
Maximum lake depth (m)	5.9	23.0
Catchment area (km^2)	0.76	3.00
Soil types (%)		
Bare rock or very thin soils	32	19
Till	60	70
Sand and gravel	0	0
Peat	8	11
Lake water quality		
pH	4.7–4.8	5.0–5.5
Alkalinity (μeq l^{-1})	<0	<20
Colour (Pt mg l^{-1})	5–10	20–30
TOC (mg l^{-1})	1.0–1.5	4.0–5.0
Ca (mg l^{-1})	1.6–2.0	1.3–2.5
Mg (mg l^{-1})	0.5–0.6	0.5–0.6
Na (mg l^{-1})	1.2–1.5	1.0–1.2
K (mg l^{-1})	0.3–0.5	0.3–0.4
Cl (mg l^{-1})	1.5–2.1	0.9–1.0
SO_4 (mg l^{-1})	6.1–9.2	6.5–7.2

exposed bedrock or very thin soils. The drainage area also contains some peatland (Table 3). The catchment is undisturbed except a modest forest clearcutting at one side of the lake. The prevailing tree species are Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*).

Materials and Methods

A formal approach to hypothesis testing, based on numerical simulation and Monte Carlo methods, has been proposed by Fedra (1983). To test a specific model, it is examined whether, for a set of ranges of initial conditions and parameters, allowable outcomes can be produced. The model has to be rejected if no allowable outcome can be generated from a statistically sufficient number of trials. If a simple model version fails to give an acceptable behaviour over the allowable input ranges, it can be modified by adding more complex process descriptions to the model.

The model version of RLM to be tested, viewed as a hypothesis, was incorporated into the Monte Carlo framework, which randomly sampled a parameter vector from the assigned allowable ranges. The model was run with a historical deposition pattern through a period of 140 years, from 1850 to 1990. All information about the run was stored. This process was repeated 1000 times for each lake. Finally, the set of runs obtained was analysed for violations of the constraint conditions in the course of the simulations. A Monte Carlo simulation is thus performed to investigate whether realistic parameter regions existed for which the model structure gives results that coincide with a predefined behaviour derived from the palaeolimnological data and recent observations.

The RLM model requires data for catchment characteristics, soil characteristics, weathering rate, runoff and sulphur and base cation deposition patterns. It was decided to vary practically all poorly known parameters, and initial conditions around their mean (shown in Table 4) in the Monte Carlo simulation. Only those parameters and variables were not randomised that can be considered well known (e.g. lake and catchment area) or strongly dependent on other variables being varied (e.g. hydraulic conductivity). Allowable input ranges for the studied catchments (Table 5) were formulated based on various data sources.

The uncertainty in the pH reconstructions was considered when assigning the constraint ranges giving the behaviour definition. The palaeolimnological reconstruction is a result of two independent somewhat uncertain measurements. First, inferring the pH of a lake from diatom occurrence using a pH index involves some uncertainty. Additional uncertainty is introduced when the age of the sediment sample to be inferred is determined.

According to Renberg and Hellberg (1982), the ancient pH of a lake can be inferred with a mean accuracy of +/−0.3 pH units by using their pH index. However, several factors, including changes in land use and special hydrological conditions can cause major errors in the pH reconstructions (e.g. Battarbee and Flower 1984). The dating of the sediment samples by lead-210 has been found to be

Table 4. Lake and catchment properties used in the Monte Carlo runs. For those variables that were randomly varied the mean is given. The actual ranges of variation around that mean are given in Table 5. Values for the equilibrium constants are given for units eq m^{-3}

Variable	Unit	Definition	Lake Orajärvi	Lake Siikajärvi
A_l	ha	Lake area	22	90
A_c	ha	Terrestrial catchment area	54	210
bs_a		Base saturation in A-layer	0.40	0.45
bs_b		Base saturation in B-layer	0.40	0.30
CEC	eq m^{-2}	Total cation exchange capacity	300	36
f		Forest coverage fraction	0.40	0.40
K_1		First dissociation constant of H_2CO_3	$10^{-3.3}$	$10^{-3.3}$
K_H		Constant of Henry's law	$10^{1.5}$	$10^{1.5}$
K_{so}		Solub. constant for solid phases of Al	948	948
k_{SO_4}		SO_4 in-lake retention rate coefficient	0.22	0.46
k_s	ms^{-1}	Hydraulic conductivity at saturation	9	200000
pCO_2	atm	Partial pressure of CO_2 in surface water	0.00123	0.00123
γ		Forest filtering coefficient	2.0	2.0
Q_{tot}	m	Total runoff	0.314	0.270
S	m m^{-1}	Surface slope	0.06	0.01
θ_f		Soil moisture content at field capacity	0.4	0.4
wr	eq m^{-3} yr^{-1}	Weathering rate of base cations	0.035	0.028
W	m	Catchment width	2376	4752
Z_l	m	Mean lake depth	3.9	15.3
Z_s	m	Soil thickness; sum of A- and B-layers	0.70	0.90

Table 5. A priori input ranges and statistics of the a posteriori accepted Monte Carlo runs for the two lakes studied. For the description of the symbols and units see Table 4

Lake Orajärvi

Variable	A priori range		A posteriori statistics			
	Min	Max	Min	Max	Mean	S.D.
bs_a	0.30	0.50	0.30	0.50	0.40	0.059
bs_b	0.25	0.55	0.25	0.55	0.41	0.081
CEC	240.0	360.0	240.4	359.3	299.3	32.29
f	0.32	0.48	0.33	0.48	0.41	0.046
K_{so}	377.7	1503.6	380.1	1466.7	903.9	332.94
k_{SO_4}	0.11	0.44	0.11	0.43	0.25	0.088
θ_f	0.28	0.52	0.28	0.52	0.40	0.069
pCO_2	2.5×10^{-4}	6.2×10^{-3}	2.7×10^{-4}	3.5×10^{-3}	1.5×10^{-3}	7.62×10^{-4}
γ	1.60	2.40	1.60	2.39	1.97	0.222
Q_{tot}	0.28	0.35	0.28	0.34	0.31	0.018
S	0.042	0.078	0.043	0.076	0.060	0.011
wr	0.024	0.046	0.025	0.045	0.036	0.006
Z_l	3.15	4.72	3.19	4.68	3.97	0.418
Z_s	0.49	0.91	0.61	0.91	0.80	0.073

Lake Siikajärvi

Variable	A priori range		A posteriori statistics			
	Min	Max	Min	Max	Mean	S.D.
bs_a	0.35	0.55	0.35	0.55	0.44	0.059
bs_b	0.15	0.45	0.15	0.45	0.31	0.099
CEC	28.8	43.2	28.8	43.2	35.9	4.50
f	0.32	0.48	0.32	0.48	0.40	0.047
K_{so}	377.7	1503.6	379.5	1491.3	905.1	325.38
k_{SO_4}	0.23	0.92	0.23	0.92	0.54	0.198
θ_f	0.28	0.52	0.28	0.52	0.40	0.071
pCO_2	2.5×10^{-4}	6.2×10^{-3}	1.1×10^{-3}	6.1×10^{-3}	3.7×10^{-3}	1.30×10^{-3}
γ	1.60	2.40	1.60	2.40	1.97	0.235
Q_{tot}	0.24	0.30	0.24	0.29	0.27	0.015
S	0.007	0.013	0.007	0.013	0.010	0.0018
wr	0.020	0.036	0.020	0.036	0.028	0.0046
Z_l	12.26	18.40	12.32	18.39	15.39	1.859
Z_s	0.63	1.17	0.64	1.16	0.88	0.131

dependent on the sedimentation conditions in the lake (Appleby and Oldfield 1978). It has, moreover, been shown that the adsorption affinity of Pb into sediment particles might decrease at low pH, which will cause errors in the sediment dating in acidified waters (Simola and Liehu 1985). Uncertainty of +/−0.3 pH units was assigned to the pH estimates and +/−10 years to the age of the sediment sample.

The historical deposition patterns, used to drive the model, were constructed by assuming that they were strictly proportional to European total sulphur emissions given by Fjeld (1976). The deposition was scaled such that the presentday deposition agreed with modelled values at each site (Sulphur Commission of Finland

1986). The historical deposition pattern for base cations was constructed in a similar way. In 1850 the deposited base cation equivalents were assumed to equal those of sulphates. From this value on the base cation deposition was scaled so that the value used for 1980 corresponded to the observed non-marine base cation deposition at each location (Järvinen and Vänni this Vol.).

Results of RLM Applications to Lakes

To illustrate the results of RLM for the two catchments, the modelled historical time evolution of lake pH is displayed in Fig. 3, together with the corresponding time evolution inferred from diatoms. The displayed three thin lines represents the minimum-maximum envelope and the mean of all behaviour giving individual runs. The thick lines represent the calculated uncertainty range for the lake pH inferred from palaeolimnological diatom remains. This pH envelope was used as the performance criterion, or constraint condition that the model output was expected to meet in order to give rise to a behaviour. The variability of the individual runs can be interpreted as the uncertainty in the model results due to the uncertainty in the input data, as well as in the measurement of the pH history. This means that some of the initial uncertainty is taken into account throughout the long term simulation. If there were no information to constrain the output, the uncertainty band would become extremely wide. This is shown in Fig. 3 as the

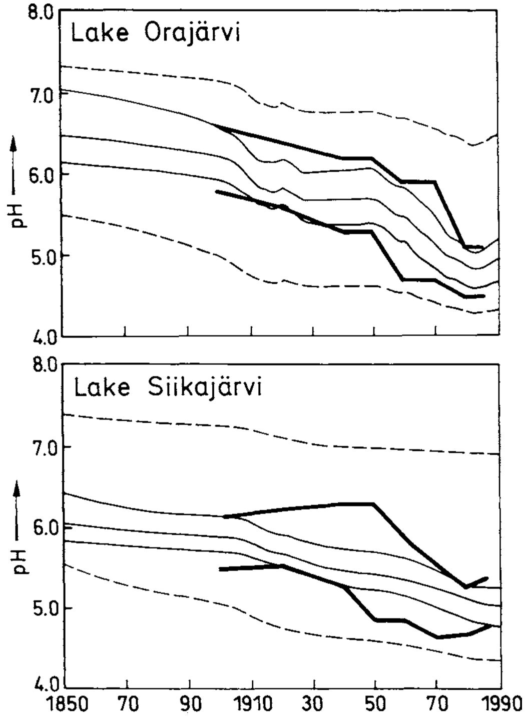

Fig. 3. Monte Carlo simulation of lake pH of the two study lakes driven by historical deposition pattern. The minimum-maximum pH envelopes as well as the median of the accepted Monte Carlo runs (*thin lines*) are displayed together with the pH history inferred from the diatoms (*thick lines*). The widest envelope (*broken lines*) represents the total variability in the model output due to uncertainty in the inputs

widest envelope (broken lines), which thus denotes the total level of uncertainty in model output due to uncertainty in model inputs.

Both independent sources of information, the model and the diatom analyses, suggest a similar lake acidification pattern for both example lakes. For both lakes, Orajärvi and Siikajärvi, a quite steep decline in pH during the last three decades is pointed out by diatoms and reproduced also by model results. The parameter statistics of the behavior giving model runs presented in Table 5 showed for Lakes Siikajärvi and Orajärvi that the RLM model could produce the required pH dynamics with a subset of parameter vectors that clustered close to the mean point in the n dimensional parameter space. The average parameter set presented in Table 4 was at least close to a behaviour giving parameter set. This can be considered promising since these prespecified mean values and the ranges around them were assigned on the basis of some, although quite uncertain, a priori knowledge of the catchments.

Concluding Remarks on RLM Application

A hypothesis can be accepted as a valuable working tool with explanatory value and predictive capabilities only if it fulfills all the constraints one can formulate as defining the systems behaviour (Fedra 1983). The required systems behaviour was defined here as the pH history of a given lake. Several constraints along the history up to recent observations were formulated. Based on the results of the Monte Carlo runs, one can conclude that there is no reason to reject the current model version since it was possible to find for all lakes from a sufficient number of trials parameter sets that gave rise to the prespecified behaviour. Only if one is prepared to increase the credibility of the diatom data and constrain the output more, could deficiences in the model versions show up that call for model refinement.

Comparison of RLM and MAGIC

Materials and Methods

Data for models. The two models described earlier were compared by applying the models to the two lakes, Lake Orajärvi and Lake Siikajärvi, discussed already in the previous section. The input values for the RLM applications are essentially those shown in Table 4. In calibrating, minor differences resulted for base saturation and weathering rate values assigned for the year 1850. The actual values used are presented by Forsius (1989). The input values used for the MAGIC model are shown in Table 6.

The yearly average values of the major cations and anions were calculated from mean monthly bulk deposition values from the years 1979–81 (Järvinen and Vänni this Vol.) from nearby monitoring stations. A dry deposition factor calculated from the difference between modelling and measured values was used to correct the sulphur concentration values in the MAGIC model. Historical lake alkalinity was

Table 6. Parameter values used for MAGIC reconstructions. Data are either measured or estimated (see text for data sources)

Catchment characteristics	Orajärvi	Siikajärvi
Precipitation	0.58	0.57
Runoff (m yr^{-1})	0.31	0.31
Quickflow (%)	95	94
Baseflow (%)	5	6
Mean temperature (°C)	5	5
Soil characteristics		
Mean depth (m)	0.8	0.9
Porosity (fraction)		
Layer 1	0.6	0.6
Layer 2	0.4	0.4
Density (kg m^{-3})		
Layer 1	1000	1000
Layer 2	1500	1500
CEC (eq m^{-3})	300	36
Total weathering rate (eq m^{-3} yr^{-3})	0.0350	0.0320
Ca (eq m^{-3} yr^{-1})	0.0180	0.0110
Mg (eq m^{-3} yr^{-1})	0.0100	0.0100
Na (eq m^{-3} yr^{-1})	0.0035	0.0075
K (eq m^{-3} yr^{-1})	0.0035	0.0035
Sulphate adsorption		
half-saturation (meq m^{-3})	170	150
maximum capacity (meq kg^{-1})	9	6
Selectivity coefficients		
layer 1: log S (AlCa)	0.3	0.0
log S (AlMg)	2.0	1.7
log S (AlNa)	−1.0	−1.5
log S (AlK)	−3.7	−3.5
aluminium solubility	8.1	8.0
layer 2: log S (AlCa)	5.7	5.9
log S (AlMg)	6.8	6.9
log S (AlNa)	1.9	1.9
log S (AlK)	0.3	−0.3
aluminium solubility	10.8	10.8
Uptake rates		
NH_4 (meq m^{-1} yr^{-1})	103	92
NO_3 (meq m^{-1} yr^{-1})	95	84
pCO_2 (atm)		
Layer 1	0.1	0.1
Layer 2	0.02	0.02
Lake characteristics		
Uptake rates		
NH_4 (meq m^{-1} yr^{-1})	96	86
NO_3 (meq m^{-1} yr^{-1})	87	70
pCO_2 (atm)	0.0006	0.0006

estimated from the pH values reconstructed from palaeolimnological diatom data according to Wright et al. (1986).

Strategy for model comparison. The aim of this study was to evaluate some aspects of the uncertainty incorporated in the RLM model, by comparing the simulation results of this model with the results of the more complex model MAGIC. In order to obtain as comparable results as possible, MAGIC was run with initially calibrated input values of RLM. The model runs of both models were also compared with the historical pH and alkalinity values obtained from the diatom stratigraphies. Furthermore, a Monte Carlo parameter estimation procedure was used in both models to evaluate the uncertainty in the model predictions.

In the first stage, a set of input values was chosen for RLM by using the Monte Carlo parameter estimation procedure, so that model predictions for lake and soil chemistry agreed with measured presentday values, and with the pH values from the diatom reconstructions. These values were then used also in the MAGIC applications. While retaining the total weathering rate of base cations obtained in the RLM calibration, the weathering rates for each individual base cation, and the selectivity coefficients determining the cation exchange reactions in MAGIC were adjusted so that the best possible fit with measured values was obtained. The parameter values determining the sulphate adsorption and nitrogen uptake rates were similarly adjusted (see Forsius 1989). The selected period for the model reconstructions was 1850–1980.

After this initial adjustment of critical model parameters, the Monte Carlo approach was used to estimate input values for those three variables that were used by both models in a similar way: total weathering rate, total cation exchange capacity (CEC) and lake retention time (or maximum lake depth in RLM). A range of 30% was chosen for all three selected, initially calibrated parameters, and 100 Monte Carlo simulations were carried out for each catchment by randomly selecting a set of input values from within these designated ranges. The equations were then solved using these particular sets of input values.

After the simulations, the model output was constrained by using measured values for lake pH in 1979–80. Only model runs for which simulated lake pH deviated at the most by 0.2 pH units from measured mean values were accepted.

Results of Model Comparison

The pH reconstructions obtained from the diatom stratigraphy at Lake Orajärvi (Tolonen and Jaakkola 1983) suggest that the "pre-acidification" pH was about 6.3 compared with measured values of 4.7–4.8 in 1979–1981. RLM and MAGIC reconstructions indicate higher initial pH and alkalinity values (Fig. 4). The simulation results of RLM show a sharper decline in these values with time than MAGIC. A rather good agreement is obtained between MAGIC simulations and diatom reconstructions of alkalinity.

The diatom curve for lake Siikajärvi (Simola et al. 1985) suggests that the lake originally had a pH of 5.8–5.9, and that acidification to presentday values of

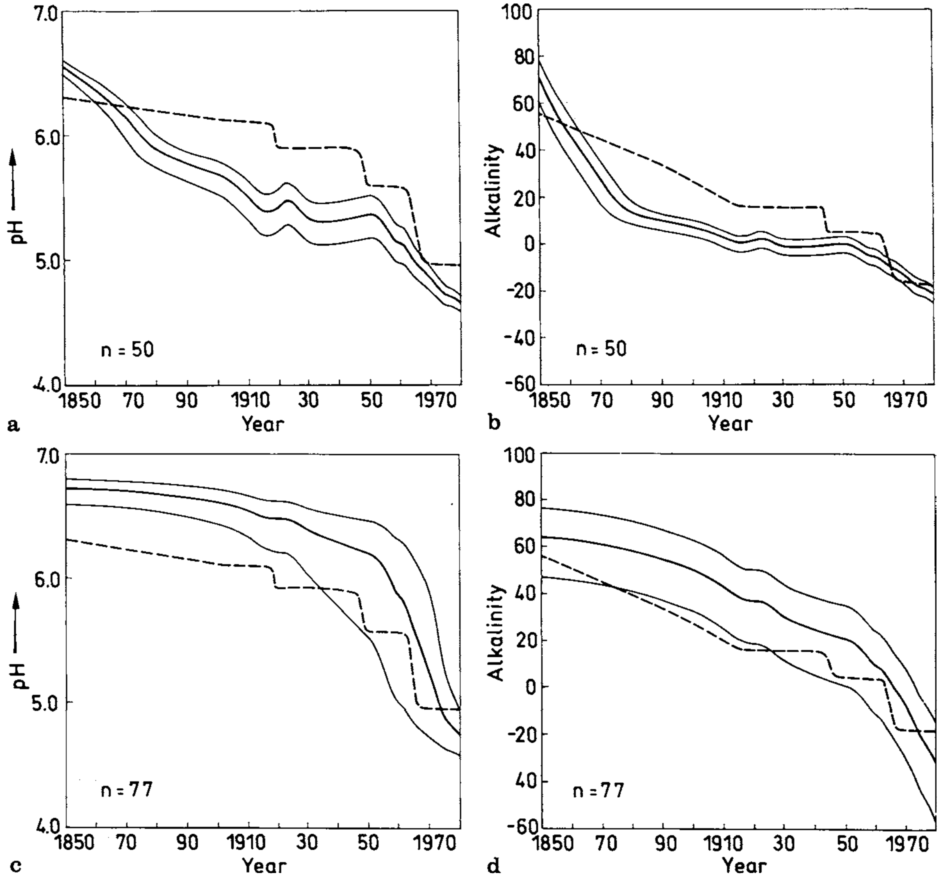

Fig. 4a–d. Reconstructed pH and alkalinity (μeq l^{-1}) for Lake Orajärvi from the diatom stratigraphy (*dotted line*) and from RLM (**a, b**) and MAGIC (**c, d**) model applications. The mean and the minimum-maximum envelope of the accepted model runs is displayed

5.0–5.1 started around 1945 (Fig. 5). However, there is some indication of mixing of the uppermost 5 cm of the sediment layer, which makes the timing of the pH decline rather uncertain. Measured pH was 5.2–5.3 during autumn overturn of the period 1979–1981. The model reconstructions indicate much higher "pre-acidification" pH and alkalinity values than has been estimated from diatoms. MAGIC simulations indicate a very sharp drop in pH around 1950. MAGIC predicts the change with time, but not the absolute values, better than RLM.

A fairly large range of variation was obtained in the model reconstructions using the Monte Carlo testing procedure. This is obvious, because both models have shown high sensitivity to variations in weathering fluxes (Cosby et al. 1985a; Gardner et al. 1990). However, allowable outcomes were reproduced in a rather high percentage of the reconstructions for the sets of ranges of initial conditions and parameters used, particularly for lake Orajärvi.

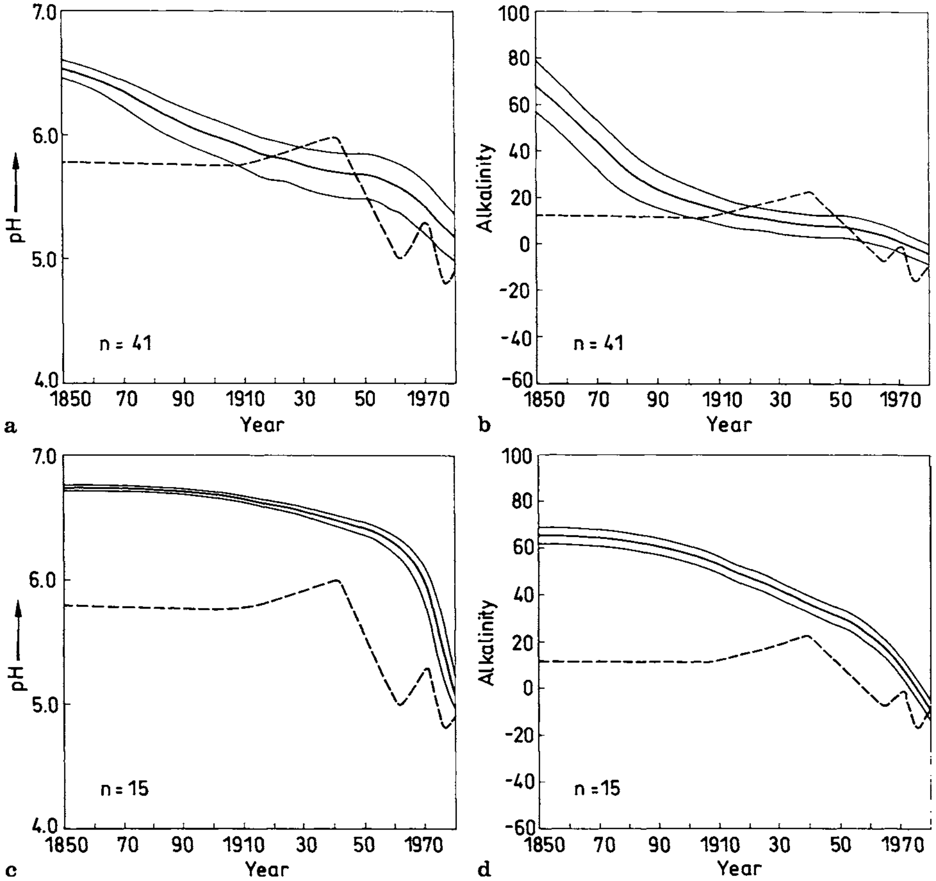

Fig. 5a–d. Reconstructed pH and alkalinity (μeq l^{-1}) for Lake Siikajärvi from the diatom stratigraphy (*dotted line*) and from RLM (**a**, **b**) and MAGIC (**c**, **d**) model applications. The mean and the minimum-maximum envelope of the accepted model runs is displayed

Some major difficulties occurred in the applications of the MAGIC model. Low values for baseflow were predicted for the Orajärvi catchment by RLM. However, somewhat larger baseflow values were used in MAGIC in order not to obtain totally unreasonable values for the selectivity coefficients. Nevertheless, high values for the selectivity coefficients, and for the coefficient determining the aluminium solubility had to be used for the B-horizon of the soils of both catchments, in order to obtain successful computations. These values were larger than those reported from other MAGIC applications (e.g. Cosby et al. 1985a, b, 1986; Wright et al. 1986), and they might not be very realistic. There is, however, very little information available on appropriate values of the Gaines-Thomas selectivity coefficients for soils likely to be impacted by acid deposition (Reuss and Johnson 1985), which makes the evaluation of the above results difficult.

In calibrating MAGIC for the two catchments, rather high parameter values for sulphate adsorption had to be used in order to match simulated and observed lake water sulphate values. This fact could naturally have several different explanations, including an overestimation of sulphate deposition, or errors in chemical water analyses. However, considerable sulphate retention has been observed in Finnish catchments having a moderate to high percentage of peatland (Kallio and Kauppi 1987), and also in bogs across eastern North America (Urban et al. 1986). Furthermore, the results from acid addition experiments conducted in pristine Norwegian catchments with thin and poorly developed soils have shown that a large proportion of the added sulphate was retained and stored in the soil (Wright et al. 1988). The finding from the MAGIC application that soils of the two Finnish forest catchments are retaining some of the incoming sulphate is thus supported by empirical evidence from similar soils from elsewhere in Scandinavia.

Concluding Remarks on the Model Comparison

Both models generally predicted similar changes in lake acidity. There were, however, some clear differences. MAGIC reconstructions usually had higher "pre-acidification" values of pH and alkalinity, and a more gradual decrease of these values with time. Some of the differences between the simulation results of the two models can obviously be explained by the fact that MAGIC was not independently calibrated to the available data. An independent calibration procedure of this model would probably have brought the simulation results closer to the values from the diatom and RLM reconstructions.

The sharp increase in acidity indicated by diatom reconstructions was more closely described by MAGIC reconstructions. This is probably due to a more detailed description of the buffer processes of the catchment soil incorporated in this model (e.g. sulphate adsorption) compared with the more simple approach in RLM. However, the computer time needed for the individual MAGIC applications is very much longer, which makes this model less suitable for extensive regional applications.

Although the use of the Monte Carlo testing procedure showed fairly large differences in the simulated acidification path of the lakes, a relatively large number of allowable outcomes were still reproduced in both RLM and MAGIC applications. This suggests that both models, using similar parameter ranges, could satisfactorily outline the general time development of lake acidity.

Regional Responses

Materials and Methods

A national assessment of future status of lake acidification should investigate broad-scale aspects of alternative policy formulations, and thus analyse the behaviour of a representative selection of catchments. As an output, the methodology should produce well-defined illustrative information which can easily be related to the effectiveness of the scenario being evaluated.

A method to regionalise the model structure has recently been introduced (Kämäri and Posch 1987). The method attempts to modify the rather uncertain a priori parameter distributions such that a satisfactory fit with observed model output distributions is obtained. The method draws on the use of Monte Carlo techniques (see Fedra 1983). Model parameters and variables having uncertainty are assigned frequency distributions. In the regional application, besides the uncertain parameters, also parameters that exhibit spatial variability are randomized within feasible a priori distributions.

The criteria for accepting or rejecting model postdictions, and thus parameter vectors used, are based on synoptic surveys of lake chemistry. Monte Carlo runs are rejected when the output falls within a bin of the measured joint frequency distribution of pH and alkalinity that has already been "filled" by the previous simulations. The accepted Monte Carlo runs, fulfilling the full joint distribution of pH and alkalinity (Fig. 6), when driven with historical deposition sequences, produce a set of theoretical lakes which are assumed to be representative for that region (Kämäri and Posch 1987; Kämäri et al. in press; Posch and Kämäri 1990). Regional lake acidification scenarios are then constructed by running the model for the desired future deposition scenario once with each of the accepted parameter

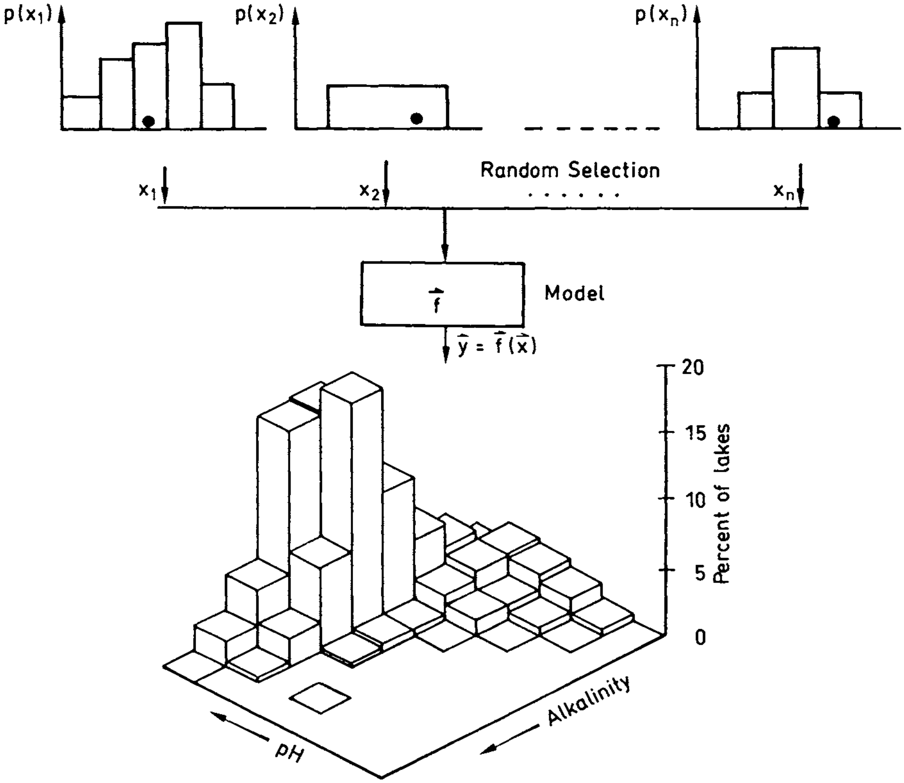

Fig. 6. Schematic representation of the regionalisation methodology

sets. This technique for selecting parameter vectors is referred to as the Monte Carlo Filter Procedure (MCFP).

The calibration procedure has several preparatory steps. First of all, ranges or distributions for unknown parameters have to be estimated. In the estimation procedure, best available information and best guesses for the input distributions are being used. Then – for the model output – a target distribution is specified on the basis of a large number of water quality observations. Finally, the filtering procedure is applied. As an input for MCFP, frequency distributions are estimated independently for the following 12 input and output parameters: (1) Lake surface area, (2) lake catchment area to lake surface area ratio, (3) mean lake depth, (4) mean catchment soil thickness, (5) mean surface slope, (6) weathering rate of base cations, (7) total cation exchange capacity, (8) base saturation, (9) solubility constant for solid aluminium phase, (10) forest coverage fraction, (11) forest filtering coefficient, and (12) partial CO_2 pressure in surface water. In addition, few variables for the regional model runs are estimated with the help of so-called transfer functions from other better-known variables. Some thermodynamic constants are kept constant in the regional runs.

In the model application to Finnish lake regions (Fig. 7), data were collected from various sources including large-scale soil (FAO-UNESCO 1974), forestry (Weltforstatlas 1975) and geological maps (UNESCO 1972), as well as soil chemistry (e.g. Nuotio et al. this Vol.), and lake chemistry (e.g. Forsius 1987) measurements. For some input parameters, there was not enough a priori information available to allow detailed distributions to be formulated. In these cases, the input variables, like the mean catchment soil thickness and the ratio of lake area to catchment area, were assigned ranges broad enough so that any reasonable value for an input could be selected from these rectangular distributions. Some parameters were assigned constant values since, based on the model analysis (see Gardner et al. 1990), they do not significantly affect the output.

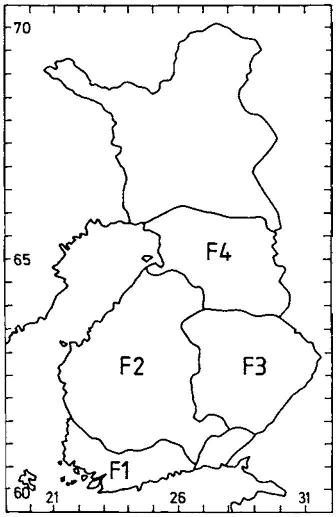

Fig. 7. Lake regions to which the regionalised model was applied

Historical deposition sequences were constructed as described earlier by assuming a proportionality between sulphur emissions and sulphur deposition (see Posch and Kämäri 1990). The dispersion of the emissions is obtained by disaggregating the emission total over the European countries on the basis of the 1980 emission per country, and applying the RAINS sulphur transport model.

Results of the Regional Model Runs

The model regionalised with the Monte Carlo Filter Procedure is applicable for providing estimates of the time patterns of regional lake acidification for any energy-emission scenario and year between 1980 and 2040. An estimate of the mean annual lake pH or lake alkalinity frequency distribution is produced as the output.

In the following, three example energy-emission scenarios are compared. The example scenarios were created using the RAINS energy-emission model, and the long-range transport model supplied by the EMEP programme. From 1900 until 1980 all the scenarios were identical. From then on the scenarios differed:

1. Reference scenario is based on the latest estimates of energy use up to the year 2000, given by the International Energy Agency (IEA 1986). No change is assumed after 2000. A reduction in sulphur deposition of more than 10% is computed to all Finnish lake regions (Table 7)
2. Current reduction plans scenario has been constructed by prescribing directly the sulphur emissions of each country on the basis of their most recent plans to reduce sulphur emissions. The reference year for the given reduction percentages is 1980 and the stated reductions in emissions are assumed to take place between 1985 and 1995. These reductions are reflected in a decrease of sulphur deposition values in Finnish lake regions by some 30% (Table 7).
3. Major pollution controls scenario assumes lower rates of energy use than the Reference scenario and, in addition, effective measures taken for the control of the sulphur emissions. These controls are defined as (1) pollution control devices on all power plants and (2) fuel cleaning in the domestic energy sector. With

Table 7. Percentage of reduction in the average sulphur deposition in the four Finnish lake regions for the three sulphur emission scenarios: Reference scenario (REF), Current reduction plans (CRP), and Major pollution controls (MPC). Computations are done by the transport model of the IIASA RAINS model system

	Reduction by 2000 from 1980 level (%)		
Region	REF	CRP	MPC
F1	11	30	48
F2	11	30	47
F3	10	28	46
F4	12	27	41

such strong measures to control sulphur emissions the depositions in Finland decrease by 41 to 48%, depending on the region (Table 7).

By the year 1980, lake acidification has been reported to be an observed phenomenon in many locations of Fennoscandia. In the worst acidified areas, in southern Scandinavia, over 30% of the total number of lakes are acidified, having summer pH values less than 5.0. In southern Finland, about 10% of the total number of lakes are that acidic. In spring, when the annual minimum pH in the surface waters occurs, the acidity of the lakes is even greater.

The time developments of the fraction of strongly acidic lakes for the three different scenarios are displayed in Fig. 8a–d separately for each lake region of Finland. When the Reference scenario, with no measures for controlling emission, was assumed, the model estimated a steady increase in the fraction of strongly acidic lakes for all lake regions. This was the case even though the deposition with this scenario decreased by 10%.

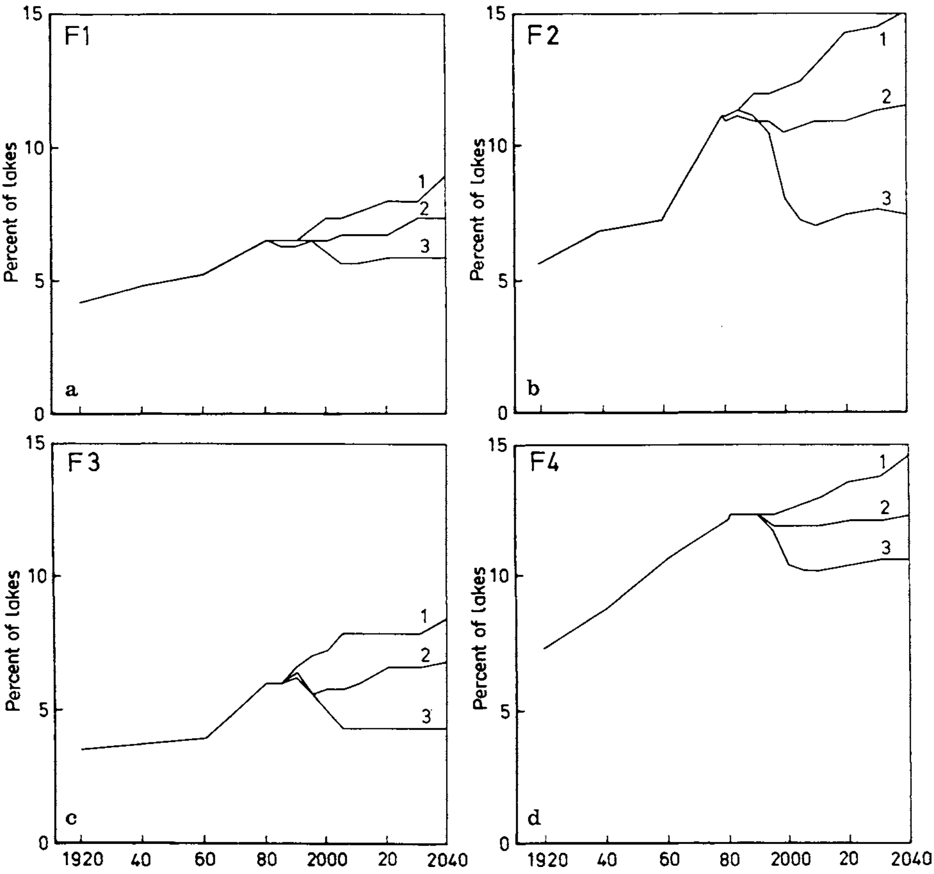

Fig. 8a–d. The time evolution of the fraction of the number of lakes below pH 5.3 for the three scenarios; (1) Reference scenario, (2) Current reduction plans, and (3) Major pollution controls scenario. Model results are displayed for Regions Fl-F4 of Finland (see Fig. 7)

The scenario assuming the current plans to reduce sulphur emissions in Europe seemed to nearly stop the lake acidification process with little recovery. For this scenario, in Regions F2 and F4, the proportion of strongly acidic lakes was estimated to decrease first and then after a few decades to turn again into a slight worsening of the acidification situation (Fig. 8b, d).

The regional model runs clearly indicated that it is feasible to expect an improvement in the state of the lake acidification as a result of major emission cuts. When strong reductions were assumed to both energy use and emissions, a recovery was predicted for practically all Finnish lake regions (curve 3 in Fig. 8a–d). It was impossible to say, however, whether the predicted recovery was permanent or whether the effect of slowly continuing soil acidification would in the long run cause the lake water quality to deteriorate.

Discussion

It is difficult to assess the uncertainties inherent in the model reconstructions despite the fact that neither model used in this study is very complicated. Both models, MAGIC and RLM, are constructed using an "average" or lumped representation of the spatially distributed catchment processes. There are two important aspects of modelling large-scale heterogeneous catchments that must be considered when assessing the adequacy of the lumped approach (Cosby et al. 1985a). The first aspect concerns the process aggregation, i.e. the degree to which a large number of the different processes which occur in a catchment can be represented by simpler conceptualisations of those processes. The second aspect concerns the scales of spatial heterogeneity in a catchment and the extent to which this heterogeneity can be neglected (spatial aggregation).

The models used in this study are examples of both types of aggregation, and therefore the processes that are included are obviously only generalisations of as yet poorly known phenomena. The dynamic non-linear interactions between the numerous mathematical descriptions included in the models make it difficult to relate the overall performance of the models to the individual equations. Several of the input parameters are also interrelated such that an acceptable range for one parameter acts to restrict the possible range for other parameters (Cosby et al. 1985a; Kämäri et al. 1986). In addition, the uncertainty in the deposition sequence is difficult to estimate. However, the problems of uncertainties are not solved by turning to more complicated models, because data on a catchment scale for many key parameters simply do not exist.

The accuracy of the model results cannot be directly addressed except to say that values produced by the model for presentday surface water quality variables are consistent with the measurements available. This is a major problem inherent in all efforts to model acid deposition effects; lack of data needed for rigorous identification of model structures and estimation of parameter values. Catchment surface water is controlled by catchment soils and complex, process-oriented models of acidification thus contain soil and soil water variables that are infrequently measured in the field. Secondly, there may be point measurements, which are not spatially representative. On the other hand, models of long-term responses can, strictly speaking, only be calibrated and verified using long time series data (decades) from natural systems, which exist for very few, if any, catchments.

In regional applications, there remains uncertainty in the accuracy of the data at two levels. First, measurements from the study area, forming the input data used, always include measurement errors. The second level has to do with the interpretation of the regional properties. Measurements can only be viewed as samples of the regional system under consideration. The aggregation and interpretation of large scale information limit the utility of regional data as such.

Despite the limitations, there is much that can be learned from the process of constructing, testing and applying the acidification models. The regional applications of the models have clearly demonstrated the importance of the emissions control on the overall chemical status of surface waters. Moreover, speculative simulation exercises have indicated new or different data that can be brought to bear on the problem (e.g. Neal et al. 1986).

Palaeolimnological data such as diatom remains in lake sediments provide independent evidence by which the relationships between acid deposition, soil acidification and surface water acidification can be tested. It has earlier been shown that both models could distinguish between acidified lakes and lakes where no indication of acidification has been observed and predict correctly the general acidification history pointed out by diatom stratigraphy, when driven by an assumed historical deposition pattern (Kämäri et al. 1986; Wright et al. 1986). The applications in this study suggest the same conclusion. The general agreement between the pH reconstruction from palaeolimnological data and that from the model outputs of both MAGIC and RLM indicate that the processes and assumptions in the models can account for observed changes in surface water chemistry. The parameter values used to drive the models are reasonable for catchment areas in Scandinavia. There remain some obvious differences, however, in the acidity levels as well as in the acidification rates of the lakes between model reconstructions and reconstructions inferred from palaeolimnological diatom remains.

Sulphate retention in the soils can be an important factor delaying the catchment response to acid deposition. However, young podzolic soils developed in post-glacial times on granitic bedrock have been considered to owe little ability to adsorb sulphate, and the choice of parameter values for the sulphate adsorption characteristics have not been seen to have critical importance in earlier MAGIC applications in Scandinavian regions (e.g. Wright et al. 1986). For the Finnish catchments, however, rather high sulphate adsorption abilities had to be assumed in the MAGIC applications in order to match the simulated and observed lake water sulphate values. This result is consistent with the latest results of the whole catchment manipulation study in Norway, where a large fraction of the sulphate added on similar podzol soils was retained in the terrestrial catchment (Wright et al. 1988). If, however, the dominating process in Finnish catchments is sulphate reduction in peatlands, rather than sulphate adsorption on mineral soils, it is to be investigated whether the description by Langmuir isotherm satisfactorily accounts for the dynamics of sulphate retention/release. The possible release of sulphate from the soils when the deposition is reduced has a significant effect on the span of the recovery of surface waters.

Deposition of sulphate in Finland in the 1970's clearly exceeded that in the 1950's (Järvinen and Haapala 1980). The palaeolimnological studies conducted in Finland suggest that the levels of acidity have increased in recent decades mainly in small oligotrophic, oligohumous lakes, but possibly also in some polyhumous lakes (Huttunen et al. this Vol.). While considerable organic acidity is present in humic waters, anthropogenic sulphate may further increase the free acidity of these waters. The results here support these findings and give an indication of future acidity in surface waters.

Despite a 40% decrease of sulphur dioxide emission levels in Finland from 1980 to 1983, mainly due to drastic decrease in the use of heavy fuel oil (Kulmala 1985), a continuing deterioration of sensitive surface waters is predicted unless further reductions in deposition are achieved.

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Ion Budgets of Small Forested Basins

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Summary

The processes important to surface water acidification in basin scale were analysed in five forested basins in Finland. Different processes were quantified on the basis of ion inputs and outputs and the role of different processes was compared by calculating hydrogen ion budgets based on the mass balances. The ions considered in mass balances were Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-, NH_4^+, HCO_3^-, and H^+. Determination of deposition was based on bulk deposition results in open field, throughfall measurements and a sulphur deposition model. Retention of sulphate was observed in all basins. The estimated production of hydrogen ions varied between 50 and 170 $keq\,km^{-2}\,a^{-1}$ and the consumption between 90 and 205 $keq\,km^{-2}\,a^{-1}$. In the basins studied deposition and dissolution of SO_2 produces more hydrogen ions than direct deposition of H^+. In basins rich in peatlands, organic acids may contribute up to half of the total hydrogen ion production.

Introduction

Chemical and hydrological properties of the surrounding drainage basin largely determine the water and sediment chemistry of surface waters. Therefore when studying surface water acidification it is important to characterize the chemical transformations of atmospheric deposition during its passage through the entire catchment.

The measurement of inputs and outputs of chemical elements in hydrologically and geologically well-defined drainage basins is a powerful tool for analysing the processes which determine the mass balance of elements in the earth's surface zone (Paces 1984, 1986). There are several examples of the use of the mass-balance approach in acidification studies from different countries (e.g. Ulrich et al. 1980; Wright and Johannessen 1980; Driscoll and Likens 1982; Van Breemen et al. 1984; Bergström and Gustafson 1985; Nilsson 1985; Paces 1985; Kelly 1988; Morgan and Good 1988). By using mass balances one can estimate the buffering properties of the basin. Long-term monitoring of mass balances and ion ratios can also serve as an early warning system. For example, the first phase of lake acidification is

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characterised by increased base cation concentrations, which indicates the consumption of cation exchange capacity of the soil in the drainage basin. In soil acidification a decreasing Ca/Al ratio implies a risk for tree growth.

This paper analyses on basin scale the processes important to surface water acidification in Finland. Different processes are quantified on the basis of ion inputs and outputs in five forested basins. In addition, the role of different processes is compared by calculating hydrogen ion budgets based on the ion inputs and outputs. Preliminary budgets of four basins were calculated already earlier for the years 1981–84 (Kallio and Kauppi 1987). Two of these basins are included in this study. After 1984, intensive water quality sampling was carried out in these two basins. In addition, the results of throughfall studies are available. These improvements make it possible to obtain more reliable budgets than in the earlier study.

Material and Methods

The ions included in the input/output calculations were: Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-, NH_4^+, HCO_3^-, and H^+. Chloride was not included in this study because of methodological difficulties in chemical analysis.

The mean annual budgets were calculated using the results from the years 1982–1987. However, in some cases the data for a certain year were too scarce to allow reliable calculations. Therefore the budgets are based on 2 to 5 years observations depending on the basin:

	Yli-Knuutila	Teeressuonoja	Huhtisuonoja	Kesselinpuro	Myllypuro
Years:	1985–87	1982–83, 1985–87	1983–85, 1987	1985, 1987	1985, 1987

Description of the Basins

The five basins included in this study belong to the network of small drainage basins of the National Board of Waters and Environment. The land use of the selected basins is forested and they are situated in southern and central Finland (Fig. 1). Since 1982, the monitoring programme of these basins has included all the main components needed for ion budget calculations. The only significant source of loading in the basins is long-range transport of airborne pollutants. Thus the basins are suitable for studying the effects of acid deposition.

There are no lakes in the basins (for other characteristics see Table 1). Forests are mainly Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*). The dominant soil type is either peat or moraine (Table 2).

Deposition

The determination of deposition to the basins was based on open field measurements, throughfall studies and a sulphur deposition model.

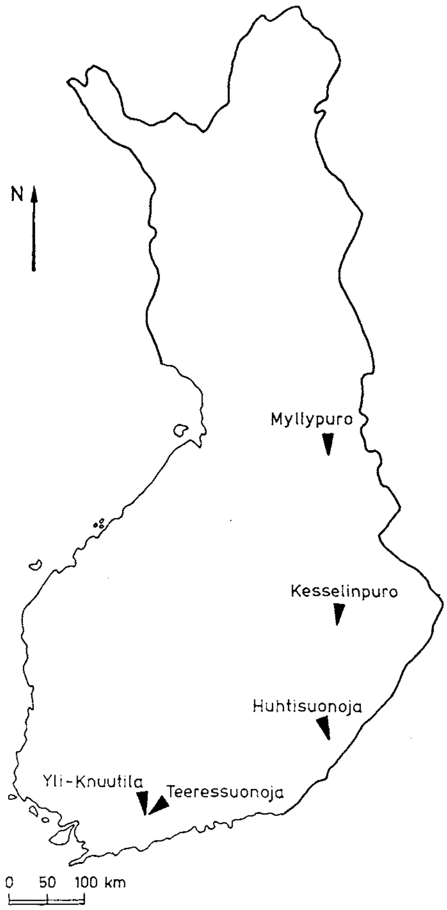

Fig. 1. Location of the basins

Deposition in Open Field

Deposition in open field was measured using bulk deposition samplers, from which samples were collected once a month. There is a deposition measuring station in or close to each basin. H^+-deposition was determined on the basis of pH of bulk deposition and the concentration of bicarbonate in rainwater was assumed to be zero. The analytical methods as well as the calculation of annual depositions have been described by Järvinen and Vänni (this Vol.).

The results of open field measurements were directly used as deposition for NO_3^-, NH_4^+, and H^+. These ions are affected by tree canopy but filtered fraction is difficult to estimate because of other processes taking place on the canopy. For other ions a forest filtering correction was made.

Effect of Forest Filtering on Deposition

Because tree canopy acts as a filter, the actual deposition to forests is higher than in open field for many ions (e.g. Parker 1983). In this study a filtering correction was

Table 1. The main characteristics of the basins

	Yli-Knuutila	Teeressuonoja	Huhtisuonoja	Kesselinpuro	Myllypuro
Drainage area (km^2)[a]	0.07	0.69	5.0	21	9.9
Forest on firm land (%)[a]	100	87	56	54	70
Tree stand ($m^3\ ha^{-1}$)[a]	162	116	39	88	59
Conifenous forest (%)[b]	96	98	100	84	91
Dominating coniferous[b]	Spruce	Spruce	Pine	Spruce	Spruce/pine
Peatland (%)[a]	0	13	44	39	27
Total S-deposition ($kg\ km^{-2}\ a^{-1}$)[c]	1100	1100	950	600	550
Runoff 1971–80 ($l s^{-1}\ km^{-2}$)[d]	3.6	7.4	6.7	7.8	10.7
pH in runoff (1981–84)[e]	6.4	6.8	5.4	4.7	5.6

[a] Seuna (1983).

[b] Mustonen (1963), Mustonen (1965).

[c] Tuovinen et al. this Vol.

[d] Hydrological yearbook (1980).

[e] Water quality data bank of the National Board of Waters and Environment.

Table 2. Distribution (%) of soil types in the basins. (Mustonen 1963, 1965)

	Yli-Knuutila	Teeres-suonoja	Huhtisuon-oja	Kesselin-puro	Mylly-puro
Peat soil	–	13	45	50	27
Moraines					
Silt	33	2	–	–	–
Fine sand	50	20	27	26	24
Coarse sand	17	53	24	21	49
Gravel	–	–	2	–	–
Graded soils	–	12	2	3	0

made for base cations and sulphate based on deposition ratios, i.e. deposition to forest divided by deposition in open field. In filtering correction calculations the specific filtering abilities of different tree species were taken into account:

$$FC = \frac{DR_s A_s + DR_p A_p + DR_b A_b + A_o}{A_{tot}}, \qquad (1)$$

where FC = filtering correction factor of a basin; DR_s, DR_p, DR_b = deposition ratio for spruce, pine and birch, respectively; A_s, A_s, A_s = area of spruce, pine and birch, respectively; A_o = area of open field; A_{tot} = total area of a basin.

Mean deposition ratios of each ion for spruce, pine and birch were obtained from throughfall studies carried out in Yli-Knuutila (Kallio and Kauppi 1990) and in four different sites in southern Finland (Hyvärinen this Vol.). To obtain the total deposition to basins, the open field depositions were multiplied by the filtering correction factor. The correction factors varied between 1.2 and 1.5 for sodium and between 1.8 and 2.0 for sulphate, depending on the basin.

Since internal cycling of Ca^{2+}, Mg^{2+} and K^+ is considerable (e.g. Parker 1983) their throughfall results cannot be used directly. Correction for these ions was made using a sodium-based filtering approach (Ulrich 1983; Ivens et al. 1989). The actual level of base cation deposition is obtained by using the filtering correction factor of Na^+ for all base cations. The approach is based on the assumptions that (1) Na^+ is not leached significantly out of the trees and (2) the aerodynamic behaviour of Ca^{2+}-, Mg^{2+}-, and K^+-bearing particles is similar to Na^+-bearing particles.

In the case of sulphate, a canopy correction factor was used in Yli-Knuutila and in the nearby Teeressuonoja because throughfall studies were carried out in Yli-Knuutila. For other basins deposition results of the EMEP/ECE-model (Lehmhaus et al. 1985) were assumed to be more reliable than the use of mean deposition ratios because the fraction of dry deposition of sulphur varies considerably in different parts of the country. The values obtained from the model varied between 770 kg S $km^{-2} a^{-1}$ in Huhtisuonoja and 230 kg S $km^{-2} a^{-1}$ in Myllypuro.

Output Fluxes

The output fluxes from the basins were estimated from the quality and quantity of the runoff water. Runoff was measured continuously with the aid of a measuring weir and a recording gauge. Mean daily runoff values were used for calculating the outputs. Water samples were taken from the overflow of the measuring weir. Because most of the runoff occurs in spring and autumn, sampling was concentrated in these seasons. The annual number of samples usually varied between 8 and 12. The variation of runoff water quality from forested basins is small (Lepistö and Seuna this Vol.). Therefore even with a fairly low sampling frequency, reasonably reliable estimates for concentrations of different ions are obtained. In addition, intensive water sampling was carried out in Yli-Knuutila and Teeressuonoja in 1985–1987 and in Kesselinpuro in 1987. Here the number of annual samples varied between 25 and 52.

pH was determined using a radiometric combination electrode GK 2401 C and NH_4^+ by a colorimetric method with hypochlorite and phenol. The analytical methods used for other ions have been described by Lepistö and Seuna (this Vol.). Bicarbonate concentration of runoff water was estimated on the basis of alkalinity.

In spring and autumn the output was calculated by the following formula (2):

$$O_1 = \sum_{i=1}^{n} \bar{q}_i c_i \Delta t_i, \qquad (2)$$

where O_1 = output in spring and autumn; $\bar{q}_i$ = mean runoff of period i; c_i = concentration of individual sample i; Δt_i = length of period i (from the middle of a sampling interval to the middle of next interval); n = number of samples.

During low runoff seasons (with no or only a few samples) the output was calculated using the mean annual concentration:

$$O_2 = \bar{q}\,\bar{c}\,\Delta t, \qquad (3)$$

where O_2 = output in winter and summer; $\bar{q}$ = mean runoff of the season in question; $\bar{c}$ = mean concentration of the year; Δt = length of the season in question. The outputs of the four seasons were summed to obtain the annual outputs.

Calculation of the Hydrogen Ion Budget

The processes considered and the reaction formulae used in the hydrogen ion budget calculations are shown in Table 3. The internal processes (processes 3 . . . 8 in Table 3) were quantified indirectly on the basis of differences between ion output and deposition. The contribution of each internal process to the hydrogen ion budget was thereafter calculated using the relevant equation. In the case of processes involving both a reaction and a counter-reaction, only the net flux could be calculated.

No estimates of biological accumulation were available in this study. Thus only the net sum of weathering, ion exchange (and eventual retention of ions) and

Table 3. Hydrogen ion producing and consuming processes considered in this study. The reaction formulae are from Van Breemen et al. (1983, 1984)

Production (Reaction from left to right)		*Consumption* (Reaction from right to left)
1. Direct deposition of H^+	$H^+[\text{aq(rain)}] \rightarrow H^+[\text{aq(soil solution)}]$	
2. Deposition and oxidation of SO_2	$SO_2 + H_2O + \frac{1}{2}O_2 \rightarrow SO_4^{2-} + 2H^+$	
3. Dissolution and dissociation of CO_2	$CO_2 + H_2O \rightarrow HCO_3^- + H^+$	
4. Nitrogen transformations	$NH_4^+ + R\text{–}OH \rightleftharpoons R\text{–}N_2 + H_2O + H^+$	Nitrogen transformations
	$NO_3^- + R\text{–}OH + H^+ \rightleftharpoons R\text{–}NH_2 + 2O_2$ (R = organic matter)	
5. Anion weathering and ion exchange	$XO_{(m+n)} + mH_2O \rightleftharpoons XO^{2m+}_{(2m+n)} + 2mH^+$	Reverse weathering and retention of anions
6. Biological accumulation of cations	$M^{n+} + nR\text{–}OH \rightarrow (R\text{–}O)_nM + nH^+$	
7. Reverse weathering of cations	$M^{n+} + \frac{1}{2}nH_2O \rightleftharpoons \frac{1}{2}nM_{2/n}O + nH^+$	Cation weathering and ion exchange
8.	$R_n\text{-}A + nH_2O \leftarrow A^{n-} + nR\text{–}OH + nH^+$	Biological accumulation of anions
9.	$H^+[\text{aq(drain)}] \leftarrow H^+[\text{aq(soil solution)}]$	Output of H^+ with drainage water

biological accumulation could be calculated:

$$O-I=W-B, \tag{4}$$

where O = output in drainage water; I = input from deposition; W = weathering, ion exchange (and retention of ions); B = biological accumulation of ions.

The ions considered in weathering, ion exchange, eventual retention and biological accumulation were: Na^+, K^+, Ca^{2+}, Mg^{2+} and SO_4^{2-}.

The net hydrogen ion flux attributed to nitrogen transformations was determined as the difference between net output of ammonium and net output of nitrate [(NH_4^+ output–NH_4^+ deposition) – (NO_3^- output–NO_3^- deposition)], a method presented by Van Breemen et al. (1983). A negative value for this quantity means that nitrogen transformations produce an equivalent amount of hydrogen ions. Dry deposition of SO_2 was obtained from the sulphur dry deposition results of the EMEP/ECE-model (Lehmhaus et al. 1985).

Hydrogen ion production due to dissociation of organic anions could not be included in the calculations because of lack of data. However, in Kesselinpuro the concentrations of organic anion in runoff water were determined using an ion balance method during a special study carried out in 1987 (Kortelainen et al. unpubl. data).

Results and Discussion

Mass Balances

There was a clear south-north gradient in the deposition: the highest deposition values were observed in Yli-Knuutila and Teeressuonoja, southern Finland and the lowest values in Myllypuro, northern Finland (Fig. 2). The same general gradient was also obvious in output. However, output can vary considerably between adjacent basins, as indicated by Yli-Knuutila and Teeressuonoja.

Generally, output exceeded input for Na^+, K^+, Ca^{2+}, Mg^{2+} and HCO_3^-. Retention was observed in case of SO_4^{2-}, NO_3^-, NH_4^+ and H^+.

Role of Different Processes

The estimated production of hydrogen ions varied between 50 and 170 $\mathrm{keq\,km^{-2}\,a^{-1}}$ and the consumption between 90 and 205 $\mathrm{keq\,km^{-2}\,a^{-1}}$ (Fig. 3). In theory, production and consumption of hydrogen ions in a basin should be equal. Budget discrepancies are due to errors in determining the ion fluxes and due to processes not considered in the calculations.

The fluxes of hydrogen ions were in general larger in the south than in the north. However, the fluxes can vary quite a lot between adjacent basins, as indicated by Yli-Knuutila and Teeressuonoja. The total fluxes are in agreement with other budget calculations of forested basins. For example in Däntersta,

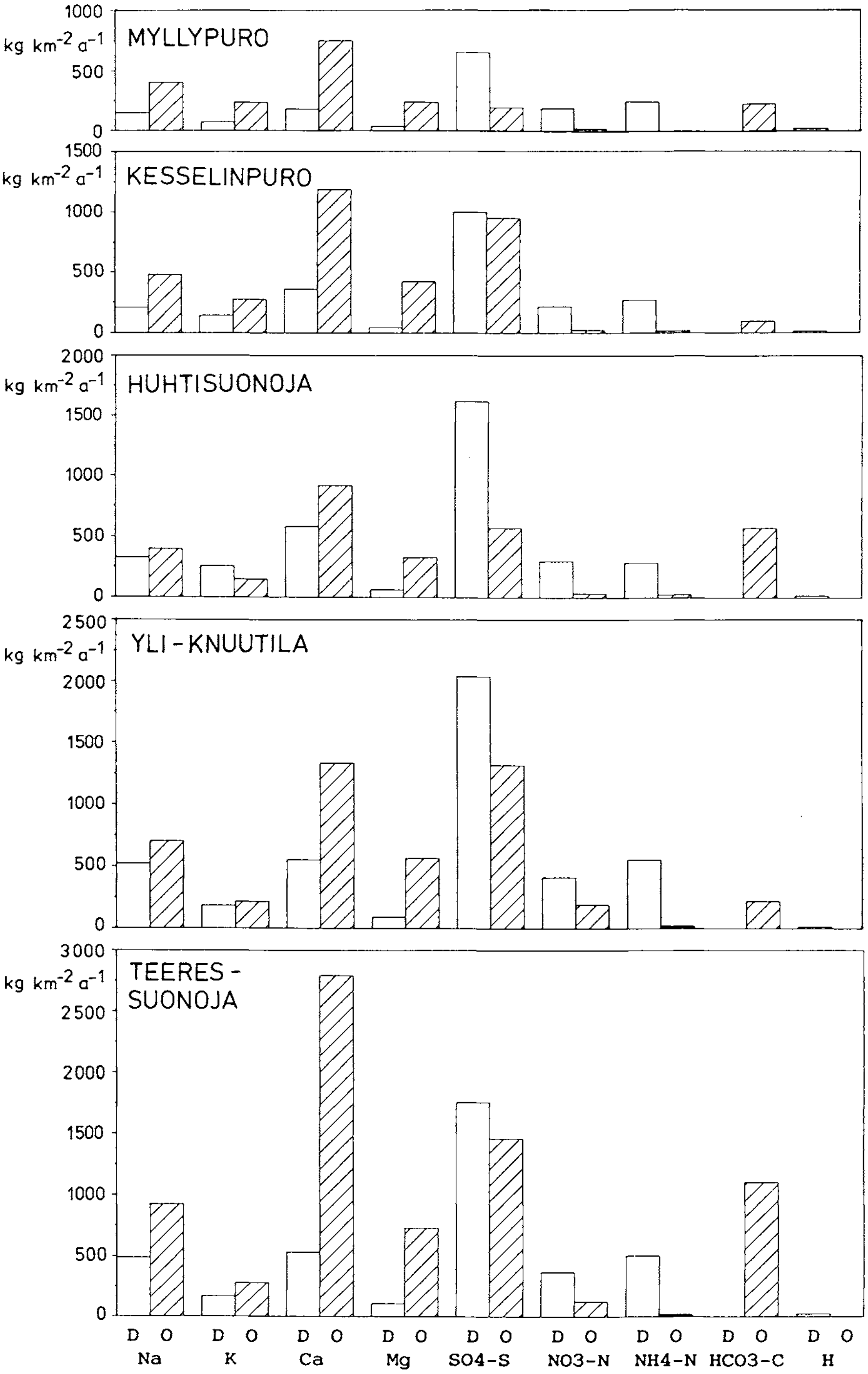

Fig. 2. The mean annual mass balances (kg km^{-2} a^{-1}) of the basins. *D* deposition; *O* output

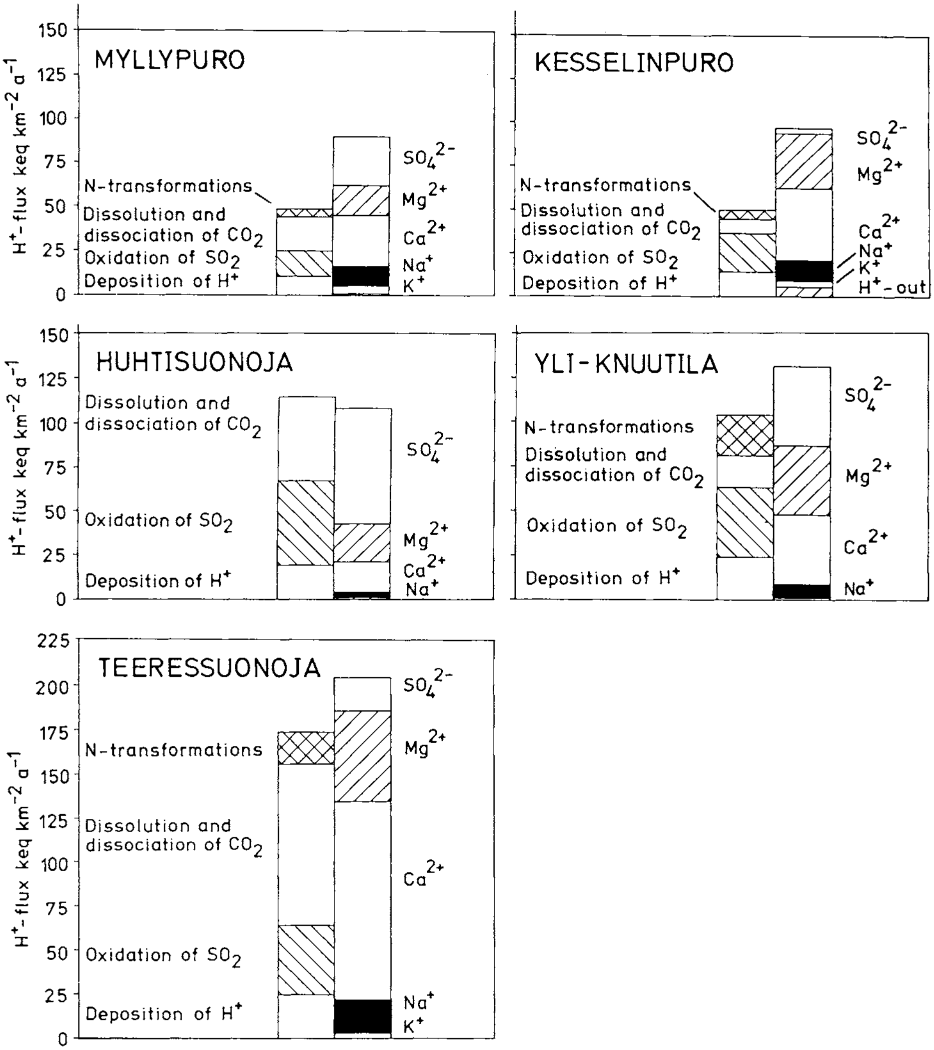

Fig. 3. The mean annual hydrogen ion production (+) and consumption (−) of the basins. The columns *on the right* represent the net contribution of weathering, ion exchange, eventual retention and biological accumulation of each ion. In Kesselinpuro direct output of H^+ with drainage water is also noticeable

central Sweden, production was 120 keq km^{-2} a^{-1} and consumption 110 keq km^{-2} a^{-1} (Bergström and Gustafson 1985). In Gårdsjön, southern Sweden, the values were 260–300 and 270–360 keq km^{-2} a^{-1}, respectively (Nilsson 1985).

Hydrogen ion production by SO_2 oxidation exceeded the direct deposition of H^+ in all basins. The role of nitrogen in hydrogen production is clearly seen in the two southernmost basins. This might indicate the increasing role of nitrogen in the acidification process. Lepistö and Seuna (this Vol.) have reported an increasing trend in nitrate concentrations in runoff water in Yli-Knuutila and Teeressuonoja during the last 25 years. In other basins, trees efficiently take up the deposited nitrogen. Dissolution and dissociation of CO_2 produced 15–50% of the calculated total production of hydrogen ions depending on the basin.

The consumption of hydrogen ions was dominated by base cations. This indicates that weathering/cation exchange is the most important buffering system in the basins. The consecutive series of buffering reactions in soil as acidification proceeds has been described by Ulrich (1983). The different categories of these reactions are called buffer ranges. In areas sensitive to acidification in southern Finland it has been reported that the buffering rate of the silicate weathering has been exceeded and the dominant buffering process is cation exchange (Nuotio et al. 1985). A small part of these sensitive areas has reached the aluminium buffer range.

The estimated weathering/cation exchange rates presented here are underestimates since biological accumulation could not be included [see Eq. (4)] due to lack of data. Biological accumulation is seldom considered in budget calculations because it is difficult to estimate. In Däntersta, central Sweden, the production of hydrogen ions due to biological accumulation was estimated to be 25 keq km^{-2} a^{-1} (Bergström and Gustafson 1985).

The output of hydrogen ions with runoff water was in all basins less than 6 keq km^{-2} a^{-1}. Sulphate retention was observed to some extent in all basins. The same has also been observed in other ion budget studies (e.g. Khanna et al. 1987; Morgan and Good 1987, Kelly 1988). However, the sulphate results of our study are partly unreliable, since humic substances in runoff water disturb the sulphate analysis (Bjärnborg and Korhonen 1985).

Processes not included in the calculations were dissociation of organic acids and aluminium transformations, which were excluded because of lack of adequate data. In the intensive study of Kesselinpuro in 1987 (Kortelainen et al. unpubl. data) the production of hydrogen ions by dissociation of organic acids was about 90 keq km^{-2} a^{-1}. This value can be regarded as an upper limit for all the basins, since in Kesselinpuro the runoff water is more humic than in other four basins. Organic acids partly explain discrepancy between production and consumption in most basins. If we use the above mentioned 25 keq km^{-2} a^{-1} (Bergström and Gustafsson 1985) as an estimate for biological accumulation, the production of hydrogen ions caused by organic acids would be ca. 50% of the total production in Kesselinpuro in 1987.

The role of Al as a source of hydrogen ions is most likely small since pH and humic matter concentration of the runoff waters studied are fairly high. Buffering in soil has also not reached the aluminium buffer range, as discussed above.

Conclusions

In the basins studied, deposition and oxidation of SO_2 produces more hydrogen ions than direct deposition of H^+. In basins rich in peatlands, organic acids may contribute up to half of the total hydrogen ion production. In southern Finland the effect of nitrogen on acidification was to be seen. Retention of sulphate was observed to some extent in all the basins, but results are partly unreliable because humic substances disturb the analytical method used. The soils in the basins are most likely in the silicate or cation exchange buffer range.

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Hydrological Characteristics Affecting the Runoff Water Acidity

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Summary

Snowmelt episodes and relationships between runoff and water quality were studied in two forested catchments (Teeressuonoja 0.69 km^2 and Yli-Knuutila 0.07 km^2) in southern Finland. Hydrograph separation using oxygen-18 was undertaken during the snowmelt periods of 1985 and 1987 in Teeressuonoja. Subsurface pre-event water was the major component of discharge even during the snowmelt period. The meltwater fraction of the total runoff during the melt periods was computed to be about 15%. During peak flow the meltwater fraction was 30–40%. The dominant mechanism in the system is the displacement of old water in the soil of catchment by incoming acidic meltwater. No significant trend was found in the acidity of the runoff water during the last 20–25 years. Acid deposition has promoted the leaching of calcium from the forest soils particularly during the low flows. Increase in nitrogen deposition is probably the main factor affecting increasing nitrate concentrations in the runoff water.

Introduction

The physical movement and the changes in chemical composition of water in catchments in response to atmospheric deposition depend on a number of factors. These include the amount, timing, and chemistry of the atmospheric deposition inputs; and catchment characteristics such as the vegetation cover, the composition and thickness of soils and regolith, the mineralogy of underlying bedrock and the flow paths of water through the catchment.

The acidification process can be divided into two time scales. Firstly, there is a short-term response during snowmelt and large storms, when the pH value decreases temporarily and elevated concentrations of sulphate and aluminium occur. Secondly, there is a long-term response to sulphur deposition over several decades, which is controlled by the buffering processes and the sulphate adsorption processes of the soil. Adsorption processes result in accumulation of sulphur before the concentration in the runoff water increases to a new, higher equilibrium level.

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In Finland, a considerable proportion of the annual precipitation falls as snow, 15–25% of the annual precipitation in the south and 25–35% in the north (Solantie 1981). The snowpack is able to store, and after melting, suddenly release large amounts of different substances. In a large variety of studies, both in the laboratory and in the natural scale, it has been found that the first fractions of the meltwater contain the highest ionic concentrations (e.g. Overrein et al. 1981; Johannessen et al. 1980; Jenkins et al. 1987). Laboratory and field experiments carried out by Johannessen and Henriksen (1978) indicated that 50–80% of the pollutants are released when the first 30% of the snow melts.

A primary factor controlling acidification is the hydrology of a basin. To estimate the effect of meltwater on terrestrial systems and on rivers and lakes, some knowledge of the contact between runoff and ground is necessary. In theory we might separate two extreme cases:

1. No contact such that the acid meltwater reaches rivers and lakes unchanged, as overland flow.
2. Acid meltwater infiltrates totally with increased discharge of "old" soil water and groundwater into the streams and watercourses, there is sufficient contact for the composition of the runoff to be completely in equilibrium with the terrestrial system.

In theory we might assume that in the forest soil overland flow (1) and surface layer flow are increased by thin soil layers, high percentage of bare rock, steep topography and a deep impermeable layer of soil frost. Catchments consisting primarily of bare rock and dominated by shallow flow systems are potentially the most sensitive type relative to alteration of water chemistry due to changes in the composition of atmospheric deposition.

Infiltration (2) is increased by the deep soil layers and high percentage of coarse, sorted soils. Groundwater-dominated systems range from relatively simple flow in fractured rock to very complex flow through thick soil in deeply weathered areas.

Usually surface waters are acidic and base flow waters well buffered; the degree of mixing of these two waters determines the water quality in the stream at the basin outlet. Water following shallow pathways may contact only highly weathered material for short periods of time, providing little opportunity for reaction. Waters following deeper pathways may contact unweathered bedrock, have a much longer residence time, and undergo more extensive reaction (Bricker 1987). Hewlett and Hibbert (1967, ref. Ward 1984) argued that over much of a catchment area, even during intense and prolonged precipitation, all precipitation infiltrates the soil surface. Then as a result of the combined processes of infiltration and throughflow through the soil profile, first the shallow water-table areas immediately adjacent to the stream channels and subsequently the lower valley slopes, become saturated as the water table rises to the ground surface (Fig. 1). In these surface-saturated areas infiltration capacity is zero so that all precipitation falling on them is excess precipitation discharging quickly to the stream channel.

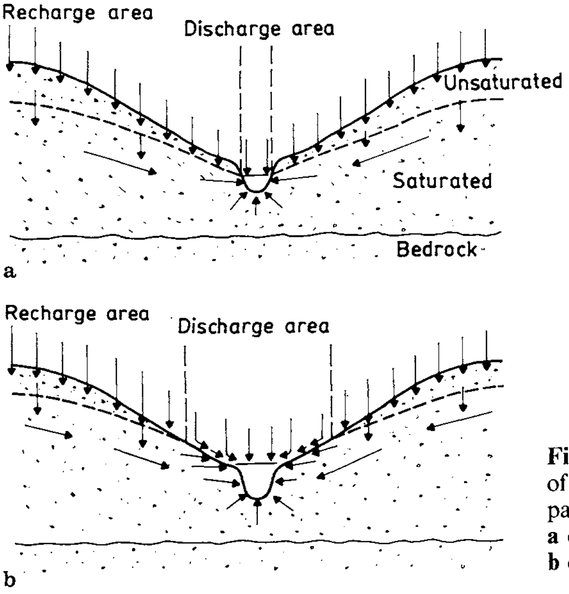

Fig. 1a,b. Schematic cross-section of catchment showing major flow paths and recharge/discharge areas, **a** during the low flow and **b** during a storm/snowmelt event

Analyses of the chemical or isotopic composition of stream water during runoff events give information on the integrated result of the various processes contributing to streamflow generation. Hydrograph separation by using isotopes has been performed since the early 1970s, predominantly in mountainous areas in central Europe and in Canada. During the last 10–20 years it has been pointed out in many isotope studies that subsurface runoff is an important component even during the high flow period. Dincer et al. (1970) concluded that during snowmelt the groundwater contribution to stream flow was as high as 70%. In a detailed study in the Bavarian Alps, Herrmann and Stichler (1980, 1982) estimated that the groundwater runoff to a stream was 70–80% during snowmelt and rainstorms. Bottomley et al. (1986) studied snowmelt runoff in the Turkey Lakes watershed, Canada, using oxygen-18 and some water quality components. In the two streams studied, 50–60% of the peak flow was contributed by groundwater recharged during the previous year or even earlier.

A number of investigations has shown that there is a seasonal variation in the acidity of rivers and lakes. This is the case in freshwater where the carbonate system is the dominant buffer as well as in more acid rivers and lakes. The variations are normally more pronounced for small brooks than for rivers and lakes (e.g. Gjessing et al. 1976). A drop in pH is often observed during snowmelt and in the autumn. The runoff during the summer is often small and pH relatively high. The first heavy autumn rain results normally in low pH particularly after a dry summer (see Overrein et al. 1981). Seasonal variation of alkalinity is clear in the large Finnish rivers discharging into the Gulf of Bothnia with very low levels during the spring high flows (Alasaarela and Heinonen, 1984). A pH drop of 0.5–1.5 units during the melt period was found by Rask et al. (1985) in small forest lakes in Evo area, in southern Finland, with considerable differences between years within a lake, mostly depending upon weather conditions. In southern Finland, about 10% of the lakes are acidified having summer pH values less than 5.0, the acidity of the lakes in spring being even greater (Kämäri 1988).

In this paper, observations from two small research catchments in southern Finland, Teeressuonoja and Yli-Knuutila, are reported. Isotopic hydrograph separations using oxygen-18 are made to estimate the contribution of snowmelt and pre-event groundwater to the stream discharging the catchment of Teeressuonoja. Hydrochemical characteristics of the streams are discussed. The effect of relatively high sulphur and nitrogen deposition on the runoff water discharging from forest soils is studied using two time scales; snowmelt episodes on the one hand, and changes during the last 20–25 years on the other. The hydrograph separation studies have recently been discussed by Lepistö et al. (1988a) and Bengtsson et al. (1989); modelling of runoff, pH and alkalinity by Lepistö et al. (1987).

Materials and Methods

Catchment Descriptions

The two adjacent forested research catchments studied are located in southern Finland (60°N, 24°E), about 50 km northwest of Helsinki (Fig. 2). Various hydrological observations began in 1953 in Yli-Knuutila and in 1963 in Teeressuonoja when measuring weirs were built. A climate station is situated between the catchments. The climate in the region is humid. Mean annual precipitation was 615 mm during 1972–85, of which 263 mm was discharged (Teeressuonoja). The average water equivalent of snow was 82 mm on 15 March during 1970–81. Usually the snow melts away in about a 2-week period in April.

The Teeressuonoja catchment (0.69 km^2) is covered by forests dominated by Norway spruce (*Picea abies*); the volume of growing stock amounts to 116 m^3 ha^{-1}. Peatland percentage is 13. There are no lakes or arable land in the catchment. Altitude ranges between 42 and 111 m, with a mean slope of 13.9% (Seuna 1982). The soil of the Teeressuonoja catchment is developed on coarse and find sand moraines (75%) with 12% graded soils and 13% peat soils. The soil depth varies from a few meters in the brook valley up to 20–25 m near the water divide south of the peat area. A considerable part of the thick soil layers has been excavated for gravel production, comprising about 8% of the total catchment area. During 1963–77 the mean maximum instantaneous runoff during snowmelt was 74-l s^{-1} km^{-2} and for summer rains 40-l s^{-1} km^{-2} (Seuna 1982).

The Yli-Knuutila catchment (0.07 km^2) next to Teeressuonoja (Fig. 2) is also covered by mainly Norway spruce; the volume of growing stock is higher, 162 m^3 ha^{-1}. The catchment is rather steep, with a mean slope of 16.0% with an altitude range of 42–92 m.a.s.l. The soils at the Yli-Knuutila are more fertile; sand and fine sand moraines (67%), the rest is silt and clay moraines (Mustonen 1963). There are no areas of arable land or lakes in the catchment, the only significant anthropo-

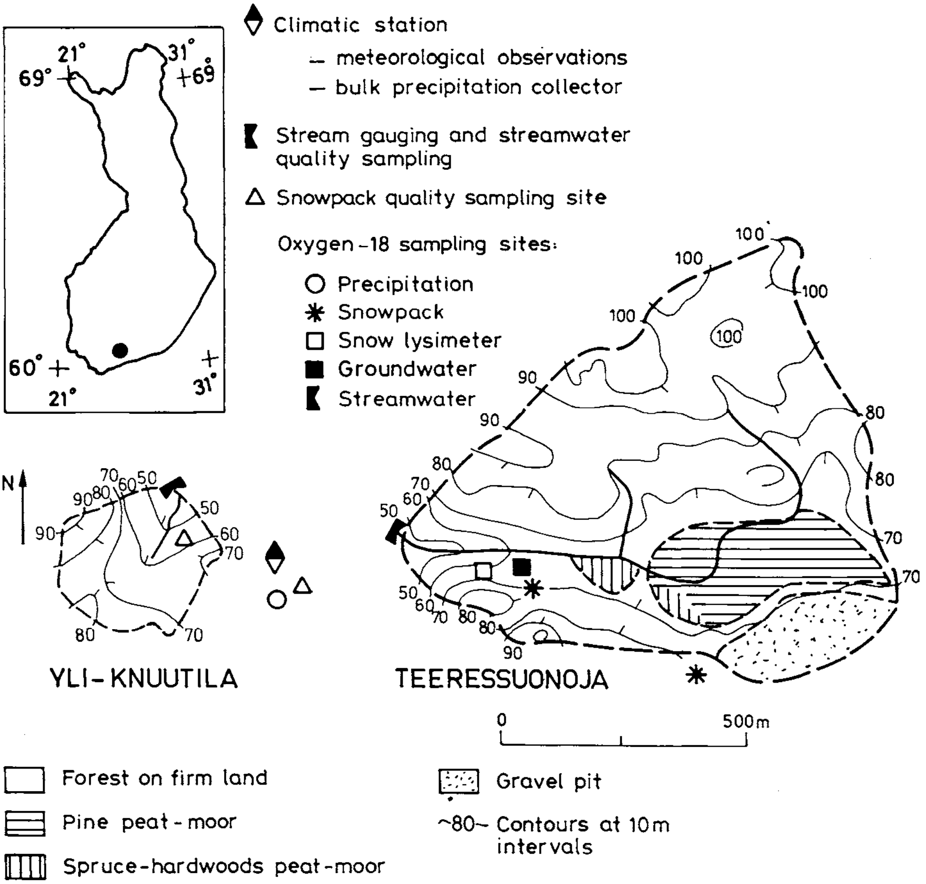

Fig. 2. Location map of the research catchments, Yli-Knuutila and Teeressuonoja

genic factor affecting the stream water chemistry is the atmospheric deposition. There was a small fertilizing experiment in 18–19 June, 1968, with 170 kg ha^{-1} of super phosphate and 140 kg ha^{-1} phosphorus-rich NPK fertilizer, from which the nitrogen input was 17.1 kg ha^{-1} together. During 1958–77 the mean annual runoff was 131 mm, the mean maximum instantaneous runoff during snowmelt 95-l s^{-1} km^{-2} and for summer rains 118-l s^{-1} km^{-2}, respectively (Seuna 1982).

Sampling

Stream water quality was sampled monthly during the period 1963–77. Since 1978, sampling was concentrated on spring and autumn high flow periods, with only 3–5 samples a year in 1978–80, and approximately 12 samples a year in 1981–84. During 1985–88, the sampling frequency increased to 40–60 samples a year. For the normal water quality analyses the stream water quality during 1985–88 was monitored two to five times a week during the snow melt period and normally once a week during summer and autumn.

Precipitation chemistry is based on 1-month bulk collections (Järvinen 1986). The chemical composition of snow was measured before the onset of melting in mid-March on samples from the snowpack in an open area, an open forested area, under the foliage in the forest, and the accumulated monthly precipitation as snow.

For oxygen-18 analysis, stream water was collected three to six times a week at the basin outlet during the melt periods, and on two 24-h occasions in 1985 every 2 h. Groundwater samples were taken from a well near the outlet. Precipitation water samples were taken from every storm event in spring 1987. In 1987 daily samples of meltwater were taken from a 1 m^2 snow lysimeter. In 1985 samples were taken only from the snowpack, assuming these samples to be representative of the meltwater.

Methods of Analyses

All the chemical analyses were made in the laboratory using the standard methods of water administration. The base cations have been measured with the same method (flame–AAS) since 1967. pH was determined with a Radiometer pH meter, NH_4^+ was measured by a spectrophotometric method with hypochlorite and phenol, SO_4^{2-} by a turbidimetric method and Cl^- by a titration with mercury nitrate. Alkalinity was determined by potentiometric titration to the pH values of 4.5 and 4.2 with HCl (National Board of Waters 1981). Nitrate-nitrogen was analyzed by the sodium salisylate method in the early phases of the monitoring period (1966–73) and later by the manual cadmium amalgam method (Erkomaa et al. 1977). Comparable results were obtained, however, by the old and new methods, with the difference of concentrations being less than 10% (National Board of Waters 1979). Due to analytical uncertainties, nitrate-nitrogen results from 1963–65 were omitted. The data are stored in the water quality data bank of the National Board of Waters and the Environment.

The oxygen–18-content of a water sample was determined by a ratio mass spectrometer at the University of Uppsala. The oxygen–18-content is expressed as the relative deviation of the isotopic ratio of the sample from that of a reference water, which is Vienna SMOW (Standard Mean Ocean Water) in our case. The accuracy of the measurements is about 0.1 δ-units.

Results and Discussion

Snowmelt Runoff in the Teeressuonoja Catchment

Snowpack in Winter 1984–85

In the snowpack the concentrations of calcium, magnesium and sodium were 60–70% of those in winter precipitation (December 1984–March 1985) (Table 1).

Table 1. The chemical composition of snowpack and precipitation in the studied areas in winter 1984–85 (December–March), during the period 1972–85, and in the spring 1988 in the open forested area and in the spruce stand

$\mu eq\ l^{-1}$	Snow-pack 26.3.85	Precipit. winter 1984–85	Precipit. 1972–85	Snow-open forested 22.3.88	Snow-spruce stand 22.3.88
Ca^{2+}	25	37	50	34	73
Mg^{2+}	6	9	18	5	14
Na^{+}	22	32	23	25	27
K^{+}	7	7	13	11	16
NH_4^{+}	–	75	72	48	64
H^{+}	–	99	50	35	56
SO_4^{2-}	69	149	127	81	137
Cl^{-}	–	27	32	23	25
NO_3^{-}	–	88	47	55	61
Cations	–	259	226	158	250
Anions	–	264	206	159	223
pH	–	4.00	4.30	4.45	4.25

The concentration of sulphate in the snowpack (69 $\mu eq\ l^{-1}$) was less than half of that compared to that in winter precipitation of 1984–85 (149 $\mu eq\ l^{-1}$). These observations indicate a significant release of sulphate and base cations from the snowpack during the thaw periods in winter.

The winter precipitation of 1984–85 was clearly more acid (pH 4.0) than the average yearly precipitation in Vihti in the years 1972–85 (Table 1). Nitrate concentration was almost double, and sulphate some 20% higher than the long-term averages. On the other hand, the concentrations of base cations, except sodium, in winter precipitation were clearly lower than these averages. The concentrations of base cations during the snow-free period are normally higher due to dust from the nearby areas, which are neutralizing the deposition to some extent.

When comparing the chemical composition of snow in open forested area and in spruce stand in spring 1988 (Table 1), it was noticed that snow under the foliage was more acid (0.2 pH units) with clearly higher concentrations of sulphate and calcium. Possible reasons might be (1) leaching of pollutants from the foliage to the snowpack and (2) more dry deposition to the canopy than to the open areas.

Snowmelt in Spring 1985

The water equivalent of snow was determined from the snow course of 60 observation points in the same area. The decrease in the water equivalent of snow during the melt period was also calculated by the modified PULSE model (Fig. 3). The area was covered by snow between 14 December 1984 and 5 May 1985. In the beginning of the winter there was a thaw period, 20–24 December, after which the

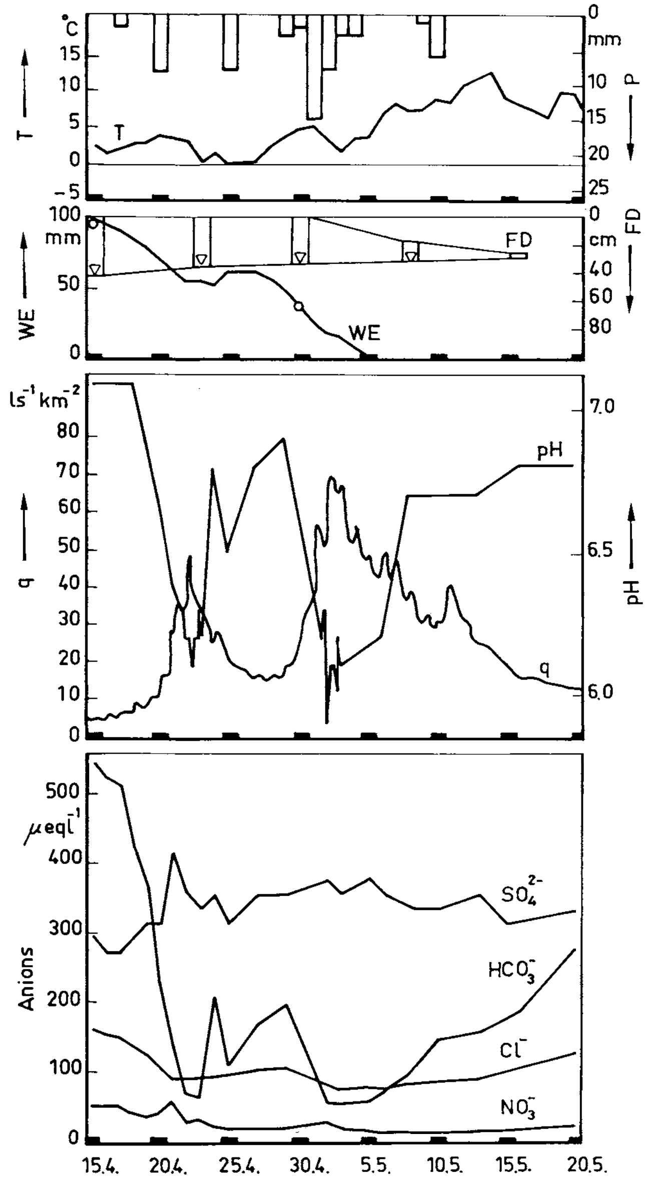

Fig. 3. Daily precipitation (*P*), daily mean air temperature (*T*), the depth of soil frost (*FD*), water equivalent of snow (*WE*), runoff (*q*), pH and concentrations of major anions of the Teeressuonoja stream during the melt period of 1985

temperature was below zero until the middle of March. The first melting pulse was observed 26–28 March, during which time runoff increased from the baseflow level of 0.8-l s^{-1} km^{-2} to 2.9-l s^{-1} km^{-2}. The water equivalent of snow was at its maximum from 8 to 13 April, 109 mm, just before the actual melting begun.

Snowmelt occurred in two separate phases; from 14 to 29 April, and from 30 April to 6 May. The first phase was dominated by melt water (55 mm) with minor inputs from precipitation (19 mm, one half as snow) (Fig. 3). During the latter phase precipitation played more important role (26 mm) being almost one half compared to meltwater (49 mm). Runoff during the first phase was 23 mm, and 29 mm during the second, respectively.

The depth of frost before the melt period was 42 cm (Fig. 3). Melting of frost occurred during 1-month until the middle of May. Before the first runoff peak, 22 April, there was very little melting. In the hydrograph separation analysis it was found that about 30% of the total runoff was "new" meltwater discharging in the upper layers of the soil. A quick discharge of the "old" water into the stream channels and the increase in the groundwater table requires an effective infiltration of the meltwater into the frosted soil. The major part of the runoff water in the beginning of melt period is probably shallow groundwater from the discharge areas nearby the channels. During the second melt peak the depth of soil frost was still 25 cm, most of the melting had occurred near the soil surface.

Separation of Event and Pre-event Water in Spring 1985 and 1987

The basic assumption of the tracer method for stream hydrograph separation is that stream flow is contributed by two sources, i.e. precipitation (as rain or snowmelt) and groundwater. From mass and tracer balance in steady state, the fraction of groundwater contribution in the stream is

$$X_g = (\delta_s - \delta_p)/(\delta_g - \delta_p), \qquad (1)$$

where δ_s, δ_p and δ_g are the tracer compositions of stream water, precipitation and groundwater, respectively.

In humid regions the isotopic composition of groundwater is about the same as the annual weighted mean content of the precipitation. During low flows the oxygen-18 content of the stream water is the same as that of groundwater. The meltwater is isotopically much lighter than the groundwater, which, in combination with the large runoff volumes of meltwater, enables rather accurate stream hydrograph separation computations. The hydrograph separation in the Teeressuonoja catchment has been discussed by Bengtsson et al. (1989).

In 1985 the $\delta^{18}O$ of stream water was -12.2‰ just before the onset of melting. The $\delta^{18}O$ of groundwater measured from a shallow well near the basin outlet varied from -12.5 to -12.6‰ during the melt period in April. Thus, the shallow groundwater was to some extent affected by oxygen-18-depleted meltwater. The initial streamwater concentration was considered to be representative of the pre-event groundwater and was used for the hydrograph separations.

In the first phase of the melt period the $\delta^{18}O$ of streamwater reached its lowest value, -13.7‰, in about 6 days and thereafter it increased to -12.5‰ (Fig. 4). After the cessation of the high flow, the $\delta^{18}O$ of stream water returned to its

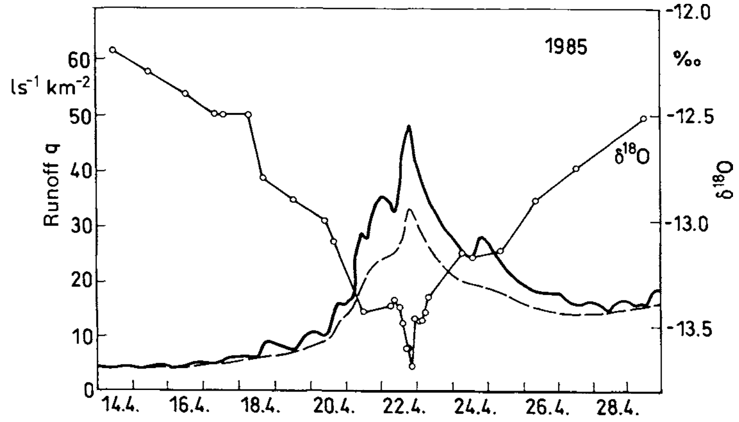

Fig. 4. Total runoff (q, *solid line*), ^{18}O content of runoff (δ^{18} O) and pre-event groundwater fraction of runoff estimated by oxygen-18 (*broken line*) in Teeressuonoja in spring 1985

pre-event value. Thus, the δ^{18}O of deep groundwater seems to have remained constant during the melt period. The isotopic input, the δ^{18}O of the snowpack, was characterized by an enrichment from -17.8 to -15.7‰ during the first melting phase. Because the meltwater oxygen-18 content was not known for this period, linear interpolation was used to obtain the value on a daily basis.

The total runoff during the first phase of the melt period (14–29 April) was 23 mm. The average computed fraction of pre-event groundwater in the stream was 85% (19 mm) and surface runoff 15% (4 mm) during the period. During a 24-h occasion on 22–23 April a detailed study revealed that the oxygen-18 content of streamwater varied between -13.4 and -13.7‰. The lowest value, -13.7‰, was measured 1.5 h after the runoff peak of 48.4-l s^{-1} km^{-2} (0.17 mm h^{-1}) at 19.00 h, 22 April. The fraction of pre-event groundwater varied from 68 to 75% during the occasion, the lowest fraction found at about the same time as the instantaneous runoff peak, which means that the largest event water contribution was 15.5 l s^{-1} km^{-2}. Another large melt period in the beginning of May could not be resolved due to isotopic perturbations caused by 15 mm rain of value -10.9‰.

Prior to snowmelt of 1987 the δ^{18}O of streamwater was -12.1‰ which was also used as a pre-event groundwater value. Two runoff peaks were observed within 2 weeks but the peaks as well as the runoff volume were much smaller than in 1985. The runoff hydrograph and the oxygen-18 variation of the stream water are shown in Fig. 5. Although the δ^{18}O of stream water varied between -12.1 and -12.9‰ only, the hydrograph separation computation could be performed because there was very little contribution from rainfall during the melt period. In the period from 30 March, when the first melt was observed, until 13 April, when the runoff started to increase considerably, the δ^{18}O of meltwater from the lysimeter increased from -17.4‰ to -14.3‰. From then on no further enrichment was assumed to occur. However, the melt proceeded faster in the lysimeter than in the basin as a whole.

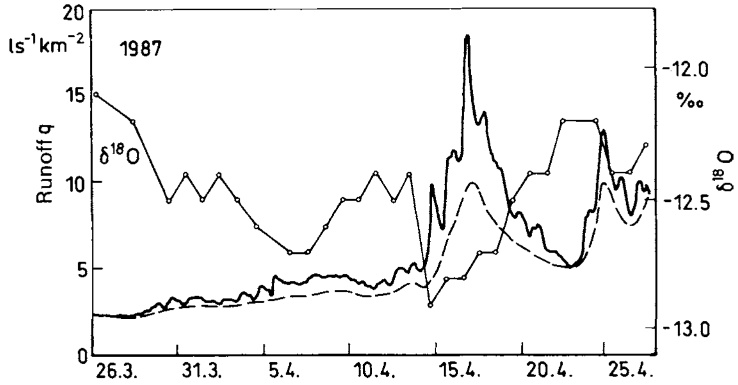

Fig. 5. Total runoff (*q, solid line*), ^{18}O content of runoff (δ^{18} O) and pre-event groundwater fraction of runoff estimated by oxygen-18 (*broken line*) in Teeressuonoja in spring 1987

The computed minimum groundwater fraction was 58% of the runoff of 7.0-l s^{-1} km^{-2} in the beginning of intensive melting around 14 April. During the peak flow on 17 April the groundwater fraction was 68% of 14.3-l s^{-1} km^{-2}, which means that the largest event water contribution was not more than 4.6-l s^{-1} km^{-2}. The groundwater fraction during 26 March–27 April was 83% (15 mm), and only about 17% (3 mm) of the total discharge was new meltwater. The dominant mechanism in the system is the displacement of old soil water and groundwater by infiltrating meltwater. The estimated pre-event water fractions agree with the results of the studies made in the comparable conditions. In Sweden, Rodhe (1987) observed that the fraction of pre-event water ranged between 32 and 95% of the discharged volumes, with a median value of 61%, in 29 snowmelt runoff events studied in ten catchments. In several Canadian basins Fritz et al. (1976) found that the groundwater contribution to rainfall-generated runoff varied from 40 to 90% of the stream flow.

Changes in the Teeresuonoja Stream Water Quality During Snowmelt 1985

Figure 3 shows runoff, pH and the anions of the Teeressuonoja stream during the melting peaks in 1985. A drop of stream pH in 1985 from a winter baseflow of 7.3 to 6.1 during the first and 5.9 during the second peak was measured, indicating that much of the acidic meltwater infiltrates the subsurface, displacing neutral groundwater to the stream. Alkalinity decreased in 5 days from 510 μeq l^{-1} on 17 April down to 70 μeq l^{-1} on 22 April due to the increase of strong acids (HNO_3 and H_2SO_4) and the dilution of bicarbonate with snowmelt water.

The depression in stream pH during spring runoff has in many studies been attributed to the rapid generation of overland flow which is produced by melting of an acid snowpack overlying frozen, impermeable soils. Environmental isotope studies indicate, however, that much of the snowmelt runoff is actually pre-event in origin (e.g. Dincer et al. 1970; Fritz et al. 1976).

Concentration of sulphate in stream water ranged from 13.0 to 20.0 mg l^{-1} (271–416 μeq l^{-1}) the highest value occurring during the first flow peak (Fig. 3). Concentration was increasing together with the increasing fraction of acid surface runoff into the stream. About 85% of the runoff water during the first snowmelt peak was pre-event water. Because the initial groundwater concentration was 250 μeq l^{-1} and the stream water concentration 416 μeq l^{-1}, the first meltwater should have had a sulphate concentration of about 900 μeq l^{-1}. The ionic separation during snowmelt has been observed in many studies, e.g. (Johannessen et al., 1980, Jenkins et al., 1987). A marked elution effect in meltwater in an upland Scottish basin was observed by Jenkins et al. (1987) with sulphate concentrations up to 550 μeq l^{-1} and a quick dilution of meltwater down to 100 μeq l^{-1} in about 1 week.

Chloride was diluted to about half of its winter baseflow value. The lowest concentration of chloride in stream during the melt period, 76 μeq l^{-1}, was high compared to average value in precipitation in 1972–85, 32 μeq l^{-1}, indicating high fraction of old, concentrated pre-event water in the stream.

Yli-Knuutila Stream Water Chemistry of the Year 1985

Ionic Balance of 1985

The ionic balance for the year 1985 was calculated for the bulk precipitation, and for the stream water of Yli-Knuutila and Teeressuonoja (Table 2). A relatively good charge balance was observed for Yli-Knuutila. There are only minor differences in the balances calculated for the different years, almost the same average

Table 2. Ionic balance of precipitation, and streamwater of Yli-Knuutila and Teeressuonoja in 1985. Values of bulk precipitation are annual averages, values of stream water are volume weighted annual averages

μeq l^{-1}	Bulk precipitation	Stream water Yli-Knuutila	Stream water Teeressuonoja
Ca^{2+}	36	378	407
Mg^{2+}	12	299	215
Na^{+}	23	167	118
K^{+}	7	49	24
NH_4^+	61	7[a]	–
H^{+}	46	1	1
SO_4^{2-}	117	570	335
Cl^{-}	27	101	108
NO_3^-	49	104	29
HCO_3^-	–	65	155
Cations	185	901	765
Anions	193	840	627
pH	4.34	5.88	6.29

[a] 1984.

concentrations were calculated for 1984 (Lepistö et al. 1988b). An anion deficit of 18% was observed for Teeressuonoja, probably due to organic anions.

Stream water of Yli-Knuutila was characterized by clearly higher concentration of sulphate and nitrate, and lower bicarbonate. Of the cations, the concentrations of Mg, Na and K were higher. One reason for the differences is higher evapotranspiration in the Yli-Knuutila catchment, particularly higher interception loss from the forest canopy. Most of the difference in sulphate might be explained by a more effective capture of atmospherically derived ions (dry deposition) by the dense forest canopy. Kallio and Kauppi (1990) measured throughfall deposition in the Yli-Knuutila catchment during the period 28.4.–2.11.1988 and found that the total sulphate deposition (wet + dry) under the spruce foliage (2780 kg km^{-2}) was over twofold compared to an open forested area (1310 kg km^{-2}).

The concentration of sulphate in the baseflow of the Yli-Knuutila catchment is high, 400–600 μeq l^{-1}. Crude approximations of steady-state sulphate concentrations for streams, assuming no internal sources or sinks of sulphate in the catchment, can be calculated using concentration of sulphate in precipitation and the ratio of precipitation to runoff to account for concentration (see Kaufmann et al. 1988). Runoff of the Yli-Knuutila catchment in 1985 was very low, 117 mm, 18% of annual precipitation, concentration factor P/Q being 5.5. One could even suspect a loss of deep groundwater from the basin, but no evidence of such a seepage exists. When multiplying annual measured concentration of 117 μeq l^{-1} in precipitation by 5.5 we obtain 647 μeq l^{-1} which is of the same order as measured, volume weighted concentration of runoff, 570 μeq l^{-1} (Table 2).

Snowmelt Episode and the Autumn High Flow Period of 1985

In the stream water of Yli-Knuutila there was a significant increase in sulphate concentration, from a baseflow level of 500 μeq l^{-1} on 26 March up to 980 μeq l^{-1} on 28 March, just when the first fractions of meltwater reached the stream (Fig. 6). At the same time, runoff increased minimally, from a winter baseflow level of 0.28-l s^{-1} km^{-2} to 0.59-l s^{-1} km^{-2}. Dilution was effective and the concentration of sulphate decreased quickly below the winter baseflow level. At the beginning of the first proper snowmelt peak, concentration doubled again, to 812 μeq l^{-1}, was then diluted and concentrated again during the second snowmelt peak in early May, now to a lower level.

Drastic changes in the anion concentrations, mostly sulphate, were mainly balanced by increased concentrations of calcium and magnesium, i.e. there were large quantities of weathering products in the soil which leached out together with the very first fractions of meltwater. Calcium and magnesium concentrations increased 30–50% from the winter baseflow values in late March, with smaller increases and dilution after that during the later parts of the melting (Fig. 6). In many studies a slight increase in the salt concentration of stream water or groundwater has been observed just at the beginning of snowmelt (e.g. Pearce et al. 1986, Johannessen et al. 1980, Soveri 1985).

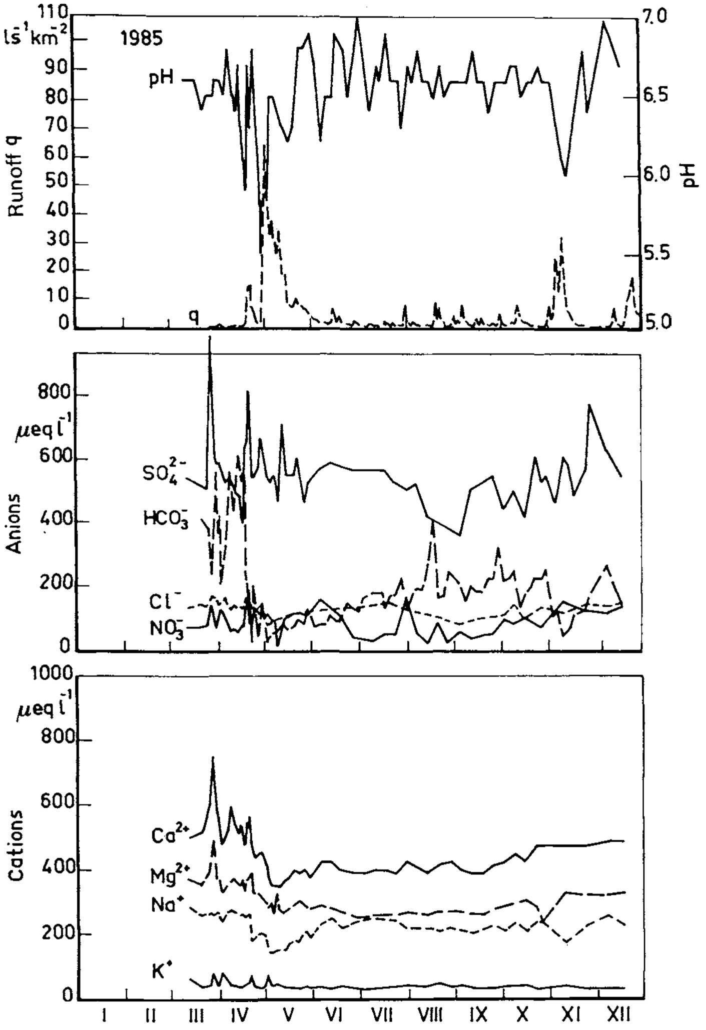

Fig. 6. Runoff (q), pH, concentrations of major anions and major cations of the Yli-Knuutila stream in 1985

A drop of stream pH from a winter baseflow of 6.6 to 5.5 and a decrease of bicarbonate from 400–500 μeq l^{-1} to close to zero occurred during the major melt peak. A drop of 0.7 pH-units was recorded together with elevated sulphate concentrations as a result of autumn rains (Fig. 6).

Nitrate increased considerably from the baseflow level of 70–80 μeq l^{-1} to 140 μeq l^{-1} in late March and up to 200 μeq l^{-1} just at the beginning of the first proper snowmelt peak on 21 April. The NO_3/SO_4-ratio was fairly high during the melt period, average being 17%, and the range 3–29%. Normally, most of the nitrate will be taken up in the catchment, except during the snowmelt period and during autumn rains, and only a small fraction will appear in runoff (e.g. Overrein et al.

1981). Thus mobile sulphate and nitrate will have different effects not only on terrestrial systems, but also for acidification of freshwater. It seems clear, however, that nitrate is becoming more important in the context of acidification, especially when monitoring fertile forest soils. In Yli-Knuutila a summer rain of 19 mm in the end of July 1985 increased the nitrate concentration quickly by over threefold to 164 μeq l^{-1} (NO_3–N 2300 μq l^{-1}). According to a Nordic working group (Nilsson 1986), to protect the most sensitive surface waters, the nitrogen deposition must not exceed the point at which it will cause leaching from the catchment at concentrations of more than 20 μeq l^{-1} as nitrate. This limit is clearly exceeded in Yli-Knuutila and also in Teeressuonoja.

Stream water Quality from the 1960's to the Present Day

During the period 1950–70 the increase in the sulphur emissions in Europe was approximately 100% and in Finland approx. 500% (Kulmala 1985). Deposition of sulphate in Finland was clearly higher during the 1970's compared to the 1950's (Järvinen and Haapala 1980). There has, however, been no distinct change in the air-borne sulphur load in southern Finland since the beginning of the 1970's (Kulmala 1985). The concentration of nitrogen compounds in the precipitation over North America and Europe has successively increased (e.g. Galloway and Dillon 1983; Söderlund and Granat 1982). The deposition of N compounds (wet + dry) is reaching 30 to 40 kg ha^{-1} a^{-1} in many areas in Central Europe and above 20 kg in the southern parts of Scandinavia (Grennfelt and Hultberg 1986). Forest growth is generally limited by N deficiency and N deposition will have a fertilizing effect. The retention of nitrogen is therefore high in forest ecosystems. High N deposition may, however, cause a nitrogen saturation which in turn may cause a considerable output of nitrate along with leaching of base cations and/or Al and H^+ from the soil.

pH and Alkalinity

No significant trend in the pH of stream water during a 25-year observation period (1963–88) occurs at Teeressuonoja (Fig. 7). The observed range of pH is 5.4–7.8. When comparing pH and the runoff of the sampling day, a highly significant ($r = -0.80^{***}$) negative correlation was found (Fig. 8) with low pH values always during the high flows connected with snowmelt or heavy autumn rains. Long-term acidification implies a continuing loss of alkalinity. Unfortunately, this kind of data does not exist.

Yearly variation of pH, alkalinity and runoff was simulated by the PULSE model (Bergström et al. 1985) using a time period of 14 years (1972–85) (Lepistö et al. 1987). The daily averages of temperature and daily totals of precipitation were used as input. Verification was carried out with data from the intensively monitored years 1984–85 ($R^2 = 0.84$ for runoff, $R^2 = 0.71$ for pH). A considerable

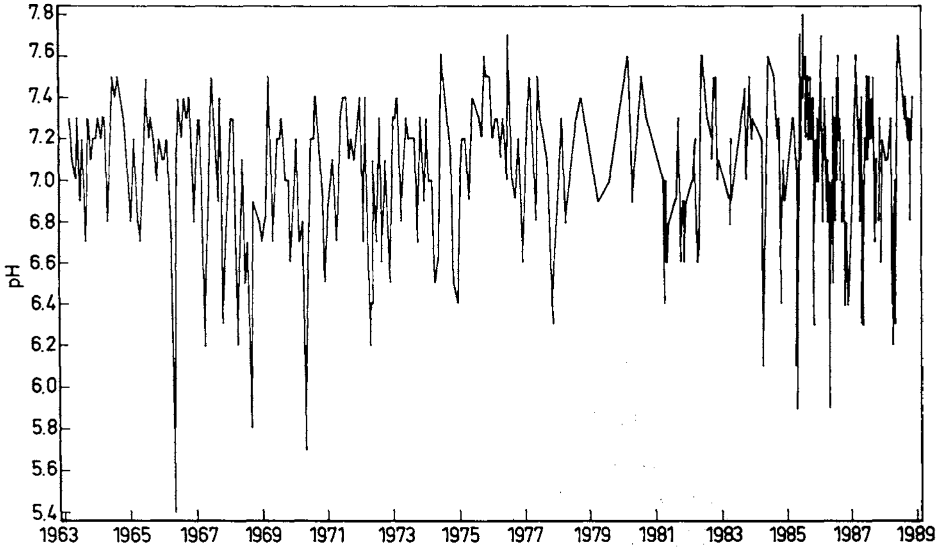

Fig. 7. pH in the stream water of Teeressuonoja during the years 1963–88

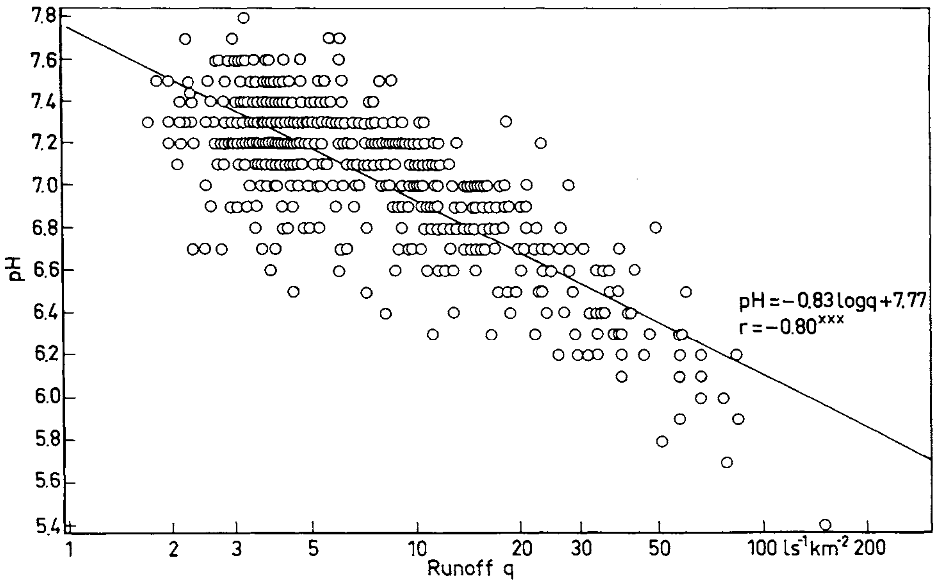

Fig. 8. Relationship between pH and daily runoff in Teeressuonoja during the years 1963–88

part of the variation of pH and alkalinity in the different hydrological years could be simulated. The model results and observations suggested that flow dominates the release of hydrogen ions, with poorly buffered runoff water every time when the flow rate was increasing.

Calcium

Calcium concentration and runoff of the sampling day in the Teeressuonoja catchment were compared, dividing the observation period into two periods; the years 1967–80 and 1981–88. Statistically highly significant negative correlation was found both during the first (r = − 0.84***) and second phase (r = − 0.95***) (Fig. 9). Three high concentrations, outliers, were not included in the regression analyses. It is obvious that concentrations have increased particularly during the low flows; e.g. with the runoff 4-l s^{-1} km^{-2} average concentration in the 1967–80 was 9.8 mg l^{-1} (490 µeq l^{-1}) and in the 1980's 13.5 mg l^{-1} (680 µeq l^{-1}). The increase during the low flows has been about 200 µeq l^{-1}. When calculating annual loads, the concentrations during the high flows dominate; however, with no clear changes between the first and second period. The increase in calcium just during the low flows is comparable to the increases in groundwater calcium concentration in the southern Finland stations (Soveri and Ahlberg this Vol.). Increased calcium concentrations have been found by many researchers in the lakes in acidified areas, e.g. Almer et al. (1978), Dillon et al. (1979). By ion exchange reactions between H^+ and metal cations and by increased SO_4^{2-} leaching, a net increase in the leaching of Ca and Mg is likely. Acid precipitation will most likely increase the weathering rates in the soil. The crucial point therefore is if the increase in weathering can compensate for the increased leaching losses (Abrahamsen 1980).

Sulphate and Nitrate

Observation series for sulphate in the streamwater of Teeressuonoja and Yli-Knuutila begin in the 1981 and 1983, and are not long enough to detect possible

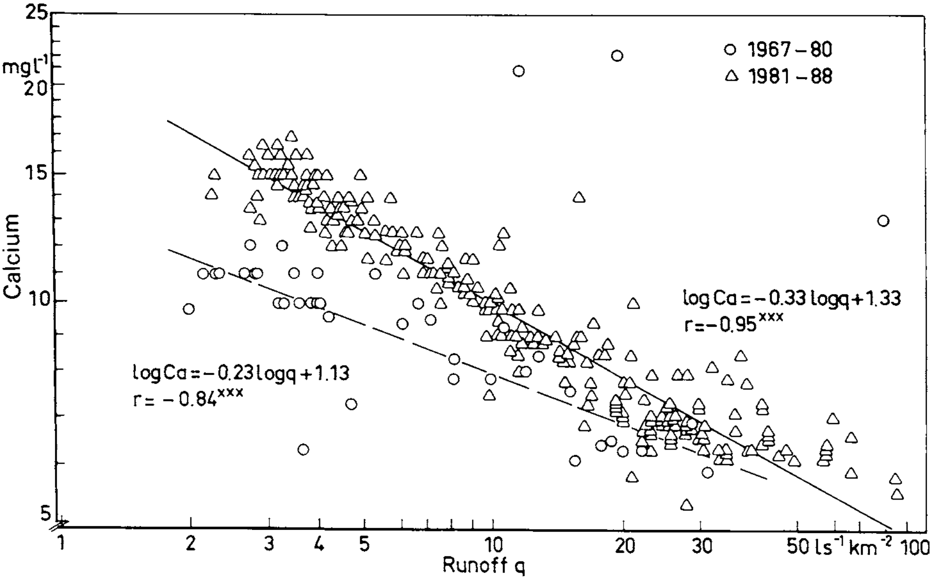

Fig. 9. Calcium vs. runoff in Teeressuonoja during the years 1967–80 (○) and 1981–88 (△)

changes. There is, however, a clear positive correlation between runoff and sulphate (r = 0.56***) in Teeressuonoja with an increase from 11 mg l^{-1} to 20 mg l^{-1} when runoff increases from 3 to 80 l s^{-1} km^{-2}.

There exist much longer data sets of nitrate-nitrogen in stream water (Yli-Knuutila 1969–88; Teeressuonoja 1966–88). A sustained increase in nitrate-nitrogen concentration was observed in both catchments. Volume weighted annual average concentration in Yli-Knuutila in 1969–74 was 500 µg l^{-1}, 1975–80-800 µg l^{-1} and 1981–87 1270 µg l^{-1} (91 µeq l^{-1}), 2.5 times that of the first period. The concentration level of nitrate in Yli-Knuutila is high considering the only anthropogenic factor affecting to the stream water is atmospheric deposition.

In Teeressuonoja, concentrations of NO_3–N are lower, but the increasing trend is comparable to that of Yli-Knuutila. The main increase is from the mid-1970's until the mid-1980's (Fig. 10). Nitrate concentration and runoff of the sampling day in the Teeressuonoja catchment were compared dividing the observation period to two periods; the years 1966–76 and 1977–88. A statistically highly significant correlation (r = – 0.48***, n = 259) was found between runoff and nitrate during the second period (Fig. 11). Correlation during the first period was weaker (r = – 0.18*, n = 128). The nitrate concentration during the first period was quite independent of the runoff, but during the second period a more negative correlation was found, with the highest concentrations during the low flows.

Figure 11 shows that concentrations have increased particularly during the low flows; e.g. with the runoff 4-l s^{-1} km^{-2} average concentration in the 1966–76 was 250 µg l^{-1} and in the 1977–88 over twofold (525 µg l^{-1}). When calculating equivalents, the change was about 20 µeq l^{-1}, one-tenth of the increase in calcium concentration. Increase in the equivalence sum of anions should be comparable to

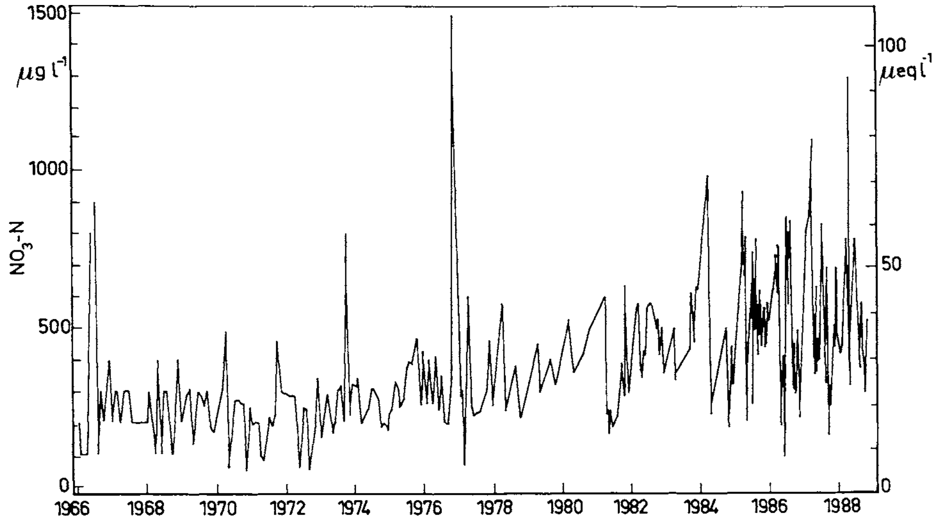

Fig. 10. Nitrate-nitrogen in the stream water of Teeressuonoja during the years 1966–88

that of increase of calcium. Nitrate plays a minor role in equivalents, so it is probable that sulphate concentrations at least during the low flows have also been increasing. This cannot be verified, however, due to the short observation series. The situation during the high flows is more variable, the variation of concentrations is clearly higher and depends much on the status of flow (increasing-decreasing flow).

The sampling frequency has been changing considerably during the study period of 1966–88, being the highest during the last 4 years, some 40–60 samples a year. The increase in NO_3–N (Fig. 11) does not appear to relate to frequency of sampling because higher concentrations during the latter period are associated with both high and low flow. The fertilizing experiment in Yli-Knuutila in 1968 was comparable to about 2 years of nitrogen deposition, with some increase in the leaching of nitrogen during the period limited to the first years of the 1970's. In Teeressuonoja there has been some excavation of sand and gravel (Fig. 2) which might have some local effect on groundwater quality (e.g. nitrate concentration) but in a catchment scale this effect can be considered negligible. Nitrate increase in a nearby undisturbed catchment, Yli-Knuutila, has been even higher, however.

In southern Finland the bulk deposition of nitrogen (mostly wet deposition) exceeds 10 kg ha^{-1} a^{-1} in many observation stations, the average of 52 stations all over Finland being 6 kg ha^{-1} a^{-1} during the years 1971–82. The deposition of nitrogen has been increasing in over 80% of the number of stations during that time (Järvinen 1986). During the years 1971–78 the annual bulk deposition of nitrogen at Vihti station (Fig. 2) was 7.4 kg ha^{-1} a^{-1} and in 1979–87 11.4 kg ha^{-1} a^{-1}, with a range of 4.2–15.0 kg ha^{-1} a^{-1} during the whole period.

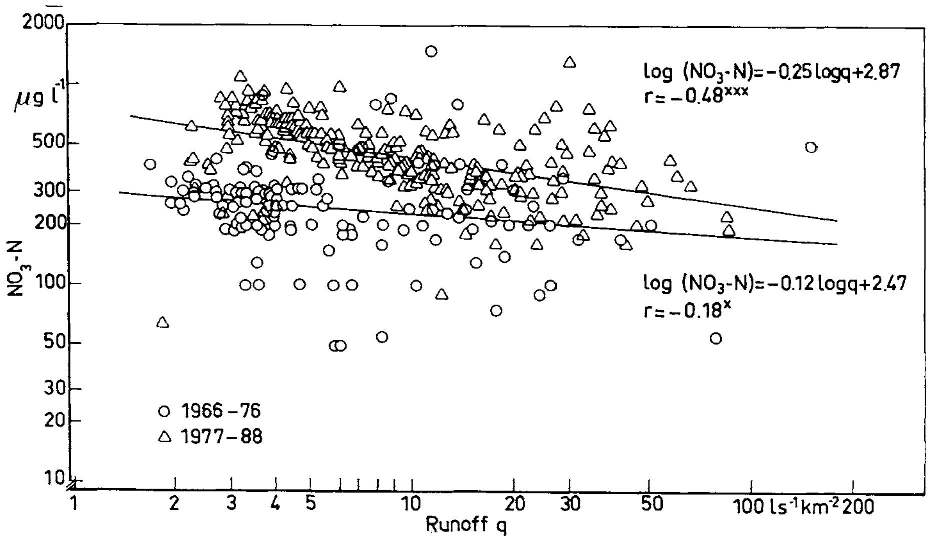

Fig. 11. Nitrate-nitrogen vs. runoff in Teeressuonoja during the years 1966–76 (○) and 1977–88 (△)

It is probable that increase in the atmospheric deposition of nitrogen has caused the increases in nitrate concentrations of the forest streams of Yli-Knuutila and Teeressuonoja. These increases in stream water nitrate could also indicate the beginning of nitrogen saturation in soils. Similarly, Kauppi (1984) reported increasing nitrate in four forested basins in southern and central Finland. According to Rekolainen (1989), the total nitrogen load has increased from 1.3 kg ha^{-1} a^{-1} in 1969–74 to 3.0 kg $ha^{-1}a^{-1}$ in 1981–85 in Yli-Knuutila catchment and from 1.9 kg ha^{-1} a^{-1} in 1965–74 to 3.1 kg ha^{-1} a^{-1} in 1981–85 in Teeressuonoja, respectively. Likens et al. (1977) studied deciduous forest catchments of Hubbard Brook and found that the annual weighted concentration of nitrate has been generally increasing during the period 1964–74. Freezing and thawing of the soils may have induced nitrification and the subsequent loss of relatively large amounts of nitrate in stream water. Another possible explanation for the increasing concentrations of nitrate in stream water is that nitrate concentrations in precipitation have also been increasing. In southern Sweden the nitrate concentration has increased by 50–100% during the last 10–20 years in deep oligotrophic lakes, which are not affected by agriculture or forest fertilizers (Dickson 1986). Henriksen et al. (1988) found that nitrate concentrations doubled in small lakes in southernmost Norway from 1974–75 to 1986, an increase that cannot be explained by increased nitrogen deposition alone.

Conclusions

Overland flow plays a minor role in the permeable soils to Teeressuonoja. The isotope studies show that snowmelt runoff consists to a considerable degree of pre-event water (70–85%) that is being pushed out from the catchment by infiltrating meltwater. Pre-event water is discharged to the Teeressuonoja stream at rates varying throughout the year. The highest rates occur during snowmelt and after heavy rain. During dry periods in summer and in winter the stream water is dominantly composed of groundwater from deeper layers with high pH values and high concentrations of base cations and bicarbonate. Dilution is effective during the melt period. It is probable that quite dilute, shallow groundwaters dominate during that time. Sulphate is transported primarily through the saturated zone of the soil.

In the study years of 1985 and 1987 the total snowmelt runoff and peakflows were smaller than the long-term averages. It can be expected that in the case of higher runoff the fraction of event water would be greater than in 1985 and 1987. From the hydrographs it is obvious that the pre-event water is pushed out without a notable lag during the snowmelt period. The catchment thus responds to water inputs more in the way of quickflow than the origin of water would indicate.

The major control on the composition of the streams is the discharge of groundwater and soil water to the streams. During snowmelt episodes, however, quick changes were noticed in the runoff water of both catchments associated with increased quantities of meltwater discharging in the surface layers of the soil. These changes include a drop in pH (up to 1.0–1.5 units) and alkalinity, and a distinct increase in sulphate concentrations particularly in Yli-Knuutila (from 500 to 1000 μeq l^{-1}), mainly balanced by increase in calcium and magnesium. The high concentrations of sulphate in the stream water of Yli-Knuutila indicate an effective capture of atmospherically derived ions (dry deposition) by the dense forest canopy, and high evapotranspiration (particularly interception).

No significant trend was found in the stream water pH of Teeressuonoja during the last 20–25 years. The observed range of pH was 5.4–7.8 for Teeressuonoja and 5.5–7.9 for Yli-Knuutila. The longer-term changes detected in the stream water quality include increased nitrate-nitrogen and calcium concentrations. The respective increase in sulphate concentration seems probable, however, but due to short observation series this could not be verified. Acid deposition has promoted the leaching of calcium from the forest soil, particularly during the low flows. The crucial point will be if the increase in weathering can compensate for the increased leaching losses. The concentrations of nitrate-nitrogen have increased clearly in both the catchments. The main changes have occurred during the low flows. Increase in nitrogen deposition is probably the main factor affecting increasing nitrate concentrations in the runoff water. These increases in stream water nitrate could also indicate the beginning of nitrogen saturation in soils.

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Organic Acidity in Finnish Lakes

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Summary

The Finnish Lake Survey, conducted in autumn 1987 and consisting of 987 randomly selected lakes, describes the average lake water quality in the country, where one-third of the land area is covered by peatlands, and where lakes are predominantly small and shallow. As a result, median TOC and colour values are high (12 mg l^{-1} and 100 mg Pt l^{-1} respectively). The proportion of lakes with TOC concentrations $\geq$ 5 mg l^{-1} in the whole country is 91%. The lower TOC concentrations in northern Finland can mainly be related to the lower primary production in colder environments. The high TOC concentrations strongly affect the acidity of lakes in Finland (median pH 6.3). Organic anion, estimated by charge balance, is the main anion in the whole country (median 89 μeq l^{-1}). For the lakes with pH < 5.3, 73% have organic anion as the dominant anion. However, in the highest deposition areas in southern Finland, minerogenic acidity exceeds the organic acidity in 76% of the lakes with TOC concentrations $\geq$ 5 mg l^{-1}.

Introduction

Humic brown-water lakes are common in the boreal landscape worldwide but are most closely associated with temperate and cold regions. The primary source of aquatic humus is terrestrial input, although decomposition products of aquatic organisms may be important in some cases. Peatlands provide a rich medium for organic matter production. High organic carbon concentrations are frequently encountered also in the soil solutions in the organic horizon of mineral soils, especially in coniferous forests (e.g. Cronan and Aiken 1985). However, organic carbon concentrations in runoff waters from well-drained mineral soils are usually much lower than from peatlands (e.g. McDowell and Wood 1984). In peatlands, surface layer runoff is the dominant form of runoff, and this encourages high leaching of organic carbon. In mineral soils, the primary source of organic carbon to the watercourses is organic-rich surface soils, whereas the lower soils appear to be a sink. Because precipitation normally passes through surface soil horizon producing drainage water with relatively high concentrations of organic carbon, it

Kauppi et al. (Eds).
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is the extent of interaction with the lower soil horizon that determines the transport of organic carbon to the watercourses (Mulholland 1988).

The climate in Finland is humid and the topography is fairly flat. Mineral soils are largely podzolic, having developed from till or glaciofluvial deposits mainly on granitic bedrock. Peatlands cover about one-third of the land area in Finland (see Fig. 1). The areal percentage of peatlands out of the total land area is higher than in any other country. The total area of peatlands in Finland is about 9 million ha (The Finnish Forest Research Institute 1989). Only in the U.S.S.R., Canada, the U.S.A., and Indonesia is the area of peatlands higher. In Finland the ditching and draining of peatlands for forestry has been very intensive: to date, about half the area of peatlands has been ditched. Coniferous forests are predominant, and 66% of the land area is presently used for forestry (The Finnish Forest Research Institute 1989). The mean total organic carbon concentration was above 10 mg l^{-1} in 18 out of the 21 rivers flowing to the Baltic Sea during the years 1974–76 (Wartiovaara 1978). The catchments of these rivers cover about two-thirds of the total area of Finland. Considering the various processes of degradation and sedimentation of organic matter occurring in lakes, the average organic carbon concentrations in Finnish headwaters are much higher. The number of lakes is high (56,000 lakes with surface area larger than 0.01 km^2), most of which are small, humic and relatively shallow.

Regional surveys of lakes conducted in North America and Scandinavia have demonstrated anthropogenic lake acidification in sensitive areas. The lake selection in Norway and in the Eastern Lake Survey in the United States was targeted at sensitive areas. Most of these lakes had low organic carbon concentrations (see Brakke et al. 1988; Eilers et al. 1988a; Eilers et al. 1988b; Henriksen et al. 1988a; Henriksen et al. 1988b; Landers et al. 1988). In some subregions in the Eastern Lake Survey, especially in northeastern Minnesota, the upper Great Lakes area and Florida, organic carbon concentrations were higher. Humic lakes are also found over large areas in eastern Canada (e.g. Jeffries et al. 1986) and in Sweden (Swedish Environmental Protection Board 1986). It has been shown that acidity in humic lakes is affected both by organic acidity from peatland catchments and by acidic deposition (e.g. Gorham et al. 1986; Kerekes et al. 1986; Brakke et al. 1987).

Several previous studies have indicated that lake acidification is a common phenomenon in small clearwater lakes in southern Finland (e.g. Tolonen and Jaakkola 1983; Kämäri 1985; Kenttämies et al. 1985; Simola et al. 1985; Tolonen et al. 1986; Forsius et al. 1987). Kortelainen and Mannio (1988) demonstrated that the pH of a set of 60 humic lakes was determined to a greater extent by individual catchment characteristics and high organic matter concentrations than by their geographical location at the present atmospheric loadings received in Finland.

A survey of 987 lakes was conducted as part of the Finnish Research Project on Acidification (HAPRO) (see Forsius et al. this Vol.). In this chapter, this large data base is used to demonstrate the TOC concentrations and the role of organic acidity in different deposition areas in Finland as well as to discuss the overall importance of organic acidity in Scandinavia and North America.

Material and Methods

Selection of Lakes

The lakes for the survey (n = 987) were randomly selected by a two-stage cluster sampling from two separate subregions, 1 and 2, which together covered the whole country. The selection was weighted by lake density. Lakes of sizes 0.01–10 km^2 were included in the statistical sampling of the southern and central Finland (Subregion 1 in Fig. 2). In northern Finland (Subregion 2 in Fig. 2) only lakes of sizes 0.1–10 km^2 were included. Moreover, the sampling intensity for northern Finland was set lower than that for southern and central regions.

The total number of lakes selected was 797 in Subregion 1 and 190 in Subregion 2. Four of the selected lakes were not visited owing to difficult field conditions. In addition, five lakes were eliminated after field sampling, due to intensive urban or industrial influence. The lake sample represents ca. 2% of the total number of lakes in the size range 0.01–10 km^2 in Subregion 1, and 5% of the lakes with surface areas 0.1–10 km^2 in Subregion 2. The median lake area of the selected lakes was 0.09 km^2 and the area of the largest lake 7.5 km^2. A detailed description of the selection of the lakes is given in Forsius et al. (1990).

Chemical Analyses

Water samples of the surface layer (1 m) of the lakes were taken during autumn overturn 1987. Twenty three chemical parameters were measured on each lake-water sample. Total organic carbon (TOC) was measured by IR gas analyzer, colour by comparative determination, and COD_{Mn} titrimetrically following oxidation with $KMnO_4$. The major inorganic cations, Ca, Mg, Na, and K, were measured by flame–AAS, and Cl and SO_4 by ionchromatography. Fluoride was measured by ion selective electrode. NO_3 and NH_4 were determined colorimetrically. Total monomeric Al and non-labile monomeric Al were measured by the method of Røgeberg and Henriksen (1985). pH was measured on a Radiometer pH meter in the laboratory, and alkalinity by Gran titration (see Forsius et al. this Vol., Forsius et al. 1990).

Non-marine sulphate, and base cations (denoted by the prefixed asterisk as, e.g., $^*SO_4$) were estimated as the differences between total concentration and concentrations attributable to marine salts, the latter based on ratios to chloride in seawater.

Estimation of Organic Acidity

The anion deficit, estimated as the difference between the sum of the main cations ($Ca + Mg + Na + K + H + NH_4 + Al_{(lab)}$) and the sum of inorganic anions ($SO_4 + Cl + NO_3 + F + HCO_3$) was used as an estimate of the dissociated organic anion concentration. Labile Al (difference between total monomeric and non-labile monomeric Al) was included in the balance with a charge value of 3 to represent cationic Al species. Gran alkalinity was used as an estimate of HCO_3.

The error in different cation and anion determinations causes uncertainty when estimating organic anion by means of ion balance calculations. Moreover, in humic samples, Gran alkalinity measurement includes, in addition to the HCO_3, also some organic alkalinity, especially in waters with high pH values (see e.g. Thompson 1986). This causes an underestimation of the organic anion concentration calculated as the difference between the main cations and inorganic anions. The deviation is to some extent compensated as both free and complexed metal concentrations are determined by atomic absorption spectrometry. If the base cations are partly complexed with organic matter, the organic anion content, estimated by ion balance calculations, will be an overestimate of the free organic anion content. In spite of these uncertainties, ion balance calculations and the model of Oliver et al. (1983) gave rather similar organic anion values (see Kortelainen et al. 1989).

Results and Discussion

Total Organic Carbon Concentrations in Finnish Lakes

As the lakes were selected by random sampling, the water quality of the lakes can be considered as representative for the average water quality in small lakes in Finland. The high values of TOC (median 12 mg l^{-1}, range 0.5–46.6 mg l^{-1}), COD_{Mn} (median 15 mg O_2 l^{-1}, range 0.6–69 mg O_2 l^{-1}) and colour (median 100 mg Pt l^{-1}, range 0–600 mg Pt l^{-1}) were the most prominent chemical characteristics of the lakes in the Finnish survey. There was a strong positive relationship between these parameters. The regression equations for TOC were:

$$\mathrm{TOC}\ (\mathrm{mg\,l^{-1}}) = 1.9 + 0.67\ \mathrm{COD_{Mn}}\ (\mathrm{mg\,O_2\,l^{-1}}) \qquad r^2 = 0.920 \qquad (1)$$

$$\mathrm{TOC}\ (\mathrm{mg\,l^{-1}}) = 3.6 + 0.086\ \mathbf{colour}\ (\mathrm{mg\,Pt\,l^{-1}}) \qquad r^2 = 0.850. \qquad (2)$$

The proportion of lakes with TOC concentrations $\geq$ 5 mg l^{-1} in the whole country was 91%. The TOC concentrations were highest in central Finland. In many lakes situated in peat-rich areas near to the Gulf of Bothnia, TOC concentrations were $\geq$ 25 mg l^{-1} (see Figs. 1 and 2).

Although it is easy to identify areas where TOC concentrations are highest, it is also typical that clearwater lakes (defined here as lakes with TOC concentrations <5 mg l^{-1}) and very humic lakes can be found close to each other, depending, e.g., on the lake morphometry, soil texture and vegetation of the catchment area. The highest TOC concentrations occurred in the smallest lakes having a large catchment area. This agrees with studies of comparable areas in North America (Gorham et al. 1986; Engstrom 1987), as well as earlier studies in Finland (Verta et al. 1986; Kortelainen and Mannio 1988). Finnish lakes are predominantly shallow, with the result that the catchment-derived organic matter is diluted in a small

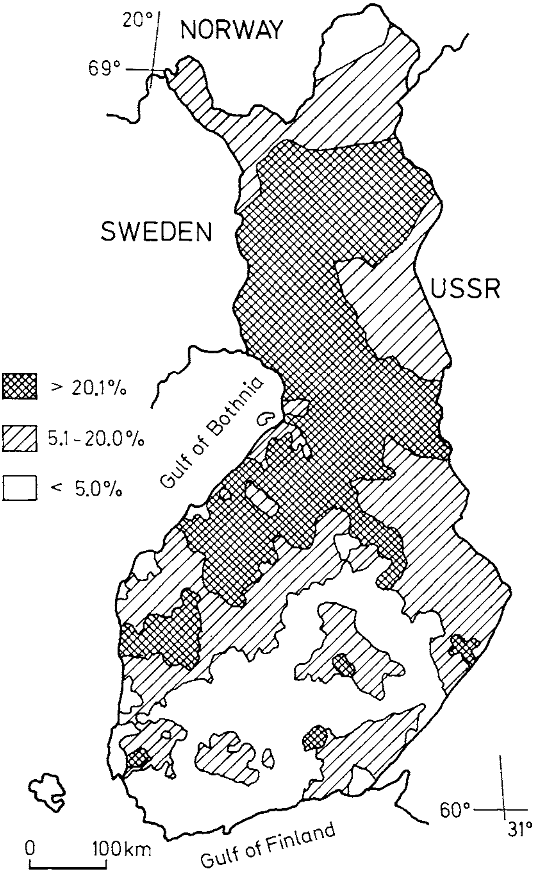

Fig. 1. The percentage of peatlands (over 0.02 km^2) of the total land area in Finland modified from Finnish Peatland Society (1983)

volume of water. In larger and deeper lakes, with longer residence times, the degradation and sedimentation processes affecting organic matter are more effective. Organic carbon concentrations are consequently lower. Even in the full data set, consisting of lakes with different hydrology, morphometry, and soil characteristics, the negative relationship between the lake area to watershed area ratio and TOC was significant (-0.337, $P<0.001$).

In southern and central Finland (Subregion 1 in Fig. 2), 44% of the lakes had TOC concentrations higher than or equal to 15 mg l^{-1}, and only 7% of the lakes had TOC concentrations lower than 5 mg l^{-1}. In northern Finland (Subregion 2 in Fig. 2), TOC concentrations were much lower, the corresponding figures were 1% and 33% respectively. The fact that the median area of the study lakes in northern Finland was higher (0.20 km^2 vs. 0.07 km^2 in Subregion 1), probably lowered the number of lakes with high TOC concentrations. However, the median TOC in Subregion 2 (6.4 mg l^{-1}) was only half of that in lakes of the same size class in Subregion 1 (11.9 mg l^{-1}).

With the exception of the northernmost Finland, the amount of peatlands is high also in Subregion 2 (see Fig. 1). One of the most important reasons for the

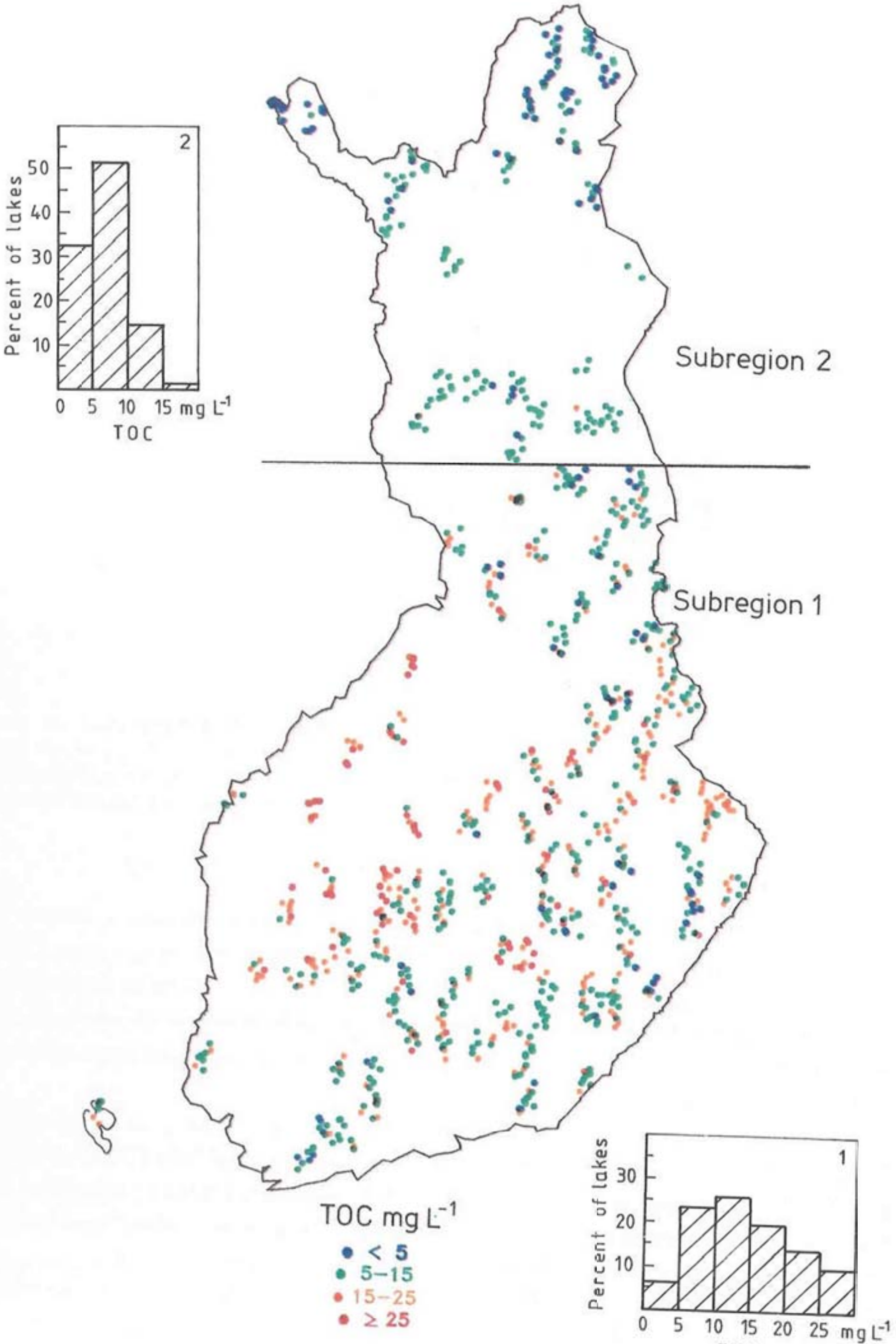

Fig. 2. Concentrations and the percentage distribution of total organic carbon in lakes in Subregions 1 and 2 (see text). The Subregions 1 and 2 are distinguished by the northern coordinate 7340 of the uniform coordinate system

lower TOC concentrations in northern Finland is probably the lower production in colder environments. In spite of the high percentage of peatlands, the leaching of organic matter in the coniferous zone north of the arctic circle is only about half of the average value in Finland (see Sallantaus 1986). Thinner soils at higher elevations in northern Finland probably also contribute to the lower TOC concentrations. In the Norwegian survey, Henriksen et al. (1988a) demonstrated that lake water TOC decreased markedly with elevation.

In southern and central Finland the summer 1987 was exceptionally cold and rainy. The total precipitation for the summer season set new records for the 20th century over wide areas of southern and central Finland. In northern Finland the conditions were not as exceptional; the summer rainfall was higher than normal in June and August, but less than normal in July. September was very rainy in southern Finland, in northern Finland the precipitation was less than normal. October was dry throughout the whole country; precipitation was only 30 to 60% of the seasonal mean (National Board of Waters and the Environment 1987). Some of the headwater lakes ($n = 59$) which were sampled in autumn 1987 were also sampled during autumn overturn in 1983 or 1986. Compared to these previous results, average TOC values were somewhat lower in Subregion 2 in autumn 1987 (6.1 mg l^{-1} vs. 7.7 mg l^{-1}, $n = 8$) and somewhat higher in Subregion 1 (11.7 mg l^{-1} vs. 10.8 mg l^{-1}, $n = 51$). In rainy years the rainwater does not penetrate very deep in the soil because of the high groundwater table. Surface water runoff is high, and this increases concentrations of organic matter in surface water (see Sallantaus 1986).

Thirty-one of the headwater lakes were sampled also during the spring and autumn overturn in 1986. In humic lakes, autumn TOC concentrations were higher than the corresponding spring values, whereas in the clearwater lakes the difference was small. The regression equation was:

$$\text{TOC(autumn)} = 1.3\ \text{TOC(spring)} - 1.4 \qquad r^2 = 0.903 \tag{3}$$

Howell (1986) found that the clearwater lakes in Nova Scotia exhibit the least seasonal variation while the coloured lakes are highly variable in colour. He concluded that the highly organic systems generally have higher water colours in the autumn compared to the spring in response to increased flushing of bog drainages following summer low flow conditions. Although the number of samples in our previous studies is very low, the results support the observations from Nova Scotia.

The Role of Organic and Anthropogenic Acidity in Different Parts of Finland

The acidity of Finnish lakes reflects the interaction of sensitivity ($^*[\text{Ca}+\text{Mg}+\text{K}+\text{Na}]$), atmospheric deposition of sulphate and the concentration of organic anions present. The main reasons for the higher base cation concentrations in southern Finland compared to the northern parts of the country are probably the thicker and more fertile soils. In addition, the higher level of acidic deposition in the south may have increased the leaching of base cations more than in northern regions. In the southeastern parts of the country also the base cation deposition and accumulation in lake sediments have been found to be higher than elsewhere in the country (see Järvinen and Vänni this Vol.; Verta et al. 1989).

The total deposition of sulphur in Finland is highest along the coastal area of southern Finland, generally above 65 keq km^{-2} yr^{-1}, and decreases on moving to the north. However, there are elevated levels of deposition also in eastern Lapland due to the extensive smelting industry in the Kola peninsula (see Tuovinen et al. this Vol.). The pattern of lake water sulphate concentration was similar to the pattern of acidic deposition; i.e. with highest concentrations in southern Finland (see Forsius et al. this Vol.; Kämäri et al. 1990). The sulphate concentrations in a few lakes scattered throughout the country were higher than would be expected from anthropogenic deposition. These high concentrations are most probably due to geological sources of sulphate in the catchments of these lakes.

Nitrate concentrations were low throughout the country (median 1.1 μeq l^{-1}), although somewhat higher in southern Finland. The median fluoride concentration was < 5 μeq l^{-1}. However, in some lakes in rapakivi granite areas in southern Finland the concentrations were high. In Subregion 1 the fluoride concentration was ≥ 10 μeq l^{-1} in 6% of the lakes, the highest value being 126 μeq l^{-1}.

Both acidic clearwater lakes and acidic humic lakes were found throughout almost the whole country in base-poor sensitive terrain (see Kämäri et al. 1990). The median pH in the full data set was 6.3 (range 4.1–8.0). Humic lakes were, on an average, more acidic than clearwater lakes. The proportion of lakes with pH values lower than 5.3 in the whole country was 17%. Of these acidic lakes 93% had TOC concentrations ≥ 5 mg l^{-1}.

The relative contributions of organic matter and non-marine sulphate to acidity were assessed by ion balance calculations. The organic anion was the main anion in the whole country (median 89 μeq l^{-1}). The median non-marine sulphate concentration was 71 μeq l^{-1} and the median bicarbonate concentration 75 μeq l^{-1}. Organic anion was the dominant anion in 42% of the lakes in the whole country. Non-marine sulphate dominated in 27% and bicarbonate in 31% of the lakes.

Organic anions dominated in acid lakes, indicating that a substantial fraction of the overall acidity of such lakes was of natural origin (see Kortelainen et al. 1989). For the lakes with $pH < 5.3$, 73% had organic anion as the dominant anion. A great number of the acidic highly organic lakes was situated in the peat-rich areas near to the Gulf of Bothnia and in the eastern parts of the country (Fig. 3). Most of these lakes were estimated to be naturally acidic (see Forsius et al. this Vol., Fig. 1).

Organic anion contributions increased with decreasing pH values ($r = -0.701$, $P < 0.001$), increasing TOC concentrations ($r = 0.593$, $P < 0.001$) and decreasing conductivity ($r = -0.413$, $P < 0.001$). Together these parameters explained 67% of the variation in the organic anion percentage. The organic anion contribution

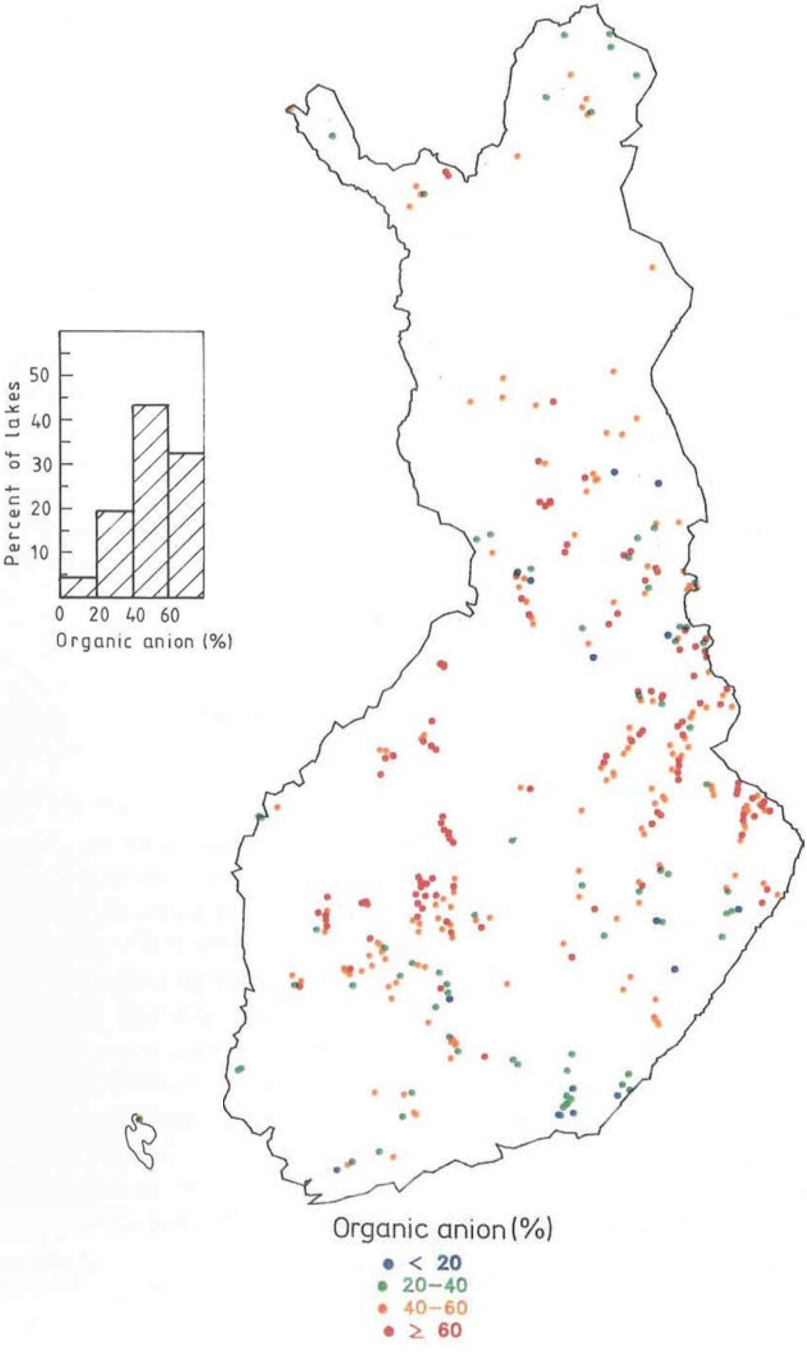

Fig. 3. Organic anion percentages [$100 \times (\Sigma^*\text{Cations} - \Sigma^*\ \text{Inorganic anions})/\Sigma^*\text{Cations}$] and the percentage distribution for lakes with Gran alkalinity $< 50\ \mu\text{eq}\,l^{-1}$

was greater than or equal to 60% in one-third of the lakes with alkalinity values lower than 50 μeq l^{-1} (Fig. 3). In southern as well as in northernmost Finland, most of the lakes had organic anion contributions lower than 40%, and in many lakes lower than 20% (Figs. 3 and 4). Bicarbonate was the dominant anion in northern Finland, whereas sulphate dominated lakes were concentrated in high deposition areas in the south (see Kämäri et al. 1990). At low elevations in southern Finland, soils are rather thick and well buffered. As a result, the number of lakes with low alkalinity is rather low, although non-marine sulphate concentrations are high (see Forsius et al. this Vol.).

Although the survey demonstrated that organic acids strongly affect the acidity of lakes in Finland, minerogenic acidity exceeded the organic acidity in high deposition areas. The high $*SO_4/A^-$-ratio in the south is further pronounced because the amount of peatlands is rather low in the southern parts of the country, whereas the peatland dominated areas are found in areas of lower deposition. In southernmost Finland (region A in Fig. 5) non-marine sulphate concentration was higher than that of organic anion in 76% of the humic lakes, while in the central and northern Finland (region B in Fig. 5) the corresponding figure was only 21%. This indicates that in high deposition areas minerogenic acidity has also increased in humic lakes.

The Importance of Organic Acidity in Finnish Lakes vs. in Other Northern Environments

In Sweden lakes with colour values >100 mg Pt l^{-1} are found throughout the country except in the northwestern mountain areas, where the lakes are clear-watered. Colour values higher than 400 mg Pt l^{-1} are found in small lakes in peatland-dominated areas (Swedish Environmental Protection Board 1986).

Compared to the Norwegian lakes (Henriksen et al. 1988a) the TOC concentrations and correspondingly organic acidity in Finnish lakes are high. In the Norwegian survey, which was targeted at sensitive areas, 90% of the lakes had TOC < 6 mg l^{-1}, and 60% of the lakes had TOC < 2 mg l^{-1}. Organic anion represented $< 10\%$ of the anions for the full data set. In southernmost Norway, where most of the acidic lakes were found, the contribution of organic anions was $< 4\%$. The maximum contribution was found in eastern Norway, where organic anions represented 20% of the anions in the pH range 5.5–6.0. Many of the differences between Norway and Finland can be related to the catchment characteristics in these two countries. The lakes in Finland are generally located at lower elevations in regions with only slight height differences in terrestrial relief, with thicker and finer-textured soils, and with higher proportion of peatlands in the catchments.

In Canada humic lakes are abundant. In eastern parts of the country, the role of humic matter on the acidity of lakes and streams has been intensively studied (e.g. Howell 1986; Gorham et al. 1986; Jeffries et al. 1986; Kerekes et al. 1986). The highest median organic anion concentration occurred in northwestern Ontario

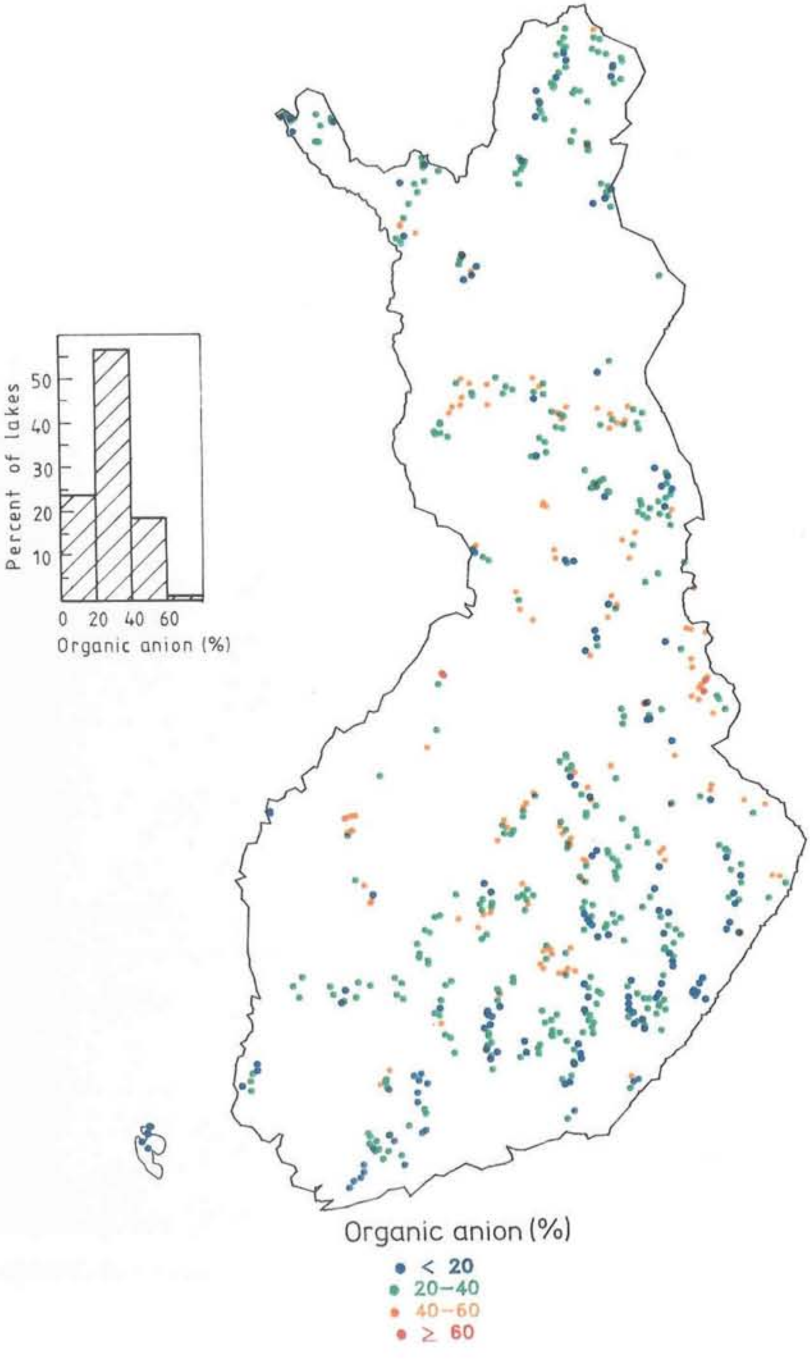

Fig. 4. Organic anion percentages and the percentage distribution for lakes with Gran alkalinity $\geq 50\ \mu\mathrm{eq\,l^{-1}}$

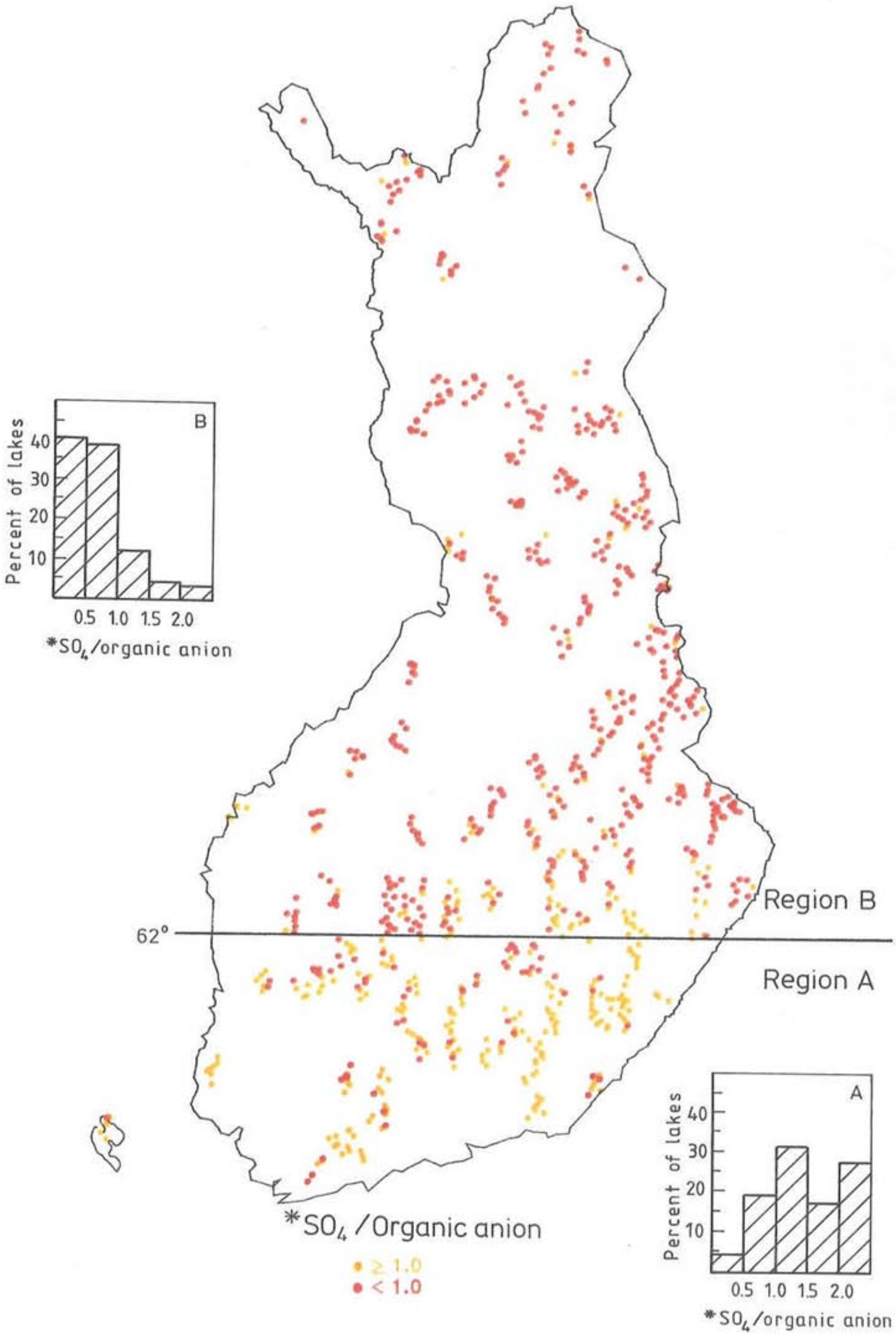

Fig. 5. Non-marine sulphate to organic anion ratios and the percentage distribution for humic lakes (TOC $\geq 5\ \mathrm{mg\,l^{-1}}$) in two regions in Finland

(94 μeq l^{-1}); in other subregions the median concentration varied between 38–56 μeq l^{-1} (Jeffries et al. 1986). In northwestern Ontario, Labrador, Nova Scotia and Newfoundland, organic anion concentrations were higher than non-marine sulphate concentrations. In other subregions sulphate dominated.

The Eastern Lake Survey in the U.S.A (autumn 1984) (Brakke et al. 1988; Eilers et al. 1988a; Eilers et al. 1988b; Landers et al. 1988), was targeted at sensitive areas. The dissolved organic carbon (DOC) concentrations were rather low in most areas. The minimum regional median DOC concentration (1.9 mg l^{-1}) was found in the southern Blue Ridge area. The highest DOC concentrations were found in northeastern Minnesota, in the upper Great Lakes area and in Florida (median DOC concentration 8.6 to 9.2 mg l^{-1}). In northeastern Minnesota 76% of the lakes had DOC concentrations higher than or equal to 6 mg l^{-1}. In most areas organic anion concentrations, estimated by ion balance calculations, were lower than sulphate concentrations. In northeastern Minnesota, upper Great Lakes area and Florida median organic anion concentrations exceeded sulphate concentrations. In Florida half of the acidic lakes (ANC ≤ 0) had organic anion as the dominant anion.

The small size of the lakes selected for the Finnish Survey (lake area 0.01–10 km^2) probably emphasized the high TOC concentrations. In the Swedish Survey lakes were larger than 0.01 km^2, and in the Norwegian Survey most of the lakes were larger than 0.2 km^2. In the Eastern Lake Survey in the United States lake area was 0.04–20 km^2.

Conclusions

The results of the Finnish survey describe the average lake water quality in the country, where one-third of the land area is covered by peatlands, and where lakes are predominantly small and shallow. As a result, humic lakes are more abundant than clearwater lakes. Humic lakes have a wide range of pH in different deposition areas, providing a unique data base to evaluate the importance of organic acidity.

The survey demonstrated high total organic carbon concentrations (TOC) throughout the southern and central parts of the country. Small headwater lakes having a large catchment area and draining peaty soils have the highest TOC concentrations. The lower TOC concentrations in northern Finland can mainly be related to the colder climate, and lower primary production.

The high TOC concentrations strongly affect the acidity of lakes in Finland. The organic acidity contribution to the lake acidity is mainly determined by the soil properties, the distribution of peatlands and the pattern of sulphate deposition. The results of this survey, conducted during autumn, may emphasize high TOC concentrations and organic acidity more than studies conducted during other periods of the year. The data collected demonstrate that the high organic matter concentrations have a decreasing effect on pH values. Compared with lake surveys in Scandinavia and North America, the number of acid humic lakes in Finland is high.

At current deposition levels of sulphate, the pH of humic lakes in Finland is determined to a greater extent by TOC concentrations than by non-marine sulphate in most areas. However, in the southern parts of the country, where the acidic deposition is highest, the anthropogenic acidity commonly exceeds the catchment derived organic acidity. The highest base cation concentrations are, however, found in the same regions. For this reason pH of the humic lakes is not essentially lower at high deposition areas.

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Effects of Air Pollutants on Chemical Characteristics of Soil Water and Groundwater

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Summary

The effects of air pollutants on the chemical characteristics of soil water and groundwater were studied at 54 groundwater stations in Finland during 1975–1988. Deposition during winter was estimated from elemental concentrations in snowpack. The bulk deposition measurements were used as estimates of annual deposition. Soil water samples were collected from different horizons down the podzol profile. High sulphate concentrations and low pH in meltwater and precipitation cause changes in the chemistry of the lower mineral soil and groundwater due to increased ion exchange and weathering. The sulphate, calcium and nitrate concentrations of groundwater have increased in the south of Finland. The median concentration of sulphate has increased during the monitoring period from 2.9 $\mathrm{mg\,l^{-1}}$ to 4.2 $\mathrm{mg\,l^{-1}}$. The pH of groundwater has decreased and the aluminium concentration increased in the areas of high local deposition.

Introduction

The chemical composition of water percolating through the soil changes as a result of weathering, ion-exchange processes, mineralization and immobilisation. As acidic meltwater percolates down through the soil it reacts with minerals. The hydrogen ions in the meltwater are replaced as a result of cation exchange by metal ions from the soil particles. According to percolation water studies made by Soveri (1985), the concentrations of metals, sulphate, alkali and earth alkali metals were higher at the early stages of infiltration than later on during the melting period. One of the reasons for the strong mobilization of material during the spring infiltration is the weathering that takes place in the soil during winter when infiltration and leaching do not take place. Helmisaari and Mälkönen (1989) have also found that in spring, when the hydrogen load is at its greatest, potassium, magnesium and calcium in particular are released in greater amounts from the humus layer than during the growing season. Aluminium has an important role in acidification. Aluminium is a common element in the bedrock and soil. The solubility of this metal is strongly pH-dependent, with a minimum solubility at pH level of about 6 (May et al. 1979). Aluminium is released from the eluvial horizon as water-soluble complexes, which are transported downwards with the water. These complexes are precipitated in the B-horizon, because the pH is higher. Nilsson and Bergkvist (1983) have reported that about 83 to 97% of the aluminium in the aqueous phase of the humus layer is organically complexed. The predominant source of inorganic Al is the lower mineral soil (Lawrence et al. 1988).

Groundwater constituted 51% of the municipal mains water in Finland in 1988. In sparsely populated areas almost all the inhabitants use groundwater. The danger of groundwater acidification is greatest in shallow groundwater basins. Signs of the acidification of groundwater have been reported by many authors, for example in Norway (Henriksen and Kirkhusmo 1982), Sweden (Aastrup and Persson 1984; Andersson and Stokes 1987), Canada (Craig and Johnston 1988) and many other countries (Alcamo et al. 1987).

This chapter presents results from a study of the effects of changes in deposition acidity on the chemistry of soil water and groundwater in Finland.

Materials and Methods

Observation Stations

The groundwater observation stations of the National Board of Waters and the Environment (Fig. 1) are usually located in areas where the groundwater quality has not been considerably affected by local disturbances. The stations were established in regions with different types of soil and climatological conditions, and the groundwater basin is well confined at each station. The size of the catchments investigated varies between 0.2 and 3.0 km^2. The area of agricultural land totals 4% of the catchment areas. Detailed information regarding bedrock and surficial materials is presented by Soveri (1985).

Analytical Programme

The analyses determined on the snow, percolation water, lysimeter solutions and groundwater, as well as the number of observations, are presented in Table 1. Alkalinity was titrated potentiometrically to the pH values 4.5 and 4.2 with HCl and pH was determined with a Radiometer pH meter in 25°C. NO_3–N, NO_2–N, N_{tot}, NH_4–N, PO_4–P, P_{tot}, Fe and Mn were measured spectrophotometrically, SO_4 was measured by a turbidimetric method, Cl by a titration with mercury nitrate. SiO_2 was measured by automatic spectrophotometry with molybdate. F was measured potentiometrically and Ca, Mg, Na, K, Cu, Pb, Ni, Cd, Al, Hg, and Zn were measured with AAS. Due to the improvement in detection limits, the heavy metal data of snow meltwater between 1975–1979 was neglected. All the chemical analyses were carried out in the laboratories of the Water and Environment Districts or Institute.

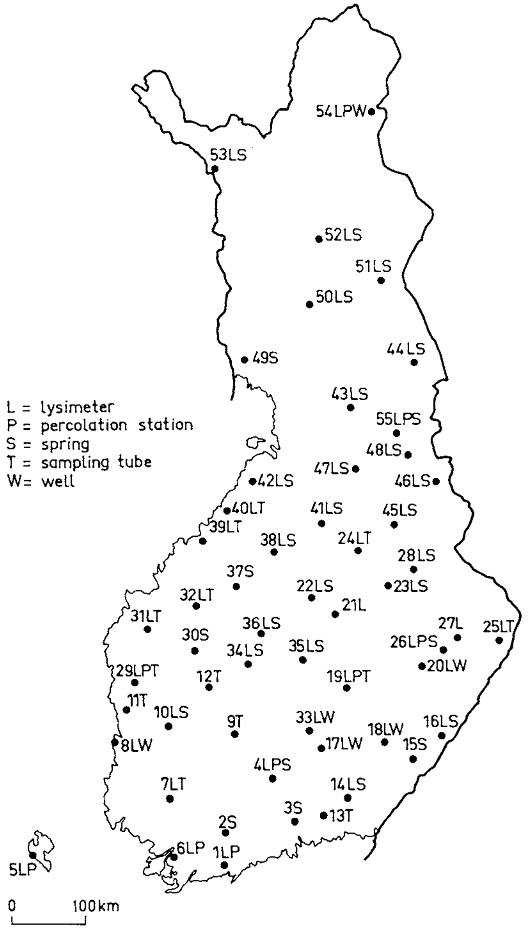

Fig. 1. The network of groundwater stations, lysimeter fields, percolation stations and groundwater sampling sites

Sampling and Data Processing

Snow samples were collected using Plexiglas samplers. The sampler was pushed vertically into the snowpack with a steady downward thrust. The snow samples were stored in polyethylene bags and transported to the laboratory, then melted at room temperature.

The percolation water tubes are made of Plexiglas with a radius of 100 mm and length of 1200 mm. The half tubes were installed horizontally in undisturbed podzol soil profiles. The tubes are slightly inclined. One tube is sited under the humus layer, a second under the illuvial horizon and a third in the subsoil (Soveri and Ahlberg 1987).

Lysimeters are galvanised iron containers coated with plastic with a diameter of 1596 mm and depth of 1700 mm. They were placed vertically in the soil profile. Both the soil type and surface vegetation in the containers correspond to those prevailing in the area. The natural stratification and podzol horizons in lysimeter

Table 1. The number of analyses made during the period 1975–1988

Parameter	Symbol	Unit	Number of analyses			
			SW	IW	PW	GW
pH value			634	503	277	3980
Electrical conductivity	γ_{25}	$\mathrm{mS\,m^{-1}}$	641	500	280	3920
Alkalinity	Alk.	$\mathrm{mmol\,l^{-1}}$	–	380	179	3637
Calcium	Ca	$\mathrm{mg\,l^{-1}}$	577	351	148	3557
Magnesium	Mg	$\mathrm{mg\,l^{-1}}$	565	351	143	3603
Sodium	Na	$\mathrm{mg\,l^{-1}}$	577	352	145	3603
Potassium	K	$\mathrm{mg\,l^{-1}}$	576	350	146	3575
Sulphate	SO_4	$\mathrm{mg\,l^{-1}}$	619	448	210	3657
Chloride	Cl	$\mathrm{mg\,l^{-1}}$	610	442	–	3793
Silicate	SiO_2	$\mathrm{mg\,l^{-1}}$	–	245	123	–
Total nitrogen	N_{tot}	$\mathrm{\mu g\,l^{-1}}$	615	354	245	–
Nitrate nitrogen	NO_3-N	$\mathrm{\mu g\,l^{-1}}$	333	470	203	3732
Nitrite nitrogen	NO_2-N	$\mathrm{\mu g\,l^{-1}}$	–	341	154	–
Ammonium nitrogen	NH_4-N	$\mathrm{\mu g\,l^{-1}}$	325	453	235	3752
Total phosphorus	P_{tot}	$\mathrm{\mu g\,l^{-1}}$	610	141	154	–
Phosphate phosphorus	PO_4-P	$\mathrm{\mu g\,l^{-1}}$	320	393	153	3743
Iron	Fe	$\mathrm{\mu g\,l^{-1}}$	–	480	–	–
Manganese	Mn	$\mathrm{\mu g\,l^{-1}}$	592	447	186	3589
Fluoride	F	$\mathrm{\mu g\,l^{-1}}$	51	272	–	2372
Lead	Pb	$\mathrm{\mu g\,l^{-1}}$	571	177	–	3386
Copper	Cu	$\mathrm{\mu g\,l^{-1}}$	551	286	–	3442
Aluminium	Al	$\mathrm{\mu g\,l^{-1}}$	161	278	152	2321
Zinc	Zn	$\mathrm{\mu g\,l^{-1}}$	559	–	152	3442
Nickel	Ni	$\mathrm{\mu g\,l^{-1}}$	51	202	–	–
Cadmium	Cd	$\mathrm{\mu g\,l^{-1}}$	161	253	154	–

SW = Snow;
IW = Infiltration water;
PW = Percolation water;
GW = Groundwater.

vessels are disturbed because of installation. Lysimeter solutions were collected directly in polyethylene bottles.

Groundwater samples were taken from the permanent observation stations either from springs or from PVC sampling tubes fixed in the soil. Samples were taken regularly during the last week of each month at a fixed depth and using the same standardized sampling procedure at each station. Samples from springs were taken directly in polyethylene bottles. From tubes they were taken by pumps when the water was clear. A detailed description of the sampling procedure is presented by Soveri (1985).

The analytical results for snow, percolation water, infiltration water and groundwater are stored in the data base of the National Board of Waters and the Environment, Helsinki.

Results and Discussion

Deposition Estimated from Snow Samples

Snow sampling was carried out at all 54 stations during 1976–1988 once a year in spring at the time, when water equivalent had its maximum. The concentrations of various constituents of snow are presented in Table 2. The concentrations were converted into fluxes using the water equivalent value and the age of the snowpack. The procedure is described in detail by Soveri (1985). The cumulative distribution of the deposition of various constituents is presented in Fig. 2.

The pH of the snow samples ranged from 4.0 to 5.9, with a mean value of 4.6, which is the same as the average pH in precipitation for the whole year between 1971–1988 (Järvinen and Vänni this Vol.). Regional variations between the northern and southern parts of the country are small (Fig. 3). The eastern parts of Finland have the lowest median values. Compared with the pH pattern recorded by Soveri (1985) for the years 1976–1984, the pH has decreased slightly during 1985–1988. The decrease is 0.1–0.3 pH units. The decrease during the same period can also be seen in the mean value of all stations (Fig. 4).

Sulphate deposition varied between 0.13–3.60 g $m^{-2}\,yr^{-1}$ with a median value of 0.60 g $m^{-2}\,yr^{-1}$ (Fig. 5). The maximum deposition of sulphate is in the south-

Table 2. Snow composition at the groundwater stations during late winter seasons 1975/76–1987/88

Parameter	Unit	Min	Max	Mean	Median	S.D.
pH		4.0	5.9	4.6	4.6	–
γ_{25}	$mS\,m^{-1}$	0.6	49.5	2.3	1.9	2.9
P_{tot}	$\mu g\,l^{-1}$	1.0	220.0	18.5	13.0	17.7
PO_4-P	$\mu g\,l^{-1}$	0	630.0	12.2	7.0	36.5
SO_4	$mg\,l^{-1}$	0	7.7	1.9	1.7	1.09
Cl	$mg\,l^{-1}$	0	5.3	0.77	0.60	0.46
Na	$mg\,l^{-1}$	0.1	1.9	0.30	0.30	0.19
K	$mg\,l^{-1}$	0	1.9	0.18	0.10	0.16
Ca	$mg\,l^{-1}$	0	2.0	0.38	0.30	0.29
Mg	$mg\,l^{-1}$	0	1.6	0.11	0.10	0.11
N_{tot}	$\mu g\,l^{-1}$	200	3300	723	670	329
NO_3-N	$\mu g\,l^{-1}$	120	1400	415	396	151
NH_4-N	$\mu g\,l^{-1}$	0	1100	234	210	155
Mn	$\mu g\,l^{-1}$	0	220.0	25.5	20.0	22.7
Cu	$\mu g\,l^{-1}$	0	70.0	2.2	1.0	4.4
Pb	$\mu g\,l^{-1}$	0	70.0	4.2	3.0	5.0
Zn	$\mu g\,l^{-1}$	0	480.0	8.5	6.0	21.3
Ni	$\mu g\,l^{-1}$	0.1	6.8	1.1	0.7	1.2
Cd	$\mu g\,l^{-1}$	0.01	3.0	0.21	0.10	0.32
F	$\mu g\,l^{-1}$	6.0	110.0	31.0	22.0	26.1
Al	$\mu g\,l^{-1}$	2.0	850.0	77.1	50.0	86.6

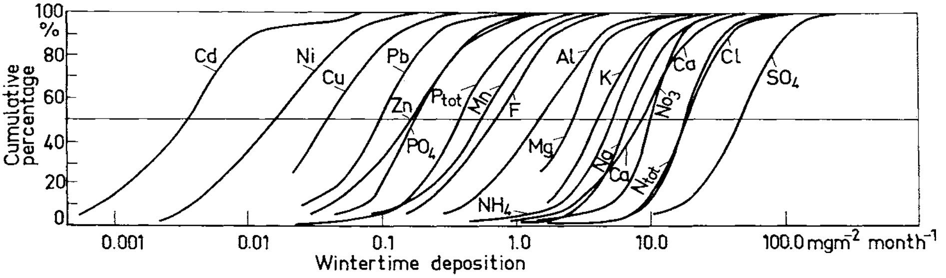

Fig. 2. Cumulative distribution of deposition for various constituents of snowpack at the groundwater stations during the years 1976–1988

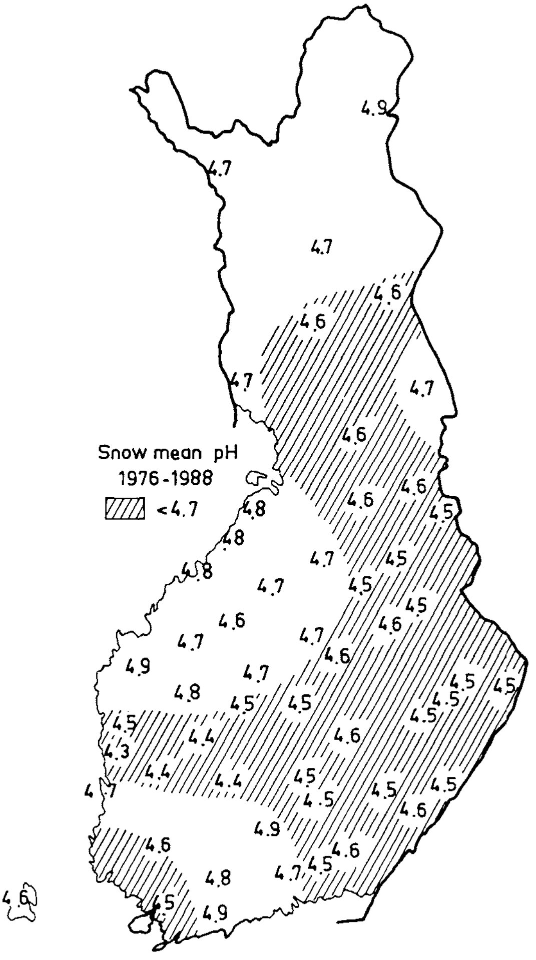

Fig. 3. The mean pH of the snowpack during the period 1976–1988 at each groundwater station

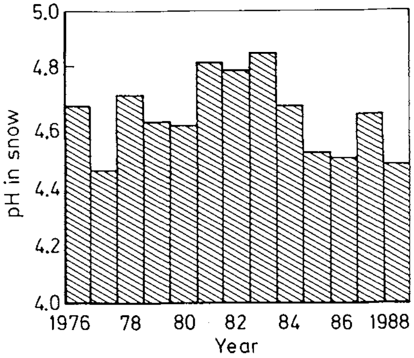

Fig. 4. The mean pH of the snowpack during the period 1976–1988 at the groundwater stations

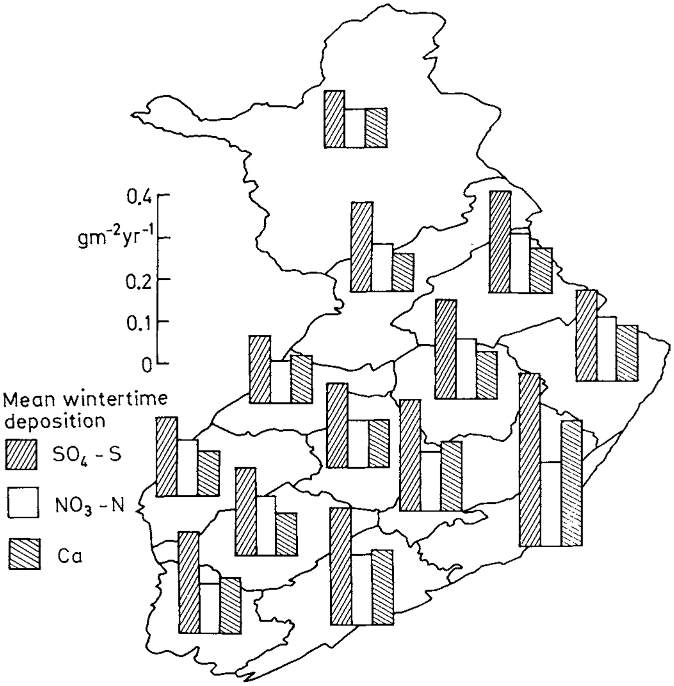

Fig. 5. Mean sulphate, nitrate and calcium deposition in winter estimated from the snowpack during the period 1976–1988 in different Water and Environment Districts

eastern Finland. The values in the southern and southwestern part are also considerably above the mean.

Nitrate nitrogen deposition varied between 0.002–0.528 g $m^{-2} yr^{-1}$, with a median value of 0.12 g $m^{-2} yr^{-1}$. Nitrate deposition has its maximum in the southern part of Finland. The values in the east of Finland are also higher than the mean value of the whole country (Fig. 5). The median of total nitrogen was 0.23 g $m^{-2} yr^{-1}$. The values varied between 0.01–1.44 g $m^{-2} yr^{-1}$.

Calcium deposition varied between 0.01–0.84 g m^{-2} yr^{-1}, with a median 0.11 g m^{-2} yr^{-1}. The values in the south of Finland are about twice as high as the values in the north (Fig. 5). The maximum of 0.41 g m^{-2} yr^{-1} was recorded at Elimäki station (No. 13) in the southeastern part of Finland.

The mean value of lead deposition was 1.14 mg m^{-2} yr^{-1}. The values varied between 0.18–42.0 mg m^{-2} yr^{-1}. The highest values occurred in the southern part of Finland, especially near the southern coast and in the Tampere region. These are areas with heavy traffic. The northernmost values are only one-quarter of the values recorded in the south.

Monthly bulk deposition in winter (XII–III) estimated by precipitation collectors at six stations of the meteorological institute and deposition estimated from snowpack at nearby (<20 km) groundwater stations during 1985–1988 were compared (Table 3). The mean values of SO_4 and NO_3 do not differ significantly, but the deviation is rather large. NH_4 is slightly lower and Na, K, Ca, Mg, Cl are higher in snow than in precipitation collectors.

Concentrations in Soil Water

According to the results of the percolation experiments, the pH of soil water changes from 4.9 to 5.9 while passing through 60–110 cm of soil (Table 4). The main reason for this increase is cation exchange processes between hydrogen ions and base cations.

Table 3. Monthly bulk deposition (mg m^{-2} month^{-1}) in winter (XII–III) at six stations of the meteorological institute (B) and deposition estimated from snowpack at nearby (<20 km) groundwater stations (S) during 1985–1988

Parameter		N	Min	Max	Mean	Median	S.D.
pH	B	18	4.0	4.6	4.3	4.4	–
	S	16	4.1	5.0	4.4	4.4	–
SO_4–S	B	17	9.0	60.0	19.8	16.6	12.0
	S	16	2.3	60.1	18.2	14.2	13.7
NO_3–N	B	17	7.3	35.3	14.8	13.5	6.3
	S	16	5.2	29.4	13.4	13.6	6.0
NH_4–N	B	17	2.8	27.0	8.4	7.6	5.5
	S	16	1.6	30.5	7.0	5.9	6.7
Na	B	17	0.8	23.4	6.3	4.5	6.2
	S	13	2.7	21.6	8.9	8.4	4.7
K	B	17	0.9	15.3	4.2	3.6	3.3
	S	13	2.4	10.6	5.3	5.4	2.0
Ca	B	16	1.4	12.9	5.7	6.2	3.3
	S	14	1.8	19.0	9.6	8.5	5.0
Mg	B	16	0.4	4.6	1.5	1.1	1.2
	S	10	2.0	8.4	3.6	3.1	1.9
Cl	B	11	6.1	25.9	10.0	8.5	5.5
	S	12	9.0	38.4	16.5	13.9	8.3

Table 4. Percolation water composition at the percolation stations during the period 1986–1988 (stations without organic topsoil layer included)

Parameter	Layer	Min	Max	Mean	Median	S.D.
pH	1	4.0	6.9	5.0	4.9	–
	2	4.5	6.7	5.4	5.4	–
	3	4.8	7.2	5.9	5.9	–
γ_{25} mS m^{-1}	1	0.9	19.6	4.2	3.8	2.4
	2	1.0	15.0	3.5	3.2	1.7
	3	1.5	9.8	4.3	3.7	2.1
N_{tot} µg l^{-1}	1	30	9600	1617	1235	1379
	2	55	7600	1118	710	1228
	3	130	6500	1159	885	1211
NO_3–N µg l^{-1}	1	0	14,100	592	50	2043
	2	2	5200	671	58	1161
	3	10	5000	668	110	1205
NH_4–N µg l^{-1}	1	1	2200	255	54	419
	2	0	1400	131	42	265
	3	0	1400	79	19	234
SO_4 mg l^{-1}	1	0.2	17.0	5.5	5.6	3.5
	2	0.5	10.8	5.8	5.7	2.1
	3	0.5	22.0	8.4	8.0	4.1
Alk. mmol l^{-1}	1	0.00	0.25	0.02	0.01	0.03
	2	0.00	0.20	0.02	0.01	0.03
	3	0.00	0.14	0.05	0.01	0.03
Na mg l^{-1}	1	0.3	24.0	1.3	0.9	2.9
	2	0.5	5.8	1.4	1.1	1.0
	3	0.6	3.9	1.7	1.6	0.8
K mg l^{-1}	1	0.2	7.3	2.0	1.9	1.2
	2	0.3	5.0	2.0	1.5	1.3
	3	0.5	6.2	2.3	2.3	1.7
Ca mg l^{-1}	1	0.3	15.5	2.3	1.6	2.4
	2	0.4	4.4	1.7	1.6	0.8
	3	1.2	4.9	2.4	2.2	0.8
Mg mg l^{-1}	1	0.0	3.3	0.7	0.6	0.6
	2	0.2	3.0	0.7	0.6	0.5
	3	0.3	7.8	1.1	0.6	1.4
Al µg l^{-1}	1	50	2800	674	615	429
	2	27	1600	529	405	357
	3	73	800	319	270	203
Zn µg l^{-1}	1	1	4700	102	24	563
	2	2	700	54	30	99
	3	1	100	17	8	23
Fe µg l^{-1}	1	10	>10,000	323	200	915
	2	5	2000	174	140	254
	3	0	180	58	39	49
Mn µg l^{-1}	1	0	1100	71	46	124
	2	1	320	76	62	68
	3	0	200	23	9	40

Table 4. (continued)

Parameter	Layer	Min	Max	Mean	Median	S.D.
Cd $\mu g\, l^{-1}$	1	< 0.01	1.04	0.14	0.05	0.18
	2	< 0.01	1.24	0.27	0.05	0.32
	3	< 0.01	0.38	0.08	0.05	0.08
P_{tot} $\mu g\, l^{-1}$	1	5	240	65	53	47
	2	4	168	30	20	33
	3	3	180	26	14	36
PO_4 $\mu g\, l^{-1}$	1	2	310	45	21	60
	2	0.5	39	6.0	4.0	7.0
	3	0.5	39	6.0	3.0	8.0

1 = organic layer; 2 = illuvial layer; 3 = subsoil; n = 25–140 obs.

The concentrations of calcium, magnesium, sodium and potassium showed the greatest relative increases in the percolation water compared to meltwater or rainwater. Calcium concentrations in the percolation water were 2.2 $mg\, l^{-1}$ in the subsoil. The chemical characteristics of the different layers of podzol cannot be separated as well in the coarse-grained soil as in the fine grained soil (Fig. 6; Soveri and Ahlberg 1987). The base cation concentrations in the uppermost layer were especially high in areas lacking organic topsoil (Fig. 7).

The increase in electrical conductivity indicated a corresponding increase in the amount of dissolved salts in the water during percolation. The values varied between 3.2 and 3.8 $mS\, m^{-1}$.

The median nitrogen concentration (110 $\mu g\, l^{-1}$, deep level) in the percolation water was much lower than that in the meltwater or precipitation in areas with an organic subsurface. The loss of nitrogen was mainly due to uptake by the vegetation and the microbiological processes in the percolation water. The nitrate concentrations were higher in areas without an organic topsoil (Fig. 7).

The sulphate concentration in meltwater or rainwater is lower than that in percolation water. The median concentration in meltwater was 1.7 $mg\, l^{-1}$, in rainwater approximately 3 $mg\, l^{-1}$ and in percolation water 5.6–8.0 $mg\, l^{-1}$. This higher concentration in soil water is caused by evapotranspiration, which is about 50% of the precipitation in Finland. The weathering of sulphide minerals is not important in Finnish soils.

The median total aluminium concentrations of the percolation water samples were between 270 and 615 $\mu g\, l^{-1}$ and for iron 39–200 $\mu g\, l^{-1}$. The highest concentrations were recorded under the organic layer. The median concentration of zinc in the humus and illuvial layers was 24–30 $\mu g\, l^{-1}$, and in the subsoil 8 $\mu g\, l^{-1}$. Zinc is released from the uppermost soil layers and is later readsorbed.

As the concentrations of copper, lead and cadmium did not change significantly during infiltration, it can be concluded that at least part of the lead and

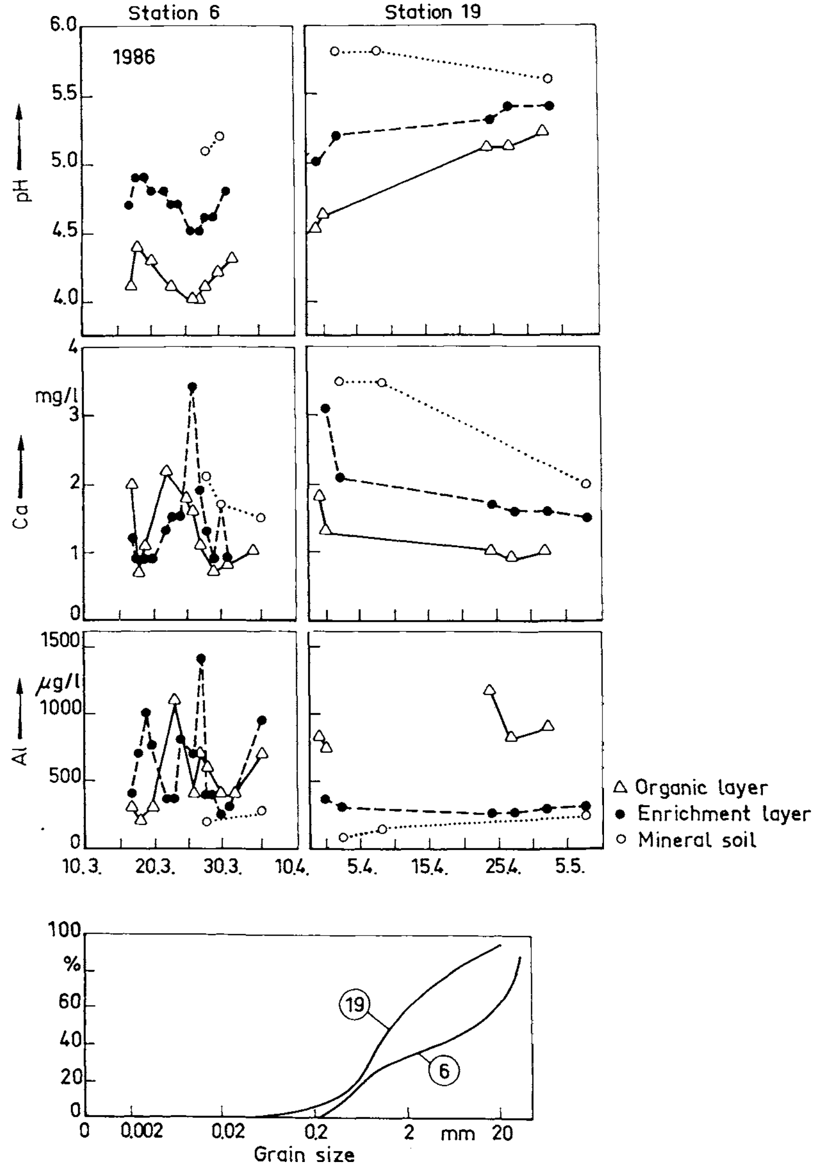

Fig. 6. Concentrations of some constituents of percolation water during the melting period in 1986 and grain size distribution at Perniö (No. 6) and Naakkima (No. 19) stations

copper in the percolation water originates from the atmosphere. Lead is absorbed very strongly by humus colloids and collidal mineral particles in the surface soil (Soveri 1989).

The composition of water from the lysimeters during 1978–1988 is presented in Table 5. The results from the percolation stations and the lysimeter stations at the

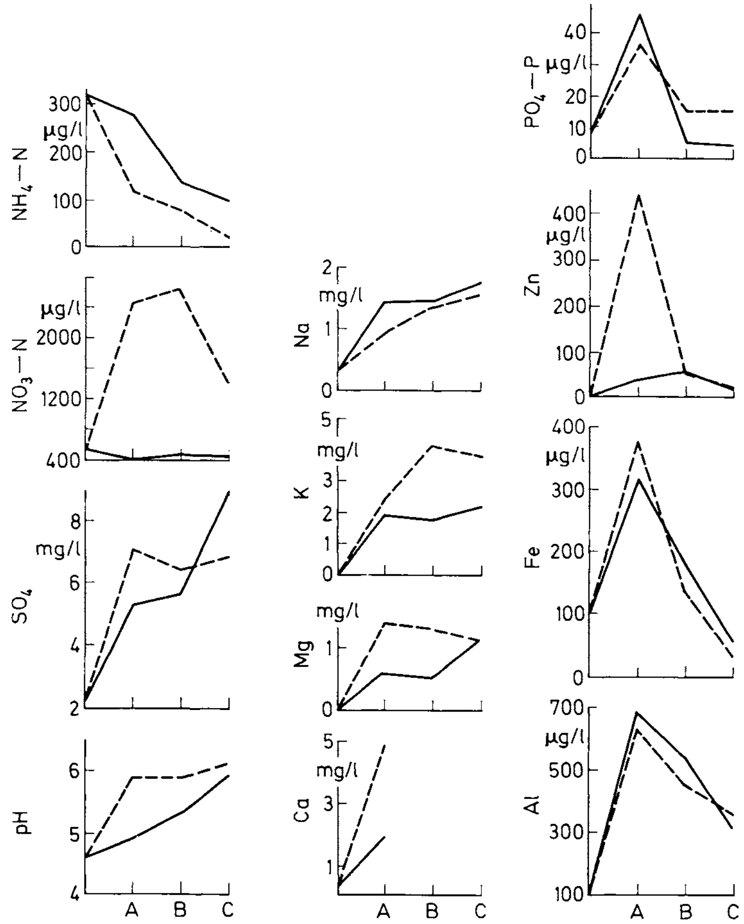

Fig. 7. Mean concentrations of some constituents of percolation water in horizons A, B and C during the period 1986–1987 at percolation stations with (*full line*) and without (*broken line*) an organic topsoil layer.

same area were compared. There are some marked differences. Alkalinity, pH, conductivity, SiO_2 and Ca in the lysimeter solutions were much higher than those of the percolation water from the deepest tubes in the subsoil. On the other hand, the concentrations of SO_4, Al, K and Na were lower. This may be somehow connected to disturbances in the soil texture during installation of the lysimeters.

Geohydrological Factors and Groundwater Acidification

The concentrations of the different substances in groundwater are presented in Table 6. Especially the sulphate and nitrate concentrations are lower than in soil water, due to losses in subsurface runoff, biological uptake and the denitrification of nitrate.

Table 5. Composition of water from the lysimeters during the period 1978–1988

Parameter	Unit	Min	Max	Mean	Median	S.D.
pH		3.2	9.0	6.7	6.8	–
γ_{25}	mS m^{-1}	1.7	60.4	8.4	7.1	6.4
P_{tot}	μg l^{-1}	0	338	12.3	6.0	32.4
PO_4	μg l^{-1}	0	345	8.9	2.0	31.2
SO_4	mg l^{-1}	0.6	144	7.1	5.5	9.2
Cl	mg l^{-1}	0.1	19.0	1.3	1.0	1.8
Na	mg l^{-1}	0.4	17.5	1.4	1.0	1.6
K	mg l^{-1}	0.2	8.8	1.8	1.3	1.5
Ca	mg l^{-1}	0.2	51.0	4.5	3.1	5.4
Mg	mg l^{-1}	0.1	16.0	1.3	0.8	1.8
N_{tot}	μg l^{-1}	38	9970	581	380	922
NO_3–N	μg l^{-1}	0	18,200	594	130	1607
NH_4–N	μg l^{-1}	0	7610	52	8	374
NO_2–N	μg l^{-1}	0	460	6.7	1.0	34
Alk.	mmol l^{-1}	0.05	6.44	0.61	0.48	0.60
SiO_2	mg l^{-1}	0.9	60.0	8.3	7.4	4.6
Al	μg l^{-1}	2	1150	91	42	130
Fe	μg l^{-1}	0	> 10,000	338	52	1206
Mn	μg l^{-1}	0	5000	112	25	307
Cu	μg l^{-1}	1	1350	69	14	159
Pb	μg l^{-1}	1	50	5.2	3.0	7.6
Ni	μg l^{-1}	1	670	14.3	4.0	52
Cd	μg l^{-1}	0.05	8.0	0.52	0.30	0.69
F	μg l^{-1}	9	580	58	44	59

Table 6. Composition of groundwater during the period 1975–1988

Parameter	Unit	Min	Max	Mean	Median	S.D.
pH		3.6	9.2	6.3	6.3	–
γ_{25}	mS m^{-1}	0.8	59	6.5	4.1	6.9
Alk.	mmol l^{-1}	0	26.1	0.32	0.22	0.59
SO_4	mg l^{-1}	0	100	6.2	3.7	10.8
Cl	mg l^{-1}	0	67	2.5	1.6	4.0
Na	mg l^{-1}	0	46	3.2	2.2	3.8
K	mg l^{-1}	0	33	1.3	0.8	1.7
Ca	mg l^{-1}	0	67	5.0	3.0	6.6
Mg	mg l^{-1}	0	36	1.6	0.9	2.7
Al	μg l^{-1}	0	9700	228	40	760
Cu	μg l^{-1}	0.1	800	6.5	2.0	18.5
Mn	μg l^{-1}	0	3900	75	11	201
Pb	μg l^{-1}	0	80	2.8	0.5	7.0
Zn	μg l^{-1}	0	9000	22.0	3.0	178
NO_3–N	μg l^{-1}	0	8500	210	46	537
NH_4–N	μg l^{-1}	0	3600	52.0	8.0	218
PO_4–P	μg l^{-1}	0	610	15.5	7.0	31.9
F	μg l^{-1}	0	5100	170	70	347

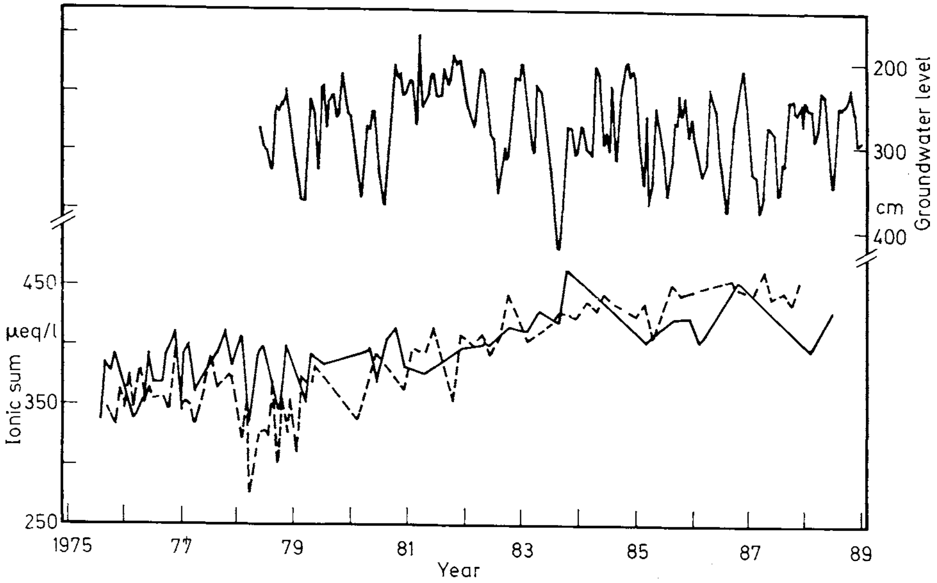

Fig. 8. Sum of cations (*broken line*) and anions (*full line*) during the period 1975–1988, groundwater level during 1978–1988 at Karkkila (No. 2) groundwater station

The Karkkila (No. 2) groundwater station in southern Finland (Fig. 8) is now at the first stage of acidification. The cation and anion concentrations have been increasing in the 1980's. Because there is still buffering capacity, the pH does not change. The increase cannot be explained by the changes in the groundwater level. The highest increase is seen in calcium and sulphate concentrations. This increase is the most typical for the southernmost stations, where the level of sulphur deposition has been high for a long time. Some changes have also been detected in stations near the eastern Finnish border. Changes of this kind have also been reported in Sweden (Andersson and Stokes 1987). The calcium concentrations in the runoff water in a forested research catchment 20 km from Karkkila have also been increasing (Lepistö and Seuna this Vol.).

The concentrations of several substances recorded at the groundwater stations in 1975–1977 and 1985–1988 were compared using the t-test. The increase in SO_4 and Ca was significant at the 99% confidence level and that of NO_3 at the 95% confidence level. A total of 1200 observations at 46 stations were used in these tests. The concentration of sulphate increased during the observation period from $2.9 \, mg \, l^{-1}$ to $4.2 \, mg \, l^{-1}$ (Fig. 9). The main reason for these increases are the increases in sulphate and nitrate depositions.

A decrease in groundwater alkalinity and an increase in sulphate concentration are often better indicators of groundwater acidification than pH values. Due to increased concentrations of hydrogen ion and sulphate ion in soil water, the base cation concentration increases, leading to increased concentrations of sulphate and base cations in groundwater without a change in pH. At the second stage the base

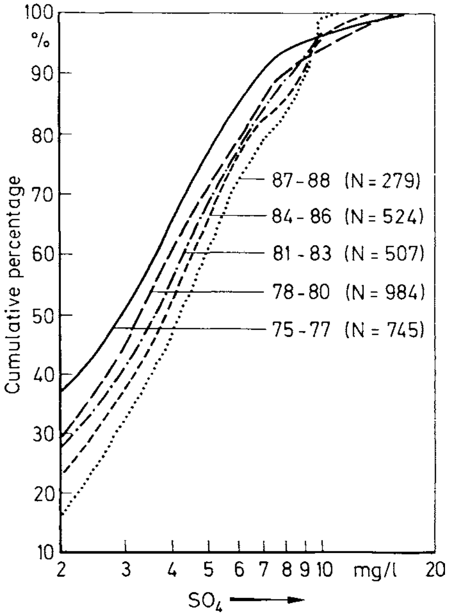

Fig. 9. Cumulative distribution of the sulphate concentration of groundwater at the groundwater stations during five periods between 1975–1988

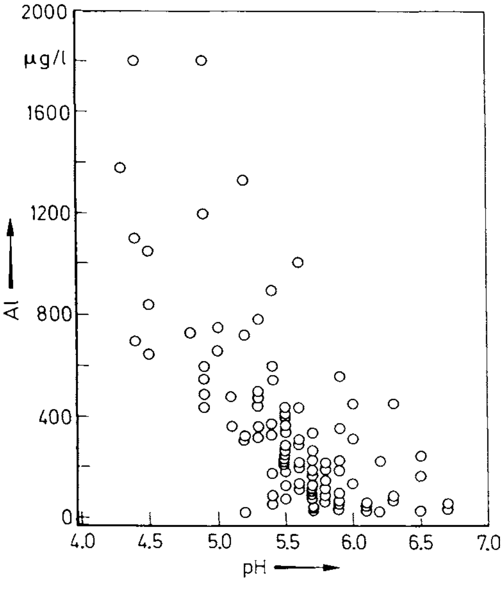

Fig. 10. Aluminium concentration and pH in groundwater in 1987 in the Porvoo area with high sulphate deposition

saturation is lowered and alkalinity decreases while acidity begins to increase.

Soil acidification may result in increased leaching of metals into the groundwater. Acidic percolation water dissolves heavy metals (e.g. Cd, Mn, Zn, Pb) and aluminium from the soil. At low pH levels (<5.5) the leaching of aluminium increases significantly. This can be seen in the well samples of Porvoo area, where the local sulphate deposition is high (Fig. 10).

Conclusions

Although groundwater in Finland is sensitive to acidification, the buffering capacity of the average Finnish soil is still sufficient to prevent considerable groundwater acidification. However, the first signs of groundwater acidification have been detected in the background stations of southern Finland. The most marked changes have occurred in sulphate and calcium concentrations. Nitrate concentrations have also increased significantly, although the mean level is still very low. The main reason for these increases seems to be increasing atmospheric deposition.

The changes have been more dramatic in areas receiving high levels of sulphate deposition from local sources, especially the oil-processing industry, pulp industry and power plants using coal. The aluminium concentrations of soil waters in these areas are very high and the pH is low.

List of Symbols

SW = snow
IW = infiltration water
PW = percolation water
GW = groundwater
γ_{25} = electrical conductivity
n = number of analyses, observations etc.
L = lysimeter
P = percolation station
S = spring
T = sampling tube
W = well

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Trace Metals in Finnish Headwater Lakes – Effects of Acidification and Airborne Load

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Summary

The study on the effects of acidification and airborne load on the concentrations of some trace metals (Al, Mn, Cd, Cu, Pb, Zn, Ni, Hg) in sediments (16 lakes), water (259 lakes) and aquatic fauna (14 lakes) of pristine Finnish headwater lakes was conducted in 1985–1989. Atmospheric trace metal load and concentrations in the water and in the sediments were higher in southern Finland than in central and northern Finland. The share of anthropogenic load according to sediments varied from 62 to 95% for Cd, Hg and Pb, was from 39 to 91% for Zn and varied from 0 to 84% for Ni and Cu in southern and central Finland. Anthropogenic load could be explained by atmospheric deposition. Acid conditions favoured high concentrations of Al, Mn, Zn, Pb and Cd in water and high concentrations of Pb, Cd, Zn, Cu and Ni in aquatic plants. Lead concentrations were usually one order of magnitude higher in liver and bones of fish from acidic lakes than in circumneutral lakes. Cadmium in liver, Hg in muscle and Al in gills also showed increased concentrations in several fish species in acidic lakes.

Introduction

Human activities have caused dramatic changes in fluxes of trace metals to the hydrologic cycle especially during this century (Nriagu and Pacyna 1988). Several industrial processes including combustion of fossil fuels, mining, metal processing and production as well as refuse incineration contribute to these emissions which are mostly concentrated in intensively populated industrial areas. Air-borne pollutants as fine particles or in gaseous form are transported over long distances and can be detected in remote areas in amounts that greatly exceed the natural background level (e.g. Johnson 1987).

Pristine headwater lakes receive atmospheric trace metals directly from precipitation, dry fallout and snowmelt, but the inflow is also dependent on the complex weathering, leaching, and retention reactions that occur in the catchment area. Many trace metals are emitted as well as deposited together with acidic compounds and acidification of soils can furthermore increase the leaching of some metals, especially Al, Mn, Zn and Cd (e.g. Berqvist 1987). Lake water acidification can

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also increase concentrations in water by decreasing trace metal gross sedimentation rates to the sediments, by mobilizing metals from the sediments, or by affecting sediment-water interactions in lakes (e.g. Norton 1984).

There are only few studies on the effects of atmospheric load of trace metals on small forest lakes in Finland before the mid 1980's (Tolonen and Jaakkola 1983; Myllymaa 1986; Myllymaa and Murtoniemi 1986; Rekolainen et al. 1986a; Rekolainen et al. 1986b; Verta et al. 1986). All these studies revealed the importance of atmospheric trace metal load on the total budget of trace metals in remote lakes in Finland.

The present paper summarises results of a project carried out in 1985–1989 in connection with the Finnish Research Project on Acidification (HAPRO). The main objectives of the study were to establish the contents of trace metals in water and aquatic fauna of pristine forest lakes susceptible to acidification or already acidified in regions of different deposition in Finland as well as to establish the effects of airborne heavy metal load and acidification on the contents in various organisms. Lastly, the historical changes in trace metal load, as reflected by lake sediments, were determined.

Materials and Methods

General Description of the Study Areas

Altogether 259 lakes were studied for trace metals in water, sediment or biota (Table 1). All the lakes included were situated in sparsely populated areas at the head of a drainage basin. Some of the southernmost lakes were, however, only some 20 km from the nearest municipalities. The lakes normally occupied about 10–20% of the watershed. Mean area of the lakes was 0.38 km^2; the largest was 10 km^2.

Table 1. General characteristics of the 259 lakes

Variable	Unit	Mean	S.D.	Range
Lake area (A)	km^2	0.38	0.86	0.005–10.0
Watershed area (W)	km^2	3.1	5.7	0.127–51.7
W/A		15	26	2.0–244
Conductivity	$mS\,m^{-1}$	2.8	1.3	0.66–10.3
pH		5.9	0.75	4.20–7.50
Gran alkalinity	$\mu eq\,l^{-1}$	53	82	− 85–525
TOC	$mg\,l^{-1}$	8.9	6.3	0.32–40.7
SO_4^a	$\mu eq\,l^{-1}$	82	48	3.0–233
Base cations[a]	$\mu eq\,l^{-1}$	200	110	28.0–907
Total N	$\mu g\,l^{-1}$	370	180	90–1360
Total P	$\mu g\,l^{-1}$	15	15	0–133

[a] Indicates non-marine concentrations.

The lakes were chosen to represent the whole lake population of Finland, but are concentrated on areas which have the highest deposition of acidic compounds. About half of the lakes were also sites of intensive studies of the effects of acidification on the biota of lakes (Heitto this Vol.; Rask and Tuunainen this Vol.). The watersheds were mostly vegetated by coniferous forests or peatlands. Morainal material is the most common soil material. Ditching operations are the main disturbance in most watersheds. Cultivated land was normally absent and in no case exceeded 10% of the watershed area.

Snow Samples

In order to study the present atmospheric load of trace metals, snow samples were collected in 1987 from March 13th to April 23th at 48 long-term snow quality monitoring stations (Soveri and Ahlberg this Vol.). Samples were collected straight into 500-ml high density polyethylene bottles (Nalgene labware) by scraping the wall of a dug trench (Ross and Granat 1986). The total depth of the snowpack was sampled. The wall of the trench had been cut by a polyethylene scraping tool. Plastic gloves were worn during sampling. The scraping tool and the bottles were kept in 10% nitric acid for 2 days followed by triple rinsing with quartz-distilled water and then put in double plastic bags for transportation. Upon arrival at the laboratory, the outer plastic bag was removed. The samples were kept frozen until analysis.

The samples were melted at room temperature and acidified with 35% suprapur nitric acid (Merck). Trace metals (Cd, Cu, Pb, Zn, Ni) were analysed using graphite furnace AAS (GFAAS). Chemical blanks were made with distilled and deionized water to ensure that no contamination occurred during analysing. Zn and Cu were high in blanks from one district, and the results were rejected.

Sediment Samples

In March–April 1986 two sediment cores were taken from the deepest points of 16 lakes (Fig. 1, Table 2) with a pistonless gravity corer (diam. 50 mm). The cores were sectioned in the field into 1.0 cm (0–10 cm) and 2.0 cm (10–30 cm) subsamples, and the two parallel samples pooled. A third core was taken from some lakes and sectioned for ^{210}Pb analysis. All the cores were taken within an area of 10 m^2. The samples were deep-frozen in polyethylene boxes.

Nine subsamples by equal volume (0–1 cm, 1–2 cm, 2–3 cm, 3–4 cm, 4–5 cm, 6–8 cm, 10–12 cm, 18–20 cm, 28–30 cm) from each core were analysed for trace metals and major cations. The lyophilised and homogenised samples (0.1–0.5 g) were digested with 10 ml of nitric acid (conc HNO_3 diluted with water 1:2) at 120°C under pressure (SFS 3044). Concentrations of Al, Na, K, Ca, Mg, Ti, Fe, Mn, Ni, Cu and Zn were determined by inductively coupled plasma (ICP) and concentrations of Cd and Pb by GFAAS. Mercury was determined by cold vapour AAS (CVAAS) technique after boiling 30 min with a mixture of conc H_2SO_4 and

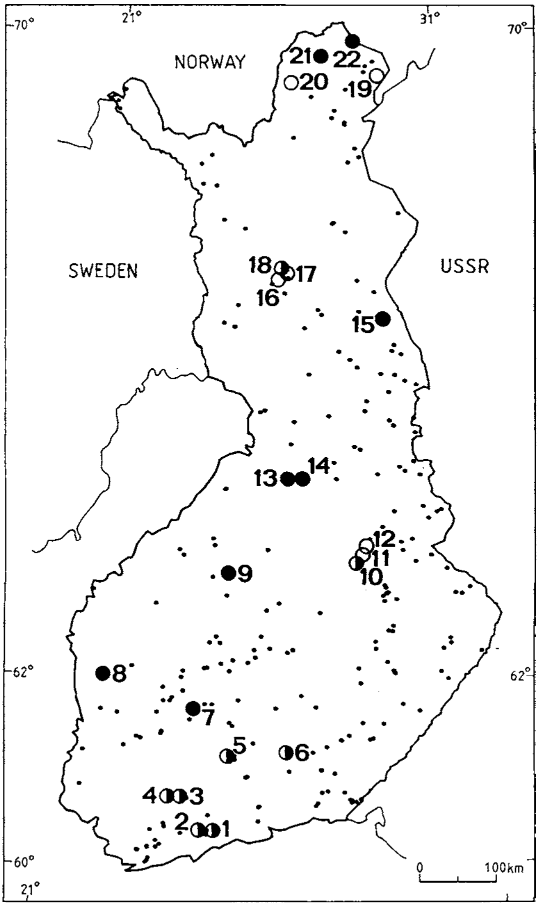

Fig. 1. The location of the study lakes. ● = lakes sampled for sediment chemistry; ○ = lakes sampled for trace metals in biota

fuming HNO_3 (SFS 5229). According to NIST (National Institute of Standards and Technology) standard reference materials (SRM 1645 and SRM 1646), the digestion method gives less than 50% of the total quantity of Al, Ti, K and Na, but from 50 to 94% of the total of Fe, Mn, Ca, Mg, Pb, Zn, Cd, and Ni in sediment samples. The relative standard deviation between replicates for all sediment samples was less than 5% for most trace metals and 11% for Hg.

Water Samples

Water samples for trace metal analyses were collected from 259 lakes included in the lake survey conducted in autumn 1987 (Forsius et al. this Vol.). All lakes were selected subjectively, either based on previous acidification studies (133 lakes) or from the statistically selected lake population of the lake survey of 1987. The objective of the selection was to cover the whole country, with emphasis put on the headwater lakes of the most acidified and acid-sensitive but unaffected areas.

Table 2. General characteristics and water quality of the study lakes sampled for sediment and biota. Lake numbers refer to Fig. 1

Lake	Sample, sediment, biota	Area, ha	Maximum depth, m	Drainage area, km^2	Dominant surficial material[a]	Water chemistry				Acidification history (diatoms)[b]
						Ca + Mg µeq l^{-1}	pH	Gran alkalinity µeq l^{-1}	TOC mg l^{-1}	
1. Iso-Lehmälampi	S, B	6	11	0.3	M	105	4.8	− 36	4.8	**
Pieni Lehmälampi[c]	B									
2. Ruuhijärvi	S, B	29	18	1.8	EB	131	5.2	− 6	4.8	**
3. Vähä-Melkutin	S, B	17	16	0.7	SG	400	6.9	388	1.5	N
4. Kaitajärvi	S, B	10	18	1.6	SG	56	4.9	− 56	0.5	N
5. Valkea-Kotinen	S, B	4	6	0.2	M	196	5.0	− 49	12.0	–
6. Sonnanen	S, B	162	12	4.4	M	196	6.6	57	1.8	N
7. Siikajärvi	S	92	23	4.0	M	106	5.2	− 6	5.0	**
8. Kangasjärvi	S	47	7	1.8	M	83	5.2	5	1.5	N
9. Valkeinen	S	94	5	2.5	SG	181	5.8	1	3.2	*
10. Suo-Valkeinen	S, B	4	8	0.2	P	51	5.2	− 8	2.7	*
11. Tiilikka	B	400	8	148.0	P	101	5.9	27	11.7	–
12. Älänne	B	450	12	15.0	M	106	6.1	30	7.0	–
13. Ahveroinen	S	4	5	0.6	SG	46	6.2	12	1.9	N
14. Jaakonjärvi	S	4	7	0.7	SG	46	6.5	30	1.5	**
15. Silpalampi	S	18	8	0.6	M	23	4.8	− 20	0.6	*
16. Iso-Venejärvi	B	238	18	19.1	M	166	7.0	120	3.5	–
17. Iso-Perälampi	B	20	6	1.1	M	106	6.6	82	6.5	–
18. Vasikkajärvi	S, B	25	17	1.6	M	41	4.9	− 8	1.0	–
19. Äälisjärvi	B	408	58	14.1	EB	83	6.6	24	1.5	–
20. Peltojärvi	B	658	47	80.8	M	142	7.0	120	3.0	–
21. Ravdojärvi	S	56	15	13.0	EB	132	6.8	83	4.5	–
22. Tsuomusjärvi	S	94	11	9.6	EB	157	7.0	93	3.6	–

[a] M = Moraine, EB = Exposed bedrock, SG = Sand and gravel, P = Peat.
[b] ** = Severely acidified, * = Slightly acidified, N = Not acidified.
[c] Water quality of Pieni Lehmälampi equals essentially that of Iso-Lehmälampi, pH is 4.5.

The bottles for trace metal analyses (125 ml polypropylene, Nalgene labware) were cleaned, stored and transported with the same precautions as with the snow sample bottles. The samples were taken below the surface layer directly in the bottles, either by hand while wearing plastic gloves or by attaching the bottle to a stick.

The samples were preserved at the District laboratories with 1 ml 35% suprapur HNO_3 (Merck). Graphite furnace AAS was used for the determination of Cd, Cu, Pb and Ni and flame AAS for Zn. Sample blanks (total 35) were made weekly from bottles filled with quartz-distilled water of the Research Laboratory and preserved as the samples. The blank values showed occasionally elevated concentrations of Zn, Cd and Pb (Table 3), but the source of the contamination could not be identified. The blank values were not substracted for two reasons: there were always lake sample values below blank values in the district in question, and all blanks were not elevated anywhere. However, in the case of an obvious contamination of the blank, all results from that district concerning that particular metal were rejected.

Iron and manganese were determined colorimetrically in district laboratories according to Finnish standards (SFS 3028, SFS 3033). Aluminium fractions were determined at the Norwegian Institute for Water Research according to methods of Røgeberg and Henriksen (1985).

Biota Samples

Fourteen lakes representing areas of different atmospheric load of acidic compounds and trace elements were chosen for study of trace elements in biota (Fig. 1, Table 2). From each area (Southern Finland–Central Finland–Northern Finland) lakes having different water quality (acidified clearwater lakes, non-acidified clearwater lakes, humic acid lakes) were sampled. The indicator species of water plants, benthic invertebrates, and fish were chosen so that each species could be found from as many lakes of different water quality as possible. There was, however, no single species that could be found in all lakes. Five lakes were sampled in the summer 1986 (lakes no. 1–5) and the rest in summer 1987. More species were collected in 1986 than in 1987. The selection of the species to be collected in 1987

Table 3. Detection limits (DL) ($\mu g l^{-1}$) and blank determinations ($\mu g l^{-1}$) of the heavy metals in water (n = 35)

Element	DL	Blanks below detection limit	Mean[a]	Max
Cd	0.01	29	0.012	0.10
Cu	0.1	26	0.088	0.60
Pb	0.01	18	0.048	0.55
Zn	1.0	27	1.73	14.7
Ni	0.1	33	0.058	0.25

[a] Values below DL are calculated as $DL2^{-1}$.

was made according to species observed to accumulate higher concentrations of trace metals, i.e. some species having low concentrations of trace metals were not collected in 1987.

Aquatic Plants

The water plants *Nuphar luteum* L. and *Sparganium* sp. were collected in July–August. The whole young leaves of *N. luteum* and segments of 10 cm from the top of the leaves of *Sparganium* sp. were cut for determination of Cd, Zn, Pb, Cu and Ni. The samples were washed with distilled water and kept deep frozen in polythene bags until analysis. A sample for analysis consisted of about ten leaves of *N. luteum* and 50–100 segments of *Sparganium* sp.

Aquatic Insects

The sampling was performed manually or with arm net from littoral areas. Most samples consisted of trichoptera larvae of *Limnophilus* sp. or *Phryganea* sp. In 1986, dragonfly larvae (Odonata) and adult water beetles (Coleoptera) were also collected. Each sample consisted of from 20 to 50 specimen of trichoptera and from 1 to 5 specimen of Odonata and Coleoptera. The samples were kept in water for 12–24 h, the trichoptera larvae were removed from the pupae, and the samples were deep frozen in polythene boxes.

Fish

Fish were captured with gill nets and the weight and the length were measured. The opercular bones or cleithral bones (*Esox lucius* L.) were removed for analysis of age and determination of Ca, Mn, Pb, Zn and Cd. The bones were cleaned by boiling in distilled water for 1–2 min, scraped clean and kept at room temperature in paper bags. The gills were removed, washed with distilled water and deep-frozen in polythene bags for determination of Al. Livers were removed and deep-frozen in polythene bags for determination of Pb, Cd, Zn, Cu and Ni. A piece of muscle was removed from under the dorsal fin from larger fish for determination of Hg. From small fish the hole muscle was removed. The samples were deep-frozen in aluminium foil. Each sample of bone, gills or liver tissue consisted of from one to three individuals of large fish or from three to nine individuals of small fish. Mercury samples were analysed individually.

The species captured for analysis were perch (*Perca fluviatilis* L.), northern pike (*Esox lucius* L.) whitefish (*Coregonus* sp.), brown trout (*Salmo trutta* L.), and lake char (*Salvelinus alpinus* L.). The large diversity of species was due to the different fish populations in the study lakes. In the most acid lakes, perch was the only species present.

Analysis Methods

The samples of aquatic plants, insect larvae, and fish gill, liver and muscle tissues were freeze dried under reduced pressure, the dry weights measured and homogenized. The bones were analysed after drying at room temperature. The results represent a mean of at least two replicates. The samples were digested by boiling with concentrated HNO_3 and 30% H_2O_2. Concentrations of Pb, Cd, Al, and Ni were determined by GFAAS technique, and concentrations of Ca, Cu, Mn, and Zn by FAAS technique. Mercury was determined by the same method as for the sediment samples.

Analyses of the NIST standard reference materials gave from 92% to 99% recoveries on SRM 1566 (Oyster tissue) for all elements. The recoveries on SEM 1572 (Citrus leaves) ranged from 63% to 105% for Cd, Cu, Zn, and Pb, and was about 150% for Ni. The relative standard deviations of replicates for all tissue samples were less than 5% for Ca, Cd, Cu, Zn, and Mn, less than 15% for Pb, and from 11 to 26% for Ni and Al.

Results and Discussion

The Atmospheric Load of Trace Metals

Snow Cover

The duration of permanent snow cover before sampling in winter 1986–1987 varied from 90 days in southern Finland to 202 days in northern Finland and the deposition values thus represent a mean of from 3 months to nearly 7 months. Three short melting periods occurred during the winter in southern Finland during which a decrease of from 10 to 20% of the thickness of the snow cover took place. The water content of the snowpack, however, increased even in southern Finland to late March, and no increase in the runoff from small catchments occurred (Water and Environment Research Institute, unpubl.).

The concentrations and the deposition of the elements studied were higher in southern Finland than in the rest of the country (Table 4). The results of Pb, Cu, Cd and Zn are in good agreement with those reported by Ross and Granat (1986) for northern Sweden, but clearly lower than those reported by Soveri (1985) for snow from the same stations in 1976–1981 and also lower than the mean concentrations and deposition found in 1980's (Soveri and Ahlberg this Vol.). The decrease may partly be caused by decreased atmospheric deposition (Rühling et al. 1987), but some contamination of the earlier samples (Soveri 1985) cannot be excluded. The stations located near some important heavy metal emission sources indicated clearly higher concentrations and deposition of those heavy metals. These were Cu, Ni and Cd in the industrial areas of Pori-Harjavalta and Cu and Ni in northeastern Lapland near the Kola peninsula.

Table 4. Concentrations and deposition of trace metals in the snowpack in southern Finland (latitude <62°) and northern Finland in winter 1986–1987

Element	Subregion south			Subregion north		
	n	Mean	(Range)	n	Mean	(Range)
Concentrations ($\mu g\,l^{-1}$)						
Al	16	133	(61–220)	26	48	(16–240)
Pb	18	4.8	(0–35)	30	2.2	(0–4)
Zn	14	6.9	(2–13)	30	4.5	(1–18)
Cu	14	2.0	(0–7)	29	0.86	(0–3)
Ni	13	1.6	(0.5–5)	27	0.45	(0.1–2)
Cd	13	0.07	(0.01–0.18)	28	0.04	(0.01–0.08)
Deposition (mg m^{-2} $month^{-1}$)						
Al	16	3.1	(1.6–5.8)	26	1.3	(0.37–6.0)
Pb	18	0.11	(0.0–0.92)	30	0.056	(0.0–0.11)
Zn	14	0.14	(0.034–0.30)	30	0.11	(0.025–0.38)
Cu	14	0.041	(0.0–0.13)	29	0.022	(0.0–0.065)
Ni	13	0.033	(0.013–0.11)	27	0.012	(0.0021–0.060)
Cd	13	0.0016	(0.0002–0.0039)	28	0.00094	(0.0002–0.0024)

Aluminium also showed a clear geographical concentration pattern with high concentrations in the south. This distinct gradient in concentration and deposition in the snowpack of this metal is probably caused by soil drift because the highest values occurred in areas of intensive cultivation in the southwestern Finland. These are also the same areas that have permanent snow cover latest during autumn, in 1986 in mid-December, and the wind-blown soil particles may easily enter the snowpack. Aluminium concentrations in snow have been reported by Soveri (1985) and Kubin and Lippo (1987) for central Finland and were of the same magnitude.

Concentrations of Pb and Cd correlated with SO_4 ($r = 0.298$ and $r = 0.364$, $p < 0.05$) and with NO_3 ($r = 0.337$ and $r = 0.672$) in the snowpack. Zn, Cu and Ni did not correlate with either SO_4 or NO_3. Only 50% of the intercorrelations between trace metals were significant ($p < 0.05$). These were Pb–Cd ($r = 0.345$), Pb–Cu ($r = 0.483$), Zn–Cd ($r = 0.417$), Zn–Ni ($r = 0.321$) and Cu–Ni ($r = 0.372$). Aluminium correlated with most trace metals; Al–Ni ($r = 0.550$), Al–Pb ($r = 0.469$), Al–Cu ($r = 0.457$), Al–Cd ($r = 0.413$) as well as with NO_3 ($r = 0.446$), possibly because the areas susceptible for soil drift are mostly the same that receive high amounts of atmospheric transported trace metals.

These intercorrelations were remarkably lower than those between Pb, Zn, Cd, and SO_4 reported by Ross and Granat (1986) in northern Sweden. Ross and Granat (1986) concluded on the basis of good correlations that the deposition of these metals is primarily due to long-range transport of anthropogenic emissions from the European continent. This was also concluded by Rühling et al. (1987)

from a decreasing concentration gradient of these metals in moss in Scandinavia from south to north. The appearance of atmospheric pollution from some local emission sources of heavy metals both in moss and in the snowpack shows, however, that the differentiation of different sources is difficult and needs more investigation. The primary emission sources of Pb to the atmosphere are automobile exhausts whereas Zn, Cd and Cu are released by metal smelting and refining and Ni by oil combustion and smelting (Nriagu and Pacyna 1988). Sulphur is predominantly released by burning of fossil fuels and nitrogen compounds by automobile exhaust. Intercorrelations of trace elements in deposition may thus not indicate the same source or transport, but reflect that most of the emissions of all these compounds are concentrated in the same areas, both in central Europe and in southern Scandinavia.

Lake Sediments

Both maximum and mean surface (0–5 cm) concentrations of Pb, Cd and Hg had a clear regional pattern showing higher concentrations in the southern Finland than in the northern Finland (Table 5). The concentrations of these three elements were also much lower in the two northernmost lakes than in the other lakes. Zn also had somewhat higher concentrations in the south than in the north. On the contrary, Cu and Ni showed no regional differences in surface sediments.

Regional differences were not found, except for higher concentrations of Zn in the north, if concentrations at a depth of 18–30 cm in the sediment profiles were compared (Table 5). The lowest concentration for Pb for all profiles were found in the deepest analysed subsample in southern Finland indicating that the "background level" may not have been found in the southernmost lake sediment profiles (cf. Verta and Mannio 1987).

The upward increase in concentration in sediment profiles was more than fivefold, with Pb in all but one lake with a maximum increase of 44 (Table 5, Fig. 2). Most of the Cd, Hg and Zn profiles showed enrichment factors (EF) between 2 and 10. Half of the EF values for Cu were less than 2 and in only three lakes were EF values of 2 for Ni exceeded. Clearly higher EF values were found in the southern part of the country than in the north, again with the exception of Cu and Ni (Fig. 2).

The sediment profiles dated with ^{210}Pb showed that the start of anthropogenic accumulation of Pb was evident in most cores by 1800 in southern Finland and was followed by a linear increase up to the 1970's (see also Verta et al. 1989). After this, a levelling off or a small decrease in the accumulation rate occurred. A prominent increase of Cd, Hg and Zn typically occurred in the 1900's and in the few cases where any prominent increase in Cu, Ni or V sedimentation occurred, it was normally after 1950.

Verta et al. (1989) also compared the recent gross accumulation rates of trace metals to the calculated background accumulation rates (non-anthropogenic) and calculated the anthropogenic deposition as the difference between these two

Table 5. Trace metal concentration in surface sediment (0–5 cm) and in deep sediment (18–30 cm) and enrichment factor (surface maximum/deep mean) in 16 lakes in Finland

Element	Subregion south			Subregion north		
	n	Mean	(Range)	n	Mean	(Range)
Surface sediment (0–5 cm) $\mu g\,g^{-1}$						
Pb	7	119	(69–204)	9	72	(0.62–146)
Zn	7	131	(60–220)	9	100	(56–166)
Cu	7	17.0	(7.5–25)	9	19.1	(7.3–31)
Ni	7	13.0	(6.9–19)	9	12.6	(4.5–25)
Cd	7	1.85	(1.0–3.4)	9	0.88	(0.32–1.7)
Hg	7	0.36	(0.14–0.57)	9	0.18	(0.01–0.33)
Deep sediment (18–30 cm) $\mu g\,g^{-1}$						
Pb	7	13.6(8.6)[a]	(2.5–43)	9	6.6 (4.4)[a]	(0.65–16)
Zn	7	29.1	(12.5–170)	9	72.7	(18–145)
Cu	7	12.5	(2.7–16)	9	17.3	(3.5–29)
Ni	7	9.2	(4.1–14.5)	9	12.8	(4.1–21)
Cd	7	0.30	(0.2–0.55)	9	0.26	(0.1–0.55)
Hg	7	0.13 (0.09)[b]	(0.05–0.37)	9	0.07	(0.02–0.15)
Enrichment factor (surface maximum/deep mean)						
Pb	7	17.8	(6.3–44)	9	14.4	(1.5–37.9)
Zn	7	6.2	(0.94–12.6)	9	2.0	(0.89–4.2)
Cu	7	1.9	(1.1–2.6)	9	1.7	(0.86–3.7)
Ni	7	1.7	(1.1–2.8)	9	1.3	(0.78–2.3)
Cd	7	8.1	(3.6–12.8)	9	4.8	(1.0–9.0)
Hg	7	6.3	(0.7–15.7)	9	2.9	(1.0–5.6)
Accumulation in 1980 ($mg\,m^{-2}\,a^{-1}$)						
Pb	4	13.4	(6.2–25)	5	6.1	(1.8–16)
Zn	4	14.4	(4.1–41)	5	7.4	(1.9–22)
Cu	4	2.3	(1.3–4.2)	5	1.2	(0.33–3.0)
Ni	4	1.5	(0.7–2.9)	5	0.75	(0.17–1.9)
Cd	4	0.19	(0.098–0.47)	5	0.077	(0.023–0.23)
Hg	4	0.040	(0.026–0.050)	5	0.016	(0.005–0.036)

[a] The mean of the deepest (26–30) subsample.

[b] The mean of six lakes. One anomalous profile (lake no. 3) rejected.

estimates. The share of anthropogenic deposition in sediments varied from 74 to 97% for Pb, from 62 to 91% for Cd, from 70 to 89% for Hg and from 39 to 91% for Zn in southern and central Finland. For Cu and Ni the variation in the anthropogenic share was much larger between different lakes ranging from 0 to 84% for Cu and from 0 to 75% for Ni. Because only slight or no disturbances have occurred in the drainage areas of the lakes, most of the anthropogenic trace metal accumulation into sediments is of atmospheric origin or is a result of increased

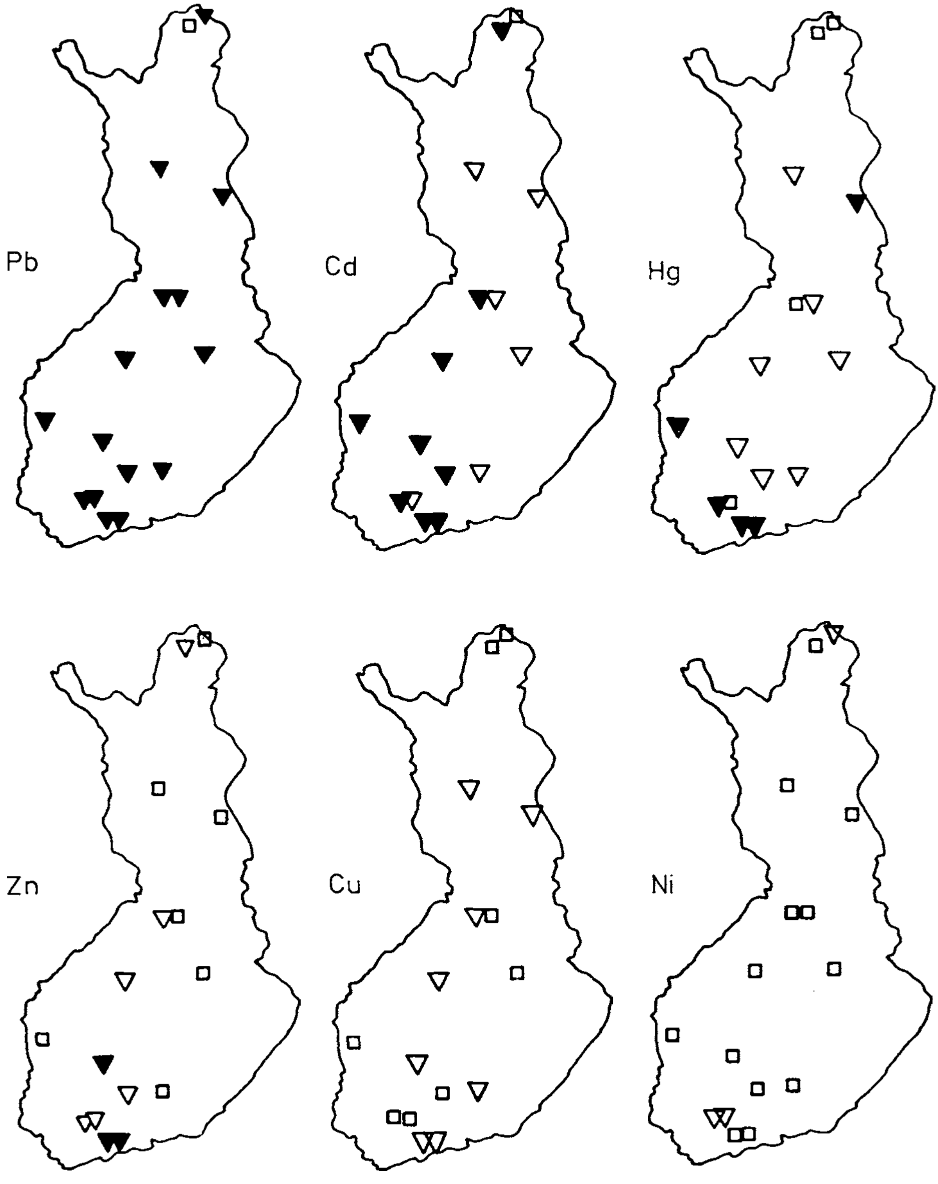

Fig. 2. The enrichment factor (*EF* = maximum concentration in surface sediments/mean concentration in deep sediments) of trace metals in lake sediments. ▼ = EF > 5; ▽ = EF = 2–5; □ = EF < 2

leaching from the catchment due to acidification and subsequent sedimentation in lakes.

When analysing intercorrelations of trace metals in surface (0–5 cm) and deep (18–30 cm) sediments clear differences in trace metal behaviour was evident. In deep sediments trace metals had only few intercorrelations (Zn–Cd, r = 0.601, Zn–Cu, $r = 0.601$). The metals showing highest anthropogenic enrichment (Pb, Cd, Hg) were normally strongly intercorrelated in surface sediment and also correlated with sediment organic matter possibly reflecting the ability of phytoplankton to scavenge these metals from the waterphase (Table 6). Cu and Ni had a strong intercorrelation in surface sediment but neither of them correlated with other trace elements.

Concentrations of trace metals in surface sediment did not correlate with concentration of the same metal in water. Instead, Pb and Hg had a weak ($P < 0.05$) positive correlation with SO_4^{2-} ($r = 0.505$ and $r = 0.593$) as well as negative correlation with pH ($r = -0.533$ and $r = -0.760$). The percentage of exposed bedrock had a strong positive ($r = 0.779$) correlation with Pb in sediment. In "bedrock-type" catchments the lack of organic soils to absorb Pb allows a greater part of the Pb deposited in the drainage area to enter the lake than in lakes with catchments of thicker organic soil layers. The study lakes in southern Finland had a notably higher proportion of exposed bedrock in the catchments than the other lakes, which may overemphasize the relationship (Table 2). The percentage of sandy soils in the catchment correlated negatively with Cu and Ni both in deep sediments ($r = -0.741$ and $r = -0.820$) and in surface sediments ($r = -0.697$ and $r = -0.635$), possibly reflecting the retention of these metals in deep soil horizons.

Water Chemistry

The general water quality of the lakes is close to the average in small Finnish lakes (Forsius et al. this Vol.). Acid-sensitive, dilute clearwater lakes are somewhat overrepresented, resulting in lower average conductivity, pH, alkalinity and TOC values in our lakes. Also the restriction to headwater lakes causes a shift to dilute water quality because of the thinner soils in the catchments.

Trace metal concentration distribution in the study lakes is presented in Table 7. The material is divided into two groups: the southern subregion (latitude < 62°) represents the more industrialized and denser-populated areas with a higher anthropogenic component in deposition (Fig. 1). The lakes in the southern subregion have higher sulphate and conductivity values, and lower pH and

Table 6. Significant correlations ($p < 0.001$) between trace metals in surface sediments (0–5 cm)

	Cd	Zn	Pb	Hg	Cu	Ni
Zn	0.771					
Pb	0.635	0.379				
Hg	0.538	–	0.522			
Cu	–	–	–	–		
Ni	–	–	–	–	0.518	
Org.	0.616	–	0.449	0.549	–	– 0.399

Table 7. Metal concentrations ($\mu g\, l^{-1}$) in water in southern and northern subregion

Element		Subregion south				Subregion north		
	n	Mean	S.D.	Max	n	Mean	S.D.	Max
Al_{r}[a]	(96)	80	76	471	(163)	48	55	311
$\mathrm{Al}_{\mathrm{il}}$[b]	(96)	34	33	163	(162)	33	39	191
$\mathrm{Al}_{\mathrm{lab}}$[c]	(96)	47	57	308	(162)	16	20	120
Fe	(95)	270	272	1400	(162)	384	424	2600
Mn	(95)	41	33	210	(161)	26	34	290
Cd	(89)	0.031	0.028	0.13	(104)	0.022	0.023	0.13
Cu	(89)	0.379	0.366	2.60	(156)	0.427	0.359	3.01
Pb	(89)	0.125	0.154	0.89	(86)	0.118	0.140	0.72
Zn	(60)	5.63	4.37	28.1	(112)	2.54	2.62	20.1
Ni	(89)	0.398	0.604	5.31	(156)	0.248	0.380	2.64

[a] Total monomeric Al.
[b] Non-labile monomeric Al.
[c] Labile monomeric Al.

alkalinity values. Also organic carbon content is slightly lower in this group, as well as watershed areas being smaller.

The concentrations of Zn, Cd and Ni in water decreased northward parallel to the pattern of atmospheric deposition as suggested by the snowpack chemistry (Table 4). This relationship is clear for Zn (Zn versus latitude, $r = -0.587$), a distribution commonly observed in Scandinavia (Henriksen and Wright 1978; Borg 1987; Mannio and Verta 1987). For Ni and Cd the correlation coefficients with latitude were -0.401 and -0.279, respectively ($p < 0.001$). Also the soil-derived metals, Mn and Al, (Fig. 3) clearly decreased towards the north.

Comparison of lake water chemistry data with metal concentration in moss (Rühling et al. 1987) revealed that Cd, Cu, Pb, Zn and Ni had significant differences in concentration in water when grouped in two to five "deposition" classes according to the areal concentrations in moss (Fig. 4). The moss data cannot be interpreted as direct estimates of deposition, because the moss retains different elements with different efficiency (Rühling et al. 1987).

The order of concentration of the trace metals was: Fe > Al > Mn > Zn > Cu–Ni > Pb > Cd, the same order as in similar Swedish lakes (Borg 1983, 1987) and in a preliminary study in Finland (Mannio and Verta 1987). The concentrations are similar to those of Swedish studies but lower than in those from the southern Norwegian survey in 1974–75 (Table 8).

Lead and to some extent Cd and Zn values in the present study are lower than reported by Mannio and Verta (1987). The latter sampling occurred in May after snowmelt, a period which very probably represents the higher concentrations of the year for anthropogenic metals. Autumn values could merely be compared to summer values, when high production and input of particulate matter increases the sedimentation and hence lowers the concentration in water (White and Driscoll

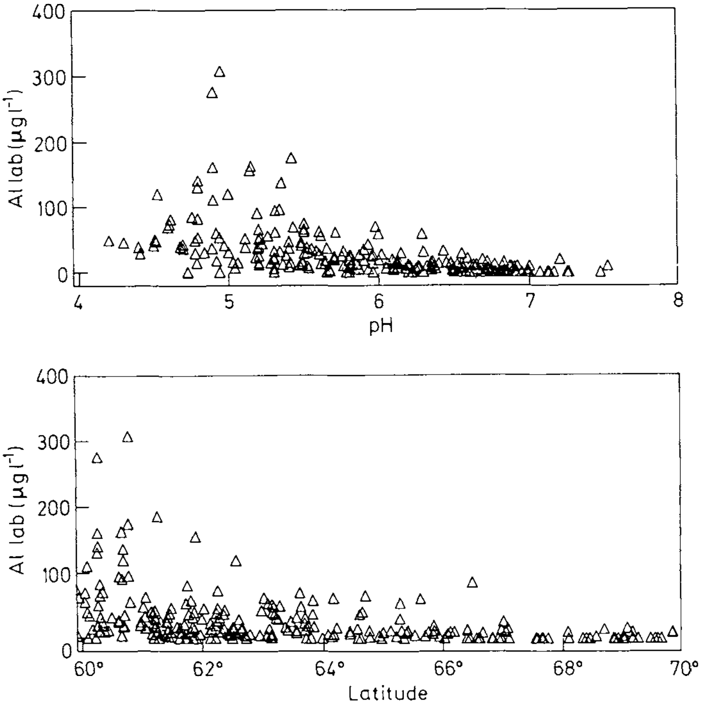

Fig. 3. Labile aluminium (Al_{lab}) concentration in lake water in autumn overturn 1987 as a function of pH and latitude

1985). Borg (1987) found on average 3.1 times lower Pb and 2.4 times lower Cd concentration in summer than in winter. The increase of concentrations of predominantly anthropogenic heavy metals in water (Cd, Zn and Pb) is simultaneous with land-derived acidification, as indicated by increased Al (Table 9). Concentrations for Ni and particularly for Cu vary more with the content of humic substances (Table 10).

Acid conditions favour significantly the high concentrations of all trace metals except Cu in both subregions and Ni in the south (Table 10). Similar, but lower correlations with trace metals were found for sulphate and Gran alkalinity. The strongest relationship was between pH and labile Al (Fig. 3), but the correlations were high also for Zn, Pb and Cd. This relationship was stronger in the southern region.

The terrestrial input of dissolved humic substances from watershed is important because of their metal complexing abilities (e.g. Benes et al. 1976; Mantoura et al. 1978). The concentrations of Cu in lake waters is more strongly dependent on total organic carbon (TOC) than is that of Cd, Zn, Pb and Ni. The concentration of the land-derived metals Al, Fe, and Mn are even more dependent on TOC, but on acidity as well. These relationships are similar to, but more significant than,

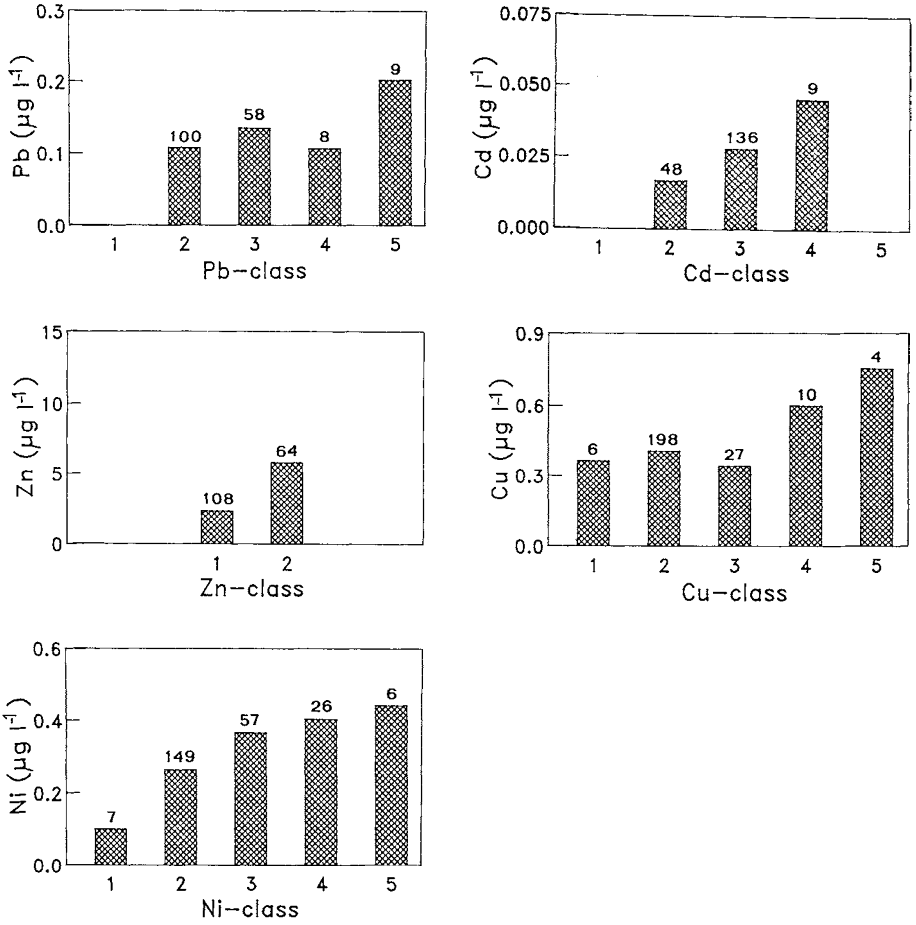

Fig. 4. Mean trace metal concentrations in lake water in areas of different atmospheric trace metal load classified according to the areal concentration of the same metal in moss (Rühling et al. 1987). No. *1* indicates the lowest concentration in moss and no. *5* the highest concentration in moss. Number of observations indicated *above the histograms*

Table 8. Mean values of trace metal concentrations in water ($\mu g\ l^{-1}$) in Scandinavian surveys of small headwater lakes

	Cd	Cu	Pb	Zn	Ni
Finland[a]	0.026	0.41	0.12	3.6	0.30
Finland[b]	0.06	0.39	0.87	7.2	0.51
S. Sweden[c]	0.04	0.68	0.67	11	< 1.0
C. + N. Sweden[d]	0.014	0.51	0.27	2.2	0.42
S. Norway[e]	0.2	2	2	15	. .

[a] Present study. [b] Mannio and Verta 1987. [c] Borg 1983. [d] Borg 1987. [e] Henriksen and Wright 1978 (median values).

Table 9. Significant correlations ($p < 0.001$) between trace metals in lake waters

	Al_{il}	Al_{lab}	Mn	Cd	Zn	Pb	Ni
Al_{lab}	0.637						
Mn	0.429	0.460					
Cd	–	0.434	–				
Zn	0.335	0.550	0.418	0.422			
Pb	0.379	0.482	–	0.499	0.333		
Ni	0.366	0.288	0.329	–	0.397	–	
Cu	0.308	–	–	–	–	–	0.279

those reported in previous studies in Sweden (Borg 1983, 1987) and Finland (Mannio and Verta 1987), because of much larger material.

Based on a review by Hultberg (1988), most common fish species have a sensitivity threshold to inorganic aluminium concentrations in the range 25–150 $\mu eq\ l^{-1}$, the lethal concentration depending on pH, calcium concentration and life stage. Several field studies conducted in southern Finland have shown that perch and roach populations have decreased in a number of Finnish lakes due to acidic deposition (Rask and Tuunainen this Vol.).

High concentrations of organic carbon and silica reduce the toxicity by complexing the toxic species of Al (Driscoll et al. 1980; Baker and Schofield 1982; Birchall et al. 1989). Seven percent of the lakes in Finnish survey had a labile Al concentration above 50 $\mu g\, l^{-1}$ and pH < 5.3, conditions generally considered as toxic for e.g. perch, brown trout, and possibly northern pike. However, 90% of these lakes were highly humic (TOC above 10 $mg\, l^{-1}$), probably much higher than in studies reviewed by Hultberg (1988).

Comparison of Snow, Water and Sediment Chemistry

The mean concentrations of Pb in the snow cover in 1987 (Table 4) were more than tenfold that in the water of the surveyed lakes in the same region in 1987 (Table 7), the difference being greater in the southern part of the country. This implies that the deposition of Pb on the lake surface can supply the concentrations of Pb in the water. For Cu, Ni, Cd and Zn the ratio of concentrations in the snowpack to in the water were from 5 to less than 2 in the southern subregion and about 2 in the northern subregion, indicating that the direct impact of atmospheric deposition of these metals on lake water chemistry is everywhere smaller than for Pb.

Deposition of metals in the snowpack in Finland in the winter 1986–1987 was less than the mean deposition in the 1980's (Soveri and Ahlberg this Vol.) for Pb, Zn, Cd and Cu but not for Ni (Table 4). The decreases for Pb, Cd and Ni are consistent with those reported for metals in moss in other Scandinavian countries (Rühling et al. 1987). For Zn and Cu no decrease in concentration during the

Table 10. Significant correlation coefficients ($P < 0.001$) between trace metals and water pH, sulphate, organic carbon and watershed area: lake area ratio in southern (1) and northern (2) subregions. R^2 is percent explained by the variables together out of the total variation of the metal concentration

	pH		SO_4		TOC		log (W/A)		R^2	
	1	2	1	2	1	2	1	2	1	2
Al_{org}		− 0.587			0.702	0.837	0.516	0.400	57	73
Al_{lab}	− 0.643	− 0.665				0.545			44	51
Fe		− 0.348			0.761	0.763	0.423	0.333	58	57
Mn		− 0.422		0.274		0.529			7	35
Cd	− 0.582	− 0.340							38	12
Cu					0.434	0.280			21	12
Pb	− 0.605	− 0.453							43	23
Zn	− 0.643	− 0.513				0.330			46	34
Ni		− 0.295		0.441		0.390			7	33

1980's in moss was discovered, but a clear decrease in Zn concentration between the 1970's and 1985 (Rühling et al. 1987). The sediment profiles for Pb show also a decrease or a levelling-off in accumulation during the 1980's (Verta et al. 1989) and thus support the results of snow and moss studies. Although Cd and Zn decrease more in concentration than Pb in the uppermost sediment layers of most southern lakes, this may not be a consequence of decreased atmospheric deposition, since pre- and post-sedimentation mechanisms may cause redistribution of these metals, at least in acidified lakes (Carignan and Tessier 1985; Norton 1984).

The mean accumulation rates of Pb, Zn, Cd, Cu and Ni per unit area of the sediment were about one order of magnitude greater at the beginning of the 1980's than deposition per unit area on the snowpack in winter 1986–1987 (compare Tables 4 and 5). Rekolainen et al. (1986b) estimated from the same snow stations that the deposition of Hg in winter 1983–1984 was from 3 to 6 $\mu g\, m^{-2}\, a^{-1}$ in southern Finland and was less than 3 $\mu g\, m^{-2}\, a^{-1}$ in northern Finland. Comparison of these figures with those of Table 5 yields a similar relationship.

Several mechanisms e.g. lower precipitation in Finland during winterime, flushing of trace elements during melting periods (Henriksen et al. 1974; Cadle et al. 1984) and higher dry deposition during the summer season, cause the total annual deposition of trace elements to be greater than deposition from the snowpack calculated out to a year's time. With the mean concentration of trace metals in the snowpack and the mean annual precipitation of 600 mm in Finland, the deposition estimates of all trace metals on the lake surface plus on the watershed (lake area = 20%) exceed, however, the mean measured trace metal accumulation into sediment at the deepest point of lakes, which certainly is an overestimation of the total trace metal accumulation rate for the entire lake. The airborne load on the lake surface and on the drainage basin can thus easily explain the anthropogenic share of trace metals accumulated into the lake bottom. Although some airborne trace metals such as Pb, Hg and Cu are trapped in the soil profile (Schut et al. 1986; Berqvist 1987; Borg and Johansson 1988; Dillon et al. 1988), a large fraction of the trace metals deposited during wintertime is flushed to the lakes during snowmelt without entering the soils. Intercorrelations between trace metals Pb, Zn and Cd in the snowpack, in the water, as well as these and Hg in surface sediments, further strongly indicate that the atmospheric load of these metals is presently of major importance to the chemistry of these elements in pristine headwater lakes.

Correlations of trace elements in snow and lake water indicated behaviour of Cu and Ni different from other trace elements. This is also obvious in clearly different sediment profiles of these elements showing increased anthropogenic accumulation in only some lakes. High concentrations of Cu and Ni were also found in the snow cover close to large emission sources. Since Cu and Ni are associated in larger particles in atmospheric emissions than Cd, Pb, Zn and Hg (Bacci et al. 1983; Chan et al. 1983), the deposition of these elements may be more affected by local emission sources than other trace elements.

Trace Metals in Biota

Aquatic Plants

The aquatic plants *Nuphar luteum* L. and *Sparganium* sp. had higher concentrations of all studied trace metals (Pb, Cd, Zn, Cu and Ni) in acid lakes versus non-acid lakes (Fig. 5). The non-acid lakes in southern Finland did not differ from those in other parts of the country. *Sparganium* sp. had notably higher concentrations of all trace metals in the only acid northern lake (Vasikkajärvi) when compared to other lakes in the area. Both these observations indicate that differences in pH rather than differences in metal load were the primary cause of increased concentrations in plants.

It seems possible that humic substances may inhibit the accumulation of Cu and Pb into water plants because the acid humic lake, Valkea Kotinen, had lower concentrations of these metals than acid clearwater lakes. The lower accumulation of Pb and Cu may be explained by the strong binding of these metals with organic

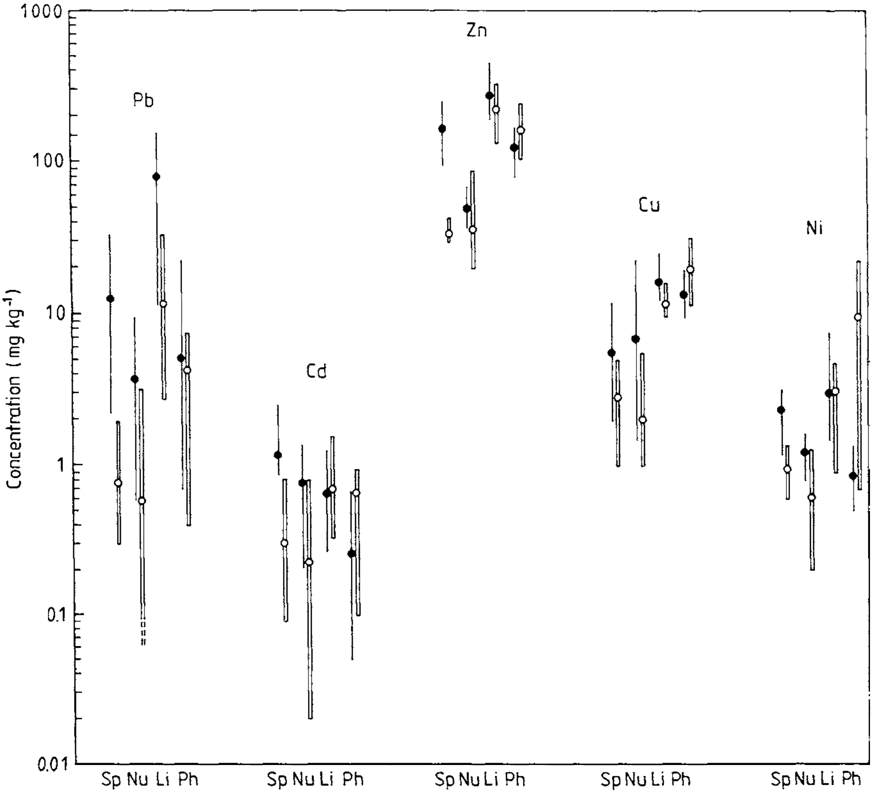

Fig. 5. Mean concentrations and ranges of trace metals in some aquatic plants and trichoptera larvae in acidic lakes (● = pH ≤ 5.2) and circumneutral lakes (○ = pH ≥ 5.9). Nu = *Nuphar luteum*; Sp = *Sparganium* sp.; Li = *Limnophilus* type; Ph = *Phryganea* type

complexes. Borg and Andersson (1984) found that the dialysable (bioavailable) fractions of Pb, Cu and Al were lower in humic lakes than in clearwater lakes.

The concentrations of Cd, Zn and Cu in *N. luteum* were in good agreement with those reported by Lehtonen (1989) for two southern Finnish small lakes with different pH. Concentrations of Cu and Zn in *N. luteum* and Cu in *Sparganium* sp. were, however, notably lower than those reported by Aulio (1986) in a polluted river, Kokemäenjoki, in southwestern Finland.

Trichoptera Larvae

Of the two genus of trichoptera larvae the *Limnophilus* sp. had clearly higher concentrations of Pb and somewhat higher concentrations of Zn and Cu in acid lakes than in non-acid lakes (Fig. 5). On the contrary, *Phryganea* sp. did not normally vary in trace metal concentrations with variable pH, except for decreased Cd content with increased lake acidity. The highest concentrations of Ni and Cu in *Phryganea* sp. were observed in Lake Äälisjärvi, situated only some 50 km west from a large nickel smelter in the Kola peninsula in the U.S.S.R., which caused the higher mean concentrations of these metals in circumneutral lakes (Fig. 5). High metal concentrations in the southern lake population occurred, as for Pb in *Limnophilus*, only in acid lakes, indicating low pH as a primary cause.

Fish

One order of magnitude or even higher concentrations of Pb both in liver and in cleithral or opercular bones of *E. lucius*, *P. fluviatilis* and *Coregonus* sp. were associated with acid versus circumneutral lakes (Figs. 6 and 7). Also Cd in liver in all species and Mn in the opercular bones of *Coregonus* sp. showed significantly higher ($p < 0.001$) concentrations in acid lakes. The only humic acidic lake had lower concentrations of Pb than did acidic clearwater lakes. No clear differences in the concentrations of Zn in liver or in bones were observed.

The trace metal concentrations in liver and bones of *E. lucius* and *P. fluviatilis* in non-acidic lakes were in good agreement with those reported in the same species in Sweden in non-polluted lakes (Håkanson 1984; Olsson and Haux 1986; Lindeström et al. 1988). This level was clearly exceeded in the case of Pb in the acidic lakes. Even higher concentrations of Pb (1.9–96 $\mu g\, g^{-1}$, d.w.) and Cd were reported by Sprenger et al. (1988) in the liver of *Perca flavescens* in some of five extremely acidic lakes (pH 4.0–4.6) in New Jersey. The increase in Mn concentration in operculum of *Coregonus* sp. at low pH is consistent with the results reported for white sucker (*Catostomus commersoni*) (Fraser and Harvey 1982) in Ontario, as well as for brook trout (*Salvelinus fontinalis*) in acidified lakes in Quebec (Moreau et al. 1983).

Hg content in the muscle of all fish species present also in acid lakes was significantly higher in acidic lakes than in non-acidic lakes (Fig. 8, Table 11). This is consistant with several other studies in Scandinavia (e.g. Lindqvist et al. 1984;

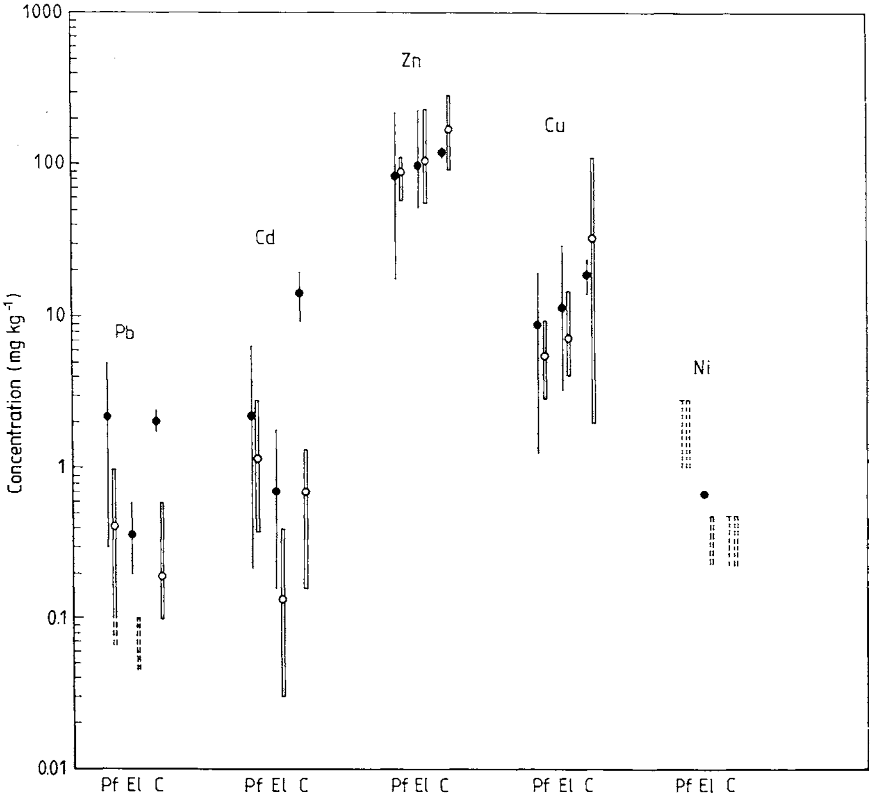

Fig. 6. Mean concentrations and ranges of trace metals in fish liver in acidic lakes (● = pH ≤ 5.2) and circumneutral lakes (○ = pH ≥ 5.9). Pf = *Perca fluviatilis*; El = *Esox lucius*; C = *Coregonus* sp.

Håkanson et al. 1988) and in North America (e.g. Akielaszek and Haines 1981). Fish from humic lakes had higher Hg content in *E. lucius* and *P. fluviatilis* than clearwater lakes, as also reported in previous studies in Finland (Mannio et al. 1986; Verta et al. 1986). Concentrations of Hg in *E. lucius* were generally between 0.5 $\mu g\,g^{-1}$ and 1.0 $\mu g\,g^{-1}$ and cause restricted use of the fish for human food.

Aluminium concentrations in the gills of fish were higher in lakes with low pH than in lakes with high pH, but were even better correlated with labile aluminium concentration in the water (Fig. 9). The reactive Al that describes the sum of all dissolved Al species in the water correlated more weakly than labile Al, indicating that labile Al, being toxic for most water organisms, is accumulated more in the gills. The studies by Booth et al. (1988) and Birchall et al. (1989) suggest that Al is accumulated mainly on the surface or subsurface of the gills. In the experiments by Booth et al. (1988) non-surviving fish had significantly higher gill Al concentrations (837 $\mu g\,g^{-1}$ w.w.) than survivors (235 $\mu g\,g^{-1}$ w.w. at water Al = 111 $\mu g\,l^{-1}$ and 413 $\mu g\,g^{-1}$ w.w. at water Al = 333 $\mu g\,l^{-1}$). These concentrations are substantially higher than those observed in the present study (Table 11) and suggest that

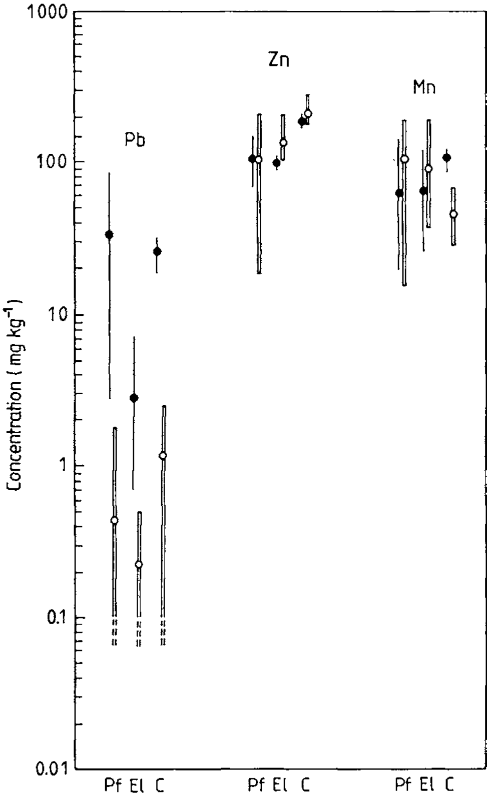

Fig. 7. Mean concentrations and ranges of trace metals in opercular bones (*P. fluviatilis*), (*Coregonus* sp.) and cleithral bones (*E. lucius*) in fish in acidic lakes (● = pH $\leq$ 5.2) and circumneutral lakes (○ = pH $\geq$ 5.9). Pf = *Perca fluviatilis*; El = *Esox lucius*; C = *Coregonus* sp.

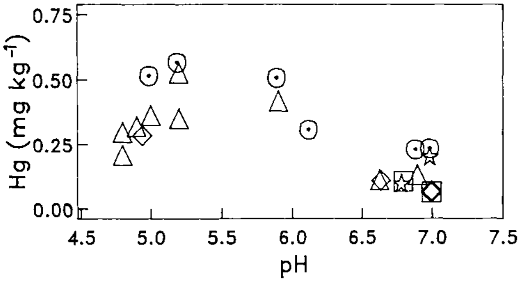

Fig. 8. Mean Hg concentrations in muscle of fish in different lakes as a function of pH in lake water. △ = *Perca fluviatilis*; ⊙ = *Esox lucius*; ◇ = *Coregonus* sp.; □ = *Salmo trutta*; ☆ = *Salvelinus alpinus*

Al accumulation on the gills of fish is not high enough to cause toxic effects on adult fish in Finnish acidified lakes.

Conclusions

The anthropogenic load of trace metals from the industrial emissions to the atmosphere have significantly increased the deposition of Pb, Cd, Hg and Zn and,

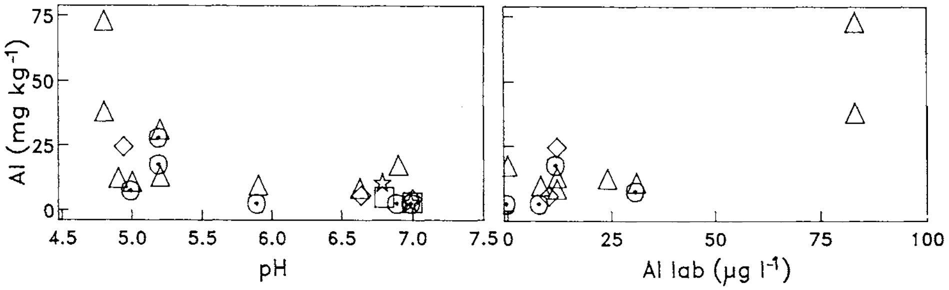

Fig. 9. Mean Al concentrations in the gill of fish in different lakes as a function of pH and labile Al in lake water. △ = *Perca fluviatilis*; ⊙ = *Esox lucius*; ◇ = *Coregonus* sp.; □ = *Salmo trutta*; ☆ = *Salvelinus alpinus*

Table 11. Mean concentrations and ranges of Al in the gills ($\mu g\,g^{-1}$ d.w.) and Hg in the muscle ($\mu g\,g^{-1}$ w.w.) of fish in acid (A: pH 4.5–5.2) and circumneutral (CN: pH 5.9–7.0) lakes

Species	Al, Gills				Hg, Muscle		
		n	Mean	(Range)	n	Mean	(Range)
Perca fluviatilis	A	25	28.6	(3–76)	58	0.33	(0.15–0.63)
	CN	15	14.2	(5–74)	22	0.19	(0.03–0.53)
Esox lucius	A	7	24.0	(8–38)	17	0.53	(0.34–0.84)
	CN	13	< 5	(–)	29	0.36	(0.15–0.67)
Coregonus sp.	A	4	24.5	(17–28)	8	0.28	(0.16–0.39)
	CN	7	4.9	(3–8)	17	0.09	(0.05–0.16)

to a lesser extent, Cu and Ni during this century. This has caused a major impact on the cycle of these metals in pristine headwater lakes in Finland. This is particularly true in southern Finland, where atmospheric deposition, concentrations in the water and accumulation in the sediment of these metals all exceed those in central and northern Finland. The deposition of trace metals in Finland occurs simultaneously with acidic compounds. Concentrations of Al, Mn, Zn, Pb and Cd are higher in the water of acidic lakes than in non-acidic lakes. Both atmospheric loading and increased terrestrial leaching of some elements (Al, Mn, Zn and Cd) due to acidification of soils have contributed to this concentration pattern. Acidic environments, rather than increased metal load, favour higher concentrations of most trace elements in aquatic plants and at least in some species of macrozoobenthos. Some trace elements also have increased concentrations in liver (Pb, Cd), in bones (Pb), in muscle (Hg) and in gills (Al) of several fish species in acidic lakes. Concentrations of labile Al in acidic water occur frequently in amounts that are considered toxic to most water organisms, including fish, and have probably contributed to the diminishing of fish species in these lakes.

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3.2 Biota in Lakes and Streams

Acid-Induced Changes in Fish Populations of Small Finnish Lakes

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Summary

A fish status survey of 80 lakes showed that acidification has affected many perch and roach populations. The perch populations in several lakes in southernmost Finland consisted of a few large and old fish, indicating that the reproduction success of perch has decreased. In extreme cases there was no offspring during the 1980's. These populations are today close to extinction. Similar patterns in roach populations were recorded in different parts of southern and central Finland. According to local residents, many roach populations are decreasing or have been lost already. In some lakes that now are very acid, roach populations disappeared 40 years ago.

This survey showed that changes of fish populations in response to acidification can be found commonly in the small lakes of southern and central Finland.

Introduction

Acid precipitation has caused major changes in aquatic ecosystems of northern Europe and North America. The decline of fish populations was first noticed in Norway in the early 1920's (Muniz 1984). Recently, the majority of fish populations have been lost from lakes (Sevaldrud and Muniz 1980) and from rivers (Leivestad et al. 1976) in southernmost Norway. In Sweden the first records of acid-induced losses of fish populations are from the 1930's (Almer 1972). It has been suggested that 9000 lakes and 10% of the total lake area in Sweden are today affected by acid precipitation (Johansson and Nyberg 1981). In eastern parts of the U.S.A and Canada, damages to fish populations have been recorded in some lake areas (Beamish and Harvey 1972; Schofield 1976) and decreases of salmon catches attributed to acidification have been also recorded from rivers on the Atlantic coast (Watt et al. 1983).

Although soils and bedrocks in central Europe are generally better buffered against acidification than those in Fennoscandia or the Canadian shield, lake acidification and resulting decreases in fish populations have now been documented from The Netherlands (Leuven and Oyen 1987), the British Isles

Kauppi et al. (Eds).
Acidification in Finland

(Turnpenny et al. 1987), France (Massabuau et al. 1987) and the Federal Republic of Germany (Fischer-Scherl et al. 1986).

The main aim of the fish survey studies in the Finnish Research Project on Acidification (HAPRO), conducted as a joint project of Finnish Game and Fisheries Research Institute, Fisheries Division and Lammi Biological Station, University of Helsinki, was to clarify if any acid-induced fish damage has occurred in Finland and to estimate the degree and extent of the effects. Also, a small-scale monitoring programme of fish populations in acidifying and limed lakes was to be initiated.

In this chapter observations on acid-induced changes in fish populations of small Finnish lakes are summarised. The data, presented here at the species level, are based on a test fishing programme of 80 lakes conducted during 1985–1987. Additional information collected from local fisheries authorities, land owners and fishermen is included.

Material and Methods

The Lakes

In the selection of lakes for the fish survey, those with a known acidification history were preferred. Palaeolimnological diatom analyses were performed in 28 of the 80 lakes (Tolonen and Jaakkola 1983; Simola et al. 1985; Tolonen et al. 1986; Huttunen et al. this Vol.). These studies indicate that 19 of the lakes have been recently acidified due to acid precipitation and 14 acidified lakes are located close to the southern coast of Finland. An assessment of chemical properties of 28 lakes in southernmost Finland (Kämäri 1985) showed that at least five or six additional lakes of the survey have undergone acidification. The rest of the lakes were chosen after examination of lake data of the National Board of Waters and Environment and Finnish Game and Fisheries Research Institute, and on the basis of a questionnaire, directed towards regional water and environment authorities.

More than half of the lakes studied are located at a distance of less than 100 km from the south coast of Finland (Fig. 1) in an area where the mean annual sulphur deposition is at the highest in Finland. Most of the lakes are small, oligotrophic and with small catchment areas, often characterized by thin soils and rocky landscapes in southernmost Finland (Fig. 2), but also by glacifluvial materials and peatland in central parts of the country. Scotch pine or spruce forest was dominant vegetation in most catchments. Only a few catchments contained some arable land.

Samples for water chemistry were taken from each lake at the time of fish samplings and analysed in the laboratory of the Fisheries Division of Finnish Game and Fisheries Research Institute according to Finnish standard methods for water analysis (SFS-standards). Aluminium analyses were made at the Helsinki University of Technology according to LaZerte (1984). The results of water analyses are summarised in Table 1 and Fig. 3.

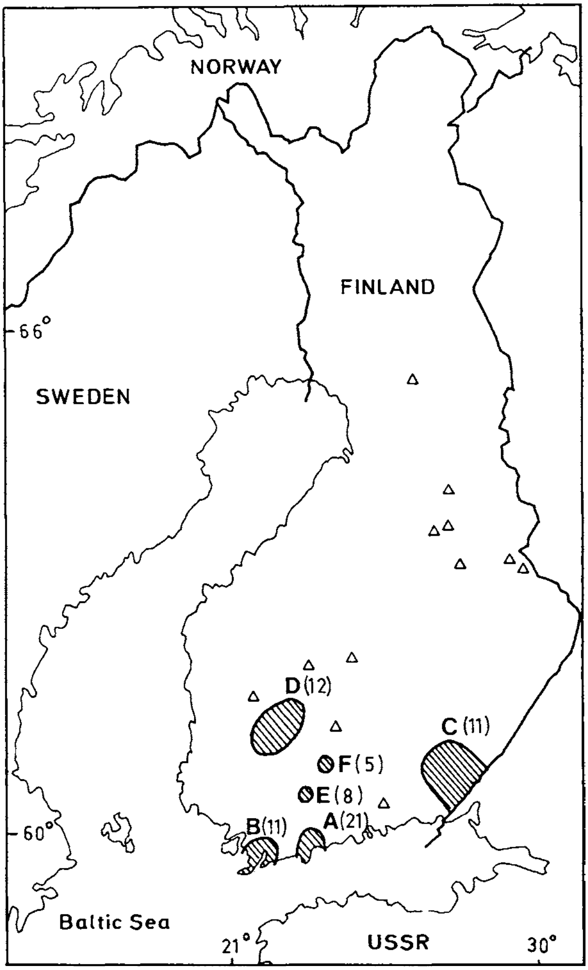

Fig. 1. The location of studied lakes. On the basis of information on rock types, soil properties, runoff and terrestrial reliefs the areas *A–D* are considered to be among the most sensitive to surface water acidification in Finland (Kämäri 1986). Areas *E* and *F* provided most of the circumneutral lakes in the survey. *Triangles* indicate single study lakes

Fish Samples

Fish were caught during the summers 1985–1987 by using a series of eight 1.8 × 30 m gill nets (mesh sizes 12, 15, 20, 25, 30, 35, 45 and 60 mm from knot to knot). Thus the smallest (< 10 cm) and the youngest (< 2-year-old) fishes were excluded. Each lake was sampled one to five times and the nets were kept at depths 2–4 m for 18 to 24 h, with an alternation of large and small mesh sizes of net.

The four most common fish species, perch, *Perca fluviatilis* L., roach, *Rutilus rutilus* L., pike, *Esox lucius* L. and ruffe, *Gymnnocephalus cernua* L., were included in an analysis of the relationships between fish measurement and acidity-related

Fig. 2. Lake Suolikas, a typical recently acidified lake in southernmost Finland (Fig. 11, lake 6). The lake was inhabited during the early 1960's by roach, burbot and crayfish. Recent pH is < 5.0 and only perch, pike and ruffe are still present

Table 1. Some characteristics of the studied lakes and their water

	Range	Mean	Median
Lake area (ha)	1–194	22	13
Altitude above sea (m)	16–218	97	89
pH	4.4–7.6	5.7	5.6
Alkalinity (mmol l^{-1})	0–0.37	0.05	0.03
Conductivity (mS m^{-1})	0.8–5.7	3.1	3.1
Colour (mg Pt l^{-1})	0–90	25	20
Ca (mmol l^{-1})	0–0.15	0.05	0.05
Al_{tot} (μg l^{-1})	0–287	110	84
Al_{lab} (μg l^{-1})	0–138	48	36

water properties using correlation analyses and analysis of variance. These species formed the entire fish assemblage in 51 lakes and together they made up 94% of the total fish biomass caught during the survey. The fish measurements were as follows: total weight per gill net series (perch, roach, pike, ruffe), mean weight (perch, roach, ruffe), mean age (perch, roach) and growth (perch, roach, pike). The growth of perch was back-calculated from opercular bones using Monastyrsky's procedure (Bagenal and Tesch 1978). For roach, back calculation was made from scales according to Fraser and Lee (Bagenal and Tesch 1978), and for pike from cleithra (Casselman 1974).

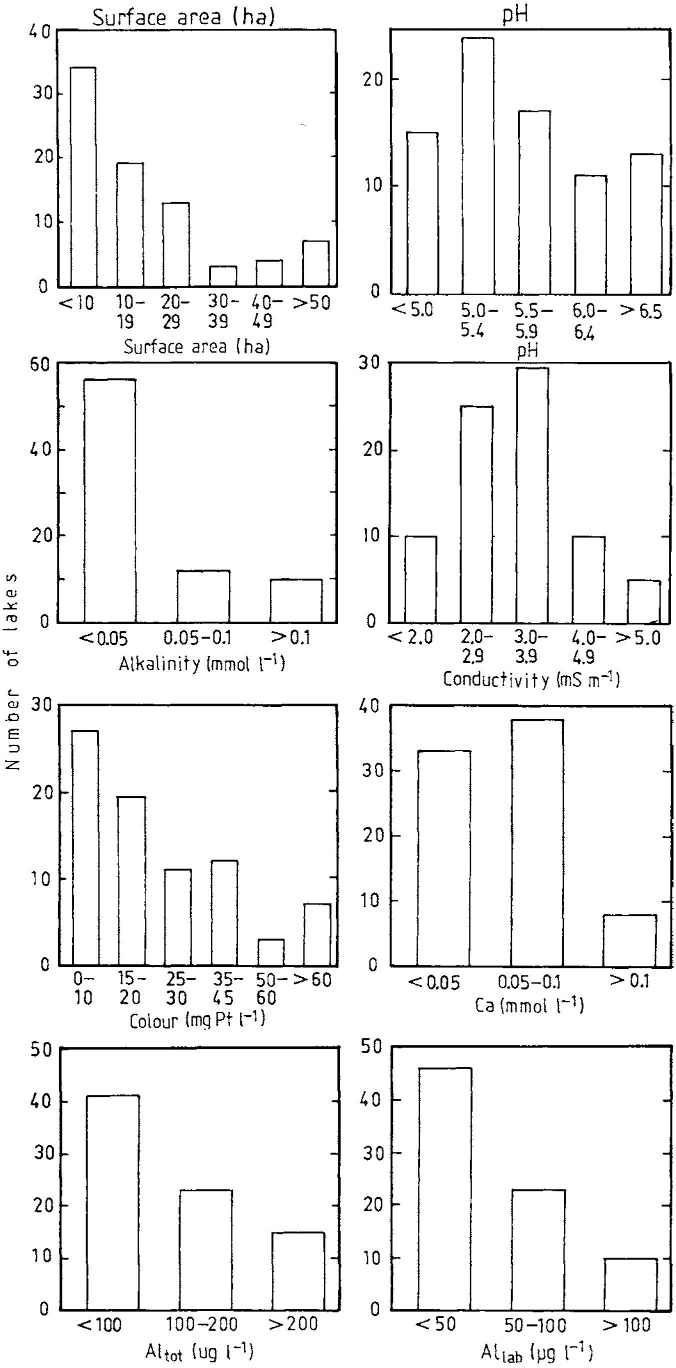

Fig. 3. Summary of the characteristics of 80 lakes as classified according to surface area and some water properties

Local land owners and fisheries authorities were interviewed about the changes in fish status of their lakes when asking for test fishing licences. Fishermen were interviewed when met in the field. Attention was paid mostly to the disappearance of fish species. Such information was thought to be quite reliable because the number of species in small lakes is generally low (one to six in this group of lakes) and usually no taxonomic difficulties exist. In some cases information on "clear" quantitative changes or changes in population structure were recorded.

Results and Discussion

Perch

Perch were caught in 77 out of 80 lakes covering a pH range of 4.4–7.6. It was the most common and also the most abundant species caught in the survey. The mean perch catch for a lake was 4.6 kg per gill net series and it formed 59.3% of the total fish biomass caught (600 kg) during the survey. The highest catches were from acid lakes: the pH and alkalinity of six lakes that yielded >10 kg perch per gill net series were <5.5 and <0.05 mmol l^{-1}, respectively (Fig. 4). In all these lakes perch was the only fish species. Therefore, the lack of interspecific competition for food may have allowed the maintenance of high perch biomasses (Sumari 1971; Svärdson 1976) if reproduction is not severely disturbed by high acidity. However, some of the smallest perch catches of <1 kg per gill net series were also from very acid lakes. This kind of wide variation resulted in insignificant differences among lakes of different pH groups of Fig. 1 (ANOVA, $p > 0.1$). Nevertheless, the weight of perch catches still correlated significantly with pH, alkalinity, calcium and total aluminium concentrations (Table 2).

The mean weight of perch in the lakes varied usually between 10 and 70 g. In some very acid lakes ($pH < 5.0$) the mean weight, however, was ≥ 100 g and in three lakes even > 300 g. In these lakes the number of perch caught was usually low. These fish were also old, the mean age being >7 years, whereas it was 3.9 years in the whole set of 80 lakes. The mean weight of perch differed significantly among different pH groups of lakes (ANOVA, $F = 8.07$, df 4, 71, $p < 0.001$).

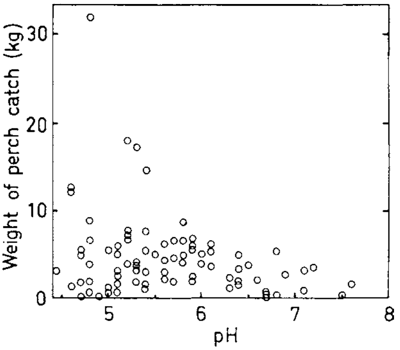

Fig. 4. The total weight of perch catches per gill net series in relation to lake pH

Table 2. Significant correlations ($p < 0.05$) between perch catch characteristics and lake properties (NS = not significant)

	Total weight of perch	Mean weight	Mean age	Mean length at age 5
Surface area	NS	NS	NS	NS
Altitude	NS	NS	NS	NS
pH	−0.288	−0.314	−0.240	−0.338
Alkalinity	−0.270	NS	NS	NS
Conductivity	NS	NS	NS	NS
Colour	NS	NS	NS	−0.439
Ca	−0.252	NS	NS	−0.299
Al_{tot}	0.237	0.329	0.343	NS
Al_{lab}	NS	0.357	0.332	NS

The catches of few large and old perch in some lakes with pH < 5.0 were interpreted to be a consequence of severe reproduction failures due to acidification (Raitaniemi et al. 1988). That these perch populations really had low densities was ascertained with marking and recapturing of perch from six lakes (Lappalainen et al. 1988). In two lakes with estimated population densities of 0 and 15 perch per hectare no successful reproduction took place during the 1980's. In two other lakes increased mortality of developing embryos were recorded, in one lake up to 100% (Lappalainen et al. 1988), indicating drastic difficulties in reproduction.

The four lakes where perch populations were close to extinction had concentrations of total and labile aluminium of >200 and >100 $\mu g\ l^{-1}$, respectively. This emphasises the importance of aluminium toxicity to fish in acidified lakes that has been stressed by several authors (Baker and Schofield 1982; Brown 1983; Henriksen et al. 1984). In some very acid lakes (pH 4.6–4.8) with low aluminium concentrations (< 50 $\mu g\ l^{-1}$), the perch catches were larger in number and consisted of fish of different size and age, which indicates that reproduction still continues (Fig. 5). Marking and recapturing of perch population in such a lake showed a density of >1000 fish per hectare (Rask 1989a).

Most of the lakes of the study and all very acid lakes (pH < 5.0) had clear water (colour < 50 mg Pt l^{-1}), indicating low amounts of humic substances. Thus, complex formation between aluminium compounds and dissolved organic carbon (Sager 1986; Hutchinson and Sprague 1987) probably did not affect the toxicity of aluminium to fish in these lakes.

The mean length of perch at the age of 5 years was usually 120–200 mm. In some cases, 200 mm were exceeded and values of > 220 mm were found in five lakes with pH < 5.0, which indicates high growth rates (Fig. 6). Because perch in small oligotrophic lakes usually form dense populations with low growth rates of individual fish (Alm 1946; Deelder 1951; Nyberg 1976; Rask 1983), special attention was paid to the lakes where the growth of perch appeared to be surprisingly high and close to those measured from pelagic predatory perch of large waters (Smirnov 1977; Thorpe 1977). In lakes with pH < 5.0, these high growth rates were

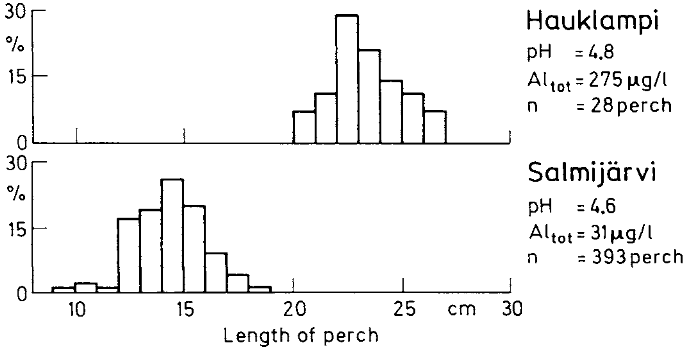

Fig. 5. The percent-length-frequency distribution of perch in two acidified lakes with different aluminium concentrations. The mean age of perch in Lake Hauklampi (Fig. 11, lake 2) was 8.2 years (Raitaniemi et al. 1988). The youngest fish were 7 years old; no more successful reproduction took place during the 1980's. In Lake Salmijärvi the mean age of perch was 3.9 years and age groups 1 to 5 were present

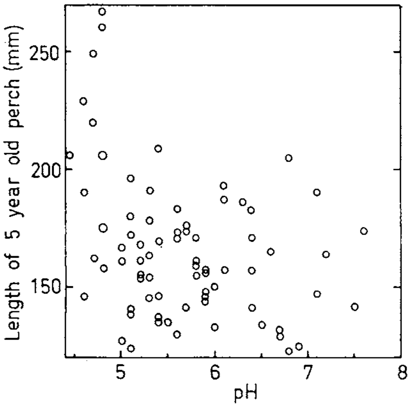

Fig. 6. The mean total length of 5-year-old perch plotted against lake pH

attributed to acid-induced reproduction failures (Raitaniemi et al. 1988; Rask and Raitaniemi 1988) that result in low fish densities and further in increased availability of food for the remaining fish (Ryan and Harvey 1980; Hultberg 1985). Because perch was the only fish species in these lakes, no competition for food, interspecific or intraspecific, occurred.

Overall, responses of perch populations to lake acidification were apparent in 10–15 of the set of 80 lakes. They were recorded as low population densities, abnormal population structures and growth rates, and increased mortality of developing embryos. There are probably still some lakes at pH levels < 5.5 where perch populations are stressed by increasing acidity but where the responses cannot yet be verified in this kind of survey type study.

Roach

Roach were caught from 32 lakes at the pH range 5.1–7.6. The mean roach catch from these lakes was 4.8 kg per gill net series and the proportion of roach from the total fish biomass of the survey was 25.5%. The largest catches, 10–13 kg, were from six lakes of pH 5.9–6.9. The total weight of roach catches did not correlate with the acidity-related water properties (Table 3).

The mean weight of roach varied from 11 to 560 g among the lakes. In eight lakes the mean weight was >100 g and seven of them had a pH < 6.0. Also the oldest roach were caught from acid lakes: the two lakes with a mean age of roach >10 years had pH values 5.1 and 5.5 (Fig. 7). These patterns in the population structure of roach at pH levels 5.0–6.0 are considered to be due to acid-induced reproduction failures (Almer et al. 1974; Johansson and Nyberg 1981; Rask 1987). Together with the absence of roach in lakes with pH < 5.0 they show that roach is one of the most sensitive fish species to acidification. This survey support earlier suggestions (Milbrink and Johansson 1975) that pH levels around 5.5 would be critical for the reproduction of roach.

Table 3. Significant correlations ($p < 0.05$) between roach catch characteristics and lake properties (NS = not significant)

	Total weight of roach	Mean weight	Mean age	Mean length at age 5
Surface area	NS	NS	NS	NS
Altitude	NS	NS	NS	NS
pH	NS	−0.506	−0.518	−0.492
Alkalinity	NS	NS	NS	−0.519
Conductivity	NS	NS	NS	−0.458
Colour	NS	NS	NS	−0.471
Ca	NS	NS	NS	−0.538
Al_{tot}	NS	0.517	0.543	NS
Al_{lab}	NS	0.588	0.672	NS

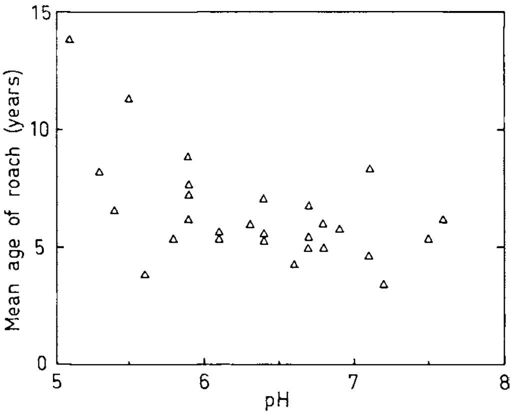

Fig. 7. The relation between mean age of roach and pH of lakes

Because the roach is so sensitive to acidity and is widely distributed, well known, and easy to observe or catch, it would be a good indicator species among fishes for acidification in Finland. In an assessment of the indicator value of different roach catch parameters the mean weight and mean length of roach were shown to be the most suitable (Rask 1989b).

The growth of roach was faster in acid than in neutral lakes (Fig. 8). The mean length at age 5 years varied from 121 to 211 mm and differed significantly among lake groups with different pH (ANOVA, $F = 3.46$, df 4, 23, $p < 0.05$). As in the case of perch, the higher growth rates of roach in acidifying waters is considered a consequence of decreased food competition in decreasing populations (Almer et al. 1974). However, in lakes of pH 5.0–6.0 there are usually high numbers of perch present. Thus, although there may be no intraspecific competition for food among the remaining roach, interspecific competition with perch still occurs (Svärdson 1976).

When a mean weight of roach >100 g or a mean length at age 5 years of >200 mm are considered as consequences of acid-induced decreases in reproduction success of roach in lakes with pH < 6.0, roach populations in eight of 80 lakes were affected by acidification.

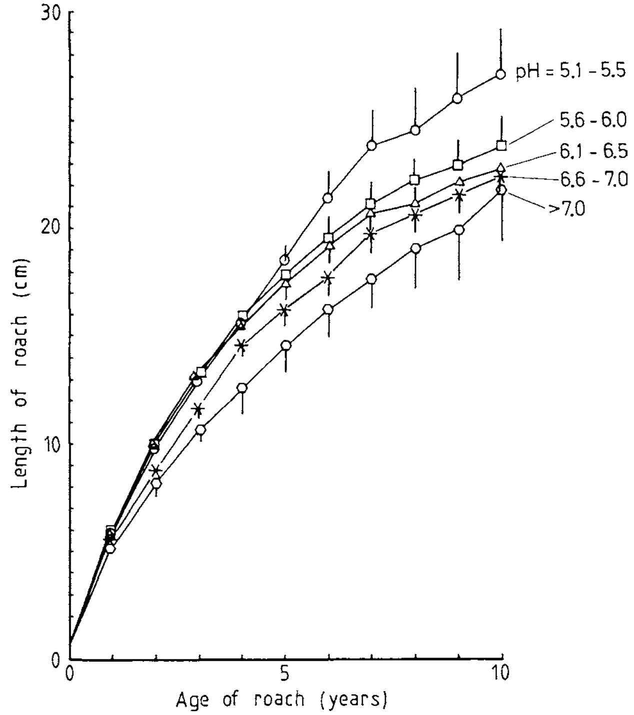

Fig. 8. Back calculated growths ($\bar{x} \pm SE$) of roach in lakes of different pH categories. The number of lakes in each pH category was four to ten

Pike

Pikes were caught from 35 lakes with a pH range of 4.6–7.6. Their proportion of the total fish biomass in the survey was 5.0%. The pike catches varied between 0.1–3.8 kg in weight and 1–10 in number per gill net series. The amount of pike in the catches may be an underestimate of their real proportion in the fish communities studied. Due to the low swimming activity of littoral pike in summertime, passive fishing gears like gill nets are not necessarily effective.

Both the wide pH amplitude of pike lakes and the lack of significant correlations between pike catch characteristics and acidity-related water properties support the view that pike is among the most acid-tolerant fish species (Muniz 1984; Magnuson et al. 1984).

According to Hultberg (1985) pikes in acid stressed lakes may show reduced growth rates. This is because of the low nutritive value of invertebrates for pike in circumstances where no more suitable prey fishes are available. In the present study one of this type of lake was found. The test fishing catch of the lake (pH 4.6) consisted of six old and large (150–300 g) perch and ten small pikes (30–190 g). Most of the pikes had fed on invertebrates, *Asellus aquaticus* and Odonata nymphs. Back-calculated length at age values of these pikes was significantly smaller when compared to those from a circum neutral lake with a dense roach population (Fig. 9). However, there were generally no significant differences in the growth rates of pike among lakes grouped according to their pH. For example, the back-calculated mean length (x̄ ± SE) of pike at age 4 years was 317 ± 43,

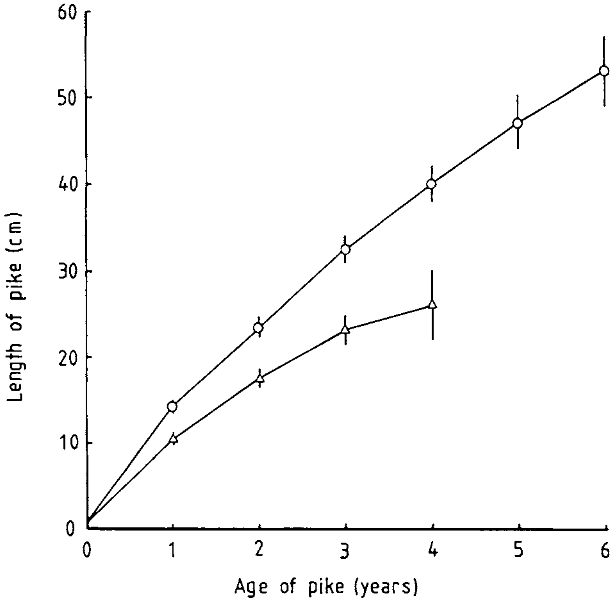

Fig. 9. The back-calculated growth (x̄ ± SE) of pike in circumneutral (pH 6.8) Lake Huhmari (*circles* n = 12) and in acidified (pH 4.6) Lake Sarkkinen (*triangles*, n = 10, Fig. 11, lake 9)

330 ± 15, 330 ± 23 and 326 ± 21 mm in pH groups < 5.0, 5.0–5.4, 5.5–5.9 and ≥ 6.0, respectively. Although variations were wide both within and among lakes, the growth of pike was slow in all lakes when compared to larger and more productive waters (Wolfert and Miller 1978; Kipling 1983; Hickley and Sutton 1984, Vøllestad et al. 1986).

Ruffe

Ruffe were present in the catches of 39 lakes with pH values 4.8–7.6. The weight of ruffe catches varied between 8–1780 g per gill net series and its proportion of the total fish biomass during the survey was 2.0%. The total weight of ruffe catches correlated significantly with the surface area of the lakes ($r = 0.46$, $p < 0.001$) but not with the altitude above sea level or with the conductivity, as reported by Degerman and Nyberg (1987) in a survey of limed lakes in Sweden. The mean areas of lakes with and without ruffe were 35 and 9 ha, respectively. Larger lakes provide more heterogeneous habitats than small ones, which may offer better possibilities for ruffe to avoid both predation (Särdson 1976) and interspecific competition for food (Hansson 1984). In addition, temporal anoxia which is common in the hypolimnia of small ($<$ 10 ha) Finnish lakes (Salonen et al. 1984) may limit the occurrence of ruffe.

Little is known about the pH tolerance of ruffe. According to this study, it is clearly more tolerant than roach but slightly more sensitive than perch and pike. The critical levels for successful reproduction of ruffe may be around pH 5.0. The higher mean weight of ruffe in acid rather than in neutral lakes (Fig. 10) might be a consequence of decreased reproduction and subsequent aging of some ruffe populations at pH levels < 5.5.

Other Species

Other native species collected during the survey in addition to perch, roach, pike and ruffe were bream *Abramis brama* L., bleak, *Alburnus alburnus* L., rudd, *Scardinius erythrophthalmus* L., crucian carp, *Carassius carassius* L., burbot, *Lota*

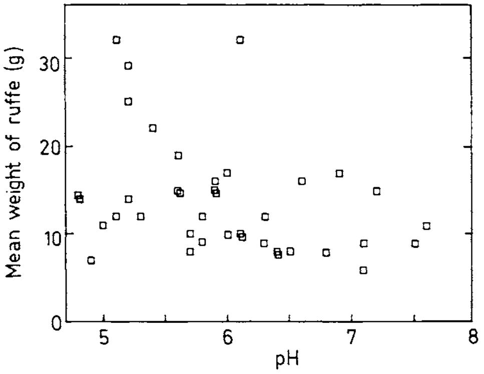

Fig. 10. The mean weight of ruffe in the gill net catches as related to lake pH

lota L., vendace, *Coregonus albula* L. and whitefish, *Coregonus sp.*. Pikeperch, *Stizostedion lucioperca* L., trout, *Salmo trutta* L. and whitefish were met as introduced species.

Bream were caught from four lakes with pH 5.9–6.7, bleak from two lakes, pH 6.7 and 7.1, rudd from two lakes, pH 5.8 and 5.9, and crucian carp from one lake with pH 5.9. The critical pH levels from successful reproduction of bream, rudd, and bleak are 6.5, 6.0 and 5.5, respectively (Leuven et al. 1987). In addition to acidity, the distribution of these species is largely controlled by the trophic status of the lakes: they are usually common in eutrophic waters. Thus, the general oligotrophy of the lakes of this survey may explain their low frequency of occurrence even in circumneutral lakes. Crucian carp is the most acid-tolerant among the cyprinids of this survey. It is able to reproduce at least at pH levels round 5.0 (Holopainen and Pitkänen 1985) but because it is very sensitive to predation it is usually common only in small seasonally anoxic ponds with no other fish species.

Most lakes in this collection are too small for the natural occurrence of vendace, whitefish and burbot. This is because they are living usually in cool hypolimnetic waters with high oxygen concentrations – circumstances that are not often provided by small lakes. Further, these species are spawning on hard, mineral bottoms that are not usually available in small lakes. Whitefish and vendace are considered acid-sensitive (Degerman and Nyberg 1987). According to the few observations on their natural populations made in this study, pH 5.2 and 7.6 for whitefish and pH 5.6 and 6.3 for vendace, critical pH levels for reproduction of these species would be 5.0–5.5. This is supported also by experimental studies (Vuorinen et al. this Vol.). Successful introductions of whitefish to lakes of pH 5.0 or even below (Rask et al. 1988) indicate that whitefish could be used in fisheries management of acidifying waters.

Information from Local Sources

Local information on the fish status of the lakes was considered important despite uncertainties in its validity. This is because there are generally no fishery statistics available from small lakes. Local information is also the only way to get some idea of fish populations that possibly have been lost recently.

Observations on the structural changes, disappearances or mortalities of adult fish were provided from 38 populations in 29 lakes of the survey. The decreases and disappearances of roach were most common (Table 4) and they were observed in all main study areas (Fig. 1A–D). The largest lake so far that has lost its roach population is one with a surface area of 1.9 km^2 (pH 5.5).

Observations on changes in perch populations were concentrated in the southernmost coastal area (Fig. 1A,B). According to local people, small perch were present during the 1960's in three lakes where perch are now close to extinction. In one lake (pH 4.4) blood and gill samples were taken from dying perch in May 1986 (Nikinmaa et al. this Vol.).

Table 4. A summary of local information on the decreases, disappearances or observed mortalities of adult fish in the fish populations of this survey

	Number of affected populations		
Fish species	Decreased	Disappeared	Fish kill
Perch	8	2	4
Roach	6	8	1
Pike	2	1	–
Ruffe	2	–	–
Burbot	1	2	–
Vendace	1	–	–

Area A close to Helsinki (Fig. 1) appeared to be the most interesting. There were 21 study lakes in a small area and information about fish status in half of them was available (Fig. 11). Some of the lakes where perch populations are now affected by acidification had also been inhabited earlier by roach. Roach populations of two lakes (pH 4.6 and 4.7 during the survey) disappeared as long as 40 years ago. Two other lakes with recent declines of pH to 4.8 and 5.1 lost their roach populations 10–20 years ago.

Conclusions

This survey of 80 lakes indicated that acid precipitation has affected fish populations of small lakes in Finland. Acidity-related impacts on perch, the most

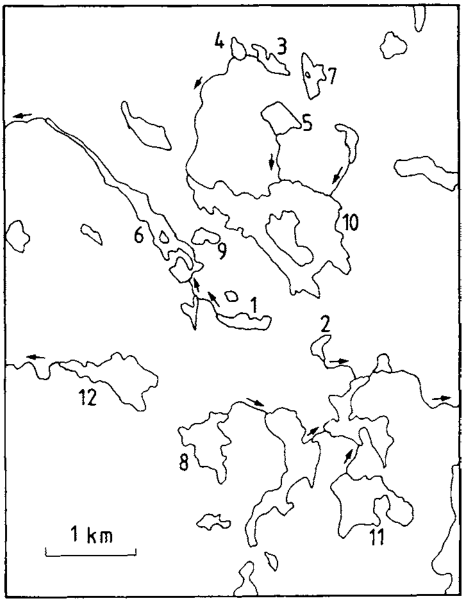

Fig. 11. A section of area A (Fig. 1) with 12 test fished lakes. Lakes 1–3 are now nearly fishless, and patterns in growth and population structure of perch and roach indicated that most fish populations are affected by the acidification. According to local people, the amounts of fish have decreased in most of the lakes and roach populations have disappeared from lakes 3–6

common and also one of the most acid-tolerant species, were concentrated to the southernmost parts of the country, where also acidic deposition has been most marked. The response of the population structure of roach to acidity in different places indicates that early impacts of acidification on fish communities can be detected in wide areas over the southern and central parts of Finland. This was also supported by local information on the decrease and disappearance of roach populations.

The proportion of lakes with affected fish populations in this survey, ca. 30%, is an overestimate because the lakes were not chosen randomly. On the other hand, in this type of a survey the first responses of fish to acidity cannot be recorded. A clear decrease in the amount of fish or a change in the population structure of a species is a result of high acid loads over many years. The disappearance of roach populations over 40 years ago from some lakes that are presently very acid suggests that the processes involved in lake acidification have been going on for even more than 50 years in parts of Finland.

The development of fish populations, both unaffected and affected, in acid sensitive lakes should be monitored further, until the emissions of acidifying substances have been restricted to levels where no more acidification is to be expected.

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Respiratory Effects of Environmental Acidification in Perch (*Perca fluviatilis*) and Rainbow Trout (*Salmo gairdneri*)

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Summary

The respiratory effects of low pH were studied in the field and laboratory. The thickness of gill epithelium was similar in perch from an acid lake to that in perch from a neutral lake. This observation suggests that gill hypertrophy was not the primary cause of death of fish in the acid lake.

A 24-h acid exposure to pH 5 did not affect the blood respiratory properties and ion concentrations of rainbow trout at all. However, when the acid-exposed fish were further subjected to hypoxia, the red cell water content and chloride concentration increased, red cell ATP concentration decreased, and plasma sodium and chloride concentration decreased. These changes were not seen in animals maintained in neutral water and subjected to hypoxia. The loss of ions may be caused by hypoxia-induced increase in the diffusion area of the gills, and hyperventilation, which initially increases the diffusion gradient across gill epithelium.

Introduction

In the absence of other environmental disturbances, pH values 4.5–5 affect the blood chemistry of salmonid fish only slightly. Malte (1986) observed a 0.15 unit drop in the arterial plasma pH in acid-exposed rainbow trout during a 102-h exposure to pH 5.0 with hardly any changes in plasma ion concentrations, blood haemoglobin concentration or red cell volume. Similarly, Wood et al. (1988a) found a 0.1 unit drop in the arterial plasma pH of brook trout during the first 40-h of a 10-day exposure to pH 4.8, with practically no other changes in the blood chemistry.

However, in most instances pH decline does not occur alone. For example, most acidified lakes in Finland, e.g. those studied by Tuunainen et al. (1986), have total aluminium levels ranging between 50 and 300 $\mu g\,l^{-1}$ (approximately 2–10 $\mu mol\,l^{-1}$). These concentrations are toxic to rainbow trout already at nearly neutral pH values (6.1–6.5; Neville 1985). The presence of aluminium in the water thus drastically increases the physiological disturbances caused by low pH.

Kauppi et al. (Eds).
Acidification in Finland

The respiratory effects of low pH or low pH and aluminium together have been largely addressed to gill damage: both low pH and aluminium act as irritants to the gills, increase the production of mucus, and ultimately cause tissue hypertrophy, which increases the diffusion distance from the environment to the gill vasculature (see e.g. Daye and Garside 1976; Ultch and Gros 1979). Additionally, poorly soluble forms of aluminium may be precipitated on the gills, causing an increased diffusion distance from water to the gill vasculature. These factors account for the decrease in blood oxygen tension, which is observed in acid + aluminium exposures both in rainbow trout (*Salmo gairdneri*) and brook trout (*Salvelinus fontinalis*) near pH 5 (see Malte 1986; Wood et al. 1988a). However, most of the available information on the gill damage is based on experiments in which fish have been subjected to low pH and aluminium without prior exposure to either. Recent data by Wood et al. (1988b) suggest that prior acclimation to acid + aluminium (pH 5.2, 150 $\mu g\ l^{-1}$ aluminium) drastically reduces the physiological disturbances caused by a further acid + aluminium shock (pH 4.8, 333 $\mu g\ l^{-1}$ aluminium). Thus, the drop in arterial oxygen tension which was seen in fish preacclimated to pH 5.2 in the absence of aluminium, and thereafter challenged with pH 4.8 and 333 $\mu g\ l^{-1}$ aluminium, did not occur in fish preacclimated to acid + aluminium. However, this study did not report the structure of the gills.

Internal hypoxia, caused by the gill damage, appears to be the primary reason for the respiratory problems (Malte 1986; Malte and Weber 1988) at pH values 5–6 (e.g. Neville 1985; Wood et al. 1988a). On the other hand, at pH values approaching 4, ionoregulatory failure may be the primary cause of death. If internal hypoxia is the primary cause of respiratory difficulties at pH values near 5, treatments which decrease environmental oxygen availability should also enlarge the acidification-induced respiratory disturbances. Up to the present, however, such studies have not been made.

In the present studies the following questions were addressed:

1. Are the gills of fish living in an acidified environment with a moderate total aluminium concentration damaged in a manner similar to the gills of acutely acid + aluminium exposed fish? This was done by comparing the structure of gills of perch from a circumneutral (pH 6.5) lake with a low (25 $\mu g\ l^{-1}$) total aluminium concentration and the structure of gills of fish from an acid (pH 4.4) lake with a moderate (50 $\mu g\ l^{-1}$) total aluminium concentration.

2. How does acute environmental hypoxia affect the responses of rainbow trout to acute acidification? This was done by exposing cannulated rainbow trout to pH 5 for 24 hours and thereafter subjecting them to hypoxia.

Gill Structure and Blood Chemistry of Perch (*Perca fluviatilis*) from an Acid and Neutral Lake

Methods

Perch (*Perca fluviatilis*) were captured with traps (1 cm square mesh) from an acid (pH 4.4; total aluminium concentration 50 $\mu g\,l^{-1}$, the number of fish 8; 59 ± 5 g) and a circumneutral lake (pH 6.5; total aluminium concentration 25 $\mu g\,l^{-1}$, the number of fish 6; 27 ± 6 g) and kept in the traps until sampling. During the time of sampling, fish were dying in the acid lake (Martti Rask persl commun.). Fish were netted from the traps, and blood and gill samples taken and treated as described earlier (Tuurala and Soivio 1982; Rask and Virtanen 1986). The gill samples were fixed in 2.5% glutaraldehyde, postfixed in 1% osmiumtetroxide, embedded in epoxy resin and cut in 1-μm sections. From the sections the mean arithmetic distance (d_A) from water to the gill capillaries was determined morphometrically as (see Weibel and Knight 1964):

$$d_A = (P_{Epi,SLR} \times 12.9)/(2 \times I_o),$$

where $P_{Epi,SLR}$ = points falling on epithelial structures in the secondary lamellae, and I_o = intersections between outer surface of the secondary lamellae and test grid lines. The points and intersections were counted using a Mertz grid with a grid constant of 12.9 μm (Mertz 1967) superimposed on the 1410 × magnified image of the gill section.

From the blood samples the blood haemoglobin concentration was determined by the cyanmethaemoglobin method, red cell water content by weighing the cells, drying them to a constant weight and reweighing (e.g. Nikinmaa and Huestis 1984), and red cell NTP (ATP + GTP) concentrations enzymatically as described by Albers et al. (1983).

Results and Discussion

As seen in Table 1, there were no differences between the mean arithmetic distance from water to blood in the gills of perch from the acid and from the neutral lake. Thus, the marked hypertrophy of gill tissue, usually observed in acid + aluminium-exposed fish was not observed in our perch from an acid lake with a moderate aluminium concentration. Earlier results on natural populations of brook trout (*Salvelinus fontinalis*) from an acid lake (Chevalier et al. 1985) suggest that the gill epithelium of the fish in an acidified lake might be affected – epithelial hyperplasia, and separation of epithelial tissue was observed. However, the thickness of secondary lamellae remained unaltered also in their study. Leino et al. (1987) reported extensive gill damage in pearl dace (*Semotilus margarita*) and fathead minnow (*Pimephales promleas*) from two experimentally acidified lakes. In their study, a chronic (129 d) laboratory exposure to a low pH (5.5) did not cause changes in the gill secondary lamellar structure. Thus, the results on the gill structure of fish during chronic exposure to acidified environments are quite variable, possibly indicating species differences. A recovery from the initial gill damage during a chronic exposure to low pH would explain why the preacclimation of fish to acid + aluminium markedly reduced the physiological effects of a further lowering of pH and increasing of aluminium concentration (Wood et al. 1988b). The major visually observable difference between the gills of fish from the acid and the neutral lake was the presence of apical crypts (apical pits) on the chloride cell surface. This has earlier been observed also by Leino and McCormick (1984) on the gills of *Pimephales promelas* after chronic exposure to acid water. Interestingly, apical crypts are present in euryhaline teleosts when they are acclimated to seawater (Foskett 1987).

The major difference in the blood values measured (Table 1) between the acid and the neutral lake was the pronouncedly higher blood haemoglobin concentration in the fish from the acid lake than in the neutral lake. In contrast, no differences between the fish were observed either in the red cell water content or in the red cell NTP concentration. This observation suggests that fish chronically acclimatized to acid + aluminium are not characterized by swollen red cells, which are a characteristic feature of blood in short term exposures (e.g. Milligan and Wood 1982).

Simultaneous Acute Exposure of Rainbow Trout (*Salmo gairdneri*) to Acidification and Hypoxia

Methods

Rainbow trout (N = 8; 765 ± 80 g) were obtained from a commercial fish farm, and acclimated to laboratory conditions (T 10–12°C, oxygen tension > 120 mmHg, pH 7.2–7.4, total aluminium concentration 25 $\mu g\ l^{-1}$, 8 : 16 light : dark cycle) for a minimum of 2 weeks before experiments. The fish were cannulated both to the

Table 1. The mean arithmetic distance from water to blood (d_A, μm), blood haemoglobin concentration (Hb, $g\ l^{-1}$), red cell NTP concentration (NTP, $mmol\ l^{-1}$ rbc), and red cell water content (H_2O, %) in perch from an acid (pH 4.4, total aluminium concentration 50 $\mu g\ l^{-1}$) and circumneutral (pH 6.5, total aluminium concentration 25 $\mu g\ l^{-1}$) lake. Means ± SEM are given. The statistical significance between the means was calculated using Student's t-test

Parameter	Acid lake	P	Neutral lake
d_A	3.02 ± 0.77	NS	2.83 ± 0.34
Hb	77.2 ± 1.85	<0.05	57.2 ± 4.60
NTP	6.00 ± 0.80	NS	4.60 ± 0.93
H_2O	76.3 ± 0.6	NS	74.4 ± 1.5

dorsal and the ventral aorta as described by Nikinmaa and Jensen (1986), and allowed to recover from the operation for 48 h before the experiments. At the onset of the experiments the animals were divided into two groups, and 100 μl (10 μCi ml^{-1}) ^{14}C-labelled 5,5-dimethyloxazolidine-2,4-dione injected into the circulation. One of the groups ($N = 4$) remained initially in normoxic, neutral water, and was sampled once (0-sample), whereafter the fish were subjected to hypoxia. Hypoxia was induced by bubbling nitrogen in the water. The desired degree of hypoxia (40% air saturation; oxygen tension 60–65 mmHg) was reached within 2 h. Hypoxic blood samples were then taken at 3 and 6 h from the onset of hypoxia. The other group of fish ($N = 4$) was transferred to acid water (acidified with HCl, and bubbled with air to expel carbon dioxide, pH 5, range 4.8–5.1, total aluminium concentration 25 $\mu g\,l^{-1}$), and sampled after 24-h exposure to acid water. Thereafter the animals were subjected to hypoxia in the same manner as the fish kept in neutral water.

The arterial and venous oxygen tensions and extracellular pH values were determined immediately after sampling using Radiometer BMS3 Mk2, PHM 72 system, the blood haemoglobin concentration with the cyanmethaemoglobin method, and blood oxygen content using Tucker's (1967) method. Thereafter plasma and red cells were separated by centrifugation at 12,000 *g*, deproteinized with perchloric acid, and stored in liquid nitrogen until the determinations of red cell and plasma ion concentrations, red cell pH and red cell ATP concentration. A portion of the blood was centrifuged in tared, dried Eppendorff tubes, plasma and the uppermost portion of the red cells removed, and the rest of the red cells weighed, dried to a constant weight, and reweighed to obtain red cell water content.

Red cell and plasma sodium concentrations were determined using Radiometer FLM 10 flame photometer, and red cell and plasma chloride concentration using Radiometer CMT 10 coulometric titrator. Red cell ATP concentration was determined enzymatically as described by Albers et al. (1983), and red cell pH from the distribution of radioactively labelled DMO in the plasma and red cells as described by Nikinmaa et al. (1987). From the molar concentrations of oxygen and haemoglobin within the cells we calculated the oxygen/haemoglobin molar ratio.

Results and Discussion

The 1-day exposure to pH 5 did not affect the blood values of rainbow trout at all. Thus, the arterial oxygen tension, arterial and venous plasma and red cell pH, red cell oxygen/haemoglobin ratio, plasma and red cell chloride and sodium concentrations, red cell water content, and red cell ATP concentration were all similar in acid-exposed and control fish (Figs. 1–5).

When control and acid-exposed fish were subjected to hypoxia, clear differences in the responses were observed between the groups. Basically, the effects of hypoxia on the blood oxygen tension and red cell oxygen saturation were similar in both groups (Fig. 1). Furthermore, the plasma pH showed only a slight decreasing

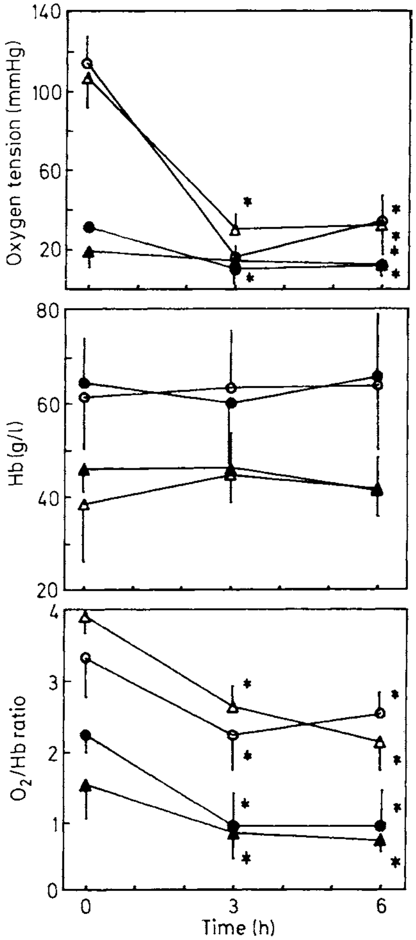

Fig. 1. The postbranchial (*empty symbols*) and prebranchial (*filled symbols*) blood oxygen tension (mmHg), haemoglobin concentration (Hb, $\mathrm{g\,l^{-1}}$), and oxygen/haemoglobin molar ratio (O_2/Hb ratio) in animals maintained at neutral pH (*triangles*) or exposed to pH 5.0 for 24 h (*circles*). After 0-samples both groups were subjected to hypoxia (environmental oxygen tension 60–65 mmHg), and samples taken after 3 and 6 h of hypoxia exposure. Means are given, *bars* indicate SEM, N = 4 except for the 6-h hypoxia samples in neutral water in which N = 3. Statistical comparisons were made between the means of 0 samples and both hypoxic samples using paired t-test. *Asterisks* indicate probability levels of less than 5%. There were no statistically significant differences between the fish kept in acid water and the fish kept in neutral water at any time point (Student's t-test was used for comparisons)

tendency in the acid + hypoxia-exposed group with no changes in the hypoxia-exposed group (Fig. 2). In both groups hypoxia exposure tended to cause an increase in the red cell pH. This is probably partly due to the increased proportion of deoxyhaemoglobin within the red cells. At constant extracellular pH a decrease in haemoglobin-oxygen saturation leads to an increase in the red cell pH (e.g. Jensen 1986). In addition, it appears that catecholamines are released to the blood stream and activate the sodium/proton exchange across the red cell membrane. The total catecholamine concentrations were below 5 nM in five measurements of normoxic fish in neutral environment, and close to 100 nM in three measurements in the plasma of fish from acid environment after 6-h hypoxia (measurements were made as described by Woodward 1982, using LKB 2150 HPLC pump, 2143 electrochemical detector, and Spherisorb ODS-2, 3 µm column 40 × 100 mm). The red cell sodium concentration increased in both the hypoxic and the acid + hypoxic group at 3-h (Fig. 3) samples. At 6-h samples, the red cell sodium concentration had started to return towards the initial values.

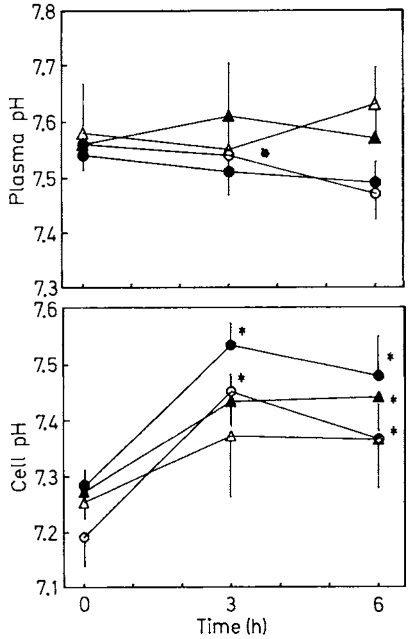

Fig. 2. The plasma and red cell pH of the postbranchial (*empty symbols*) and prebranchial (*filled symbols*) blood in animals maintained at neutral pH (*triangles*) or exposed *to* pH 5.0 for 24 h (*circles*). After 0-samples both groups were subjected to hypoxia (environmental oxygen tension 60–65 mmHg), and samples taken after 3 and 6 h of hypoxia exposure. Means are given, *bars* indicate SEM, N = 4 except for the 6-h hypoxia samples in neutral water in which N = 3. Statistical comparisons were made between the means of 0 samples and both hypoxic samples using paired t-test. *Asterisks* indicate probability levels of less than 5%. There were no statistically significant differences between the fish kept in acid water and the fish kept in neutral water at any time point (Student's t-test was used for comparisons)

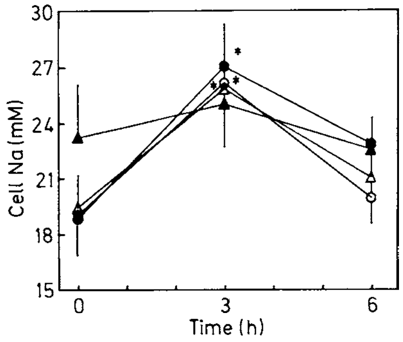

Fig. 3. The red cell sodium concentration (mmol l^{-1} RBC) in the postbranchial (*empty symbols*) and prebranchial (*filled symbols*) blood of animals maintained at neutral pH (*triangles*) or exposed to pH 5.0 for 24 h (*circles*). After 0-samples both groups were subjected to hypoxia (environmental oxygen tension 60–65 mmHg), and samples taken after 3 and 6 h of hypoxia exposure. Means are given, *bars* indicate SEM, N = 4 except for the 6-h hypoxia samples in neutral water in which N = 3. Statistical comparisons were made between the means of 0 samples and both hypoxic samples using paired t-test. *Asterisks* indicate probability levels of less than 5%. There were no statistically significant differences between the fish kept in acid water and the fish kept in neutral water at any time point (Student's t-test was used for comparisons)

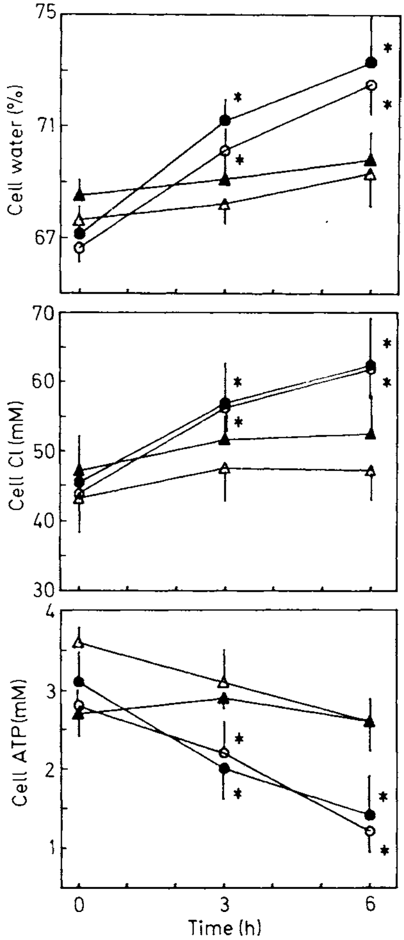

Fig. 4. The red cell water content (%), chloride concentration (mmol l^{-1} rbc), and ATP concentration (mmol l^{-1} rbc) of the postbranchial (*empty symbols*) and prebranchial (*filled symbols*) blood of animals maintained at neutral pH (*triangles*) or exposed to pH 5.0 for 24 h (*circles*). After 0-samples both groups were subjected to hypoxia (environmental oxygen tension 60–65 mmHg), and samples taken after 3 and 6 h of hypoxia exposure. Means are given, *bars* indicate SEM, N = 4 except for the 6-h hypoxia samples in neutral water in which N = 3. Statistical comparisons were made between the means of 0 samples and both hypoxic samples using paired t-test. *Asterisks* indicate probability levels of less than 5%. After 6 h hypoxia exposure the red cell ATP concentration of fish exposed to acid water was significantly ($P < 0.05$) lower than that of the fish maintained in neutral water (Student's t-test was used for comparisons)

The first major difference between the hypoxia and acid + hypoxia-exposed fish was in the red cell water content. The red cell water content showed only a slight, non-significant, increasing tendency in fish subjected to hypoxia alone, but increased drastically in acid + hypoxia exposed animals (Fig. 4). The increase in acid + hypoxia exposed animals was mainly due to influx of chloride into the red cells. The red cell chloride concentration increased pronouncedly in the acid + hypoxia exposed animals with little changes in animals exposed to hypoxia

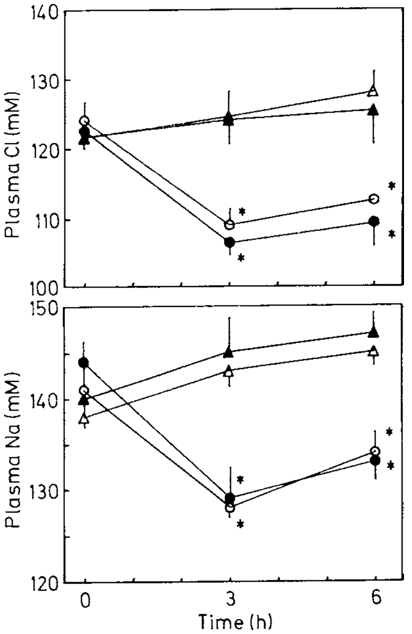

Fig. 5. Postbranchial (*empty symbols*) and prebranchial (*filled symbols*) plasma chloride and sodium concentration of animals maintained at neutral pH (*triangles*) or exposed to pH 5.0 for 24 h (*circles*). After 0-samples both groups were subjected to hypoxia (environmental oxygen tension 60–65 mmHg), and samples taken after 3 and 6 h of hypoxia exposure. Means are given, *bars* indicate SEM, N = 4 except for the 6-h hypoxia samples in neutral water in which N = 3. Statistical comparisons were made between the means of 0 samples and both hypoxic samples using paired t-test. *Asterisks* indicate probability levels of less than 5%. Both the postbranchial and the prebranchial values of acid exposed fish were significantly ($P < 0.05$) lower than the values of fish maintained at neutral water at both hypoxic samples (Student's t-test was used for comparisons)

alone. The most likely reason for the net chloride influx was the drop of red cell NTP concentration occurring in acid + hypoxia-exposed animals. Although the red cell swelling as such contributes to the drop in ATP concentration, a metabolic drop also occurred, because the ATP/haemoglobin molar ratio decreased from ca. 0.7 before hypoxia exposure in the acid-exposed animals to less than 0.4 after the 6-h hypoxia exposure. In animals exposed to hypoxia alone, the red cell ATP concentration did not change significantly.

The second major difference between hypoxia and acid + hypoxia exposed animals was in the plasma sodium and chloride concentration (Fig. 5). There were no changes in the plasma sodium and chloride concentrations of the animals subjected to hypoxia alone. In contrast, both the sodium and chloride concentration of the acid + hypoxia-exposed animals decreased by approximately 15 mM. Although some of this drop is due to the net chloride (and sodium) influx into the red cell, the changes in the red cell concentrations are far too small to account for the whole decrease.

A possible cause for the hypoxia-induced drop in the plasma sodium and potassium concentrations of acid-exposed animals is the hypoxia-induced hyperventilation. The increased flow of water past the secondary lamellae of the gills initially maintains the diffusion gradient for sodium and chloride between blood and the environment great. The "functional" secondary lamellar surface increases in hypoxia either as a result of lamellar recruitment (Booth 1979) or as a result of a decrease in the relative proportion of basal channels in the secondary lamellae (Tuurala et al. 1984). This increase in "diffusion area" of gills may increase the ion losses in the acid environment, because ion gradients favour ion efflux. Simultaneously, active ion uptake may be reduced, because the ion gradients in acid environment are unfavourable.

Interestingly, the drop of plasma sodium and chloride concentrations resembles that observed in acid + aluminium exposure in brook trout. Wood et al. 1988 observed that acid + aluminium exposure in low calcium (pH 4.8, total aluminium concentration 333 $\mu g\, l^{-1}$, calcium concentration 12.5 μM) caused a marked drop of plasma ions, but had practically no effect on plasma pH. The blood oxygen tension and oxygen/haemoglobin ratio started to decrease only in animals nearing death. Walker et al. (1988) observed that acid-exposed animals increased their ventilation volume pronouncedly. Booth et al. (1988) have observed that the effect of aluminium on the net ion fluxes is predominantly to increase the efflux component. All of these observations are compatible with a hyperventilation-induced increase in diffusion of sodium and chloride ions to the environment also in the acid + aluminium exposed animals.

Conclusions

Our studies of dying fish from an acid lake with a moderate aluminium concentration suggest that aluminium-induced gill damage is not the cause of death in fish chronically exposed to low pH and aluminium. In fact, the gill structure of the animals from the acid lake was remarkably similar to that of the animals from the neutral lake.

The experiment with acutely acid + hypoxia-exposed fish suggests that an increased ventilatory requirement causes pronounced decrease in the plasma chloride and sodium concentrations. Thus, the responses caused by hypoxia in acid water are similar, and apparently as drastic, as those caused by acid + aluminium exposure. In addition to suggesting that the ion losses may, in both cases, be caused by hyperventilation, the results may have also ecological relevance. In addition to aluminium, any other environmental change which either decreases oxygen availability or increases oxygen requirement in acid water, may cause the plasma ion losses. Thus, the hypoxic environment, encountered by fish in ice-covered small lakes in spring may be an important factor in increasing "acid toxicity". Also, the rapid increases in environmental temperature, which occur at the spawning time (period with a high oxygen consumption) in spring may also markedly contribute to the "acid toxicity". Up to date, the possible importance of these factors has not been studied.

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Long-Term Exposure of Adult Whitefish (*Coregonus wartmanni*) to Low pH/Aluminium: Effects on Reproduction, Growth, Blood Composition and Gills

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Summary

Adult whitefish (*Coregonus wartmanni* sensu Svärdson 1979) were exposed for 143 days before and during spawning time to an acidity of pH 5.75 or 4.75 with or without aluminium (150 μg Al l^{-1}) added in water containing 0.23 mmol Ca l^{-1}. Ovulation was delayed on the average 10 days at pH 4.75 with Al and also somewhat at pH 5.75 with Al and at pH 4.75 without Al. The regression of testes was delayed at pH 4.75 and most prominently at pH 4.75 with Al. In both sexes, plasma Na and Cl concentrations were greatly reduced and glucose concentration greatly elevated at pH 4.75. Extremely reduced plasma Na and Cl concentrations and an elevated blood glucose concentration in addition to the smallest growth at pH 4.75 with Al seen in females suggest that the female reproductive functions made them highly susceptible to Al at low pH. In the gill epithelium, deposits of Al were detected in fish exposed to Al and the gill epithelial cells showed hypertrophy at pH 4.75.

Introduction

The decreased survival of early life stages has been proposed as the main reason for the losses of fish populations in acidified waters (Schofield 1976). Effects of acidification have been attributed to impaired fertilisation, lowered survival of embryos and fry and decreased hatching success (e.g. Leivestad et al. 1976; Runn et al. 1977; Peterson et al. 1980; Rosseland et al. 1980; Rask 1983; Daye and Glebe 1984; Cleveland et al. 1986; Tuunainen et al. 1987, 1988). Sevaldrud et al. (1980) state that over 1400 Norwegian lakes have lost their brown trout (*Salmo trutta* L.) populations and 118 lakes their perch (*Perca fluviatilis* L.) populations due to effects on reproduction. In addition, some observations of mass mortalities of adult fish in lakes exist. In Sweden, the main part of vendace (*Coregonus albula*) population was wiped out after heavy rains in two lakes having rather low pH (4.9–6.0) and low (< 0.02 mmol l^{-1}) buffering capacity (Grahn 1980).

In their widely cited study Beamish et al. (1975) stated that in acidified lakes with changed fish population structures, fish had not spawned during their normal spawning time, and they attributed that effect to the lowered serum calcium levels

Kauppi et al. (Eds).
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in female fish. Wiener et al. (1985) detected, before spawning, lower serum calcium levels in female white suckers (*Catostomus commersoni*, Lacepède) from acidified lakes compared to circumneutral lakes, but they did not make observations of the spawning of the fish. In another study white suckers were observed to mature at older ages and larger sizes in three acid lakes than in two circumneutral lakes (Trippel and Harvey 1987). These three studies relate reproductive effects to only lake water acidity and tell, except for Beamish et al. (1975), little about the lake water chemistry; no one mentions aluminium. Acidified lakes usually have rather high water aluminium concentrations (Dickson 1975), and for instance, adult vendace that died in two acidic lakes had high aluminium concentrations in their gills (Grahn 1980). The forms of aluminium present in water are related to the water chemistry, especially to its pH, and inorganic forms are considered to be most toxic (Baker and Schofield 1980).

Earlier, as well as some recent experimental studies have focussed on the reproduction of fish in acidic conditions with fathead minnow, *Pimephales promelas* (Mount 1973; McCormick et al. 1989), brook trout, *Salvelinus fontinalis* (Menendez 1976; Tam and Payson 1986; Tam et al. 1987), flagfish, *Jordanella floridae* (Craig and Baksi 1977; Ruby et al. 1977; 1978) and rainbow trout, *Salmo gairdneri* (Lee et al. 1983; Weiner et al. 1986). However, the combined effects of acidity and aluminium on the reproductive success have been conducted only fairly recently with brook trout (Mount et al. 1988a; 1988b).

In the fisheries survey programme (Rask and Tuunainen this Vol.) of the Finnish Research Project on Acidification (HAPRO), thinning, ageing and even disappearance of populations of fish species were observed in small acidified lakes. In these small clear water lakes the water aluminium concentration was higher the lower the water pH was (Tuunainen et al. 1987).

In the fisheries subproject of HAPRO, the effects of water acidity and aluminium on different life stages of fish species have been conducted as experimental studies. Test fish were selected among the species that inhabit small Finnish lakes. One of the objectives of these studies has been to clarify the mechanisms of the action of acidification on fish species and in turn population structures. This knowledge might then be used in management of fish stocks in acidified and acidifying lakes.

In this long-term laboratory study the effects of acidity and aluminium on whitefish (*Coregonus wartmanni* sensu Svärdson 1979) reproduction, growth and on some blood and plasma parameters and on gills were examined. Whitefish was selected as a test fish, because it is commercially and recreationally important in Finland, and some of acidifying lakes studied in the fisheries subproject are inhabited by this species as a native population. Up until this point, there has been little knowledge about the reactions of whitefish to acidity. Nieminen et al. (1982) measured blood glucose and lactate levels in whitefish (*C. peled*) after short-term (3–17 h) exposure at pH levels of 3.0–9.5 and Scherer et al. (1986) exposed lake whitefish (*C. clupeaformis*) at pH levels of 4.1–5.0 for 2 weeks and studied behavioural effects and changes of some plasma variables. According to our experiments with sac fry, whitefish is relatively resistant towards acidity and aluminium (Tuunainen et al. 1987, 1988).

Materials and Methods

Fish

Whitefish (*Coregonus wartmanni* sensu Svärdson 1979) were caught from Lake Paasivesi at the beginning of June in 1986. Fish were transported to the nearby Central Fish Culture Station for Eastern Finland in Enonkoski where the experiment was performed and the fish were distributed into five circular fibre-glass tanks. The diameter of the tanks was 2.7 m and water volume about 2000 l. Fish were acclimated for 1 month to test conditions and fed on commercial dry feed before the experiment was begun. The fish were in these same tanks during the test. About a week before the start of the test all the whitefish were anaesthetized in $NaHCO_3$-buffered tricaine methane sulphonate (MS-222) solution ($0.13\ mg\ l^{-1}$; 3 min) individually and weighed and measured, and 40 whitefish that were healthy and in good condition were left in each of the five tanks (Table 1). The age of the fish was 3.6 ± 0.1 years (mean ± SE), as determined from the scales in the final sampling. During the experiment fish were fed on commercial dry feed (Ewos) 4% of their body weight per day in two portions and the test basins were cleaned after every feeding.

Exposure

Fish were exposed to one of the four treatments and one group served as a control. The treatments were: pH 5.75 ("pH 5.75"); pH 5.75 plus aluminium $150\ \mu g\ l^{-1}$ ("pH 5.75 + Al"); pH 4.75 ("pH 4.75") and pH 4.75 plus aluminium $150\ \mu g\ l^{-1}$ ("pH 4.75 + Al"). The test was performed as a flow-through test. The lowering of pH and aluminium addition were made by pumping appropriate stock solution by peristaltic pumps (Desaga 132100) into a mixing chamber where dilution water (lake water from Lake Ylä-Enonvesi) was also led. The water in the mixing chamber was aerated vigorously to expell carbon dioxide. The flow of the dilution water was $18\ l\ min^{-1}$, hence 90% replacement time in the test basins was about 4 h

Table 1. The mean (± SE) weight, total length and condition factor of whitefish at the beginning of exposure in different treatments

	Control	pH 5.75	pH 5.75 + Al	pH 4.75	pH 4.75 + Al
Length, cm	23.2 ± 0.3	23.6 ± 0.4	23.5 ± 0.3	23.1 ± 0.3	23.4 ± 0.3
Weight, g	112 ± 7	107 ± 7	107 ± 7	110 ± 8	108 ± 8
CF	0.87 ± 0.03	0.78 ± 0.03	0.79 ± 0.03	0.84 ± 0.03	0.79 ± 0.03
N	40	40	40	40	40

(calculated according to Sprague 1969). Stock solutions for acid exposures were made by diluting analytical grade sulphuric acid (Merck No 731) in lake water and for acid-aluminium treatments first dissolving $Al_2(SO_4)_3 \times (16–18)H_2O$ (Merck No 1100). pH-meters (Schott CG817T, electrode N37) connected to recorders (Goertz SE-120) were used to monitor pH in the test basins. pH values, 4 h apart, were recorded from the charts, and mean pH values were calculated from these readings after converting to hydrogen ion concentration. Water samples from the five basins were taken three times, about every 6th week. Conductivity, colour and chemical oxygen demand and calcium and iron concentrations were analysed according to Finnish water analysis standards (SFS-standards). The determinations of aluminium speciation were made in the Helsinki University of Technology according to the method of LaZerte (1984) by atomic absorption spectrometry (graphite furnace). The results of all these measurements are given in Table 2. Water temperature varied according to the lake water temperature which was at its maximum (ca. 22°C) at the beginning of August, decreasing down to ca. 2°C towards the end of the exposure. The photoperiod was natural. Dissolved oxygen content (DO) in the water of test basins was monitored at first daily but later more seldom with a dissolved oxygen meter (Yellow Springs Instruments model 57). Percentage saturation of DO was mostly 85–95%, but decreased down to 70% during the warmest water temperature values in early August. However, the variations in DO were similar in all basins. The exposure was started on 8 July 1986 and was finished on 28 November 1986 after the spawning time of whitefish. The duration of the exposure was 143 days (143-d).

Gonad Products

Fish were stripped artificially after ovulation had occurred in individual females from 29 October to 7 November. The occurrence of ovulation was determined every other day by gently pressing the sides of the fish near the anus. If some eggs were easily expelled and if the expelled eggs were clear, i.e. lipid droplets were

Table 2. The water quality (mean ± SE) in the test basins based on three measurements about 6 weeks apart: conductivity, colour (measured as Pt mg l^{-1}), chemical oxygen demand (COD) and concentrations of iron (Fe), calcium (Ca), total aluminium (Al_{tot}) and labile aluminium (Al_{lab}). The mean pH values were calculated from daily recordings 4 h apart after converting to hydrogen ion concentrations

	Control	pH 5.75	pH 5.75 + Al	pH 4.75	pH 4.75 + Al
Cond., mS m^{-1}	7.4 ± 0.0	7.9 ± 0.2	8.1 ± 0.1	8.8 ± 0.6	8.8 ± 0.3
Colour	35 ± 0	37 ± 2	37 ± 2	38 ± 2	37 ± 2
COD, mg O_2 l^{-1}	6.9 ± 0.4	6.5 ± 0.5	6.7 ± 0.6	6.5 ± 0.6	6.8 ± 0.4
Fe, μg l^{-1}	74 ± 1	77 ± 6	72 ± 6	82 ± 5	71 ± 10
Ca, mmol l^{-1}	0.23 ± 0.00	0.23 ± 0.01	0.23 ± 0.00	0.23 ± 0.00	0.22 ± 0.00
Al_{tot}, μg l^{-1}	8 ± 2	11 ± 3	134 ± 6	16 ± 3	176 ± 13
Al_{lab}, μg l^{-1}	3 ± 1	4 ± 0	54 ± 1	5 ± 1	96 ± 3
pH	7.07 ± 0.00	5.69 ± 0.00	5.77 ± 0.00	4.75 ± 0.01	4.75 ± 0.01

coalesced, the eggs were considered ready for stripping. Those females that were empty, i.e. delivered only a few eggs with plenty of ovarian fluid, were considered to have already spawned; those that delivered plenty of ovarian fluid and a few grams of eggs were considered to be partly spawned; those that easily delivered quite a lot of eggs were considered ready for stripping; those that delivered eggs quite easily at first but did not deliver all the eggs, were considered partly unovulated, and those that did not deliver any ripe eggs despite of enlarged belly were considered unovulated. The proportional weight of the eggs per female was calculated only from females considered to be ready for stripping. Every fish that delivered either milt or eggs was marked individually by Carlin tags for subsequent sampling. On 26–28 November at fish sampling, all fish including those which were not stripped, were killed for examination of sexual maturity and completeness of ovulation. The number of spawned or stripped fish and fish having nearly mature but unovulated eggs was considered to be the total number of sexually mature fish in each test basin. The proportions of spawned or stripped, partly spawned, ready-to-strip, partly unovulated or unovulated fish in each sampling day were calculated on this basis.

A sample of unfertilised eggs was taken for the determination of fresh and dry weight and water content (after drying in 105°C for 24 h). Eggs from each female were fertilised by milt from three males of the same tank. Eggs and milt were mixed by a small amount of water from the control tank in a plastic vessel. After 3 min of gently shaking, the eggs were rinsed and put into a small glass funnel mounted into a Plexiglas box, the drain of which was supplied with a stainless steel wire net to prevent eggs or hatched sac fry from escaping. Eggs were incubated in lake water (Lake Ylä-Enonvesi) until hatching in late spring in 1987. During incubation water temperature changed from 4.6°C to 1.3°C between November and April and rose to 4.0°C at hatching time. Numbers of hatched sac fry were counted and percentage hatches were calculated. Newly hatched sac fry were collected for the determination of wet weight and total length.

Sampling of Fish

From 26 to 28 November, fish were randomly caught successively by a dip net from the five basins and anaesthetized individually for 3 min in MS-222 solution (0.13 mg l^{-1}), buffered to the pH of the test solution of the appropriate tank, and a blood sample by heart puncture was drawn into an heparinized 1 ml syringe (needle No 16; 0.6 × 25 mm). The fish was measured and weighed and its liver and gonads were also weighed. The proportional weights of liver (LSI, %) and gonads (GSI, %) per the body weight of fish were calculated. Condition factors were calculated by the formula $CF = 100^*$ (weight, g)* (length, cm)$^{-3}$. The mean specific rate of increase in live weight (G_W% d^{-1}) and in length (G_L% d^{-1}) were calculated according to Elliott (1975) for the males and females from the initial combined mean values (Table 1). Some scales were removed for age determination and for back calculation of growth using the formula by Fraser and Lee (Tesch 1971).

From the male fish in each tank the second and third left gill arches were fixed in buffered 4% formaldehyde for light microscopy. Gill arches were dehydrated, embedded in paraffin and sectioned in 7 μm slices and stained by haematoxylin-eosin as a routine procedure. Periodic acid Schiff reagent (PAS) was applied to stain goblet (mucus-secreting) cells. The number of goblet cells was counted in 15–20 filaments per fish and results were calculated as numbers of goblet cells per secondary lamella. A special staining technique for aluminium introduced by Havas (1986) for staining aluminium deposits in whole animals (invertebrates) and plants was also applied in sectioned gill slices (10 μm). Aluminium deposits were counted in 5–15 filaments on two slides per fish so that about 100 deposits per fish were counted and results were calculated as a number of deposits per filament.

After the blood sample from a fish was drawn, subsamples were taken from it immediately for the haematocrit reading (centrifuged by Heraeus Haemofuge A 12,000 rpm for 3 min) and pipetted for the determinations of haemoglobin, glucose and lactate concentrations. The rest of the blood was centrifuged (Beckman Microfuge B; 11,600 rpm for 1.5 min) twice to separate plasma and the blood cells. Plasma was preserved in liquid nitrogen until analysed. Blood haemoglobin concentration was determined as cyanmethaemoglobin, glucose and lactate concentrations by Boehringer Mannheim GmbH test kits No 124 028 and No 124 842, respectively. Plasma total protein concentration was determined by the biuret method, calcium and magnesium concentrations by Wako test kits (Wako Chemicals GmbH), sodium by flame photometry (Flame Photometer FLM3, Radiometer), and chloride by coulometric titration (chloride titrator, Radiometer CTM 10).

One-way ANOVA was applied to test the effect of the treatments, and the differences between means were tested successively by Scheffe's test at the 95% level. The effects of pH and aluminium were tested by two-way ANOVA. Statistical Analysis System (SAS 1985) was used to perform statistical calculations.

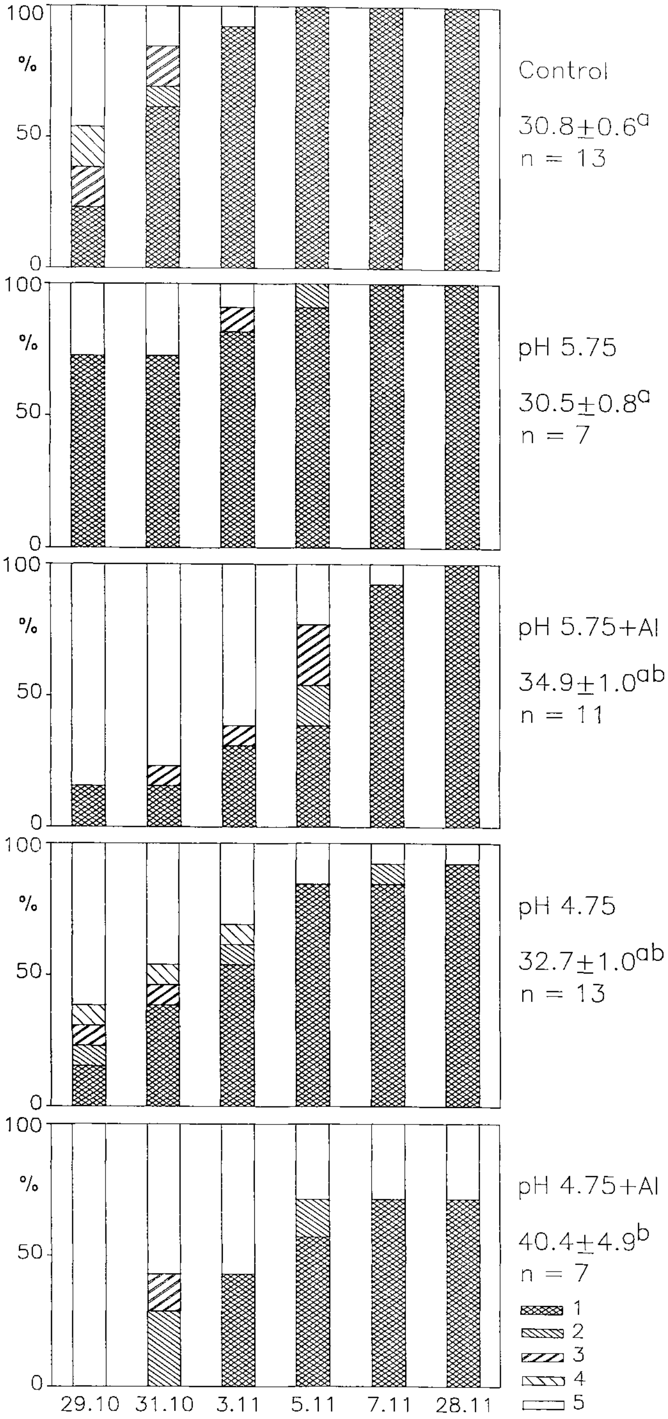
Results and Discussion

Reproduction

Ovulation was significantly delayed in the group pH 4.75 + Al and somewhat as well in the groups pH 5.75 + Al and pH 4.75 (Fig. 1). Thus acidity alone seemed to have only a slight effect, but aluminium combined with low pH delayed ovulation clearly. In the group pH 4.75 + Al the delay was, on the average, 10 days. One whitefish female in the group pH 4.75 + Al died about 2 weeks and one about 4 weeks after the beginning of stripping. In addition, one female in the group pH 4.75 died after 1 week. Only a fraction of the ova in these females had ovulated. In the control group all the females matured in a week. In rainbow trout exposed for 6 weeks to pH 4.5, only partial ovulation had been observed in two fish at sampling when all the fish at higher pH had ovulated (Weiner et al. 1986). Tam and Payson (1986) reported brook trout ovulation occurring 5 days later at pH 4.48 and even about 2 weeks later at pH 5.16 compared to the control group. The proportions of the ovulated females were 69 and 50% respectively against 75% in the control group; however, an outbreak of tail rot disease at pH 5.16 evidently contributed to the extensive delay of ovulation in that brook trout group, as suspected by the authors. The water used in the experiment of Tam and Payson (1986) had a rather high background aluminium concentration (95 $\mu g\, l^{-1}$), and Weiner et al. (1986) did not give any background levels of aluminium in rainbow trout test water. It is therefore possible that aluminium has contributed to the delayed and partial ovulation also in those experiments. Mount et al. (1988b) observed a slight delay in ovulation in brook trout exposed to different combinations of acidity and aluminium and calcium concentrations, but unfortunately, they do not state any numbers concerning delay. In another study of Mount et al. (1988a), brook trout females tended to mature slightly later compared to the control in exposure to aluminium (monomeric, 169 $\mu g\, l^{-1}$) at pH 5 with low water calcium (0.5 mg l^{-1}). In the present study, water calcium concentration was moderately high (0.23 mmol l^{-1}, 9.2 mg l^{-1}) compared to levels usual in acidified waters (approximately 1.5 mg l^{-1} at pH 4.75 and 2.6 mg l^{-1} at pH 5.75; Tuunainen et al. 1988). It remains to be elucidated if the ovulation of whitefish would have been delayed even more if water calcium concentration had been lower. On the other hand, a slight delay of ovulation in brook trout occurred at low pH with elevated aluminium irrespective of water calcium concentration (0.5, 2 or 8 mg Ca l^{-1}; Mount et al. 1988b).

A field study of the spawning of perch in lakes with different degrees of acidification revealed that spawning occurred later in a lake having a low pH (4.5–4.8) with total aluminium concentration of 62–193 $\mu g\, l^{-1}$ and water calcium 0.4–1.6 mg l^{-1} (Rask et al. 1990). More extensive delay, even about 1 month, was found in perch spawning in a lake having very high total aluminium concentration (275–580 $\mu g\, l^{-1}$) and low pH (ca. 4.5) with water calcium 1.2–2.0 mg l^{-1} (Tuunainen et al. 1987). Earlier, Beamish et al. (1975) reported that fish had not released their eggs in acidified lakes when studied after the normal spawning time. However, it remains unresolved if the spawning of those fish had only been delayed, because they were examined only on one occasion.

There were no significant differences in the amount of eggs produced per female whitefish between the groups, although the amount was smallest in the group pH 4.75 + Al (Table 3). The numbers of female per group in this calculation were small, because only those females that were supposed to give all their eggs at stripping were included. There were no significant differences between the groups in the fresh weight or water content of unfertilised eggs either, but the egg dry weight in the groups pH 5.75, pH 4.75 and pH 4.75 + Al was significantly smaller than in the control (Table 3). The small amount and small size of eggs in the group pH 4.75 + Al suggest perhaps some disturbance in vitellogenesis in this group,


100
%
50
0
Control
30.8±0.6a
n = 13
pH 5.75
30.5±0.8a
n = 7
pH 5.75+Al
34.9±1.0ab
n = 11
pH 4.75
32.7±1.0ab
n = 13
pH 4.75+Al
40.4±4.9b
n = 7
1
2
3
4
5
29.10
31.10
3.11
5.11
7.11
28.11

supported by the fact that the liver index (LSI) of female whitefish in this group was smallest, approximately the same size as in males (Table 4). Liver size increases in female fish during vitellogenesis because yolk protein (vitellogenin) is synthesised in liver (Mommsen and Walsh 1988), but in addition to the reproductive cycle, liver size can be affected by the feeding status (Gingerich 1982). In warm-water flagfish, both primary and secondary yolk deposition were strongly inhibited at pH 5.5 and below that (Ruby et al. 1977). Mount et al. (1988b) did not observe any relation between water quality (acidity, aluminium and calcium) and egg size or egg numbers per body weight, although fecundity was reduced. In that study reduced fecundity was attributed to decreased growth. In a field study, perch fecundity was not found to be related to the stage of acidification of a lake (Lappalainen et al. 1988).

Lowest percentage hatches in whitefish were recorded in the groups pH 4.75 and pH 4.75 + Al; however, mean hatching percentages were rather low in all groups, and no significant differences existed due to large within-group variation (Table 5). Hatched sac fry in the control and in the group pH 5.75 + Al were significantly bigger in weight and length than in the other groups (Table 5), as expected on the basis of bigger dry weights of eggs for these same groups (Bagenal 1969). Mount et al. (1988b) did not find any effect on brook trout egg viability (survival to hatch) in exposure to different acidity and aluminium and calcium concentrations. On the contrary, Menendez (1976) reported that brook trout egg viability (determined as development until the gastrula stage) was reduced significantly at pH 5.0 compared to the control. In that study, brook trout were allowed to spawn in the exposure basins so it was possible that, for example fertilisation was

Table 3. The mean (± SE) percentage weight of eggs produced per the body weight of female (= amount of eggs, %) and the mean (± SE) fresh and dry weight of eggs and their water content. Number of females in parenthesis. The different letter as a superscript indicates that the mean values differ significantly ($p < 0.05$)

	Control	pH 5.75	pH 5.75 + Al	pH 4.75	pH 4.75 + Al
Amount of eggs, %	21.8 ± 3.6^a (6)	20.7 ± 14.5^a (2)	20.9 ± 3.8^a (8)	22.5 ± 6.8^a (3)	16.5 ± 7.7^a (3)
Fresh weight, mg	6.5 ± 0.5^a (8)	5.7 ± 0.7^a (3)	6.9 ± 0.3^a (8)	6.1 ± 0.4^a (6)	5.3 ± 0.2^a (5)
Dry weight, mg	2.0 ± 0.1^a (8)	1.6 ± 0.1^b (3)	2.2 ± 0.1^a (8)	1.7 ± 0.1^b (6)	1.6 ± 0.1^b (5)
Water content, %	69.3 ± 0.4^a (8)	72.1 ± 1.4^a (3)	68.0 ± 1.9^a (8)	72.1 ± 1.2^a (6)	69.7 ± 0.2^a (5)

◁ **Fig. 1.** The proportions of spawned or stripped (*1*), partly spawned (*2*), ready-to-strip (*3*), partly unovulated (*4*) and unovulated (*5*) females of each exposure group at dates when stripping was tried or at the final sampling date (28 November). The nominal pH values are given and *Al* signifies to 150 $\mu g l^{-1}$ total aluminium added. The mean (±SE) ovulation time in days from 1 October is given and the *different letter as a superscript* indicates significant ($p < 0.05$) difference between treatments

Table 4. The mean (± SE) weight, total length, condition factor and proportional weight of liver (LSI, %) of female and male whitefish at sampling, 3 weeks after the end of stripping, at the end of 143-d exposure. The specific rate of increase in weight (G_W % d^{-1}) and length (G_L % d^{-1}) was calculated from the final and initial (Table 1) mean weights and lengths in each treatment. The different letter as a superscript indicates that the mean values differ significantly between the treatments ($p < 0.05$). The mortality figures represent the total mortality of fish in each treatment during the whole exposure

	Control	pH 5.75	pH 5.75 + Al	pH 4.75	pH 4.75 + Al
Mortality, %	2.5	10.0	12.5	2.5	17.5
Females					
Length, cm	28.7 ± 0.5^{a}	27.5 ± 1.1^{a}	28.5 ± 0.6^{a}	27.8 ± 0.7^{a}	27.4 ± 0.7^{a}
Weight, g	218 ± 15^{a}	181 ± 24^{a}	191 ± 13^{a}	180 ± 16^{a}	164 ± 15^{a}
CF	0.90 ± 0.03^{a}	0.82 ± 0.02^{b}	0.81 ± 0.02^{b}	0.81 ± 0.02^{b}	0.79 ± 0.02^{b}
LSI, %	1.51 ± 0.08^{a}	1.45 ± 0.08^{a}	1.34 ± 0.05^{a}	1.41 ± 0.07^{a}	1.29 ± 0.11^{a}
N	13	11	13	12	4
$G_W\%\ d^{-1}$	0.466	0.368	0.405	0.344	0.292
$G_L\%\ d^{-1}$	0.149	0.107	0.135	0.130	0.110
Males					
Length, cm	27.2 ± 0.4^{a}	27.4 ± 0.4^{a}	27.9 ± 0.7^{a}	27.8 ± 0.3^{a}	28.0 ± 0.5^{a}
Weight, g	183 ± 8^{a}	180 ± 9^{a}	200 ± 14^{a}	181 ± 8^{a}	196 ± 14^{a}
CF	0.91 ± 0.02^{a}	0.87 ± 0.01^{ab}	0.92 ± 0.03^{a}	0.84 ± 0.02^{b}	0.87 ± 0.02^{ab}
LSI, %	1.25 ± 0.06^{a}	1.16 ± 0.07^{a}	1.26 ± 0.07^{a}	1.14 ± 0.06^{a}	1.26 ± 0.05^{a}
N	15	15	6	13	17
$G_W\%\ d^{-1}$	0.343	0.364	0.437	0.348	0.417
$G_L\%\ d^{-1}$	0.111	0.104	0.120	0.130	0.126

Table 5. The mean (± SE) hatching percentage and mean length and fresh weight of sac fry from female whitefish exposed for 143 days at given treatments before spawning time. Number of observations in parenthesis. The different letter as a superscript indicates that the mean values differ significantly ($p < 0.05$)

	Control	pH 5.75	pH 5.75 + Al	pH 4.75	pH 4.75 + Al
Hatch-%	36.7 ± 18.7^{a} (4)	45.2 ± 8.9^{a} (2)	64.3 ± 12.8^{a} (8)	19.8 ± 6.8^{a} (5)	29.5 ± 17.4^{a} (4)
Length, mm	11.9 ± 0.1^{a} (71)	11.0 ± 0.1^{b} (21)	12.0 ± 0.1^{a} (112)	11.0 ± 0.1^{b} (32)	10.9 ± 0.3^{b} (32)
Weight, mg	7.7 ± 0.1^{a} (71)	5.5 ± 0.1^{b} (21)	7.5 ± 0.1^{a} (112)	5.7 ± 0.1^{b} (32)	5.7 ± 0.2^{b} (32)

affected. The whitefish egg fertilisation rate decreased in very soft water at pH 5.0 and below that (Tuunainen et al. 1989).

Regression of testes was delayed in acid water and aluminium augmented this effect. When fish were sampled 3 weeks after stripping was finished, plenty of milt was still running from most of the males in the group pH 4.75 + Al and from many in the group pH 4.75. Then the proportions of males with milt in the testes were in these groups 100 and 85%, respectively, against 13% in the control, 20% in the group pH 5.75 and 33% in pH 5.75 + Al. The proportional weight of testes of

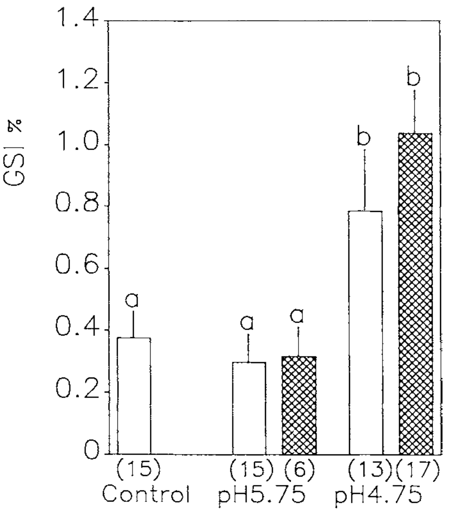


Fig. 2. The proportional weight of testes of whitefish males at the end of 143-d exposure, 3 weeks after the end of stripping. The *shaded columns* represent treatments with 150 μg $Al l^{-1}$ added and *blank columns* treatments without aluminium. The *vertical bar* indicates standard error of the mean and the *different letter above the bar* indicates significant ($p<0.05$) difference between the means. The number of observations is *in parenthesis*

males in the pH 4.75 groups were significantly bigger than in the other groups, and biggest testes were detected in the group pH 4.75 + Al (Fig. 2). The delay in regression of testes might, partly at least, result from the delay in ovulation. Pheromones probably mediate information of ovulation to males to induce spawning. In goldfish (*Carassius auratus*) the presence of ovulatory females was necessary for males to exhibit a normal gonadotropin surge and spawning (Kobayashi et al. 1986). Although whitefish were stripped, they also spawned by themselves. Evidently, spawning began later in basins where females matured later and therefore regression of testes in these basins perhaps got started later as well. However, it requires elucidation whether acidity and aluminium exposure have direct effects on spermatogenesis and/or regression of testes. Tam and Payson (1986) did not observe any delay of sperm production in brook trout exposed at pH levels of 4.48–5.56. In flagfish, production of sperm was reduced at pH levels 4.5–6.0 compared to pH 6.7 (Ruby et al. 1978).

Growth

The weight of the whitefish females at the end of the 143-d exposure was smallest in the group pH 4.75 + Al, but, due to a wide individual variation and especially the small number of females in the group pH 4.75 + Al, the differences were not significant (Table 4). The length and weight of males and the length of females in the exposure groups were of about the same magnitude as in the control (Table 4). Exposed females were leaner then control females, which can be seen in significantly lower condition factors in all the exposure groups. In males, the condition factor of only the group pH 4.75 was significantly smaller than in the control and in the group pH 5.75 + Al (Table 4). The acid exposure diminished whitefish growth ($p < 0.05$; two-way ANOVA) as was back-calculated from scales, males and females combined. Aluminium exposure at the pH 4.75 decreased growth even more but increased it somewhat at pH 5.75 ($p < 0.05$; two-way ANOVA; Table 6). The specific rates of increases in weights revealed that aluminium exposure at pH 4.75 decreased weight gain drastically only in females (Table 4). Apparently the energy costs for the production of eggs in females under exposure to stress had diminished the energy available for growth, or there may have been differences in feed intake between exposed females and males although that was not detected. Mount et al. (1988b) observed that adult brook trout in severe acidity plus aluminium exposures left most of the offered feed uneaten. In a study of Tam and Payson (1986), the body weights of both male and female brook trout at pH 5.16 and 4.48 (background aluminium concentration 95 $\mu g\, l^{-1}$) were smaller than in the control at the end of a 10-month exposure. According to Mount et al. (1988a, b), reduction in growth of adult brook trout was related only to aluminium and calcium concentrations at low pH levels, and although the effect of calcium was significant, aluminium accounted more for the effect.

In the 15 lakes that our test fishing survey revealed as having whitefish populations, in those lakes with pH > 5.5, the mean lengths of whitefish at age tended to be higher than in those with pH < 5.5 (Rask et al. 1988). On the contrary, the growth of juvenile whitefish, stocked as one-summer-olds, was better in an acidified lake (pH ca. 4.6, total aluminium ca. 180 $\mu g\, l^{-1}$ and water calcium 1.4 $mg\, l^{-1}$) than in a circumneutral lake that had a fairly dense perch population in addition to a population of older whitefish (Tuunainen et al. 1988). Comparison of growth data from lakes with those from laboratory experiments is obscured by the fact that lakes usually have several and different fish populations so that competition and predation pressures affect the growth of fish in lakes in complex ways.

Blood and Plasma Parameters

After 143-d exposure, the plasma chloride and sodium concentrations of both female and male whitefish were significantly lower and blood glucose concentration higher in the groups pH 4.75 and pH 4.75 + Al than in the control (Figs. 3 and 4). Decreases in plasma sodium and chloride concentrations are well-documented responses in fish experiencing acid stress (e.g. Leivested and Muniz 1976; Muniz and Leivested 1980). In rainbow trout females exposed to acidity for

Table 6. The mean (± SE) growth increment of whitefish during the 143-d exposure as back-calculated from scales (females and males combined). The different letter as a superscript indicates that the mean values differ significantly ($p < 0.05$)

	Control	pH 5.75	pH 5.75 + Al	pH 4.75	pH 4.75 + Al
Growth, cm	6.9 ± 0.4^{ab}	6.5 ± 0.4^{ab}	7.6 ± 0.5^{a}	6.7 ± 0.4^{ab}	5.4 ± 0.3^{b}
N	27	22	16	24	22

42 d, the plasma sodium concentration was lowered only at pH 4.5 of the tested (4.5, 5.0 and 5.5), compared to the control (Weiner et al. 1986). Brook trout females, exposed for 193 d to aluminium at low pH and low water calcium (pH 5.0, monomeric aluminium 169 $\mu g\,l^{-1}$ and calcium 0.5 mg l^{-1}) before spawning, showed lower plasma sodium concentration compared to the control, but low pH exposure alone did not affect this parameter (Mount et al. 1988a). Elevated blood glucose indicates stress in general (e.g. Wedemeyer and McLeay 1981), but it might also be a response to try to maintain plasma osmolality when plasma ion concentrations decline (McDonald 1983; Scherer et al. 1986). In lake whitefish, plasma glucose concentration was greatly elevated in exposure for 2 weeks to the most acidic (pH 4.1 and 4.4) waters but not at pH 4.7 and 5.0 (Scherer et al. 1986). Extremely low plasma sodium and chloride concentrations and high blood glucose concentration in females in the group pH 4.75 + Al (Figs. 3 and 4) suggest that exposure to aluminium at pH 4.75 had stressed whitefish females more than males. In whitefish females, the mean plasma sodium concentration at pH 4.75 + Al was 26% and the chloride concentration 24% smaller than in the control, and in males 19% and 20%, respectively. According to Wood and McDonald (1987), death of brook trout was preceded by a 35% decrease in plasma sodium and chloride levels. In the present study, the greatest mortality of whitefish (17.5%; four females and three males) occurred in the exposure to aluminium at pH 4.75 (Table 4).

There were no significant differences between groups in plasma magnesium concentrations either in whitefish females or males (Figs. 3 and 4). The plasma calcium concentration of females tended to be lower (Fig. 3) in those groups where ovulation was delayed, but differences were not significant because of a wide individual variation. Coefficients of variation were greatest in the group pH 4.75, 40.9% and in the group pH 4.75 + Al, 37.3 against 24.9% in the control. Similarly, Weiner et al. (1986) detected wide variation in plasma calcium in rainbow trout females at spawning time after 42-d exposure to pH 4.5 in soft water. In brook trout females, after 193-d exposure to aluminium at low pH and low water calcium (pH 5.0, monomeric aluminium 169 $\mu g\,l^{-1}$ and calcium 0.5 mg l^{-1}), plasma calcium concentration was significantly lower compared to the control at the end of stripping, and in this same group the maturation of eggs was slightly delayed (Mount et al. 1988a). Beamish et al. (1975) found serum calcium concentrations of female fish in acidic lakes to be lower than in circumneutral lakes around spawning time, and attributed the disturbed calcium metabolism of females to the inability to release eggs. Vitellogenin binds calcium ions, necessary for vitellogenin to be transported via the blood flow from the liver to be deposited in oocytes during exogenous vitellogenesis (Ng and Idler 1983). Disturbances in calcium metabolism may thus interfere with exogenous vitellogenesis that could be expected to appear as lower numbers and/or smaller sizes of eggs. As discussed above, such effects seemed to appear in the present study, although this could not be confirmed statistically. The sampling was performed about 3 weeks after stripping, so vitellogenesis was already over when plasma calcium levels were measured. Further studies are needed to clarify the physiological mechanisms

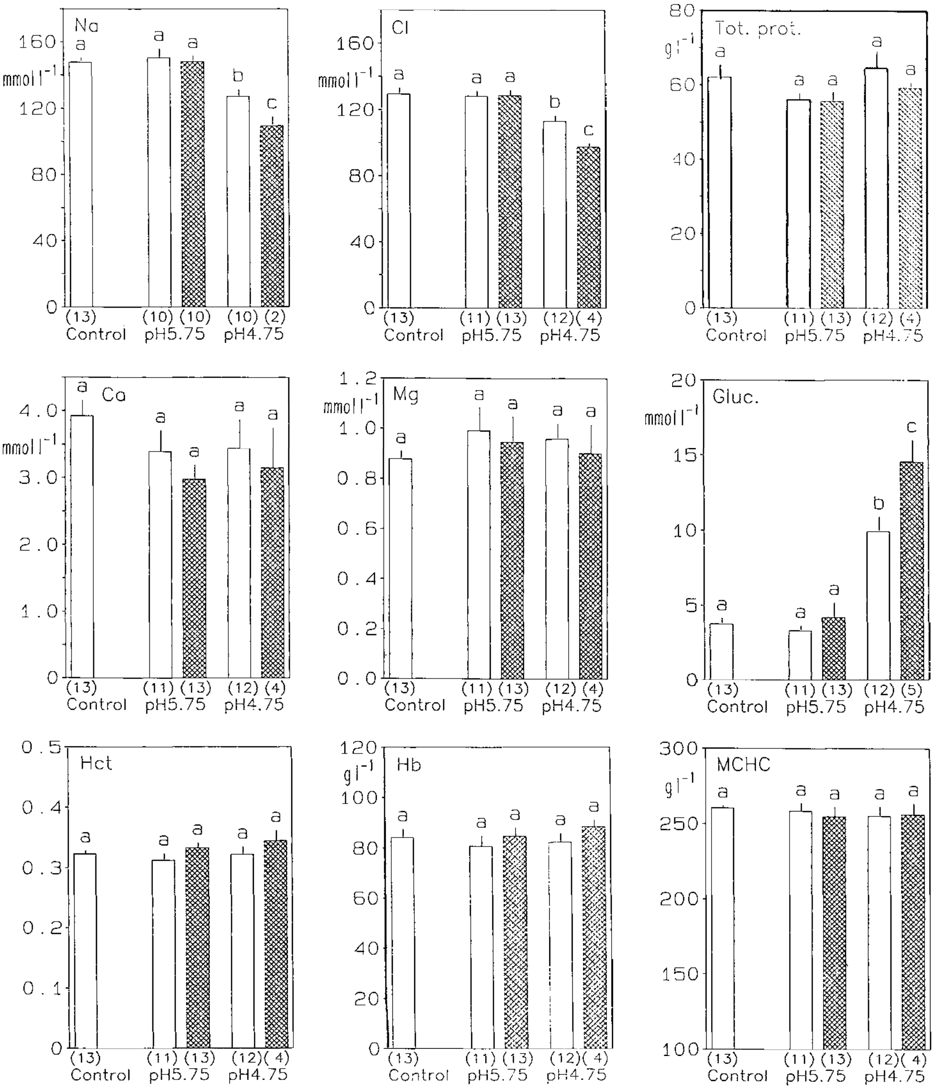


Fig. 3. The blood and plasma variables of female whitefish at the end of 143-d exposure, 3 weeks after the end of stripping: the mean (±SE) plasma sodium (*Na*), chloride (*Cl*), total protein (*Tot. prot.*), calcium (*Ca*) and magnesium (*Mg*) concentration and blood haematocrit value (*Hct*) and haemoglobin (*Hb*), mean corpuscular haemoglobin (*MCHC*) and glucose (*Gluc.*) concentration. Symbols used are the same as in Fig. 2

behind the delayed ovulation; possibly disturbances in vitellogenesis and/or in the hormone-mediated processes of ovulation.

In haematological values of whitefish females, there were no significant differences between the groups (Fig. 3). In accordance, Mount et al. (1988a) did not find 193-d acid plus aluminium exposure to affect brook trout female blood haematocrit value. In whitefish males, blood haematocrit values were significantly higher in

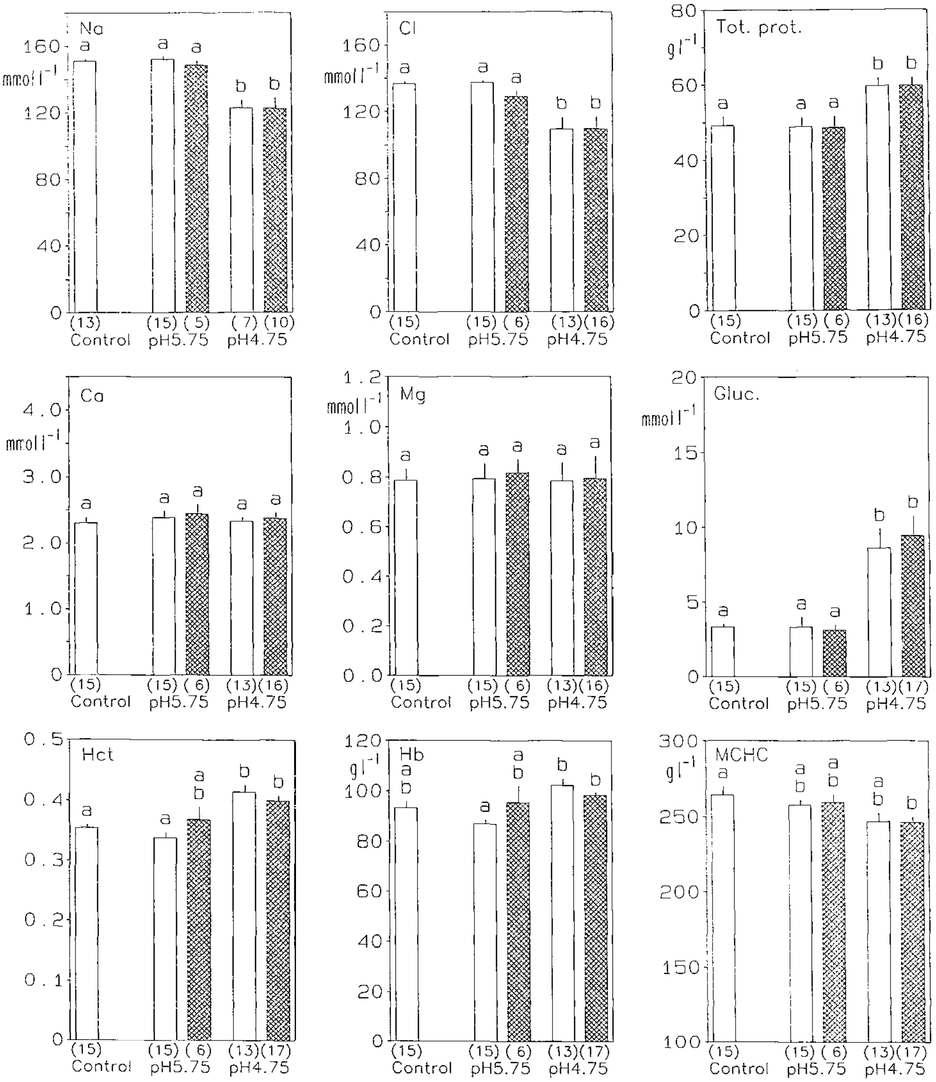


Fig. 4. The blood and plasma variables (see Fig. 3.) of male whitefish at the end of 143-d exposure, 3 weeks after the end of stripping. Symbols used are the same as in Fig. 2

the groups pH 4.75 and pH 4.75 + Al than in the control group and haemoglobin concentrations tended to be higher. MCHC was significantly smaller in the group pH 4.75 + Al than in the control and plasma total protein concentration was significantly higher in the pH 4.75 groups (Fig. 4). Elevated plasma protein levels as well as increased blood haematocrit value together with increased haemoglobin concentrations may indicate haemoconcentration (Wedemeyer and McLeay 1981), a response to declined plasma ion concentrations. In that case, the lowered MCHC might result from the release of young erythrocytes, containing less haemoglobin than the older ones (Lehmann and Sturenberg 1975), into the circulation. On the other hand, lowered MCHC, while the haematocrit reading is elevated, indicates the swelling of erythrocytes, a mechanism by which blood oxygen transport capacity is increased (Nikinmaa 1982). This response would suggest that male whitefish experienced slightly hypoxic conditions at pH 4.75. However, there were no significant differences in blood lactate concentrations between the groups.

Gills

On slides stained with an aluminium-specific technique, purple-stained deposits were found in the gill epithelium of the fish that had been exposed in test solutions with aluminium added. Very seldom did deposits occur in the epithelium of secondary lamellae, but were mostly in the epithelium of filament trunk (Fig. 5). The number of deposits per filament was significantly higher ($p < 0.05$) in the gills of fish exposed at pH 4.75 (10.0 ± 1.6; mean ± SE; N = 17) than at pH 5.75 (3.3 ± 0.7; N = 6). Youson and Neville (1987) detected electron-dense particles on and within pavement and chloride cells in rainbow trout gills at pH levels 4.5–6.1 in all aluminium treatments; the X-ray microanalysis showed that these deposits contained aluminium. Aluminium in chloride cells may hinder their normal function and indeed, aluminium has been detected to inhibit gill Na/K-ATPase activity in acidic water (Staurnes et al. 1984).

The number of PAS-positive epithelial cells per secondary lamella was significantly ($p < 0.05$) bigger in the group pH 4.75 + Al (2.5 ± 0.5; N = 7) than in the control (1.6 ± 0.2; N = 9) and aluminium increased the number of PAS-positive cells at pH 4.75, but decreased it at the pH 5.75 ($p < 0.05$; two-way ANOVA). In addition to the hypertrophy of the gill epithelial cells, increased gill mucus production was also observed when farmed brown trout were exposed to acidic (pH 5.8)

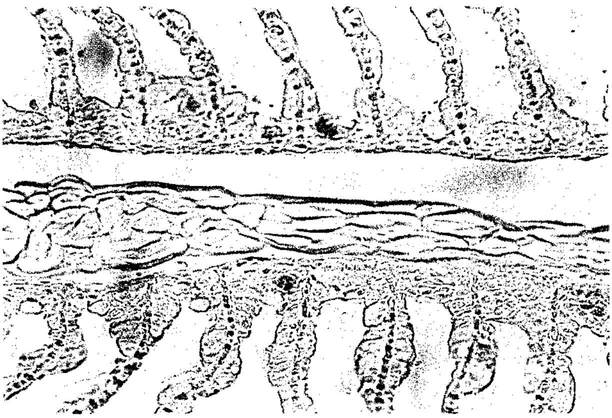


Fig. 5. Gill section of male whitefish exposed for 143-d at pH 4.75 with aluminium (150 $\mu g\,l^{-1}$) showing deposits stained purple with a technique specific for aluminium (Havas 1986). The extensive hypertrophy of epithelial cells at the base of secondary lamellae is also seen

aluminous (Al_{tot} 216 µg l^{-1}, Al_{lab} 80 µg l^{-1}) water (Karlsson-Norrgren et al. 1986b). The amount of mucus on the gills of whitefish was not detected at sampling, but the increased amount of PAS-positive cells, possibly being mucous cells (Daye and Garside 1980), in the pH 4.75 + Al suggest that these fish secreted more mucus than fish in the control group. Hughes (1985) proposed that the stress-induced mucus production might be protective of the fish because of the aluminium binding properties of mucus, i.e. the irritating aluminium would be washed away with mucus. There was, however, no correlation between the aluminium deposits and the amount of PAS-positive cells in gills of whitefish when each fish was screened individually.

Cell hypertrophy at the base of secondary lamellae as well as in the filament epithelium was prominent in the group pH 4.75 + Al (Fig. 5) and to a little lesser extent in the group pH 4.75. On the other hand, aluminium did not increase hypertrophy at pH 5.75. Hypertrophied chloride cells have been reported to appear when brown trout (Karlsson-Norrgren et al. 1986a) and rainbow trout (Youson and Neville 1987) were exposed to acid water and aluminium. Leino and McCormic (1984) concluded that hypertrophy of chloride cells in gills of fathead minnow could amplify the surface area of chloride cells for improved Na^+ and Cl^- uptake. Increased diffusion distance caused by the hypertrophy of epithelial cells in gill lamellae may, in turn, hinder the diffusion of oxygen between water and blood (Tietge et al. 1988). The high haematocrit together with low MCHC in the acid-aluminium exposed whitefish males suggests that fish were subjected to less effective gas exchange. The apparent increase in the diffusion distance in the gills of whitefish was not quantified, but even so, the changes observed in the gill epithelium were consistent with toxicological and physiological effects caused by low pH and aluminium.

Conclusions

The increase in blood glucose and decrease in plasma sodium and chloride concentrations were the most conspicuous changes in blood chemistry in whitefish under long-term exposure to water comparable to that in acidified lakes. At pH 4.75 without aluminium these effects were pronounced and, at this pH level with aluminium, were even more prominent in females. This was evidently due to the reproduction stress making females more sensitive. That was also seen as decreased growth. Above all, preparing to spawn or spawning of fish coincides with the worst conditions in respect to acidic deposition: in the autumn during heavy rains and in the spring after snow melting. Exposure at low pH to aluminium may affect calcium metabolism and vitellogenesis in females. Whether the disturbed calcium metabolism is the reason for the delayed ovulation and delayed spawning of fish requires elucidation. Delayed regression of testes might result from delayed ovulation through pheromone action from ovulatory females, but direct effects of acidification on male reproductive physiology is not excluded.

Delay of spawning is apparently one mechanism by which acidification affects the survival of fish populations, especially the ones that spawn in spring time. In the spring, waters warm up rapidly and delayed spawning might then lead to temperatures too high for successful embryonic development and fry survival. Delayed spawning, if resulting in viable fry, might also shorten the growth period of fry and thus decrease chances to survive over the winter. Because of delayed ovulation and delayed regression of testes, the beginning of the next oogenesis and spermatogenesis is most likely postponed. In addition to causing the delay of spawning, acidity and aluminium also affect detrimentally the fertilisation of eggs and the early life stages of fish, thereby decreasing fish populations.

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Macrophytes in Finnish Forest Lakes and Possible Effects of Airborne Acidification

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Summary

Macrophytes in 71 lakes were surveyed in 1984–1986 as part of the biological survey of the Finnish Research Project on Acidification. The aim was to obtain information on the macrophyte composition of lakes susceptible to acidification and the possible effects of lake water acidification on macrophytes. The acidic lakes differed from the circumneutral lakes in species composition, but in most lakes the composition was influenced more by factors such as lake morphometry and trophic status than by acidity itself. *Sphagnum* mosses had invaded some lakes as a consequence of acidification, but there were no other obvious acidophilic species. *Juncus bulbosus* was abundant in one very acid lake ($pH < 5.0$) only. Suppression of isoetids could not be assessed because of the lack of earlier vegetation data, but it may have happened in some lakes. Most elodeids were absent from the acidic lakes, and one species, *Myriophyllum alterniflorum*, may have suffered from acidification.

Introduction

Macrophyte surveys in acidic lakes have shown clearly that the aquatic vegetation of many poorly buffered water bodies has changed because of acidification. A common feature in European lakes has been the abundant growth *Sphagnum* moss (Raven 1988) and *Juncus bulbosus* (Nilssen 1980; Melzer and Rothmeyer 1983), which have in some cases suppressed the isoetid vegetation (Roelofs 1983; Grahn 1986). In the Netherlands the water bodies studied have been small, shallow and highly acidic (often $pH < 4.0$) due to high deposition of ammonium, and under these circumstances the changes in macrophyte communities have been even more drastic. Not only the isoetids but also the lemnids, ceratophyllids, nymphaeids and elodeids have disappeared in some pools, and nowadays only *Juncus bulbosus* and *Sphagnum* mosses are found in many cases, while there are some that have lost all their macrophytes (Arts and Leuven 1988).

The aim of this survey was to study the macrophytes in Finnish lakes which are susceptible to acidification in order to obtain information on their aquatic vegeta-

Kauppi et al. (Eds).
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tion and trends which might be similar or dissimilar to those pointed out elsewhere in Europe.

Material and Methods

Macrophytes in a total of 135 lakes were surveyed during July to mid-September 1984–86 as part of the biological lake survey of the Finnish Research Project on Acidification. Of these lakes 71 were studied thoroughly, and in the others the aquatic vegetation was estimated along a couple of transects. Since comparison of the methods showed that the most reliable results were obtained when lakes were studied in detail (Heitto 1989), the results for these 71 lakes are presented here. Most of them are situated in southern and central Finland.

Samples for surface water chemistry were taken both at the same time as the botanical survey was made (July–September 1984–86) and in autumn 1987, during the overturn in the water. The chemical data from 1987 [conductivity, pH, Gran-alkalinity, colour, TOC, COD, base cations, total nutrients (P, N), NO_3, NH_4, SiO_2, SO_4, reactive aluminium] are used here as they allow better comparisons between the lakes. For the analytical methods, see Forsius et al. (this Vol.).

The lakes selected were almost entirely headwater lakes where exposed bedrock was the most common substrate type in the catchment areas, followed by till, sand, peatland and clay. They were on average quite small (median area 16 ha, range 0.6–201 ha), and their water was clear (median colour value 30, range 0–200, median TOC 5.2 mg l^{-1}, range 0.5–17.2 mg l^{-1}), oligotrophic (median total phosphorus 10 μg l^{-1}, range 2–110 μg l^{-1}), poorly buffered (median alkalinity 5 μeq l^{-1}, range -16–490 μeq l^{-1}) and acidic (median pH 5.5, range 4.5–7.5). In a statistically selected material of 988 Finnish lakes of area less than 10 km^2 the median size was 9.2 ha, median pH 6.3 and median colour value 100 (Forsius et al. this Vol.), so that in this sense the present lakes were not representative of their size class. The median maximum depth of the lakes was 9.0 m (range 0.6–42.0 m).

Macrophytes in the 71 lakes were studied from a boat by means of a viewing box and a rake. A rough estimate of the abundance of the taxa was recorded on a scale of 1 to 5 (1 = rare, 2 = occasional, 3 = frequent, 4 = common, 5 = abundant), and the taxa identified were recorded on vegetation maps. The macrophytes dealt with here comprise lemnids, ceratophyllids, isoetids, nymphaeids, elodeids and helophytes and also *Sphagnum* mosses. Mosses other than *Sphagnum* and macroalgae were not included. To avoid errors in identification *Sphagnum* spp., *Sparganium* spp., *Nymphaea* spp, *Callitriche* spp., *Utricularia* spp. and *Isoetes* spp. were not designated to species.

The lakes were divided into five botanical types. The classic categorization of Finnish lakes on the basis of their aquatic macrophyte vegetation proposed by Maristo (1941) did not suit this lake group very well, mainly because these lakes were on average smaller than those studied by Maristo. Rintanen (1982) surveyed

484 lakes in Finnish Lappland to elaborate and extend Maristo's classification, and these were more similar to the present lakes. The five lake types recognized here are:

1. Nuphar lakes (n = 21, pH = 5.1 ± 0.4 (mean ± standard deviation), alkalinity = -1 ± 37 μeq l^{-1}, colour value = 75 ± 63). This was botanically the poorest lake group. They had some nymphaeids (*Nuphar lutea*, *Nymphaea* spp, *Sparganium angustifolium*), some sparse helophytes (*Phragmites australis*, *Equisetum fluviatile*, *Lysimachia thyrsiflora*) and almost all (17 out of 21) had some *Sphagnum* spp. Most of them represented the clearwater variants described by Rintanen (1982). Although Rintanen excluded lakes with isoetids and *Potamogeton natans* from the clearwater variants, six lakes with a rare isoetid vegetation and four lakes with rare *P. natans* were included here.
2. Lobelia lakes (n = 25, pH = 5.5 ± 0.5, alkalinity = -2 ± 29 μeq l^{-1}, colour value = 20 ± 21). Lobelia lakes are clearwater lakes usually situated on sandy soils. They have a dense isoetid (*Lobelia dortmanna*, *Isoetes* spp.) vegetation. *Juncus bulbosus* was encountered in half of them, and *Myriophyllum alterniflorum* in five, but no other elodeid species was present. *Sphagnum* occurred in ten lakes, and helophytes (*P. australis*, *E. fluviatile*) were abundant in some cases.
3. Equisetum lakes (n = 8, pH = 5.6 ± 0.3, alkalinity = 8 ± 17 μeq l^{-1}, colour value = 54 ± 21). Helophytes (*P. australis*, *E. fluviatile*) form denser stands in this lake group than in the Nuphar lakes. Isoetids form scattered patches, and elodeids are almost totally lacking. *Sphagnum* spp. grew in five out of the eight lakes.
4. Equisetum-Phragmites lakes (n = 5, pH = 6.1 ± 0.4, alk. 70 ± 29 μeq l^{-1}, colour value = 63 ± 15). These lakes are better buffered than types 1–3, and they have denser stands of helophytes than the Equisetum lakes. Isoetids were quite common. The nymphaeid *Potamogeton natans* was encountered in three lakes. Elodeids were lacking in two, and the number of elodeid species was relatively low. *Sphagnum* had only a rare occurrence in the littoral zone of one lake.
5. Eutrophic lakes (n = 12, pH = 6.7 ± 0.4, alk. = 206 ± 135 μeq l^{-1}, colour value = 65 ± 59). This is a composite type including some of the eutrophic lake types described by Maristo (1941). These lakes are very well buffered. There were many elodeids (*Potamogeton* species, *Elodea canadensis*) and meso-eutrophic and eutrophic helophytes (*Typha angustifolia*, *Sagittaria sagittifolia*, *Alisma plantago-aquatica*, *Iris pseudacorus*), but no *Sphagnum*.

This classification was not used in order to compare the results with the work of Maristo (1941) and Rintanen (1982), since the survey was not detailed enough to give results of a kind required for an accurate lake typology. The classification merely gives an impression of the natural differences between the lakes, e.g. the bottom of the littoral zone in Lobelia lakes is often sandy, whereas that in Nuphar lakes is very soft. The slope may also be typical of a particular lake group, e.g. Nuphar lakes are often steep-sided, with a narrow littoral zone.

Ordination analysis of vegetation data was performed using detrended correspondence analysis (DCA). Those species, occurring in less than three lakes, were assigned negligible weight in the ordination. Detrending was performed by segments. To interpret the DCA axis, Pearson correlations were calculated between the axis and a variety of environmental variables (e.g. water chemistry, features of the catchment area).

The weighted average and weighted standard deviation of pH were calculated for all taxa occurring in more than two lakes (for equations, see Huttunen and Turkia this Vol.).

Results and Discussion

The lakes mostly represent oligotrophic types, while the botanical lake types can be separated quite easily in the DCA ordination diagram, the floristically poorest types Nuphar, Equisetum, Lobelia being located on the right-hand side and the more eutrophic ones on the left (Fig. 1). The first DCA axis showed a highly significant negative correlation with pH, alkalinity, base cations, silica and conductivity, and the second with TOC, colour, silica, sodium, sulphate, labile aluminium and conductivity (Table 1). The first axis accounted for 54% of the variation explained by the first four axes and the second for 28%.

Since alkalinity, base cations, and conductivity correlated positively and highly significantly with pH (Table 1), the first DCA axis was interpreted as representing acidity. The highly significant positive correlation of the first axis with the total coverage of exposed bedrock in the drainage basin and its negative correlation with the area of that basin supports such as interpretation, as acid lakes often have a small catchment area mostly with an exposed bedrock surface (Table 1). Since all the variables which correlated markedly with the second axis were highly positively correlated with lake water colour (Table 1), this was interpreted as the colour axis, although the correlation is much weaker than between acidity and the first axis.

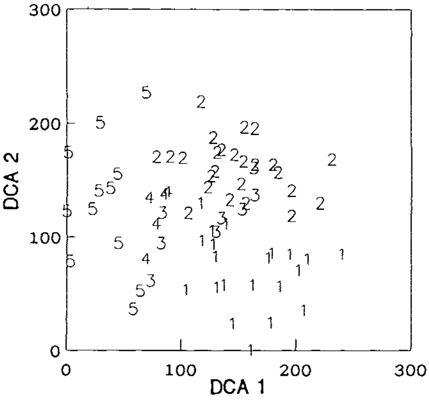

Fig. 1. The DCA ordination diagram of the lakes. *DCA 1* the first DCA axis; *DCA 2* the second DCA axis. *1* Nuphar lakes; *2* Lobelia lakes; *3* Equisetum lakes; *4* Equisetum-Phragmites lakes; *5* Eutrophic lakes

Table 1. Correlation coefficients of the first and the second DCA axis with a variety of environmental variables

Variable	DCA-1	DCA-2	pH	Colour
pH	−0.88***			
Alkalinity	−0.79***		0.83***	
Colour		−0.55***		
Conductivity	−0.49***	−0.43***	0.39***	0.51***
Total nitrogen	−0.28*	−0.37**		0.71***
Nitrate nitrogen	−0.36**	−0.25*		0.43***
Sodium	−0.49***	−0.43***	0.41***	0.50***
Potassium	−0.55***	−0.29*	0.41***	0.42***
Magnesium	−0.57***	−0.29*	0.56***	0.47***
Calcium	−0.67***	−0.34**	0.60***	0.45***
Silica	−0.58***	−0.45***	0.44***	0.60***
Sulphate		−0.42***		0.43***
Labile aluminium	0.34**	−0.46***	−0.47***	0.39***
Total organic Carbon		−0.57***		0.93***
Drainage area	−0.56***		0.41***	
Lake area		0.33**		
Max depth		0.43***		−0.32**
Exposed bedrock[a]	0.45***	−0.26**	−0.31**	
Till[a]				0.31**
Sand[a]	−0.36**	0.34**	0.26*	
Clay[a]	−0.32**	−0.28*		

[a] Proportion of drainage area.

Macrophyte surveys of acidic lakes in other countries performed using multivariate methods have given similar results (Catling et al. 1986; Arts and Leuven 1988; Jackson and Charles 1988), whereas surveys of more circumneutral lakes have shown conductivity to be more important than acidity for explaining floristic differences (Seddon 1972; Crowder et al. 1977).

The total number of taxa decreased markedly along the first DCA axis, i.e. with increasing acidity. The life forms that decreased most were the elodeids and helophytes (Fig. 2) and that which increased most was the *Sphagnum* mosses (Fig. 3).

There are probably two main reasons, which cannot easily be separated, for the absence of elodeids in the acidic lakes. Firstly, many elodeids prefer eutrophic water because of its high nutrient status (P, N, Ca), and secondly elodeids suffer from low inorganic carbon concentrations in acidic water (Roelofs et al. 1984), being unable to utilize inorganic carbon sources from the sediment as effectively as isoetids, for instance. They can withstand short-term acid pulses (Blomdal and Egerhei 1983), but when alkalinity decreases to zero along with lake water acidification, many of them will disappear (see Hinneri 1976).

Most of the ten elodeid taxa recorded here were present in the lakes of the eutrophic type, *Myriophyllum alterniflorum* and *Juncus bulbosus* being the most

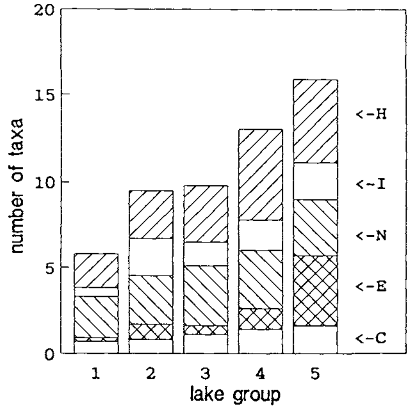

Fig. 2. The mean total number of taxa in different lake groups. *H* Helophytes; *I* Isoetids; *N* Nymphaeids; *E* Elodeids; *C* Ceratophyllids. For explanation of lake groups, see Fig. 1

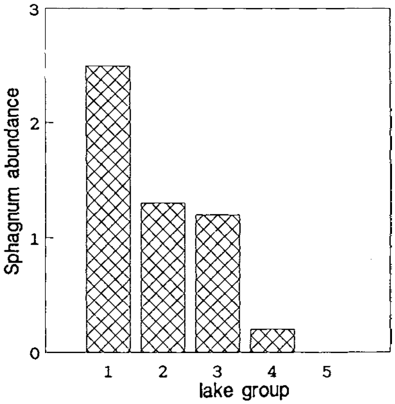

Fig. 3. The mean abundance of *Sphagnum* spp. in different lake groups. For abundance values: *1* rare; *2* occasional; *3* frequent. For explanation of lake groups, see Fig. 1

common elodeid species present in the oligotrophic lakes. *Myriophyllum alterniflorum* has disappeared from acidified lakes in the Netherlands (Arts and Leuven 1988) and in Germany (Melzer and Rothmeyer 1983). In one acid lake the abundance of *Myriophyllum alterniflorum* had decreased between 1984 and 1988, and it seems that the species is at its lower limit with respect to inorganic carbon concentration, and may well disappear without an increase in carbon supply (increase in pH).

Acidification has been found to favour *Juncus bulbosus* especially in the Netherlands (Roelofs 1983). This species was abundant in one of the present zero alkalinity lakes (alkalinity < 0 μeq l^{-1}), frequent in two and occasional in two while it was not recorded at all in 24 such lakes. Thus is could not be regarded as an indicator species for acidic conditions. *J. bulbosus* has been found to favour acidic water in some lakes in Finland (e.g. Aulio 1987), however, so that it would be worth investigating further.

The other life form that tended to decrease in terms of the number of species and abundance with increasing acidity was the helophytes. Almer et al. (1974) state that the helophyte species *Phragmites australis* may have suffered from acidification in Sweden, but the effect of acidification on helophytes is probably a very minor one. In a situation of sudden acidification in western Finland, for example, where the pH of the water dropped from 7.5 to 4.5 over a couple of years due to the oxidation of sulphate-rich deposits in one drainage basin, no effects on helophytes could be observed, even though almost all the elodeids disappeared (Aulio 1987). Similarly *Phragmites australis* was present in a highly acid river in Denmark (Sand-Jensen and Rasmussen 1978). The presence of helophytes depends greatly on the nutrient content of the sediments, so that the lack of helophytes in acidic lakes is obviously because of their natural oligotrophy (low supply of P and N).

Sphagnum spp. was the only macrophyte taxon recognized here that was clearly acidophilic. *Sphagnum* mosses utilize only free carbon dioxide for their inorganic carbon supply, and thrive under acidic conditions, in which all the inorganic carbon is in the form of free CO_2. *Sphagnum* occurred in 38 lakes (pH range 4.5–6.7) and its weighted average was 5.18 (Table 2). *Sphagnum* spp. are very common species on the shores of Finnish forest lakes and belong to the flora of naturally acidic lakes (Maristo 1941). Thus it is quite natural that they will increase along with lake water acidification. Due to a lack of information of the vegetational history of most of the lakes studied here, it is difficult to evaluate *Sphagnum* growth as a consequence of acidification. Earlier vegetation records were available regarding one acidic clearwater lake which now has an abundant growth of *Sphagnum* and *Juncus bulbosus*, and comparison shows that these species are recent elements of the lake flora. Diatom analysis of the sediments has confirmed that the lake has become acidified in the course of time (Tolonen and Jaakkola 1983).

There were some very acid lakes with little or no *Sphagnum* growth, however, and an abundant occurrence of *Sphagnum* was noted in only two lakes. Thus it seems that the *Sphagnum* invasion has not been as strong in Finland as in Sweden, for instance (Grahn 1986).

No suppression of isoetids (*Lobelia dortmanna*, *Isoetes* spp.) because of invasion of *Sphagnum* or other acidophilic species was recorded in the lake from which earlier vegetation data were available, although this may have happened in some lakes. One shallow Nuphar lake (max depth 3.0 m) situated in an esker region has its bottom totally covered with mosses (mostly *Warnstorfia* spp., but also *Sphagnum* spp. in shallow water), and there are a few *Isoetes lacustris* individuals present.

Utricularia species have been found in many acidic lakes (Iversen 1929; Halvorsen 1977; Melzer et al. 1985), and are almost the most abundant species in many such lakes in North America (Roberts et al. 1985). *Utricularia* spp. were abundant in two of the present zero alkalinity lakes, frequent in three and occasional in two, and failed to be recorded in 24 such lakes. Thus these cannot be regarded as indicator species for acidic water in this region.

There is also one nymphaeid and one isoetid species which deserve attention. The nymphaeid species, *Potamogeton natans*, had a rare occurrence in three lakes with $pH < 5.5$, and was otherwise found only in lakes with $pH > 5.7$ (weighted mean pH 6.3 ± 0.6) (Table 2). Halvorsen (1977) also reports that *P. natans* was present only in lakes with $pH > 6.0$, while Melzer and Rothmeyer (1983) quote

Table 2. The weighted averages (pH) and weighted standard deviations (s) of pH of the recorded taxa and the number of lakes (n) in which taxa occurred

	Taxa	n	pH	s
Bryids				
	Sphagnum spp.	38	5.1	0.4
Ceratophyllids				
	Utricularia spp.	26	5.9	0.6
Nymphaeids				
	Nuphar lutea	68	5.7	0.7
	Sparganium spp.	60	5.8	0.7
	Nymphaea spp.	49	5.8	0.6
	Potamogeton natans	21	6.3	0.6
Isoetids				
	Isoetes spp.	44	5.6	0.6
	Lobelia dortmanna	40	5.7	0.6
	Eleocharis acicularis	7	6.2	0.7
	Ranunculus reptans	12	6.5	0.4
Helophytes				
	Lysimachia thyrsiflora	53	5.8	0.7
	Phragmites australis	57	5.9	0.7
	Equisetum fluviatile	45	6.0	0.6
	Spargnium emersum	15	6.1	0.6
	Eleocharis palustris	10	6.1	0.8
	Iris pseudacorus	8	6.3	0.6
	Schoenoplectus lacustris	8	6.3	0.4
	Typha angustifolia	5	6.3	0.4
	Alisma plantago-aquatica	8	6.5	0.5
	Sparganium erectum	3	6.5	0.8
Elodeids				
	Hippuris vulgaris	6	5.9	0.7
	Juncus bulbosus	23	6.0	0.7
	Callitriche spp.	3	6.3	0.5
	Potamogeton gramineus	4	6.4	0.9
	Myriophyllum alterniflorum	17	6.5	0.6
	Ranunculus peltatus	3	6.7	0.8
	Potamogeton berchtoldii	8	6.8	0.2
	Elodea canadensis	6	6.8	0.2
	Potamogeton alpinus	5	6.8	0.4
	Potamogeton perfoliatus	8	6.9	0.3

Seven species that occurred in less than three lakes (*Lemna minor*, *Potamogeton praelongus*, *Littorella uniflora*, *Subularia aquatica*, *Glyceria fluitans*, *Polygonum amphibium*, *Sagittaria sagittifolia*) were excluded from this table.

earlier vegetation records which indicate the disappearence of this species from Kleiner Arberseen, which has become acidified in recent times. *P. natans* may suffer from low inorganic carbon concentrations in acidic water before its floating leaves reach the surface. The isoetid species *Ranunculus reptans* occurred only in lakes with pH > 5.7 (weighted mean pH 6.5) (Table 2). It is a common species in oligotrophic Lobelia lakes, but seems not to tolerate acidic conditions.

Conclusions

Although the species composition of the macrophytes in acidic lakes was different from that in the circumneutral lakes and acidity seemed to explain observed differences very well, the effects of lake water acidification on species composition has probably not been very great. *Sphagnum* mosses have invaded a few lakes as a consequence of acidification, but the invasion has not been as extensive as in Sweden or the Netherlands, for instance. *Juncus bulbosus*, a common species in many acidified lakes, especially in the Netherlands, was abundant in one acidic lake only. Suppression of isoetids as a consequence of *Sphagnum* invasion could not be assessed due to the lack of previous vegetation data, but it may have happened in a few lakes. Elodeids were absent from the acidic lakes, and one oligotrophic elodeid, *Myriophyllum alterniflorum*, may have decreased in a few lakes because of acidification.

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Phytoplankton and Acidification in Small Forest Lakes in Finland

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Summary

The aim of this study was to find out how water acidity influences the phytoplankton biomass and composition in small forest lakes in Finland and to assess the usefulness of phytoplankton investigations for monitoring the effect of acidification.

One phytoplankton sample was taken from small forest lakes each during the summer stagnation period in 1984–1986. Samples were counted by the inverted microscope method of Utermöhl (1959).

It is difficult to assess the acidity stage of a lake from its total phytoplankton biomass, for this is influenced by total phosphorus, total nitrogen and colour values, and pH is of only minor importance. However, acidity can be evaluated from the biomasses of the various phytoplankton groups since pH is the factor that determines the occurence of dinoflagellates, the other groups being regulated largely by water colour, total phosphorus and total nitrogen. Following taxa were typical for acid lakes: *Peridinium inconspicuum*, *Peridinium* sp., *Gymnodinium* sp., *Oocystis borgei*, *Monoraphidium minutum*, *Chlamydomonas* sp., *Dinobryon pediforme* and *Dinobryon* sp.. The most reliable estimate of water acidity is to be obtained by examining the species composition of the phytoplankton. Although the results suggest that, alongside acidity, water colour has an effect on total phytoplankton biomass and the biomasses of the various algal groups in acid lakes, the main determinant of species composition may nevertheless be said to be pH.

Introduction

The phytoplankton community is considered a good indicator of physicochemical characteristics of the surrounding water. Thus there is a lot of interest in how water acidity influences the composition of phytoplankton (Almer et al. 1974; Crisman et al. 1980; Kelso et al. 1982). Algal species in particular vary greatly in their relation to water quality and their tolerance of low pH (Prescott 1962). Acidic lakes are often oligotrophic, and it is sometimes difficult to separate such effects from those of depressed pH.

Kauppi et al. (Eds).
Acidification in Finland

On the other hand, there are many lakes with dark water in Finland, and it has not been determined how water colour influences phytoplankton composition in acidic lakes.

The aim of this work was to find out how water acidity influences the phytoplankton biomass and composition in small forest lakes in Finland and to assess the usefulness of phytoplankton investigations for monitoring the effects of acidification.

Material and Methods

One phytoplankton sample was taken from each of 133 small forest lakes during the summer stagnation period, mainly in July and August, in 1984–1986. Each composite sample consisted of five subsamples taken with a Ruttner sampler at 0.5-m intervals from surface to a depth of 2 m. This minimized vertical variations in phytoplankton occurrence. No account was taken of possible horizontal patchiness (Ilmavirta 1983). Phytoplankton composition during the summer stagnation period does not change much from year to year within one lake (Hörnström et al. 1986), and consequently a single summer stagnation sample describes certain characteristics of a lake quite well.

The phytoplankton samples were fixed with acetic Lugol solution in the field, in addition to which buffered formalin was added to the samples collected in 1984 and 1985 in the laboratory. The samples collected in 1986 were fixed only with Lugol solution. All samples were kept at 20°C in the dark until being counted 6–12 months later.

Phytoplankton was counted by the inverted microscope method of Utermöhl (1958). Algae were identified and counted from 50, 75 or 100 randomly chosen fields to a total of 500 items (cells, colonies or 100 μm filaments), and large items from the whole sedimentation chamber were counted at a lower magnification of 200 × .

Biomass was calculated using standard individual cell volumes as quoted by Naulapää (1972), with numerous corrections. The taxonomy and names used are according to Tikkanen (1986), although the outdated taxonomy of the data bank of the National Board of Waters and Environment had to be used in a few cases for technical reasons. The phytoplankton data are kept in the phytoplankton data bank of National Board of Waters and Environment.

Water samples for physicochemical analysis were collected at the same time as the phytoplankton samples.

Detrended correspondence analysis, DCA (Hill 1979), was used to study the phytoplankton composition in the lakes, the results were tested using Pearsson's correlation coefficients. pH optima and tolerances for the phytoplankton taxa were determinated by weighted averaging using the equations presented by Oksanen et al. (1988) (see Huttunen and Turkia this Vol.).

Results and Discussion

Phytoplankton in Lakes of Different Colour and pH Classes

The lakes were divided into three water colour classes: 1 = clear water lakes (< 20 mg Pt/l), 2 = mesohumic lakes (20–50 mg Pt/l), and 3 = polyhumic lakes (> 50 mg Pt/l). The terms "mesohumic" and "polyhumic" are used here to describe these colour classes; however, other chapters in this volume describe different kinds of classification.

Each colour class was divided into four acidity classes: A (pH ≤ 5.3), B (pH 5.4–5.9), C (pH 6.0–6.9) and D (pH ≥ 7). Some characteristic features of water quality in the subclasses are presented in Table 1.

Total Biomass

Between the subclasses the total biomass of phytoplankton ranged from 0.38 mg l^{-1} to 6.10 mg l^{-1} between subclasses. The total biomass was higher in polyhumic lakes than in mesohumic or clearwater lakes, and there was a highly significant positive correlation between total biomass and colour (0.34***). The biomasses in the different lake classes are presented in Fig. 1.

The total biomass seemed to be lower at lower pH, although no significant correlation was found between the two. The acidic lakes were also mostly oligotrophic (Table 1), which was probably one reason for their low biomasses. Total

Table 1. Surface water quality, by lake classes

Subclass	Number of lakes	Mean pH	Mean colour	Mean totP	Mean totN
1A	13	5.0	7.3	7.3	203
1B	14	5.6	7.5	6.8	204
1C	21	6.5	9.8	7.4	303
1D	9	7.2	7.6	8.1	337
1	57	6.1	8.3	7.3	264
2A	4	5.1	25.0	8.3	283
2B	10	5.8	33.5	10.3	300
2C	30	6.4	33.5	10.3	351
2D	10	7.2	36.0	13.7	343
2	54	6.3	33.3	10.8	335
3A	2	5.2	80.0	17.5	390
3B	8	5.7	101.3	20.4	499
3C	9	6.5	70.6	23.8	498
3D	3	7.1	70.0	51.3	687
3	22	6.1	82.5	25.7	514
tot	133	6.2	31.1	11.8	33

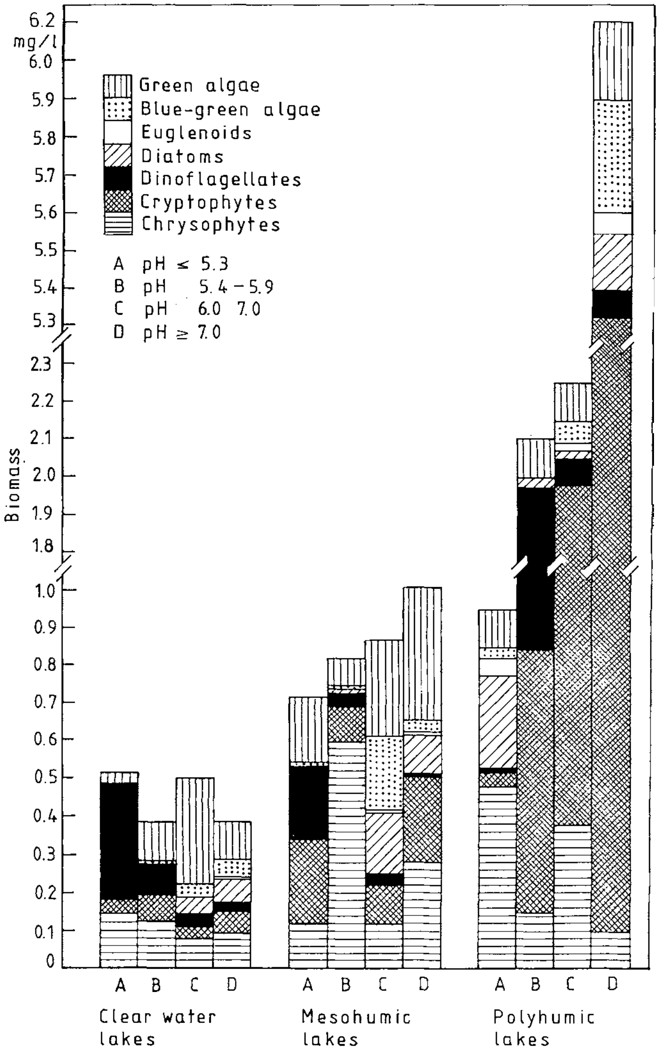


Fig. 1. Total biomass and biomass of the different algal groups by lake classes. Prymnesiophyceae and undetermined flagellates and monads are included here in the Chrysophyceae

biomass showed highly significant positive correlations with total phosphorus (0.56***) and total nitrogen (0.40***).

According to many authors, acidification does not affect the total biomass of phytoplankton (Hörnström et al. 1973; Hörnström 1979; Yan 1979; Raddum et al. 1980; Schindler et al. 1980; Stokes 1986). A more important reason for low biomasses in acidic lakes is oligotrophy (Almer et al. 1974). This was also seen here.

Biomasses of the Phytoplankton Groups

The biomasses of the algal groups in the different lake classes are given in Fig. 1.

Blue-green algae were almost absent in the acid lakes (summer pH ≤ 5.3), but became more abundant with increasing pH and colour values (Fig. 1). Blue-green algae do not favour oligotrophic water (Tikkanen 1986), although their total biomass showed no significant correlations here with pH, colour, total phosphorus or total nitrogen. This may be due to the fact that the biomass of the blue-green algae was generally low in the present lakes, which were poor in nutrients (Table 1).

The biomass of the green algae varied irregularly from one lake class to another, and was especially high in group 1C (clearwater lakes, pH 6.0–6.9). It was lowest in the acidic clearwater lakes (Fig. 1). There was a significant positive correlation between the biomass of green algae and total phosphorus (0.25**), but none between biomass and pH, colour or total nitrogen. There was a significant positive correlation between biomass and total nitrogen (0.39**) in the clearwater lakes, however.

Green algae form a heterogeneous group ecologically. Some species prefer oligotrophic environments and some eutrophic (Rosén 1982, Tikkanen 1986). As a group, they seem to occur mainly in eutrophic neutral or alkaline waters (Ilmavirta 1980; Havens and DeCosta 1986). A positive correlation between the biomass of green algae and phosphorus was noted here, but the lakes included in subclass 1C, in which the biomass of green algae was highest, were mostly oligotrophic. The high biomass of green algae in this subclass was mostly due to one sample, in which 98% of the phytoplankton biomass consisted of chlorophycean algae. When this sample was excluded, the biomass of green algae in lake class 1C was of about the same magnitude than in the other subclasses rich in green algae, 2C and 2D. The appearance of green algae in neutral and alkaline waters was not clearly distinguishable here.

The total biomass of Chrysophyceae varied greatly from one lake class to another. Either lake pH or colour seemed to be connected with their biomass, and there were no significant correlations between the biomass of Chrysophyceae and total phosphorus or total nitrogen either.

According to Ilmavirta (1980) and Rosén (1981), chrysophycean algae are typical of oligotrophic waters. The investigations of Ilmavirta also show that chrysophytes are typical of humic oligotrophic waters. The artificial character of the chrysophycean group in the present material probably affected the results so that the above feature could not be confirmed.

No diatoms occurred in the samples from the acid lakes, but they became more abundant with increasing pH values and trophic level. Nevertheless, no significant correlations were found between the biomass of diatoms and pH, colour, total phosphorus, or total nitrogen.

Diatoms can be found in all kinds of waters, but as a group they are typical of eutrophic waters (Ilmavirta et al. 1984; Havens and DeCosta 1986). Although there are also acid-tolerant species (Mills and Schindler 1986), the relative biomass of diatoms tends to decrease as pH decreases (Stokes 1986).

Cryptophycean algae were most abundant in lakes with pH > 6 and dark water (subclasses 3C and 3D), where the amounts of nutrients were high (Table 1). There were highly significant positive correlations between the biomass of Chryptophyceae and total phosphorus (0.76***), total nitrogen (0.42***) and colour (0.33***), but not between the former and pH.

Flagellated phytoplankton species appeared to be typical of humic lakes (colour > 50 mg Pt/l) in southern and eastern Finland also in earlier studies (Ilmavirta 1984, 1985). Kwiatkowsky and Roff (1976) investigated six lakes near Ontario in Canada and noticed that algae belonging to the Pyrrophyta became more abundant as pH increased. Since their Pyrrophyta group included both Cryptophyceae and Dinophyceae, however, it is not possible to compare these two sets of results.

The biomasses of Dinophyceae were highest in the acidic lakes, and were the dominating phytoplankton group in the acidic clear water lakes. There was an almost significant negative correlation between the biomass of dinoflagellates and pH (−0.20*), which was stronger in the case of clearwater lakes (−0.44**). No significant correlations were found between biomass of dinoflagellates and colour, total phosphorus or total nitrogen.

Biomasses of dinoflagellates have been observed to increase as pH decreases in many other investigations (Hörnström et al. 1973; Almer et al. 1974; Yan and Stokes 1978; Yan 1979; Hörnström 1979; Johansson and Nyberg 1981; Willén 1983; Hörnström et al. 1984; Morling 1984; Hörnström and Ekström 1986; Havens and DeCosta 1986; Stokes 1986).

The biomass of Euglenophyceae was low in this material, these occurring mainly in lake classes 3C and 3D, in which most of the lakes were mesotrophic or eutrophic (Table 1). Their biomass had a highly significant or significant correlation with total phosphorus (0.39***), total nitrogen (0.29**) and colour (0.23**) in surface water, but no correlation with pH. Euglenoids are considered typical of eutrophic waters (Järnefelt 1952).

Number of Taxa

The number of taxa increased with increasing pH and colour values. The acid clear water lakes (1A) had an average of ten phytoplankton taxa per sample, whereas the acid lakes with dark water (3A) had an average of 30. Eighteen to 24 taxa occurred in lakes with pH 5.4–5.9 (1–3B), 30–34 in lakes with pH 6.0–6.9 (1–3C), and 30–41 in the most alkaline lakes. According to many authors, there are on average 5–15 phytoplankton taxa in acidic lakes (Hörnström et al. 1973; Almer et al. 1974; Yan 1979; Raddum et al. 1980; Johansson and Nyberg 1981; Rosén 1981; Hörnström et al. 1984; Hörnström and Ekström 1986), while 30–70 phytoplankton taxa have been reported in lakes with pH 6 (Almer et al. 1974). Surface water colour also seems to influence the number of phytoplankton taxa in this material.

Phytoplankton Species Composition

Some deviant samples which were dominated by only one species had to be removed from the data before the analysis, which meant the exclusion of 16 lakes in which one species made up over 90% of the total cell number.

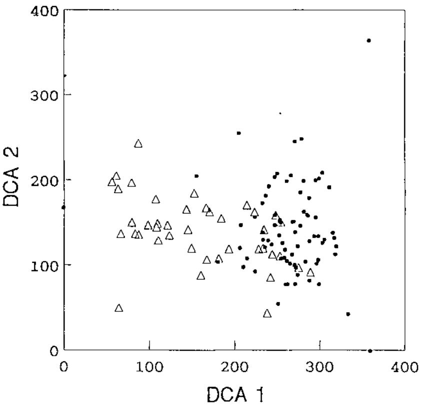
The DCA ordination diagrams for the lakes and phytoplankton taxa are presented in Figs. 2 and 3. In the diagrams, acidic lakes and taxa typical for them are located on the left-hand side. The coefficients of correlations between the environmental variables and the cell numbers of the taxa suggest that pH is critical for the first axis (Table 2), with which it shows a highly significant positive correlation (0.66***).

No highly significant correlations were found between the second DCA axis and any environmental variable, i.e. pH, colour, total phosphorus, total nitrogen or surface area of lake (Table 2). Thus, none of these variables alone seemed to be critical for the second axis.

The 54 phytoplankton species located furthest towards the left-hand side of the first axis (Fig. 3) were chosen for more detailed study, and Pearsson's correlation coefficients were calculated for the relationship between cell number of these species and surface water pH. Only the species whose cell number correlated negatively with pH are considered here to be of possible value as indicators. pH optima and tolerances, estimated by weighted averaging, were assigned to these species (Table 3).

The phytoplankton communities of the acidic waters consisted mainly of green algae, dinoflagellates and undetermined, mostly flagellated, species.

The dinoflagellates *Peridinium inconspicuum*, *Peridinium* sp. *Gymnodinium* sp. and cells attributed to the Dinophyceae (representing various developmental



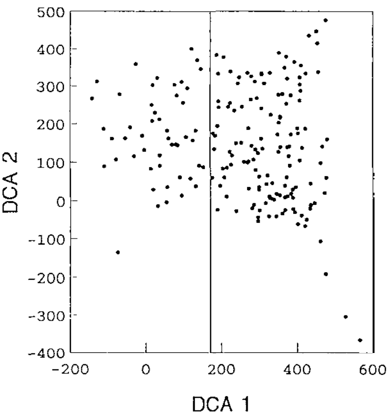


Fig. 2. DCA ordination diagram for the lakes studied. *Triangle* lakes with $\mathrm{pH} < 6.0$; *point* lakes with $\mathrm{pH} \geq 6.0$

Fig. 3. DCA ordination diagram for the phytoplankton taxa. Taxa located on the *left-hand side* of the line are typical for acid lakes

Table 2. Correlations between the first and the second DCA axis and environmental variables

Variable	Correlations First axis	Second axis
pH	0.67***	−0.10
Colour	0.14	−0.10
totP	0.24*	0.10
totN	0.20*	0.15
Lake surface area	0.10	−0.03

Table 3. Species typical of acidic lakes, their correlations with surface water pH, weighted pH averages and weighted standard deviations. Phytoplankton taxa which were abundant in < 3 lakes are omitted from the table. Taxa with relative frequencies not > 1% in any lake were excluded from DCA analysis and weighted averaging and taxa which occurred in only lake were omitted from the weighted averaging

Species	n[a]	Corr.	Weighted pH aver.	Weighted S.D.
Peridinium inconspicuum	51	−0.37***	5.73	0.77
Peridinium sp.	10	−0.20*	5.51	0.75
Gymnodinium sp.	31	−0.21*	8.81	0.72
Dinophyceae[b]	50	−0.24**	5.90	0.68
Chlamydomonas sp. 7 µm	15	−0.26**	5.57	0.55
Oocystis borgei	18	−0.16°	5.84	0.70
Monoraphidium minutum	13	−0.23*	5.61	0.65
Protococcales[c]	13	−0.21*	5.68	0.52
Dinobryon pediforme	7	−0.17*	5.59	0.75
Monad 3 µm	37	−0.28**	5.81	0.70
Flagellate < 6 µm	63	−0.17*	6.02	0.71

[a] Number of lakes, where species was abundant.
[b] Different development stages of dinoflagellates.
[c] Green algae which were not identified to species.

stages of dinoflagellates) appeared to be typical of the acidic lakes, and *Peridinium goslawiense* was also an acid-tolerant species in terms of the DCA diagram although it was abundant only in one sample, an acidic one. These results concerning dinoflagellates support those of many other investigations (Hörnström et al. 1973; Almer et al. 1974; Yan and Stokes 1978; Yan 1979; Hörnström 1984; Ilmavirta K et al. 1984; Hörnström and Ekström 1986).

Among the green algae taxa, *Oocystis borgei*, *Monoraphidium minutum*, *Chlamydomonas* sp. and undetermined green algae assigned to the Protococcales were typical of acidic water. The *Oocystis* species (*O. submarina*, *O. lacustris*, *O. marssonii* and *O. rhomboidea*) and some *Monoraphidium* species (*M. dybowskii* and *M. griffithii*) have also been observed to be the most acid-tolerant green algae elsewhere (Almer et al. 1978; Rosén 1981; Hörnström and Ekström 1986). Fängström and Willén (1987) similarly demonstrate that *Monoraphidium dybowskii* is typical of acid and humic lakes, but it was *Monoraphidium minutum* that appeared to be typical of acid lakes in the present material. The group Protococcales consists of algae which were not identified to species, and is not examined in detail here.

Dinobryon pediforme seemed to be typical of acid lakes. It was not abudant in very many lakes, but made up over 90% of the total number of cells in one case. *Dinobryon* species have been seen to be abundant in other acid lakes, notably *Dibobryon sertularia* in Pennsylvania, U.S.A. and Ontario, Canada (Bradt et al. 1986; Findlay and Kasian 1986).

Small undetermined monads ($< 3\,\mu m$) and flagellates ($< 6\,\mu m$) also were common in the acidic samples.

A further seven species out of the 54 taxa to emerge from the DCA analysis had a weighted pH average < 5.9, but showed no correlations between their numbers and surface water pH. They are therefore not examined further here.

Conclusions

The total phytoplankton biomass was lower in the acid clearwater lakes than in the lakes with higher pH and darker water, but this was due rather to the nutrient levels than pH as such. The biomasses of the different phytoplankton groups varied with acidity and water colour. Dinoflagellates and chrysophytes formed the major part of the total biomass in the lakes which were most acidic and had the clearest water, while cryptophycean algae became more abundant in the acidic lakes with darker water. The lakes which had the most alkaline and clearest water had a variety of groups represented in their phytoplankton biomass, while the alkaline lakes with darker water again had cryptophycean algae as dominating element in the phytoplankton. pH was the factor which influenced the biomass of dinoflagellates, while total phosphorus, total nitrogen and colour had the greatest effect on the biomass of Cryptophyceae, Euglenophyceae and Chlorophyceae.

It is difficult to assess the acidity stage of a lake from its total phytoplankton biomass, for this is influenced by total phosphorus, total nitrogen and colour values, and pH is of only minor importance. Acidity can be evaluated with relative certainty from the biomasses of the various phytoplankton groups, however, since pH is the factor that determines the occurrence of dinoflagellates, the other groups being regulated largely by water colour, total phosphorus and total nitrogen.

The total number of taxa increased with increasing pH and colour values. It was the surface water pH that had the greatest effect on phytoplankton species composition, which did not seem to depend on surface water colour, total phosphorus or total nitrogen.

Dinoflagellates *Peridinium inconspiccum*, one undetermined *Peridinium* and *Gymnodinium* species and undetermined developmental stages of Dinophyceae were typical of the samples from acid lakes, as also were the green algae *Oocystis borgei*, *Monoraphidium minutum*, *Chlamydononas* sp. (7 µm) and small undetermined algae assigned to the Protococcales. There was also one *Dinobryon* species, *Dinobryon pediforme*, which seemed to favour acid water. Small undetermined monads (3 µm) and flagellates (< 6 µm) were likewise common in the acidic lakes.

The most reliable estimate of water acidity is to be obtained by examining the species composition of the phytoplankton, in addition to which counting of the number of representatives of the given taxa enables one to avoid the sources of error which arise when converting absolute numbers to biomasses. Although the results suggest that, alongside acidity, water colour has an effect on total phytoplankton biomass and the biomasses of the various algal groups in acid lakes, the chief determinant of species composition may nevertheless be said to be pH.

All in all, experiences with the present material point to the usefulness of phytoplankton as an indicator for monitoring acidification and determining the degree of acidity of specific bodies of water.

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Periphytic Diatoms in the Acidification Project Lakes

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Summary

Periphytic diatoms growing attached on the solid substrata in the littoral are sensitive indicators of the recent water quality, especially of the water pH. In the most acid lakes planktonic diatoms are missing but periphytic diatoms can be still abundant in the littoral of these lakes. Periphytic diatom communities reflect besides the water pH and alkalinity also the content of organic matter in the water. Acidophilic and acidobiontic taxa dominated both in the clear- and brown-water lakes with zero or negative alkalinity (and low pH), whereas in lakes with positive alkalinity the periphytic diatom communities have higher species richness and the relative proportions of neutrophilic and alkaliphilic taxa are higher. Using K-means clustering eight community types were formed. The number of diatom taxa per sample decreased with decreasing water pH. For the interpretation of water pH by periphytic communities an equation was calculated:

$$\mathrm{pH} = 0.355 + 0.037^{*}\ \mathrm{acb\%} + 0.054^{*}\ \mathrm{acf\%} + 0.070^{*}\ \mathrm{neutr\%} + 0.068^{*}\ \mathrm{alkf\%} + 0.094^{*}\ \mathrm{alkb\%};\ r^2 = 0.548;\ n = 135;\ \mathrm{S.E.}_{e} = \pm 0.484.$$

In the acidification studies periphytic diatoms are very useful due to easy sampling and lack of old and allochthonous material which can interfere with results using deep lake sediment samples.

Introduction

Periphytic algae are good indicators of water quality and its changes. Water discharging from the surrounding passes first the littoral zone where periphytic algae are found. Periphyton samples always represent actual algal communities, whereas sediment samples also contain representatives from several past years and often abundant allochthonous diatom material carried by running water discharging into the lake.

Diatom communities in a lake may contain very variable amounts of planktonic forms, epipelic unattached forms and attached, real periphytic forms. The relative proportion of each group in the lake depends on many factors such as water currents, littoral types (types of sediment and vegetation) and water quality.

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Diatoms are often abundant in the littoral zones of the acid lakes, whereas in the plankton of these lakes they are a minor component in algal communities or they are totally absent. Many small forest lakes have a shoreline with a steep peat or moss edge, whereas others may have sandy or rocky shores all around. In these lakes the variability of the substrata is low. The aquatic macrophyte vegetation may be sparse, providing only little surface for the attaching epiphytic algae. Thus the periphytic diatom communities are affected not only by the water quality but also by the lake morphology and especially by the shore structure. The same factors cause even more diversity in the diatom assemblage in deep sediments where the total collection of taxa representing all communities should be found. Thus in acidification studies the variability of the algal communities caused by the shore structure should be distinguished from that caused by the water chemistry (pH, alkalinity etc.).

In this chapter the relation between the water pH and the community structure of the periphytic algae is studied using the most frequent and abundant taxa representing different pH categories. Some comparisons were also made between the results from periphyton diatoms and results from deep lake sediment diatoms. Some general results from acidification studies of periphytic communities in these project lakes and results from studies on the relations between the acidobiontic indicators and water quality have been reported in earlier papers (Eloranta 1987a, b, 1988, 1989).

Methods

Periphyton samples were collected during the summer months (once per lake) with a small brush from different substrata (macrophytes, rocks, wood) from the lake littorals and pooled to a single sample of each lake. Then the samples were preserved with ca. 5 ml of concentrated formalin/200 ml sample. In the laboratory the samples were studied in two steps. First, filamentous algae were analysed using inverted microscope and counting chamber techniques. Second, diatom samples were cleaned using a boiling acid mixture (conc. nitric acid and sulphuric acid in ratio 2:1; boiling time ca. 2–4 h). Diatom slides were mounted using Dirax as a mounting resin.

The relative abundances of diatoms were plotted against measured water chemistry and lake characteristic data of each lake. The grouping analyses were made using a data set of the 20 most common and abundant diatom taxa. The relative abundances were transformed to octave scale, and K-means clustering (Hartigan 1975) was carried out to produce eight community types.

Results

Studied Lakes

Periphytic algae in 135 lakes were studied in 1984–1986. The average area of the lakes is 29.6 ha, ranging from 1 to 201 ha. Most of the lakes (70) are located at the uppermost parts of their drainage basin, 33 are throughflow lakes and 27 are groundwater lakes without any outlet. The lakes represent a rather wide range of water quality from alkaline to acid and from clear to brown lakes.

Water colour and chemical oxygen demand (COD) were in strong positive correlation, illustrating mostly the occurrence of humic substances (Fig. 1). These variables were joined by total nutrients, iron and aluminium. Alkalinity and water pH represent a second factor. The first two factors explained 50.2% of total variation. The size of the lake and its drainage basin correlated positively with the pH factor (Factor 2 in Fig. 1).

Diatom Taxa

Periphyton samples contained, with a few exceptions, rather small quantities of planktonic forms or epipelic forms. Thus the species assemblages and the number of taxa recorded from the periphyton samples differed significantly from those in sediment samples (Turkia 1987; Fig. 2). The number of taxa in the periphyton samples correlated best with the water pH (Table 1; $r = 0.507$; $p < 0.001$) (Eloranta 1989).

Planktonic diatoms were not very common and abundant in the periphytic diatom samples, with a few exceptions. *Asterionella formosa* Hassal dominated only in one lake (41.0%). The others, like *Cyclotella* spp., *Fragilaria* spp., *Melosira* spp. and *Synedra* spp., were rather common in weakly acid and neutral lakes but not abundant. Neutrophilic taxa like *Achnanthes* spp. [*A. flexella* (Kütz.) Brun, *A. linearis* (W. Sm.) Grun. in Cleve & Grun., *A. minutissima* Kütz.], *Anomoeoneis exilis* Cleve and *Cymbella gracilis* (Rabenh.) Cleve occurred frequently and also

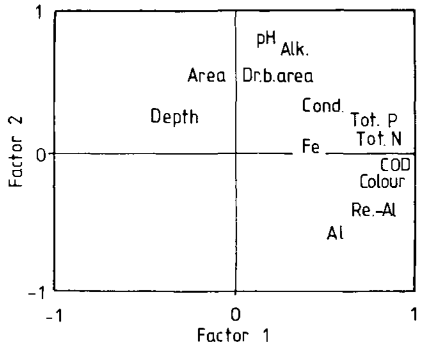

Fig. 1. Factor loading plot of some chosen water quality variables of the studied lakes indicating mutual relations (*Factor 1* COD and colour; *Factor 2* pH and alkalinity; *Alk.* alkalinity; *Dr. b. area* drainage basin area; *Cond.* conductivity; *Re.-Al* reactive aluminium)

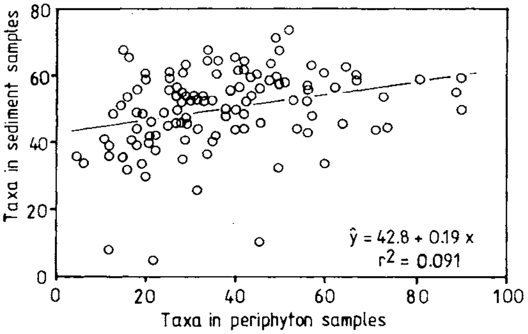

Fig. 2. Comparison between the numbers of taxa recorded from the sediment surface samples (Turkia 1987) and from the periphyton samples taken from the corresponding lakes

Table 1. The average number of diatom taxa in the periphyton samples from lakes belonging to different pH classes

pH class	n	Taxa	±SD
≥ 7.0	24	50.6	20.0
6.0–6.9	60	41.8	18.1
5.2–5.9	34	27.9	10.6
<5.2	17	19.9	7.1

very abundantly in weakly acid and neutral lakes. Acidophilic taxa were surprisingly common and abundant also in lakes with a water pH close to 7 (Eloranta 1989). The most abundant taxa of this group were *Anomoeoneis serians* var. *brachysira* (Breb. ex Rabenh.) Hust., *Eunotia lunaris* (Ehr.) Grun. in Van Heurck, *E. tenella* (Grun in Van Heurck) A. Cleve, *E. veneris* (Kütz.) O. Müller, *Frustulia rhomboides* (Ehr.) De Toni, *F.rh.* var. *saxonica* (Rabenh.) De Toni and *Tabellaria flocculosa* (Roth) Kütz. and T. *quadriseptata* Knudson. *Actinella punctata* Lewis, *Eunotia exigua* (Breb. ex Kütz.) Rabenh., *Navicula subtilissima* Cleve and *Tabellaria binalis* (Ehr.) Grun. in Van Heurck were the most characteristic acidobiontic taxa.

Periphyton Communities

The community structure was studied using K-means clustering and the results of the 20 above-mentioned most common and abundant taxa, representing different pH categories. The analysis was carried out for eight types from which two were represented only by one lake (Table 2). The ordination of lakes was made using canonical discriminant analysis. Lakes with a different periphyton community type were grouped mainly corresponding to differences in water pH (Fig. 3) but with wide overlapping.

The B and H lake groups consisted of the largest lakes with ± neutral water and higher conductivity (Table 2). The lakes of group B were the clearest but in group H the water colour value was higher most obviously due to the turbidity, not

Table 2. The means of the lake water variables in different diatom community lake groups (A–H) formed using K-means clustering and the results of the 20 most common and abundant taxa

Community type	A	B	C	D	E	F	G	H
n	40	30	29	11	1	1	10	13
Lake area (ha)	21	48	19	20	25	201	27	35
Drainage basin (ha)	154	502	161	144	256	921	275	1024
pH	6.1	6.8	5.3	6.1	5.9	6.4	6.2	7.1
Colour (mg l^{-1} Pt)	27	23	28	48	50	5	58	41
Total P (μg l^{-1} P)	10.4	10.0	8.9	14.6	15.0	4.0	17.1	22.8
Total N (μg l^{-1} N)	333	339	260	339	290	430	407	414
Conduct. (mS/m; 25°C)	3.6	3.8	2.8	3.2	1.8	3.4	3.5	4.3
COD (mg l^{-1} O_2)	6.4	6.2	4.9	9.4	11.0	2.7	10.9	7.3
Fe (μg l^{-1} Fe)	251	301	240	614	100	340	341	307
Total Al (μg l^{-1} Al)	96	25	112	63	105	35	87	21
Reactive Al (μg l^{-1} Al)	41	16	31	37	79	0	55	11

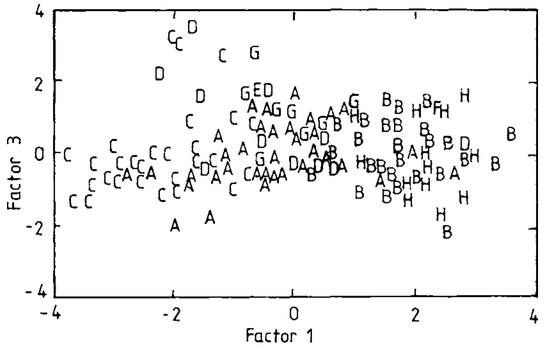

Fig. 3. Plot of studied lakes belonging to different periphyton community types (A–H) against their values from two canonical discriminant functions (*Factor 1* pH; *Factor 3* water colour)

by the humic matter. The ground and soil of the drainage basin of group B lakes were composed of different materials, with the exception of silt. Silt had its highest relative contribution in the drainage basins of group H lakes, which explains the high pH and highest average nutrient concentrations among the groups. The diatom community of group H consisted of several alkaliphilic and neutrophilic taxa (Table 3). Acidobiontic taxa were missing and acidophilic taxa occurred only in low quantities. Characteristic for group B was the dominance of neutrophilic taxa (esp. *Achnanthes* spp.) with low abundance of both alkaliphilic and acidophilic forms. The community type in group A was characterized by representatives from all pH categories between alkaliphilic and acidobiontic. The average water quality in lakes of this group was close to the average values of the entire material (135 lakes) with wide variation among the groups. Thus group A spreads in the ordination analysis over all the other groups (Fig. 3). The group C community represented the smallest and most acidic lakes with the lowest average values of conductivity, nutrient and iron concentrations and COD (Table 2). The periphytic diatom community in the lakes of this group was dominated by acidophilic taxa (*Frustulia rhomboides* var. *saxonica* with *Eunotia lunaris* and *E. tenella*); however, acidobiontic taxa were also represented. Alkaliphilic and neutrophilic taxa were absent in this group. Group D has a wide pH range with an average pH of 6.1

Table 3. Average number of taxa and average relative contributions of diatom indicator groups in lakes with different periphyton community type, A–H

Community type	A	B	C	D	E	F	G	H
n	40	30	29	11	1	1	10	13
Number of taxa	32.6	47.5	22.4	26.5	27.0	18.0	45.1	64.7
Acb-%	2.0	0.4	10.3	0.6	34.9	14.9	0.6	0.05
Acf-%	77.1	41.8	86.6	86.7	61.7	82.9	66.1	25.9
Neutrophil-%	17.2	48.8	2.5	6.2	3.1	0.5	19.1	43.4
Alkf%	3.8	8.8	0.5	6.4	0.3	0.0	14.2	29.3
Alkb-%	0.001	0.2	0.03	0.0	0.0	0.0	0.1	1.2

acb = acidobiontic, acf = acidophilic, alkf = alkaliphilic, alkb = alkalibiontic.

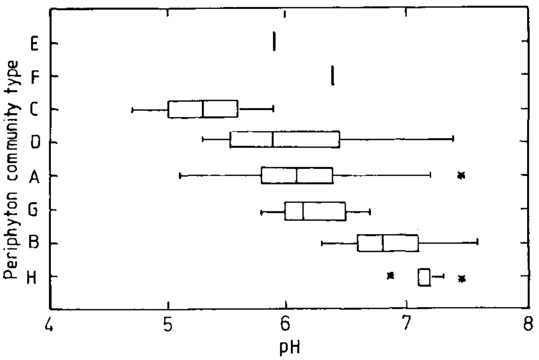

Fig. 4. Box plot of water pH for lakes with different periphyton community types (*A–H*). The center line of the box is the median, the edges of the box are the upper and lower hinges, the *whiskers* show the range of points within 1.5 × the distance between the hinges; points outside this range are marked with *asterisks*

(Fig. 4). These lakes were rather brown and small. The periphyton community in these groups was dominated by *Tabellaria flocculosa*. The group G lakes had the highest average colour and COD values. The pH was mainly 6.0–6.5. Besides the clear dystrophy, these lakes had some mesotrophic features (higher total P and total N concentrations). The diatom community of this group had many similarities with group B and with many alkaliphilic forms and had a low abundance of acidophilic forms with the exception of *Frustulia rhomboides* var. *rhomboides* and *Tabellaria flocculosa*.

The Effects of Total Organic Carbon (TOC) and Alkalinity on the Periphytic Community Structure

The lakes were grouped according to the TOC and Gran alkalinity of the water into six groups (with TOC classes <5, 5–10 and >10 mg$\,l^{-1}$ and alkalinity classes <0 and >0 meq$\,l^{-1}$). The number of taxa was rather low in all lakes with negative Gran alkalinity. In lakes with positive alkalinity the number of taxa per sample was very variable. In those lakes (groups 2, 4 and 6) the median number of taxa was somewhat higher in meso- and polyhumic lakes than in clearwater lakes (TOC <5 mg$\,l^{-1}$). Acidobiontic diatoms were more abundant in clearwater lakes (group 1) and mesohumic lakes (group 3) with negative alkalinity but their contribution was low in the other groups including polyhumic lakes with negative alkalinity (group 5; Fig. 5). Similarly, the relative proportion of acidophilic diatoms was very high ($>80\%$) and of the neutrophilic diatoms (circumneutral) very low ($<10\%$) in most lakes with negative alkalinity, and clearly lower but very variable in the other lake groups. This situation indicates clearly that for diatoms alkalinity is a more important factor than the humic content of the water.

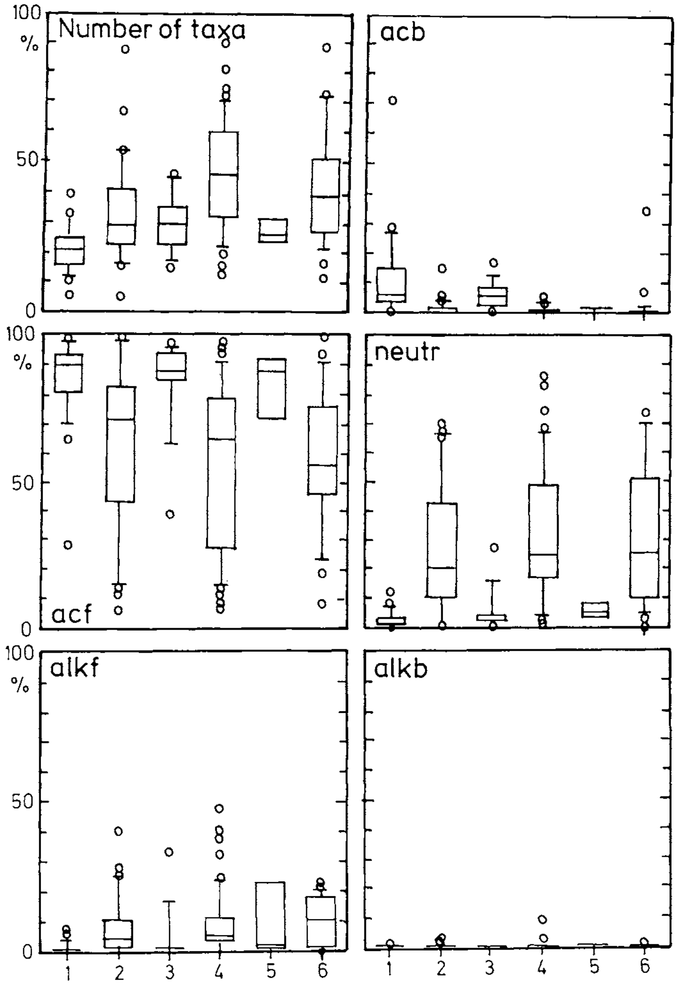

Fig. 5. Box plots of the number of taxa and relative proportions (%) of diatom pH classes (*acb* acidobiontic; *acf* acidophilic; *alkf* alkaliphilic; *alkb* alkalibiontic) in lake groups with different TOC concentrations and Gran alkalinity (*groups 1 and 2* TOC <5 mg l^{-1}; *groups 3 and 4* TOC 5–10 mg l^{-1}; *groups 5 and 6* TOC >10 mg l^{-1}; *groups 1, 3 and 5* alkalinity <0 meq l^{-1}; *groups 2, 4 and 6* alkalinity >0 meq l^{-1})

Interpretation of Water pH by Periphytic Communities

The equations given in the literature to calculate the water pH using diatom results are inadequate when used with results from periphytic diatom communities only (cf. Eloranta 1988). The best result was obtained using the multiple regression equation:

$$\text{pH} = 0.355 + 0.037^{*}\ \text{acb\%} + 0.054^{*}\ \text{acf\%} + 0.070^{*}\ \text{neutr\%} + 0.068^{*}\ \text{alkf\%} + 0.094^{*}\ \text{alkb\%};\ r^2 = 0.548;\ n = 135;\ \text{S.E.}_{e} = \pm 0.484$$

(see also Fig. 6).

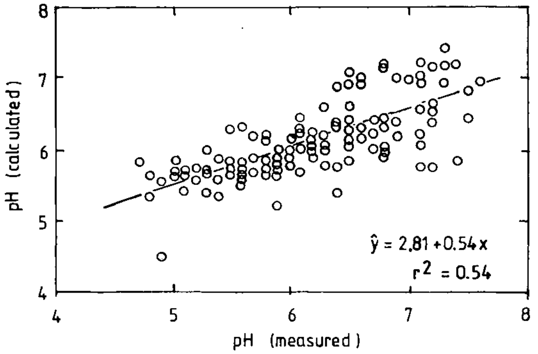

Fig. 6. The linear relationship between the measured summer pH and the pH calculated using the multiple regression equation given in the text

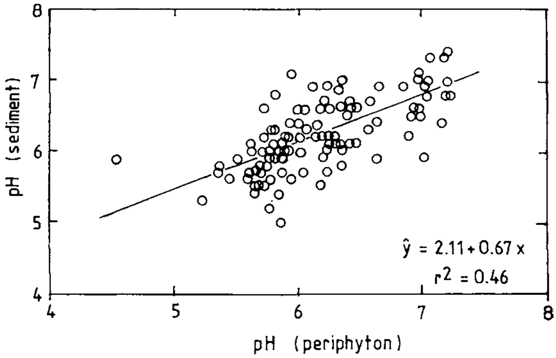

Fig. 7. The relationship between the calculated pH values using sediment surface samples (Turkia 1987) and periphyton samples

The pH values calculated using periphytic diatoms correlated highly significantly with those obtained from sediment diatoms analyses (cf. Turkia 1987) but the values for some single lakes varied notably from each other (cf. Fig. 7).

Discussion and Conclusions

In the acidifications studies the diatom samples are typically taken from the deep lake sediments. These, however, contain members from different communities and, in the throughflow lakes, also variable amounts of allochthonous material carried by water discharging into the lake. On the other hand, sediment samples may contain material of differing ages due to the mixing of sediments by currents and animals.

Periphytic communities represent the actual situation, but the samples can contain some mixed material from plankton and littoral sediments. The variability of periphytic communities in the same lakes within different habitats has not been studied. However, the epilithic, epiphytic and epipelic communities differ to some degree and thus the diatom results can vary, depending on the substratum from which the samples have been collected. To obtain a general view of the periphytic communities in one lake several samples should be taken representing different shore and substratum types.

The correlations between the diatom communities and water-quality variables are usually calculated using samples from sediments of the lake middle. Water coming from the surroundings by the soil surface or groundwater may clearly differ from that in the main waterbody of the lake. Thus the littoral communities may reflect the local water quality and thus cause some variation in the results, but simultaneously, they reflect the actual situation at the location.

Acid conditions seem to be more inhibitory on diatoms in clearwater lakes than in humic lakes. Further, low alkalinity and low pH affect diatoms stronger than humic content (TOC). In conclusion, the use of periphytic communities instead of samples from deep lake sediments as indicator of lake acidification is proposed. Periphytic communities are rich in taxa, and periphytic diatoms can still be found in acid lakes where planktonic diatoms are already missing. Sampling from the lake littoral is easier than from lake deeps. In monitoring studies artificial substrate can also be used for more precise and comparative results.

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Surface Sediment Diatom Assemblages and Lake Acidity

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Summary

The diatom composition of surface sediments from 125 lakes was studied in relation to lake water acidity. According to the results of canonical correspondence analysis (CCA), the structure of the diatom assemblages correlates closely with the pH and the pH-related factors of lake water. Hustedt's classification of diatoms seems to reflect pH fairly well. Acidobiontic diatom taxa, for example, clearly indicate acidic conditions. On the basis of weighted averaging, however, some diatom species classified to acidophilous can tolerate low pH to an equal degree. Contrariwise, euplanktonic diatoms, most of which are either alkaliphilous or circumneutral, appear sensitive to acidification since they are usually rare or totally absent in lakes of low pH. Comparing different pH-indicator methods based on diatom assemblages, pH was predicted more precisely by canonical correspondence analysis and by weighted averaging based on the optimum and tolerance of species than by multiple regression or diatom indices α and B.

Introduction

Diatoms (Diatomae, Bacillariophyceae) are small, microscopic algae with siliceous cell walls that are called frustules. The structure of the frustules is the most important classification criterion in diatom taxonomy. In most waters, diatoms are common. Some taxa are planktonic, others are periphytic, living attached to macrophytes, stones, sand, etc. at the littoral zones of lakes. Sediment samples from deepwater areas contain diatoms that originate from various habitats within the lake. Diatom frustules are usually well preserved in lake sediments.

Information on the relationship of diatom taxa to habitat and water quality has been accumulating for decades. Consequently, the basic ecological requirements of common diatom species are known. The distribution of diatoms is clearly related to the acidity of lake water. This relationship was already discovered by Hustedt who examined over 650 diatom samples from Java, Bali and Sumatra. In this classical work Hustedt (1937–39) founded the pH classification for freshwater diatoms:

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Alkalibiontic: Occurring at pH greater than 7.
Alkaliphilous: Occurring at pH about 7 with widest distribution at $pH > 7$.
Indifferent or circumneutral: Occurring equally above and below pH 7.
Acidophilous: Occurring at pH about 7 with widest distribution at $pH < 7$.
Acidobiontic: Occurring at pH below 7 with optimum distribution at pH 5.5 or less.

On the basis of this classification, Nygaard (1956) presented three diatom indices for the estimation of pH values. He stressed that the percentage frequencies of individual taxa should be used, and all taxa should be taken into consideration when pH is predicted from diatom assemblages. Acidobiontic and alkalibiontic diatom taxa were considered to be much better indicators than acidophilous and alkaliphilous taxa. Therefore, the relative frequencies of each acidobiontic and alkalibiontic taxon are arbitrarily weighted by a factor of 5. For example, acid units are calculated by adding the relative frequency of acidobiontic taxa multiplied by five to the relative frequency of acidophilous taxa. Alkaline units are calculated accordingly.

Nygaard's indices:

$$\alpha = \frac{\text{acid units}}{\text{alkaline units}}$$

$$\omega = \frac{\text{acid units}}{\text{number of acid taxa}}$$

$$\varepsilon = \frac{\text{alkaline units}}{\text{number of alkaline taxa}}.$$

Meriläinen (1967) calibrated Nygaard's indices with Finnish lakes using pH values measured during the autumnal circulation period when pH is less affected by differences in primary production. In this way he made a contribution to the strengthening of the pH reconstruction technique. The accuracy of the pH estimation was around one pH unit.

Renberg and Hellberg (1982) developed index B where circumneutral diatom taxa are included:

$$B = \frac{\%\ \text{circumneutral} + 5 \cdot \%\ \text{acidophilous} + 40 \cdot \%\ \text{acidobiontic}}{\%\ \text{circumneutral} + 3.5 \cdot \%\ \text{alkaliphilous} + 108 \cdot \%\ \text{alkalibiontic}}.$$

From index B, pH can be inferred according to the following equation based on a calibration dataset of surface sediment diatom assemblages and the corresponding pH values from 30 Scandinavian lakes:

$$\text{pH} = 6.40 - 0.85 \log \text{index B}$$
$$r^2 = 0.91 \quad \text{SE} = \pm 0.30.$$

Index B and the pH equation have been widely used. In Finland, too, pH reconstructions have been made from sedimentary diatom assemblages by index B in order to trace the acidification due to acidic deposition (Tolonen and Jaakkola

1983; Simola et al. 1985; Tolonen et al. 1986; Liukkonen 1989). Recently, multivariate methods have been employed in diatom studies (Huttunen and Meriläinen 1986a). Provided that a local calibration dataset is available, it is possible to produce more precise and more accurate equations that are most applicable to the study region or lakes.

In this study, the aim was to examine the relationship of diatom taxa to the quality of lake water, especially pH, and to study the suitability of surface sediment diatom assemblages for biological monitoring of acidification or recovery.

Material and Methods

Sediment Sampling

Surface sediment samples were collected from 125 out of the 140 lakes in the Finnish Acidification Research Project. Five short cores were taken from the deepest basin of each lake. The topmost 1–2 cm of these were combined in the field to make one surface sediment sample. In 1984 when sampling was initiated, the top 2 cm section was removed carefully from the middle of the sediment core (52 lakes). In 1985 and 1986, however, only the top 1 cm was taken to obtain a sample that would contain only the quite recent diatoms. Sediment samples were stored in Minigrip plastic bags in about +5°C.

Sediment Digestion and Slide Preparation

Small subsamples of sediment, less than 0.5 ml, were placed in Pyrex test tubes and about 5 ml of concentrated nitric acid (65% HNO_3) was added. Samples were heated in flame one by one until boiling for 1–2 min. After allowing the samples to cool, a few drops of concentrated sulphuric acid (95–97% H_2SO_4) were added. In case a sample was not yet clear enough, heating was repeated. Occasionally, organic material formed clumps. More nitric acid and a longer heating time were then needed.

Following digestion, nitrogen and sulphuric acids were rinsed from diatom suspensions. At first, suspensions were poured into centrifuge tubes which were then covered with Parafilm. Tubes were centrifuged for 5 min at 2000 rpm. Acid was poured off with care not to resuspend diatoms. Distilled water was added and the tubes were shaken manually. Next, the samples were spun at 3000 rpm for 5 min. Supernatant was removed carefully and rinsing was repeated two more times.

Diluted diatom suspensions were dried on coverslips by gentle warming on a hotplate. Dried coverslips were allowed to cool. With a glass rod, a few drops of Hyrax mounting medium was placed in the centre of each cover slip. Again, samples were slowly heated on a hotplate, increasing the heat gradually until the solvent was evaporated.

Cleaned glass slides were heated to ensure that they were completely dry. One cooled cover slips was placed diatom side down in the centre of each slide. A slide was heated until the mounting medium had flowed to the edges of the cover slip. After cooling, the density of diatoms was checked under a microscope. When necessary, the concentration of diatom suspension was modified and slide preparation procedure was repeated. Slides were labelled with the following information: lake number, lake name, district, sampling date and water depth.

Diatom Identification and Counting

Diatoms were identified and counted under oil immersion at 1500X magnification using Wild M 20 microscope with 100X Wild Fluortal objective (N.A. = 1.30) and phase contrast optics. For each sample, transects across the centre of two cover slips were examined until 300 to 400 valves were counted. Any valve fragment containing characteristic features of the valve structure was included in the count, even if the valve was not entirely within the transect. Sometimes, one or two species were extremely common and additional counting was necessary to determine the percentage frequencies of other taxa.

Diatom identification and taxonomy is based mainly on the following publications: Hustedt (1930; 1927–66); Cleve-Euler (1951–55); Mölder and Tynni (1967–73); Tynni (1975–80); Germain (1981); Meriläinen (1969).

Assignment of Diatoms to Hustedt's pH groups

Diatom taxa are divided into five pH groups according to the information on diatom ecology (e.g. Hustedt 1937–39; Jørgensen 1948; Foged 1948; 1953; 1954; Meriläinen 1967; 1969; Cholnoky 1968; Battarbee 1984). The following ten taxa are classified as acidobiontic diatoms: *Actinella punctata* Lewis, *Amphicampa hemicyclus* (Ehr.) Karsten, *Anomoeneis serians* (Bréb.) Cleve, *Eunotia bactriana* Ehrenberg, *Eunotia exigua* (Bréb.) Rabenhorst, *Navicula hoefleri* Cholnoky, *Navicula subtilissima* Cleve, *Pinnularia subcapitata* var. *hilseana* (Janisch) O. Müller, *Tabellaria binalis* (Ehr.) Grunow and *Tabellaria quadriseptata* Knudson.

Data Management

Results of lake water quality from surface samples (1 m) collected during the autumnal circulation period in 1987 were used in this study. Autumnal pH optima and tolerances for diatom taxa were estimated by *weighted averaging* using the equations presented by Oksanen et al. (1988). The weighted average (w_i) for species i which occurs at abundance y_{ij} at site j where the quantity of ecological factor x i.e. pH is x_j, is defined by

$$w_i = \Sigma y_{ij}\, x_j / \Sigma y_{ij}$$

The weighted standard deviation (s_i):

$$s_i = [(\Sigma y_{ij}\, x_j^2 - (\Sigma y_{ij}\, x_j)^2/\Sigma y_{ij})/\Sigma y_{ij}]^{1/2}.$$

These equations were also used in estimating pH from diatom assemblages.

Canonical correspondence analysis, CCA (CANOCO, Ter Braak 1987) is a direct gradient analysis. It allows one to study the part of the variation in diatom assemblages that can be explained by the measured environmental variables. From diatom assemblages, pH was estimated according to the following equation (Ter Braak 1987):

$$\text{est}\ (z_{i1}) = \bar{z}_1 + \frac{s_1 \cdot x_i^*}{c_1},$$

where $\bar{z}_1$ and s_1 are the mean and standard deviation of the calibration variable, c_1 is the canonical coefficient for the standardized calibration variable, i.e. pH and x_i^* is the sample score on the first axis.

In addition, pH was predicted by *multiple regression analysis* and by two diatom indices: *index* α and B. These pH-indicator methods are based on the Hustedt classification of freshwater diatoms. The regression equations were:

$$\text{pH} = 2.72 + 0.007\text{acb} + 0.246\text{alkb} + 0.042\text{ind} + 0.039\text{alkph} + 0.022\text{acph}$$
$$\text{pH} = 6.25 - 0.572\ \alpha$$
$$\text{pH} = 6.33 - 0.776\ \text{B}.$$

Results and Discussion

Number of Taxa

A total of 257 diatom taxa were identified from surface sediment samples. The number of taxa per sample ranged between 3 and 74, the mean value being 50. The primary data of a complete list of taxa in the 125 study lakes is filed at Joensuu University, Finland.

It has been shown that acidification may cause decrease of diversity in diatom assemblages (e.g. Van Dam et al. 1981). In this study, however, no significant correlation was found between the number of diatom taxa per sample and lake water pH. Only a small number of taxa was found in many acidic lakes, but also in some lakes with pH well over 6.0, where one or two planktonic species were dominant.

When the number of taxa is small, ecological interpretations are not as reliable, and estimated pH may differ considerably from measured pH. In studies of lake acidification, the silica scales of chrysophytes in the family Mallomonadaceae have also been used. Charles and Smol (1988) suggest that in the samples dominated by only a few diatom taxa, chrysophytes may be better indicators. In comparison to diatoms, however, far fewer chrysophyte taxa are usually identified in lake sediments.

Planktonic Diatoms

Depending on the information in different diatom floras about diatom ecology, only the following ten diatom species have here been classified as euplanktonic: *Asterionella formosa* Hassal, *Asterionella gracillima* (Hantzch) Heiberg, *Asterionella ralfsii* W. Smith, *Cyclotella comta* (Ehr.) Kützing, *Diatoma elongatum* (Lyngb.) Agard, *Melosira ambigua* (Grun.) Müller, *Melosira granulata* (Ehr.) Ralfs, *Rhizosolenia longiseta* Zacharias, *Synedra acus* Kützing and *Tabellaria fenestrata* (Lyngb.) Kützing. The number of these diatom species seems to be related to the pH of lake water: The higher the pH, the more euplanktonic species were found ($r = 0.37$); only a few euplanktonics were encountered in acidic clear water lakes with TOC < 5.0 mg l^{-1} (Fig. 1). Meroplanktonic diatoms, too, e.g. *Cyclotella kützingiana* Thwaites and *Melosira distans* (Ehr.) Kützing were less common in acidic lakes. As compared with lake water pH, too many planktonic species were found in the 2-cm samples from acidic lakes. These samples taken in 1984 contained diatom taxa with different ecology suggesting that the algae originate from different environmental conditions. Therefore, a surface sediment sample of 1 cm or 0.5 cm is better for collecting the recent diatom flora.

According to several studies (e.g. Almer et al. 1974; Flower and Battarbee 1983; Charles 1985; DeNicola 1986), planktonic diatoms are very rare or totally absent at low pH values. The reason for this is still unknown, but it may be related to decreased nutrient availability. Unlike periphytic diatoms, planktonic species take all their nutrients directly from water and silicon or phosphorous may be the limiting factor. Moreover, increased concentrations of aluminium and heavy metals in acidic lakes may be toxic for planktonic species. Associated with acidification, there are probably several factors that may cause decrease of planktonic diatoms.

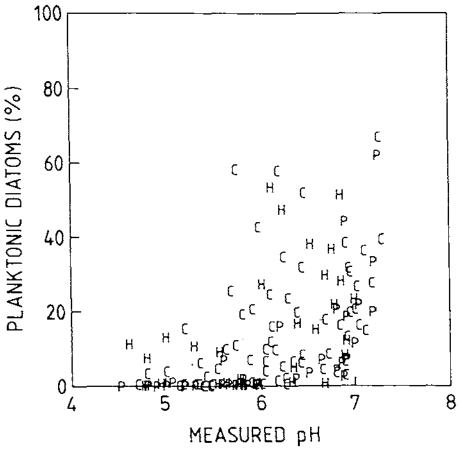

Fig. 1. The percentage of euplanktonic diatoms in relation to lake water pH. *C* clearwater lakes (TOC $< 5.0\,\mathrm{mg\,l^{-1}}$); *H* humic lakes (TOC 5.0–$10.0\,\mathrm{mg\,l^{-1}}$); *P* polyhumic lakes (TOC $> 10.01\,\mathrm{mg\,l^{-1}}$)

Measured pH and the Hustedt Classification of Diatoms

The study 125 lakes were divided into three lake groups according to the measured autumnal pH: (1) pH <5.2, (2) pH 5.2–5.9, (3) pH ≥ 6.0. In each lake group, the composition of diatom assemblages was examined by the mean division of diatoms into Hustedt's groups: acidobiontic, acidophilous, circumneutral, alkaliphilous and alkalibiontic. This diatom classification based on the information about diatom ecology seems to reflect lake water acidity fairly well (Fig. 2). The relative abundance of acid units (acidobiontic + acidophilous diatoms) is highest in acidic lakes (lake group 1): 73%, but less acid units were found in lakes with autumnal pH ≥ 6.0 (lake group 3): 32%. Compared to lake group 1, the diatom communities in lake group 3 contained considerably more alkaliphilous diatoms. Alkalibiontic diatom taxa, however, were extremely rare in this material.

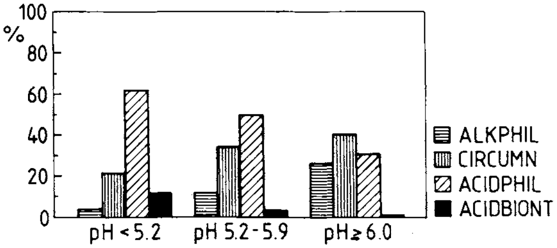

Fig. 2. The composition of diatom assemblages in lakes of different autumnal pH by the Hustedt classification of diatoms. Lake groups: (1) pH<5.2, (2) pH 5.2–5.9, (3) pH≥ 6.0. Alkalibiontic taxa were extremely rare and are therefore not presented

Weighted Averaging

For each diatom taxon, a pH optimum and tolerance was estimated by the method of weighted averaging. In Table 1 the autumnal weighted pH averages and the weighted standard deviations of selected diatom taxa are presented.

The lowest weighted pH averages, below pH 5.00, were calculated for the acidophilous diatom taxa *Navicula söhrensis* Krasske (4.89) and *Eunotia tenella* (Grun.) Hustedt (4.97). The latter low value is partially explained by including the acidobiontic *Eunotia rhomboidea* Hustedt in *Eunotia tenella*. In this material, the asymmetrical valves of *E. rhomboidea* seemed to differ little from *E. tenella* and gradual transitions between the two species frequently occurred (see also Van Dam et al. 1981).

For five acidobiontic taxa, a weighted pH average below 5.30 was calculated. According to the results, *Eunotia bactriana* Ehrenberg, *Navicula subtilissima* Cleve, *Anomoeoneis serians* (Bréb.) Cleve, *Tabellaria binalis* (Ehr.) Grunow, as well as *Tabellaria quadriseptata* Knudson are good indicators of acidic conditions. When compared with a Norwegian material (Berge 1985), however, considerably higher weighted pH averages were here calculated for most diatom taxa including the

Table 1. A selection of diatom taxa indentified, their pH categories, weighted pH averages (WA) and weighted standard deviations (S). The number of lakes in which the taxa occurred is also given.

Diatom taxon	pH category	pH WA	S	No. of lakes in which taxon was observed
Navicula söhrensis Krasske	acph	4.89	0.27	16
Eunotia tenella (Grun.) Hustedt	acph	4.97	0.38	37
Eunotia bactriana Ehrenberg	acb	5.00	0.30	19
Eunotia microcephala Krasske	acph	5.06	0.39	31
Navicula subtilissima Cleve	acb	5.17	0.44	73
Anomoeoneis serians (Bréb.) Cleve	acb	5.23	0.44	32
Tabellaria binalis (Ehr.) Grunow	acb	5.23	0.39	23
Tabellaria quadriseptata Knudson	acb	5.29	0.56	59
Navicula tenuicephala Hustedt	acph	5.29	0.30	38
Asterionella ralfsii W. Smith	acph	5.30	0.58	15
Actinella punctata Lewis	acb	5.31	0.39	27
Navicula hoefleri Cholnoky	acb	5.31	0.52	65
Frustulia rhomboides v. *saxonica* Rabenhorst	acph	5.33	0.59	115
Cymbella hebridica (Greg.) Grunow	acph	5.34	0.53	44
Eunotia exigua (Bréb.) Rabenhorst	acb	5.39	0.48	57
Eunotia veneris (Kütz.) O. Müller	acph	5.44	0.59	106
Eunotia lunaris (Ehr.) Grunow	ind	5.45	0.58	92
Navicula heimansii van Dam & Kooyman	acph	5.47	0.40	18
Pinnularia subcapitata v. *hilseana* (Janisch) O. Müller	acb	5.47	0.61	16
Frustulia rhomboides (Ehr.) De Toni	acph	5.47	0.53	110
Anomoeoneis styriaca (Grun.) Hustedt	ind	5.55	0.48	32
Pinnularia interrupta W. Smith	acph	5.56	0.59	108
Pinnularia gibba Ehrenberg	ind	5.59	0.63	63
Pinnularia hemiptera (Kütz.) Cleve	ind	5.62	0.66	37
Stenopterobia intermedia Lewis	acph	5.63	0.58	83
Amphicampa hemicyclus (Ehr.) Karsten	acb	5.64	0.45	36
Navicula mediocris Krasske	ind	5.66	0.55	94
Peronia heribaudi Brun & Peragallo	acph	5.70	0.43	66

Tebellaria flocculosa (Roth) Kützing	ind	5.74	0.54	166
Anomoeoneis serians v. *brachysira* (Bréb.) Cleve	acph	5.77	0.47	100
Anomoeoneis exilis f. *lanceolata* A. Mayer	ind	5.82	0.47	100
Cymbella gracilis (Rabh.) Cleve	ind	5.90	0.50	101
Cymbella turgida (Greg.) Cleve	alkph	5.92	0.57	33
Stauroneis phoenicenteron (Nitzch) Ehrenberg	ind	6.01	0.50	48
Anomoeoneis follis (Ehr.) Cleve	ind	6.03	0.45	23
Stauroneis anceps Ehrenberg	ind	6.06	0.66	62
Anomoeoneis exilis (Kütz. Grun.) Cleve	alkph	6.13	0.49	76
Fragilaria construens (Ehr.) Grunow	alkph	6.14	0.64	67
Tabellaria fenestrata (Lyngb.) Kützing	alkph	6.14	0.38	53
Asterionella formosa Hassal	alkph	6.16	0.48	52
Achnanthes linearis W. Smith	ind	6.24	0.45	51
Cymbella naviculiformis Auerswald	ind	6.25	0.47	32
Cyclotella stelligera Cleve & Grunow	ind	6.26	0.30	36
Melosira ambigua (Grun.) Müller	alkph	6.34	0.43	52
Amphora ovalis Kützing	alkph	6.38	0.55	30
Achnanthes minutissima Kützing	ind	6.42	0.43	63
Navicula radiosa Kützing	ind	6.52	0.43	41
Cyclotella comta (Ehr.) Kützing	alkph	6.61	0.20	30
Cymbella cuspidata Kützing	ind	6.66	0.26	12
Gyrosigma acuminatum (Kütz). Rabenhorst	alkb	6.87	0.08	6

acidobiontic diatoms. This is probably due to the lower number of acidic lakes in this material.

In comparison to acidobiontic diatom taxa, some of the acidophilous diatoms are apparently able to tolerate low pH to an equal degree. Besides *Navicula söhrensis* and *Eunotia tenella*, pH averages less than 5.30 were also calculated for *Eunotia microcephala* Krasske and for *Navicula tenuicephala* Hustedt. In this material, these acidophilous diatom taxa are better indicators of acidic conditions than the acidobiontic *Amphicampa hemicyclus* (Ehr.) Karsten and *Pinnularia subcapitata* var. *hilseana* (Janisch) O. Müller.

CCA ordination

Because CCA is sensitive to rare species and deviant samples, they should be removed from the data before the analysis (see Ter Braak and Prentice 1988). When the relative abundance of a diatom taxon was less than 1.0% of all counted frustules in the sample, it was excluded from the analysis. Some diatom assemblages were dominated by only one or two species. It was also necessary to remove these deviant samples from the data. Thus, five lakes were excluded from CCA.

In the ordination diagrams of diatom assemblages (Fig. 3) and species (Fig. 4), some lake water characteristics are presented by arrows. Each arrow can be regarded as an environmental axis by extending the arrow in both directions. The arrow indicates the direction of variation of the environmental variable as well as the rate of change through the two-dimensional subspace. Comparing the arrow lengths, one may get an idea of the importance of the presented lakewater characteristics. According to our results, pH seems to be determinative for the composition of the diatom assemblages. Good correlation exists between the horizontal CCA axis 1 and autumnal pH of lake water (r = 0.97). Axis 1 correlates negatively with labile (inorganic) monomeric aluminium (r = −0.57) as moderately high levels of this aluminium fraction were found in acidic lakes. The less

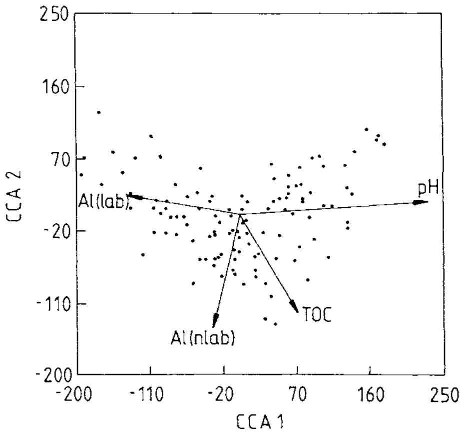

Fig. 3. CCA ordination diagram of diatom assemblages with respect to four lake water characteristics: labile monomeric aluminium *Al(lab)*, non-labile monomeric aluminium *Al(nlab)*, total organic carbon TOC, and pH.

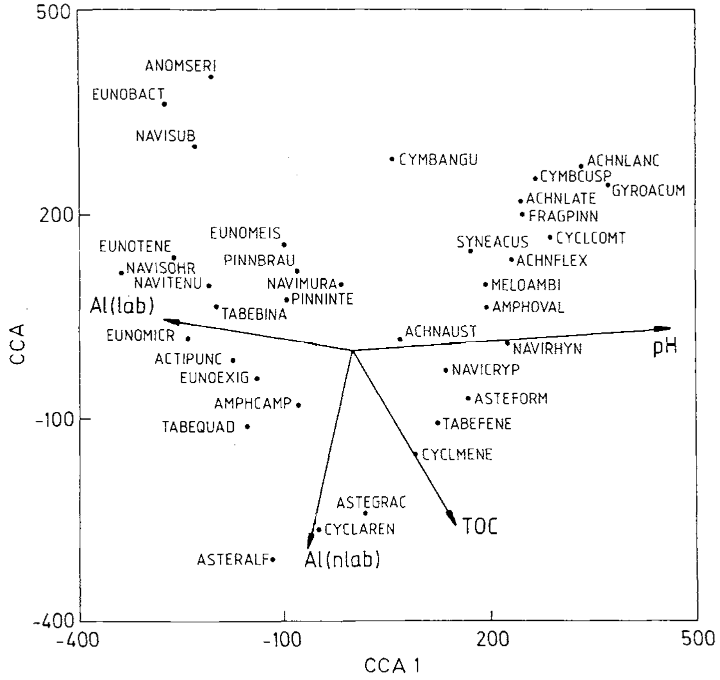

Fig. 4. CCA ordination diagram of diatom taxa with respect to four lake water characteristics, see Fig. 3. Only the extreme species of the included 180 diatom taxa are plotted, because those near the centre are of minor importance, occurring in lakes of intermediate pH

toxic non-labile monomeric aluminium correlates with the second axis ($r = -0.85$) and with total organic carbon ($r = 0.79$).

The diatom assemblages indicating acidic conditions lie on the left-hand side of the diagram (Fig. 3). These assemblages are from lakes of low pH. The diagram of the species ordination (Fig. 4) allows us to infer which species occur primarily in acidic lakes, and which in circumneutral-alkaline lakes. On the whole, acidobiontic and acidophilous diatom taxa are typical for the lakes on the left and are extremely rare or missing in the remaining samples which lie more to the right. For example, the following diatom species have a low weighted average with respect to pH: *Navicula söhrensis* Krasske, *Eunotia tenella* (Grun.) Hustedt, *Eunotia bactriana* Ehrenberg, *Eunotia microcephala* Krasske, and *Navicula subtilissima* Cleve. Accordingly, these species are inferred to be negatively correlated with pH. In addition, they seem to tolerate high levels of labile aluminium. On the basis of the TOC axis, the acidobiontic taxa *Anomoeoneis serians* (Bréb.) Cleve and *Eunotia bactriana* are largely restricted to clearwater lakes.

Estimation of pH by Diatom Indices and by Multivariate Methods

Two diatom indices, index α and B were used to infer pH from diatom assemblages. In addition, pH was estimated by multiple regression analysis, weighted averaging and canonical correspondence analysis. Multiple regression and the diatom indices are based on the pH classification of diatoms created by Hustedt.

Our results indicate (Table 2) that pH can be predicted more precisely by multiple regression than by diatom indices α and B. The most precise estimations, however, were achieved by weighted averaging (see also Oksanen et al. 1988) and canonical correspondence analysis with standard errors of 0.16 and 0.29 pH units, respectively.

Diatom indices are useful where local surface sediment diatom assemblage data are absent. A comparison between different pH-indicator methods based on surface sediment diatom assemblages was made by Huttunen and Meriläinen (1986b): Inferred pH from indices α and B failed considerably in the most acidic lakes. When a reliable calibration dataset is available, the use of diatom indices and foreign pH equations can be avoided. Instead, it is possible to produce local pH equations that are likely to be more appropriate for the region under consideration.

Conclusions

Effects of acid precipitation on lake ecosystems are being studied intensively. Microscopic algae including diatoms are considered suitable for biological water assessment, because by their mode of nutrition, they are more dependent on water quality than other aquatic organisms. Moreover, their life-cycle is short and changes in environment are soon registered in the composition of the communities. Therefore, (see Van Dam 1974) microphytes are valuable indicators of water quality including the environmental factors which may fluctuate sharply, such as pH.

Diatoms are common in most waters and their distributions are closely correlated with the pH of lake water (e.g. Hustedt 1927–66; Huttunen and Meriläinen 1983; Charles 1985; Davis and Anderson 1985). In lake sediments, diatoms are usually abundant and well preserved. Thus, the number of palaeoecological

Table 2. A comparison of the pH-indicator methods used in estimating pH from diatom assemblages. Correlation coefficients and standard errors of estimation are for regressions between estimated pH and measured autumnal pH

Method	r	r^2	SE
Index α	0.76	0.58	0.30
Index B	0.79	0.62	0.29
Multiple Regression	0.81	0.66	0.29
Canonical Correspondence Analysis	0.88	0.78	0.29
Weighted Averaging	0.88	0.78	0.16

For equations, see methods.

investigations on acidification has been increasing and there are already over 50 lakes in Finland where sedimentary diatoms and the inferred pH/alkalinity have been studied (Tolonen and Jaakkola 1983; Simola et al. 1985; Tolonen et al. 1986; Huttunen et al. this Vol.).

Surface sediment diatom assemblages are promising for biological monitoring of lake acidification. They contain recently deposited diatoms from different habitats of the lake reflecting the average conditions of the particular water body. When collecting representative samples of modern plankton or periphyton flora, one must pay more attention to the spatial and seasonal variation of algal communities (see e.g. Jones and Flower 1986). More sampling is then needed. Consequently, surface sediment diatom assemblages seem to be very competitive. They also provide the best source of analogues for the interpretation of fossil diatom assemblages (see e.g. Metcalfe 1988).

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Crustacean Zooplankton of Finnish Forest Lakes in Relation to Acidity and Other Environmental Factors

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Summary

The abundance and species diversity of crustacean zooplankton in 138 Finnish forest lakes were significantly reduced in lakes with a low pH (< 5.2); especially the abundance and species number of calanoids and *Daphnia* declined. The impoverishment of zooplankton fauna at low pH was less pronounced in polyhumic lakes, which also harbored much higher abundances of zooplankton than clearwater lakes. Sample size (in terms of individuals studied) had a major effect on the variation of species numbers. In spite of statistically significant relationships, abiotic environmental parameters could explain only a relatively minor fraction of the observed variation of zooplankton community structure; direct and indirect biotic interactions were probably more important.

Introduction

Zooplankton is an important trophic link between phyto- and bacterioplankton and fish. The most valuable fish species in the lake fisheries in Finland – vendace and whitefish – are planktivorous, and the young of most other species rely heavily on zooplankton food during their first summer. The crustacean zooplankton community of a lake is usually very stable, if there are no major environmental changes (Pejler 1975). Kratz et al. (1987) showed that crustacean zooplankton populations were more variable among lakes than among years, whereas rotifer populations were more variable in time. Plankton crustaceans might therefore be superior to rotifers as indicators of environmental disturbances.

Acidification is known to change the abundance and species composition of zooplankton communities (Nilssen 1980; Stenson and Oscarson 1985). Low pH as such may be deleterious for certain species, but often indirect effects such as increased heavy metal concentrations, temperature changes or varying nutrient ratios (Malley et al. 1982; Keller and Pitblado 1984), or shifts in competitive advantages or predation pressure may be more important (Nilssen and Sandøy 1986). The effects of acid deposition on zooplankton are also dependent on the buffering capacity of water and on the levels of nutrients and humic matter. High

Kauppi et al. (Eds).
Acidification in Finland

levels of humic substances are typical of most Finnish lakes. Humus may ameliorate the toxic effects of heavy metals. In naturally acidic, humic lakes the carbonate buffer system is replaced by a buffering system due to humic matter. The organic matter of humus is also a significant source of food for zooplankton (Salonen and Hammar 1986).

There are few earlier published reports on the zooplankton of Finnish forest lakes (Kenttämies et al. 1985). As part of the Finnish Research Project on Acidification the zooplankton communities in 138 northern forest lakes were examined in relation to environmental factors, especially pH, nutrient level and humic content. Special attention was paid to a search for possible "early warning organisms" which might be used to identify the impact of acidification.

Methods

In all, 138 lakes were sampled in 1984–1986, between mid-June and mid-September. Of these lakes, 45 were common to fish studies (Rask this Vol.) and 133 to phytoplankton studies (Kippo-Edlund and Heitto this Vol.). Each lake was sampled only once during daylight. A vertical water column was collected with a Sormunen tube sampler (described in Hakkari 1978; height 1 m, volume 7 l) from the surface to 1 m above the bottom, or in lakes deeper than 10 m, to the depth of 10 m. In lakes deeper than 6 m the water column was divided in two samples, 0–5 m and from 5 m to the deepest sampling level. Zooplankton was concentrated with a 50 μm plankton net and preserved in 4% formaldehyde.

In the laboratory, zooplankton crustaceans were identified (according to Flössner 1972) and counted with an inverted microscope. Large samples were subsampled, and successive aliquots counted until at least 200 individuals were encountered. However, the whole sample was always scanned through to complete the species list.

A preliminary clustering of lakes and species, based on a subset of 116 lakes, was accomplished with the Biomedical Computer Programs (BMDP; Dixon 1983); final statistics were calculated with the Statistical Analysis System Programmes (SAS Institute 1985). Because crustacean abundance and species number and most of the environmental variables were not normally distributed even after a logarithmic transformation, the correlation and regression analyses were based on ranks. Correspondence analysis (CA) and detrended correspondence analysis (DCA) were run with the programme DECORANA (Cornell Ecology Programme; Hill 1979; Gauch 1982), and a principal coordinates analysis (PCO; Mather 1976) with M. Williamson's program (Williamson 1978, 1983). Zooplankton species composition was related to environmental factors by DCA followed by correlations with autumn water chemistry, and by canonical correspondence analysis CCA, performed with the programme CANOCO (ter Braak 1986, 1988). Taxa found in less than four lakes, and lakes with less than three taxa, were omitted from the analyses, so that in all 133 (134 in DCA) lakes and 18 taxa were used. Of the authors, SH did part of the field sampling, all zooplankton counting, and the preliminary statistical analyses; JS was responsible for the final analyses and the preparation of this chapter.

Results

Abundance and Number of Taxa

Altogether 21 planktonic crustacean taxa were identified in the samples (Table 1). Cyclopoid copepods were not identified to species. Due to their unsettled taxonomy, *Bosmina* forms were treated at the genus level; however, most of our *Bosmina* observations refer to *B. longispina* (sensu Nilssen and Larsson 1980). The true

Table 1. Limnetic crustacean zooplankton species in 138 Finnish forest lakes. Column A denotes the number of lakes, in which a species was found, and column B denotes the number of lakes in which the species was one of the dominants (> 10% of total crustacean numbers). The last column gives the abbreviated code used in Fig. 5

	A	B	Code
Cladocera			
Leptodora kindti (Focke)	34	–	Lkin
Limnosida frontosa (Sars)	36	–	Lfro
Diaphanosoma brachyurum (Liévin)	90	10	Dbra
Holopedium gibberum (Zaddach)	80	28	Hgib
Daphnia longispina (O.F. Müller)	1	–	Dspp
D. cf. *hyalina* (Leydig)	3	–	Dhya
D. galeata (Sars)	9	–	Dgal
D. cucullata (Sars)	1	–	Dspp
D. cristata (Sars)	95	37	Dcri
D. longiremis (Sars)	45	7	Dlon
D. sp. (unidentifiable)	66	14	Dspp
Ceriodaphnia quadrangularis (O.F. Müller)	54	23	Cqua
Bosmina spp.	132	69	Bos
Chydorus cf. *sphaericus* (O.F. Müller)	20	2	Csph
Polyphemus pediculus (Linnaeus)	16	–	Pped
Bythotrephes longimanus (Leydig)	16	–	Blon
Copepoda			
Eudiaptomus gracilis (Sars)	81	51	Egra
E. graciloides (Lilljeborg)	25	16	Egds
E. sp. (unidentifiable)	22	13	Espp
Heterocope appendiculata (Sars)	78	7	Happ
H. borealis (Fischer)	1	–	Hbor
Eurytemora lacustris (Poppe)	3	–	Elac
Calanoida spp. (unidentifiable)	1	–	Cal
Cyclopoida spp.	132	103	Cyc

identity of the taxa provisionally named as *Daphnia hyalina* and *Chydorus sphaericus* requires re-examination (cf. Frey 1980; Cotten 1985; Flössner and Kraus 1986). *Bosmina* and cyclopoids occurred in almost every lake. Species typical for large and deep lakes (e.g. *Heterocope borealis* and *Eurytemora lacustris*) were only occasionally found. In addition to the plankton species, a number of littoral species were found in some samples: *Alona affinis* Leydig, *Alonella nana* (Baird), *A. excisa* (Fischer), *Acroperus harpae* Baird, *Alonopsis elongata* Sars, *Eurycercus lamellatus* (O.F. Müller), *Sida crystallina* (O.F. Müller), and *Streblocerus serricaudatus* (Fischer).

Cyclopoids were found at all pH levels, while the numbers of calanoids decreased with increasing acidity (Fig. 1). *Eudiaptomus gracilis*, *E. graciloides* and *Heterocope appendiculata* were seldom found in acid lakes (pH < 5.2), and the rare *E. lacustris* and *H. borealis* were only found in circumneutral lakes.

In Cladocera, *Leptodora kindti*, *Bythotrephes longimanus*, *Limnosida frontosa*, and *Daphnia* species decreased with increasing acidity, and *Chydorus sphaericus* was lacking in lakes with pH < 5.2 (Fig. 1). Of the *Daphnia* species, *D. cristata* was the least sensitive to acidity, while *D. galeata* was only common in lakes with pH > 6.0. High humic content counteracted acidity effects: in polyhumic lakes *D. cristata* and *D. longiremis* were found at pH 4.8, although in clearwater lakes they did not occur below pH 5.4.

Holopedium gibberum, *Diaphanosoma brachyurum*, *Ceriodaphnia quadrangula*, *Polyphemus pediculus* and the genus *Bosmina* were indifferent in relation to pH in this data set.

The averge abundance of planktonic crustaceans was 25 individuals l^{-1} [standard deviation (SD) 26], of which 12 were copepods and 13 cladocerans. As expected for single column zooplankton samples (Pinel-Alloul et al. 1988), the variability was high (range 0.03–157 ind. l^{-1}). Though part of the variation was certainly due to the extended sampling period (3 months), this did not bias the data: there were no systematic, statistically significant changes in the abundance over the summer.

In humic lakes, zooplankton was more abundant in the 0–5 m than in the 5–10 m layer, while the opposite was true of clear lakes. In the most acid lake group, the contribution of planktonic cladocerans was higher, and that of calanoids lower (Fig. 2).

Average abundance decreased with increasing acidity, decreasing humic influence and decreasing nutrient levels (Fig. 3). The abundance showed highly significant, albeit low, positive correlations to alkalinity, phytoplankton total biomass, total organic carbon, total nitrogen, total phosphorus, pH, water colour, and calcium. The average abundances were highest in shallow lakes: there was a highly significant negative correlation with the lake depth (Table 2).

A stepwise multiple regression of crustacean abundance on the environmental variables (lake depth; conductivity; alkalinity; pH; chemical oxygen demand; iron; total, nitrite, nitrate and ammonium nitrogen; water colour; total and phosphate phosphorus; manganese; natrium; potassium; magnesium; calcium; silicate; chlor-

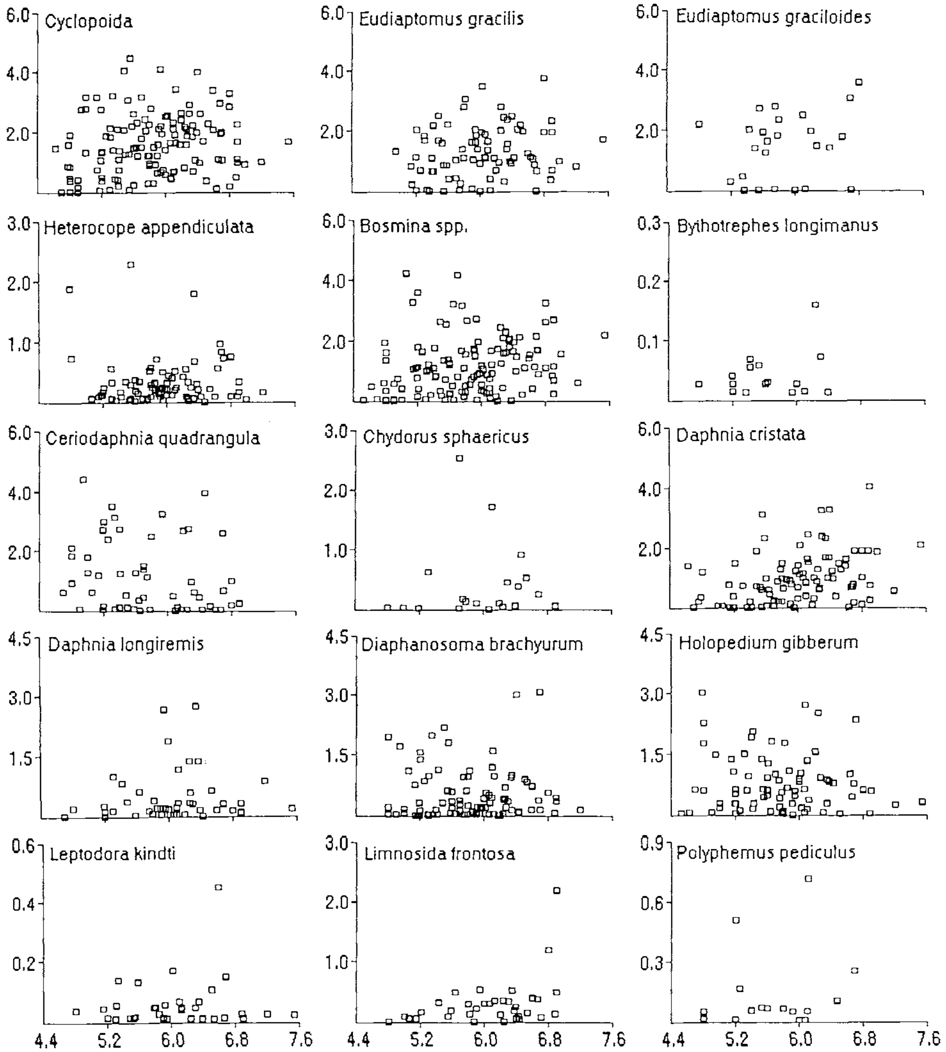

Fig. 1. The abundance [*vertical axis*: $\log_e(\text{ind. } l^{-1}+1)$] of the most common crustacean zooplankton taxa in Finnish forest lakes in relation to the autumn pH of water (*horizontal axis*). Each *square* denotes one lake; only positive finds are shown

ide; sulphate; total organic carbon; total and labile aluminium; all values except pH $\log_e$-transformed), resulted in a model with four significant independent variables: total organic carbon (partial $r^2 = 0.30$), lake depth ($r^2 = 0.10$), pH ($r^2 = 0.02$) and water colour ($r^2 = 0.01$). This model accounted for 48% of the total variance of abundance. A stepwise multiple regression based on ranks yielded only three significant independent variables, total organic carbon, lake depth and labile aluminium, which altogether accounted for 38 % of the total variance.

The number of crustacean zooplankton taxa per lake varied from 1 to 11 (median 7, quartile range 6–9; mean 7.1, SD 2.1, including 4.6 cladoceran and 2.4

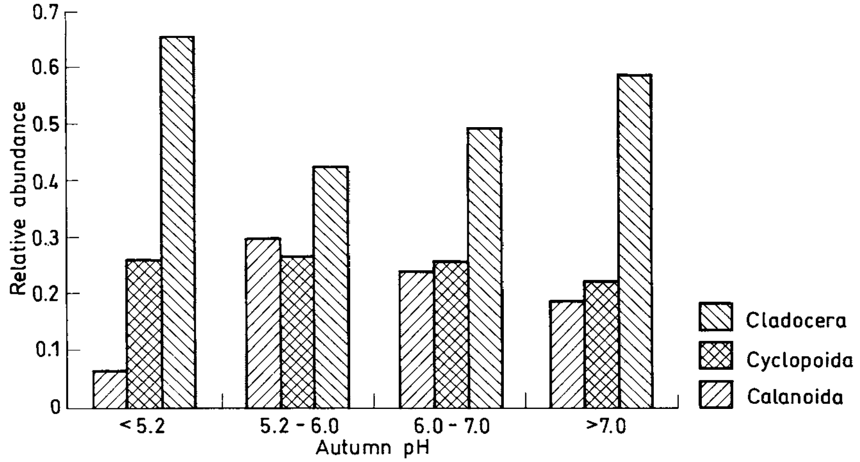

Fig. 2. The proportion of Cladocera, Cyclopoida and Calanoida in the total numbers of crustacean zooplankton in different pH classes of Finnish forest lakes

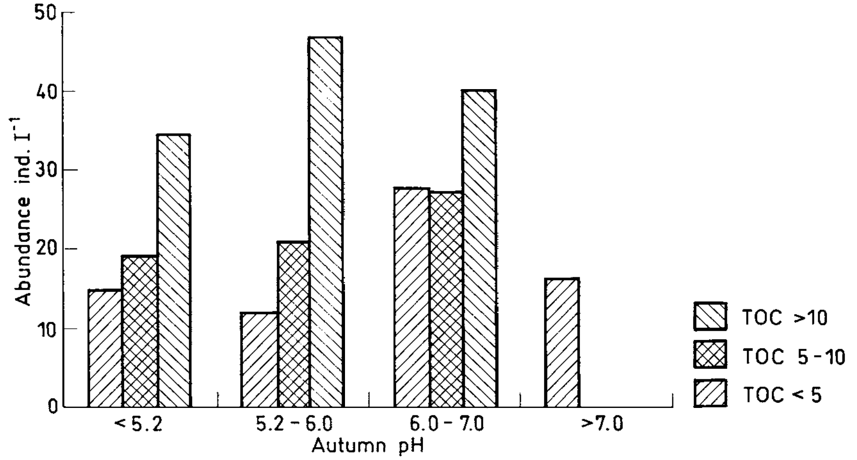

Fig. 3. The abundance of crustacean zooplankton in Finnish forest lakes in relation to pH and total organic carbon content of water

copepod taxa). The number of taxa was not dependent on the date of sampling, but differed between six geographical areas (one-way analysis of variance: $F_{5,109} = 3.06^*$), being lowest in the northernmost lakes and highest in the south-central lake area (provinces of North Häme and Central Finland). The number of taxa showed a highly significant correlation (based on ranks) with the number of individuals studied, water pH, alkalinity and lake depth, a weaker correlation with crustacean abundance, conductivity and calcium, and a negative correlation with labile aluminium (Table 2). The correlation with lake depth probably partly reflects the higher probability of catching the rarer species in larger sample volume.

Table 2. Rank correlations (r; P = probability level) of the abundance and the number of species of crustacean zooplankton with the number of individuals studied and key environmental variables in Finnish forest lakes. N = 138, except for phytoplankton biomass (112) and sulphate (137)

	Abundance		Number of species	
	r	P	r	P
Number of individuals studied	0.79	0.0001	0.43	0.0001
Lake depth	– 0.32	0.0001	0.34	0.0001
Total phytoplankton biomass	0.38	0.0001	0.14	0.147
Conductivity	0.26	0.0024	0.17	0.045
Calcium	0.30	0.0003	0.23	0.007
Alkalinity	0.39	0.0001	0.36	0.0001
pH	0.32	0.0001	0.40	0.0001
Sulphate	0.05	0.581	0.15	0.088
Labile aluminium	– 0.11	0.202	– 0.23	0.007
Total nitrogen	0.35	0.0001	0.03	0.733
Total phosphorus	0.33	0.0001	– 0.05	0.563
Colour	0.31	0.0002	0.08	0.343
Total organic carbon	0.36	0.0001	0.14	0.101

A stepwise multiple regression of the number of taxa on environmental factors gave a model with six significant independent variables (in decreasing order of importance): the number of individuals studied (partial $r^2 = 0.49$), pH ($r^2 = 0.04$), depth ($r^2 = 0.03$), total organic carbon ($r^2 = 0.02$), total nitrogen ($r^2 = 0.02$) and sulphate ($r^2 = 0.01$). This model accounted for 60% of the total variation. A stepwise multiple regression based on ranks gave a model with three significant independent variables, alkalinity, lake depth and the number of individuals studied. This model accounted only for 34% of the total variation.

In lakes with a high humus content even the acid sensitive species (e.g. *Eudiaptomus* and *Daphnia* spp.) tolerated notably lower pH. Accordingly, at the lowest pH level, there were more crustacean zooplankton species and individuals in the humic than the clearwater lakes while in the more neutral group (pH > 6.0) there was little difference between brown and clear lakes (Fig. 4). The contribution of *Daphnia* to the total crustacean zooplankton was significantly higher in neutral than acid clear lakes, while there was no difference between neutral and acid brown-water lakes.

Multivariate Analyses

Cluster analysis of 116 lakes (K-means clustering of cases, programme BMDPKM), based on $\log_e$ (abundance + 1) of the zooplankton species, gave the clearest classification with three clusters of 54, 16 and 46 lakes. Geographical location or date of sampling did not influence the clusters. The number of taxa was lowest and the proportion of cladocerans highest in the third cluster, which

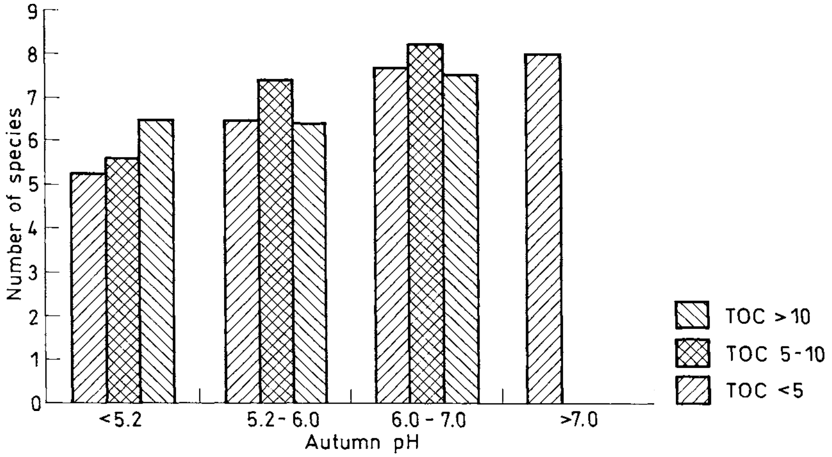

Fig. 4. The number of crustacean zooplankton species in different pH and total organic carbon (TOC) classes of Finnish forest lakes

included most of the acid study lakes (13 out of 16); however, this cluster also contained 33 other lakes with variable environmental conditions. The heterogeneity of the clusters was confirmed in a stepwise multiple discriminant analysis. The pH of water (F = 12.6***) and lake depth (F = 9.2***) discriminated best between the clusters; other discriminant variables were not significant. However, most of the lakes were allocated to wrong clusters, suggesting only a weak correspondence between the environmental conditions and the zooplankton communities.

The first two axes of a principal coordinates analysis of the same 116 lakes ($\log_e$-transformed counts of zooplankton taxa, cos theta as distance measure) explained 50.7% of the total variation between the lakes; in an analysis of species, the first two axes explained 55.6% of the total variation. The first two clusters were separated on the first two ordination axes, but the third cluster was overlapping and partly surrounding the two others.

A detrended correspondence analysis ($\log_e$-transformed counts, downweighting of rare taxa) gave a practically identical scatter plot of lakes on the first two axes as the principal coordinates analysis. In an ordinary correspondence analysis ($\log_e$-transformed counts), the first two clusters were more tightly packed and slightly overlapping, while the third cluster was widely scattered over the space defined by the first two axes.

None of these ordinations separated the group of truly acid lakes from the other lakes. The acid lakes were shown as an oblique band on the first two axes, and correlations between environmental parameters and all ordination axes were weak. Date of sampling or lake depth did not seem to influence the ordination.

Species were ordered in all three ordinations in a similar way. Common species were aggregated in the middle, and rare species tended to be isolated. In spite of the downweighting of rare species, they still largely determined the ordination axes.

The axes of a DCA of the whole data set, 134 lakes and 18 taxa (rare species and deviant samples excluded; see methods), showed only relatively weak (although statistically significant) correlations with environmental factors (Table 3). The first two axes of a species-environment biplot explained 46% of the total variation. *B. longimanus*, *D. longiremis*, *L. frontosa*, *H. appendiculata*, *E. gracilis*, and also *E. lacustris*, *H. borealis* and *D. hyalina* not used in the calculation of the axes, received high scores on the first axis. High scores on the second axis were obtained for *E. graciloides* and *D. galeata*, and low scores for *C. quadrangularis*, *P. pediculus* and *C. sphaericus*, all of which, together with *D. brachyurum*, had low scores on the first axis.

Higher species-environment correlations were obtained in the CCA, but the eigenvalues were much smaller than in DCA (Table 3), indicating a poor correspondence of environmental and species data. Many of the measured 24 environmental variables in the autumn chemistry data showed mutual correlations (Kenttämies et al. this Vol.). Conductivity was positively correlated with potassium, calcium, magnesium, manganese and silicate concentrations, pH correlated positively with alkalinity, natrium, chloride, potassium and calcium, and negatively with labile aluminium and sulphate, while total organic carbon correlated positively with chemical oxygen demand, water colour, iron, manganese, magnesium, calcium and total nitrogen and phosphorus. Seemingly superfluous environmental variables were identified from high correlation coefficients and variance inflation factors, and the number of environmental variables for the final analyses was reduced from 24 to only 5: pH stood for acidity variables, calcium for ionic strength, total phosphorus for nutrient availability and total organic carbon for humic content. Labile aluminium was included because of its toxicity, although it

Table 3. Comparison of the results of ordinations by detrended correspondence analysis (DCA) and canonical correspondence analysis (CCA) and detrended canonical correspondence analysis (DCCA) of the zooplankton data: eigenvalues and species-environment correlation coefficients for the first three axes

	Axis 1	2	3
	Eigenvalues		
DCA	0.23	0.17	0.13
CCA	0.07	0.03	0.01
DCCA	0.07	0.02	0.01
	Correlation coefficients		
DCA	0.49	0.36	0.53
CCA	0.67	0.46	0.24
DCCA	0.67	0.46	0.40

was correlated with pH. The use of conductivity instead of calcium resulted in a practically identical ordination. The reduction of the number of environmental variables from 24 to 5 decreased the first eigenvalue from 0.09 to 0.07 and the second eigenvalue from 0.06 to 0.03, and the correlations between the first and second species and environment axes decreased only from 0.72 to 0.67 and from 0.60 to 0.46. The third and fourth eigenvalues were insignificantly small.

Several environmental parameters showed significant correlations with lake depth, but its inclusion as a covariable in the analysis had a minor effect on the ordination. The two first axes of the species-environment biplot accounted for 88% of the total variance in CCA. The canonical coefficients of pH and labile aluminium obtained the highest absolute values (of opposite sign) on the first axis (Table 4); total organic carbon also had a large negative coefficient. The species-environment biplot (Fig. 5) shows that the first species axis was mainly related to pH and labile aluminium, while the second axis was related to total organic carbon, total phosphorus and calcium; the same result can be seen also in the interset correlations; pH and labile aluminium showed the highest correlation with the first species axis, total organic carbon, total phosphorus and calcium on the second species axis. The DCA axes could be interpreted similarly (Table 4). Thus, the first axis represented acidity and the second axis was a combination of humic influence and nutrient level.

An examination of the species-environment biplot (Fig. 5) shows that *C. quadrangularis*, *P. pediculus*, *B. longimanus* and *H. gibberum* were associated with low pH and high concentrations of labile aluminium, whereas *Daphnia* species, *L. kindti*, *C. sphaericus*, *L. frontosa*, *E. lacustris* and *H. borealis* were associated with relatively high pH and low aluminium concentrations. *C. sphaericus* was typical of waters with high conductivity, calcium, and/or organic carbon as were also *E. lacustris*, *D. galeata*, *H. borealis*, *L. kindti*, *C. quadrangularis* and *D. cristata*. *B. longimanus*, *H. gibberum*, *E. graciloides*, *H. appendiculata* and *D. longiremis* were associated with lower than average conductivity, calcium, and total organic carbon and also with low phosphorus waters. *C. quadrangularis*, *C. sphaericus* and *E. lacustris* were associated with the highest total phosphorus.

Discussion

Abundance and Number of Species

Most published studies on the effect of acidity on zooplankton report a decrease in the number of species with increasing acidity (Sprules 1975; Wright et al. 1976; Fryer 1980; Hobaek and Raddum 1980; Confer et al. 1983; Chengalath et al. 1984; Keller and Pitblado 1984; Arvola et al. 1986; Havens and DeCosta 1987), while the reports on abundance changes are more variable. Schindler et al. (1985) did not find any consistent changes in crustacean abundance or biomass in a whole-lake acidification experiment, while Carter (1971) found higher biomasses of crustacean

Table 4. Canonical coefficients and the intraset correlations of environmental variables with the first two axes of canonical correspondence analysis (CCA) and the detrended correspondence analysis (DCA)

	CCA Canonical coefficients		Correlation coefficients		DCA Regression coefficients			Correlation coefficients		
Axis	1	2	1	2	1	2	3	1	2	3
Variable										
pH	– 0.22	– 0.07	– 0.56	0.04	0.15	0.08	– 0.15	0.38	0.01	0.42
TOC	– 0.17	0.08	– 0.11	0.32	0.03	– 0.03	– 0.16	– 0.19	– 0.21	– 0.26
Calcium	0.06	0.14	– 0.23	0.30	– 0.04	– 0.13	– 0.04	– 0.09	– 0.26	– 0.24
Total phosphorus	0.08	0.08	0.11	0.32	– 0.10	– 0.07	– 0.02	– 0.24	– 0.28	– 0.07
Labile Al	0.13	– 0.02	0.39	0.15	– 0.11	0.03	0.07	– 0.37	– 0.10	0.21

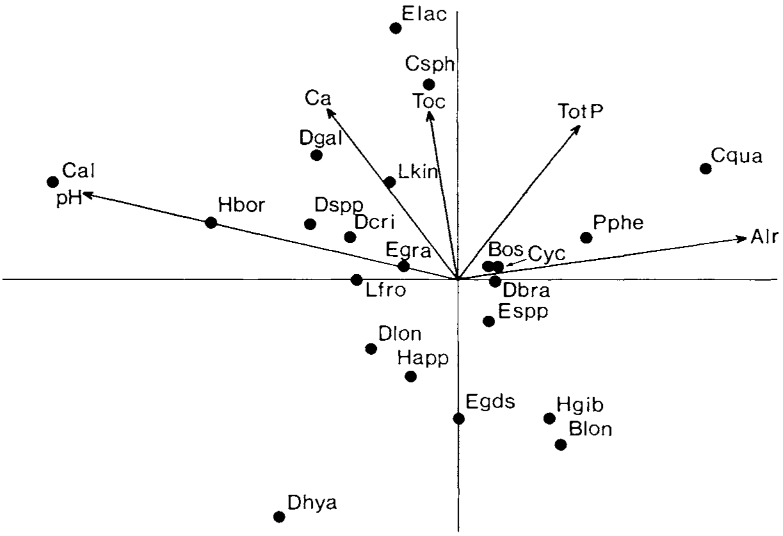

Fig. 5. Species-environment biplot based on canonical correspondence analysis of the crustacean zooplankton abundances with respect to the main water chemistry variables (*arrows*). *Ca* calcium; *TOC* total organic carbon; *TotP* total phosphorus; *Alr* labile aluminium. Species codes are given in Table 1

zooplankton in acid lakes than in neutral or close-to-neutral lakes. However, in agreement with the present study, decreasing abundance of crustacean zooplankton with increasing acidity was reported by Sprules (1975), Roff and Kwiatkowski (1977), Yan and Strus (1980), Keller and Pitblado (1984) and Arvola et al. (1986).

According to Wright et al. (1976) and DeCosta and Janicki (1978), the number of species starts to decrease when pH decreases below 6.0, and the decrease accelerates below pH 5.0, which was true also for the present study. Because we treated cyclopoids and *Bosmina* as collective units, the real decrease may have been steeper; at least cyclopoid species have been found to decrease with increasing acidity (Roff and Kwiatkowski 1977). On the other hand, the number of species found is a function of the lake size (e.g. Browne 1981) and, especially, the number of individuals studied (this chapter; Sarvala 1986). Samples from the most acid lakes contained only few individuals, which automatically leads to low species numbers per sample, even though the total number of species in the lake might be higher. In the present study, the apparent decrease of diversity with increasing acidity could thus be mostly due to the effects of acidity on the abundance of zooplankton. Our species numbers mainly describe species density.

The number of crustacean zooplankton species found in the different pH classes in our study was relatively high compared to several published regional accounts (Sprules 1975; Wright et al. 1976; Brezonik et al. 1984; Keller and

Pitblado 1984), especially considering that in the studies mentioned cyclopoids and usually also *Bosmina* were identified to species. Even higher species numbers were found in surface sediment samples of 46 lakes in eastern Finland (Cotten 1985; average 7.6 limnetic cladoceran species per lake, range 3–11; three *Bosmina* species distinguished, but *Daphnia* only as two species groups). South Finnish lakes seem to harbour an unusually high diversity of benthic copepods, too (Sarvala 1986). Viewing lakes as islands, these findings are consistent with the theory of island biogeography (MacArthur and Wilson 1967). The large number and density of lakes in Finland are expected to shift the equilibrium of colonization and extinction towards high species numbers. The highest species numbers in our data came from the southwestern part of the Finnish Lake District, where the percentage of lakes of the total surface area is at its highest.

The loss of species from acid lakes may have several reasons, either abiotic, such as toxicity of hydrogen ion concentrations or of other chemical substances, or biotic, such as changes in food conditions or in competitive and predatory interactions (Eriksson et al. 1980; Nilssen 1984; Stenson and Oscarson 1985). Zooplankton have been shown to be sensitive to such low concentrations of labile aluminium as are commonly found in acidified waters (e.g. 50–300 $\mu g\ l^{-1}$; Baudoin and Scoppa 1974; Hörnström et al. 1984; Kenttämies et al. this Vol.).

Acid lakes are often nutrient-poor compared to more neutral lakes (Almer et al. 1974; Gran et al. 1974; Wright et al. 1976; Jansson et al. 1986). Low availability of nutrients leads to low primary production, which may be more important than the low pH as such in restricting zooplankton numbers and diversity in acid lakes (Pejler 1965; Hörnström et al. 1984). In the same vein, the present data showed a correlation between nutrient concentrations and both the number of crustacean species and the proportion of *Daphnia*. More important than the nutrient concentrations and the ensuing level of primary production per se may be the quality of phytoplankton and other food available for zooplankton (e.g. Havens and DeCosta 1987). In the present data, there were important differences in phytoplankton species and abundance between lakes grouped according to acidity and humus content: in humic lakes, the average biomass decreased with increasing acidity, and in clear lakes the proportion of the largely inedible Dinophyceae increased with acidity (Kippo-Edlund and Heitto this Vol.). The larger species counts of zooplankton in humic water may reflect the more efficient heterotrophic food chains; in humic water zooplankton may obtain 80% or more of their carbon requirements from allochthonous dissolved organic matter (Salonen and Hammar 1986).

Other biotic factors are more difficult to measure. However, acidification changes competitive and predatory relationships. Fish, *Chaoborus* larvae and predatory zooplankton, such as cyclopoids and *Heterocope*, are the main predators on zooplankton (Hakkari 1978; Eriksson et al. 1980; Henrikson et al. 1984; Nyberg 1984). With increasing acidity, fish are the first to disappear, increasing the impact of the invertebrate predators on zooplankton (Nyman et al. 1985; Stenson and Oscarson 1985).

Responses of Individual Species

Daphnia species, especially, *D. cristata*, seem to be suitable indicators of acidification. *Daphnia* fill most of the requirements of a good indicator organism (Raddum and Fjellheim 1984). They are common and relatively easy to identify. Laboratory studies suggest that their disappearance from acid lakes may be due to purely physiological reasons (Davis and Ozburn 1969; Potts and Fryer 1979; Walton et al. 1982; Nilssen et al. 1984); interactions of pH and calcium may be important (Havas et al. 1984). In most field studies, *Daphnia* species have been found to be lacking in acid lakes (e.g. Pejler 1965: especially *D. cucullata*; Almer et al. 1974; Hobaek and Raddum 1980; Delisle et al. 1984; Hörnström et al. 1984); in Finland, however, *D. cristata* and especially *D. longispina* seem to be more acidity-tolerant. Arvola et al. (1986) observed *D. longispina* as a dominant at pH 5 in a polyhumic lake, and Uimonen-Simola and Tolonen (1987) found it abundant still at pH 4.7 in a clearwater lake. In the present study, *D. longispina* was found in a single, polyhumic, relatively acid (pH = 5.4) lake, which was the only one of the study lakes with no catch in experimental fishing, and also one of the very few lakes without any *Bosmina*. Usually, the absence of competition by *Daphnia* (DeMott and Kerfoot 1982) favours the acidity-tolerant *Bosmina* (e.g. Havens and DeCosta 1987), but this does not necessarily apply to the relationship between *Bosmina* and *D. longispina* (Uimonen-Simola and Tolonen 1987).

Cotten (1985) found that *Diaphanosoma* and *Holopedium* were most consistently abundant in highly coloured, acidic lakes. In our study *H. gibberum* was associated with acid but clear lakes, and *D. brachyurum* was quite indifferent to both factors. According to Cotten (1985), *Bosmina coregoni* and *B. longirostris* were associated with more nutrient-enriched lakes, while *B. longispina* was more abundant in the less enriched lakes. In Estonia, Mäemets (1961) found *B. coregoni* seldom in humic waters and never at pH < 6. In the present study, in a subset of 19 lakes in which the *Bosmina* forms were identified, *B. longispina* was dominant in 15 lakes, and *B. longirostris* was dominant in five lakes and present in one additional lake. *B. coregoni* was lacking altogether in the whole data set. In Cotten's (1985) data, species of the *Daphnia longispina* group were most abundant in moderate to low nutrient and moderate to high colour lakes, and these characterisations were true in our material, too. The taxon called here *Chydorus sphaericus* may contain several ecologically differentiated species (Frey 1980; Cotton 1985), and, therefore, not much weight can be attached to its occurrence.

The most common cyclopoid species in southern Finland, *Thermocyclops oithonoides* (Sars) and *Mesocyclops leuckarti* (Claus), are probably not very vulnerable to the early stages of acidification, because they spend late autumn and winter in diapause in the sediments (e.g. Sarvala 1979), and do not become active until after the break-up of ice in spring. Consequently, the hatching of larvae, which is probably the most sensitive phase of the life cycle, occurs after the most extreme acid pulse caused by the snowmelt waters. In contrast, other species, such as *Cyclops kolensis* Lilljeborg and *C. strenuus* Fischer, which spend the summer in diapause and start their reproductive period close to the shoreline in early spring, might be more vulnerable. At low pH (< 5.2–5.5) all copepod populations have been found to decline, cladocerans becoming the dominant crustaceans (Nilssen 1980; Havens and DeCosta 1987); such was also the case in this study. However, Nyman et al. (1985) and Stenson and Oscarson (1985) showed that, when fishes disappear, invertebrate predators can reduce the cladoceran populations and invert the dominance relations.

Community Responses

Stenson and Oscarson (1985) found many common features in the crustacean zooplankton community of SW Swedish acidified lakes. There were few species and low abundance of cyclopoids. Few cladocerans were found, but some of them were abundant (*Bosmina coregoni* s.l. and *Diaphanosoma brachyurum*). Daphnids were totally missing, and one calanoid species (*Eudiaptomus gracilis*) dominated the grazer community. In contrast, in our study lakes, *Eudiaptomus* species were practically absent at pH < 5.0, in agreement with Nauwerck (1980).

A similar community developed also in a well-buffered lake, where the fish population had been experimentally eliminated (Stenson and Oscarson 1985). *Holopedium gibberum* and *Daphnia cristata* were especially sensitive to invertebrate zooplankton predators, the numbers of which were determined by fish. The appearance of littoral species in the open water is typical of acidified lakes (Nilssen 1980; Stenson and Oscarson 1985). Likewise, in the present study, the open-water occurrence of *P. pediculus*, which is normally bound to the littoral, was related to acidity (and probably reduced planktivorous fish stocks), but the observations of littoral chydorids were too sporadic for further conclusions.

Changes in cladoceran communities, revealed by studies of dated sediment cores, have been successfully used to infer past lake water pH conditions (e.g. Brakke 1984; Cotten 1985; Krause-Dellin and Steinberg 1986; Huttunen et al. 1988; Oksanen and Huttunen in press). Cladoceran remains in the sediment are quantitatively dominated by a few planktonic species, but most of the species found typically belong to littoral chydorids. The response of chydorid Cladocera to acidification is an elimination of species characteristic of higher pH, and decreased diversity and numbers of species (Brakke 1984). Cotten (1985) and Huttunen et al. (1988), who analysed subfossil sediment cladoceran assemblages in relation to environmental conditions in a set of 46 lakes in eastern Finland, claimed that cladoceran assemblages incorporate the same quality and degree of information about lake conditions as do diatom assemblages. Cotten (1985) found a good correspondence between the results of detrended correspondence analysis (DCA), minimum variance clustering and multiple discriminant analysis. The first DCA axis showed a highly significant correlation with nutrient parameters and pH, while the second axis was correlated with water transparency. The most important variables discriminating between cladoceran assemblage types in multiple discriminant analysis were calcium, catchment area, conductivity, lake area, total nitrogen, pH, Secchi depth, forest percentage in drainage area, and maximum lake depth. Oksanen and Huttunen (in press) analysed this data set further, finding that cladoceran remains in the surface sediment were more correlated with the overall water chemistry, especially nutrient status, than acidity.

Janicki and DeCosta (1979) found in their multivariate analyses that both the differences between partly isolated lake basins and the seasonal changes of crustacean zooplankton were related to H^+ concentrations and in vivo fluorescence, indicative of productivity. In the principal component analysis of crustacean zooplankton by Sprules (1977), the first two components showed highly significant correlations with pH and transparency of water in a regional set of acid lakes, with transparency, surface area, maximum depth and water colour in a second region, and with mean depth, transparency and total spring phosphorus in a third lake region. In addition, there were weaker correlations with a number of other limnological variables.

Conclusions

The abundance and species diversity of crustacean zooplankton in Finnish forest lakes were significantly related to acidity, whereby the influence of acidity was substantially modified by humic matter. As found in earlier studies, certain crustacean species disappear from the most acid lakes. However, in spite of the statistically significant relationships, the environmental parameters could explain only a relatively minor fraction of the variation in zooplankton community structure. The low explanatory power can certainly be attributed in part to methodological factors. Samples were available only from single dates, and species with pronounced seasonality may have been missed. Sample size also had a major effect on the variation of species numbers. Especially for abundance estimates of zooplankton, but also for more reliable data of the community structure, a different study strategy would be needed. The samples should consist of several (around ten) vertical water columns from surface to bottom, divided at the thermocline if necessary, and several such samples, at least three or four, should be taken throughout the summer (Yan 1986).

However, part of the weak relationship of the crustacean zooplankton species composition to environmental parameters was certainly due to the biological characteristics of zooplankton. Limnetic species are few and they form a relatively homogeneous ecological group. Further, the zooplankton community structure is strongly dependent on various biotic factors: the availability of suitable food and the character and intensity of invertebrate and vertebrate predation (Stenson and Oscarson 1985; Henrikson et al. 1984; Nilssen and Sandøy 1986). Therefore, the effects of acidification on zooplankton are mostly indirect, and may be difficult to interpret because of the diffuse food web effects. Especially the role of humic matter seems to be considerable but is poorly understood. As noticed by Pejler (1981), environmental indication is mostly based on superficial correlations, but a deeper understanding must be based on more detailed studies on ecology and physiology (cf. Schindler et al. 1985).

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Benthic Invertebrates in Relation to Acidity in Finnish Forest Lakes

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Summary

In order to examine the effects of acidity on abundance and community structure of the benthic invertebrates in forest lakes and to evaluate the applicability of certain benthic animals as early warning indicators of lake acidification, 140 lakes, situated mainly in southern Finland, were studied by quantitative and qualitative sampling methods.

The biomass and number of animals showed no significant correlation with lake acidity, although the number of species decreased markedly with increasing acidity in the littoral zone of the lakes. The fauna in the deeper zones was often reduced as a result of poor oxygen conditions, and it was not possible here to separate the effects possibly attributable to acidity from those of other factors.

There are certain acid-sensitive species, especially among the snails, mayflies and small mussels, by means of which it would be possible to evaluate the stage of acidification of a lake. The presence of these key species is closely related to minimum pH, the acid peak in a lake usually occurring as the snow is melting. This means that the acid periods can be detected also afterwards, which is a considerable advance compared with physico-chemical monitoring of water quality. The comparison of the sampling methods indicated that the qualitative hand net offers a superior method for sampling the littoral invertebrates, making it much easier to obtain samples containing a high number of individuals and species than with the Ekman grab.

Introduction

Our knowledge of acidification as a phenomenon has increased tremendously during the past 20 years, and numerous attempts have been made to identify its effects on the quantity and quality of freshwater biota. Much attention has also been paid to benthic invertebrates and the opportunities for using these for the biological assessment of acidification in lakes and streams.

Research concerning benthic invertebrates in relation to acidity has been carried out most of all in Norway, Sweden and North America (e.g. Wiederholm and Eriksson 1977; Mossberg 1979; Mossberg and Nyberg 1979; Drabløs and

Kauppi et al. (Eds).
Acidification in Finland

Tollan 1980 (includes many papers); Økland and Kuiper 1980; Raddum and Saether 1981; Havas and Hutchinsson 1982; Otto and Svensson 1983; Raddum and Fjelheim 1984; Dermott 1985; Dermott et al. 1986; Økland and Økland 1986; Bendell and McNicol 1987; Bradt and Berg 1987; Wickham et al. 1987), with some contributions in other countries (e.g. Sutcliffe and Carric 1973; Hall et al. 1980, 1987; Townsend et al. 1983; Buskens et al. 1986; Leuven et al. 1986; Dickman et al. 1987). There have been only a few investigations dealing with this theme in Finland, however. Meriläinen (1984, 1988) examined the effects of acidic, aluminium-contaminated river water on the quantitative and qualitative distribution of freshwater invertebrates in a low-saline estuary in the Bothnian Bay, and Aho (1984) published a comprehensive review on the relative importance of water chemistry and the equilibrium model of island biogeography for explaining the local diversity of freshwater gastropods in southern and western Finland.

The data of this study were collected from 140 forest lakes, situated mainly in southern Finland, which serve well to represent the small forest lakes of this country. The aim was to examine the effects of acidification on abundance and community structure of the zoobenthos in these lakes and to evaluate the applicability of certain benthic groups as early warning indicators of lake acidification. It was also evident that recommendations for proper sampling methods to be used in monitoring would be needed, and therefore tests were carried out to determine the sampling efficiency of the methods commonly used. The roles of labile aluminium and humus are usually considered to be of great importance in northern forest lakes, and the roles of these as well as other environmental factors, including the geomorphological data and water quality, were thus examined.

Material and Methods

The Lakes Studied

The 140 forest lakes investigated were mainly distributed over southern Finland. All of them were small, ranging in area from 0.01 to 2.01 km^2, and 97% of them were less than 1.0 km^2. The catchment areas of a major proportion of the lakes were composed of bare rocks and thin till layers, but some lakes from peatland areas and fluvial sand areas were also studied. Most of these were headwater lakes with a distinct inlet and outlet.

The 140 lakes were poor in nutrients, the phosphorus concentration averaging 12 µg/l and ranging from 2 to 110 µg/l. The corresponding values for total nitrogen were 403 µg/l and 85–1000 µg/l. Water colour averaged 54 mg Pt/l, ranging from below 5 to 250 mg Pt/l, mean COD being 8.2 mg/l O_2. The correlation of colour on COD and total organic carbon (TOC) was high, 0.94*** and 0.92***. This indicates that the water colour in these lakes is largely determined by the concentration of organic matter, i.e. humus. Ca and Mg concentrations were low, the mean values (± SD) being 2.6 ± 1.5 mg/l and 0.8 ± 0.5 mg l^{-1}. The concentration of monomeric inorganic Al ranged from below 10 to 314 µg l^{-1}, the mean value being 42 µg l^{-1}, and its negative correlation on pH was highly significant, $r = -0.52^{***}$.

Two different values are given for lake acidity. (1) "pH" indicates the present autumn pH as measured in 1987, and (2) "minimum pH" the minimum value recorded in the given lake during the past 5 years. Figure 1 shows that the stated pH in some lakes may be as much as one pH unit higher than the minimum pH. The pH values ranged from 4.5 to 7.5 and minimum pH from 4.3 to 7.3.

Animal Material

Each lake was sampled once in the course of the summers 1984–1986, three replicate quantitative samples being taken with an Ekman grab in each of two depth zones, 1 m and about 4–5 m. The latter value represented the maximum depth in a number of lakes.

A preliminary study of 55 lakes was made in 1984 (Kenttämies et al. 1985). Only certain animal groups in that material were identified to species, namely gastropods, mayflies, caddis flies, dragonflies and alderflies.

A more comprehensive survey of a further 86 lakes was carried out in 1985–1986. In addition to the quantitative Ekman samples, the littoral fauna at 0.5–1.0 m was sampled with a hand net for about 1 min at a time. All the samples were sieved through a 0.5-mm mesh and preserved in alcohol. The animals

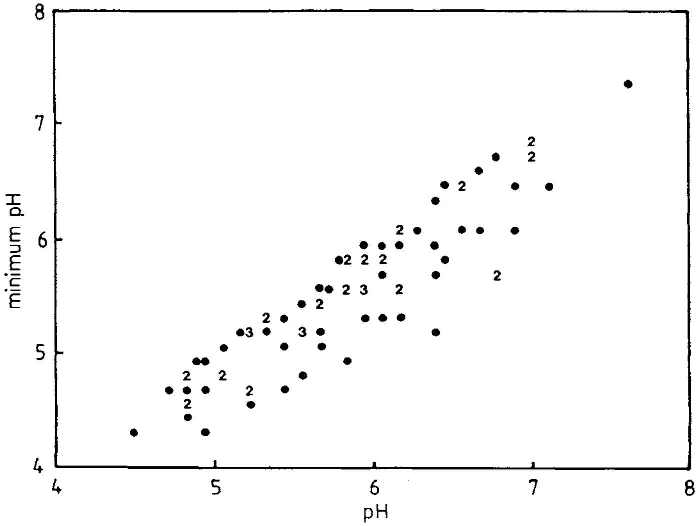

Fig. 1. Relationship between observed minimum pH and autumn pH in 86 lakes (*numbers* indicate overlapping observations)

(excluding water mites) were identified to species or in some cases to genera. In the animal material collected from 22 lakes during the last year of investigation species-level identification was restricted to those groups which were regarded as key organisms in relation to lake acidification, i.e. gastropods, sphaeriids and mayflies. The animals were kept in a bath of deionized water for a few minutes before wet mass determination to remove the alcohol.

Statistical Methods

To examine possible patterns in the assemblage of the benthic species, the quantitative abundance data were subjected to DCA ordination (Hill 1979). The most comprehensive data, including the species-level identifications and complete data on geomorphology and water quality, were available for 62 lakes. One lake was omitted as an outlier, since the abundant fauna was composed almost entirely of *Einfeldia* species, which were very rare in the other lakes. Rare species were downweighted in the analysis. In order to interpret the most effective environmental gradients, the correlations of the data on water quality and geomorphology were calculated with the ordination axes produced by the DCA. The reliability of the results is substantially reduced by the fact that the samples from these lakes were taken at different times during the period from June to September 1986. A considerable proportion of a benthic community usually consists of insect larvae, and their emergence causes great variation in the species assemblage in a given habitat during the growing season.

The efficiency of the sampling methods used was tested in four small lakes, one of which was non-acidic and the others moderately acidic. The material was collected with an Ekman grab at about 1 m and with a hand net at 0.5–1.0 m. The vegetation was usually somewhat sparser at 1 m than in the shallower areas. In order to examine the sampling efficiency of these methods (the increase in expected number of species with an increasing number of individuals), rarefaction curves for both methods in each lake were calculated by the method of Simberloff (1978). The original Fortran program was compiled in Microsoft QuickBasic for a PC.

Results

Fauna

The benthic invertebrates found in the lakes represented 220 taxa, a major proportion of which consisted of chironomids. The species list is given in the Appendix. The figure excludes water mites (Acari, Hydrachnellae) which were not identified to species. The numbers of taxa by groups were:

Gastropoda	9
Lamellibrachiata	12
Oligochaeta	16
Hirudinea	3
Crustacea	4
Ephemeroptera	13
Odonata	17
Trichoptera	29
Chironomidae	107
Others	10

The main interest was focussed on the littoral zone, animals restricted to the deeper bottoms being poorly represented in the material, although of the relict crustacean species common in large, deep lakes were represented by finds of *Pallasea quadrispinosa* in six lakes and *Mysis relicta* in one lake (see Särkkä et al. 1990).

Benthic Invertebrates in Relation to Environmental Factors

DCA ordination of the quantitative data sampled at 1 m revealed no distinct lake clusters, although the most acidic lakes were grouped to the right (Fig. 2). According to the correlation analyses, the variation on axis 1 was best explained by lake

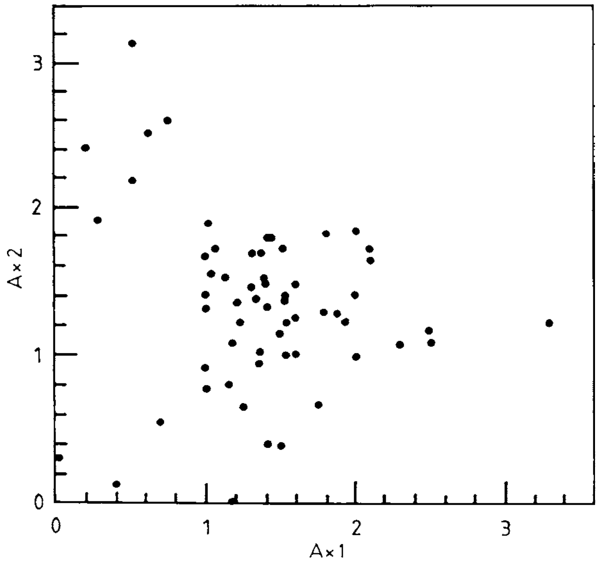

Fig. 2. DCA ordination for the quantitative material sampled at 1 m in 62 lakes. Ax1 represents increasing acidity, while the variation in Ax2 is best explained by the soil quality of the catchment area and by the differences in sediment quality (see text)

acidity, the correlation of minimum pH with axis 1 being − 0.40***. The proportion of rocks and thin till layers in the catchment areas had the best correlation on axis 2 (r = − 0.45***). Actually, it may be assumed that the variation on axis 2 is more closely related to sediment quality, although this could not be demonstrated here since only a rough classification was available based on the visual appearance of the sediments.

The ordination and correlation analyses of the data for the deeper zone (4–5 m) showed that retention time and interrelated factors such as the colour of the water and concentration of total phosphorus, which both had strong negative correlations on retention time, were the main factors explaining the variation on axis 1. Thus, axis 1 was interpreted as a loading gradient, since loading generally increases with increasing water flow, i.e. with decreasing retention time. None of the environmental factors studied showed any significant correlation on axis 2. It was nevertheless possible to separate two distinct patterns from the basic group, a "*Chaoborus flavicans* group" and a "*Zalutschia zalutschicola* group", both of which included lakes characterised by poor oxygen conditions in their deeper areas. Those lakes where the fauna in the deeper zone was mainly composed of *Chaoborus* suffered oxygen depletion during the summer, while those in which the *Zalutschia* larvae were the dominant species retained an oxygen saturation above 20% at this depth zone.

As stated above, the seasonal variation in the benthic assemblages disturbs the community analyses and may bias the results, but even so it may be concluded that the littoral fauna was greatly affected by the acidity of the water, while the fauna in the deeper zone in these small lakes was largely determined by factors other than acidity, e.g. the trophic level of the lake and the availability of oxygen.

Correlation and Regression Analyses

The benthic biomass at 1 m averaged 2.22 g m^{-2}, ranging from 0.01 to 14.5 g m^{-2}. None of the environmental variables studied could explain the observed variation in biomass. The number of individuals, which averaged 1604 ind m^{-2}, showed a non-significant correlation on minimum pH. It is interesting to note that lake acidity was the determining variable for the number of species, in the form of pH in most cases but minimum pH for the gastropods and mayflies (Table 1). The large-sized insect larvae such as dragonflies, caddis flies and alderflies (including *Sialis lutaria* and the rare *S. sordida*) seemed to be indifferent to lake acidity. The number of dragonfly species was even somewhat higher in the acidic lakes, the correlation on minimum pH being − 0.22*.

The relationship between the number of species of mollusks and the acidity was still stronger when the humic lakes (water colour $\geq$ 50 mg Pt/l) were excluded. In this case the correlation of minimum pH with the number of species was 0.68*** for the gastropods and 0.70*** for the mussels (n = 46 lakes).

Calcium concentration is usually regarded as one of the main factors determining the distribution and abundance of freshwater mollusks, especially gastropods

Table 1. Stepwise regression analysis for the abundance of benthic invertebrates at 1 m and the numbers of species of different groups found in the lakes.

	Step	Determining Variable	R	R^2	n
Benthic biomass	1	[a]			86
No. of individuals	1	pH_{min}	− 0.21 NS	0.04	86
No. of species					
Gastropoda	1	pH_{min}	0.60***	0.36	86
Lamellibranchiata	1	pH	0.57***	0.32	86
	2	pH + Mg	0.65***	0.42	86
Ephemeroptera	1	pH_{min}	0.64***	0.41	86
Chironomidae	1	pH	0.44***	0.20	65
Oligochaeta	1	pH	0.2*	0.08	65
	2	pH + Mg	0.36*	0.13	65
	3	pH + Mg + Ca	0.42**	0.18	65
Total	1	pH	0.54***	0.29	65
	2	pH + Mg	0.57***	0.32	65

[a] No variables meet the criteria.
Statistical significances: *, $P \leq 0.05$; **, $P \leq 0.01$ and ***, $P \leq 0.001$

(Aho 1984). The correlation of the species number of snails with the Ca concentration was fairly low in this material (r = 0.27*) in relation to that with lake acidity. Snails were absent from lakes with a Ca concentration below 1.7 mg l^{-1} and with a Mg concentration below 0.5 mg l^{-1}. The corresponding values for mussels were 1.0 mg l^{-1} Ca and 0.4 mg l^{-1} Mg.

Species in Relation to Acidity

Gastropods were the most sensitive to acidity, even the most tolerant species, *Lymnaea peregra*, being absent from lakes with a minimum pH below 5.3 and a mean pH below 5.7 (Table 2). Small mussels were very much more tolerant than snails, but they were also absent from the most acidic lakes. The most tolerant among the common mussels were *Pisidium casertanum*, *P. hibernicum*, *P. henslowanum* and *P. nitidum*.

Lumbriculidae and Enchytraeidae oligochaetes were found in the most acidic lakes, while the common species, *Peloscolex ferox*, *Limnodrilus hoffmeisteri* and *Stylaria lacustris*, were more sensitive and were absent from lakes with a minimum pH below 4.7 and a mean pH below 5.3 (Table 3). *Helobdella stagnalis* seemed to be the most sensitive of the leeches.

Leptophlebia marginata and *L. vespertina* were found in the most acidic lakes, but the other mayfly species were absent from acidic water. The most common species in our material, *Ephemera vulgata*, was found only in lakes with a minimum pH above 5.2 and a mean pH above 5.5 (Table 4). The other insects were in general fairly tolerant of acid water. Although the number of chironomid taxa decreased markedly with increasing acidity (Table 1), only four of the approx. 30 most

Table 2. Lowest pH limits for the most common mollusck species on the basis of observed minimum pH and mean pH, n = 140 lakes for Gastropoda and n = 86 for Sphaeriidae

	pH	
	Minimum	Mean
Lymnaea peregra	5.3	5.7
Myxas glutinosa	5.5	5.7
Gyraulus albus	5.7	5.9
G. laevis	5.7	5.9
Lymnaea stagnalis	5.7	6.0
L. auricularia	5.8	6.2
Valvata piscinalis	6.2	6.8
V. pulchella	7.2	7.3
Pisidium casertanum	4.5	5.0
P. hibernicum	4.8	5.3
P. henslowanum	4.9	5.0
P. nitidum	4.9	5.0
P. obtusale lapponicum	5.0	5.5
P. milium	5.1	5.3
P. lilljeborgii	5.1	5.5
P. moitessierianum	5.1	5.5
P. obtusale	5.2	5.4
P. subtruncatum	5.3	5.6
P. pseudosphaerium	5.4	5.5
Sphaerium corneum	5.7	6.0

Table 3. pH limits for the most common Oligochaeta and Hirudinea, as in Table 2, n = 63 for Oligochaeta and 140 for Hirudinea

	pH	
	Minimum	Mean
Lumbriculidae	4.3	4.5
Enchytraeidae	4.4	4.8
Stylaria lacustris	4.7	5.3
Limnodrilus hoffmeisteri	4.7	5.3
Peloscolex ferox	4.7	5.3
Erpobdella octoculata	4.8	5.3
Glossiphonia complanata	4.8	5.3
Helobdella stagnalis	5.5	6.1

common taxa being absent from lakes with a minimum pH below 4.7 and a mean pH below 5.2. These were *Polypedilum bicrenatum* gr., *P. convictum* gr., *Phaenopsectra flavipes* and *Stictochironomus* spp. Several midge taxa such as *Ablabesmyia longistyla*, *Procladius* spp., *Psectrocladius limbatellus* gr., *Chironomus plumosus* gr., *C. thummi* gr., *Dicrotendipes pulsus*, *Microtendipes* spp., *Tanytarsus* spp. and *Chaoborus flavicans* continued to be numerous in the acidic lakes.

Table 4. pH limits for the most common Ephemeroptera species, as in Table 2, n = 140 lakes

	pH	
	Minimum	Mean
Leptophlebia spp.	4.3	4.5
Ephemera vulgata	5.3	5.6
Caenis horaria	5.3	6.0
Cloeon dipterum	5.4	5.5
Caenis luctuosa	5.7	6.2

Sampling Efficiency

The number of individuals caught in four hand net samples was 784 in the non-acidic Lake Harviolampi, with a pH of 6.7, while only 46 were caught in six Ekman samples (Fig. 3), and the number of species was similarly much higher in the hand net samples, 55, than in Ekman samples, 14. The situation was somewhat different in the moderately acidic lakes, in which the pH ranged from 5.0 (in Lake Mäkilampi) to 5.4 (in Lake Vuorilampi), the differences in catches between the two methods being smaller than those in Lake Harviolampi (Fig. 4). The hand net method nevertheless gave more species in relation to the number of individuals in every lake than did the Ekman grab, or at least the same number of species. The probability of obtaining specimens of the rarer species is thus higher when using a hand net method.

The higher efficiency of the hand net is probably largely due to the fact that it also collects animals attached to submerged stems and leaves of the aquatic vegetation, e.g. many gastropods and active swimmers which are able to escape the grab. The catch of representatives of the acid-sensitive groups such as gastropods, small mussels and mayflies was very much better using the hand net (Table 5).

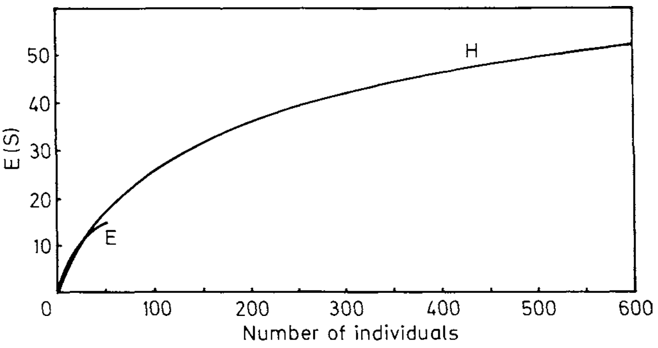

Fig. 3. Rarefaction curves $E(S)$, expected number of species with increasing number of individuals for the quantitative Ekman samples (E) at 1 m and for the qualitative hand net samples (H) at about 0.5–1.0 m in the non-acidic Lake Harviolampi

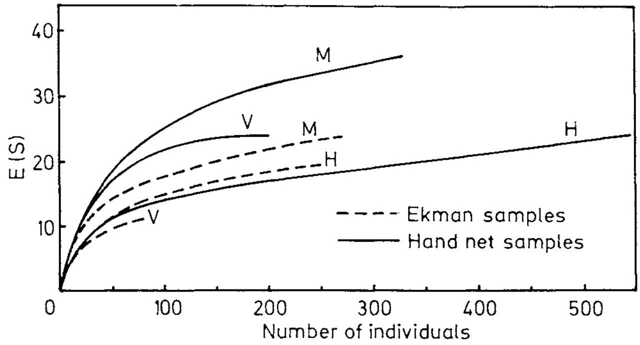

Fig. 4. Rarefaction curves in moderately acidic lakes, as in Fig. 3, Vuorilampi (*V*), Hirvilampi (*H*) and Mäkilampi (*M*)

Table 5. Number of species of the most acid-sensitive groups, total numbers of species and individuals caught with the Ekman grab and hand net. Numbers of samples taken are shown in parentheses. The Ekman samples were taken at about 1 m and hand net samples at 0.5–1.0 m.

	No. of taxa				Individuals
	snails	mussels	mayflies	total	
Lake Harviolampi (pH 6.7)					
Ekman (6)	–	1	–	14	46
Hand net (4)	2	4	3	55	784
Total catch	2	4	3	56	830
Lake Hirvilampi (pH 5.2)					
Ekman (6)	–	1	1	20	283
Hand net (2)	–	3	1	24	548
Total catch	–	3	1	27	831
Lake Mäkilampi (pH 5.0)					
Ekman (3)	–	–	–	24	283
Hand net (4)	–	–	1	36	330
Total catch	–	–	1	40	613
Lake Vuorilampi (pH 5.4)					
Ekman (3)	–	–	–	11	82
Hand net (2)	–	–	1	24	162
Total catch	–	–	1	26	244

Discussion

Abundance of Zoobenthos in Acid Water

As observed here, benthic biomass shows no significant correlation with water pH. This has also been so in many earlier works (Wiederholm and Eriksson 1977; Mossberg and Nyberg 1979; Dermott 1985; Dermott et al. 1986; Buskens et al.

1986; Bradt and Berg 1987), although findings which point to the opposite conclusion also exist, so that at least four theories have been put forward to explain this disagreement (see details in Økland and Økland 1986).

The importance of fish predation for the structuring of animal communities is stressed by many authors (Grahn et al. 1974; Mossberg and Nyberg 1979; Eriksson et al. 1980), and Bendell and McNicol (1987) even concluded that fish predation is the most immediate factor structuring aquatic insect assemblages and is responsible for the changes in these coincident with lake acidification. We were not able to examine this phenomenon in the present material. It is apparent, however, that the acidified parts of the Kyrönjoki estuary harbour low abundance of zoobenthos even though fish predation is low due to the acid, Al-contaminated water entering the area from the river (Meriläinen 1988), and it is concluded in this case that the high concentrations of monomeric inorganic aluminium during the acid periods (200–320 µg/l and over 2000 µg/l in places) were mainly responsible for the low benthic biomass in the acidic freshwater area of the estuary.

Impact of Acid Water on Species Numbers

The most acid-sensitive animal groups and species in the material, the gastropods, small mussels and mayflies (except *Leptophlebia*), were those known also to be absent from acid water bodies in many other countries (Wiederholm and Eriksson 1977; Mossberg and Nyberg 1979; Økland and Kuiper 1980; Engblom and Lingdell 1984; Raddum and Fjellheim 1984; Leuven et al. 1986; Økland and Økland L1986). The lower pH limits obtained for some species here cannot be regarded as absolute values, but they do give a general idea of the sensitivity of the species to acidic water. These limits nevertheless come very close to those given by Økland (1980) and Økland and Kuiper (1980) for different species of mollusks in Norway and the experimental and empirical values given for different species of mayflies in Scandinavia (Engblom and Lingdell 1984; Raddum and Fjellheim 1984).

Observations made on the most common tubificid species such as *Peloscolex ferox* and *Limnodrilus hoffmeisteri* (including immature specimens of the genus), show that they are not tolerant to acidity. On the other hand, *Limnodrilus* can survive in areas with periodical acidity (Meriläinen 1988). This may indicate that the duration of the acid period is an important factor for benthic species living in sediments. Experiments have shown that several invertebrates (Hall et al. 1980, 1987) and amphibian embryos (Clark and Hall 1985) die within a short time if exposed to low pH and high concentrations of monomeric inorganic Al.

Many chironomid species will tolerate an acidity of pH 4–4.5, usually they make up the major part of the macrobenthos in acidified water, especially in lakes (Wiederholm and Eriksson 1977; Mossberg 1979; Mossberg and Nyberg 1979; Buskens et al. 1986; Bradt and Berg 1987). As shown here and by Raddum and Saether (1981) and Leuven et al. (1986), however, the number of midge taxa in a lake decreases with increasing acidity. There are also indications that the number of species of both leeches (Raddum and Fjellheim 1984; this chapter) and water mites (Meriläinen 1988) decreases in acidic water. In other words, the benthic diversity decreases with increasing acidity. The littoral zones of highly acidic lakes harbour a rather simple assemblage of benthic invertebrates, consisting mainly of the large-sized insects living on the bottom such as larvae of dragonflies, alderflies, caddis flies and some midges, and also freely swimming water bugs and beetles, which are common in acidic lakes (Leuven et al. 1986; Bendell and McNicol 1987).

We were not able to distinguish the effects of acidity on the benthic fauna in the deeper zone of the lakes. The hypolimnion in small forest lakes is usually very small in volume, which means that the deeper bottoms suffer from an oxygen deficit, especially at the end of the stagnation periods in late winter and late summer. The surface water of these sheltered lakes soon warms up in spring, which may result in an incomplete overturn and poor oxygen conditions in hypolimnion during the summer. Due to the low oxygen concentration, the deeper areas in these lakes harbour a sparse fauna usually consisting of certain midge species, mainly *Chironomus* spp., *Chaoborus flavicans* and Tanypodinae chironomids. All these are common in acidified lakes (Mossberg and Nyberg 1979; Dickmann et al. 1987; Wickham et al. 1987).

The effects of acid water can be divided simply into direct and indirect effects. The acidity can directly affect the physiology of the species, or it may indirectly increase the toxic effects of other substances or the concentrations of the toxic forms of substances. It can be concluded that acidity is the primary factor leading to a decline in the fauna and a reduced community structure in acidified water, although indirect chemical and biological effects are undoubtedly also important.

Acid water may affect the food supply to the extent that the quantity and/or quality of the food is insufficient for some animals (see Sutcliffe and Carric 1973; Ziemann 1975; Townsend et al. 1983). Otto and Svensson (1983) suggest the low quality of leaf material in acid streams may be responsible for the low number of shredder species, and they also hold the food shortage, i.e. reduced growth of periphytic algae, to be partly responsible for the absence of mayflies from acidic, brown-water streams. The reduced community structure in turn affects the occurrence of a number of carnivorous animals. The absence and scarcity of leeches in acidic water is an example of this, as their occurrence is largely determined by the presence of snails, the main prey organisms of the most common leech species (Raddum 1980).

Many investigators have concluded that mobilized aluminium, as well as low pH, is a major determinant of the abundance and distribution of aquatic invertebrates in acidified water (Hall et al. 1980, 1987; Herrmann and Baron 1980; Harriman and Morrison 1982; Havas and Hutchinson 1982; Burton and Allan 1986; Wicham et al. 1987).

Monomeric inorganic Al is the most toxic Al fraction in water. Driscoll et al. (1980) and Baker and Schofield (1982) have shown in laboratory experiments with fish that the most toxic forms are AlOH species, AlF complexes were moderately toxic, and organically complexed Al was non-toxic. The experiments performed by Clark and Hall (1985) suggest that AlF complexes are toxic to amphibians. This means that the pH and the availability of different complexing ligands such as fluoride, sulphate and organic matter will ultimately determine the toxicity of labile aluminium for animals. Birchall et al. (1988) have shown recently in experiments with Atlantic salmon fry that the availability of Al at pH 5 is reduced by an excess of Si over Al and its acute toxicity is eliminated. This effect was achieved at a Si:Al (exchangeable Al) ratio of 15.5, but positive effects were not observed when the ratio ranged from 0.4 to 5.

The present material included 13 acid lakes ($pH \leq 5.3$) with a high concentration of labile aluminium (95–308 $\mu g\, l^{-1}$ or 3.5–11 $\mu mol\, l^{-1}$). The concentration of SiO_2 in these lakes ranged from 0.5 to 7.1 $mg\, l^{-1}$ (10–118 $\mu mol\, l^{-1}$), so that the Si:labile Al ratio was from 1.3 to 14.9. The total number of benthic taxa present in these lakes bore no relationship to the Si:Al ratio. This may indicate that the positive effects of silica remain low in our forest lakes, but further investigation is needed to explain the importance of silicates to Al toxicity under natural conditions. Investigations are also needed to determine the suitability of the present analytical methods for the labile fraction of Al in humic water.

Conclusions

The community structure of benthic invertebrates is reduced with increasing acidity in small forest lakes, and there are certain acid-sensitive species, especially among the snails, mayflies and small mussels, by means of which it would be possible to evaluate the stage of acidification of a lake. In most cases the presence of these species is more closely related to minimum pH, the acid peak in a lake usually occurring as the snow is melting, than to average or autumn pH. This represents a considerable advance compared with the results achieved by physicochemical monitoring of water quality. The difference between minimum pH and average or autumn pH may be great and a very comprehensive system for monitoring water quality is needed to identify the most pronounced acid periods.

The fauna in the deeper zones of these forest lakes is usually highly reduced, often as a result of poor oxygen conditions, and it was not possible here to separate the effects possibly attributable to acidity from those of other factors.

The hand net offers a superior method for sampling the littoral benthos at about 0.5–1 m, making it much easier to obtain samples containing a high number of individuals and species than with the Ekman grab. It can be estimated that two hand net samples taken for about one minute each from different parts of a lake will be appropriate for practical purposes when assessing acidification in lakes.

It is recommended that several regions distributed over the whole country should be included in the monitoring system and each should contain a number of lakes. Identification of the “key groups”, snails, mussels and mayflies, is usually appropriate for monitoring purposes, although examination of the whole material will naturally give more information about the ecological relationships between the animals and their environment.

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Appendix. The species list and the lowest observed pH limits for the occurrence of the common species (frequency ≥ 10% of the studied lakes) in the data collected from 85 acid and acid-sensitive forest lakes situated mainly in southern Finland

	Minimum pH
Porifera	
Spongilla lacustris (L.)	5.4
Gastropoda	
Valvata pulchella Studer	
V. piscinalis Müll.	
Lymnaea auricularia L.	5.8
L. palustris Müll.	
L. peregra Müll.	5.3
L. stagnalis L.	
Myxas glutinosa Müll.	
Gyraulus albus Müll.	5.7
G. laevis (Adler)	5.7
Lamellibranchiata	
Pisidium casertanum Poli	4.5
P. henslowanum Shepp.	4.9
P. hibernicum Wstl.	4.8
P. lilljeborgii Cl.	5.1
P. milium Held	5.1
P. moitessierianum Palad.	
P. nitidum Jenyns	4.9
P. obtusale C. Pf.	
P. obtusale lapponicum Cl.	
P. pseudosphaerium BJ-K.	
P. subtruncatum Malm	5.3
P. spp.	
Sphaerium corneum (L.)	5.7
Oligochaeta	
Stylodrilus heringianus Clap.	4.5
Lumbriculidae	4.3
Tubifex sp.	4.4
Psammoryctides albicola (Mich.)	
P. barbatus (Grube)	5.3
Limnodrilus hoffmeisteri Clap.	4.7
L. udekemianus Clap.	
L. spp. (immature)	
Peloscolex ferox (Eisen)	4.7
Arcteonais lomondi (Martin)	
Nais spp.	
Ripistes parasita (Schmidt)	
Slavina appendiculata (Od.)	
Stylaria lacustris (L.)	4.7
Uncinais uncinata (Oerst.)	
Vejdovskyella comata (Vej.)	
Enchytraeidae	4.4
Hirudinea	
Glossiphonia complanata (L.)	4.8

Appendix (continued)

	Minimum pH
Helobdella stagnalis (L.)	5.5
Erpobdella octoculata (L.)	4.8
Acari, Hydrachnellae	4.3
Crustacea	
Mysis relicta Lovén	
Asellus aquaticus L.	4.3
Gammarus lacustris Sars.	
Pallasea quadrispinosa Sars.	
Ephemeroptera	
Siphlonurus alternatus (Say)	
Baetis vernus Curtis	
Cloeon dipterum (L.)	5.4
C. sp.	
Procloeon bifidum (Bgts.)	
Heptagenia fuscogrisea (Retz.)	
Leptophlebia spp.	4.3
Paraleptophlebia cincta (Retz.)	
Ephemera vulgata (L.)	5.3
Caenis horaria (L.)	5.3
C. luctuosa (Burm.)	5.7
C. lactea (Burm.)	
Odonata	
Coenagrion hastulatum (Charp.)	
C. spp.	
Erythromma najas (Hansem.)	
Enallagma cyathigerum (Charp.)	
Gomphus vulgatissimus (L.)	
Aeschna grandis (L.)	
Ae. caerulea (Ström)	
Ae. cyanea (Mull.)	
Epitheca bimaculata (Charp.)	4.3
Somatochlora metallica (V.d.L.)	
S. arctica (Zett.)	
Cordulia aenea (L.)	4.5
Libellula depressa L.	
L. sp.	
Sympetrum sp.	
Leucorrhinia rubicunda (L.)	
L. sp.	
Neuroptera	
Sialis lutaria (L.)	4.5
S. sordida Klingst.	4.5
Trichoptera	
Oxyethira sp.	
Tinodes waeneri (L.)	
Ecnomus tenellus (Ramb.)	
Polycentropus flavomaculatus (Pict.)	
Holocentropus dubius (Ramb.)	4.5

Appendix (continued)

	Minimum pH
Cyrnus flavidus McL.	4.5
C. trimaculatus (Curt.)	
Agrypnia pagetana Curt.	
A. obsoleta (Hagen)	
A. varia (Fabr.)	
A. sp.	4.5
Phryganea bipunctata Retz.	4.5
P. sp.	
Limnephilidae	4.7
Nemotaulius punctatolineatus (Retz.)	
Molanna angustata Curt.	4.5
M. albicans (Zett.)	
M. submarginalis McL.	
Molannodes tinctus Zett.	
Athripsodes aterrimus (Steph.)	
A. cinereus (Curt.)	
A. sp.	
Mystacides azureus (L.)	4.3
M. longicornis (L.)	4.8
M. niger (L.)	
Triaenodes bicolor (Curt.)	
Erotesis baltica McL.	
Oecetis ochracea (Curt.)	
O. furva (Ramb.)	
O. lacustris (Pict.)	
O. testacea (Curt.)	
Coleoptera	
Haliplus sp.	
Oulimnius sp.	
Coleoptera, others	4.5
Diptera	
Chaoborus flavicans (Mg)	4.5
Tanypodinae	
Ablabesmyia longistyla Fitt.	4.5
A. monilis (L.)	4.5
A. phatta (Egger)	4.5
Anatopynia plumipes (Fries)	
Apsectrotanypus trifascipennis (Zett.)	5.7
Arctopelopia spp.	4.7
Clinotanypus nervosus (Mg.)	4.7
Conchapelopia spp.	5.0
Guttipelopia guttipennis (v.d.W.)	
Labrundinia longipalpis (Goetgh)	
Macropelopia nebulosa (Mg.)	
M. notata gr.	4.5
Paramerina cingulata (Walk)	
Procladius gr. a	4.5
P. gr. b	4.3

Appendix (continued)

	Minimum pH
P. gr. c	4.5
P. spp.	4.5
Thienemannimyia spp.	5.7
Diamesinae	
Protanypus morio (Zett.)	4.7
Prodiamesinae	
Monodiamesa bathyphila (K.)	5.0
Orthocladiinae	
Acamptocladius submontanus (Edw.)	
Chaetocladius dentiforceps gr.	
Corynoneura lacustris Edw.	4.5
C. scutellata gr.	
C. sp.	
Cricotopus bicinctus gr.	
C. cylindraceus gr.	
C. festivellus gr.	
C. (*C.*) spp.	4.9
C. intersectus gr.	
C. sylvestris gr.	
Epoicocladius flavens (Mall.)	
Heterotanytarsus apicalis (K.)	5.0
Heterotrissocladius grimshawi (Edw.)	
H. maari Br.	
H. marcidus (Walk.)	4.5
Limnophyes prolongatus gr.	
Metriocnemus sp.	
Nanocladius bicolor (Zett.)	
Orthocladius sp.	
Parakiefferiella smolandica (Br.)	
P. sp.	
Psectrocladius (*Allospsectrocladius*) sp.	
P. (*Mesospsectrocladius*) sp.	
P. (*Monopsectrocladius*) sp.	
P. calcaratus (Edw.)	4.5
P. limbatellus gr.	4.3
P. psilopterus gr.	4.4
P. septentrionalis gr.	
P. sordidellus gr.	4.9
Synorthocladius semivirens (K.)	
Tokunagayusurica komensis Zvereva	
Zalutschia zalutschicola Lipina	4.6
Z. korosiensis gr.	
Chironomini	
Chironomus plumosus (L.)	
C. p. (*semireductus*) gr.	4.5
C. salinarius gr.	
C. thummi gr.	4.3
Cladopelma viridula (L.)	4.3

Appendix (continued)

	Minimum pH
C. sp.	
Cryptochironomus defectus gr.	4.4
Cryptotendipes sp.	
Demicryptochironomus vulneratus (Zett.)	4.3
Dicrotendipes lobiger (K.)	
D. pulsus (Walk.)	4.3
Einfeldia gr. a	
E. gr. *b*	
Endochironomus albipennis (Mg.)	5.2
E. impar (Walk.)	5.7
E. sp.	
Glyptotendipes spp.	4.4
Harnischia curtilamellata (Mall.)	5.7
Lauterborniella agrayloides (K.)	
Microchironomus tener (K.)	
Microtendipes spp.	4.4
Nilothauma brayi (Goetgh.)	
Omisus caledonicus (Edw.)	
Pagastiella orophila (Edw.)	4.5
Parachironomus arcuatus gr.	4.8
P. vitiosus gr.	
Paracladopelma camptolabis gr.	
P. nigritula gr.	
Paralauterborniella nigrohalteralis (Mall.)	
Paratendipes albimanus (Mg.)	
P. nudisquama (Edw.)	
Phaenopsectra flavipes (Mg.)	4.7
Polypedilum sordens gr.	
P. bicrenatum gr.	4.7
P. convictum gr.	4.7
P. pullum (Zett.)	4.8
Sergentia coracina (Zett.)	4.5
Stenochironomus sp.	4.7
Stictochironomus rosenscholdi (Zett.)	
S. spp.	4.9
Tribelos intextus (Walk.)	4.5
Xenochironomus xenolabis (K.)	
Pseudochironomini	
Pseudochironomus prasinatus (Staeg.)	4.5
Tanytarsini	
Cladotanytarsus spp.	4.5
Corynocera ambigua Zett.	
Paratanytarsus spp.	
Stempellina bausei (K.)	
Stempellina subglabripennis (Br.)	
Stempellinella minor (Edw.)	
Tanytarsus chinyensis gr.	

Appendix (continued)

	Minimum pH
T. gregarius gr.	
T. lugens gr.	
T. spp.	4.3
Ceratopogonidae	4.3
Brachycera	4.8

Estimation of Acidity in Streams by Means of Benthic Invertebrates: Evaluation of Two Methods

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Summary

The distribution of benthic invertebrates was studied in relation to stream acidity. The object was to evaluate use of invertebrates in assessing stream acidity. Of two methods applied, the first is tolerance limit (TL) method based on presence/absence of indicator species. The second method is weighted averaging based on species optima and tolerances, which were estimated by maximum likelihood (ML) and weighted averaging (WA) methods, assuming unimodal relationship between relative abundance of invertebrate taxa and the stream pH.

The total number of taxa increased with increasing stream pH. Within the same pH range, the number of taxa appeared to be higher in humic versus clearwater streams. At the species level, the distribution of *Baetis* mayflies also indicated that humic substances may ameliorate the harmful effects of low pH. According to the tolerance limits, few highly acid sensitive taxa were found, but differences in stream acidity could be demonstrated by observing the appearance of species with different sensitivity. The predicted minimum pH with both ML and WA estimates showed a highly significant relationship to the observed stream pH. The results suggest that also the pH in lake surface water during the spring snowmelt period can be assessed by use of outlet invertebrate assemblages. The results do not reveal the order of superiority of the two methods in detecting acidity level. The method of weighted averaging was, however, considered more informative in monitoring acidification.

Introduction

Many species of freshwater benthic invertebrates are shown to be sensitive to low pH and, consequently acid deposition has impoverished the benthic fauna in numerous lakes and streams (Økland and Økland 1986). The effects of acid precipitation are likely to be observed first in streams where the rainwater often forms a great part of the water volume. The pH in streams usually attains the annual minimum in spring when a rapid melting of accumulated low pH snowpack occurs (Gjessing et al. 1976; Haapala et al. 1978; Jeffries et al. 1979). These acid pulses, even of short duration, can be deleterious to the sensitive invertebrate

Kauppi et al. (Eds).
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species (e.g. Bell 1971; Engblom and Lingdell 1983). Studies using multivariate statistical analysis (Townsend et al. 1983; Wright et al. 1984; Ormerod and Edwards 1987) suggest that of many environmental variables, pH, or factors closely related, best explain the variation of stream benthos. In Scandinavia, both spatial and temporal variation in faunal composition have been well documented and attributed to surface water acidification (Engblom and Lingdell 1984; Raddum and Fjellheim 1984; Degerman et al. 1987; Raddum et al. 1988). In these studies the lower limit of pH tolerance for many species was derived mainly from field observations and the level of acidification of a given site was judged by presence/absence of these species.

In this study we observed the distribution of benthic invertebrates in small streams as related to stream pH. The main objective of the study was to evaluate methods for acidification monitoring by use of benthic fauna. We attempted to predict the stream minimum pH as a measure of acidity level. In addition to the tolerance limit method, used earlier, we tried a new one based on species pH optima and tolerances, recently applied in the prediction of lake acidity by means of diatom assemblages (Oksanen et al. 1988; Ter Braak and van Dam 1989). In this method species relative abundances were taken into account, which was thought to give some advantages if compared to simple presence/absence observation. We also tried to ascertain the most suitable sampling season for the monitoring survey.

Materials and Methods

Study Sites and Data Sampling

Benthic invertebrates and water samples were collected from a total of 54 small streams in southern and eastern Finland in 1985–88 (Fig. 1). The streams were divided into two separate groups, the first of which consists of 32 streams and will be referred to as the estimation set. The remaining 22 streams were used in assessing the predictions by different methods based on data from the estimation set. This group will be referred to as the prediction set.

Except for three first-order streams in the estimation set (numbers 27–29), all streams studied are lake outlets. Some of the streams within the estimation set and all among the prediction set discharge lakes which are also targets of other subprojects of the Finnish Research Project on Acidification. The water chemistry of the streams is presented in Huttunen and Hämäläinen (1989).

Macroinvertebrate samples were collected with a hand-net (mesh size 0.5 mm), and preserved in alcohol. In the laboratory, all animals were picked by the aid of an illuminated magnifying glass (4 ×). Current velocity and the dominant substratum type varied between streams, but an attempt to standardize these factors was made by choosing each sampling site from the most rapidly flowing section where at least some gravel and scattered stones existed. The objective of the sampling strategy was to obtain species lists and relative abundances of the species

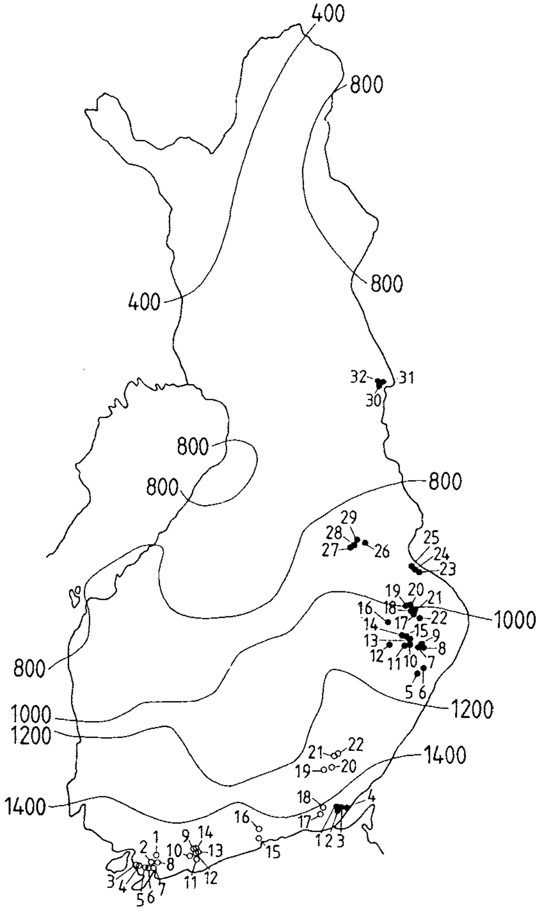

Fig. 1. Location of the study sites. The estimation (*filled circles*) and the prediction data set (*open circles*). The sulphur deposition (mg $m^{-2} a^{-1}$) in 1985 is indicated by *isoclines*

in each stream. Each of the streams of the estimation set was sampled three times (in spring, summer and autumn) in one year during the investigation period. The streams of the prediction set were sampled only once in the autumn of 1986. Except for Oligochaeta and Diptera, the invertebrates were identified mostly to species or genus.

Water samples for chemical analyses were collected from streams at the time of benthic sampling. In order to detect the lowest prevailing pH value, the streams of the estimation set were first visited during snowmelt period in spring. Some streams were sampled more than once during that period. The standard methods of the Finnish water authority were used for water analysis (National Board of Waters, 1981).

Estimation of Indicator Values

The indicator values were derived from the estimation data set. The tolerance limit (TL) of a species was defined as the lowest measured pH value among those streams where the species was present. According to their tolerance limits species were further arranged into four pH categories: (1) < 4.5, (2) 4.5–4.9, (3) 5.0–5.4, (4) > 5.4.

The optima with respect to stream minimum pH were estimated by two methods. Assuming the Gaussian response model (Gaugh and Whittaker 1972), the optima, tolerances and expected maximum abundances for species were estimated by the maximum likelihood (ML) method. The lowest measured pH was used as an explanatory factor. The GLIM programme (Payne 1986) was applied to fit the model. The mathematical approach of Oksanen et al. (1988) was followed. The optima and tolerances were also estimated with the more simple and less elaborate method of weighted averaging (WA). Here, the abundance weighted average minimum pH is the estimate of the optimum and the abundance weighted standard deviation is the measure of the species amplitude comparable with tolerance (Ter Braak and Looman 1986; Oksanen et al. 1988). The formulas for WA are given by Huttunen and Turkia in this Volume. The relative abundances of species in combined samples of the three seasons were used in parameter estimation. The oligochaetes and dipterans were not included in calculations. ML estimates were determined for those species and genera which occurred at least in seven streams within the estimation set. WA estimates and tolerance limits are given for species and genera which were found in at least three streams.

Prediction Methods

The estimated indicator values were used in predicting minimum pH for streams in both data sets. The first and most simple prediction method is based on species pH categories. For each stream the species with the highest category number was considered to indicate the lowest encountered pH value at the corresponding accuracy of category. The method is basically similar to that represented by Engblom and Lingdell (1983, 1984, 1987) and Raddum et al. (1988). We also used tolerance limits as such instead of pH categories to obtain more precise predictions. The latter will be called tolerance limit (TL) predictions.

The second method of weighted averaging is based on the assumption that in a given stream, taxa with an optimum close to the stream pH are most abundant. By this method the minimum pH of a stream was given as the abundance weighted average of the optima of occurring species. Predictions were made separately with WA and ML optima. The inverses of squared tolerances were used as additional weights to give more stress to "good" indicators, i.e. species with narrow tolerance (Ter Braak and Barendregt 1986; Oksanen et al. 1988; Huttunen Turkia and this Vol.). One of the required conditions for unbiased calibration by the weighted averaging is the equal maximum abundances of the species (Ter Braak and

Barendregt 1986). This assumption is obviously violated here, because species of different trophic levels are included. When predicting with the ML estimates we tried to correct this defect by use of the inverses of expected maximum abundances as second additional weights.

The reliability of predictions was assessed by comparing measured and predicted pH values. The TL, WA and ML predictions were plotted against the observed pH values, and regression analysis was performed. Additionally, the mean and standard deviation of differences (predicted minus observed pH) were used as measures of the goodness of prediction (see Oksanen et al. 1988). Within the estimation set comparisons were made between the predicted and the lowest measured pH values, but in the prediction set only autumn pH was available. However, eight of the lakes above these streams were sampled for water chemistry by Tuunainen et al. (1987) during the snowmelt period in spring 1986. In these cases we also compared the predicted pH with the arithmetic mean of lake littoral and surface pH, which was assumed to correspond to the outflow pH. In the estimation set the predictions were done both with combined samples and with samples from the three time periods separately, in order to ascertain the best sampling season.

Results

Benthic Invertebrates and Their Indicator Values

The number of animals collected per stream ranged between 835 and 4423 (mean 2088) in the estimation set and between 126 and 1171 (mean 553) in the prediction set. 125 taxa were represented in the samples. In the estimation set the number of taxa per stream varied between 12 and 48. On average, the autumn samples included 73% of the total taxa detected and the spring and summer samples yielded 66 and 59% of the taxa, respectively. The total number of taxa was significantly positively correlated with the minimum pH (estimation set) and the autumn pH (prediction set). In the estimation set an abrupt decline in taxonomical richness occurred at a minimum pH of about 5. The number of taxa within a given pH range appeared to be higher in humic (colour > 50 Pt mg$\,l^{-1}$) versus clear-water streams (Fig. 2).

Distribution of the selected taxa (occurrence ≥ 3) as related to stream minimum pH is shown in Fig. 3. According to their tolerance limits, 14 taxa were assigned to pH category 1, and 21, 28 and 8 taxa to categories 2, 3 and 4, respectively. WA estimates were calculated for all of these 71 taxa and ML estimates for 42 taxa (Table 1). ML estimates for a few species are missing, irrespective of sufficient number of recordings, through a failure to fit the model. In general the WA and ML optima as well as tolerances were in good agreement (Table 1). The greatest difference between the two optima obtained was in alderfly *Sialis fuliginosa*, for which the WA estimate was 0.76 pH units higher than ML.

There was a significant positive correlation between pH and the number of mayfly (Ephemeroptera) taxa in both the estimation set ($r = 0.55$, $p < 0.001$) and prediction set ($r = 0.79$, $p < 0.001$). *Leptophlebia marginata* and *L. vespertina* were often the sole representatives of the order in the most acidic streams. All species, except for *Centroptilum luteolum*, *Caenis horaria*, and some of those recorded only once or twice, were found in streams with the minimum pH of 5.0 or less (Table 1). However, as indicated by the optima, most species occurred more frequently or abundantly, or both, in less acidic streams; e.g. *Baetis rhodani* the obtained TL was pH 4.9 and the optima 6.3. This species occurred in all but three streams with the minimum pH above 5.5, but only in four streams below that. All those streams with minimum pH < 5.5 and with a population of *B. rhodani* or any other *Baetis*-species, were brown-coloured.

There was no correlation between stonefly (Plecoptera) taxa and the minimum pH in the estimation set, but in the prediction set the number of taxa tend to increase with increasing autumn pH ($r = 0.52$, $p = 0.013$). None of the species proved to be particularly sensitive to acidity, since all were found in streams with a minimum pH of 5.0 or less (Table 1). *Nemoura flexuosa*, *Isoperla* spp. and *Leuctra fusca* had the highest estimated optima and they were clearly more frequent and abundant in less acidic streams. *Leuctra digitata* is an example of taxa with high WA optimum, but almost even distribution along the pH gradient. This is indicated by a wide standard deviation and by the failure to fit the unimodal model in ML (Table 1). Of the highly tolerant stonefly species, *Leuctra nigra* and *Nemurella pictetii* were almost completely restricted to the most acidic streams. *Nemoura cinerea* inhabited less acidic streams as well, but was more dominant in more acidic ones.

There was a significant positive correlation between taxonomical richness of caddisflies (Trichoptera) and pH in both the estimation set ($r = 0.57$, $p = 0.001$) and the prediction set ($r = 0.56$, $p = 0.007$). The most acid-sensitive taxa, judging

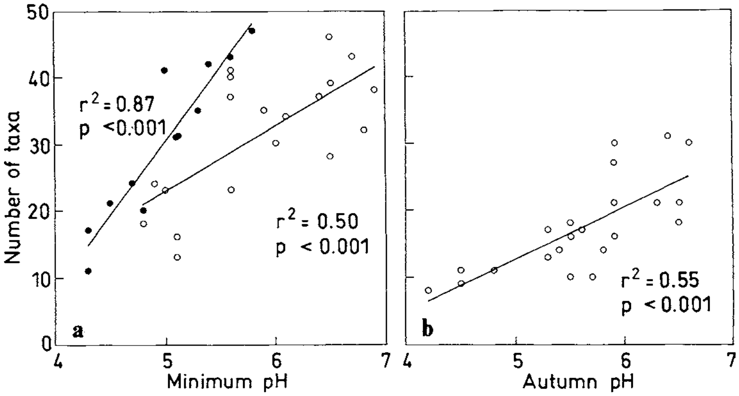

Fig. 2. **a** Number of invertebrate taxa in relation to minimum pH in the estimation set. The streams with water colour >50 Pt mg l^{-1} indicated by *filled circles*. **b** Number of taxa in relation to autumn pH in the prediction set

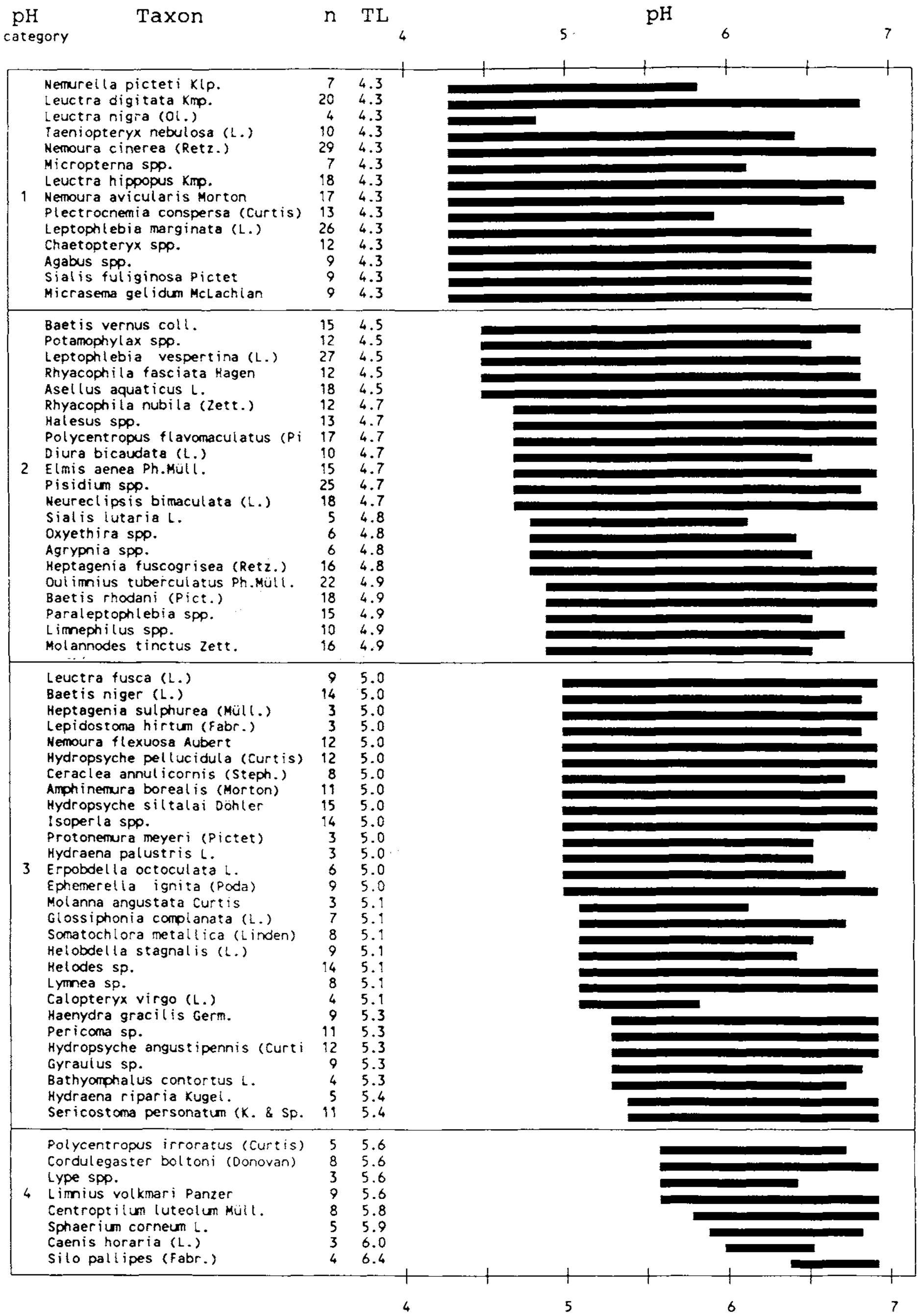

Fig. 3. Incidence of occurrence of selected taxa in relation to stream minimum pH in the estimation set. *TL* lower pH tolerance limit

Table 1. Estimated indicator values by different methods: lower pH tolerance limit (TL), Optimum and tolerance estimated by weighted averaging (WA) and maximum likelihood (ML)

	n	TL	WA	ML
Bivalvia				
Pisidium spp.	25	4.7	5.4 ± 0.43	5.6 ± 0.43
Sphaerium corneum L.	5	5.9	6.1 ± 0.31	– –
Gastropoda				
Lymnea spp.	8	5.1	6.2 ± 0.40	6.2 ± 0.44
Bathyomphalus contortus L.	4	5.3	5.6 ± 0.23	– –
Gyraulus spp.	9	5.3	5.7 ± 0.33	6.0 ± 0.32
Hirudinea				
Erpobdella octoculata L.	6	5.0	5.8 ± 0.34	– –
Helobdella stagnalis (L.)	9	5.1	5.8 ± 0.40	5.8 ± 0.32
Glossiphonia complanata (L.)	7	5.1	5.6 ± 0.50	5.8 ± 0.52
Crustacea				
Asellus aquaticus L.	18	4.5	5.5 ± 0.57	5.7 ± 0.50
Ephemeroptera				
Leptophlebia marginata (L.)	26	4.3	5.5 ± 0.46	5.5 ± 0.42
Leptophlebia vespertina (L.)	27	4.5	5.3 ± 0.36	5.5 ± 0.40
Baetis vernus coll.	15	4.5	4.9 ± 0.50	– –
Heptagenia fuscogrisea (Retz.)	16	4.8	5.9 ± 0.47	5.9 ± 0.47
Baetis rhodani (Pict.)	18	4.9	6.3 ± 0.51	6.3 ± 0.39
Paraleptophlebia spp.	15	5.0	5.7 ± 0.53	5.8 ± 0.41
Baetis niger (L.)	14	4.9	6.0 ± 0.45	6.1 ± 0.34
Ephemerella ignita (Poda)	9	5.0	5.4 ± 0.62	5.7 ± 0.69
Heptagenia sulphurea (Müll.)	3	5.0	5.8 ± 0.71	– –
Centroptilum luteolum Müll.	8	5.8	6.3 ± 0.36	6.3 ± 0.35
Caenis horaria (L.)	3	6.0	6.1 ± 0.09	– –
Plecoptera				
Nemoura cinerea (Retz.)	29	4.3	5.1 ± 0.59	– –
Nemoura avicularis Morton	17	4.3	4.9 ± 0.66	– –
Leuctra digitata Kmp.	20	4.3	6.1 ± 0.86	– –
Taeniopteryx nebulosa (L.)	10	4.3	4.8 ± 0.31	– –
Nemurella picteti Klp.	7	4.3	4.5 ± 0.24	– –
Leuctra nigra (Ol.)	4	4.3	4.4 ± 0.20	– –
Leuctra hippopus Kmp.	18	4.3	5.8 ± 0.85	– –
Diura bicaudata (L.)	10	4.7	5.1 ± 0.42	5.1 ± 0.64
Nemoura flexuosa Aubert	12	5.0	6.1 ± 0.57	6.2 ± 0.49
Amphinemura borealis (Morton)	11	5.0	5.8 ± 0.68	5.9 ± 0.52
Protonemura meyeri (Pictet)	3	5.0	5.5 ± 0.68	– –
Leuctra fusca (L.)	9	5.0	5.9 ± 0.62	6.1 ± 0.59
Isoperla spp.	14	5.0	6.0 ± 0.55	6.2 ± 0.52
Odonata				
Somatochlora metallica (Linden)	8	5.1	5.7 ± 0.58	5.8 ± 0.44
Calopteryx virgo (L.)	4	5.1	5.4 ± 0.24	– –
Cordulegaster boltoni (Donovan)	8	5.6	6.1 ± 0.42	6.1 ± 0.32
Coleoptera				
Agabus spp.	9	4.3	4.7 ± 0.57	– –
Elmis aenea Ph. Müll.	15	4.7	6.2 ± 0.60	6.7 ± 0.78
Oulimnius tuberculatus Ph. Müll.	22	4.9	5.4 ± 0.50	5.7 ± 0.47

Table 1. (continued)

	n	TL	WA	ML
Hydraena palustris L.	3	5.0	6.4 ± 0.38	– –
Helodes spp.	14	5.1	5.9 ± 0.52	6.1 ± 0.43
Haenydra gracilis Germ.	9	5.3	5.6 ± 0.39	5.9 ± 0.38
Hydraena riparia Kugel.	5	5.4	5.8 ± 0.51	– –
Limnius volckmari Panzer	9	5.6	6.5 ± 0.31	6.6 ± 0.39
Megaloptera				
Sialis fuliginosa Pictet	9	4.3	5.0 ± 0.48	4.3 ± 0.97
Sialis lutaria L.	5	4.8	5.3 ± 0.46	– –
Trichoptera				
Plectrocnemia conspersa (Curtis)	13	4.3	4.8 ± 0.42	4.5 ± 0.55
Micropterna spp.	7	4.3	5.0 ± 0.47	4.6 ± 0.68
Micrasema gelidum McLachlan	9	4.3	4.6 ± 0.40	– –
Chaetopteryx spp.	12	4.3	5.3 ± 0.64	5.1 ± 0.83
Potamophylax spp.	12	4.5	5.3 ± 0.59	5.3 ± 0.89
Rhyacophila fasciata Hagen	12	4.5	5.8 ± 0.36	– –
Polycentropus flavomaculatus (Pictet)	17	4.7	5.1 ± 0.41	4.9 ± 0.71
Neureclipsis bimaculata (L.)	18	4.7	5.8 ± 0.64	5.8 ± 0.43
Rhyacophila nubila (Zett.)	12	4.7	6.0 ± 0.79	– –
Halesus spp.	13	4.7	5.8 ± 0.66	6.1 ± 0.76
Agrypnia spp.	6	4.8	5.8 ± 0.77	– –
Oxyethira spp.	6	4.8	5.5 ± 0.28	– –
Molannodes tinctus Zett.	16	4.9	5.7 ± 0.42	5.7 ± 0.35
Limnephilus spp.	10	4.9	5.7 ± 0.39	5.8 ± 0.42
Lepidostoma hirtum (Fabr.)	3	5.0	5.8 ± 0.88	– –
Ceraclea annulicornis (Steph.)	8	5.0	6.1 ± 0.31	6.1 ± 0.27
Hydropsyche siltalai Döhler	15	5.0	5.7 ± 0.76	6.2 ± 1.02
Hydropsyche pellucidula (Curtis)	12	5.0	6.5 ± 0.29	6.5 ± 0.38
Molanna angustata Curtis	3	5.1	6.0 ± 0.30	– –
Hydropsyche angustipennis (Curtis)	12	5.3	5.9 ± 0.40	6.1 ± 0.31
Sericostoma personatum (K. & Sp.)	11	5.4	6.3 ± 0.43	6.3 ± 0.38
Lype spp.	3	5.6	5.9 ± 0.33	– –
Polycentropus irroratus (Curtis)	5	5.6	5.7 ± 0.30	– –
Silo pallipes (Fabr.)	4	6.4	6.6 ± 0.23	– –

by the tolerance limits, were *Silo pallipes*, *Lype* spp., *Polycentropus irroratus*, *Sericostoma personatum* and *Hydropsyche angustipennis*, which were restricted to streams with a minimum pH > 5.2 (Fig. 3, Table 1). At least one *Hydropsyche* species was recorded in all but one stream with pH > 5.2 within estimation set, only in three streams below that, but never below pH 5.0. Of those species with high WA optima (Table 1), not mentioned above, *Rhyacophila nubila* and *R. fasciata* were found in streams with the minimum pH down to 4.7 and 4.5 respectively. *Ceraclea annulicornis* was found only once below pH 5.6. The most regular inhabitant of acidic streams was *Plectrocnemia conspersa* and it was not found in less acid streams with minimum pH > 5.4 (Fig. 3).

Small bivalves of the genus *Pisidium* were common and found down to pH 4.7. *Sphaerium corneum* was absent from streams with minimum pH < 5.9. Snails

(Gastropoda) as a group did not occur below pH 5.1. The latter were found only occasionally, making up a negligible part of the total fauna.

Asellus aquaticus was the only crustacean found in the estimation set. This species was common also in acidic streams down to pH 4.5. Of the three leech species (Hirudinea), none was found below pH 5.0. The two most common dragonflies (Odonata) were *Somatochlora metallica* and *Cordulegaster boltoni*, of which the latter seems to avoid acidic streams, since it was not found below pH 5.6. The tolerance limits of alderflies (Megaloptera) were well below pH 5. Of these, *Sialis fuliginosa* was more frequent in the most acidic streams.

Elminthid beetles *Elmis aenea*, *Oulimnius tuberculatus* and *Limnius volckmari* (Coleoptera) were common and usually abundant, but were absent from the most acidic streams. *L. volckmari* was restricted to streams with the lowest pH > 5.6. *Hydraena* species also tend towards less acidic streams. Oligochaetes, as well as the dipteran families Simuliidae and Chironomidae occurred in all streams studied. The latter two groups often formed a considerable proportion of invertebrates in the samples. They were, however, neglected in this chapter.

Predictions with Tolerance Limits

The percentages of taxa belonging to each pH category are given for streams of both data sets (Tables 2 and 3). Predicting minimum pH for the estimation set streams by pH categories or tolerance limits is somewhat circular logic, because the values are derived from the same data. The predicted pH can never be higher than the measured pH. However, the taxa of the right (measured) pH category might be missing, which causes an underestimate of pH as a consequence. When the combined samples were used, the classification was successful, i.e. in every stream one or more taxa of the pH category corresponding to the lowest measured pH was found (Table 2). The autumn samples alone led to the same result except for stream no 20, where none of the category 4 taxa were found. In spring and summer samples there were 5 and 4 inconsistent cases respectively. The inferred pH categories for the prediction set streams were in accordance with, or lower than the measured autumn pH. In those cases where comparison was possible, the inferred categories were in agreement with the spring pH of the lake above (Table 3).

Tolerance limits as such were not used in predicting minimum pH for the estimation set streams, but the TL predictions showed highly significant relationship to stream autumn pH in the prediction set (Fig. 4; Table 4). The average bias (predicted minus autumn pH) was strongly negative (Table 4), which could be expected. There were, however, three streams for which the predicted minimum pH by TL was higher than the measured autumn pH (Fig. 4), which means that some taxa were found there at a lower pH than in the estimation set. The most acidic stream of these (pH 4.2) was out of the range of the estimation set and in the other two streams (pH 4.5) *Pisidium* spp. (obtained TL 4.7) was found. The TL predictions were closely related to the spring pH of the lake and both the average bias and random error (S.D. of differences) were small (Fig. 4; Table 4).

Table 2. The percentages of taxa in pH categories in the combined samples of the estimation set

Stream no.	pH categories (%) 1	2	3	4	Measured min pH
28	100.0	–	–	–	4.3
27	100.0	–	–	–	4.3
12	94.7	5.3	–	–	4.5
26	46.6	53.4	–	–	4.7
29	97.6	2.4	–	–	4.8
3	83.7	16.3	–	–	4.8
18	26.1	73.9	–	–	4.9
2	36.5	27.4	36.1	–	5.0
24	15.1	53.4	31.6	–	5.0
1	59.9	39.9	0.2	–	5.1
4	58.1	41.5	0.3	–	5.1
25	16.9	81.8	1.3	–	5.1
23	9.3	78.0	12.7	–	5.1
9	51.6	31.5	16.9	–	5.3
7	33.8	51.3	14.9	–	5.4
13	45.3	26.9	26.9	0.9	5.6
21	19.7	51.0	29.2	0.1	5.6
17	17.5	65.7	15.4	1.3	5.6
6	17.2	66.5	13.3	3.0	5.6
16	15.7	50.8	31.9	1.6	5.6
8	15.3	34.8	48.8	1.0	5.8
19	24.3	8.2	11.1	56.4	5.9
20	43.0	23.6	33.3	0.1	6.0
15	31.5	58.6	8.0	1.9	6.1
14	8.4	36.6	54.6	0.4	6.4
5	6.1	41.8	44.6	7.4	6.4
31	4.3	38.6	21.4	35.7	6.5
30	3.3	81.6	8.8	6.3	6.5
32	2.5	65.6	31.7	0.2	6.5
11	20.0	44.1	24.3	11.6	6.7
10	39.3	37.8	21.9	1.0	6.8
22	8.7	48.8	31.3	11.2	6.9

Predictions with Optima and Tolerances

In the estimation set, significant linear relationships were observed between the measured pH and the minimum pH inferred by both the WA and ML estimates (Fig. 5; Table 4). Predictions with the WA estimates showed a slightly stronger relationship to the measured minimum pH and the random error was also smaller. With both WA and ML estimates the differences were clearly systematic in nature: too high predictions were obtained for streams with low pH and vice versa (Fig. 5). The additional weighing by inverses of expected abundances only slightly improved the relationship between ML predictions and pH, but the random error and especially the average bias became smaller (Table 4). The sampling times did

Table 3. The percentages of taxa in the pH categories in autumn samples of the prediction set

Stream no.	pH categories (%) 1	2	3	4	Autumn pH	Lake pH
5	100.0	–	–	–	4.2	4.4
12	93.1	6.9	–	–	4.5	4.6
13	99.5	0.5	–	–	4.5	4.5
10	97.9	2.1	–	–	4.8	
3	74.7	24.6	0.7	–	5.3	
9	27.6	72.4	–	–	5.3	4.7
8	72.6	27.1	0.3	–	5.4	
4	94.0	6.0	–	–	5.5	
6	20.5	78.6	0.9	–	5.5	4.9
11	87.8	11.7	0.4	–	5.5	
18	65.2	34.5	–	0.3	5.6	
2	54.4	43.9	1.8	–	5.7	
21	66.8	32.7	0.5	–	5.8	
16	18.9	80.6	0.5	–	5.9	5.2
22	6.5	53.2	39.8	0.5	5.9	
14	2.6	54.8	37.6	4.9	5.9	5.4
1	38.2	45.2	9.5	7.1	5.9	
15	47.9	28.7	20.6	2.8	6.3	
7	10.9	69.3	8.8	10.9	6.4	5.6
17	12.3	56.3	0.4	31.0	6.5	
20	6.4	28.3	62.2	3.1	6.5	
19	2.9	71.2	20.7	5.2	6.6	

not differ remarkably from each other with regard to correlation coefficients or standard errors. The predictions derived from summer samples showed the generally weakest relationship to the measured pH. The smallest average bias and random error were obtained by using the combined or autumn samples (Table 4).

In the prediction set, the inferred minimum pH by the WA and ML estimates showed a highly significant linear relationship to autumnal stream pH (Fig. 4, Table 4). Predictions with the WA estimates were clearly weaker related to measured pH than those with ML estimates. Mean bias of predictions by both estimates was negative. There was, however, a similar trend as in the estimation set: the greatest negative differences were obtained for streams with high pH and the predicted values for most acidic streams were too high (Fig. 4).

There were also significant linear relationships between the inferred stream minimum pH and the spring pH of the lake above (Fig. 4, Table 4). The random errors were even smaller than in the estimation set. The predictions were systematically too high, this feature being stronger with the WA optima. The range of lake pH is rather narrow and the relationships between pH and the predictions by both WA and ML estimates are actually very similar to those in the estimation set within corresponding pH range (cf. Figs. 4 and 5).

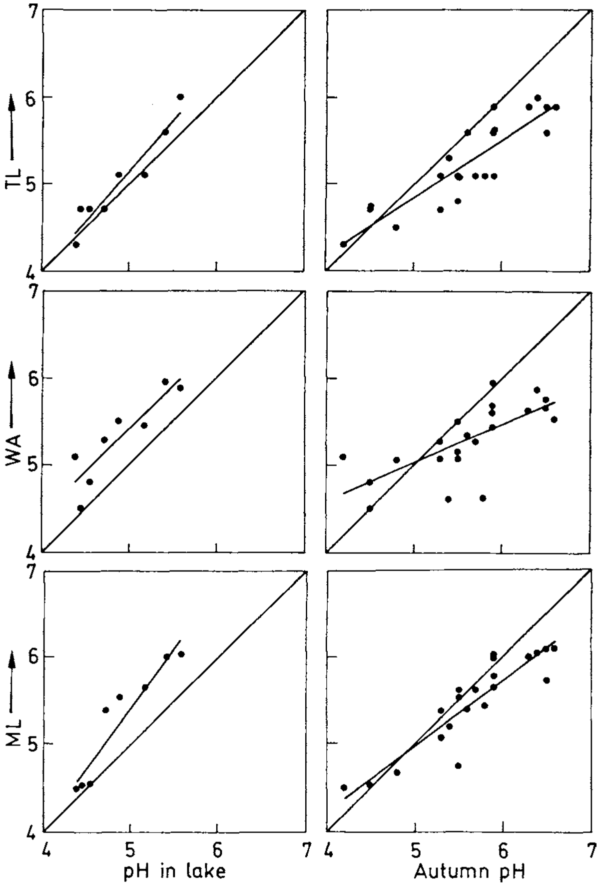

Fig. 4. The TL, WA, and ML predictions vs. measured pH in lake (*left*) and versus measured stream pH in autumn (*right*) in the prediction set

Discussion

As summarized by Økland and Økland (1986), there is no absolute lower pH limit for a given species due to differences in sensitivity of populations and life cycle stages, due to other external factors modifying the effect of pH, and due to gradual thinning out of species in acidified waters. Moreover, a given species may be absent in acidic streams because of indirect rather than direct effects of low pH, as suggested in the case of the mayfly *Ephemerella ignita* (Willoughby and Mappin 1988) and several other insects (Raddum 1979). Consequently, a given species cannot be expected to disappear from a stream at the very moment a given pH value is attained. The tolerance limits determined by us are, however, in fairly good agreement with those given by other Scandinavian workers (Otto and Svensson 1983; Raddum and Fjellheim 1984; Engblom and Lingdell 1983, 1984, 1987). One

Table 4. Descriptive statistics on the performance of prediction methods. ML2 = additional weighing by inverses of expected maximum abundance

Estimation set, predicted vs. measured minimum (n = 32)

Method		Regression statistics			Differences			
		r	s.e.	p	mean	s.d.	min	max
WA	Combined	0.92	0.19	< 0.001	− 0.011	0.363	− 0.79	0.47
	Spring	0.90	0.21	< 0.001	− 0.035	0.391	− 0.90	0.72
	Summer	0.89	0.24	< 0.001	0.068	0.376	− 0.69	0.69
	Autumn	0.91	0.21	< 0.001	0.005	0.372	− 0.80	0.60
ML	Combined	0.87	0.24	< 0.001	0.181	0.410	− 0.68	0.80
	Spring	0.90	0.20	< 0.001	0.195	0.403	− 0.60	0.88
	Summer	0.80	0.36	< 0.001	0.152	0.452	− 0.61	0.84
	Autumn	0.84	0.28	< 0.001	0.166	0.431	− 0.69	0.79
ML2	Combined	0.90	0.20	< 0.001	0.138	0.396	− 0.65	0.71
	Spring	0.89	0.20	< 0.001	0.166	0.409	− 0.66	0.84
	Summer	0.83	0.32	< 0.001	0.088	0.431	− 0.65	0.75
	Autumn	0.88	0.26	< 0.001	0.109	0.386	− 0.68	0.77

Prediction set, predicted minimum pH vs. measured autumn pH (n = 22)

Method	Regression statistics			Differences			
	r	s.e.	p	mean	s.d.	min	max
WA	0.71	0.30	< 0.001	– 0.309	0.475	– 1.16	0.89
ML	0.91	0.20	< 0.001	– 0.182	0.320	– 0.88	0.29
ML2	0.92	0.23	< 0.001	– 0.184	0.278	– 0.78	0.29
TL	0.88	0.24	< 0.001	– 0.359	0.325	– 0.90	0.20

Prediction set, predicted minimum pH vs. measured lake pH (n = 8)

Method	Regression statistics			Differences			
	r	s.e.	p	mean	s.d.	min	max
WA	0.90	0.24	0.002	0.415	0.223	0.06	0.70
ML	0.91	0.28	0.001	0.396	0.285	0.06	0.77
ML2	0.94	0.24	< 0.001	0.370	0.275	– 0.01	0.66
TL	0.96	0.17	< 0.001	0.128	0.177	– 0.09	0.41

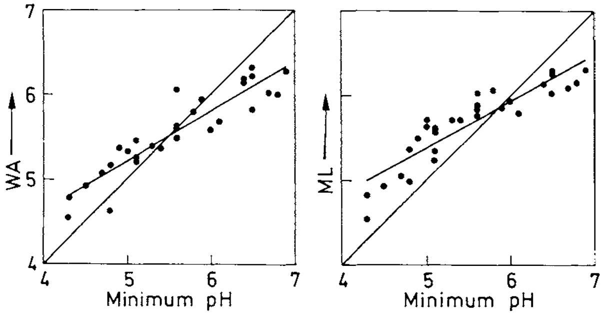

Fig. 5. The WA and ML predictions vs. measured minimum pH in the estimation set

reason for existing inconsistencies is probably the differences in the size of data sets. For example, the tolerance limits given by Engblom and Lingdell (1983, 1984, 1987), generally lower than ours, are based on data from several thousand streams supplemented by experimental data. Because of the small number of streams in our study the TL values for many species are probably overestimated. A cautious attitude should be taken to the TL values of rare species, especially.

One of the many external factors possibly modifying the effect of acidification on invertebrates is humic substances in water. This is indicated here by the different species richness in brown versus clearwater streams within the same pH range (Fig. 2). Acidification is usually accompanied by elevated concentrations of aluminium, which is toxic to some species of invertebrates (Herrmann 1987). The results of experiments by Burton and Allan (1986) show that addition of an organic ligand reduces susceptibility of some invertebrates to Al at low pH by altering Al speciation. Weatherley et al. (1988) and McCahon and Pascoe (1989) have shown that organic ligand in acid waters containing aluminium reduce harmful effects on mayfly *Baetis rhodani*. We found *B. rhodani* below pH 5.5 only in brown-coloured streams, which is consistent with results of Lingdell and Engblom (1987), who recorded the species below that pH only in streams with colour > 50 Pt mg l^{-1}. In Norway, this species is also absent from non-humic soft water streams with pH < 5.5 (Raddum et al. 1988). In brown-coloured acid streams humic substances may act as a ligand reducing the toxicity of Al and allowing *B. rhodani* to survive at lower pH than could be possible in low-organic water. This may hold true for other *Baetis* species too, since we found *B. vernus*, considered one of the most sensitive mayfly species by Engblom and Lingdell (1984) and Raddum and Fjellheim (1984), in four strongly coloured (140–350 Pt mg l^{-1}) streams with a minimum pH 5.0 or less. (In these cases *B. vernus* was distinguished from other representatives of the collective species.) Those streams where the collective species or *B. niger* were found below pH 5.5 were also brown-coloured (> 50 Pt mg l^{-1}). The considerably low tolerance limits for the *Baetis* species given by Otto and Svensson (1983) are also based on data from brown water streams. There is no reason to suppose the possible effect of humic substances is restricted solely to *Baetis* species, but the present data is insufficient for further species-specific considerations.

We found very few highly acid-sensitive taxa, when judged by tolerance limits (TL > 5.5). Therefore it could be even expected that some of the streams in the estimation set with measured minimum pH > 5.5 were missing the taxa of the corresponding pH category. However, this was not the situation if samples were combined and in autumn samples there was only one such case. In some streams the proportion of taxa of the highest pH category was very small (Table 2), indicating the need for effective sampling to find these taxa without depending on chance alone. The disadvantage might be alleviated if more taxa were taken into account. We found many species which were earlier reported to be acid-sensitive (Otto and Svensson 1983; Raddum and Fjellheim 1984; Engblom and Lingdell 1983, 1984, 1987) only once or twice and they were ignored. Nevertheless, in the prediction set the inferred pH categories were generally reliable, if the measured autumn pH is regarded to indicate the stream acidity level. Moreover, the predicted pH categories were in accordance with the lake water spring pH. The predictions with the tolerance limits as such showed highly significant relationship to the measured autumn pH and they were especially close to the spring pH in lake.

The predictions by weighted averaging with both WA and ML estimates were closely related to the observed minimum pH in the estimation set. The prediction power may be overestimated if the estimation set is used in assessing the method because the parameters are derived from the same data (see Oksanen et al. 1988). Data from the prediction set was independent and therefore valid in assessing the predictions. The data was, however, poorly adapted to this purpose because the minimum pH, which we actually tried to predict, was not measured. Autumnal pH and minimum pH are usually strongly related to each other ($r = 0.92$, $p < 0.001$ in the estimation set, see also Meriläinen and Hynynen this Vol.). Therefore the highly significant relationships between autumn pH and predicted minimum pH by WA and ML estimates (and by TL) are of some value and they can be considered as indirect proof of the reliability of predictions. The strongly negative average bias was what one would expect, since the autumn pH is generally higher than the minimum pH. More evidence of the usability of the methods was obtained by comparing the predictions with spring (minimum) pH of the lake where the stream started from.

In the prediction set, unlike in the estimation set, the inferred pH with WA estimates was clearly weakest related to the measured pH. This may indicate unreliability of the derived WA estimates for those species missing ML estimates, either due to small number of observations (< 7) or lack of clear relationship to pH (e.g. *Leuctra digitata*).

The systematic nature in differences of predictions with WA estimates (too high inferred values for streams with low pH and too low for those with high pH) can partly be explained by a drawback of the weighted averaging method. WA produces optimum estimates which are inevitably within the pH range of the estimation set and which tend to shift towards the mean. Accordingly, predictions with the WA estimates tend to move towards the centre of the range (see Oksanen et al. 1988). ML, in contrast can produce optimum estimates which lie outside the range. Such optima were in fact obtained for a few species but they were unreliable (e.g. pH − 3.71 for *Nemoura cinerea*) and these species were removed from the ML predictions. Moreover for some species with the highest relative abundance near the edge of the pH range, the Gaussian model could not be fitted. Consequently, all ML optima were within the pH range of the estimation set and only few very high or low optima were obtained (Table 1). This may explain the fairly similar pattern of predictions with ML and WA estimates. This "edge effect" could have been less strong if the pH range of the estimation set had been wider.

There were no substantial differences between the predictions derived from the samples of different seasons. As a rule, the autumn samples, however, produced the best predictions and they were almost as good as the combined samples in this respect. One representative invertebrate sample collected in autumn seems to be a sufficient basis for the prediction of the minimum pH in streams. The minimum pH as such is not of particular interest and we could not predict it exactly by means of benthic fauna. Differences in acidity level of the studied streams, however, were clearly demonstrated by both methods applied here. The predicted minimum pH from outlet invertebrate assemblages also proved to reflect the pH of lake water during the period of snow melt.

The stream invertebrates can be used in mapping regional differences in acidity of watersheds (Johansson and Nyberg 1981; Engblom and Lingdell 1984; Degerman et al. 1987; Raddum et al. 1988), but they are also suitable for acidification monitoring of fixed sites. The method based on species tolerance limits has already proved to be useful. Engblom and Lingdell (1984) showed the acidification of Swedish mountain streams by documenting changes in ephemeropteran fauna between 1971 and 83. Hall and Ide (1987) suggested that the acidification of some streams in Canada had occurred within the last decades by comparing ephemeropteran and plecopteran fauna of 1937–42 and 1984–1985. In both studies some acid-sensitive species had disappeared and they were partially replaced by acid tolerant species (e.g. *Leptophlebia* spp.). Raddum et al. (1988) demonstrated both increased and decreased acidification in Norwegian watersheds by observing presence/absence of acid sensitive invertebrates over a period of 5 years.

An advantage of the tolerance limit method is its simplicity. However, most invertebrate species seem to tolerate pH well below 5.5, which is regarded as a critical point in freshwater acidification (Johansson and Nyberg 1981, see Raddum and Fjellheim 1984) and few species seem to be totally eliminated before pH declines below that value (Fig. 3). Raddum et al. (1988) specified only four taxa of this category. These few taxa can disappear or be absent for many reasons other than low pH. Therefore the earlier stages of acidification may sometimes be difficult to detect solely by observing the appearance of the sensitive taxa. The predictions by weighted averaging are based on the whole assemblage (all species with indicator values) and are thus less dependent on detecting any particular species. Moreover, abundances may be affected long before even the sensitive species are eliminated (see Mierle et al. 1986). In this respect the method based on species optima and taking into account each taxon's contribution to total abundance might be more informative. Relative abundance of species may, however, change for reasons other than pH. Concurrent monitoring of invertebrates and water quality at fixed sites is needed to evaluate the performance of the two methods in demonstrating changes in acidity. Extension of data, covering a large number of streams of wider pH range might be necessary to derive more reliable indicator values and to obtain them for more species. However, trends and regional differences in Finnish watersheds may be demonstrable by either method employed here and by using the indicator values given in Table 1.

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Palaeoecological Evaluation of the Recent Acidification of Susceptible Lakes in Finland

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Summary

The aims of this study were to reveal the causes of lake acidification and to study the acidification history and areal distribution of acidification of Finnish lakes. The 30 lakes selected for this study were mainly oligotrophic forest lakes. They do not represent statistically all lakes in Finland but are the most interesting, sensitive lakes. Estimates of inferred pH and alkalinity from sediment diatom assemblages were based on a calibration set of 92 lakes with surface sediment diatom assemblages and the corresponding chemistry of autumnal water samples. Of the studied 30 lakes, 43% had a significant recent decrease in alkalinity, 20% were naturally acidic, and 27% were with no acidification trends. Lakes with sediment with poorly preserved diatom frustules were 10% of the whole material. At all sites where recent acidification was recorded and the lake was deep enough, the proportion of planktonic diatoms decreased remarkably. In naturally acidic lakes, abundances of diatom plankton have also declined during the last century. In this study the chemical models used showed both larger and smaller acidification than the estimates from the palaeoecological approach. The recent acidification of small forest lakes is restricted to southern Finland where almost all acidic lakes have acidified since 1900. In central and northern Finland, on the other hand, the proportion of naturally acidic lakes is higher.

Introduction

The regional occurrence of acidic lakes and streams has recently been proved to be fairly common in areas of granitic bedrock and sensitive soils both in Europe and in North America (Merilehto et al. 1988). However, the common lack of any monitoring records from small lakes makes it difficult to time the chemical history of acidification and its possible causes. The effects of anthropogenic acidity in

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deposition are not easily separable from the consequences of changes in land-use and natural acidifying processes in soils. Podzolisation, paludification and oxygenation of soil sulphides are the most common natural processes which may cause gradual or temporary acidification of lakes and streams.

In conditions prevailing in Finland, the natural acidification of lakes and streams has been very common. About one-third of the land area of Finland is covered by peatland. The paludification process has been very rapid soon after the latest glacial era from 10,000 to 6000 B.P., most of the small forest lakes have brown water, and have relatively low pH-value and high total organic carbon (TOC) concentration. According to Kortelainen and Mannio (1988), TOC is a better predictor of pH than non-marine sulphate in Finnish forest lakes. Another type of natural acidification in Finland arises from the oxidation of sulphides in the sulphur-rich sediments of the ancient Litorina-sea. This phenomenon is limited to the coastal clay areas lower than 80 m above sea level, it typically causes temporary, severe acidification of lakes and streams followed by fishkills. On the other hand, the deposition of sulphur has increased especially in southern Finland from 1 to 2 g $m^{-2} a^{-1}$, causing acidification in sensitive regions (Järvinen and Vänni this Vol.).

The sediment deposited in lakes is an archive of nature that may be used to trace pH history. The dated sediment with fossil remains of taxa whose abundance is pH-dependent analysed with contemporary anthropogenic pollutants, like heavy metals and carbonaceous particles, support the hypothesis of the recent airborne acidification of lakes. Also the slower rate of natural acidification makes it separable from man-induced causes.

In recent years the palaeolimnological approach has been applied in many acidification studies in Europe and North America. Comprehensive reviews of these studies are given by Battarbee and Charles (1987) and Charles et al. (1989).

Diatom frustules preserved in lake sediments provide an excellent tool for interpretation of past conditions in aquatic environments. Diatoms respond rapidly to changes in water chemistry and also reflect disturbances in the drainage areas of lakes. A strong relationship between diatom assemblages and lake acidity is well established and documented. This knowledge has been used in developing inference techniques for the reconstruction of the past pH of lakes (e.g. Nygaard 1956; Meriläinen 1967; Renberg and Hellberg 1982; Charles 1985). Recently new multivariate methods make possible a more precise estimation of pH and of other water parameters, e.g. alkalinity and total organic carbon, TOC (Davis and Anderson 1985; Oksanen et al. 1988; Stevenson et al. 1989; Huttunen and Turkia 1989). Also several dating methods based on the measurement of isotopes (e.g. ^{210}Pb, ^{137}Cs) in sediment are now available for establishing the timing of acidification trends.

The first diatom-based acidification studies in Finland were conducted by Tolonen and co-workers (Tolonen and Jaakkola 1983; Tolonen et al. 1986). These papers dealt with the sediments of 15 weakly buffered oligotrophic forest lakes, and showed that eight of the lakes had been clearly acidified in recent times.

Simola et al. (1985) studied the diatom stratigraphy of ten sensitive lakes. Three of the studied lakes seemed to have acidified recently from a constant background level that was in the range pH 4.8–5.7. The pH decline was 0.3–0.8 units. Three others had also acidified recently, but the decline was interpreted rather as a recovery from a transiently elevated pH level. Of the remaining cases three showed no definite trends in pH and one was undecipherable because of apparent dissolution of diatom frustules in the sediment.

Materials and Methods

Study Lakes

The 30 study lakes presented here were selected from the set of research and monitoring lakes of the Finnish Research Project on Acidification. The lakes are situated in southern and central Finland, in the regions of high and moderate airborne sulphur deposition (Fig. 1). Most of the lakes are small, from 2 ha to 107 ha, headwater, drainage lakes with the exception of some seepage lakes. Clearwater, oligotrophic lakes were preferentially selected at the expense of more dystrophic lakes. The highly coloured humic lakes have acidified naturally long ago; the palaeolimnological methods are more useful for analysing the history of clearwater lakes (Simola et al. 1985). Thus the lakes selected for this study do not represent all lakes in Finland, but the more sensitive ones.

Methods

The sediment was sampled by coring in late winter 1985 and 1986 from the lake's deepest point using a modified Züllig corer with an inner diameter of 7.5 cm. From each lake a core with no visible disturbance in the surface sediment was chosen for subsampling. In the field, the core was extruded in 0.5 cm intervals from 0 to 5 cm. Below 5 cm longer intervals were used: 1-cm intervals to 16 cm, 2-cm intervals to 30 cm, and when the core was longer, 5-cm intervals to the end of the core.

For diatom slide preparation, a small sediment sample was separated from the middle part of each slice. The sediment samples for diatom analyses were cleaned by oxydating the organic material with hot, concentrated nitric acid. If needed, some drops of concentrated sulphuric acid were added for complete oxidation. The undigestible part of the sediment was separated after centrifuging at 2000–3000 rpm for 2–3 min. Before slide preparation, the frustules were washed carefully three times in distilled water and then mounted in Hyrax. From each slide 300–500 single valves were counted by microscope with a magnification of at least × 1000.

The taxonomy and identification of diatoms mainly follow Hustedt (1930, 1927–1966, 1937–1939 and 1957), Cleve-Euler (1951–1955), Meriläinen (1967, 1969), Mölder and Tynni (1967–1973), and Tynni (1975–1980).

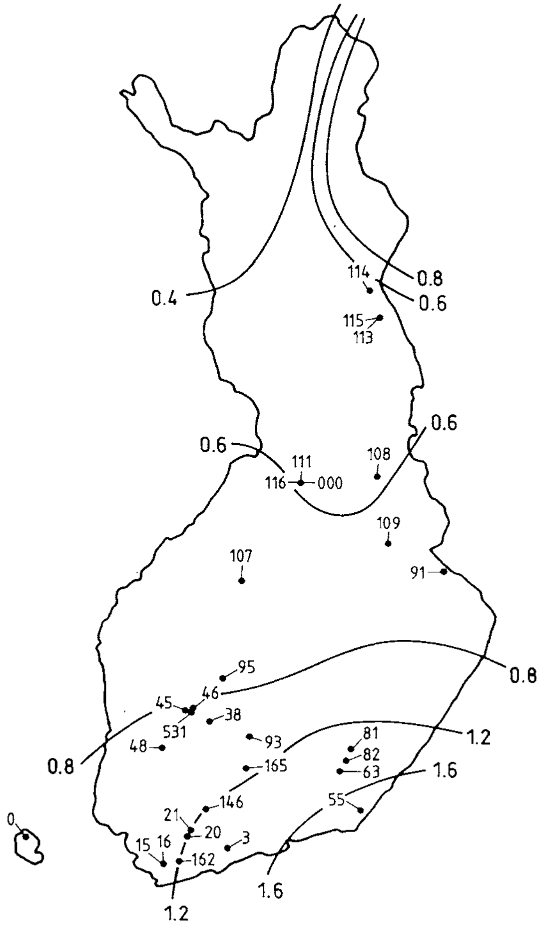

Fig. 1. Location of the study lakes (*closed circles*). The regional sulphur deposition in 1980 ($g\,S\,m^{-2}\,a^{-1}$) has been included. (After Tuovinen et al. this Vol.)

For dating the cores, the total ^{210}Pb content of subsamples was measured through its α-emitting grand-daughter, ^{210}Po, using isotope dilution and ^{208}Po as an internal tracer (Häsänen 1977). One core from each lake was analysed except the five lakes (16, 3, 107, 116 and 115) from which two parallel ^{210}Pb datings were done. For calculating sediment chronologies the C.R.S. (constant rate of supply) model and in some cases also the C.I.C. (constant initial concentration) model (see Oldfield and Appleby 1984) was used. Both C.R.S. and C.I.C. give identical results in cases where the accumulation rate has been constant.

Estimations of inferred pH and alkalinity from sedimentary diatom assemblages are based on a calibration dataset of 92 lakes. This calibration dataset consists of surface sediment (1 cm) diatom assemblages and the corresponding values of pH and alkalinity which have been determined from surface water samples (1 m) collected during the autumnal circulation period in 1987. Alkalinity was determined by Gran titration. About half of the lakes presented in Huttunen and Turkia (this Vol.) are included in calibration supplemented by a set of more alkaline lakes. The average pH was 6.01 ranging from 4.7 to 7.3, and mean alkalinity was 82 μeq l^{-1} ranging from −49 to 405 μeq l^{-1}.

Canonical correspondence analysis (CCA) and the equations presented by Ter Braak (1987) were used in estimating pH and alkalinity (for formulae, see Stevenson et al. (1989), and Huttunen and Turkia, this Vol.).

When the abundance of a diatom taxon was less than 1.0% of all counted diatom frustules, it was excluded from the analysis. Octave transformation was performed to change the relative frequencies of diatoms into a logarithmic scale. The relationship between measured and CCA-estimated values were highly significant in the calibration dataset (for pH $r^2 = 0.89$, SE 0.27; for alkalinity $r^2 = 0.88$, SE 0.041).

Results

The Dating of Cores

The background activities for ^{210}Pb (12–57 mBq g^{-1}) agree well with the known uranium distributions of bedrock in Finland. The dating results of six lakes (146 Salmijärvi, 111 Jaakonjärvi, 63 Hautalampi, 000 Leväsoppinen, 113 Leusjärvi, 20 Riituksenjärvi) were discarded for various reasons. In two cases (63 Hautalampi, 000 Leväsoppinen) supposed mixing or abrupt increase in accumulation rate of sediment caused rejection. In two acidic lakes (111 Jaakonjärvi, 146 Salmijärvi) dissolution of ^{210}Pb due to acidification (see e.g. Nriagu 1984) seemed to be apparent. Residual ^{210}Pb activity in the sediment of 111 Jaakonjärvi was much lower than that of adjacent 116 Ahveroinen although the lakes are similar in size and have similar soil in drainage area. The ^{210}Pb activity in surficial sediment of 20 Riituksenjärvi was 1190 mBq g^{-1}, but at the depth of 5 cm and lower down the sediment the activity of 51 mBq g^{-1} only. This indicated such an abnormally low sediment accumulation rate that dating was rejected. Erosion of sediment from the large drainage area with fields could be the reason of extremely low ^{210}Pb activities (204 mBq g^{-1}) of the surficial sediment in 113 Leusjärvi.

The results of this study show that for evaluating the reliability of ^{210}Pb dating knowledge of conditions in the catchment area is as essential as are chemical and physical parameters in the lake.

Acidification Trends

The lakes are classified into four groups according to current water chemistry and the amount of acidification.

Lakes with Significant Recent Decrease in Alkalinity

All lakes in this group have been clearly acidified. In many cases acidification started prior to 1900 but has accelerated after 1960. The reconstructions of pH and alkalinity history are presented in Fig. 2 and characteristics of lakes in Table 1 and Table 2.

The greatest change in inferred pH (1.2 pH units) and alkalinity (− 148 μeq l^{-1}) is found in lake 111 (Jaakonjärvi). The lake is a small kettle lake lying on glaciofluvial sandy soil. The timing of the onset of the decreases is not clear as the dating results of this lake were discarded. However, we assume that acidification started before 1900 because the composition of the diatom assemblages in the sediment is changing clearly since the depth of 20 cm. The inferred pH decreases gradually to the present and there was no ANC left before a slight liming of the lake was carried out in June 1982. The liming raised the water pH from 5.2 to 6.2 for 3 years. In 1988 pH was back at 5.4. The temporary rise of pH is not reflected in the diatom-inferred pH from the core taken in spring 1985, because it only had minor effects on the diatom assemblage.

Lake 20 (Riituksenjärvi) is a small, clearwater kettle lake surrounded by mostly sandy soils with exposed bedrock and some peat. The core was not dated but the acidification process started hundreds of years ago with a clear acceleration in the uppermost part of the profile. The lake has lost its ANC recently, measured recent pH is 5.8 and alkalinity −8 μeq l^{-1}.

Lake 0 (Långträsk) is situated on Åland island. The lake is a small clearwater lake entirely surrounded by exposed rapakivi-granite bedrock. Present pH is 6.1 and alkalinity 58 μeq l^{-1}. The acidification of the site started before this century and has continued to the present. The total loss of alkalinity from 1900 is 115 μeq l^{-1}.

Lake 146 (Salmijärvi) is the most acidic lake of this group (pH 4.8, alkalinity −31 μeq l^{-1}). The lake is a small kettle lake on sandy soil. Dating results are lacking, but loss of ANC must have started before 1900 (Fig. 2). There is sharp lowering of pH to the present. Total decrease of pH is one of the greatest of all sites, 0.7 pH units from pre-1900.

Lake 16 (Malarijärvi) is an acidic clearwater lake (pH 5.6, alkalinity −4 μeq l^{-1}). Its catchment consists of exposed bedrock with some sandy and peaty soils. The acidification of lake started hundreds of years ago staying at a stable level until around 1900. An abrupt decrease in ANC took place since 1960.

Lake 15 (Krailan Pitkäjärvi) is a slightly humic (TOC 7.0 mg l^{-1}) lake surrounded by rocky and till soils. Its recent water pH is 5.4 and alkalinity −9 μeq l^{-1}. The ANC of the lake has been fairly constant and inferred pH even increased after 1900. However, a drastic acidification occurred at the site after 1960. The decline of pH since then is 0.4 units and for alkalinity is 56 μeq l^{-1}.

Lake 3 (Kattilajärvi) is a weakly buffered clearwater lake with a pH of 6.0 and alkalinity 10 μeq l^{-1}. It drains rocky and moraine-covered catchment. The pH history indicates that the lake was very stable until around 1900, when an abrupt decline of pH about 0.3 units occurred. No clear change since 1960 to the present. The diatom inferred pH values are slightly lower than that measured from lake water.

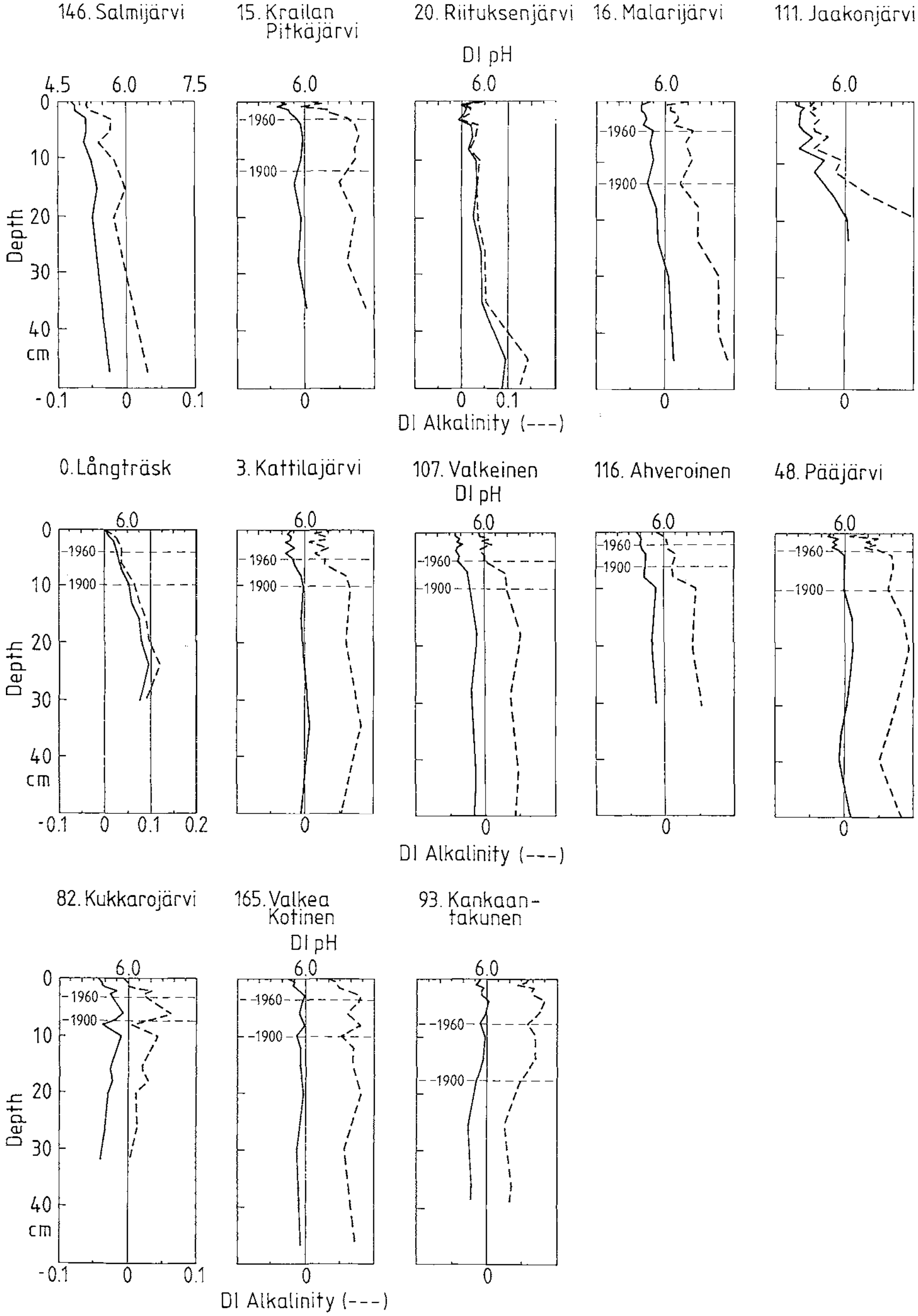

Fig. 2. Diatom-inferred pH and alkalinity in lakes with significant acidification trend. Level of 1960 and 1900 are indicated for the dated profiles

Table 1. Lake and catchment area characteristics

Number	Lake	Catchment area ha	Lake area ha	Max depth m	Percentage of each soil type				Type of dominating bedrock
					Exposed bedrock/ areas with soil thickness less than 1 m	Till	Sand/ gravel	Peat	
146	Salmijärvi	102	27	11	–	–	80	20	Microclinegranite
15	Krailan Pitkäjärvi	93	9	6	64	16	–	20	Granite
20	Riituksenjärvi	48	21	19	13	9	68	10	Acid gneiss
16	Malarijärvi	206	42	15	79	–	8	13	Granite
111	Jaakonjärvi	68	3	8	–	–	100	–	Migmatitegranite
0	Långträsk	60	13	6	100	–	–		Rapakivigranite
3	Kattilajärvi	166	34	10	43	40	11	7	Granodiorite
107	Valkeinen (Lestijärvi)	254	94	5	–	–	65	35	Granodiorite/diorite
116	Ahveroinen	60	3	6	–	–	100	–	Migmatitegranite
48	Pääjärvi	364	24	24	18	64	–	18	Micagneiss
82	Kukkarojärvi	31	9	9	100	–	–	–	Gneissgranite
165	Valkeakotinen	24	4	7	–	100	–	–	Micagneiss
93	Kankaantakunen	174	42	15	29	71	–	–	Fyllite/micagneiss
115	Silpalampi	58	16	7	–	100	–	–	Granitegneiss/gabro
109	Matojärvi	289	15	6	–	49	–	51	[a]
21	Tervakka	179	14	15	15	42	35	8	Granodiorite
55	Mäkilampi	50	11	11	91	–	–	9	Rapakivigranite
46	Honkajärvi	78	15	6	30	59	–	11	Granodiorite
91	Melalampi	256	27	10	–	81	–	19	Quartz-feldspar-schist
38	Ukonjärvi	988	34	17	67	22	–	11	Pegmatite/porfyritegranite
63	Hautalampi	352	13	17	7	81	–	12	Granite/micagneiss
114	Ruuhijärvi	172	68	4	–	–	43	57	Diabase/amfibolite
000	Leväsoppinen	53	2	8	–	–	100	–	Migmatitegranite
95	Valkeinen (Keuruu)	83	26	8	16	–	65	19	Granite
162	Sahajärvi	112	27	12	75	–	18	7	Granite
531	Iso Koukeri	94	13	14	12	71	–	17	Granite
81	Yläkuolimo	338	34	9	82	18	–	–	Gneiss
108	Kuikkalampi	16	3	7	–	–	86	14	[a]
113	Leusjärvi	427	107	2	–	27	–	73	[a] [b]
45	Saari-Soljonen	22	5	5	–	–	19	81	Granodiorite

[a] Areas with no open bedrock areas or no previously published bedrock maps.
[b] Includes 62-ha area drained for farming use.

Table 2. Lake water characteristics during the autumnal overturn 1987

Lake		pH	alkalinity[a] μeq l^{-1}	conductivity mS m^{-1}	SO_4^{2-} mg l^{-1}	Ca^{2+} mg l^{-1}	Mg^{2+} mg l^{-1}	Na^+ mg l^{-1}	K^+ mg l^{-1}	TOC mg l^{-1}
146	Salmijärvi	4.8	−31	1.8	3.7	1.0	0.2	0.6	0.3	1.2
15	Krailan Pitkäjärvi	5.4	−9	2.8	4.7	1.9	0.6	1.6	0.4	7.0
20	Riituksenjärvi	5.8	−8	2.6	5.7	1.7	0.5	1.4	0.4	1.1
16	Malarijärvi	5.6	−4	2.7	5.3	1.9	0.6	1.3	0.3	3.8
111	Jaakonjärvi[b]	6.4	30	1.1						
0	Långträsk[c]	6.1	58	4.9	6.2	2.3	0.7	3.0	0.5	
3	Kattilajärvi	6.0	10	3.3	8.1	2.6	0.8	1.6	0.4	3.6
107	Valkeinen	5.9	11	1.3	3.0	0.7	0.3	0.7	0.2	3.1
116	Ahveroinen	6.2	12	0.9	1.9	0.6	0.2	0.7	0.1	2.0
48	Pääjärvi	6.0	26	3.0	6.3	1.9	0.9	1.5	0.6	6.6
82	Kukkarojärvi	5.8	31	3.2	6.8	2.2	1.2	1.2	0.4	9.3
165	Valkea-Kotinen	5.0	−49	3.7	8.0	2.6	0.8	1.4	0.4	12.0
93	Kankaantakunen	5.6	11	2.9	5.4	2.3	0.7	1.2	0.4	8.3
115	Silpalampi	4.8	−20	1.3	0.3	0.3	0.1	0.3	0.1	0.6
109	Matojärvi	4.8	−14	2.1	2.2	1.0	0.4	0.9	0.4	15.5
21	Tervakka	5.4	−2	3.3	6.3	2.4	0.8	1.4	0.3	7.8
55	Mäkilampi	5.0	−13	3.0	7.5	2.1	0.4	0.9	0.4	4.2
46	Honkajärvi	5.1	3	4.8	7.7	3.7	1.0	1.7	0.8	9.0
91	Melalampi	5.8	25	1.8	2.8	1.5	0.5	1.0	0.4	10.1
38	Ukonjärvi	5.3	20	3.3	6.6	2.3	0.9	1.5	0.6	13.2
63	Hautalampi	6.5	85	3.9	6.5	3.3	0.9	1.7	0.8	5.6
114	Ruuhijärvi	6.8	64	1.6	1.1	1.3	0.5	0.6	0.5	3.3
000	Leväsoppinen[d]	6.7	542							
95	Valkeinen	5.8	1	2.6	4.5	1.9	0.5	1.1	0.5	3.2
162	Sahajärvi	6.1	19	2.7	5.9	1.8	0.6	1.8	0.3	3.5
531	Iso Koukeri	5.5	11	2.7	5.1	1.7	0.7	1.4	0.6	9.3
81	Ylä-Kuolimo	6.1	55	3.1	5.6	2.4	1.1	1.3	0.6	9.4
108	Kuikkalampi	4.7	−20	1.4	2.0	0.3	0.1	0.3	0.0	0.8
113	Leusjärvi	6.9	213	3.9	1.9	4.0	1.3	1.5	1.0	10.4
45	Saari-Soljonen	4.8	−21	1.8	2.7	0.9	0.1	0.5	0.2	4.6

[a] By Gran's method.
[b] Water chemistry 25.09.1984, slightly limed.
[c] Water chemistry 17.09.1986.
[d] Water chemistry 13.03.1989.

Lake 107 (Valkeinen) is also a weakly buffered, clearwater lake (pH 5.9, alkalinity 11 μeq l^{-1}). It is one of the largest (94 ha) of the studied lakes, lying mostly on sandy soil with some peat. The pH was fairly constant until 1950. Then took place a rapid loss of ANC. Total decline of pH from pre-1900 is 0.5 units, and since 1950 to the present it is 0.3 units.

Lake 116 (Ahveroinen) is a small kettle lake on sandy soil. The lake is less acidic (pH 6.2, alkalinity 12 μeq l^{-1}) but there are measurements from earlier years indicating that the lake has been many times below pH 6 during autumnal and vernal circulation. The onset of acidification with a sharp decline in alkalinity predates the year 1900 and acidification has continued to the present.

Lake 48 (Pääjärvi) is a slightly humic lake (pH 6.0, alkalinity 26 μeq l^{-1}, TOC 6.6 mg l^{-1}) with a large drainage area consisting of rocky till and some peat. The inferred pH history shows quite constant conditions until 1960, when a rapid decrease in pH and loss of alkalinity occurred.

Lake 82 (Kukkarojärvi) is a small headwater lake on totally exposed bedrock. It is slightly acidic and mesohumic (pH 5.8, alkalinity 31 μeq l^{-1}, TOC 9.3 mg l^{-1}). The inferred pH history indicates increasing pH until 1900, then a steady decrease to the present. The lake is losing its ANC. The total decrease of pH from 1960 is 0.5 units an for alkalinity 48 μeq l^{-1}.

Lake 165 (Valkea Kotinen) is a small humic lake on morainal material (pH 5.0, alkalinity −49 μeq l^{-1}, TOC 12.0). Interpretation and reconstruction of acidification history may be in error because of the mass occurrence of some planktonic diatoms (*Rhizosolenia longiseta, Asterionella formosa*) in the topmost sediment samples. The inferred pH and alkalinity are clearly higher than that measured from the lake recently. But the inferred values show a clear decrease since 1960 to the present.

Lake 93 (Kankaantakunen) is also a humic headwater lake (pH 5.6, alkalinity 11 μeq l^{-1}, TOC 8.3 mg l^{-1}). The pH history shows increasing ANC until 1980, then a sharp decline. As in Valkea Kotinen, a mass occurrence of *Asterionella* species affects the inferred values. According to ^{210}Pb-dating, the accumulation rate in the lake is the highest recorded in this study. The lake is receiving waters from several small lakes with some recent disturbances (forest cutting, ditching) in their drainage area.

Naturally Acidic Lakes

Six of the study lakes have been acidic (without alkalinity) for the time covered by the short sediment cores (Fig. 3).

Lake 115 (Silpalampi) is the northernmost of the studied lakes, located in South Lapland. It is a small acidic, clearwater lake on moraine ground (pH 4.8, alkalinity −20 μeq l^{-1}, TOC 0.6 mg l^{-1}). The inferred pH in this century is constant, but inferred alkalinity shows a weak decline from 1900 to the present.

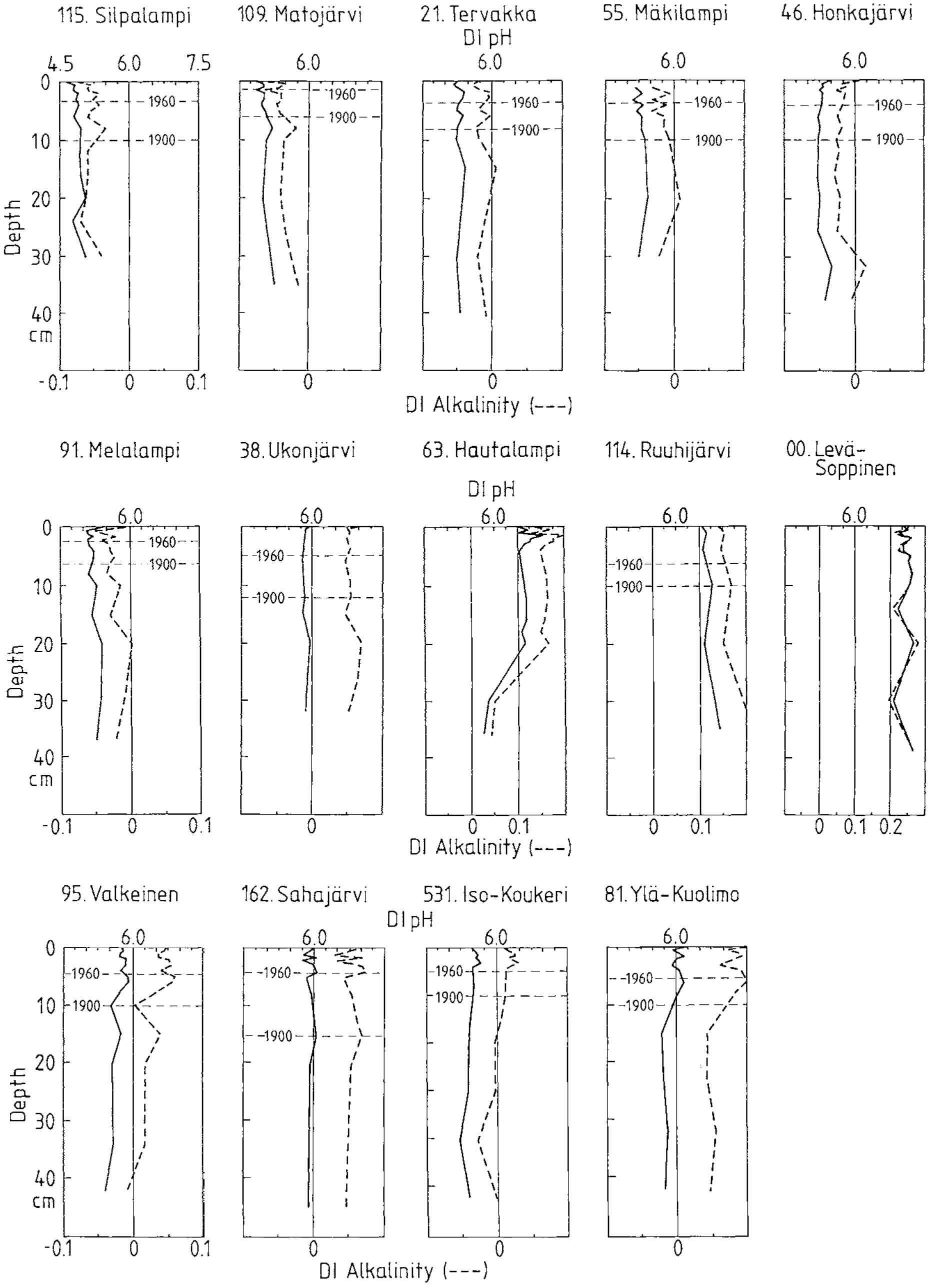

Fig. 3. Diatom-inferred pH and alkalinity in naturally acidic lakes and in lakes with no acidification trend

Lake 55 (Mäkilampi) is a clearwater lake in southeastern Finland. Its catchment consists of exposed bedrock and some peat. The recent pH is 5.0 and alkalinity $-13\ \mu\text{eq}\ \text{l}^{-1}$. The inferred acidification trend indicates a slight but somewhat fluctuating lowering in ANC.

Lake 21 (Tervakka) is a small moderately humic lake (pH 5.4, alkalinity $-2\ \mu\text{eq}\ \text{l}^{-1}$, TOC 7.8 mg l^{-1}). Its catchment consists of moraine, sand and peat. The lake has no ANC now; there has been slight lowering of alkalinity since 1960.

Lake 46 (Honkajärvi) is a small humic lake (pH 5.1, alkalinity 3 μeq l^{-1}, TOC 9.0 mg l^{-1}) with a rocky, moraine and peaty drainage area. The pH has been very stable for a long time. A slight increase in ANC since 1960 could be caused by land use. There are small fields in the drainage area.

Lake 91 (Melalampi) is distinctly a humic lake (pH 5.8, alkalinity 25 μeq l^{-1}, TOC 10.1 mg l^{-1}) with a large drainage area consisting of moraine and peat. The inferred pH values have been constant for a long time. A slight decline has occurred for ANC since 1960, with a slight recovery in the topmost sample.

Lake 109 (Matojärvi) is truly a brown-water lake (pH 4.8, alkalinity $-14\ \mu\text{eq}\ \text{l}^{-1}$, TOC 15.5 mg l^{-1}). Its drainage area is large including some lakes and peatlands. The acidification history shows a lowering of ANC since 1900. The diatom-inferred values could be misleading here, as in most brown-coloured lakes, because the proportion of brown-coloured lakes in the reference database is too small. The response of species to acidification in humic lakes may also be different from those in clearwater lakes.

Lakes with No Acidification Trends

The lakes in this group have relatively high ANC. Most of the lakes show increasing inferred pH since pre-1900 (Fig. 3), indicating disturbance or changes in land use in their drainage area.

Lakes 63 (Hautalampi), 114 (Ruuhijärvi), and 000 (Leväsoppinen) are the most alkaline of the studied lakes ($\text{pH} \geq 6.5$). Ylä-Kuolimo (81) is fairly buffered at present. Lake 95 (Valkeinen), 38 (Ukonjärvi), and 162 (Sahajärvi) are not so well buffered but inferred values indicate no clear acidification trends.

Lakes with Poorly Preserved Diatom Frustules

In sediment cores of the three lakes, diatom valves in the topmost samples have been only partly preserved. Therefore, an interpretation of the acidification history of these lakes has not been done. It is noteworthy, however, that two of the lakes, 108 (Kuikkalampi) and 45 (Saari-Soljonen) are seepage lakes and presently acidic and 113 (Leusjärvi) is the most alkaline of all lakes studied (pH 6.9). Causes for poor preservation might be different in each case.

Changes in the Proportion of Planktonic Diatoms

The abundance of planktonic diatoms in lakes depends on the lake acidity and probably on water colour or humic content of water. As a lake acidifies, the proportion of planktonic diatoms in the sediment assemblages decreases abruptly. In acidic lakes planktonic forms have generally a minor or no role (e.g. Flower and Battarbee 1983; Charles 1985).

The classification of diatoms into planktonic or non-planktonic is in some cases problematic because the same species can grow both in the plankton and benthos, depending on prevailing lake conditions. In this paper the following species are classified as euplanktonic: *Asterionella formosa*, *A. gracillima*, *A. ralfsii*, *Cyclotella comta*, *Diatoma elongatum*, *Melosira ambigua*, *M. granulata*, *Rhizosolenia longiseta*, *Synedra acus* and *Tabellaria fenestrata*, but also meroplanktonic *Cyclotella kützingiana* and *Melosira distans* are included. Most of these species are absent in acidic lakes except *Asterionella ralfsii*, which can be abundant also in acidified waters.

The abundances of planktonic diatoms in the short cores varied greatly (Fig. 4). Excluding the sites where serious dissolution of frustules was found, planktonic diatoms have been absent or in very low proportion in two lakes, 0 (Långträsk) and 107 (Valkeinen), which have been acidified, and in one lake, 114 (Ruuhijärvi),

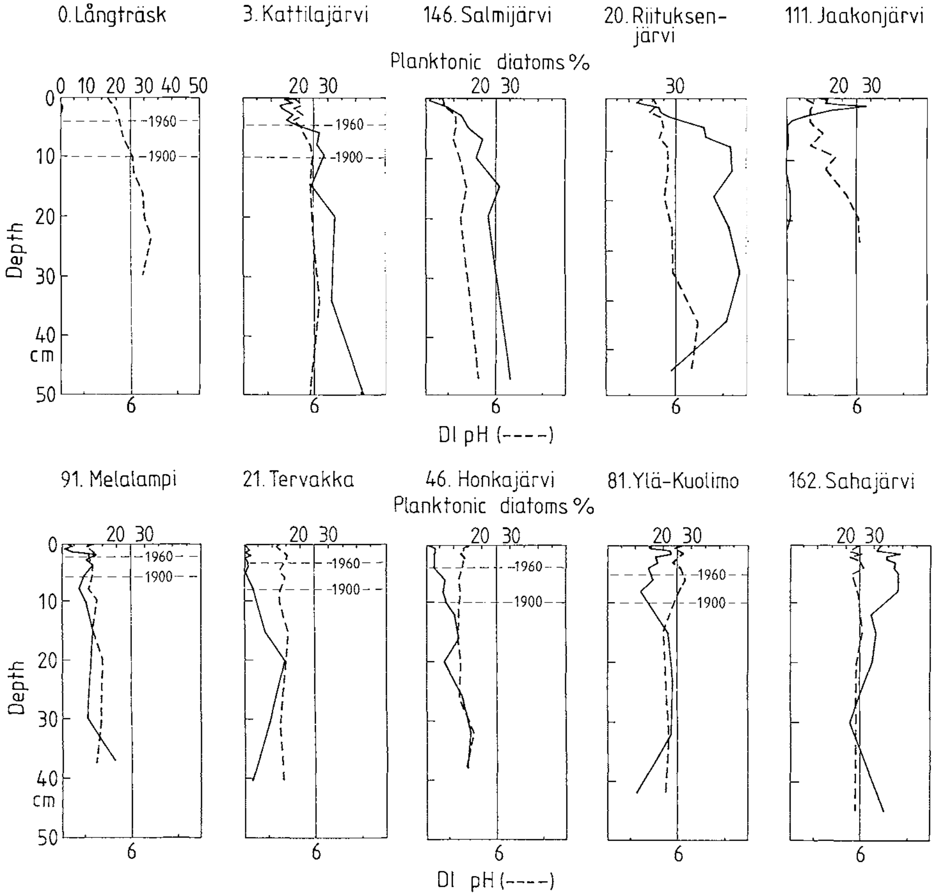

Fig. 4. Percentage of planktonic diatoms and inferred pH in ten selected lakes

where the acidification trend is not as clear. Absence of planktonic diatoms may be caused by a weaker turbulence in the shallow forest lakes. Maximum depth of these lakes is 6 m or less (Table 1).

At all sites where recent acidification is recorded and the lake is deep enough, ca. 8 m, the proportion of planktonic diatoms decreases remarkably (146 Salmijärvi, 20 Riituksenjärvi, 16 Malarijärvi, 3 Kattilajärvi and 48 Pääjärvi).

In naturally acidic lakes the abundance of planktonic diatoms has declined during the past century (lakes 109, 21, 55, 63, and 91). Proportion of planktonic species has always been less than 20% in these lakes.

For lakes which have not acidified or where the inferred alkalinity has increased for the last 100 years, the proportion of planktonic diatoms increased or fluctuated between adjacent sediment levels. This could indicate a rapid and positive response of planktonic diatoms to the changing water regime. An example of this behaviour is the dramatic increase of planktonic forms found in the topmost samples of lake 111 (Jaakonjärvi), possibly at a time when the lake was limed. In the older sediment samples planktonic diatoms are almost absent.

Changes in the proportion of planktonic diatoms are sharper and occur slightly earlier compared to changes in inferred pH estimated from the whole diatom assemblage. Using this response of planktonic species, together with the structure of the whole diatom assemblage, it may be possible to predict lake acidification processes or to trace the recovery of an acidified lake in a more detailed way.

Chemical Models for Estimating Lake Acidification

The present chemical characteristics of lakes have been used in calculations about the past pre-acidification state. Empirical models of estimating acidification have been developed by Henriksen (1979, 1980) and Wright (1983). Both methods make use of the ionic balance of major ions, subtraction sea salts from ionic concentrations, and empirical statistical relationships of major ions in lakes of unaffected reference areas.

The base cation model of Henriksen (Henriksen 1979, 1982) defines the relationship between the past alkalinity and modern calcium and magnesium concentrations as follows

$$\mathrm{Alk}_o = 0.91\ ([\mathrm{Ca}^{2+}]^* + [\mathrm{Mg}^{2+}]^*). \tag{1}$$

The asterisks (*) denote the non-marine fractions, corrected from measured concentrations by substracting the sea salt fraction on the basis of the fixed ratio Cl:Ca (or Mg) μeq 1^{-1} in seawater and the actual concentration of $[\mathrm{Cl}^-]$ in lakewater.

If the growing acidic deposition has added the weathering rate and thus released more cations from lithological components within a watershed, a correction term is needed in Eq. (1). The ratio of unequivalent change in $[\mathrm{Ca}^{2+}]^* + [\mathrm{Mg}^{2+}]^*$ to change in $[\mathrm{SO}_4^{2-}]^*$ is defined as: (Henriksen 1984)

$$F = \Delta \frac{([\mathrm{Ca}^{2+}]^* + [\mathrm{Mg}^{2+}]^*)}{\Delta\ [\mathrm{SO}_4^{2-}]^*} \tag{2}$$

and thus

$$\Delta\ ([\mathrm{Ca}^{2+}]^* + [\mathrm{Mg}^{2+}]^* = \mathrm{F}\ \Delta[\mathrm{SO}_4^{2-}]^*. \tag{3}$$

The empiric relationship between the original alkalinity and modern base cation concentrations [Eq. (1)] is thus (Henriksen 1982)

$$\begin{aligned}&\mathrm{Alk}_o = 0.93\ ([\mathrm{Ca}^{2+}]^* + [\mathrm{Mg}^{2+}]^* -\\ &\mathrm{F}\ ([\mathrm{SO}_4^{2-}]^* - [\mathrm{SO}_4^{2-}]_o^*) - 14.\end{aligned} \tag{4}$$

In Norway the original, pre-acidification or background sulphate concentration ($[\mathrm{SO}_4^{2+}]_o^*$) has been estimated to be about 20 μeq l^{-1} by Henriksen (1982), or calculated from an empiric equation (Henriksen, pers. commun. cf. Forsius et al. this Vol.)

$$[\mathrm{SO}_4^{2-}]_o^* = 14 + 0.16\ ([\mathrm{Ca}^{2+}]^* + [\mathrm{Mg}^{2+}]^*). \tag{5}$$

The F-value depends on catchment characteristics getting values from zero to 1. It approaches zero in the areas of extremely low weathering rate and is 1 if acidic load is totally compensated by base cations from soils. The equation for F-value is defined by Brakke et al. (in press, cf. Forsius et al. this Vol.)

$$\mathrm{F} = \sin\left(\frac{90[\mathrm{BC}]^*}{\mathrm{S}}\right), \tag{6}$$

where BC* is the sum of concentrations of modern basic cations (Na, K, Ca, Mg); S is the point at which F = 1 (200 or 400 μeq l^{-1}).

In the calculations of pre-acidification alkalinity according to Eq. (4), values of 200 and 400 for S were used. Equation (5) was used when predicting original (background) sulphate concentration.

The results from base cation method calculations show clear acidification in almost all the studied lakes (Table 3). This method does not indicate anything about the time of acidification, only the total measures. Generally, the chemical method show both larger and smaller acidification than the diatom method. The biggest differences are in humic lakes. This chemical model does not apply to such cases, where anions other than sulphate and bicarbonate are abundant.

Discussion

Of the 30 lakes, 13 indicate a strong, recent acidification during this century. Together with corresponding studies of Tolonen and Jaakkola (1983), Simola et al. (1985) and Tolonen et al. (1986), the total number of palaeoecological acidification histories of lakes in Finland is now over 50 (Fig. 5). The recent acidification of small forest lakes seems to be restricted to southern Finland, where almost all acidic lakes have also acidified since 1900. In central and northern Finland naturally acidic lakes are more common. The distribution of catchment types is, however, not the same all over the country. In southern Finland exposed bedrock

Table 3. Measured alkalinity (μeq l^{-1}) in 1987, changes of alkalinity based on diatom and empiric, base cation models with two F-values (F_1, S = 200 μeq l^{-1}, F_2, S = 400 μeq l^{-1})

	Acid-neutralizing capacity (ANC), μeq l^{-1}					
	Measured alkalinity	Diatom-inferred			Base cation model[a]	
Lake		1985	Change since 1960	Total change	Change with F_1	Change with F_2
146 Salmijärvi	−31	−55	nd	−84	−46	−59
15 Krailan Pitkä	−9	6	−59	−80	−63	−83
20 Riidtuksenjärvi	−8	40	nd	−103	−26	−56
16 Malarijärvi	−4	25	15	−65	−48	−77
111 Jaakonjärvi	3	−46	nd	−148	–	–
0 Långträsk	6	4	−33	−115	–	–
3 Kattilajärvi	10	30	1	−49	−33	−54
107 Valkeinen	11	−7	−7	−59	−5	−15
116 Ahveroinen	12	−10	−16	−62	−6	−10
48 Pääjärvi	26	26	−21	−66	−25	−45
82 Kukkarojärvi	31	−5	−25	−48	−57	−68
165 Valkea-Kotinen	−48	33	−44	−48	−91	−117
93 Kankaantakunen	11	59	0	−24	−59	−80
115 Silpalampi	−20	−72	−21	−33	−28	−27
109 Matojärvi	−14	−58	1	−43	−60	−66
21 Tervakka	−2	−19	−16	−25	−72	−92
55 Mäkilampi	−13	−30	0	−38	−10	−52
46 Honkajärvi	3	−1	17	−14	−118	−130
91 Melalampi	25	−15	25	−16	−39	−50
38 Ukonjärvi	20	70	22	1	−43	−63
63 Hautalampi	85	138	nd	−67	−39	−42
114 Ruuhijärvi	64	143	−3	−67	−23	−11
112 Leväsoppinen	542	280	nd	−27	–	–
95 Valkeinen	1	47	−12	−12	−49	−71
162 Sahajärvi	9	62	−7	−11	−14	−44
531 Iso-Koukeri	11	12	−3	−20	−34	−56
81 Ylä-Kuolimo	55	95	4	−6	−58	−64
108 Kuikkalampi	−20	−73	−37	−47	−21	−24
113 Leusjärvi	213	283	nd	−4	−58	−72
45 Saari-Soljonen	−21	−26	−8	−8	−37	−45

nd = no dating

[a] Henriksen (1979, 1982), Brakke et al. (in press)

catchments are much more common and in inland areas of central and eastern Finland acidic lakes are more often seepage lakes. The northernmost, recently acidified lakes 111 Jaakonjärvi and 116 Ahveroinen are situated in the region of moderate sulphur deposition from 0.6 to 0.8 g m^{-2} a^{-1}. Their catchments are extremely sensitive to acidification. However, even if the role of acidic deposition is clear both in the acidification history and in the regional distribution of recent lake acidification, it is not possible to give any numerical values of critical loads for acidification.

A slight acidification trend was found in almost all lakes (mean 46 μeq l^{-1}), even in the previously naturally acidic sites. Using four different chemical acidification models, Kämäri (1985) found a general trend of decreasing alkalinity in small

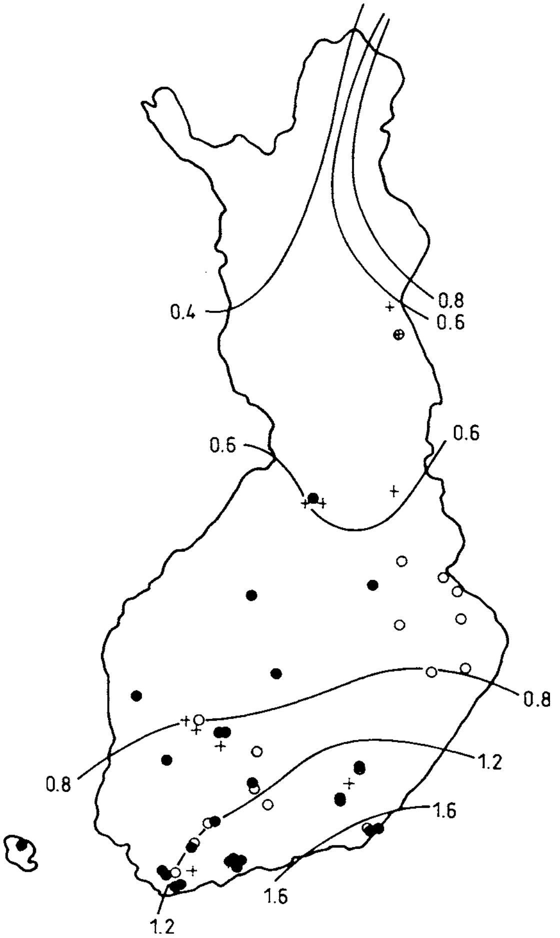

Fig. 5. The sites studied for history of lake acidification in Finland (Tolonen and Jaakkola 1983; Simola et al. 1985; Tolonen et al. 1986; this chapter). Recently acidified lakes are indicated by (*closed circles*), naturally acidic lakes by (*open circle*), and lakes with no acidification trends (**cross**). The regional sulphur deposition in 1980 ($g\,S\,m^{-2}\,a^{-1}$) has been included. (After Tuovinen et al. this Vol.)

acid-sensitive forest lakes in south Finland ranging from 50 to 100 $\mu eq\,l^{-1}$. In our study the chemical model showed the mean of 50 $\mu eq\,l^{-1}$ absolute acidification (Table 3).

According to data from 375 small oligotrophic lakes and their catchments Kämäri (1984) concluded that the type of surficial soil material is the most critical parameter for the sensitivity of Finnish lakes to acidification. A large proportion of naturally acidic peat in the catchment area usually increases the humic content of lake water and lowers the pH. The share of organic anions can be well over 10% in humic lakes where TOC is about 10 $mg\,l^{-1}$ (Kortelainen and Mannio 1988). For example in lake 91 Melalampi TOC was 10.1 $mg\,l^{-1}$ and in lake 109 Matojärvi 15.5 $mg\,l^{-1}$.

Miscellaneous granite and gneiss bedrock dominate in the most catchment areas of the sites studied. Only in one case, the lake 114 Ruuhijärvi, more easily weathered rock types such as diabase and amphibolite dominate in the catchment. At present this lake is well buffered, neutral (pH 6.8) clearwater lake with very low aluminium concentration.

If soils are thin, cation exchange reactions cannot totally neutralize the acidic deposition. In such cases aluminium release from soils with low pH may increase. A large percentage of exposed bedrock (or areas with soil thickness $\leq$ 1 m) in drainage areas shortens the reaction time between seepage water and soil particles and leads to incomplete neutralization of acid rain. For example recently acidified lakes 16 Malarijärvi, 82 Kukkarojärvi, 15 Krailen Pitkäjärvi and 0 Långträsk are situated in this kind of open bedrock areas.

The reaction time between seepage water and soil increases as the particle size, and thus permeability decreases. In fine-grained soils, such as silts and clays, the cation exchange processes are effective enough if soil compaction does not occur.

In very coarse mineral soil, neutralization is not effective due to lack of exchange surfaces. Many of the recently acidified lakes, according to diatom-based pH-reconstruction, are situated in areas of coarse-grained sand or gravel as a dominant soil type (e.g. 20 Riituksenjärvi, 146 Salmijärvi, 116 Ahveroinen and 111 Jaakonjärvi).

Despite the low to moderate ANC of coarse grained soils, a large catchment/lake area and a thick soil layer can neutralize strong acid loads because of the increase in reaction time. Only slight recent changes in diatom assemblages or inferred pH-values were found in lakes with relatively large catchment areas (e.g. 38 Ukonjärvi, 63 Hautalampi, 81 Ylä-Kuolimo and 113 Leusjärvi).

The traditional slash-and-burn method has been used in Finland since the onset of agriculture, which dates according to pollen analyses and radiocarbon dating to approximately 4000 B.P. (Huttunen 1980; Tolonen 1983; Vuorela 1986). Although in certain areas the traditional methods of cultivation had gone out of practice by the 18th century, they still continued to be practiced in eastern Finland as late as in the beginning of the 20th century. The declining pH may indicate a gradual return from an elevated pH level caused by land use change and forest succession. In the United Kingdom Battarbee et al. (1988) state that although there have been changes in burning and grazing practice in many studied catchments, there is no correlation between changes in moorland management and lake acidification. However, the conifer afforestation seems to have some acidifying effects.

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PART 4 LIMING

Alleviation of Forest Soil Acidification Through Liming

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Summary

The results of 40, long-term broadcast liming experiments (2 t ha^{-1}) in Scots pine and Norway spruce stands on mineral soil sites, and of two experiments in Scots pine stands on peatland (2, 4 and 8 t ha^{-1}), are reviewed.

Liming resulted in considerable accumulation (10–50% increase) of organic matter in the humus layer, but no changes in the mineral soil. The C/N ratio of the humus increased on the most productive mineral soil sites, but either remained unchanged (after 60 years) or decreased (after 30 years) on the peatlands. Almost all of the added Ca was still present in the humus and 0–10 cm mineral soil layers, but a considerable proportion had been leached from the surface layers of the peatlands. Of the added Mg, 70–80% had been removed from the 0–30 cm layer in the peatlands. Liming brought about a long-term decrease in acidity and corresponding increase in base saturation of the surface layers on both types of substrate. Sulphur was found to have been immobilized to a considerable extent in the humus of the mineral soils, presumably as aluminium sulphate.

Introduction

Finnish forest soils are naturally acid. The mean $pH(H_2O)$ of the humus layer of mineral soil sites is about 4, and that of the A, B and C horizons 4.5, 5.0 and 5.4 respectively (Urvas and Erviö 1974). The $pH(H_2O)$ of peat soils varies considerably according to depth and site type, but in the 0- to 20 cm-thick peat layer on the most common types of pine mires it lies between 4.1 and 4.6 (Westman 1981). The moist and cool climate, coupled with the relatively high acidity, means that the rate of decomposition of organic matter is slow. This is even more pronounced in peat soils owing to the high water content and anaerobic conditions deeper in the peat. The rate of mineralization of plant nutrients, especially nitrogen, is very slow and, in many cases, there is net immobilization of nutrients. Thus, although the soil contains considerable reserves of nutrients, the levels of available nutrients (especially nitrogen) are usually limiting for tree growth.

During the past few years considerable attention has been paid to the use of liming as a means of counteracting the detrimental effects of acidic deposition on

Kauppi et al. (Eds).
Acidification in Finland

mineral soils (see Andersson and Persson 1988) for a comprehensive review. In long-term experiments carried out in Sweden, limestone has been applied to the soil surface at rates ranging from 3 to 20 t $CaCO_3$ ha^{-1}. As expected, liming increased pH and base saturation, and decreased titratable acidity (Hallbäcken and Popovic 1985). Matzner et al. (1985) have studied the short-term effects of broadcast liming on mineral soil properties in Germany. They also found marked increases in base saturation. Broadcast liming had little short-term effects on C and N storage in the humus layer, primarily due to the slow dissolution of the limestone in the surface humus. In contrast, limestone mixed into the topsoil on both mineral soils (Palmgren 1984) and peat soils (Kaunisto and Norlamo 1976) has had a considerable stimulating effect on soil microbiology. Despite the apparent positive effects of liming on soil characteristics, a slight decrease in tree growth has been reported in several studies (e.g. Derome et al. 1986). Persson (1988) concludes that the main reason for the decrease is that slow dissolution of the limestone applied to the soil surface results in an increase in N mineralization in the mineral soil, but a decrease in the litter and humus layers. In the long term, however, the overall decrease in net N mineralization down the soil profile will turn into an increase. The increase in the pH of the humus layer is also associated with a decrease in P availability through precipitation as calcium phosphate (Nihlgård 1988).

The aims of this study are to investigate the long-term effects of broadcast forest liming on the chemical properties of mineral and peat soils in Finland.

Material and Methods

Liming Experiments

Mineral Soils

The material used in this part of the study comprises 40 of the fertilization experiments, established on mineral soil sites by the Department of Soil Science, the Finnish Forest Research Institute, where limestone has been added as one of the treatments (Fig. 1). The experiments, set up at the end of the 1950's and beginning of the 1960's, are in either Scots pine (*Pinus sylvestris* L.) or Norway spruce (*Picea abies* (L.) Karst.) stands growing on sites of varying fertility.

Soil samples have been taken from these fertilization experiments after certain intervals, but not at the time of establishment. The experiments have been selected for this study so as to provide material representing a time period of ca. 20 years between liming and soil sampling. In addition, the samples are for the period before reliming was carried out, i.e. only one dose of limestone (2 t limestone ha^{-1}) has been applied. The size of the plots was 30 × 30 m.

Table 1. Distribution of the material according to tree species and site type (see Cajander 1949 for explanation of site types)

Tree species	Site type OMT	MT	VT	CT	Total
Pine	–	12	10	4	26
Spruce	8	6	–	–	14
Total	8	18	10	4	40

OMT = *Oxalis-Myrtillus* forest site type, MT = *Myrtillus* type, VT = *Vaccinium* type, CT = *Calluna* type

Peat Soils

The experiments used in this part of the study consist of 60 plots established in different years on peat soils in two experimental areas: Vilppula in 1929, and Muhos in 1955–56 (Fig. 1). Although dolomitic limestone has been used (25% Ca, 11% Mg) in most cases, there is some uncertainty about the composition of the limestone applied on a number of plots. Limestone has been applied at doses of 2, 4 and 8 t ha^{-1}. The unfertilized plots were used as controls. The experiments were established on relatively nutrient-poor pine mires where the dominating tree species was Scots pine. The mires at Vilppula were old peatland forests, and at Muhos transitional drained peatlands.

Sampling

Mineral Soils

Sampling was done along three lines running parallel across each plot. Fifteen humus and four mineral soil samples (0- to 10-cm-thick layer) were taken. Five of the spruce and five of the pine experiments were subjected to more comprehensive sampling in 1983 in order to determine changes in aluminium levels down the soil profile. Humus samples were taken from 40 sampling points along the border surrounding the plots, and mineral soil samples (0–5, 5–10 and 10–20 cm) from every second sampling point.

Peat Soils

Volumetric samples were taken of the peat profiles at five points on each plot: in the centre and two each from the diagonals. The profiles were divided into five layers (raw humus, 0–5, 5–10, 10–20 and 20–30 cm), and combined to form composite samples for each layer.

The humus, mineral soil and peat samples were taken to the laboratory, air-dried and weighed. The peat samples were stored in a deep freeze. The humus samples were milled to pass through a 1 mm sieve, and the mineral soil samples sieved to remove roots and gravel (> 2 mm).

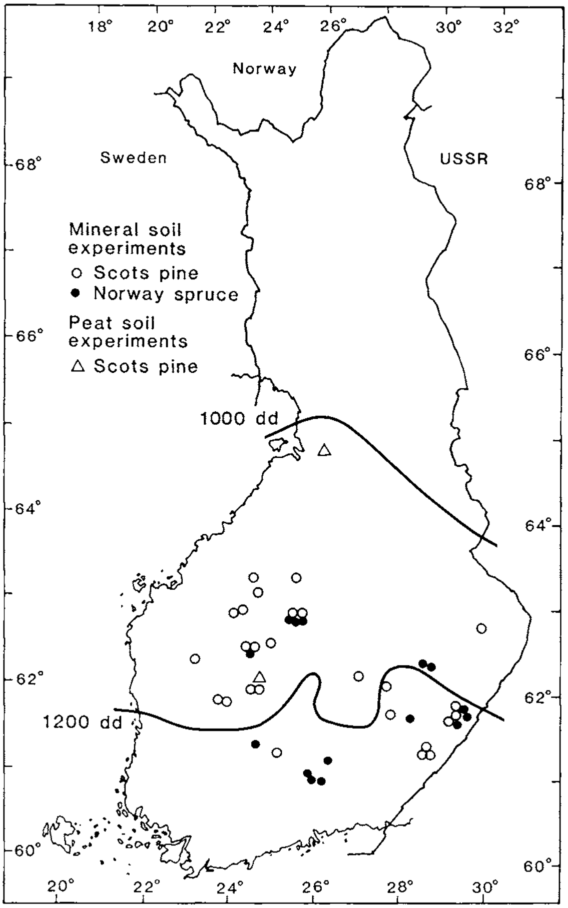

Fig. 1. Location of the liming experiments

Chemical Analyses

The moisture content of the samples was determined by drying in an oven at 105°C. pH(H_2O) and pH(KCl) were determined from a slurry consisting of 10 ml humus/mineral soil or 15 ml of peat (fresh) and 25 ml of deionized water or 1.0 M KCl.

Extractable aluminium was determined by extraction with 1 N KCl and titration following the addition of NaF (Black 1965).

Total nutrients were determined by ashing 1.5 g air-dry humus or peat in a muffle furnace at 550°C for 3 h. The residue was dissolved in a small amount of conc. HCl, evaporated to dryness on a water bath to precipitate silica, and then extracted with 0.1 N HCl to give a final volume of 100 ml. Total Ca, Mg, K and inorganic S and P were determined by inductively coupled plasma atomic emission spectrophotometry (ICP/AES) (ARL, model 3580 OES). Total C and N were determined on an automatic CHN analyser (Leco).

Available nutrients were determined by shaking 5 g air-dry humus or peat or 15 g air-dry mineral soil for 2 h (after standing overnight) with 150 ml 1 M NH_4OAc, pH 4.65. After filtering, Ca, Mg and K were determined by ICP/AES. Acidic ammonium acetate extractable S was determined from the extract by ICP/AES.

Potential cation exchange capacity and base saturation were determined from the peat samples in neutral (pH 7.00) 1 M NH_4OAc.

Calculations

In order to eliminate the considerable differences between soil parameter levels on the control plots of the separate experiments, the differences between certain parameters on the control and limed plots on mineral soils were calculated as the change (in percent) on the limed plot compared to the control plot in each experiment separately. The percentage values for all the limed plots in the same group were then averaged and their distribution compared to the zero level for the controls tested using the t-test.

In the case of the peat soils the nutrient contents of the limed plots (30 and 60 years interval) were compared directly with those from the control plots in each experiment.

Results and Discussion

Liming Experiments on Mineral Soils

Organic Matter Accumulation and Organic Matter Quality

Liming resulted in statistically significant accumulation of organic matter in the humus layer of both the pine and spruce experiments (Fig. 2). The change was the greatest on the most and the least productive sites. Liming had no effect on the amount of organic matter in the 0–10-cm-thick mineral soil layer.

Although this aspect has not been studied here, the most plausible explanation for the high level of organic matter accumulation in the humus layer is an increase in the litterfall and root biomass of the ground vegetation (e.g. Nihlgård and Popovic 1984). Liming tends to increase the coverage of annual plants which return large amounts of dead biomass to the litter layer each autumn. As liming has had either no effect or only a slightly negative one on stand growth (Derome et al. 1986), litterfall from the tree stand could not explain this accumulation.

The quality of the organic matter in the humus layer was estimated on the basis of the total C and N content (% of organic matter) and the C/N ratio (Fig. 3). Liming clearly increased the carbon content of the organic matter in both the pine and spruce experiments, and had a progressively stronger effect with increasing site fertility. This is an unexpected result when we consider that higher pH values should increase decomposition activity. In Swedish liming experiments no changes were detected in the C/N ratio of the humus layer (Andersson and Persson 1988).

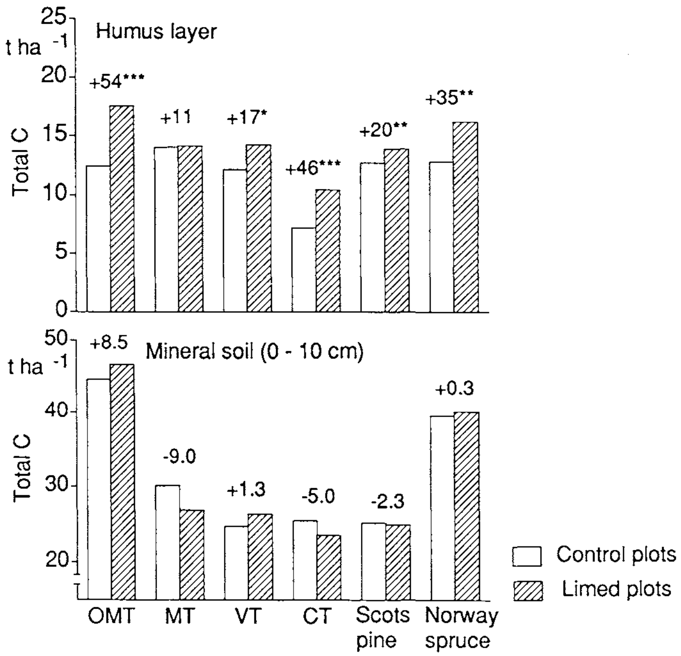

Fig. 2. The change in the amount of elemental carbon in the humus and mineral soil layers by tree species and site type. *OMT* Oxalis-Maianthemum site type; *MT* Myrtillus type; *VT* Vaccinium type; *CT* Calluna type. The *values above the columns* indicate the mean change (in %) on the limed plots compared to the control plots. The mean change is the average of the percentage change for the individual experiments. (*** = highly significant difference, ** = very significant, * = significant)

The total nitrogen content in the humus layer was not affected at all by liming. The C/N ratio for the whole material did not change but, owing to the large increase in the C content on the most productive sites, their C/N ratio increased significantly. Hallbäcken and Popović (1985) were not able to find any clear changes in C, N or the C/N ratio in their studies in Sweden owing to the high variation in the material. The reason for the increase in C content but not N content would suggest that changes have taken place in the quality of the humus (cf. Hallbäcken and Popović 1985), and the increase is not merely a result of compression of the humus on the limed plots caused by the accumulation of organic matter.

Long-term liming experiments differ from short-term field or laboratory incubation experiments in that changes in the quality and quantity of the litterfall will have a decisive effect on the quality of the organic matter after extended periods, e.g. the 20 years period examined here. The C/N ratio in these experiments may have initially fallen due to immediate stimulation of the soil microbes. However, any such effect will have disappeared after a new equilibrium was reached. Although the humus layers of mineral soils and peat are not directly comparable, it

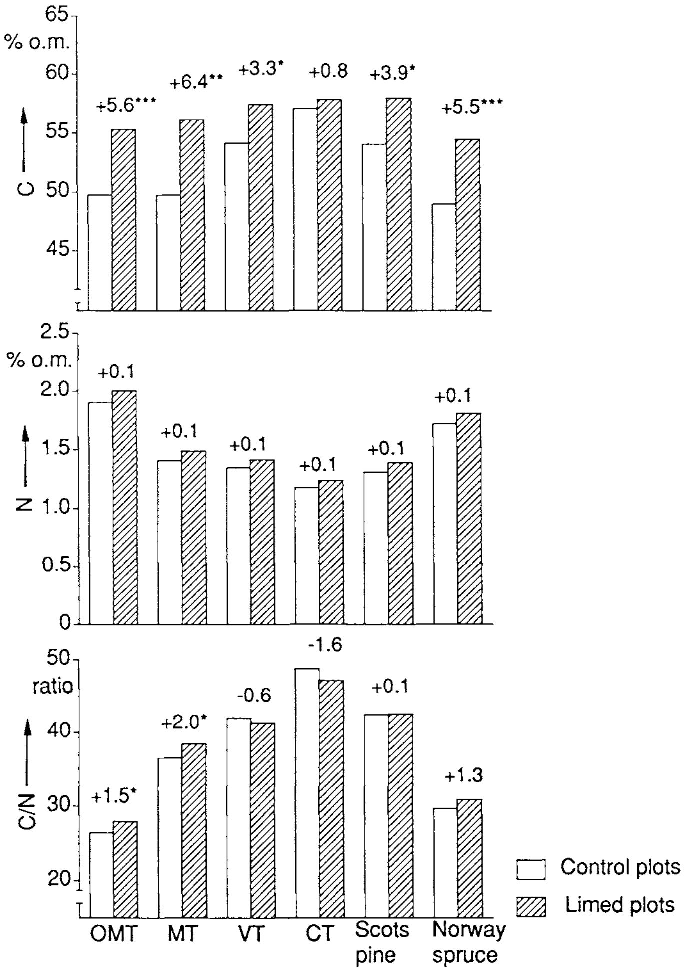

Fig. 3. The change in the content of total carbon, total nitrogen and the C/N ratio in the humus layer by tree species and site type. The *values above the columns* indicate the absolute difference between the limed and control plots. See Fig. 2 for explanation of site type abbreviations

is interesting to note that the C/N ratio of peat in the Muhos experiment (limed 1956) decreased following liming (see Table 8).

Soil Acidity

Liming has increased the pH(H_2O) of the humus layer in both the pine and spruce experiments by more than 0.5 pH-units (Table 2). On the other hand, only the pH(H_2O) of the mineral soil in the pine experiments has been increased significantly. As expected, liming has had the greatest effect on the pH(H_2O) of the humus layer on the least productive site type (CT), which has a thin cover of humus and tree stand consisting only of pines. The pH(H_2O) of the mineral soil of this same site type has also increased the most. The pH(H_2O) of the mineral soil of the most productive site type (OMT) has not been affected at all. These results are in full agreement with those obtained in Swedish liming experiments (Andersson and Persson 1988) in that limestone applied directly to the soil surface has an immediate and long-term effect on humus pH, and the time lag before the mineral soil is affected is determined primarily by the thickness of the humus layer.

Although exchange acidity of the soil from the pine and spruce experiments has not been determined, pH(KCl) does provide some information about the total amount of hydrogen ions in the different layers. There is a close relationship between pH(KCl) and exchange acidity in the humus owing to the low proportion of exchangeable Al (Derome et al. 1986). In the mineral soil, on the other hand, many of the protons displaced during extraction with KCl are lost through dissolution of aluminium and iron hydroxides, and an underestimate is obtained.

The trends for the change in pH(KCl) closely follow those for pH(H_2O). The magnitude of the decrease in H^+ for the humus layer calculated on the basis of the change in pH(KCl) is, as expected, much stronger. The long-term effects of liming thus lie in the ability of the limestone to gradually neutralize a fairly high proportion of the protons occupying exchange sites, and not only free protons. The change in the mineral soil is smaller than that for pH(H_2O).

Aluminium

The results presented here are from a smaller material consisting of five pine and five spruce experiments. Even though the mean humus thickness on the control plots (4.3 cm for spruce, 3.5 for pine) was not the same as the sampling depths used in the mineral soil, the extractable aluminium levels in the humus layer were proportionately much lower than those in the 5-cm-thick layers of the mineral soil. Most of the aluminium in the humus layer is complexed with organic matter (i.e. not readily extractable with KCl) and the proportion of extractable Al is low (Nilsson and Bergkvist 1983). In the mineral soil, on the other hand, much of the aluminium is in the form of aluminium hydroxides, and equivalent amounts of aluminium will be dissolved by the hydrogen ions liberated from the exchange sites during KCl extraction.

Liming significantly reduced the amount of extractable aluminium in the humus and mineral soil layers in the pine and spruce stands (Fig. 4). The percentage reduction was fairly uniform down the soil profile in the pine stands. In contrast, the reduction in the spruce stands was concentrated in the humus and 0- to 5-cm-thick mineral layers. Similar marked reductions in extractable Al levels in the uppermost soil layers have been reported in Swedish experiments (Andersson and Persson 1988). The reduction in Al levels brought about by liming is clearly dependent on the neutralizing effect of liming. In a more detailed study carried out on ten of these liming experiments (Derome et al. 1986), highly significant negative correlation was found between the extractable aluminium content and soil pH in

Table 2. Effect of liming on pH(H_2O) and pH(KCl) in the humus and mineral soil (0–10 cm) layers by tree species and site type. See Fig. 2 for explanation of site type abbreviations

Site type or tree species	Treatment	Humus layer pH(H_2O)	Change $H^+ \times 10^{-5}$	pH(KCl)	Change $H^+ \times 10^{-5}$	Mineral soil pH(H_2O)	Change $H^+ \times 10^{-5}$	pH(KCl)	Change $H^+ \times 10^{-5}$
OMT	0	4.16		3.50		4.39		3.73	
	Ca	4.61	−4.5***	4.01	−21.8***	4.45	−0.5	3.75	−1.1
MT	0	3.78		3.09		4.37		3.79	
	Ca	4.39	−12.6***	3.82	−67.1***	4.82	−2.8*	4.13	−8.9**
VT	0	3.61		2.86		4.42		3.96	
	Ca	4.27	−19.2***	3.68	−118.7***	4.91	−2.6**	4.21	−4.8*
CT	0	3.62		2.87		4.60		4.29	
	Ca	4.60	−21.3***	3.99	−126.0***	5.12	−1.7*	4.45	−1.5*
Scots	0	3.68		2.94		4.47		3.91	
Pine	Ca	4.36	−16.8***	3.77	−98.8***	4.96	−2.3**	4.23	−5.9**
Norway	0	3.99		3.32		4.31		3.75	
spruce	Ca	4.51	−7.2***	3.95	−34.4***	4.51	−1.8	3.85	−3.7

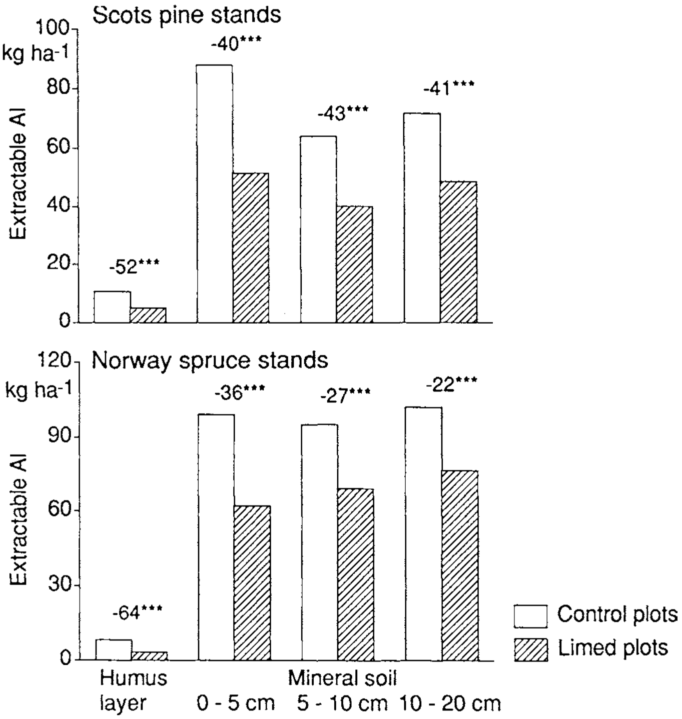

Fig. 4. The change in the amount of extractable aluminium in the humus and uppermost mineral soil layers of ten Scots pine and Norway spruce liming experiments. The *values above the columns* indicate the mean change (in %) on the limed plots compared to the control plots. The humus and mineral soil samples were bulked to give one sample per layer per plot

the humus and 0- to 5-cm-thick mineral soil layers. The pH was, in turn, dependent on the distribution of the added Ca down the soil profile. Most of the added Ca was still in the humus and 0- to 5-cm-thick mineral soil layers in the spruce experiments, but was fairly evenly distributed down the soil profile in the pine experiments. The retention of a higher proportion of the added Ca in the humus layer was attributed to the greater thickness of the humus layer and finer texture of the mineral soil layer in the spruce experiments.

Calcium Balance

An attempt has been made to determine how much of the Ca, added as limestone (2 t ha^{-1}), is still present in the humus and uppermost mineral soil layers. Owing to insufficient documentation, however, it is not known with any certainty which experiments have received limestone (31–35% Ca) and which dolomitic limestone (22% Ca). The probable doses of calcium applied during liming have been calculated by assuming that those experiments with an increase in the available Mg concentrations in the humus layer of the limed plots of over 100% have been given

440 kg Ca ha^{-1}, and all the others 660 kg Ca ha^{-1}. A calcium balance sheet for the humus and 0- to 10-cm-thick mineral soil layer is given in Table 3.

Almost all of the Ca added as limestone was still present in the humus and uppermost mineral soil (0–10 cm) layers after 20 years. The Ca was rather evenly divided between the humus and mineral soil layers in both the spruce and pine experiments. The distribution according to site type, however, did not appear to follow a regular pattern because the proportion of Ca was lowest in the humus layer of the MT sites, and highest in the humus layer of the CT sites. These results conflict somewhat with those presented in an earlier study carried out on ten of the liming experiments (Derome et al. 1986), in which 65–75% of the added Ca was found to be present in the humus and 0–20-cm-thick mineral soil layers. Despite the fact that there is some uncertainty concerning the actual amounts of Ca applied and the technical problems associated with determining total amounts of Ca in mineral soil samples, the results for the study in hand are from a much more comprehensive and representative material. It would thus appear that the hydrogen ion load in Finland during the 20-year period (approx. 1960–1980), combined with the production of H^+ through natural soil processes, has not been able to displace, to any appreciable extent, the Ca added in liming at doses of 2 t ha^{-1} from the humus layer and uppermost mineral soil layer.

The values obtained in Swedish studies (Hallbäcken and Popović 1985) concerning the retention of added Ca in the topmost layers of the soil are lower than those obtained here. They report losses from the humus and 20-cm-thick mineral soil layers of between 50 and 400 kg $CaCO_3$ over a 25-year period in experiments which received between 3 to 10 t limestone ha^{-1}. Acidic deposition in southern Sweden is, however, much higher than that in southern and central Finland, and the addition of limestone at levels much higher than those used in the experiments in Finland will undoubtedly result in the movement of excess Ca down to deeper depths in the soil.

Base Cations

Cation exchange capacity and base saturation were not determined for these experiments. Total available base cations (Ca + K + Mg) was used here as a measure of the soil's ability to withstand acidic deposition.

As expected, liming strongly increased Ca and Mg concentrations in the humus layer of both the pine and spruce experiments on all site types (Table 4). Liming had no effect on K concentrations in the humus layer, apart from the significant increase on the most productive site type. Liming considerably increased total base cations in the humus layer, because Ca and Mg are the major base cations in the calculations. The increase was the greatest on the least productive sites. These results were, as expected, in full agreement with those for pH(KCl).

The situation in the mineral soil was very similar, except that the increase was not as large as that in the humus layer. The fact that the results for the mineral soil do not agree very well with those for pH(KCl) is due, as mentioned earlier, to the

Table 3. Distribution of the calcium added as limestone between the humus and uppermost mineral soil layers by site type and tree species

Site type or tree species	Treatment	Humus layer kg Ca ha^{-1}	Diff.	% of Added Ca	Mineral soil kg Ca ha^{-1}	Diff.	%	Total kg Ca ha^{-1}	% of Added Ca	Added kg Ca ha^{-1}
OMT	0	215			796					
	Ca	524	309	(50)	1084	315	(50)	624	(100)	570
MT	0	148			509					
	Ca	358	210	(35)	831	322	(54)	532	(90)	593
VT	0	82			289					
	Ca	371	289	(53)	546	257	(47)	546	(100)	540
CT	0	25			375					
	Ca	341	316	(66)	514	139	(29)	455	(95)	480
Scots	0	103			404					
pine	Ca	360	257	(45)	683	279	(49)	536	(94)	568
Norway	0	193			658					
spruce	Ca	466	273	(48)	955	297	(52)	570	(100)	557

Table 4. Effect of liming on available calcium, potassium, magnesium and total base cations (available Ca + K + Mg) in the humus and uppermost mineral soil layers by site type and tree species. All values are calculated per 100 g of organic matter (o.m.).

Site type or tree species	Treatment	Humus layer				Mineral soil (0–10 cm)			
		Ca	K	Mg	(Ca + K + Mg)	Ca	K	Mg	(Ca + K + Mg)
		mg	(100 g o.m.)$^{-1}$		meq (100 g o.m.)$^{-1}$	mg	(100 g o.m.)$^{-1}$		meq (100 g o.m.)$^{-1}$
OMT	0	2897	466	270	17.9	27.0	3.85	3.79	1.76
	Ca	6242***	547**	359**	35.5***	44.7**	4.00	4.58*	2.71**
MT	0	920	301	108	6.25	14.4	3.17	1.72	0.94
	Ca	2371***	318	184***	14.2***	33.8**	2.92	2.31*	1.95**
VT	0	243	98.7	31.9	1.73	5.19	2.06	0.74	0.37
	Ca	1001***	97.9	70.4***	5.82***	21.1***	1.89	1.82**	1.25***
CT	0	137	73.9	18.3	1.02	1.43	1.95	0.38	0.15
	Ca	1443***	63.2	102***	8.21***	14.1***	1.75	1.59***	0.88***
Scots pine	0	295	99.0	36.3	2.01	10.3	2.42	1.13	0.67
	Ca	1123***	101	70.3***	6.44***	28.6**	2.29	1.93*	1.64***
Norway spruce	0	2540	556	260	16.2	19.1	3.81	2.92	1.29
	Ca	5674***	620	387***	33.1***	35.0***	3.64	3.76***	2.15***

fact that this parameter does not give a true measure of the amount of hydrogen ions on exchange sites in the mineral soil.

In an earlier study on ten of these fertilization experiments (Derome et al. 1986), liming was found to have increased the base saturation of the humus layer from 21 to 35% in the pine experiments, and 25 to 39% in the spruce experiments over a period of 23 years. The corresponding values for the 0–20-cm-thick mineral soil layer were 7.5 to 19% and 8 to 15%.

In theory, increased amounts of Ca and Mg on exchange sites and subsequently in the soil solution should increase K leaching as a result of K displacement. In Finnish soils, however, almost all of the available K is already free in the soil solution (Derome 1989) and, owing to its lower affinity, K is not able to compete for exchange sites with other cations. Although considerable amounts of K are lost from the humus layer under normal conditions, most of this K is reclaimed in the mineral soil (Helmisaari and Mälkönen 1989) and presumably recycled back into the tree stand and ground vegetation. The results obtained in this study concerning the effect of liming on available K concentrations indicate that K is relatively unaffected by the presence of relatively high concentrations of Ca and Mg.

Sulphur

The different S fractions examined here are not based on precise methods for determining sulphur owing to the fact that the data have been obtained from analyses originally intended for other purposes. The residual sulphur following dry combustion (550°C) of the samples and extraction with HCl is here called total inorganic sulphur (TIS). Although this is not a very exact method, most of the residual sulphur will be sulphate. Similarly, the sulphur extracted with acid ammonium acetate (AES) will also be primarily in the form of sulphate, although some easily soluble organic S will be present. The difference between these two parameters is considered here to be sulphur in the form of sparingly soluble inorganic sulphate compounds, i.e. immobilized inorganic sulphur (IIS).

Liming has resulted in a considerable accumulation of TIS in the humus layer (Fig. 5). As the proportion of TIS has increased (on average by 49%) more than that of total C (on average 27%, Table 1), TIS has accumulated as a direct result of liming and not merely as an indirect effect of organic matter accumulation. The amount of AES has hardly changed at all, despite the considerable increase in the amount of organic matter in the humus layer. The concentration of AES can thus be considered to have been "diluted" as a result of liming. The component representing the difference between TIS and AES, i.e. IIS, has increased the most – on the average by 69%. Owing to the high corresponding increase in total Ca in the humus layer (Table 3), IIS presumably represents sulphate immobilized as sparingly soluble aluminium sulphate. Part of the excess IIS is presumably derived from sulphur removed from the sulphur cycle in the forest ecosystem, and part from the sulphate input in acidic deposition. If this is the case, then liming can be considered

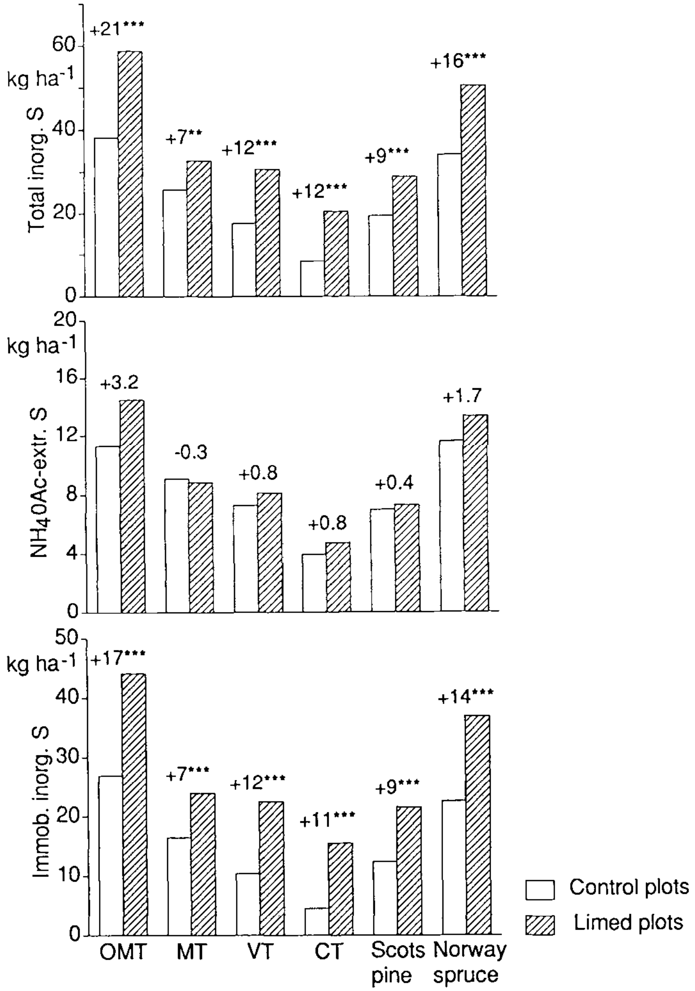

Fig. 5. Distribution of sulphur into total inorganic sulphur (TIS), ammonium acetate (pH 4.65) extractable sulphur (AES), and immobilized inorganic sulphur (IIS) in the humus layer by tree species and site type. The values above the columns indicate the absolute difference between the limed and control plots. See Fig. 2 for explanation of site type abbreviations

to alleviate the threat of cation leaching by totally or partially "fixing" the input of sulphate in acidic deposition that is assumed to increase cation leaching.

Liming Experiments on Peat Soils

The results concerning nutrient contents (kg ha^{-1}) in peat soils are mean values for plots which received the same limestone dose within each experiment.

Calcium and Magnesium

The time which had elapsed since liming had no effect on the total amount of calcium in the 0 to 30-cm-thick layer on any of the plots (Fig. 6). The amount of calcium on the plots given the highest doses of dolomitic limestone (8 t ha^{-1}, ca. 2 t Ca ha^{-1}) was double that on the control plots at both Vilppula (limed 1929) and at Muhos (limed 1956). Application at levels of 2 or 4 t ha^{-1} had no effect on the total amount of calcium down the peat profiles at Muhos, and only a small effect at Vilppula (20–25% of the added limestone remaining). The apparent decrease in the amount of calcium in the Muhos experiments may be due to the high variation in peat quality within the experimental area.

There were clear differences in the distribution of the added Ca between the Muhos and Vilppula experiments. In the Muhos profiles (1956) the calcium was clearly concentrated in the uppermost 10-cm-thick layer, and especially in the raw humus. At Vilppula (1929) there was no relationship between the amount of calcium in the raw humus and the size of the limestone dose. In contrast, the effects of limestone addition were clearly evident in the deeper layers.

Both this study and Swedish experiments show that the calcium added as limestone is effectively retained in the uppermost layers of mineral soil sites. In peat soils, however, retention does not seem to be as effective. Even in the case of 8 t of limestone, only about 50% of the calcium was present in the uppermost 10-cm-thick layer after 30 years.

The amounts of magnesium on the control plots at Muhos and Vilppula were similar, but there were differences as regards the effect of different limestone doses

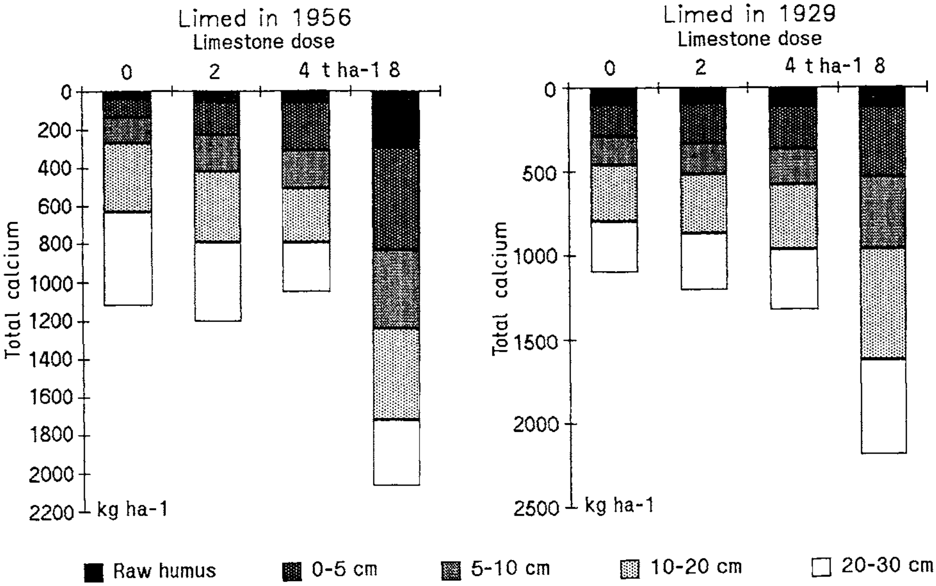

Fig. 6. Total calcium (kg ha^{-1}) at different depths on the plots limed in 1956 and 1929

(Fig. 7). The increases in the amount of magnesium due to liming in the 30-cm-thick soil profile on the plots limed 30 years ago were ca. 50, 100 and 250 kg ha^{-1} with limestone applications of 2, 4 and 8 t ha^{-1} respectively. Assuming that the magnesium content of the dolomitic limestone was 11%, then the corresponding Mg additions would have been equivalent to ca. 220, 440 and 880 kg ha^{-1}. This indicates that 70–80% of the added magnesium has been removed (Mg uptake and/or leaching) from the topmost 30-cm-thick layer during the 30-year period. In the case of the 60-year-old liming experiments, elevated amounts of magnesium were found only on the plots given the highest dose of limestone. The vertical distribution of magnesium down the soil profile shows that magnesium has been leached to a greater extent than calcium during the 30-year period.

Greater leaching of magnesium compared to calcium has also been documented in Swedish experiments (Hallbäcken and Popović 1985), especially in areas of high acid deposition. In organic soils, however, the stronger retention of calcium compared to that of magnesium may be explained by the higher affinity of calcium for exchange sites in the organic exchange complex (e.g. Jungk 1964). Calcium and magnesium are mainly responsible for the available base pool in peat (Starr and Westman 1978). Available Ca and Mg can be reliably estimated from total values using the high correlation between total and available concentrations of these elements. The results for the amounts of available Ca and Mg show that the reserves of available bases (Ca and Mg) in the 30-cm-thick peat layer are similar on the control and limed plots, apart from those given 8 t ha^{-1} (Table 5).

If we assume that the dolomitic limestone used in both experiments has the same Ca and Mg content, then nearly all of the bases added in applications of

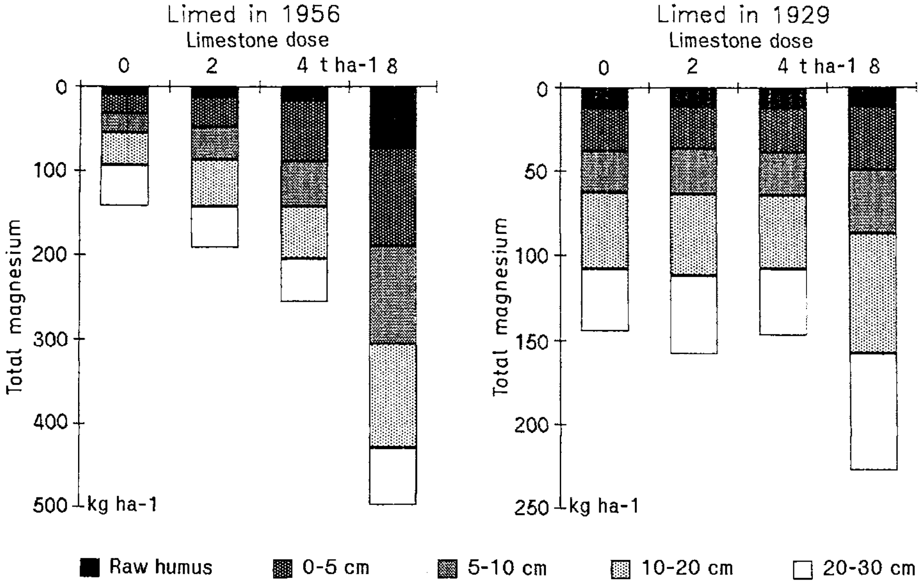

Fig. 7. Total magnesium (kg ha^{-1}) at different depths on the plots limed in 1956 and 1929

Table 5. Amount of bases (keq ha^{-1}) in the uppermost 30 cm-thick peat layer of the plots limed in 1956 and 1929, and the amount of bases added as dolomitic limestone

	Limestone dose t ha^{-1} 0	2	4	8
	Amount of bases keq ha^{-1}			
Muhos (−56)	43	49	48	126
Vilppula (−29)	42	46	49	81
Bases added	–	43	86	172

2 t ha^{-1} and 4 t ha^{-1} limestone have been leached out from the profiles during the 60-year period. The results for the plots given the largest doses of limestone support this conclusion because the plots at Muhos lost 46 keq bases ha^{-1} during 30 years, and at Vilppula 91 keq bases ha^{-1} during 60 years. The only anomaly in the material are the plots at Muhos given 4 t ha^{-1}, which had less Ca in the peat than those given 2 t ha^{-1} or the control plots. The assumption is made in these calculations that Ca and Mg uptake by the vegetation has been of the same order of magnitude in both experiments. However, the values presented above demonstrate that the effect of adding 2 t dolomitic limestone ha^{-1} lasts for about 30 years in a 30-cm-thick layer of a typical pine mire. The loss of bases in both the 60 and 30-year-old experiments was ca. 1.5 keq ha^{-1} a^{-1}, which is rather low compared to that reported in Sweden, 1–8 keq Ca ha^{-1} a^{-1} for mineral soils (Hallbäcken and Popović 1985).

pH and Base Saturation

The effects of liming on pH and base saturation were still visible after 60 years even at the lowest limestone dose, 2 t ha^{-1}, (Tables 6 and 7). The vertical distribution of the increase in pH and base saturation followed that of calcium in the peat profiles. Base saturation on the plots given the largest limestone dose (8 t ha^{-1}) was double after 60 years in the 0- to 30-cm-thick layer, and was three times higher after 30 years in the raw humus and 0- to 10-cm-thick layer compared to the control plots. The neutralizing effect of limestone on the peat was thus rather strong compared to that in cultivated sedge peat soil where limestone was added at doses of 0–6 t ha^{-1} (Kaila and Ryti 1968). In their experiments the pH increase in the uppermost 18-cm-thick layer 38 years after application was 0.1 units at 2 t $CaCO_3$ ha^{-1}, 0.4 units at 4 t $CaCO_3$ ha^{-1} and 0.6 units at 6 t $CaCO_3$ ha^{-1}. The increases in base saturation were 3%, 13% and 18% respectively.

Nitrogen and Phosphorus

Estimates of the effect of liming on total nitrogen, phosphorus and the C/N ratio are not directly comparable in the Vilppula and Muhos experiments because

Table 6. pH(H_2O) at different depths on the plots limed in 1956 and 1929

Depth	Experiment	Limestone dose t ha^{-1} 0	2	4	8
		pH(H_2O)			
Raw humus	Muhos (−56)	3.98	4.13	4.30	5.06
	Vilppula (−29)	3.96	3.93	4.02	4.11
0–5 cm	Muhos	3.93	4.10	4.26	4.98
	Vilppula	3.49	3.79	3.78	3.87
5–10	Muhos	4.03	4.21	4.23	4.99
	Vilppula	3.44	3.63	3.56	3.90
10–20	Muhos	4.27	4.34	4.26	4.64
	Vilppula	3.39	3.54	3.52	3.91
20–30	Muhos	4.66	4.62	4.26	4.56
	Vilppula	3.49	3.52	3.60	3.97

Table 7. Base saturation (BS) at different depths on the plots limed in 1956 and 1929

Depth	Experiment	Limestone dose t ha^{-1} 0	2	4	8
		BS%			
Raw humus	Muhos (−56)	15	20	23	45
	Vilppula (−29)	21	25	25	32
0–5 cm	Muhos	13	19	22	42
	Vilppula	15	21	18	29
5–10	Muhos	10	14	16	29
	Vilppula	11	15	14	25
10–20	Muhos	10	12	11	16
	Vilppula	10	11	13	22
20–30	Muhos	16	15	8	13
	Vilppula	9	11	12	20

nitrogen and phosphorus fertilizations were carried out in 1955–56 and 1973 in Muhos. However, the limed plots in Muhos received the same amounts of fertilizer P and N, and are thus comparable with each other. The original total nitrogen and phosphorus contents of the peat were much higher in Muhos than in Vilppula. This might also have had an effect on the nitrogen and phosphorus status of the limed peat.

There were no clear effects of liming on either the N content or the C/N ratio of the plots limed 60 years ago (Fig. 8, Table 8). In contrast, there was a clear increase in the total nitrogen content and decrease in the C/N ratio on the plots limed 30 years ago. The phosphorus results were similar; there were only small differ-

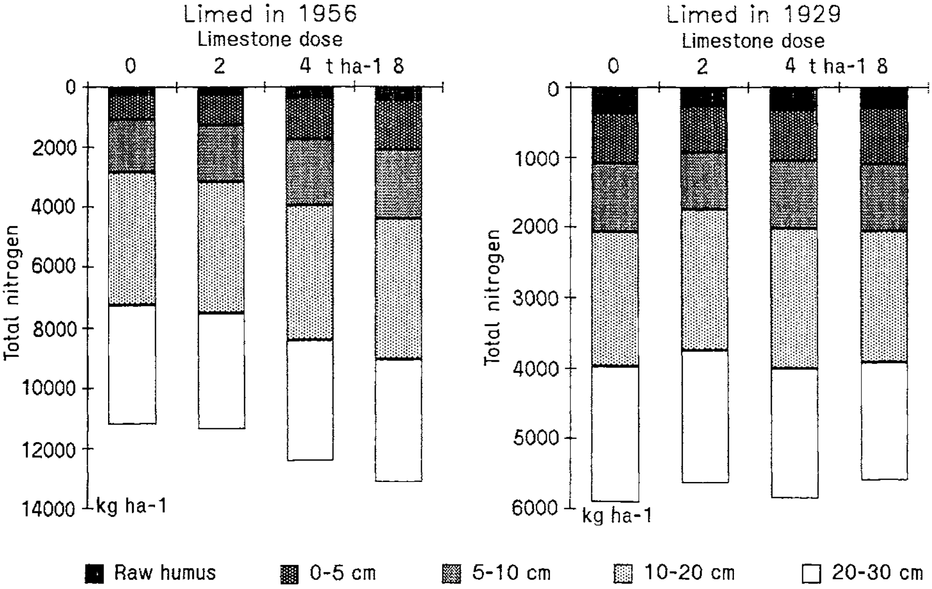

Fig. 8. Total nitrogen (kg ha^{-1}) at different depths on the plots limed in 1956 and 1929

Table 8. C/N-ratio at different depths on the plots limed in 1956 and 1929

Depth	Experiment	Limestone dose t ha^{-1} 0	2	4	8
		C/N-ratio			
Raw humus	Muhos (−56)	35	33	29	30
	Vilppula (−29)	40	43	39	37
0–5 cm	Muhos	32	28	26	24
	Vilppula	40	39	38	37
5–10	Muhos	25	25	24	23
	Vilppula	36	38	35	36
10–20	Muhos	24	26	27	25
	Vilppula	40	37	37	39
20–30	Muhos	25	27	28	26
	Vilppula	40	39	41	40

ences in the P content of the peat between the plots treated with limestone 60 years ago, but there was a clear increase in total P on the plots limed 30 years ago (Fig. 9).

The results concerning the nitrogen and phosphorus status at the Muhos experiment limed 30 years ago are not easily interpreted in the light of older liming experiments carried out on peat soils in Finland. In earlier experiments, mostly

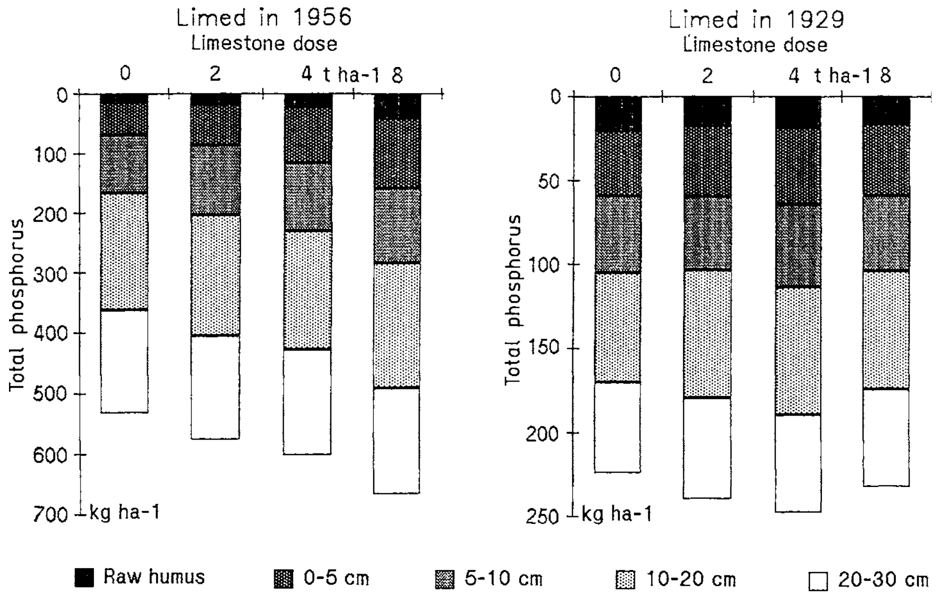

Fig. 9. Total phosphorus (kg ha^{-1}) at different depths on the plots limed in 1956 and 1929

carried out on cultivated peat soils, liming has not increased the total nitrogen content of the peat although nitrification has slightly increased with the largest doses of limestone (Kaila and Ryti 1968; Kaila et al. 1954). Neither has the C/N ratio decreased; on the contrary, there has been a clear increase in the C/N ratio of the limed sedge peat samples (Lakanen and Vuorinen 1963).

Mineralization of organic phosphorus does not seem to have significantly increased as a result of liming according to these older experiments (Kaila 1965). One possible reason for this could be the effective immobilization of phosphorus with iron or aluminium at elevated pH levels of cultivated peat soils (Lakanen and Vuorinen 1963).

Conclusions

The accumulation of organic matter in the humus layer of mineral soil sites is presumably of benefit on the least productive sites from the point of view of the quality of runoff water. Organic matter accumulation is probably caused by increased litterfall from the ground vegetation. As reported earlier (Derome et al. 1986), spruce stands especially suffer from a growth decline following liming, either because their shallow root systems are unable to compete with the ground vegetation for the mobilized nutrients, or because their mycorrhizal associations are disturbed by the higher pH conditions. Pine, which grows on the dry, infertile sites where liming is most likely to be used first, is relatively unaffected. Nowadays the main reason why limestone would be applied in forest ecosystems is to alleviate or prevent accelerating soil acidification caused by acidic deposition. In this respect the results obtained here on mineral soils and peatlands are rather promising. The effects of liming on the chemical properties of the soil included a long-term reduction in acidity of the surface soil, considerably elevated base saturation values down to a depth of at least 20 cm, considerably reduced extractable Al levels, and the immobilization of sulphate in the humus layer. The less desirable effects of liming included immobilization of phosphorus, and subsequent deterioration in phosphate availability in peat soil. To this must be added the possibility of immobilization of certain other essential nutrients (e.g. B, Mn, Cu, Zn). If liming is to be adopted in the near future as a means of controlling accelerating soil acidification, then some of the adverse effects could be partly avoided by mixing it into the surface soil during reforestation of mineral soils.

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Neutralization of Acidified Watercourses

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Summary

In this study particular attention has been paid to the solving of neutralization problems in Finnish lakes with two special characteristics: the typically high humus content, and the 4–6 months for which the watercourses are covered by ice. The effect of organic content on the specific neutralization demand was studied by means of laboratory experiments. The specific neutralization demand increases with increasing organic content. Laboratory tests were also carried out to compare three different liming methods, the results then being applied to the neutralization of three small lakes. Liming of the lake ice proved to be almost as efficient a method as wet application, and distinctly better than dry application. Cost assessments were also made to compare the different liming methods. Finnish neutralization practice and lake liming projects have also briefly been described.

Introduction

Acidification of sensitive watercourses in Finland is mainly caused in by airborne pollutants and to some extent by intensive draining of sulphate-rich soils. Airborne acidification has affected small headwater lakes and streams throughout the country (Kenttämies and Kämäri 1986), while the latter problem is restricted to the coastal areas of western Finland (Alasaarela 1982).

Today international measures to reduce the emissions of acidifying substances to an acceptable level are considered the only way to a final solution of the problem. As acceptable emission levels will take decades to achieve, other possibilities for reducing harmful effects of acidification on water ecosystems must also be considered. For this purpose neutralization is the only practical countermeasure today. The main purpose of all water neutralization projects is to restore and maintain the normal functioning of the threatened ecosystem until the acidifying deposition has been sufficiently reduced.

Liming experiments have been carried out over the last 10 years in Finland. Finnish research and operations have mostly been based on Swedish and Norwegian liming experiences, but particular attention is now being paid to the special characteristics of Finnish lakes and streams, such as the high humus content

Kauppi et al. (Eds).
Acidification in Finland

typical of Finnish inland waters, and the 4–6 months for which the watercourses are covered by ice in the winter.

Most Finnish watercourses have a high organic matter content, and their average colour value 91 Pt mg/l (Laaksonen 1970) ranks high on a global scale. The dissolved organic matter in this organically coloured water consists mainly of humic substances (HS) (Thurman 1985). HS possess the properties of weak acids, and average pH values in natural humic waters are generally lower than in clear waters. Although some small humic ponds and lakes in Finland have been limed for many years to improve the conditions for fish, the general opinion is that naturally acidic humic waters should not be neutralized.

The environmental impacts of neutralization in humic waters, and the planning the liming of such bodies of water are not fully understood. Humic lakes require higher lime doses than clearwater lakes (Sverdrup 1985). Colour and organic matter levels increase in some limed humic waters (Berzins 1960; Broberg 1978; Hasselrot and Hultberg 1984; Wright 1985), probably due mainly to the dissolving of HS from sediments as a consequence of increased decomposition of organic matter, and to the increase in the colour values of HS with decreasing acidity. On the other hand, losses of organic matter and colour (increase in transparency) from the water column have been reported in some lakes following liming with high doses of $CaCO_3$ (Broberg 1978; Swedish National Board of Fisheries 1981; Driscoll et al. 1982), and these have been attributed to flocculation and precipitation of HS caused by calcium complexation and the increased decomposition of HS. Losses of iron from the epilimnion, probably via co-precipitation with HS, have similarly been reported (Hoell et al. 1984). The changes in the organic content and in the nature of the humic substances probably depend on the neutralization dose applied and the special characteristics of humic substances in different drainage basins. Further research will be necessary to achieve cost-effective and ecologically safe neutralization of humic waters.

A second special consideration in Finland, as noted above, is the long winter, during which lime can be spread on the ice. This possibility inevitably creates a need for research into the efficiency and economy of this method in comparison to liming of open water, as mainly practised in other countries.

The purpose of the present work was to study neutralization problems in Finnish lakes, paying particular attention to the two special characteristics discussed. The project included two subprojects: (1) Neutralization of acid humic water and (2) Neutralization in winter. Their results have been presented. Finnish neutralization practice and lake liming projects have also briefly been described.

Neutralization Practice in Finland

Some 100 watercourses have been limed in Finland to date. Most neutralization operations have been managed privately, and government support has been restricted to research projects. Some financial support for neutralization has recently been introduced regionally (e.g. in the cities of Tampere and Vaasa).

Mostly fishponds and small headwater lakes (Table 1) have been limed in Finland, but a few streams have also been treated. Watercourses with variable hydrological and hydrographic features have been neutralized, and both clear water ecosystems and extremely humic waters have been included, as well as lakes with varying retention times.

With a few exceptions, finely ground calcitic or dolomitic limestone has been used as the major liming agent. In some projects technical lime products such as burnt lime (calcium oxide) have been used to neutralize highly acidic water draining from acid sulphate soils.

Neutralization has mostly been carried out in winter, when the ice on the lakes is normally strong enough to carry agricultural limespreaders. The mean maximum thickness of the lake ice in Finland is 0.5–0.8 m (Laasanen 1982). Agricultural equipment can be used for lake neutralization without modification in most winters more or less throughout the country. The method has given good results at fairly low cost.

The majority of the limestone powder distributed during the open water period has been spread pneumatically several hundred metres from the container truck using compressed air and suitable hoses. Lake liming from special boats, which are able to spread a lime-water mixture, has not so far been used in Finland. A few small headwater lakes and wetland areas have been limed from a helicopter, a method which, although rather expensive and requiring special equipment, has proved to be the best way of reaching targets located in difficult terrain. The method will become more common as strategies become directed more towards liming watersheds. Screw dosers for continuous dosing with lime are used in most stream liming projects.

HAPRO Subprojects

Neutralization of Acid Humic Waters

In this HAPRO subproject (1) the effect of organic content on the specific neutralization demand in acid lake waters, and (2) changes in the concentration and nature of humus (dissolved organic carbon, DOC) in the water after liming were examined.

Materials and Methods

Samples were taken in summer and autumn 1987 (July 22–November 5) from 58 small lakes located in southern, central and eastern Finland. Most of the sites were also included in the sampling programme for the HAPRO subproject National inventory of lake acidification. The samples with the highest organic content were chosen for the evaluation of changes in the concentration and nature of dissolved organic carbon.

Table 1. Characteristics of Finnish lake liming projects

	Lake Terva-järvi	Lake Iso Nuoluan-järvi	Lake Matala-järvi	Lake Hauki-järvi	Lake Saari-järvi	Lake Havise-van-järvi	Lake Kallio-järvi	Lake Valki-järvi	Lake Syvä-järvi	Lake Suur-lampi	Lake Ahven-järvi
Lake surface (ha)	8	82	72	11	10	39	12	5.7	26.8	4.9	11.7
Lake volume (10^6 m^3)	0.056	0.601	2.50	0.625	0.167	2.35	1.03	0.280	1.07	0.290	0.450
Av. residence time (a)	0.1	1.1	1.6	0.6	1.0	0.7	6.8	3.1	3.5	1.3	1.6
Type of water[a]	h	h	sh	h	c	h	c	sh	c	c	h
Time of liming (m/a)[b]	3/75	4/79	3/83	4/85	4/85	5/86	4/87	8/88	4/87	6/87	8/87
Liming agent[c]	DLP	DLP	CLP	CLP	CLP	CLP	CLP	CLP	CLP	CLP	CLS
Application dose (g m^{-3})	1000	21.6	24	30.4	65.9	12.8	24.7	39.6	22	21	12.1
Total lime amount (t)	56	13	60	19	11	32	25.3	11.1	23.4	6.1	5.5
Distribution method	icesp.[f]	icesp.	icesp.	icesp.	icesp.	doser[e]	icesp.	pneum.[g]	icesp.	pneum.	boat
Water quality											
pH before liming[d]	5.2	5.2	4.8	4.7	4.9	5.1	5.2	5.3	5.3	5.5	5.1
pH after liming[e]	7.5	5.9	6.5	6.0	6.9	6.3	6.8	6.8	6.8	7.1	6.8
duration until pH 5.5 (a)	10	5	3	1	2						

[a] c = clear, sh = semihumic, h = humic. [b] Month/year. [c] DLP = dolomitic limestone powder, CLP = calcitic limestone powder, CLS = calcitic limestone slurry. [d] Value at first turnover after liming. [e] Continuous liming of incoming water, [f] Spreading on ice, [g] Spreading pneumatically.

Chemical analyses included dissolved (DOC) and particulate organic carbon (POC), chemical oxygen demand (COD_{Mn}), pH, conductivity, alkalinity, calcium, total iron and colour. Specific neutralization demand (dN/dpH) was assessed potentiometrically by titration with 0.005 M Na_2CO_3 (Hindar 1985). The neutralization chemical used was fine grade 99% $CaCO_3$ powder. The samples were neutralized approximately to pH 6.50, as in most liming projects. The concentration and nature of the organic matter was evaluated before and 5 days after lime addition. The corresponding changes were also monitored in reference samples. The precipitation of organic matter was studied by filtering initial and limed water samples and the reference samples through Whatman GF/F glass fibre filters. The nature of the dissolved organic carbon was assessed by ultrafiltration with an Amicon Diaflo membrane PM10, with a quoted molecular weight cut-off of 10000.

Results

All the water samples, which differed in their organic content (Fig. 1), were acid and poorly buffered (Table 2). The colour values of the filtrates ranged from 5 to 590 Pt mg l^{-1} and TOC from 2.7 to 24.4 mg l^{-1}.

DOC accounted for an average of 93% of TOC. Iron in the filtrates accounted for an average of 84% of total iron, and was probably complexed with humic substances in these oxic water samples (see Shapiro 1964; Ghassemi and Christman 1968). The DOC and iron in the apparent molecular weight fraction $> 10{,}000$ accounted for 34–59% and 47–79% of the corresponding concentrations in the initial water samples.

The specific neutralization demand increases with increasing organic content (Fig. 1). It is over twofold in the humic lake waters (colour 200–350 Pt mg l^{-1}) as compared to the clear lake waters (colour 5–20 Pt mg l^{-1}). The effect of the iron is not significant as compared with that of the organic matter. This may be due mainly to the complexation of iron with humic substances.

There was a small increase ($< 10\%$) in colour values in the limed samples, and also in the colour values of the apparent molecular weight fraction $> 10{,}000$. The

Table 2. Average water quality in the samples studied for specific neutralization demand (n = 58)

	x	S	Min	Max
pH	4.9	0.4	4.2	5.8
Alkalinity mmol l^{-1}	0.03	0.02	0	0.12
Conductivity mS m^{-1}	2.8	1.2	0.8	9.1
Ca mg l^{-1}	1.9	1.5	0.3	10.2
Colour Pt mg l^{-1}	230	160	5	590
TOC mg l^{-1}	13.2	6.3	2.7	24.4
COD_{Mn} mg l^{-1}	17.6	12.0	0.3	41.2
tot. Fe µg l^{-1}	480	370	20	1290

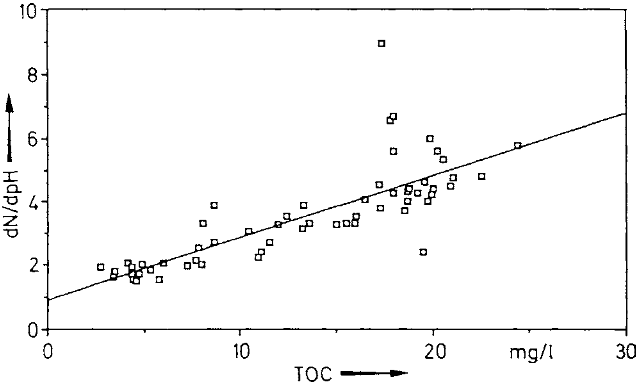

Fig. 1. Organic carbon concentration (TOC) and specific neutralization demand (dN/dpH) in acidified Finnish lakes

precipitation of DOC and iron due to liming during the 5-day period was not substantial, always under 7% of the initial DOC and iron concentrations. Liming slightly increased the proportions of DOC (<7%) and iron (<10%) in the apparent molecular weight fraction >10,000 in most samples, which may indicate further precipitation, because the flocculation and precipitation of these substances may be slow.

Neutralization in Winter

Laboratory tests were carried out to compare the solubility of three types of Finnish limestone products of different grain size when used with different liming methods, the results then being applied to the neutralization of three small lakes. Cost assessments were also made to compare the different methods.

Materials and Methods

The tests were carried out in the Tampere District Office of the National Board of Waters and the Environment in 1986. The efficiency of neutralization was studied using four plastic tanks of depth 3.00 m and diameter 0.2 m. These were filled with water from Lake Musta-Tokamojärvi, which corresponds in quality (pH 4.8, acidity 0.21 mmol l^{-1}, colour 120 Pt mg l^{-1}) fairly well with that of the lakes selected for the liming trials in the field (see Table 3). The three Finnish limestone products of different grain size used in the tests were 2H/Vampula, Finncarb 90101 and Parfill P8. The limestone doses tested employing both a wet and a dry method were calculated as recommended by Sverdrup et al. (1985). Attempts were made to take account of the practical procedures involved in liming in the field when spreading the limestone powders. The dry method comprised direct scattering of the powder on the surface of the water in an even manner, while in the wet method the powder was mixed mechanically with water before application. Application to an ice surface was tested by freezing small quantities (approx. 0.0015 m^3) of the lake water in plastic dishes of the same diameter as the tanks and sprinkling the powder on this surface. The ice was then allowed to melt sufficiently to moisten the powder, after which it was frozen again. This melting and freezing routine was repeated twice more before the block of ice, still containing its powdered limestone, was placed in a tank of water and allowed to melt entirely. The efficiency of the liming was monitored by measuring pH, alkalinity and calcium content. Two lakes, Lake Kalliojärvi and Lake Rukojärvi (Table 3) were limed in winter 1987 via the ice calculating lime doses by the wet method (Sverdrup et al. 1984). The lime was spread on the ice with agricultural lime spreaders.

Lake Valkijärvi (Table 3) was limed in summer 1988 by the dry method, pumping the powdered limestone about 300 m out into the lake by means of a compressor fitted to the tanker lorry. The 2H/Vampula grade of powdered limestone was used throughout. Target pH values were 6.8 in Lake Kalliojärvi and Lake Rukojärvi and 7.0 in Lake Valkijärvi. Restrictions imposed by the dosage equipment meant that somewhat larger amounts of powder had to be used than were prescribed in the calculations. The costs attached to the various techniques were also assessed.

Efficiency and Costs of Neutralization

Liming of the lake ice proved to be almost as efficient a method as wet application, and distinctly better than dry application. The mean amounts of powder required to achieve the desired change in pH in the experimental tanks employing the wet method, ice surface method and dry method respectively were in the ratio 1:1.1:2.1.

According to these experiments (Table 3), Sverdrup's model is sufficiently accurate for practical liming purposes, in spite of the slight "overdosing" of limestone.

The costs entailed in the liming of lakes comprise material costs, transport, spreading costs and the costs of various preparatory stages, e.g. clearing of the snow from the surface of the ice.

Transport accounts for a significant proportion of the total costs, the sum represented per tonne of limestone distributed being dependent both on the distance over which it has to be transported and on the amount of limestone to be spread. These costs become lower as the amount of limestone used approaches the maximum single load. Thus where small lakes are concerned, this item can become as expensive as the material itself.

The liming operations carried out suggest that, at least where small lakes of 10–100 ha are concerned, the choice of the most economical approach will depend primarily on the bearing capacity of the local roads and their location in relation to the lake. If there is a road suitable for heavy vehicles, dry application in summer will usually be most economical. If the only suitable road is some distance away

Table 3. Calculated and actual doses of powdered limestone and effects of liming on the pH of the lake water.

	Lake Kalliojärvi[a]	Lake Rukojärvi[a]	Lake Valkijärvi[b]
Initial pH value	5.3	4.9	5.3
Acidity, mmol l^{-1}	0.12	0.30	0.10
Colour, Pt mg l^{-1}	20	160	35
Calculated dosage, t	22.9	21.8	10.6
Actual dosage, t	25	26	11
Target pH value	6.8	6.8	7.0
pH after breakup of ice	7.0	6.7	
pH 2 weeks after liming			7.0

[a] Liming of lake ice, May 31 1987.
[b] Dry application August 11 1988

from the lake, however, the natural and most economical method will be spreading lime on the surface of the ice in winter.

Conclusions

The specific neutralization demand increases with increasing organic content. It is over twofold in the humic lake waters (colour 200–350 Pt mg l^{-1}) as compared with the clear lake waters (colour 5–20 Pt mg l^{-1}). The limed humic lake waters showed small increases in colour values. DOC and iron were also slightly precipitated, and there was a slight increase in the proportions of DOC and iron in the largest apparent molecular weight fraction of dissolved organic matter. Further research will be necessary to achieve cost-effective and ecologically safe neutralization of humic waters.

Liming of the lake ice proved to be almost as efficient a method as wet application, and distinctly better than dry application. The mean amounts of limestone powder required to achieve the desired change in pH in the experimental tanks employing the wet method, ice surface method and dry method respectively were in the ratio 1:1.1:2.1.

The choice of the most economical liming approach will depend primarily on the bearing capacity of the local roads and their location in relation to the lake. If there is a road suitable for heavy vehicles, dry application in summer will usually be most economical. In other cases the most economical method will be spreading on the surface of the ice in winter.

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Liming of the Acidic Lake Valkealampi in Eastern Finland: Effects on Water Chemistry and Phytoplankton

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Summary

Lake Valkealampi, an acidic lake in eastern Finland, was limed with $CaCO_3$ in July 1983. Prior to liming, its water was clear and acidic (median pH 4.91) with no alkalinity and low levels of Ca, P_{tot} and chlorophyll a. pH, alkalinity and Ca increased most markedly after liming. COD_{Mn}, colour, γ_{25}, SO_4, N_{tot} and P_{tot} in the surface water were also significantly greater after liming, whereas Al_{tot} in the whole water body remained constant. Liming was followed by a decrease in the abundance of Peridinae and an increase in chlorophycean and chrysophycean species. This change persisted for at least 4 years. The number of phytoplankton taxa increased from 5 to 17 in the third year after liming. The trophic status of the lake in terms of chlorophyll a levels, became mesotrophic for 2 years after liming, and although the chlorophyll a level subsequently seemed to diminish, the lake had not yet reached its pre-treatment state after 5.5 years.

Introduction

A number of techniques for neutralizing acidic lakes (most frequently liming) have been developed to protect water resources from the impact of acid deposition. The national liming policies in Scandinavia have been presented by Hindar and Rosseland (1988) for Norway and Nyberg and Thørneløf (1988) for Sweden. Only a small number of lakes in Finland have been neutralized so far (Heikkinen and Alasaarela 1988), and no official national policy exists for the liming of surface waters.

The aim of this work was to examine the effect of liming on water quality and phytoplankton in an acidic clearwater lake, Lake Valkealampi, in Eastern Finland. The lake belongs to the network of small, oligotrophic lakes sensitive to acidification monitored regularly by the National Board of Waters and the Environment. Lake Valkealampi is situated in the acidic Karelian schist area consisting of mica schist, partly phyllite (Geological Map of Finland 1:100,000 Pre-quaternary Rocks 1967). Palaeolimnological evidence suggests that Lake Valkealampi has been acidic for a long time (Simola 1986).

Kauppi et al. (Eds).
Acidification in Finland

Study Area and Treatment

Lake Valkealampi (62° 17′N, 30° 23′E) is located in the Jänisjoki river basin in North Karelia, Eastern Finland. It is a seepage lake with no inlet or outlet, and is dimictic, small and shallow ($A = 9.8$ ha, $\bar{z} = 3.8$ m, $z_{max} = 6.5$ m, $V = 300\,700$ m^3). The lake is situated at 94 m a.s.l. on the Salpausselkä ridge, with a drainage area of 229 ha, of which 84.7% is mineral soil, 10.0 % peatland and 5.3 % lakes (Fig 1.). The area has quite a cold, snowy forest climate, moist all the year round, with a cool, short summer (in the Köppen classification). The snow depth reaches its maximum in early March, when it is approximately 60–70 cm (Heikkilä and Koivukangas 1979). The average length of the growing season is 155 d, from 2nd June to 4th October. The average monthly temperature ranged from −23.6°C in January to +18.8°C in July during the period studied here, the long-term means (1931–1960) being from −10.5°C to +16.1°C, respectively. Annual mean temperatures during the years 1983–1988 in Tohmajärvi, about 10 km south of the lake, varied from 0.1°C to 3.4°C, and annual precipitation from 619 mm to 755 mm (Monthly Meteorological Report for Finland 1983–1988).

The lake bottom is covered by a thick mat of the moss *Drepanocladus fluitans* (L.) Warnst. down to a depth of 5.5 m. The vegetation of the catchment area consists mainly of coniferous forest (dominated by *Pinus silvestris*) and there is an ombrotrophic bog on the southwest shore of the lake. Human influence on the lake consists of three summer cottages, a public swimming beach, and a country road

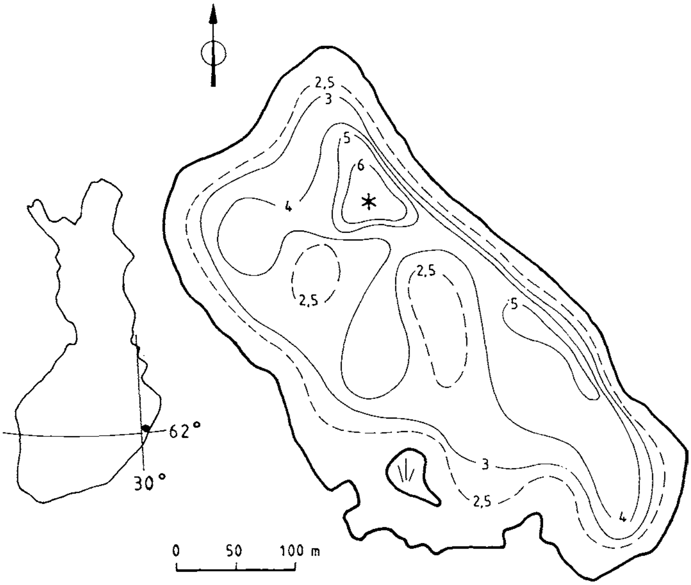

Fig. 1. Location and bathymetric map of Lake Valkealampi. *indicates the sampling station

Table 1. Annual mean temperature and precipitation in 1983–1988 and the long-term means (1931–1960) at Tohmajärvi, North Karelia (Monthly Meteorological Report for Finland 1983–1988)

Year	Mean temperature °C	Annual precipitation mm a^{-1}
1931–1960	2.2	612
1983	3.1	738
1984	3.4	619
1985	0.3	755
1986	2.0	650
1987	0.1	749
1988	2.8	717

near the southern shore. Slash-and-burn cultivation was probably practiced around it during the 19th century (Simola 1986).

Perch (*Perca fluviatilis* L.) were recorded in Lake Valkealampi up until the 1950's, but had disappeared by the mid-1970's (Simola 1986). On 13th July 1983, the land-owners treated the water of the lake with 10 tons of granulated calcium carbonate (33 g m^{-3}) distributed by helicopter (Hannu Kivivuori pers. commun.).

Materials and Methods

Water quality data were collected nine times from 1976 to June 1983 and 31 times after liming of the lake. The chemical analyses were carried out by the Water and the Environment District of North Karelia. Two post-liming periods were studied, the first 2.5 years from July 1983 to December 1985 and the whole 5.5-year period from July 1983 to December 1988. Differences between the pre-treatment and post-treatment water properties were tested using the t-test. All the data analyses reported were completed using the SAS programme package (SAS 1984a,b). Differences were regarded as significant if $P \leq 0.05$.

All the water samples were taken with a Ruttner-type sampler from the deepest part of Lake Valkealampi (Fig. 1), at depths of 1 m (= surface water), 3 m, and 1 m above the bottom (= hypolimnion). A sample from a depth of 0–2 m was collected during the summer for chlorophyll a analysis. The sampling and water quality analyses were performed according to the standard methods used by the National Board of Water and the Environment (National Board of Waters 1981, 1984), all the analyses being performed under laboratory conditions using non-filtered samples. Calcium (Ca) and total aluminium (Al_{tot}) analyses were carried out at the Research Laboratory of the National Board of Water and the Environment, Helsinki. Al_{tot} was determined by a spectrophotometric method based on reaction with pyrocatechol until 1983, and by graphite furnace atomic absorbtion spectrophotometry (GFAAS) in 1983–1988. Alkalinity was titrated potentiometrically to pH values of 4.5 and 4.2 with HCl.

Phytoplankton samples were taken once a year in July in 1979 and 1983–1987 (in August 1987). This period of maximum water temperatures and minimum surface inflows (the lake has no inlet stream) represents the stable summer stagnation period. All the samples were collected from depths of 0–2 m (combined sample). Since the depth of the euphotic zone may reach 5 m, the sample represents only its upper part. The samples were preserved with Lugols solution in the field, and 2 ml of 37% formaldehyde was later added to each 100 ml to ensure the preservation. After sedimentation in 50 ml settling chambers, the phytoplankton species were identified and counted using inverted microscopy (Utermöhl 1958). The algal volumes were taken from Naulapää (1972).

Results

Water Chemistry

Before liming, Lake Valkealampi was an acidic clearwater lake (median pH 4.91) with mean transparency (Secchi depth) of 4.7 m and a mean colour value of 6 Pt mg l^{-1} (Table 2). The water had no buffering capacity. Conductivity (γ_{25}), chemical oxygen demand (COD_{Mn}), total nitrogen (N_{tot}), total phosphorus (P_{tot}) and Ca concentrations were all low. Al_{tot} concentrations varied from 30 to 110 µg l^{-1} in the surface water and from 20 to 130 µg l^{-1} in the hypolimnion (Fig. 2).

pH values in August 1983, after liming, were highest at depths of 3–4 m. The Secchi depth decreased from 4.0 m (in June) to 2.3 m in August 1983 and the colour value increased two-to-four-fold at the same time. The pH value at 1 m increased dramatically to 6.58 in 1 week after liming, and to 7.00 in 2 weeks (Fig. 3). After 3 weeks, on 9th August, pH reached its maximum, 7.30, at a depth of 3 m. pH reached its lowest value during the first post-treatment period, 6.29, in January 1984, and it was as high as 8.80 in July 1984. pH values in the hypolimnion ranged from 6.03 to 7.05 (Fig. 3). During the whole post-treatment period pH ranged from 5.00 to 8.80 in the surface water from 5.52 to 7.05 in the hypolimnion (Table 2).

Alkalinity in the hypolimnion reached its maximum, 0.14 mmol l^{-1}, in August 1983, 3 weeks after liming (Fig. 4). Alkalinity values remained at almost the same level in the whole water body until November 1983, but increased to 0.15–0.20 mmol l^{-1} at depths of 3–5 m in winter 1984. Ca reached its maximum values simultaneously (Figs. 4, 5). Conductivity increased with increasing Ca during the first post-treatment period (Table 2).

Alkalinity, pH, Ca, γ_{25}, COD_{Mn}, colour, N_{tot}, P_{tot} and sulphate (SO_4) were significantly greater in the post-liming samples, whereas Al_{tot}, oxygen (O_2), temperature, and iron (Fe) were similar in both the pre-treatment and the post-treatment samples (Table 2). Transparency, on the other hand, was significantly lower during the immediate post-treatment period than prior to neutralization. Changes of the same kind occurred in the hypolimnion as in the surface water,

Table 2a. Water characteristics of Lake Valkealampi (surface water)

	Before liming					After liming July 1983–Dec. 1985					After liming July 1983–Dec. 1988				
	$\bar{x}$	Min	Max	SD	n	$\bar{x}$	Min	Max	SD	n	$\bar{x}$	Min	Max	SD	n
Transparency m	4.7	3.0	6.0	1.0	9	3.7*	2.0	6.0	1.1	20	4.1	2.0	6.0	1.2	31
Alkalinity mmol l^{-1}	0.0	0.0	0.0	0.0	8	0.10*	0.04	0.14	0.04	17	0.07*	0.0	0.14	0.05	27
pH	4.91[a]	4.60	5.72	0.33	9	6.76[a]*	6.29	8.80	0.51	20	6.70[a]*	5.00	8.80	0.67	31
Colour Pt mg l^{-1}	6	2	10	2.7	9	11*	5.0	20	4.0	20	11*	5.0	20	4.0	30
γ_{25} ms m^{-1}	1.6	1.2	1.9	0.2	9	2.7*	2.0	3.3	0.4	20	2.4*	1.7	3.3	0.5	31
O_2 mg l^{-1}	9.9	8.3	11.4	1.2	9	10.0	8.3	12.4	1.3	19	10.3	8.2	13.8	1.6	30
$\mathrm{Al_{tot}}$ µg l^{-1}	48	30	110	27.8	8	43	15	95	19.0	16	49	15	110	21	26
Ca mg l^{-1}	0.68	0.0	1.6	0.5	8	2.9*	1.9	3.7	0.5	16	2.4*	1.5	3.7	0.7	25
$\mathrm{COD_{Mn}O_2}$ mg l^{-1}	2.0	1.3	2.8	0.0	9	3.2*	1.7	4.8	1.1	18	3.5*	1.7	4.8	1.0	29
$\mathrm{N_{tot}}$ µg l^{-1}	334	250	460	72	9	520*	360	871	136	18	470*	278	871	152	29
$\mathrm{P_{tot}}$ µg l^{-1}	8	4	12	2.4	9	11*	6	17	2.7	18	11*	6	35	5.2	29
Fe µg l^{-1}	80	10	200	55	9	87	11	410	89	18	72	11	410	72	29
$\mathrm{SO_4}$ mg l^{-1}	3.5	2.8	4.2	0.5	8	4.9*	4.0	6.1	0.5	17	4.9*	3.3	6.1	0.6	28
Chlorphyll a µg l^{-1}[b]	1.5	1.5	1.5	11	1	5.6	1.6	10.4	3.3	11	4.5	1.5	10.4	3.0	18

[a] Md. * $P \leq 0.05$ (t-test)

[b] 0–2 m.

Table 2b. Water characteristics of Lake Valkealampi (hypolimnion)

	Before liming					After liming July 1983–Dec. 1985					After liming July 1983–Dec. 1988				
	x̄	Min	Max	SD	n	x̄	Min	Max	SD	n	x̄	Min	Max	SD	n
Alkalinity mmol l^{-1}	0.02	0.00	0.16	0.06	8	0.11*	0.03	0.20	0.01	17	0.09*	0.00	0.20	0.06	27
pH	4.98^{a}	4.76	5.30	0.18	9	6.55^{a}*	6.03	7.05	0.32	20	6.22^{a}*	5.52	7.05	0.46	31
Colour Pt mg l^{-1}	7	0	15	4.5	9	14*	5	35	7.2	20	13*	5	35	6.5	31
γ_{25} ms m^{-1}	1.6	1.3	1.9	0.2	9	2.7*	1.9	3.7	0.5	20	2.5*	1.7	3.7	0.6	31
O_2 mg l^{-1}	9.3	1.5	13.3	3.4	9	7.6	1.3	12.2	3.3	19	7.4	0.0	12.2	3.7	30
Al_{tot} µg l^{-1}	54	20	130	34	8	41	20	70	15	16	48	20	100	18	25
Ca mg l^{-1}	0.6	0	1.6	0.5	8	3.0*	2.1	3.8	0.5	16	2.6*	1.5	3.8	0.7	25
$COD_{Mn}O_2$ mg l^{-1}	2.1	1.2	3.5	0.8	9	3.2*	1.6	6.1	1.2	18	3.5*	1.6	6.1	1.1	29
N_{tot} µg l^{-1}	349	260	540	102	9	624*	360	1640	296	18	546*	256	1640	270	29
P_{tot} µg l^{-1}	9	5	14	2.9	9	14*	7	27	5.7	18	13	6	27	5.4	29
Fe µg l^{-1}	126	22	490	147	9	143	24	422	135	18	140	23	452	132	29
SO_4 mg l^{-1}	3.5	3.0	3.8	0.3	8	4.4*	3.7	5.0	0.4	17	4.5*	3.5	6.7	0.6	27

^{a} Md. * $P \leq 0.05$ (t-test)

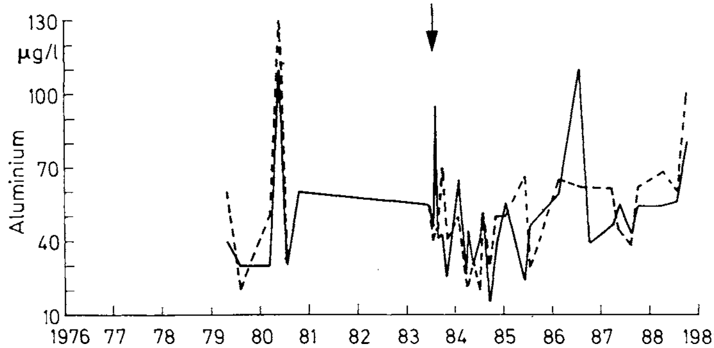

Fig. 2. Aluminium concentrations in the surface water and hypolimnion of Lake Valkealampi in 1976–1988. The *arrow* indicates liming on the 13th of July 1983. *Solid line* surface water (1 m); *dotted line* hypolimnion

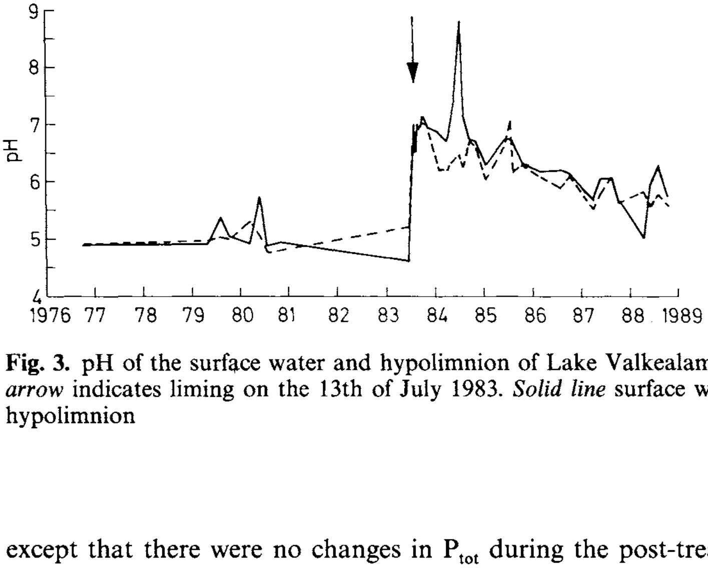

Fig. 3. pH of the surface water and hypolimnion of Lake Valkealampi in 1976–1988. The *arrow* indicates liming on the 13th of July 1983. *Solid line* surface water (1 m); *dotted line* hypolimnion

except that there were no changes in P_{tot} during the post-treatment period. The median pH value during the whole post-treatment period was 6.70, mean alkalinity 0.07 mmol l^{-1}, and mean Ca concentration 2.4 mg l^{-1} (Table 2).

Phytoplankton

Species Composition

The total number of phytoplankton taxa in Lake Valkealampi before liming was 5 (Table 3). The phytoplankton community was dominated by Peridiniales *Peridinium inconspicuum* and *Gymnodinium* sp., the only representative of the Chrysophyceae being *Dinobryon pediforme*, with a moderate abundance. The numbers of Cryptomonads (*Cryptomonas marssonii* and *Cryptomonas* sp.) were small (Table 3).

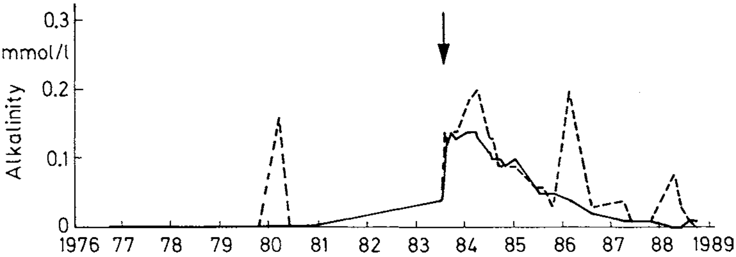

Fig. 4. Alkalinity of the surface water and hypolimnion of Lake Valkealampi in 1976–1988. The *arrow* indicates liming on the 13th of July 1983. *Solid line* surface water (1 m); *dotted line* hypolimnion

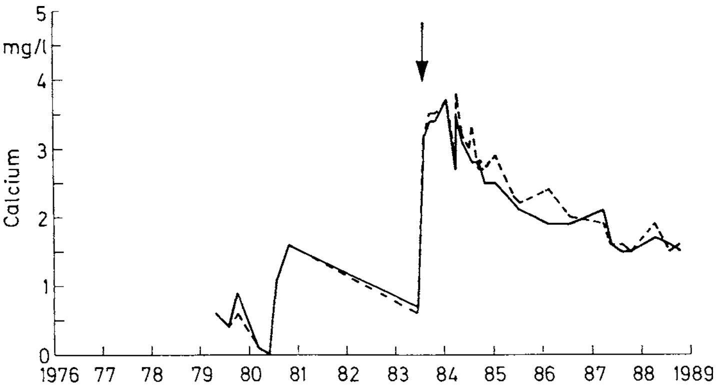

Fig. 5. Calcium concentrations in the surface water and hypolimnion of Lake Valkealampi in 1976–1988. The *arrow* indicates liming on the 13th of July 1983. *Solid line* surface water (1 m); *dotted line* hypolimnion

The number of phytoplankton taxa increased after liming, to 9 in 1983 and 17 in 1985 (Table 3). Numerically most abundant in 1983–1987 were the small chrysophyceans, dominated by *Chrysomonadinae* sp., *Chrysidiastrum catenatum, Dinobryon crenulatum, D. cylindricum, Uroglena americana* and Chlorococcales (*Oocystis* spp., *Monoraphidium dybowskii, Westella botryoides*). Some cyanophytes (*Anabaena flos-aquae* and *Gomphosphaeria lacustris*) were present in the samples in 1984 and 1985 and also desmidiales from 1984 onwards (Table 3). Peridineans made up only a small part of the community during this period.

Biomass

The biomass of the phytoplankton was low (range 0.3–1.7 g m^{-3} FW, Fig. 6), with its peak in 1979, before liming and decreasing slightly thereafter. The majority of phytoplankton biomass in 1979 consisted of a few large Peridineans, i.e. of a relatively small number of cells. After liming the phytoplankton community was dominated by small-sized species, the number of cells increasing up to tenfold

Table 3. Phytoplankton composition (percentage of total) in Lake Valkealampi in 1979 and 1983–1987

Taxa	30.7. 1979	27.7. 1983	30.7. 1984	15.7. 1985	28.7. 1986	13.8. 1987
Cyanophyceae						
Chroococcales						
Gomphosphaeria lacustris Chodat				+		
Nostocales						
Anabaena flos-aguae Brébisson			+	+		
Cryptophyceae						
Cryptomonadales						
Cryptomonas marssonii Skuja	+	+			1	
Cryptomonas spp.	+	1	+	3	16	1
Katablepharis ovalis Skuja			+	3	4	+
Rhodomonas lacustris Pascher & Ruttner			+	+	3	
Dinophyceae						
Peridiniales						
Gymnodinium spp.	10	+			+	+
Peridinium inconspicuum Lemmermann	86	+	+	1	+	+
Chrysophyceae						
Ochromonadales						
Chrysidiastrum catenatum Lauterborn					1	37
Chrysomonadinae sp.				21	27	14
Dinobryon crenulatum West & West					21	1
D. cylindricum Imhof						13
D. pediforme (Lemmermann) Steinecke	4	+				
D. suecicum Lemmermann					+	
Kephyrion boreale Skuja					9	
Mallomonas crassisquama (Asmund) Fott			+			
M. sp.				+		
Pseudokephyrion entzii (Conrad) Schmid					+	
Uroglena americana Calkin			95			

Table 3. (Continued)

Taxa	30.7. 1979	27.7. 1983	30.7. 1984	15.7. 1985	28.7. 1986	13.8. 1987
Diatomophyceae						
Bacillariales						
Tabellaria flocculosa (Roth) Kützing		+				
Synedra sp.			+			
Euglenophyceae						
Euglenales						
Trachelomonas hispida (Perty) Stein			+			
Chlorophyceae						
Volvocales						
Eudorina elegans Ehrenberg			+	4		
Gonium pectorale O.F. Müller				+		
Chlorococcales						
Oocystis lacustris Chodat				2		3
O. rhomboidea Fott		1			+	
O. submarina Lagerheim		1			+	
O. spp.	95					
Monoraphidium dybowskii (Woloszynska) Hindák & Komárková-Legenerová			3	+	15	1
Scenedesmus brasiliensis Bohlin				+		
S. ecornis (Ehrenberg) Chodat				+		
Westella botryoides (W. West) De Wildeman				62		20
Ulotrichales						
Elakatothrix gelatinosa Wille			+			7
Conjugatophyceae						
Desmidiales						
Spondylosium planum (Wolle) W. & G.S.West			+	2		
Staurodesmus incus (Brébisson) Teiling						+
Teilingia granulata (Roy & Bisset) Bourrelly			+	+		
Total number of taxa	5	9	14	17	15	13

Table 4. Phytoplankton, chlorophyll a, total nitrogen, total phosphorus, pH and transparency in Lake Valkealampi before and after liming

	30.7. 1979	27.7. 1983	30.7. 1984	15.7. 1985	28.7. 1986	13.8. 1987
Phytoplankton biomass mg m^{-3}	1717	400	679	362	291	617
Phytoplankton exx ml^{-1}	745	2293	7726	1082	658	1147
Chlorophyll a μg l^{-1}	..	1.6	10.4	..	1.5	4.3
pH	5.4	7.0	7.1	6.7	6.2	6.1
P_{tot} μg l^{-1}	10	9[a]	13	11	12	8
N_{tot} μg l^{-1}	320	360[a]	871	508	354	278
Transparency m	4.7	5.0	2.6	5.0	6.0	6.0

[a] 22.8.1983.

(Tables 3, 4). The majority of the biomass consisted of Chrysophyceae (Fig. 6), the biomass of which was greatest in 1984, 1 year after liming, and in 1987. The biomass of Chlorophyceae (Volvocales and Chlorococcales) increased later, in 1985. The biomass of cyanophytes was high (15 % of the total biomass, Fig. 6, Table 2a) at the time of the highest pH values, which coincided with the highest nutrient contents (Table 4), in the summer 1984. The biomass of the diatoms was low during the whole period.

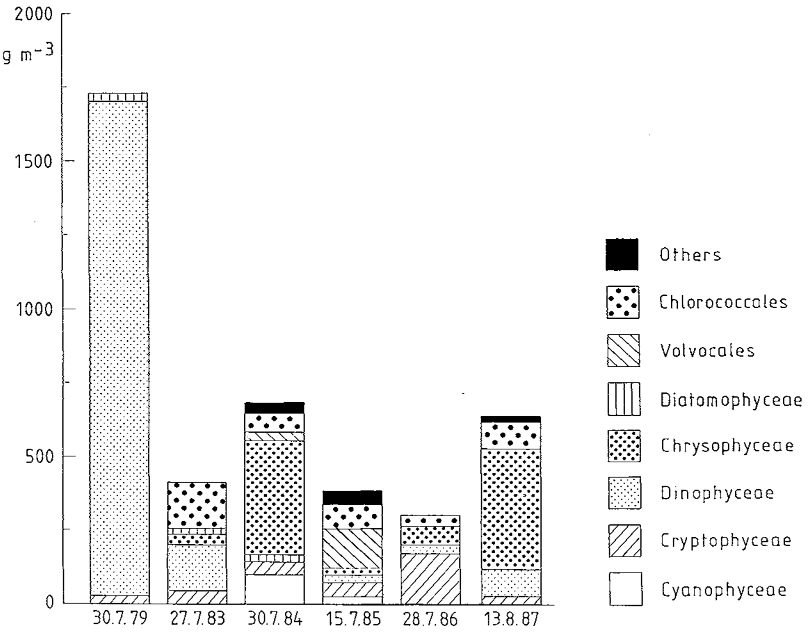

Fig. 6. Biomass and composition of phytoplankton in the surface water of Lake Valkealampi (0–2 m).

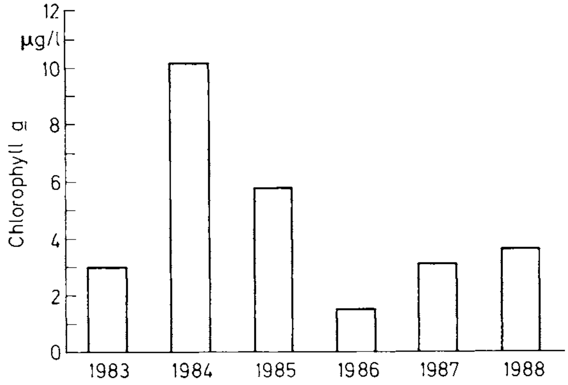

Fig. 7. Annual means for chlorophyll a concentration during the growing season in Lake Valkealampi at a depth of 0–2 m in 1983–1988

Chlorophyll a

In June 1983, and before liming, chlorophyll a was 1.5 μg l^{-1}. Within 1 week after liming, chlorophyll a increased to 6.2 μg l^{-1}. Two weeks after liming it returned to 1.6 μg l^{-1}. It increased in August and in September, varying between 2.2 μg l^{-1} – 4.3 μg l^{-1}. Mean chlorophyll a in 1983 was 3.0 μg l^{-1} (Fig. 7) and the maximum value, 10.4 μg l^{-1}, occurred in July 1984, about 1 year after liming. The level was still high in 1985, 2 years after liming but seemed to decrease in the summers of 1986–1988 (Fig. 7).

Discussion

Water Chemistry

Before liming, Lake Valkealampi was one of a group of pristine acidic clearwater lakes in Eastern Finland located on the acidic Karelian schist (Ilmavirta et al. 1984), where atmospheric deposition likely is not important.

The most dramatic effects of liming were, as expected, increases in pH, alkalinity and Ca values, as noted elsewhere (e.g. Dillon et al. 1979; Wright 1985; Broberg 1988; Marcus 1988).

Liming stimulates decomposition processes, and this may have reduced oxygen concentrations in the hypolimnion. This is a risk in lakes with a high organic matter content, while no such adverse effects have been reported in clearwater lakes (Wilander and Ahl 1972). There were no significant differences between the pre-treatment and post-treatment oxygen values in Lake Valkealampi (Table 2).

In Lake Valkealampi, increases in COD_{Mn} and colour were significant throughout the 5.5 years post-treatment period, whereas transparency decreased during the first 2.5-year period. This may partly be due to decomposition of *Drepanocladus* moss debris. Wright (1985) also reported increases in TOC levels during the first 2 years after liming. Phytoplankton biomass in Lake Valkealampi remained low after liming, so that was not responsible for the increased COD_{Mn} and colour values. Increases in DOC have also been unaccounted for changes in phytoplankton biomass (Dillon et al. 1979; Wright 1985).

The fact that maximum pH values were recorded about 1 year after liming (Fig. 3) can be partly attributed to high primary production, as reflected in the high chlorophyll a values (Fig. 7). Another reason may be the continued dissolving of calcium carbonate. Ca was still > 2.5 mg l^{-1} in the whole water body when pH was at its maximum, and throughout 1984 (Figs. 4, 3). It then decreased fairly rapidly, but remained greater than 1.5 mg l^{-1} for the whole post-treatment period. Since alkalinity values were still slightly above zero and pH values about 5.50 in the hypolimnion in 1987–1988, with the exception of October, 1988, it can be assumed that the lake has not yet reached the pre-treatment state. The pH of the surface water was 5.00 in April 1988, however, and simultaneously alkalinity reached zero (Figs. 4, 3).

The decreases in Al_{tot} after liming were not significant, but decreases in the maximum values were detected during the post-treatment periods both in the surface water and in the hypolimnion (Table 2). It should be noted that Al_{tot} values in Lake Valkealampi before liming were smaller than in many other limed Scandinavian lakes (e.g. Hasselrot and Hultberg 1984; Wright 1985; Larsson 1988). In common with our observations, post-treatment Al_{tot} was not reduced in the 2 years following liming in the clearwater Lake Suurilampi in southeastern Finland (Silvo and Weppling 1989). Driscoll et al. (1989) observed a slow decrease in Al_{tot} concentrations during the first summer after liming in two acidic lakes in Adirondack, New York State, U.S.A., but it was difficult to discern any difference in Al_{tot} between their pre-treatment and post-treatment results. The catchment area of Lake Valkealampi as such was not limed, which allowed for continued transport of Al_{tot} due to interactions between the soil/bedrock and runoff (cf. Rosseland and Hindar 1988). This may play an important role in the present Al_{tot} values.

A significant increase in SO_4 concentration was observed during the 5.5-year post-treatment period (Table 2). Other studies (Wright 1985; Marcus 1988) have shown that SO_4 levels did not change after liming. Liming stimulates mineralization processes (e.g. Hultberg and Andersson 1972), and decomposition of moss debris may party be due to the SO_4 increase in Lake Valkealampi. Greb and Garrison (1988), using plant tissue analysis from Crystal Lake, Wisconsin, U.S.A., reported that total sulphur in the dead *Drepanocladus* moss fraction was about double that found in living tissue. Another reason for higher SO_4 concentrations after liming may also partly be due to the dissolving of trace amounts of sulphur contained in the $CaCO_3$ (unknown in this case). A third reason for higher SO_4 values in Lake Valkealampi after liming might be higher deposition of sulphate and/or increased runoff. The post-treatment period was rainy as compared with the long-term mean (Table 1). The loading of acidic deposition may also be episodic in this region. However, deposition is not measured in the drainage area of the lake.

A significant increase in N_{tot} concentrations was found during the whole post-treatment period (Table 2), possibly resulting to some extent from decomposition of *Drepanocladus* moss debris, as liming is reported to stimulate mineralization (Wilander and Ahl 1972; Hultberg and Andersson 1982; Broberg 1988). *Sphagnum* mosses practically vanished and benthic felt mats were degraded after liming in Lake Gårdsjön, Sweden (Grahn and Sangfors 1988), leading to increased transport of ammonium from the lake and a gradual increase in organic nitrogen concentrations (Broberg 1988). Because of the lack of data on the various nitrogen fractions, it is not possible to explain their behaviour in our material, but the post-treatment period was rainy as compared with the long-term mean (Table 1) and the increasing runoff and/or higher deposition of nitrogen may also partly explain the higher N_{tot} values (Table 2). Increases in N_{tot} after liming are similarly reported by Marcus (1988) in some lakes in the U.S.A., although Dillon et al. (1979) demonstrated increases in N_{tot} in some lakes and decreases in others.

Some authors point to increased nutrient levels, particularly phosphorus, after liming (Wilander and Ahl 1972), but there is also evidence that P_{tot} may remain unchanged after liming (Dillon et al. 1979; Silvo and Weppling 1989). The post-treatment increases in P_{tot} in Lake Valkealampi were significant over both periods in the surface water, but only during the first phase in the hypolimnion (Table 2). This may reflect the fact that the increase was due to the dissolving of trace amounts of phosphorus contained in the $CaCO_3$ (in this case about 1%). The other explanation would be a release of phosphorus from the sediment and from the degradation of the benthic flora (e.g. Broberg 1988).

Phytoplankton

The low number of phytoplankton species in Lake Valkealampi before liming, only five taxa, is in accordance with results from naturally acidic lakes in Sweden (Almer et al. 1978), where the number of species was lower in lakes with a low pH. The present low number of species was partly due to the lack of algal immigration via an inlet. The dominant species, *Peridinium inconspicuum* and *Gymnodinium* sp., are typical of acidic lakes poor in nutrients ($P_{tot} < 10\ \mu g l^{-1}$, see Rosen 1981).

The phytoplankton composition was similar to that commonly found in acidic, clearwater lakes in eastern Finland in late summer (Ilmavirta et al. 1985; Ilmavirta 1988), and similar to that of many other acidic lakes investigated, although the number of taxa in our late summer samples was even smaller (Raddum et al. 1986; Larsson 1988; Bukaveckas 1989).

The number of species in Lake Valkealampi increased in the second year after liming (1984) and reached its maximum in the third year (1985), after which it started to decrease together with the pH, although it was still higher in 1987 than before liming (Table 3, Table 2a). According to Larsson (1988), liming increased the number of phytoplankton species in certain Swedish lakes during the first 3 years, with the maximum species diversity found in the 2nd year.

The effects of liming on phytoplankton have been similar in many lakes, i.e. a decrease in Peridinae and an increase in chlorophycean and chrysophycean species (Raddum et al. 1986; Larsson 1988; Bukaveckas 1989). The cyanophytes seem to avoid lakes with low pH (Almer et al. 1978), and cyanophytes were present in Lake Valkealampi only in the samples in 1984–1985 with the highest pH values (pH 6.7–7.1). The change from large to small species noted here is in agreement with the results of Larsson (1988) from Lake Gårdsjön.

The effects of liming on the phytoplankton species composition are obvious for at least 4 years afterwards, but the biomass does not necessarily change, since the limiting factor in these poor waters seems to be phosphorus not the low pH (Raddum et al. 1986).

The chlorophyll a, which averaged 3.0 $\mu g\ l^{-1}$ in 1983, was 10.2 $\mu g\ l^{-1}$ in 1984 and 5.8 $\mu g\ l^{-1}$ in 1985 (Fig. 7). This may reflect increased availability of nutrients to the phytoplankton for a short time after liming (cf. Wright 1985; Broberg 1988), especially in view of the lower values in 1987–1988 (Fig. 7), although even these were still two to three times the pre-treatment figure of 1.5 $\mu g\ l^{-1}$. It is assumed that after 5.5 years Lake Valkealampi has not yet reached its pre-treatment state. On the other hand, the chlorophyll a data are too limited to allow interpretation of the trophic status of Lake Valkealampi after liming. Bukaveckas (1988) also reported increased summer chlorophyll a levels following liming in two small acidic ($pH < 5.0$) lakes in Adirondack, New York State, U.S.A., but mentions at the same time a case of lowered chlorophyll a levels after liming in another lake. Some other authors also report reduced chlorophyll a levels (Scheider and Dillon 1976; Stenson 1984), and others no significant changes or only slight ones (Yan and Dillon 1984). No changes in chlorophyll a or other water quality variables could be observed between the years 1983 and 1985 or 1983 and 1988 in Lake Kakkisenlampi, another acidic clearwater lake in North Karelia which would serve as a reference in this respect, being left without any treatment (Simola et al. 1985; unpubl. data of the Water and the Environment District of North Karelia).

Conclusion

Liming an acidic clearwater lake with no alkalinity and low concentrations of Ca, P_{tot} and chlorophyll a affected both water chemistry and biota of the lake. Some effects of liming on water chemistry remained after 5.5 years, and effects on phytoplankton species composition lasted for at least 4 years. The role of submerged vegetation and interactions between soil/bedrock and runoff seemed to have an important role in reacidification. Liming of an acidic lake may cause mesotrophication. However, more detailed knowledge of the lake ecosystem and its drainage area is required to understand and predict all of the consequenses of liming.

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Effects of Liming on the Chemistry and Biology of a Small Acid Humic Lake

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Summary

A small humic lake was limed on ice in winter. The treatment elevated the water pH after ice melt from ca. 5 to ca. 6.5. Compared with a similar reference lake, the only other noticeable chemical changes were in calcium concentration and alkalinity. Due to the short retention time of the lake, the chemical effects of liming persisted for only 1 year. The most remarkable biological change was an increase in bacterioplankton by ca. 50% after liming. In the phytoplankton, the relative biomass of dinophytes, chlorophytes and cryptophytes increased and an acidophilic diatom, *Asterionella ralfsii*, decreased, but the changes were only moderate. After liming, the abundance of algal species increased, but decreased again 1 year later. A cladoceran, *Daphnia longispina*, increased markedly, followed by other changes in the zooplankton community. In small headwater lakes the catchment area, rather than the lake itself, should be limed in order to produce a more persistent increase in water pH.

Introduction

The effects of liming on the chemistry and biology of acidic lakes have been studied largerly in clearwater lakes (e.g. Wilander and Ahl 1972; Dillon et al. 1979; Hultberg and Andersson 1982; Scheider and Brydges 1984; Wright 1985; Hörnström and Ekström 1986; Raddum et al. 1986; Broberg 1987a,b; Larsson 1987). Only few such studies have been carried out with humic lakes (cf. Waters 1956; Waters and Ball 1957; Hillbricht-Ilkowska 1977).

In Oligo-mesohumic lakes liming has sometimes increased water colour (Berzins 1960; Myllymaa 1984). This might be a consequence of the solubilization of humic substances after lime treatment (Hasselrot and Hultberg 1984) or the release of humic compounds from sediment due to the improved bacterial decomposition (Broberg 1978). Also co-precipitation of DOM with iron and aluminium complexes (Stumm and Morgan 1981; Broberg 1987a) and photoreduction of iron favoured by low pH (Collienne 1983), will be less important at higher pH. However, in some cases liming has decreased water colour (Driscoll et al. 1982).

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This may be attributed to photo-oxidation (cf. Gjessing 1971, 1976) and improved bacterial decomposition of DOM (Broberg 1978).

The effect of liming on decomposers is of particular interest in humic lakes, in which allochthonous organic matter can play a major role (Salonen and Hammar 1986). Both Kalinin (1974) and Hillbricht-Ilkowska et al. (1977) observed intensified decomposition of organic matter by bacteria after liming. In this paper we describe the effects of liming on the plankton of a humic lake with special attention paid to the vertical and temporal distributions of populations in order to take into account interactions between different organisms.

Materials and Methods

Study Site

Lake Pussijärvi (61°13′N, 25°12′E) is a small (0.003 km^2) acidic humic lake in the Evo district of southern Finland (Table 1). The lake is surrounded by a floating *Sphagnum* peat raft so the water is 2–4 m deep at the shoreline. The lake has a small inlet and one outlet. Primary rock is granodiorite and gneiss, soil is morainic and the surrounding forest is composed of Scots pine and spruce. The reference lake Ruuttanajärvi (61°13′, 25°13′E) is also a small (0.01 km^2) humic lake with its drainage area adjacent to that of Pussijärvi. The lake has a small inlet and outlet. Primary rock, soil and surrounding forest are similar to Pussijärvi. Ruuttanajärvi has a dense (51.7 $kg\,ha^{-1}$; Lappalainen et al., 1988) population of perch, *Perca fluviatilis* L. while Pussijärvi is without fish. Circulation of the lakes might be incomplete particularly in spring due to their small surface area and sheltered position.

One week before ice-melting at the end of April 1987 850 kg of powdered limestone (particle size 80% $< 74\ \mu m$) was spread on the ice of Pussijärvi with a 1–2-m-broad stripe around the lake. The aim of the liming was to increase pH above 6.0

Physical, Chemical and Biological Measurements

Water samples for physical, chemical and biological analyses were collected during June–August, 1986, and May–August, 1987–1988. Lakes were sampled weekly in

Table 1. The morphometrical characteristics of the study lakes

	Pussijärvi	Ruuttanajärvi
Surface area (km^2)	0.0029	0.01
Drainage area (km^2)	0.10	0.14
Max. depth (m)	8.0	11.2
Mean depth (m)	6.6	4.9
Volume (m^3)	19,000	47,000

1986–1987 but monthly in 1988. All samples, except for metazoan zooplankton, were taken at three stations with a Patalas-type sampler (volume 0.9 l) from depths of 0.1, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 and 6.0 m. Samples pooled for each depth were transported to the laboratory in the dark in cool boxes.

Metazoan zooplankton samples were taken with a 1 m long, 6.4 l tube sampler as 0–1, 1.2, 2–3, 3–4 and 4–5 m columns profiles, filtered through 50-µm mesh net and preserved in 3–4% formaldehyde. The samples from each depth of the three stations were combined.

Temperature and oxygen were measured in situ with a combined probe (Yellow Springs Instruments) at the deepest part of the lakes. Colour of filtered (Whatman GF/C) water was measured spectrophotometrically (Hitachi/model 101) at 420 nm using platinum-cobalt standards as a reference.

Dissolved nutrients were determined immediately upon return to the laboratory. The samples were filtered through Whatman GF/C glassfibre filters, which were first rinsed with 0.5 l of deionized water. The first 200 ml of filtrate were discarded and only the last fraction was used for determination of inorganic phosphorus (Murphy and Riley 1962) and nitrate-nitrite (Wood et al. 1967) with an AKEA autoanalyser. Total nitrogen and phosphorus were determined after persulphate digestion (Koroleff 1979). Total aluminium was measured photometrically using catechol violet reagent (Dougan and Wilson, 1973). Iron and other cations were determined with a Varian Techtron 1000 atomic absorption spectrophotometer. Water pH was measured in the laboratory with an Orion Research 701 (1986–1987) and SA 720 (1988) pH meter (electrode 91–62). Alkalinity was measured by Gran titration (Mackereth et al., 1978). Sulphate and chloride were determined with an ion chromatograph (Dionex 2000i). Sulphate, chloride, aluminium and cations were sampled once a month. Dissolved inorganic carbon (DIC), dissolved organic carbon (DOC) and particulate organic carbon (POC) were determined according to Salonen (1979, 1981). For POC 5–25 ml of samples were filtered through 7 mm precombusted Whatman GF/C glassfibre filters.

Phytoplankton samples were immediately fixed with acid Lugol's solution. The species composition and biomass were determined with an inverted microscope using the settling chamber technique (Utermöhl 1958). Depending on the density of algae, 50 or 10 ml of water were sedimented for 24 h and 20 randomly selected fields were counted at 400 × magnification and 20 fields at 200 × magnification. Phytoplankton biomass was calculated as wet weight from algal volumes measured for the dominant species or for the others as given by Naulapää (1972).

Chlorophyll a (Chl-a) was determined from ethanol extracts (cf. Arvola 1981) with a Shimadzu UV-240 spectrophotometer (1986–1987) at 665 and 750 nm wavelengths or a Hitachi F-4000 Fluorescence spectrophotometer (1988) with excitation at 430 nm and emission at 671 nm. Bacterio-chlorophyll d (Bchl-d) was determined as above at 654 nm and 750 nm or with excitation at 430 nm and emission at 662 nm. The ratio between Chl-a/Bchl-d was calculated to indicate the shift from Chl-a to Bchl-d in the hypolimnion.

Primary production of phytoplankton was estimated in situ at the depths of 0.1, 0.5, 1.0, 1.5 and 2.0 m by the acidification and bubbling modification of the radiocarbon method (Schindler et al. 1972). 0.20 ml of $Na_2{}^{14}CO_2$ solution was injected for 130-ml bottles. Incubation time was 24 h from morning to morning. Samples were counted with a Wallac 1210 Ultrobeta scintillation counter.

Bacterioplankton samples were fixed in 2% formaldehyde. Samples of 1 ml were filtered together with 5 ml prefiltered deionized water onto black Nuclepore filters (pore size 0.2 µm; diameter 25 mm). Bacteria were stained by acriflavine (Bergström et al. 1986), and 20 fields were counted (200–1000 cells) with an epifluorescence microscope (light source HBO 100, magnification 1250 ×).

Rotifers were counted with an inverted microscope (150 × magnification) and crustaceans with a dissecting microscope (25 × magnification) with the aid of a grooved disk (Hakala 1971).

Results

Physical and Chemical Properties

The thermal and chemical stratification pattern in both lakes was similar (Fig. 1, Tables 2–5). In Pussijärvi the temperature difference between the surface and 2 m often exceeded 10°C, and the upper limit of the anoxic hypolimnion usually occured at 1.5–2.2 m. In 1986 in Ruuttanajärvi the thickness of the oxic water layer was similar, but in the later years mixing was more complete and in early summer anoxic water was found to be only under 2–5 m.

In 1987 in Pussijärvi pH, alkalinity, conductivity and Ca^{2+} increased markedly due to liming (Tables 2, 4, Figs. 2, 3), whereas epilimnetic DOC concentration was rather stable. Quite soon, however, epilimnetic pH began to decrease, although Ca^{2+} concentration was high the whole summer. In both lakes aluminium concentrations doubled in 1987 (Fig. 3, Tables 4 and 5), because of high precipitation, which ameliorated total Al input to the lake from the drainage area. The changes in other cations were similar in both lakes (Tables 4, 5). Dissolved inorganic nitrogen and phosphorus were also rather stable except that in Ruuttanajärvi inorganic P concentration was considerably lower in 1986 than in the following years, possibly due to the higher primary production in 1986.

In 1988 pH and alkalinity in Pussijärvi were again at their original levels, while Ca^{2+} remained at higher levels than before liming.

Phytoplankton

In the year following liming, primary production in both lakes was lower than in the two other years (Table 6). Thus the differences between the years in Pussijärvi were more probably due to variation in light conditions than liming. In Pussijärvi primary production was highest at 0.1–0.5 m depth despite maximum biomass

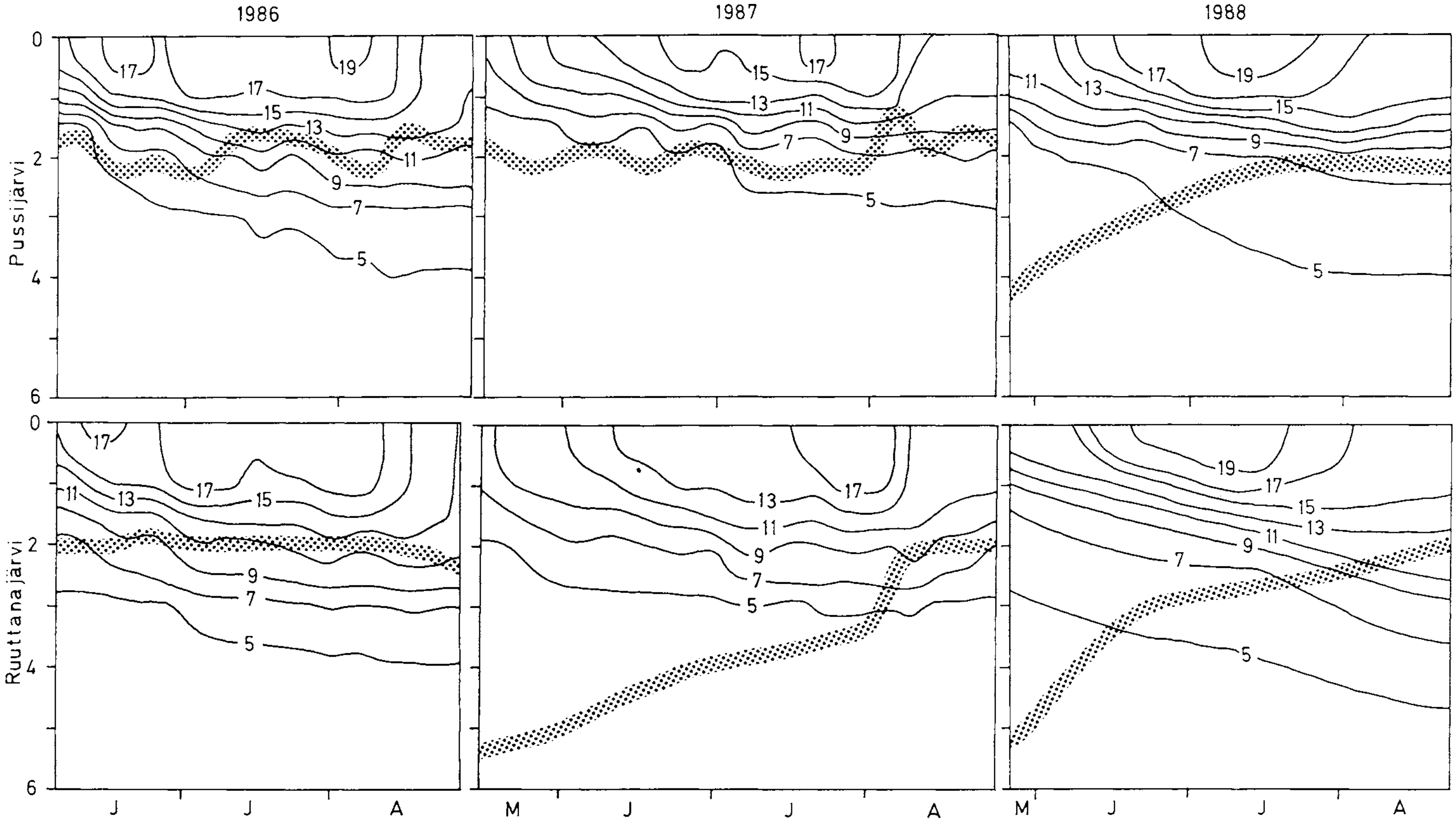

Fig. 1. Thermal stratification and the upper level of the anoxic water layer (*dashed line*) in Pussijärvi and Ruuttanajärvi

Table 2. Some characteristics of water chemistry in Pussijärvi at 0–1 m and 3–4 m depth in 1986–1988 (mean ± SD)

	1986		1987		1988	
	0–1 (n = 12)	3–4 (n = 12)	0–1 (n = 12)	3–4 (n = 12)	0–1 (n = 4)	3–4 (n = 4)
pH	4.9 ± 1.0	5.6 ± 0.1	6.3 ± 0.4	5.7 ± 0.1	4.7 ± 0.3	5.1 ± 0.3
Alkalinity (μeq l^{-1})	−0.007 ± 0.01	0.089 ± 0.02	0.220 ± 0.02	0.114 ± 0.01	−0.004 ± 0.01	0.011 ± 0.01
Conductivity (mS m^{-1} 20°C)	2.6 ± 0.1	3.3 ± 0.1	4.0 ± 0.2	3.7 ± 0.2	3.0 ± 0.2	3.4 ± 0.1
Colour (mg Pt l^{-1})[a]	168 ± 0	–	150 ± 17	221 ± 7	139 ± 38	196 ± 8
DIC (mg l^{-1})	2.3 ± 0.4	8.9 ± 0.7	4.2 ± 0.8	9.3 ± 0.8	2.2 ± 0.2	6.6 ± 3.8
DOC (mg l^{-1})	13.2 ± 0.5	19.8 ± 1.3	14.0 ± 0.7	20.2 ± 1.3	14.0 ± 1.8	18.3 ± 2.0
POC (mg l^{-1})	–	–	–	–	0.48 ± 0.15	0.81 ± 0.24
Cl^- (mg l^{-1})[b]	0.78 ± 0.44	1.29 ± 0.09	0.66 ± 0.04	0.97 ± 0.03	1.02 ± 0.18	1.09 ± 0.01
SO_4^{2-} (mg l^{-1})[b]	6.2 ± 1.9	6.7 ± 0.2	6.3 ± 0.2	7.3 ± 0.1	8.8 ± 0.0	9.0 ± 0.3
$NO_3^-+NO_2^-$ (μg l^{-1})	32 ± 10	42 ± 15	10 ± 5	16 ± 26	12 ± 11	10 ± 4
PO_4^{2-} (μg l^{-1})	5 ± 2	45 ± 19	5 ± 2	16 ± 5	3 ± 1	22 ± 3
TOT-P (μg l^{-1}	15 ± 2	106 ± 22	21 ± 7	81 ± 23	17 ± 5	54 ± 12
TOT-N (μg l^{-1})	–	–	458 ± 35	605 ± 97	464 ± 64	504 ± 26

[a] 1986 n = 1.

[b] 0–1 m: 1986–87 n = 3, 1988 n = 4; 3–4 m: 1986–87 n = 3, 1988 n = 4,

Table 3. Some characteristics of water chemistry in Ruttanajärvi at 0–1 m and 3–4 m depth in 1986–1988 (mean ± SD)

	1986		1987		1988	
	0–1 (n = 12)	3–4 (n = 12)	0–1 (n = 12)	3–4 (n = 12)	0–1.5 (n = 4)	3–4 (n = 4)
pH	5.9 ± 0.2	6.0 ± 0.2	5.8 ± 0.1	5.7 ± 0.1	5.1 ± 0.2	5.3 ± 0.3
Alkalinity (μeq l^{-1})	0.041 ± 0.007	0.190 ± 0.03	0.033 ± 0.005	0.084 ± 0.007	0.022 ± 0.007	0.071 ± 0.013
Conductivity (mS m^{-1} 20°C	3.5 ± 0.1	4.4 ± 0.2	3.5 ± 0.1	3.8 ± 0.2	3.5 ± 0.1	3.8 ± 0.2
Colour (mg Pt l^{-1})[a]	226 ± 7		200 ± 9	215 ± 14	179 ± 12	199 ± 8
DIC (mg l^{-1})	0.7 ± 0.4	6.7 ± 1.1	1.6 ± 1.0	5.2 ± 0.3	1.0 ± 0.5	5.3 ± 2.0
DOC (mg l^{-1})	18.7 ± 2.1	18.7 ± 2.2	18.0 ± 2.1	18.0 ± 2.1	15.0 ± 0.4	16.0 ± 0.6
POC (mg l^{-1})	–	–	0.81 ± 0.49	0.49 ± 0.25	0.85 ± 0.41	0.71 ± 0.16
Cl^- (mg l^{-1})[a]	1.63 ± 0.4	1.1 ± 0.49	1.24 ± 0.05	1.02 ± 0.50	1.02 ± 0.01	1.32 ± 0.04
SO_4^{2-} (mg l^{-1})[a]	7.51 ± 1.9	5.9 ± 3.1	8.8 ± 0.2	8.2 ± 0.1	10.1 ± 0.1	9.23 ± 0.0
$NO_3^- + NO$ (μg l^{-1})	38 ± 16	44 ± 18	12 ± 5	141 ± 58	15 ± 7	17 ± 14
PO_4^{2-} (μg l^{-1})	10 ± 8	96 ± 47	23 ± 14	80 ± 15	23 ± 6	65 ± 21
TOT-P (μg l^{-1})	43 ± 17	149 ± 43	63 ± 8	106 ± 11	49 ± 4	74 ± 9
TOT-N (μg l^{-1})	–	–	706 ± 151	701 ± 73	678 ± 36	579 ± 17

[a] See Table 2.

Table 4. The major cation concentrations (mg l^{-1}) at 0–1 m and 3–4 m depth in Pussijärvi in 1986–1988 (mean ± SD)

	1986		1987		1988	
	0–1 (n = 4)	3–4 (n = 4)	0–1 (n = 4)	3–4 (n = 4)	0–1 (n = 4)	3–4 (n = 4)
Na^+	1.21 ± 0.39	1.67 ± 0.18	1.07 ± 0.08	1.30 ± 0.04	0.94 ± 0.06	1.11 ± 0.04
K^+	0.22 ± 0.24	0.67 ± 0.24	0.27 ± 0.15	0.55 ± 0.02	0.14 ± 0.15	0.48 ± 0.03
Ca^{2+}	2.64 ± 0.66	4.50 ± 0.14	7.49 ± 0.82	6.45 ± 0.28	3.35 ± 0.48	4.28 ± 0.69
Mg_2^+	0.77 ± 0.02	0.81 ± 0.04	0.98 ± 0.07	0.70 ± 0.04	0.70 ± 0.04	0.98 ± 0.27
$Fe^{2/3+}$	0.13 ± 0.00	0.35 ± 0.00	0.19 ± 0.05	0.38 ± 0.03	0.10 ± 0.05	0.21 ± 0.02
tot-Al	0.06 ± 0.05	0.10 ± 0.01	0.12 ± 0.04	0.18 ± 0.05	0.09 ± 0.02	0.15 ± 0.02

Table 5. The major cation concentrations (mg l^{-1}) at 0–1 and 3–4 m depth in Lake Ruuttanajärvi in 1986–1988 (mean ± SD)

	1986		1987		1988	
	0–1 (n = 4)	3–4 (n = 4)	0–1 (n = 4)	3–4 (n = 4)	0–1 (n = 4)	3–4 (n = 4)
Na^+	1.57 ± 0.21	1.40 ± 0.34	1.41 ± 0.13	1.49 ± 0.12	1.21 ± 0.04	1.35 ± 0.03
K^+	0.55 ± 0.09	0.60 ± 0.03	0.62 ± 0.07	0.65 ± 0.07	0.53 ± 0.06	0.60 ± 0.01
Ca^{2+}	4.32 ± 0.45	5.70 ± 1.98	5.04 ± 0.12	5.79 ± 0.20	3.91 ± 0.24	4.66 ± 0.24
Mg^{2+}	0.86 ± 0.12	0.81 ± 0.38	0.97 ± 0.07	1.06 ± 0.07	0.88 ± 0.05	1.00 ± 0.02
$Fe^{2+/3+}$	0.21 ± 0.08	0.68 ± 0.11	0.33 ± 0.04	0.50 ± 0.06	0.25 ± 0.02	0.43 ± 0.05
tot-Al	0.12 ± 0.01	0.13 ± 0.02	0.18 ± 0.02	0.20 ± 0.03	0.17 ± 0.02	0.18 ± 0.01

being below 1.5 m (Fig. 4). Only in 1986 did primary productivity differ markedly between our study lakes (Table 6).

The hypolimnetic phytoplankton biomass in Pussijärvi increased after liming and was composed of the flagellates *Chlamydomonas* spp. (usually more than 60% of the total biomass), *Scourfieldia cordiformis* Takeda, *Glenodinium* sp. and phototrophic green sulphur bacteria. Also in Ruuttanajärvi Chl-a increased towards the hypolimnion (except in 1987 after more complete mixing), but biomass was always higher in the epilimnion (Fig. 4). The high biomass and productivity in Ruuttanajärvi in 1986 was mainly caused by the green alga *Oocystis lacustris* Chodat. In both lakes there were no clear differences in Chl-a concentrations between the years, but Bchl-d occurred at greater depth in 1987 and 1988 than in 1986 (Fig. 5).

In Pussijärvi the cell numbers of dinophytes, chlorophytes and cryptophytes increased after liming. In the following year the cell abundance of chrysophytes and cryptophytes was still high but that of cyanophytes and chlorophytes had already decreased. In 1987 only diatoms decreased and reached their relative and absolute minimum in 1988. The high proportion of diatoms in 1986 was largely due to the acidophilic *Asterionella ralfsii* W. Smith (Fig. 6), which decreased after

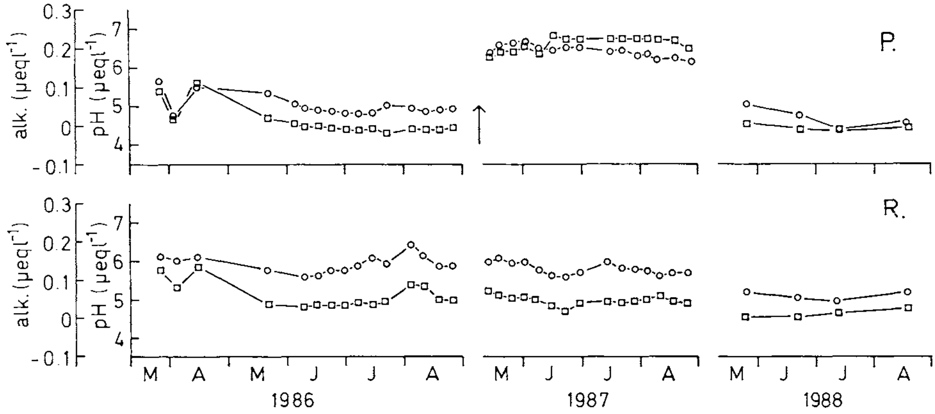

Fig. 2. Variation of alkalinity (*squares*) and pH (*circles*) in Pussijärvi (*P.*) and Ruuttanajärvi (*R.*)

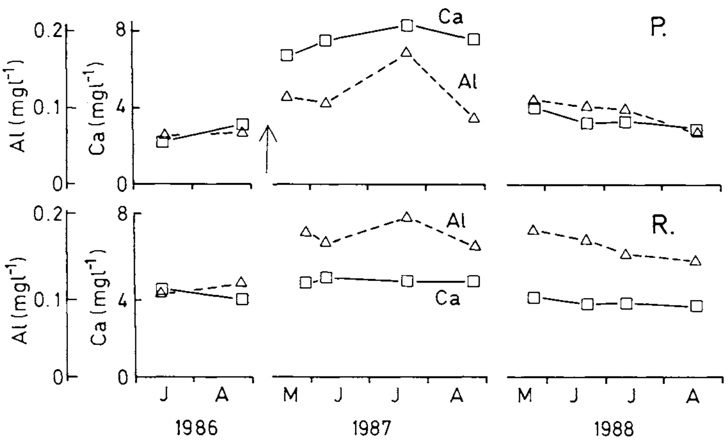

Fig. 3. Variation in calcium (*Ca*) and aluminium (*Al*) concentrations in Pussijärvi (*P.*) and Ruuttanajärvi (*R.*) *Arrow* indicates the time of liming

liming. A dinophyte, *Glenodinium* sp., was abundant every spring, whereas *Gymnodinium* spp. had its highest biomass in the liming year. After liming, the relative abundance of crypsophytes slightly decreased although their cell biomass increased. In the late summer of the liming year species of *Cryptomonas* (Figs. 6, 7) accounted for over 50% of the total biomass. *Dinobryon divergens* Imhof var. *divergens* and *Pseudopedinella* spp. were abundant in the liming year compared to the years before or following the treatment. *Mallomonas punctifera* Korshikov, M. *heterospina* Lund, *Mallomonas* spp., *Pedinella* spp. and *Spiniferomonas* spp. increased in the year following liming whereas *Chrysococcus cordiformis* Naumann decreased (Fig. 6). In the hypolimnion the dominance of chlorophytes was partly replaced in 1988 by cryptophytes and chrysophytes.

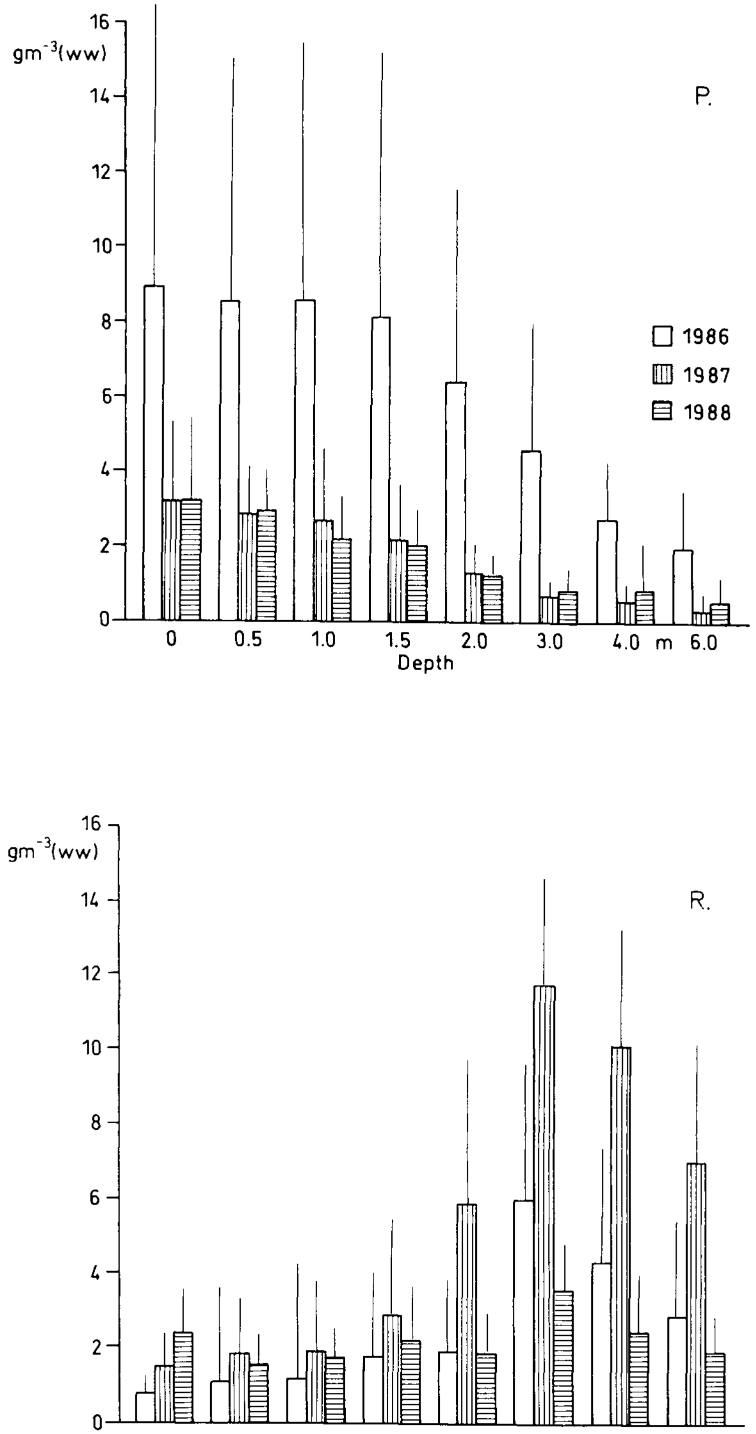

Fig. 4. Mean biomass of algae at different depths in Pussijärvi (*P.*) and Ruuttanajärvi (*R.*)

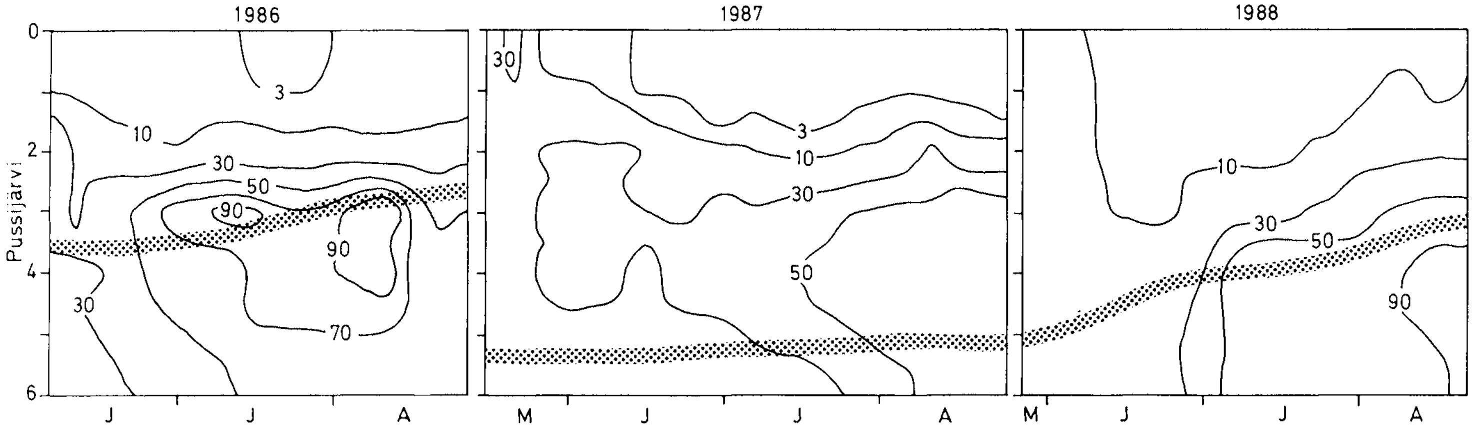

Fig. 5. Vertical distribution of total chlorophyll a and the upper level of bacterio-chlorophyll d (*dashed line*) in Pussijärvi

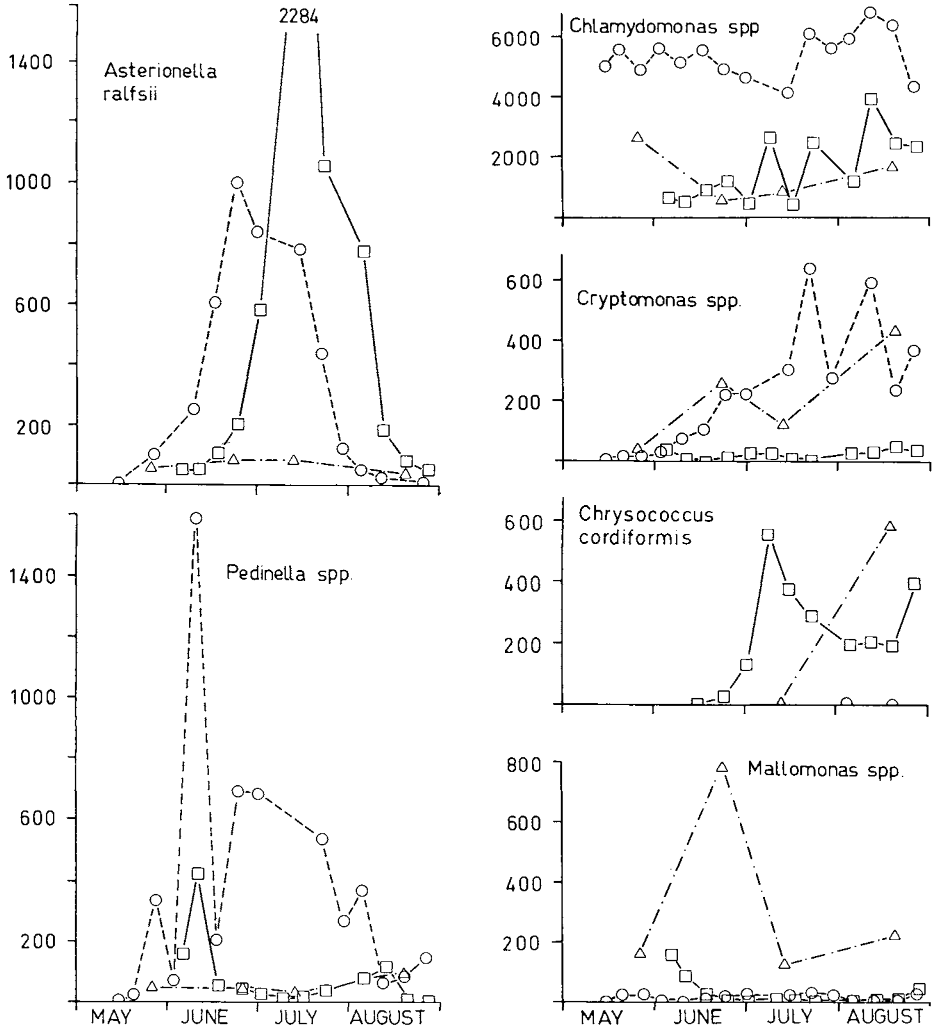

Fig. 6. The densities (cells ml^{-1}) of the most abundant phytoplankton taxa in Pussijärvi in 1986 (*squares*), 1987 (*circles*) and 1988 (*triangles*)

In Ruuttanajärvi cryptophytes, chrysophytes and diatoms dominated in June 1986, which was followed by conjugatophytes (Fig. 7) and chlorophytes (> 90% of the biomass). The high biomass in 1986 was due to *Oocystis lacustris*, *Closterium gracile* Brebisson and *C. macilentum* Brebisson. In 1987 chlorophytes dominated during the spring bloom, and chrysophytes and particularly cryptophytes during the rest of the summer with the exception of the blue-green alga *Anabaena circinalis* Rabenhorst in July. In 1988 biomass was maintained mainly by cryptophytes. The same taxa dominated in both epi- and hypolimnion.

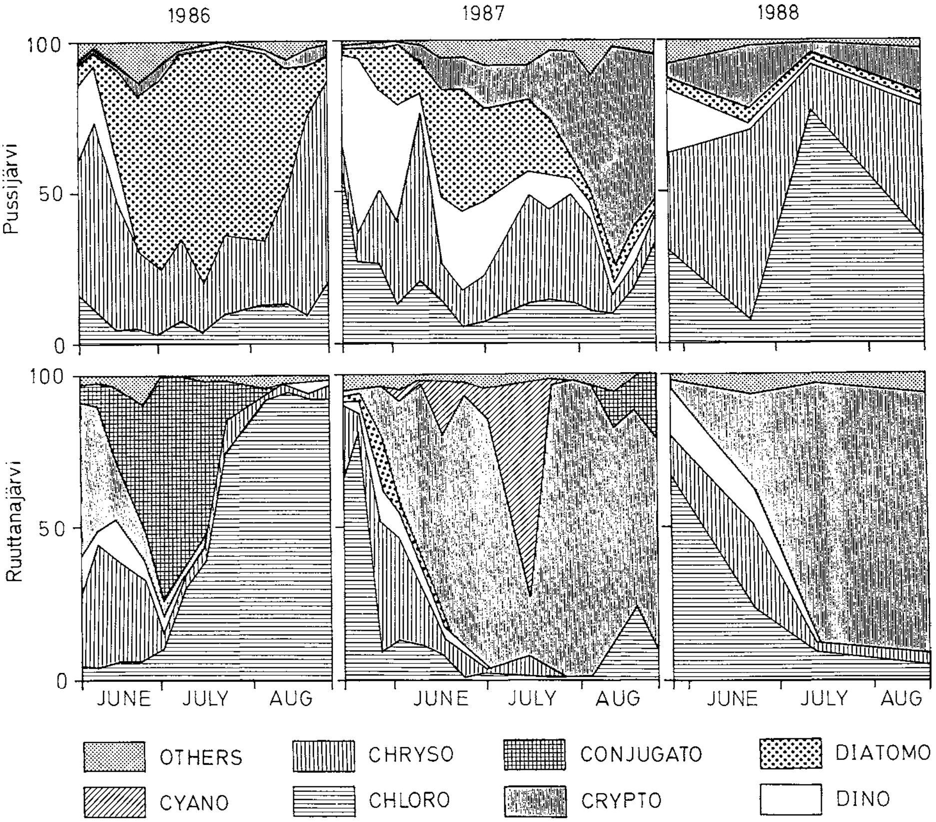

Fig. 7. Relative biomasses of the most important phytoplankton groups in Pussijärvi and Ruuttanajärvi

In Pussijärvi phytoplankton species richness increased slightly after lime treatment but decreased again one year later (Table 6). In Ruuttanajärvi the number of species was similar to Pussijärvi in 1986 and 1988, but was lower in 1987.

Table 6. Mean epilimnetic (0–1 m) chl-a, primary production, biomass of phytoplankton, species richness and numbers of bacteria (with standard deviations) in Pussijärvi and Ruuttanajärvi in 1986–1988

	Pussijärvi			Ruuttanajärvi		
	1986 (n = 12)	1987 (n = 12)	1988 (n = 4)	1986 (n = 12)	1987 (n = 12)	1988 (n = 4)
Chl-a ($\mu g\ l^{-1}$)	4.8 ± 2.3	1.4 ± 1.9	7.4 ± 4.5	21.2 ± 8.0	9.3 ± 7.9	18.0 ± 17.2
Primary production (mg C m^{-3} d^{-1})	73 ± 39	54 ± 25	121 ± 22	203 ± 94	80 ± 50	78 ± 6
Biomass of phytoplankton ($\mu g\ l^{-1}$ WW)	3.2 ± 4.2	2.1 ± 1.0	2.0 ± 0.2	9.2 ± 6.7	2.8 ± 1.4	2.4 ± 1.3
Phytoplankton species richness	22.3 ± 4.1	29.3 ± 5.0	23.7 ± 5.8	23.1 ± 7.4	19.1 ± 9.0	24.1 ± 11.2
Bacteria (10^6 cells ml^{-1})	2.8 ± 0.3	4.7 ± 1.6	2.2 ± 0.5	5.2 ± 1.4	4.0 ± 1.6	4.3 ± 0.8

Bacterioplankton

After liming of Pussijärvi the number of bacteria increased by about 50% (Anova $p < 0.001$). In the following year their number decreased (Anova $p < 0.001$) particularly in deeper layers (Table 6), where bacteria were most abundant (Fig. 8).

In Ruuttanajärvi bacteria were vertically more evenly distributed and their numbers remained more or less stable over the whole study period (Fig. 8). In 1988 the density of bacteria was lower than in 1986, as also found in Pussijärvi.

Zooplankton

After liming, the vertical distributions of zooplankton species in Pussijärvi remained similar to those prior to treatment. Most animals were in the uppermost

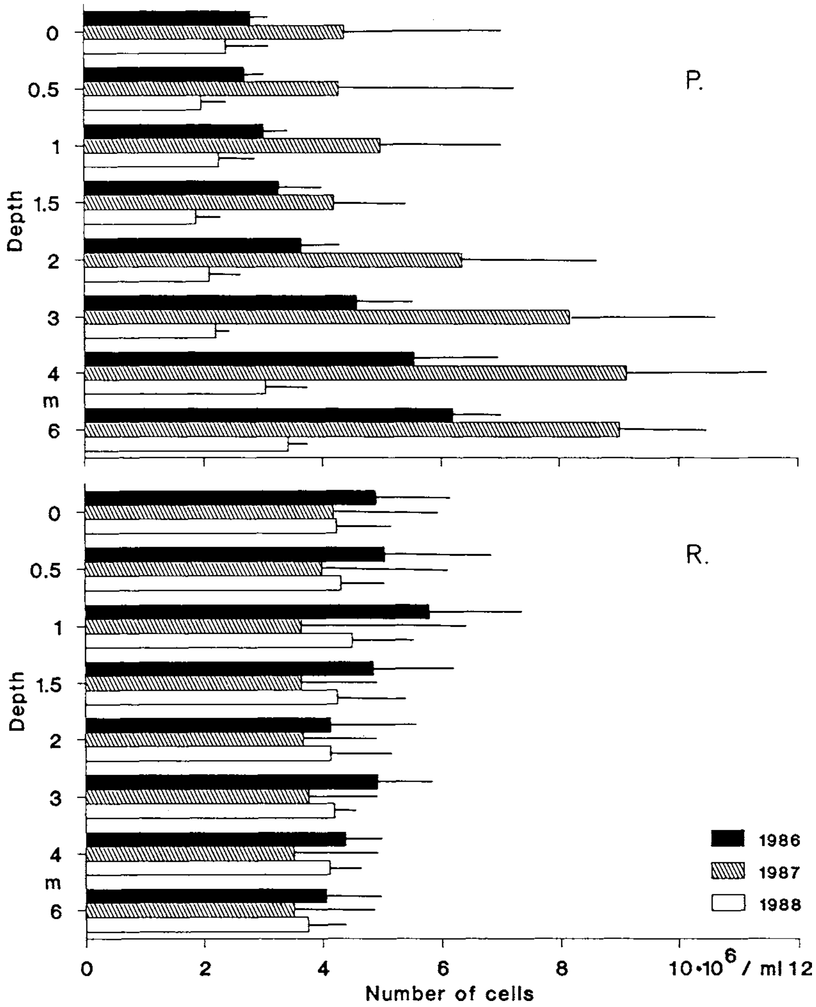

Fig. 8. Mean densities of bacteria at different depths in Pussijärvi (*P.*) and Ruuttanajärvi (*R.*)

2-m water layer with the exception of cold-stenotherm species, *Keratella cochlearis* f. *tecta* Gosse and *Keratella hiemalis* Carlin.

In Pussijärvi the density of filter-feeding crustacean zooplankton was generally low. Cladocerans were dominated by large *Daphnia longispina* Muller, which started to increase only in late summer of the liming year, probably due to their long generation time. The highest abundance of *D. longispina* appeared the next year in early summer. *Bosmina longispina* Leydig was very rare during the whole study period and liming did not affect this species. *Ceriodaphnia quadrangula* Muller was a little more abundant in 1987, but its density was constantly low (ca. 150 ind. m^{-2}). A few littoral species, *Polyphemus pediculus* L. *Chydorus sphaericus* Muller and *Simocephalus vetulus* Muller were regularly found.

In Ruttanajärvi cladocerans were ca. 30 times more numerous than in Pussijärvi, but instead of *Daphnia longispina* the dominating species was the smaller *Bosmina longispina*. In the summers 1986–1987 its population density was rather stable with a mean ca. 450 ind. m^{-2}, but in 1988 it was only ca. 150 ind. m^{-2}. *Daphnia cristata* Sars increased during the study period (mean densities in summers 1986, 1987 and 1988 ca. 10, 20 and 90 ind. m^{-2}, respectively). The corresponding densities for *Ceriodaphnia quadrangula* were ca. 20, 200 and 50 ind. m^{-2}.

In Pussijärvi the proportion of rotifers in metazoan zooplankton numbers was generally over 90%, with 12–13 species. In the liming year the conspicuously dominant species, *Keratella cochlearis* Gosse (including the form *tecta*), started to decrease in late summer at the same time as *Daphnia longispina* began to increase and in 1988 its population was much lower. Among other rotifers, the previously rare *Conochilus hippocrepis* Schrank increased strongly, while *Polyarthra* spp. (including *P. vulgaris* Carlin) and *Trichocerca similis* Wierz declined significantly (Anova $p < 0.001$ and $p < 0.01$ respectively) after liming (Fig. 9). During the first 2 years the population of *Asplanchna priodonta* Gosse was stable, but in 1988 it virtually disappeared (Fig. 9). Other less abundant species in Pussijärvi were *Ascomorpha ecaudis* Perty, *Gastropus stylifer* Imhof, *Keratella hiemalis*, *K. quadrata*, *Monommata* sp., *Synchaeta* spp. and *Trichocerca capucina* Wierz.

In Ruuttanajärvi there were ca. 18 rotifer species, though their abundance was comparable with Pussijärvi. *Polyarthra* spp., especially *A. vulgaris*, dominated among rotifers. In 1987 their density increased significantly (Anova $p < 0.01$). *Keratella cochlearis* was also abundant in 1986, but in 1988 it almost disappeared. No differences were noticed in the numbers of *Keratella hiemalis* and *K. quadrata* between the study years. Other common, though not abundant, species in Ruuttanajärvi were *Asplanchna priodonta*, *Gastropus stylifer*, *Kellicottia longispina* Kellicott, *Conochilus hippocrepis*, *Filinia longiseta* Ehrenberg, *Collotheca* sp. and *Synchaeta* spp.

In Pussijärvi cyclopoids (only copepodite stages) were most abundant copepods. Their numbers started to decrease 1 year after liming. No changes in the numbers of a calanoid, *Eudiaptomus graciloides* Lilljeborg, or of copepod nauplii were found between the study years (Fig. 9). In Ruuttanajärvi the cyclopoids

Cyclops abyssorum Sars and *Thermocyclops oithonoides* Sars were the most abundant copepods. The only calanoid, *Heterocope appendiculata* Sars, was scarce. In 1987 there was a slight decrease in the abundance of nauplii (Anova $p < 0.05$).

Discussion

Changes in water chemistry following liming were limited to pH, alkalinity and calcium concentration in Pussijärvi. This is in agreement with the results of Wright

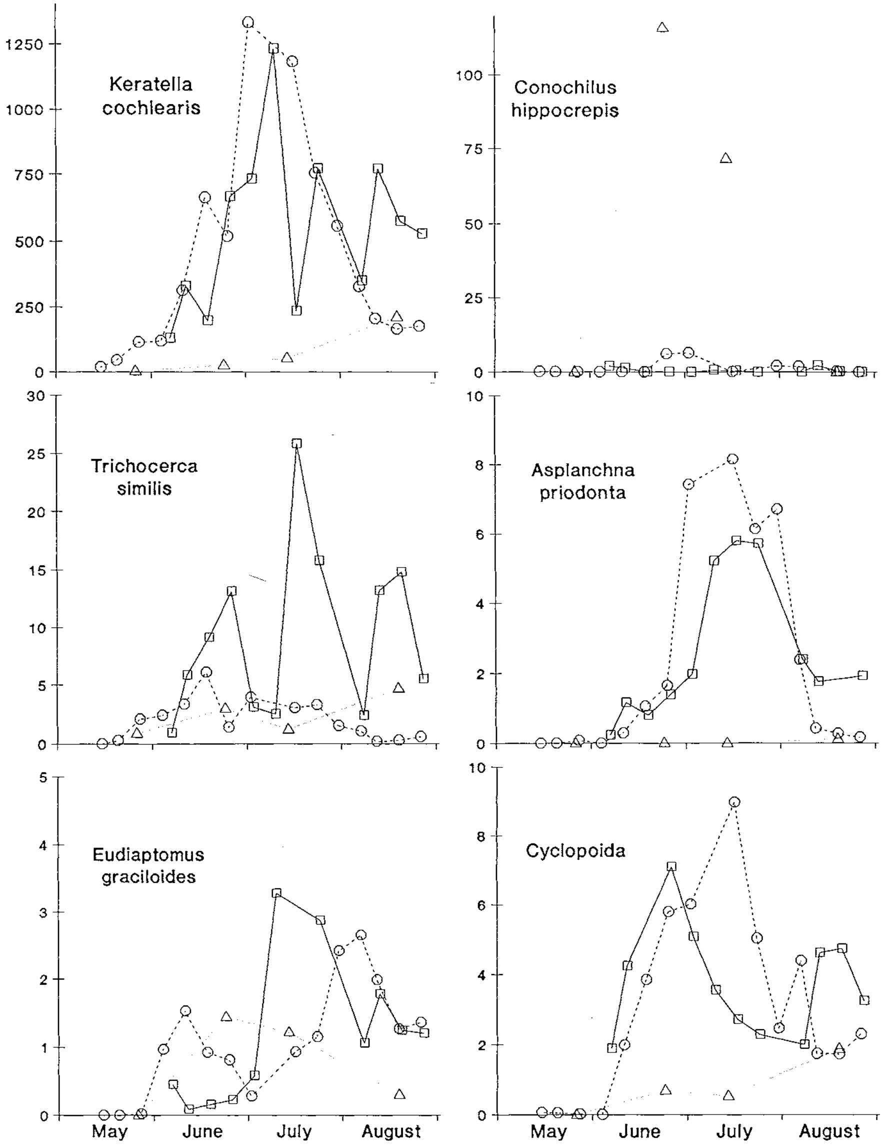

Fig. 9.

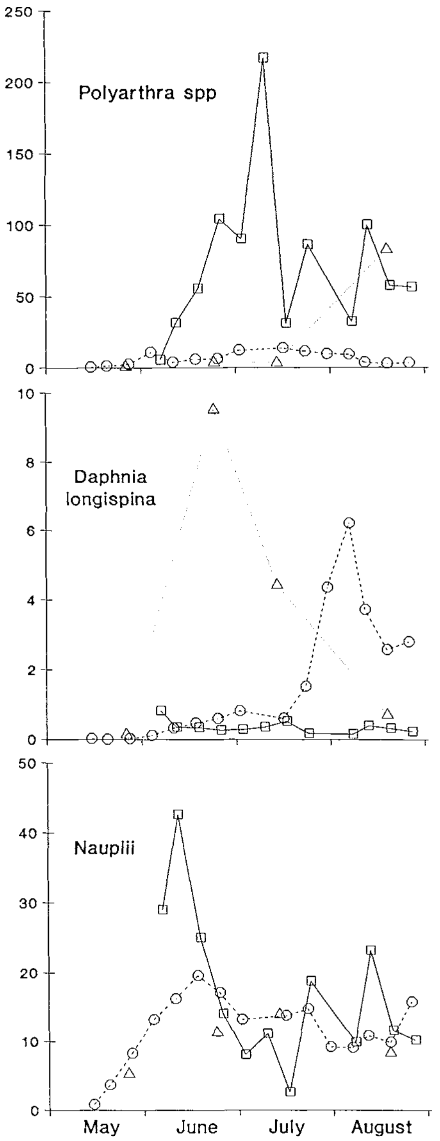

Fig. 9. Densities of the most abundant zooplankters (10^3 ind. m^{-1}) in Pussijärvi during the summer seasons 1986 (*squares*), 1987 (*circles*) and 1988 (*triangles*)

(1985) and Kullberg and Pettersson (1987), who observed no remarkable change in the concentration of major cations (except Al), DOC and water colour after liming. Broberg (1987a) reported increased concentration of DOC after liming of a clear water lake in Sweden, while Myllymaa (1984) found both declines and increases of water colour in 18 limed lakes in northern Finland.

In contrast to our study, Hillbricht-Ilkowska et al. (1977) found a small increase in inorganic phosphorus and a marked increase in inorganic nitrogen in a humic lake. They suggested that increased concentration of calcium caused the release of those from humus. On the other hand, the laboratory experiments of

Hörnström et al. (1984) indicated that after liming humic substances reduce the loss of phosphorus by precipitation and consequent sedimentation.

The increase in Al concentration in 1987 in Pussijärvi cannot be attributed to liming, because the same was also observed in the reference lake. It seems to have followed from high precipitation in 1987. Driscoll et al. (1989b) and Wright (1985) observed reduced concentrations of aluminium after liming, possibly due to precipitation. They concluded that although variations in total aluminium were subtle, changes in aluminium speciation shifted from acid-soluble to monomeric aluminium.

Rapid re-acidification, as found in Pussijärvi, was also observed by Driscoll et al. (1989a) in two North American lakes. In Pussijärvi this was caused by the short retention time, particularly in the epilimnion, which is characteristic of highly stratified forest lakes (cf. Arvola et al. 1987, 1989; Similä 1988). Altogether, the results of this study demonstrated the importance of hydrology on the chemistry of a small humic lake, which is consistent with the results of Arvola et al. (1989).

The clearest biological effect of liming in Pussijärvi was the increase in the density of bacteria. This is in line with the observations that liming generally increases microbial activity (Kalinin 1974; Scheider and Dillon 1976; Hillbricht-Ilkowska et al. 1977; Dillon et al. 1979).

The decrease of primary production in 1987 in the limed and reference lakes might be attributed to increased aluminium levels. However, in humic water aluminium is mostly bound to humic compounds and is then less toxic (e.g. Hörnström et al., 1984); thus less favourable illumination in 1987 seems a more likely explanation. Like Hillbricht-Ilkowska et al. (1977), we observed practically no change in chlorophyll a concentration or phytoplankton biomass in the epilimnion after liming. However, an increase was observed in the hypolimnion. A reduction in the density of phytoplankton after liming has been reported (Hultberg and Andersson 1982; Larsson 1987; Bukaveckas 1989). This may be attributed to mortality induced by rapid chemical changes (e.g. pH shock) or physical removal by cell adsorption onto sinking mineral particles (Fordham and Driscoll 1989). Differences between the results are certainly at least partly due to differences in liming. For example in our case, final pH (ca. 6.5) was much lower than in most other experiments (e.g. ca. 9.5 in those of Bukaveckas 1989). It is also necessary to distinguish between short-term (time scale of days, e.g. Bukaveckas 1989) and long-term effects (time scale months or longer) as in our study.

The most noticeable change in the phytoplankton of Pussijärvi was the replacement of *Asterionella ralfsii*, an acidophilic species, by chrysophytes and cryptophytes. In contrast, below the thermocline no change in the species composition was found. This is in accordance with the observations of Arvola (1986) that the dominating taxa *Chlamydomonas* spp. has a wide pH tolerance. In some previous studies chrysophytes also increased after liming (Hillbricht-Ilkowska et al. 1977; Eriksson et al. 1983; Stokes 1986; Bukaveckas 1989). In her review, Stokes (1986) found an increase in the relative biomass of chrysophytes and diatoms while dinophytes (especially Peridinae) decreased at high pH. Species richness seems to increase with increasing pH (Eriksson et al. 1983; Stokes 1986), as was the case in Pussijärvi. However, because the number of species also increased in the reference lake, it is probable that besides water chemistry the species composition of phytoplankton was affected by other factors such as epilimnetic flushing (Arvola et al. 1987; Similä 1988).

Sprules (1975) suggested that the effect of pH on the structure of zooplankton communities is highest below pH 5.0. In Pussijärvi such acidity was reached before liming and again 1 year later. In this study the higher level of pH lasted only one summer and it is difficult to know which of the few changes observed in zooplankton could be considered as natural fluctuation due to other factors rather than as a consequence of liming.

Crustacean zooplankton of Pussijärvi was typical of fishless lake, where the predator-prey system is characterized by invertebrate predators such as *Chaoborus* spp. and *Corixidae* (Stenson and Oscarson 1985; Nyberg 1983; Nyman et al. 1985). The mean body size of crustaceans was larger than in Ruuttanajärvi, where the selective predation by fish probably largely determines crustacean size distribution (Henrikson et al. 1985). The scarce population of *Daphnia longispina* in Pussijärvi and its high increase after liming is in agreement with the conclusion that *Daphnia* species are sensitive to acidification (e.g. Keller and Pitblado 1984; Stenson and Oscarson 1985; Arvola et al. 1986). The high densities of rotifers in Pussijärvi may have been due to the low density of filter-feeding crustaceans (Erikson et al. 1983) and a phytoplankton assemblage rich in chrysophytes (Pourriot 1977) and nanoplankton (Moore 1980). Gilbert and Stemberger (1985) and Burns and Gilbert (1986) suggested that *Daphnia* species can inhibit population growth of *K. cochlearis* even when shared food between these species is abundant so that competition of food is not the only possible explanation (May and Jones, 1989). However, the decreases in *Polyarthra* spp. and *Trichocerca similis* were apparent before the appearance of high densities of *D. longispina* and may thus be explained by liming. In contrast to our results, liming has been usually found to increase *Polyarthra* (e.g. Henrikson et al. 1985) as well as *T. similis* (MacIsac et al. 1986). Also in some other previous studies a marked increase of rotifers after liming has been observed (e.g. Hillbricht-Ilkowska et al. 1977; Eriksson et al. 1983; Henrikson et al. 1985; Raddum et al. 1986). In Pussijärvi the decrease of most rotifers may be explained by the absence of fish, which allowed large *Daphnia longispina* to outcompete rotifers.

Following the drastic decrease of *Keratella cochlearis* their predator, *Asplanchna priodonta*, almost vanished. A similar disappearance after liming was found by Hillbricht-Ilkowska et al. (1977), while Hultberg and Andersson (1982) observed an increase. The only rotifer which increased strongly during the maximum of *Daphnia longispina* was *Conochilus hippocrepis*. It may have gained an advantage of the decrease of *K. cochlearis* probably using similar food (Pourriot 1977) and/or from the decrease of predatory *A. priodonta* and cyclopoid copepods. Because *C. hippocrepis* is colonial, it is not so susceptible to predation by the former species. The stability of the densities of *Eudiaptomus graciloides* is not unexpected, since, in contrast to *D. longispina*, it is a coarse filtrator and is not so strongly affected by competition from the latter. The decrease of cyclopoids 1 year after liming may have resulted from lower density of rotifers.

The lower number of calanoids in Ruuttanajärvi compared with Pussijärvi may be explained in terms of fish population. Stenson and Oscarson (1985) have concluded that the copepod group is dominated by small cyclopoids in the well-buffered lakes with fish. Yan et al. (1977), Henrikson et al. (1984) and Raddum et al. (1986) found only a small effect on the copepod population shortly after liming. Slow reactions of copepods to changes in the environment are, at least partly, due to their long life history.

Comparison between the results of different studies or even different years within one study is hampered by random weather effects like the amount of precipitation or the degree of autumnal mixing of water in this study. Other important difficulties arise from the complex biological interactions within the food webs of lakes and the effect of organisms on their environment. The biological reactions are often dependent on the structure of the community at the time of treatment and the effects may only become evident after various time intervals. Thus although some chemical changes may be instantaneous, their final biological consequences may only appear after many years (e.g. Hillbricht-Ilkowska 1977).

Thus single-lake liming experiments, even with a reference lake, can provide few firm conclusions despite much work. We feel that it would be more informative to investigate a larger number of lakes of which part would be treated by lime and part untreated to obtain results which can be analysed using statistical methods. The rapid disappearance of the chemical effects of liming makes neutralization of small headwater lakes too transitory. The only reasonable way to produce longer-term effects would be to treat the catchment area. Although that is more costly, it would also ameliorate problems caused by acidification at their origin in the soil, leading to a more complete cure of the problems.

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PART 5 SECONDARY EFFECTS AND ASSESSMENT

Development of an Integrated Model for the Assessment of Acidification in Finland

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Summary

An integrated model to consider the future development of acidifying emissions and their impacts on forest soils and lakes is being prepared in close collaboration with several Finnish research institutes and IIASA. The model system (HAKOMA) covers SO_2 and NO_x emissions from energy use, industrial processes, and transportation, and also NH_3 emissions from agriculture, animal farming, and industry. Future emissions are estimated on the basis of different scenarios for energy, traffic, industry and agriculture and on the basis of alternative reduction strategies.

The sulphur deposition due to emission sources in Finland and nearby areas is calculated using source-receptor matrices computed with a mesoscale model developed at the Finnish Meteorological Institute, and the sulphur deposition due to the long-range transport is estimated using source-receptor matrices based on the results of EMEP. A mesoscale model is under development for nitrogen oxide emissions. The deposition due to ammonia emissions and the long-range fraction of nitrate deposition will be described with the results of the EMEP nitrogen model.

Most forest soils in Finland are in the cation buffer range. The main factors considered in the soil model are sulphur and nitrogen deposition, base cation deposition, depletion of the base cation inventory through outflow of sulphate ions and biomass harvesting, and supply of base cations from mineral weathering. In the lake model, the fluxes of anions and cations to the lake from catchment soils and directly from the air as well as from the in-lake alkalinity generation processes have been considered. The parameter values describing soils and lakes are selected on the basis of survey programmes.

The preliminary results of the simulations suggest that the current reduction plans of sulphur emissions in different countries would not stop the acidification of forest soils in Finland. Also if Finland alone applied very strict reduction measures, the acidification would be somewhat slower, but a considerable change could be effected only if all countries contributing to the deposition in Finland would strictly reduce their emissions.

Kauppi et al. (Eds).
Acidification in Finland

Introduction

An integrated model system to assess the development of acidifying emissions and different processes leading to acidification of forest soils and lakes is under preparation. The model system (the Finnish Integrated Acidification Assessment Model, HAKOMA from the Finnish name of the model) covers sulphur and nitrogen oxide emissions from energy use, industry, and transportation, ammonia emissions from agriculture and animal farming, emission abatement measures, atmospheric dispersion and transformation, and impacts on forest soils and lakes (Fig. 1) (Johansson et al. 1989). All the emission models and the calculation chain from the sulphur emissions to the impacts are presently operational. The atmospheric models for nitrogen oxides and ammonia, and the emission control cost model are planned to be in operation later.

The objectives of the integrated model system are:

- to obtain quantitative relationships between different factors and processes relevant to acidification; to identify the most important factors and the greatest contributors to uncertainties;

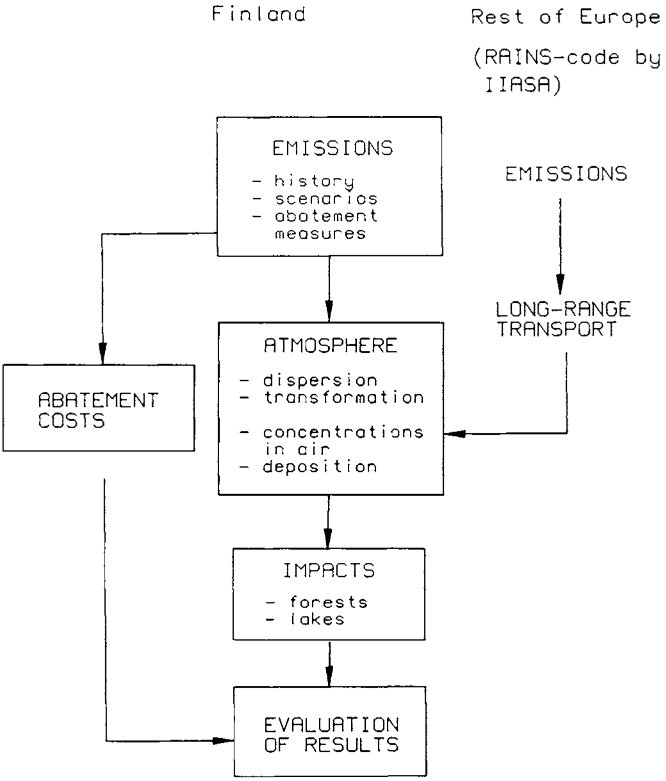

Fig. 1. The main parts of the Finnish integrated acidification assessment model (HAKOMA)

- to obtain estimates on the future development of emissions, deposition, and impacts on forest soils and lakes; e.g. for the planning of emission criteria and emission abatement strategies; and
- to collect and present data relevant to acidification in a form which is informative and easy to use.

The model system is being developed at the Technical Research Centre of Finland, in co-operation with the International Institute for Applied Systems Analysis (IIASA) and several national institutes in Finland such as the Finnish Meteorological Institute (FMI), the National Board of Waters and Environment, the Finnish Forest Research Institute, Helsinki University, and the Geological Survey.

In the following a description of the integrated model system and some preliminary results are given. Sulphur and nitrogen oxide emission models and emission scenarios for the future, as well as the forest soil model and the lake model, are described in more detail in other articles of this volume. Therefore, only a short overview of these topics is given here.

Emissions

Emissions of Sulphur Dioxide and Nitrogen Oxides

Emissions of sulphur dioxide and nitrogen oxides originate mainly from energy use, industry, and transportation. Sulphur emissions are principally due to sulphur contents of fuels. In conventional burning processes the sulphur in the fuels is released to a large extent or totally to the atmosphere. Some fraction of the sulphur emissions originates from raw materials of industrial processes as from the ore in the basic metal industry. The nitrogen oxide (NO_x) emissions are caused by combustion processes mainly, and the origin of the nitrogen in the NO_x of the exhaust gases can be both the nitrogen in the fuel and the nitrogen in the inlet air in burning process. Energy production by boilers, and especially road traffic, are the most important sources of nitrogen oxide emissions.

In the integrated model system the emissions of sulphur dioxide and nitrogen oxides in Finland are estimated on the basis of energy use and transport performance scenarios and on the basis of alternative emission control strategies (Savolainen and Tähtinen 1989; Savolainen and Tähtinen this Vol.). The energy use scenarios include also assumptions on the development of the production volumes of the process industry.

The main objective of the emission models of the HAKOMA system is to produce future emission estimates to be used as source terms to the atmospheric dispersion models and further in the forest soil and lake impact studies. In this way the model system can be used to study how various energy use and traffic scenarios and control strategies affect the development of emissions, deposition, and acidification of forest soils and lakes. To be used as source term, the emission estimates of the future should be distributed both geographically and according to effective emission heights.

Emission Model

The basis for the emission calculations for the stationary sources is a plant file made from the register of the Ministry of the Environment. It includes data from about 190 power and industrial plants (about 500 boilers) in Finland. The plant file has also data about the used fuels for each boiler in the reference year, which is presently 1986. The plant file is used to give the information needed for the geographical and elevational distributions of the emissions.

The emission model considers five energy use sectors which are: industry, electricity production, district heating, domestic heating, and transportation. The industry sector includes also more detailed information for some subsectors for the estimation of process emissions. These subsectors are: forest (pulp) industry, oil refining, basic metal industry, and basic chemical industry. The sector of electricity production consists of conventional condensation power plants only. The industry and district heating sectors produce also electricity which is accounted in the fuel use of the respective sectors. The domestic heating sector also considers the energy use of agriculture, forestry, and households. The fuels considered in the model are: heavy fuel oil, light fuel oil, diesel oil, gasoline, natural gas, hard coal, peat, waste liquors from the pulp industry, and others (mainly wood). Nuclear and hydro power have been accounted for in the energy balance.

Sulphur Emissions

The reference energy use scenario considered is based on the long-term prognosis of the Ministry of Trade and Industry (1988) (KTM, from the Finnish name of the ministry). In addition to this, two other scenarios have been developed (Savolainen and Tähtinen this Vol.). One assumes a high increase in the consumption of natural gas replacing mainly coal, and the other strong energy conservation measures in industry and space heating. The objective of these two scenarios is to explore the emission reduction potential which can be achieved with high increase in the use of natural gas and strict energy conservation. The model has also been used to study emissions from energy use scenarios assuming a slow economic growth (Savolainen and Tähtinen 1988).

In the calculation of the sulphur emissions in Finland, three alternative reduction strategies have been considered: no reduction measures as a theoretical reference to show the effectiveness of the reduction measures; reduction measures mandated by the Finnish government; and very strict measures to test the effect of the maximum reductions which can practically be achieved with the employment of the present control techniques. Figure 2 shows the total sulphur emissions in Finland for the three reduction strategies in the case of the reference (KTM) energy

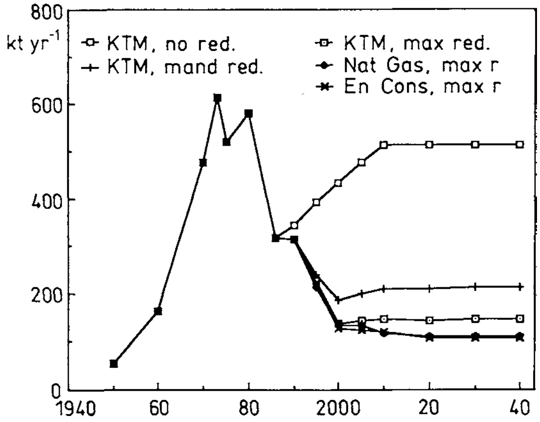

Fig. 2. Estimates for the future development of the sulphur emissions (kt SO_2 yr^{-1}) in Finland. Three reduction strategies (no reductions, mandated reduction measures, and maximum reduction measures) are shown for the reference (KTM) energy use scenario, one strategy (maximum reduction measures) for natural gas and energy conservation scenarios

use scenario, and the emissions for the maximum reduction strategy in the cases of natural gas and energy conservation scenarios.

Sulphur emission scenarios for other parts of Europe are mainly based on the information obtained from IIASA (Alcamo et al. 1987) and EMEP (Eliassen et al. 1988) (EMEP is an abbreviation for the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe). The estimates are based on data of the OECD International Energy Agency and the UN Economic Commission for Europe. Three control strategies were defined: no emission reductions; current reduction plans as announced by various countries (typically a reduction of 30–70% in each country compared to the emissions of 1980); and maximum reductions estimated by assuming that all potential emission reductions achievable with the present control technologies are realized but no measures are taken for energy conservation and fuel substitution. In the last case the reductions would typically be about 80 to 90%, varying from country to country. A summary of sulphur emissions in the considered scenarios both for Finland and for other parts of Europe is presented in Table 1.

Nitrogen Oxide Emissions

Transportation causes about half of the total nitrogen oxide emissions in Finland. The emission estimates for road traffic are based on traffic performance and emission factors. The vehicles have been divided on the basis of car and engine types into the following six groups: passenger cars (gasoline/diesel), vans (gasoline/diesel), buses (diesel), and trucks (diesel). Urban and highway driving are considered separately. For the geographical distribution of the traffic performance, a distribution by municipalities in Finland for the reference year has been formed

Table 1. Summary of the emissions of SO_2, NO_x, and NH_3 in the calculational scenarios considered (see text)

SO_2(kt yr^{-1})

Year/scenario	Finland	Other European countries
1980	590	54,000
1986	320	51,000 (1985)
2000/no reductions	430	55,000
/mandated reductions or current plans	190	44,000
/maximum reductions	140	11,000
/energy conservat., max. reds.	120	
/natural gas, max. reds.	120	

NO_x(kt NO_2 yr^{-1})

Year/scenario	Finland	Other European countries
1980	250	24,000
1986	240	26,000 (1985)
2000/no reductions	320	31,000
/assumed red. measures or current plans	240	23,000
/energy conservat., assumed meas.	210	
/natural gas, assumed meas.	220	

NH_3(kt yr^{-1})

Year/scenario	Finland	Other European countries
1980	45	12,000
1986	43	12,000 (1985)
2000/reference scenario	39	14,000
/reduction scenario	32	11,000

on the basis of information from the National Road and Waterways Authority (TVH). The prognosis of the traffic performance is based on the estimates by provinces made by TVH.

The estimates of nitrogen oxide emissions from boilers are based on fuel consumptions and emission factors which are assumed to depend on main fuel, burning technique, and size of the boilers. Two cases regarding emission reductions have been considered: no reductions as a theoretical reference; and assumed reduction measures which include mainly primary, although relatively strict, methods for existing and new boilers. Selective catalytic reduction is assumed to be required for big new coal-fired plants only. The assumed measures (Savolainen and Tähtinen this Vol.) are proposed by a state committee. For mobile sources, catalytic converters are assumed to be required in gasoline-fuelled passenger cars. Considerable reductions in the emission factors of trucks and buses are assumed, mainly to be reached with the development of engines. The total nitrogen oxide emissions in Finland are presented in Fig. 3 for the reference (KTM) energy use scenario with and without the assumed reduction measures, and for the natural gas and energy conservation scenario with the reduction measures. For road traffic, only one traffic performance scenario has been used. It is easy to apply the model to other scenarios assuming e.g. slow economic growth or strong increase of railway traffic, if data of these kinds of scenarios were available.

Nitrogen oxide emissions from the parts of Europe other than Finland will be described with the estimates obtained from the studies of IIASA and EMEP as in the case of sulphur dioxide emissions. A summary of the emissions in different scenarios is presented in Table 1.

Ammonia Emissions

Ammonia emissions originate mainly from agriculture. The most important sources are livestock manure and artificial fertilizers (Fig. 4). These sources are considered to be responsible for 90% or more of the anthropogenic ammonia emissions (Buijsman et al. 1986b). Fertilizer and ammonia production plants are industrial sources of atmospheric ammonia. The total industrial ammonia emissions are small compared to the agricultural emissions, but they can be significant locally. In Finland fur animals contribute considerably to the ammonia emissions, especially on the local scale in some municipalities in the western coast.

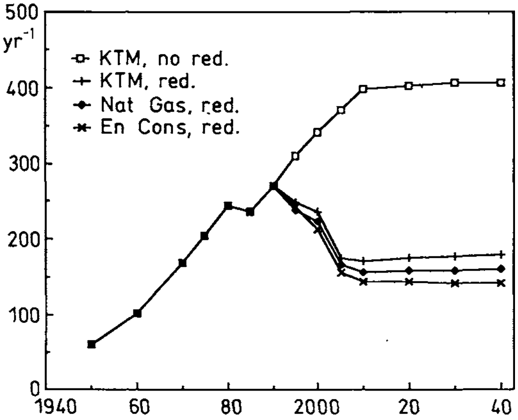

Fig. 3. Estimates for the future development of the nitrogen oxide emissions (kt NO_2 yr^{-1}) in Finland. Two strategies (no reductions, and assumed reduction measures) are shown for the reference (KTM) energy use scenario, one strategy (assumed reduction measures) for natural gas and energy conservation scenarios

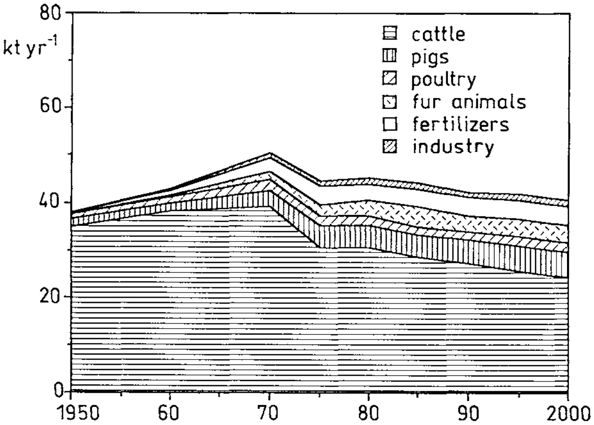

Fig. 4. Estimated development of ammonia emissions (kt NH_3 yr^{-1}) in Finland (reference scenario)

Emissions in Finland

Finnish ammonia emissions are estimated from municipal data for the reference year (1985) on the basis of animal numbers and industrial emissions. Estimates for the other years (1950–2040) are made using provincial correction factors assuming the emission sources to be distributed in the same way in the municipalities of the province considered as for the reference year.

Emissions from livestock manure are calculated for cattle, pigs and poultry. Keränen et al. (this Vol.) have estimated the Finnish agricultural ammonia emissions in the 1980's. In the model emission factors calculated on the basis of these estimates are used. Finnish ammonia emissions from the livestock manure are estimated to be about 30 kt of nitrogen (about 35 kt of ammonia) for the reference year.

In Finland mostly combined artificial fertilizers are used. The total amount of nitrogen sold in artificial fertilizers was 205 kt for the reference year. Using the emission factors given by Buijsman et al. (1986b) the emission would be about 1.5% of the nitrogen content, that is about 3 kt nitrogen (3.7 kt NH_3) in 1985.

In 1985 about 6.5 million furs were produced in Finland. Using an emission factor of 0.65 kg NH_3/fur produced, estimated on the basis of data given by Helin (1982), the total amount of ammonia emitted from fur farms is about 3.2 kt nitrogen (about 4.0 kt ammonia) for the reference year.

Data on industrial ammonia emissions were obtained from the Ministry of Environment. The industrial emissions in Finland were about 1.1 kt N (1.3 kt NH_3) in 1987. Emission data was available only for the year 1987. The emissions for the reference year were estimated to be the same as in 1987. Historical emission data (1950–1985) were taken from Buijsman's estimates (Buijsman 1986a) which are based on the ammonia and fertilizer production in Finland.

Two emission scenarios are used to describe future ammonia emissions in Finland. The reference scenario is based on forecasts made by a committee (Ministry of Agriculture 1987). The number of cattle is expected to decrease by

15%, the number of fur animals by 10% from the reference year to the year 2000. The numbers of pigs and poultry are assumed to increase by 15 and 20% respectively, and industrial emissions are assumed to remain the same as for the reference year. Emission factors are assumed to be same as for the reference year. The other scenario assumes all emissions to decrease by 25% from the values of the reference scenario (Table 1). The forecasts are made to the year 2000. In both scenarios emissions are assumed to be constant from 2000 to 2040.

Emissions in Other Countries

Data on emissions from other European countries for the period 1950–1980 were taken from estimates made by Buijsman (1986a). The emissions are estimated from statistical data (animal numbers, use of artificial fertilizers and industrial production of ammonia and fertilizers) by using emission factors. The emission data given by Buijsman was multiplied with a factor of 1.4 on his recommendation to avoid underestimation. Recent data on ammonia emission factors for livestock have been considerably higher than those used by Buijsman (Thomas et al. 1988). For the reference year data from EMEP (Eliassen et al. 1988) were used. These data are also based on Buijsman's estimates. The total emissions in Europe excluding Finland were about 12 Mt NH_3 in the year 1985.

Two scenarios are used also for the European countries other than Finland. The first scenario assumes that emissions in the EC and Nordic countries will remain constant and increase by 30% in the Eastern European countries by the year 2000. The total emissions would be about 14 Mt in 2000. The second scenario assumes that emissions in the EC and Nordic countries will decrease by 30% and remain constant in the Eastern European countries by the year 2000. The total emissions would be about 11 Mt in 2000. In both scenarios emissions after the year 2000 are constant (Table 1).

The scenarios are based on the information that there is agricultural overproduction in the EC and Nordic countries. Also, the emissions in many European countries are very high and abatement policies are expected. The Eastern European countries are not self-sufficient in their agricultural products and some increase in production can be expected (Csáki 1982). Also population growth in these countries is expected to be larger than in the EC and Nordic countries.

Atmospheric Processes and Deposition

Atmospheric processes of acidifying compounds, i.e. transport, transformation and deposition, are represented by source-receptor transfer matrices in HAKOMA. These matrices describe the strength of the atmospheric link between a source or a source area and deposition at certain locations due to that source. The transfer matrices are calculated using dispersion models, the application of which is described in this chapter.

Sulphur

Mesoscale Transport

The sulphur deposition due to the sources in Finland and nearby areas has been estimated using the mesoscale sulphur model developed at the Finnish Meteorological Institute (Nordlund et al. 1985b; Nordlund and Tuovinen 1988). The model is of hybrid type, i.e. it contains Eulerian (fixed coordinate framework), Lagrangian (moving coordinate framework) and statistical features.

The basic principle of the mesoscale sulphur model is to numerically solve the steady-state partial differential equation describing atmospheric dispersion of a gaseous pollutant emitted from a continuous point source, or the so-called K-theory equation of diffusion. Sulphur dioxide and particulate sulphate are the compounds modelled; they are connected by a first-order conversion rate. Dry deposition is included as a boundary condition for the diffusion equation, and wet deposition is treated as a first-order process determined by the scavenging coefficient.

For the calculation of long-term sulphur deposition, dispersion conditions are classified into a set of discrete events, for which the model equations are solved. The precalculated deposition distributions are then weighted according to their frequency of occurrence. The dispersion events consist of combinations of three stability classes, four wind speed classes, three precipitation classes, and four seasons which have different values for transformation and deposition parameters. The frequencies of these combinations were calculated in twelve wind direction classes from the synoptic meteorological observations over the period 1972–1981. For a detailed description of the model and values of the parameters, see Nordlund et al. (1985a) or Nordlund and Tuovinen (1988).

Originally, six effective emission height classes were used in the model. On the basis of sensitivity tests, it was concluded that in this application, only one source height is needed when farther than 100 km from the source. The source height has then only a marginal effect on the annual average deposition. Closer than 100 km three classes are used (below 50 m, 50–100 m and over 100 m).

The matrices describing the relation between SO_2 emission and sulphur deposition were calculated in 14 × 14 km grid squares for four climatological regions, i.e. for four different sets of frequencies of wind direction and dispersion events. The sulphur deposition field in Finland is formed by adding up the separate fields induced by 44 emission areas. The deposition fields for each emission area are obtained by scaling the transfer matrices of the fixed climatological region by the emission rate of the area considered and placing the field according to the location point of the area. Figure 5 gives the estimated sulphur deposition in 2000 due to

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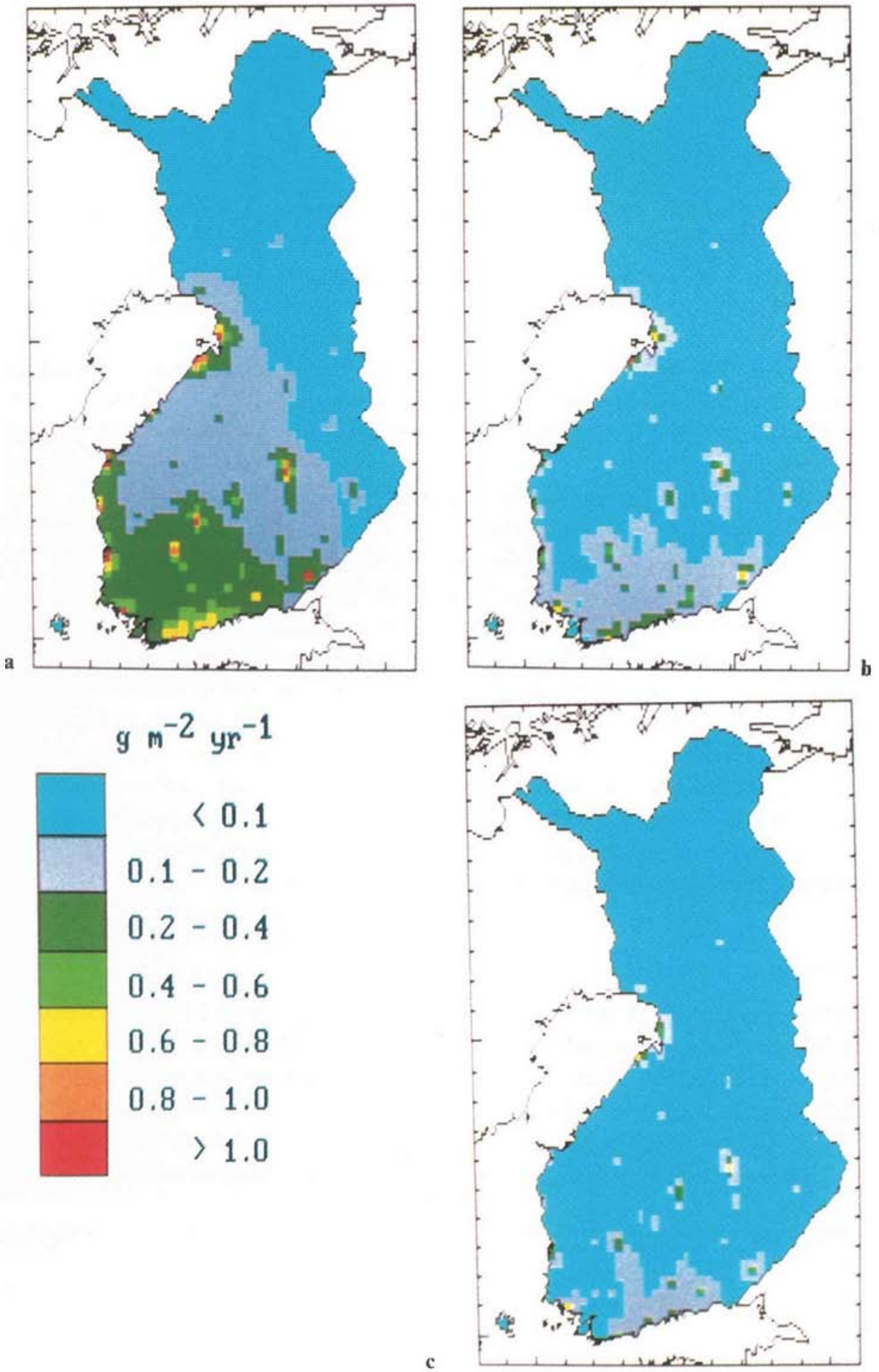
Fig. 5a–c. Estimated sulphur deposition (g m^{-2} yr^{-1}) due to the emission sources in Finland in the year 2000. The reference (KTM) energy use scenario. **a** with no emission reduction measures; **b** with mandated emission reduction measures; **c** with maximum emission reduction measures ▷


a
b
c
g m^{-2} yr^{-1}
< 0.1
0.1 - 0.2
0.2 - 0.4
0.4 - 0.6
0.6 - 0.8
0.8 - 1.0
> 1.0

emission sources in Finland for three emission scenarios. The deposition level due to Finnish sulphur sources is rather low in the cases which include emission reduction measures.

Long-Range Transport

The source-receptor relation for sulphur emitted far from Finland is calculated using the long-range transport (LRT) sulphur model of Western Meteorological Synthesizing Centre (MSC-W) of EMEP (Eliassen and Saltbones 1983; Eliassen et al. 1988). In the model, Europe is covered with a grid with squares of ca. 150 × 150 km, and the European countries are defined as source areas. Transfer matrices are obtained as country-to-grid deposition fields, so that the smallest emitter area that can be treated separately is a country.

For the present calculations, a modification of the model was applied (Tuovinen et al. this Vol.). In order to increase the spatial flexibility and the applicability of the scaling principle, the western parts of the Soviet Union were split into several source areas. Also new emission data were available from the regions of the Soviet Union nearby the Finnish border (Kulmala 1989).

The new division makes it possible to apply the mesoscale model in the regions of the USSR where detailed emission data are available. Assuming the Finnish meteorological data to be representative of the nearby regions of the Soviet Union, the finer scale features of the deposition pattern can be estimated. This is especially important in the northeastern Lapland where two isolated sources in the Kola Peninsula within 100 km from the Finnish border produce very high deposition maxima. Examples of the resulting deposition distribution under different emission scenarios are shown in Fig. 6 for the year 2000. The current reduction plans in Europe and in Finland seem to reduce the highest deposition values below 0.8 $\mathrm{g\,m^{-2}yr^{-1}}$ with the exception of some industrial areas.

Nitrogen

An Eulerian mesoscale dispersion model for nitrogen oxides is being developed at the Finnish Meteorological Institute (Tuovinen et al. 1989) which will be applied within the HAKOMA model system. At the moment, deposition of both oxidized and reduced nitrogen is calculated by FMI using the LRT nitrogen model of EMEP/MSC-W (Eliassen et al. 1988; Hov et al. 1988). The calculations presented by Tuovinen et al. (this Vol.) provide country-to-grid transfer matrices for the

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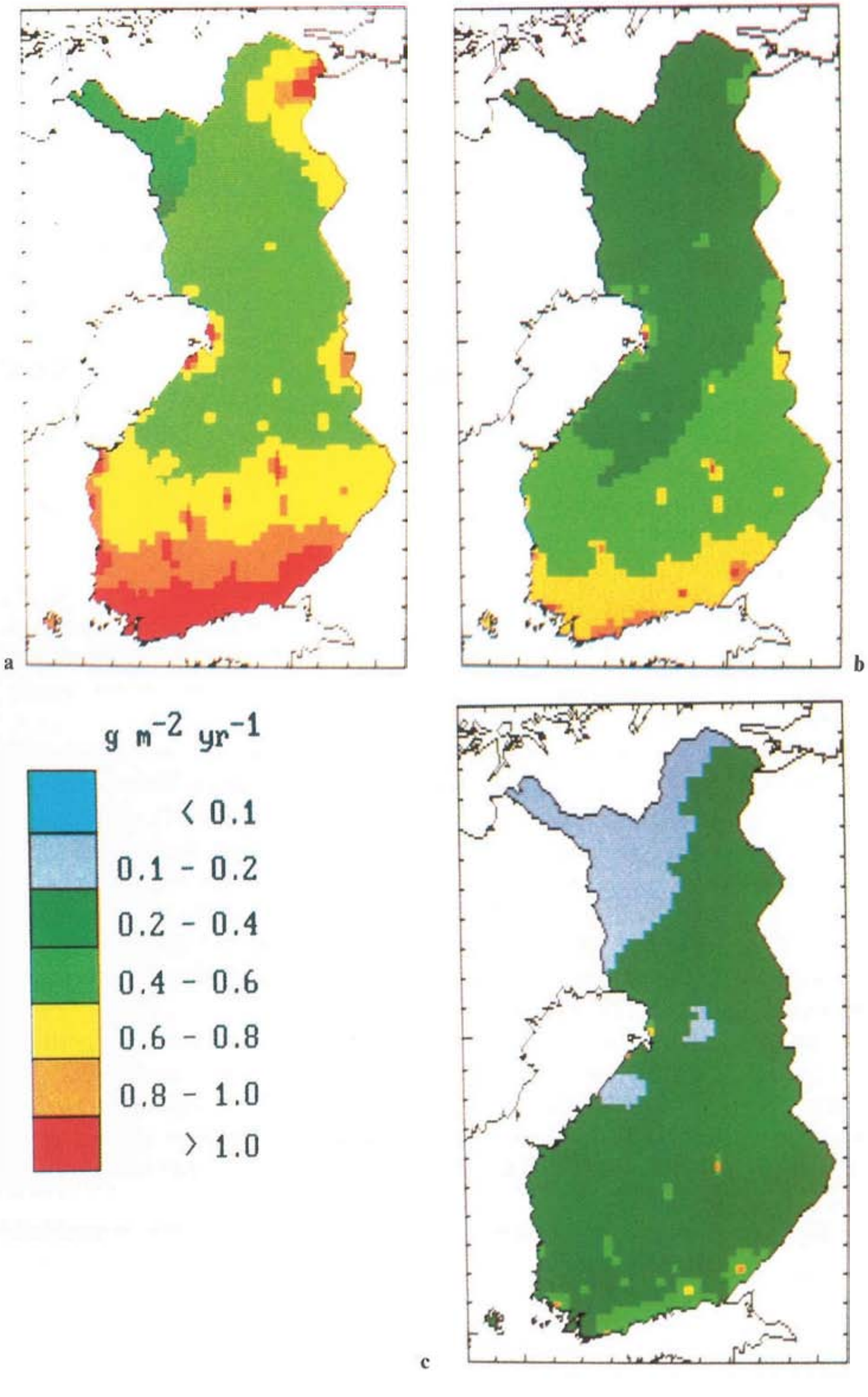
Fig. 6a–c. Estimated total sulphur deposition ($\mathrm{g\,m^{-2}\,yr^{-1}}$) in Finland in the year 2000. ▷ **a** No emission reduction measures. The reference (KTM) energy use scenario is used for Finland and "Official Energy Pathway" (Alcamo et al. 1987) for other European countries. **b** As above but the mandated emission reduction measures are applied for Finland and the current reduction plans for other countries. **c** As above but the maximum reduction measures are applied for Finland and the maximum feasible reductions for other countries (see text)


a
b
g m^{-2} yr^{-1}
< 0.1
0.1 - 0.2
0.2 - 0.4
0.4 - 0.6
0.6 - 0.8
0.8 - 1.0
> 1.0
c

countries in Europe for 1985. Calculations for one year are only available, but according to Tuovinen et al. (this Vol.), the year 1985 seems to be climatologically quite representative of average long-term weather conditions in the Northern Europe.

A first estimate for the source-to-grid matrices for ammonia was obtained by calculating the deposition caused by a single grid square in Finland. As the model in principle is non-linear due to the link between the chemistries of reduced and oxidized nitrogen, the matrix was estimated in an indirect way. Instead of using one emitter grid square, the emission value was set at zero in one square chosen as the source square. The deposition field calculated this way was subtracted from the field calculated with unaltered emissions, yielding the influence of one grid square emission. The atmospheric models for nitrogen, however, are not yet operational in the HAKOMA framework.

Impacts on Forest Soil

Soil Model

The buffer range concept presented by Ulrich (1983) is used in the soil model. In Finland, however, the soils are mostly in the cation buffer range. The soils start to shift to the aluminium range in low base saturation values. In this case, base cation nutrients are scarce and the vitality of forests is affected.

The forest soil model was originally developed by IIASA for the RAINS code (Kauppi et al. 1986). The time span in the application is 50 years. The calculations are made in a grid of 1/4 degrees (longitude) × 1/8 degrees (latitude), which makes about 14 × 14 km in Southern Finland close to the latitude of 60 degrees. At present, only sulphur deposition can be used as acid input term in the model. Later, depositions caused by NO_x and NH_3 emissions will be included. The soil model itself will be replaced in the near future with a more detailed model, which in addition considers, e.g. the weathering of aluminium hydroxides and other processes described later (De Vries et al. 1989b).

The most important factors considered in the soil model are the H^+ deposition (calculated on the basis of sulphur emissions and atmospheric processes), base cation deposition, depletion of the base cation inventory through outflow with sulphate ions and harvesting of tree stems, and supply of base cations from weathering of minerals. The soil model is described in more detail by Johansson and Savolainen (this Vol.).

The geographical distribution of base cation deposition is based on measurements from 38 stations over a 10-year period. The samples consist of bulk deposition. The values of calcium, magnesium, sodium, and potassium are summed and the effect of chloride of sea salt subtracted. However, a considerable fraction of the resulting base cation deposition might be either internal circulation in the forest ecosystem or insoluble, thus not participating in the buffering process.

The dry deposition consists of relatively large particles, for which the atmospheric transport distance is limited (Anttila this Vol.). Therefore, the amount of wet deposition is assumed here as a level of an external source to the system considered. It was estimated on the basis of measurements of the Finnish Meteorological Institute that the fraction of wet deposition is about 30–50% of the bulk deposition. An estimate of 30% has been taken as the effective external base cation deposition. However, it has been realized that further research is needed on this topic.

The geographical distribution of the production of base cations due to the weathering of minerals is described with the mineral composition of the bedrock. The absolute level of the supply of base cations due to weathering is scaled with the catchment wide testing of lake model against the diatom analysis of the lake sediments (Kämäri et al. in press).

The base cation contents of forest soils are estimated on the basis of forest site types. Data for determining the base cation inventory in different site types has been provided by the Finnish Forest Research Institute. The values used in the soil model have been calculated from the results of an intensive survey covering southern and central Finland. Three base cation classes were selected for the test runs. The classes represent rich and poor mineral soils and peat lands. The soil layer thickness considered is 50 cm including humus for mineral lands and 20 cm for peat lands. The geographical distribution of the base cation classes is computed on the basis of forest site type distributions from the Seventh National Forest Survey conducted in 1977–1984.

The removal of base cations from soil due to net accumulation in stems and their loss through harvesting is included in the model. The net uptake of base cations by stem and bark is taken into consideration as a function of forest site types and the effective temperature sum. The effective temperature sum can be assumed to be linearly dependent on the latitude. Based on information of the Seventh National Forest Survey, separate latitude-dependent values for all three base cation classes are used to describe the loss of base cations via harvesting.

Simulation Results

Figure 7 shows the result of a test simulation in the year 2040 of the soil model. The map indicates where more than 20% of the forested area of a grid cell has a base saturation value below the value given in the legend. The sulphur emissions considered in the calculation assume the current reduction plans which various countries have announced. These plans include measures to be passed before the year 2000, after which the emissions are assumed to remain constant. Below the base saturation of 5% it can be estimated that buffering of acid deposition is shifting to the aluminium range. By then the health of the forest is likely to be affected due to increase of soluble aluminium in soil solution and nutritional disturbances. The most affected areas according to the simulation are in the areas

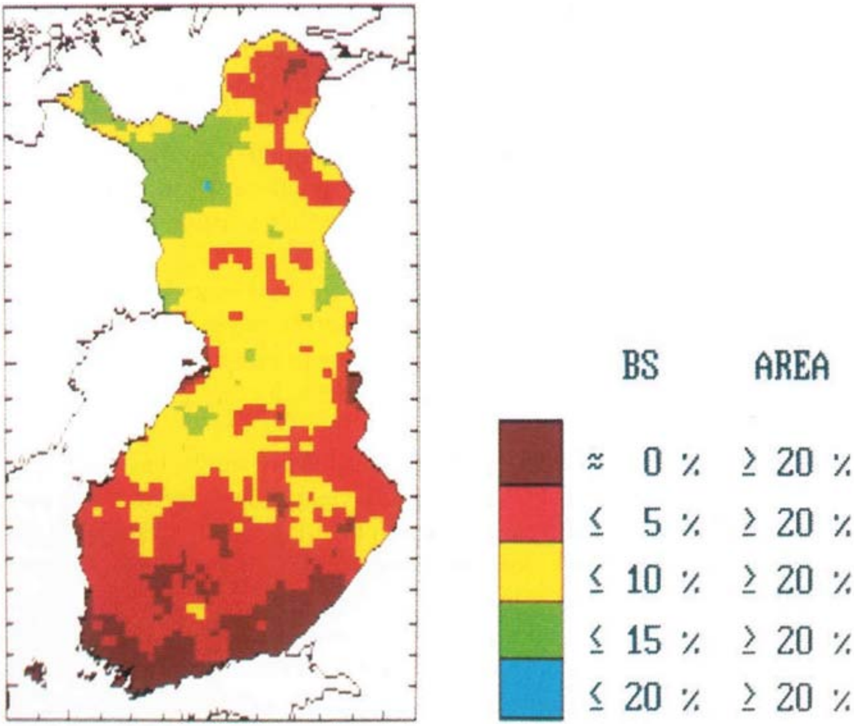


Fig. 7. Result of the soil model simulation showing the areas in 2040 where over 20% of the forest soils have a base saturation value lower than the value indicated in the legend. Emissions in Finland base on the reference (KTM) energy use scenario with the mandated reduction measures. Emissions in other countries correspond to the current reduction plans

of high deposition in the south and southeast and to some extent on soils where the base cation content is small, like in the north, and where the weathering rate is low.

Preliminary results of different emission scenarios are compared in Fig. 8 in respect to forest soil acidification. The criterion considered is the percentage of total forested area below the base saturation level of 5%. In the theoretical case of no sulphur emission reductions, practically all forests seem to acidify relatively rapidly. In the case of current reduction plans both for Finland and for other European countries still a large fraction of forest soils in Finland would continue to acidify. If emissions were strictly reduced in Finland with maximum practical control measures and even with strong energy conservation, the area of base saturation below 5% would diminish by about 10% compared to the case of the current reduction plans. A considerable change would be reached if maximum reductions were performed in the other countries also. The model tests (Johansson and Savolainen this Vol.) have shown, however, that the results are sensitive to variations in parameter values. The uncertainties of many important parameters, like base cation deposition and weathering rate, are large. Therefore, the preliminary results should be considered with caution and as of a relative nature.

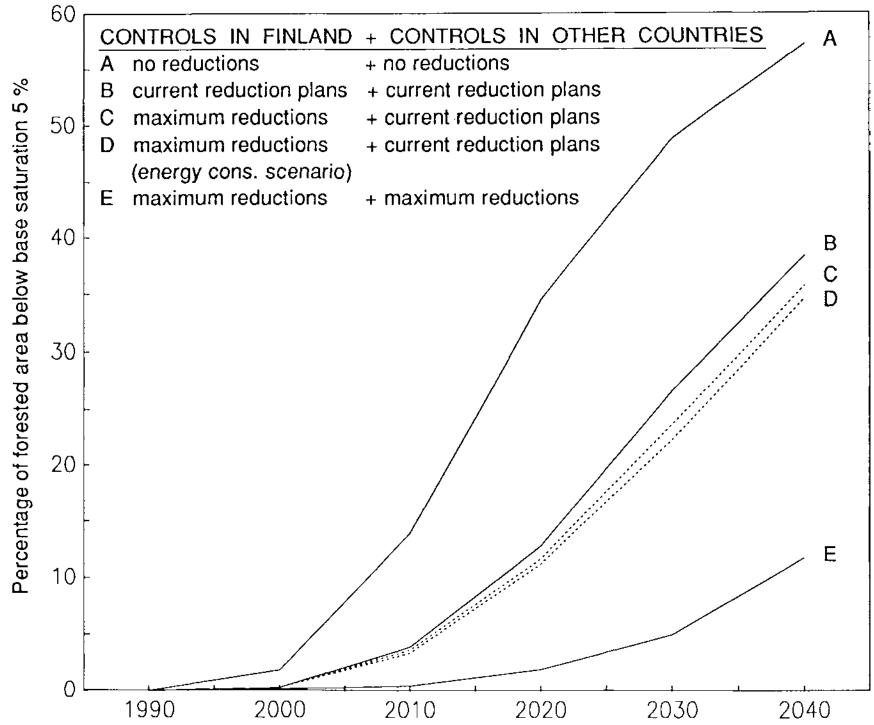


Fig. 8. Estimated temporal development for the percentage of the total forested area in Finland below the base saturation of 5%. Five combinations of emission scenarios for Finland and the other countries have been considered. For Finland the reference (KTM) energy use scenario has been used in four cases, and the energy conservation scenario in one case

Impacts on Lakes

The SMART Model

An acidification model, termed the Simulation Model for Acidification's Regional Trends (SMART), has recently been developed in order to estimate long-term chemical changes in soil, soil water as well as surface water in response to changes in atmospheric deposition (De Vries et al. 1989b). This model is later on intended to replace the RAINS Soil Module used above as it has a more detailed description of soil processes. As a first step the model is applied to regional lake data as part of HAKOMA.

Apart from net uptake and net immobilization of nitrogen, the processes accounted for in SMART are restricted to geochemical interactions, including weathering of carbonates, silicates and aluminium hydroxides, sulphate adsorption, cation exchange and CO_2 equilibria. The model structure is based on the anion mobility concept and incorporates the charge balance principle (Reuss et al.

1986). State variables depict the quantities of chemical constituents in minerals (carbonates, silicates and hydroxides) and on the exchange complex, as well as the ion concentrations in the soil solution. Rate variables depict the processes influencing state variables. These include the net input of elements and water and various neutralizing reactions, i.e. the dissolution (weathering) of carbonates, silicates and aluminium hydroxides, and cation exchange.

SMART includes the effects of natural soil acidification due to dissociation of CO_2 and the impact of the deposition due to SO_2, NO_x and NH_3 emissions. Sulphate adsorption may not be quantitatively significant in Finnish surface soils, but on a catchment scale the low SO_4^{2-} concentrations in some acidified lakes suggest significant SO_4^{2-} adsorption. Therefore, sulphate adsorption was incorporated to SMART even though it was not part of the calculations in the first versions of the model (cf. De Vries et al. 1989b). SMART is designed so that it can easily be applied for estimating long-term development of soils and stream waters as well as lakes on a large regional scale. The model predicts the major components of the soil solution and surface water, i.e. H^+, Al^{3+}, BC^{2+}, NH_4^+, NO_3^-, SO_4^{2-} and HCO_3^-. BC^{2+} represents the sum of divalent base cations.

Table 2 shows which ions are included in which processes. The concentrations of ions in soil solution are generally controlled by the input of elements into the soil and chemical interaction within the soil (e.g. sulphate adsorption, weathering and cation exchange). The HCO_3^- concentration is based on an equilibrium approach with CO_2 and regulated by both the CO_2 pressure and the pH. The precipitation surplus affects all ion concentrations. Atmospheric deposition, net removal of N and BC^{2+} by uptake and immobilization and net release of BC^{2+} by silicate weathering are not described by processes, but are required as input to the model. Apart from silicate weathering, all neutralization reactions are described by equilibrium reactions. The equilibrium reactions included play a role in specific buffer ranges as defined by Ulrich (1983).

A complete overview of the various soil process formulations, including the initialization procedure and the solution methods in the soil part of SMART are described by De Vries et al. (1989a, b). The application of SMART to individual

Table 2. Overview of the ions included in the processes in SMART

Process	H^+	Al^{3+}	BC^{2+}	NH_4^+	NO_3^-	SO_4^{2-}	HCO_3^-
Atmospheric deposition	+	–	+	+	+	+	–
Sulphate adsorption	–	–	–	–	–	+	–
Uptake	+	–	+	+	+	–	–
Immobilization	+	–	–	+	+	–	–
Nitrification	+	–	–	+	+	–	–
Dissociation	+	–	–	–	–	–	+
Carbonate weathering	+	–	+	–	–	–	–
Silicate weathering	+	+	+	–	–	–	–
Al hydroxide weathering	+	+	–	–	–	–	–
Cation exchange	+	+	+	–	–	–	–

+ : ion included in the respective process; – : ion not included.

lakes, testing of the model against palaeolimnological diatom data, as well as the complete description of the regional model application to Finnish lake regions will be described in forthcoming scientific papers.

Regional Application as Part of HAKOMA

The data available on a large regional scale are characterized by a high degree of heterogeneity and generalization. Even though the actual measurements would be reliable and the measurement error would be small, the observations are still only samples of the systems under consideration. A method called the Monte Carlo Filter Procedure (MCFP) is used for regional calibration. Model parameters and variables having uncertainty are assigned frequency distributions. In the regional application, besides the uncertain parameters, also parameters that exhibit spatial variability are randomized within feasible a priori ranges. The criteria for accepting or rejecting model postdictions, and thus parameter vectors used, are based on a synoptic survey of lake chemistry. The accepted Monte Carlo runs produce a set of theoretical lakes which are assumed to be representative for that region (Kämäri and Posch 1987). Regional lake acidification scenarios are then constructed by running the model for the desired deposition scenario once with each of the accepted parameter set.

The basic water quality data for constraining the output is provided by the statistical survey of 984 lakes conducted in fall 1987 (Forsius et al. this Vol.). The lakes for the survey were chosen by random sampling and the selection was weighted by lake density. The water quality of the surveyed lakes can thus be considered as representative for the approximately 56,000 lakes with surface areas between 0.01 and 10 km^2 in Finland. The joint distributions that the model is expected to meet include chemical elements, alkalinity, SO_4^{2-} and BC^{2+}.

The major driving variables (source terms) are the atmospheric deposition patterns of SO_2, NO_x and NH_3, which have to be estimated for all regions considered. Spatial variation of these patterns within the regions considered cannot be avoided. Therefore, parallel deposition time developments are drawn randomly from designated present deposition distributions, given by the atmospheric transport models for the region under consideration.

All the soil information needed by the model is extracted from the data used by the soil model described previously. Weathering rate of base cations, total cation exchange capacity, base saturation and net uptake of base cations are assigned distribution according to the grid-based data that the soil model uses.

The third major source of input information is the statistical lake survey itself. Distributions for the partial CO_2 pressure in surface water and the solubility constant for inorganic aluminium are estimated from the results of the survey. Moreover the measured total organic carbon concentrations are used in calculating the organic anion contributions.

The remaining influential model inputs are assigned wide rectangular distributions so that any reasonable value can be selected. The objective is to enable any combination of inputs needed for fitting the five marginal output distributions simultaneously. The maximum sulphate adsorption capacity as well as the half-saturation constant belong to this group. All other inputs, such as equilibrium and dissociation constants, are assigned realistic constant values.

The output of the application of SMART to Finnish lake data will consist of regional estimates of the time development of acidification in Finnish lakes. In practice this means lake acidity or alkalinity distributions as functions of time, or, fractions of lakes violating some predetermined criteria in the future. At the moment, the regional application of the SMART model is at a testing phase and no model results are shown in this chapter.

Discussion and Conclusion

The assessment of impacts of acidifying emissions to forest soils and lakes includes uncertainty in various phases of the study. First, the emission estimates contain inaccuracy for the future, and even for the presentday situation. Sulphur emissions for a given energy use can be estimated on the basis of fuel sulphur contents and emission controls or control limits relatively well. The nitrogen oxide emission estimates base on emission factors which have relatively great uncertainty due to different burning techniques and burning conditions. This concerns both stationary emission sources, like energy production plants and industrial plants, and mobile sources. For future emission estimates, however, energy demand and how it will be fulfilled, volume of the production in the processing industry, development of the transportation sector, and reduction measures will probably make major contributions to the uncertainty of the development of emissions. The uncertainty involved in these activities has been covered at least to some extent with various energy use scenarios and alternative emission reduction strategies considered.

Ammonia emissions are estimated on the basis of emission factors which probably have relatively great uncertainty. The factor values used are totally based on measurements in central Europe, where at least the climatological conditions are different from Finland.

Concerning atmospheric dispersion, transformation and deposition, validations of the models in general exist. The results of the atmospheric models are in relatively good agreement with the measurements. Possible discrepancies can often be explained by the inaccuracy of emissions and local effects which are beyond the resolution of the models. However, the linearity between emissions and deposition assumed in the models may become questionable in situations where considerable emission reductions have been made. In the long term, reviews of model parameters and the validation of the models under Finnish conditions could improve the reliability of the applied atmospheric models.

Soil and lake models apparently contain relatively large uncertainty. The data describing soil properties still base on a quite small number of samples. The soil model has been tested against measured values over a longer period of time in only few cases (Posch et al. 1989). Some important parameters like effective external base cation deposition and production of new base cations through weathering of minerals are inaccurately known. Validation of the impact models with measurement data covering a period of several years or decades is greatly desirable. The lake model has been tested against data describing lake pH histories obtained with diatom analyses of lake sediments and reasonable agreement of model results and measurements has been found (Kämäri et al. in press). This gives also some validation to the soil model which has been used as a part of the lake model in the description of the catchment. In model tests the soil model was found to be relatively sensitive to changes in the parameter values. To obtain more information about the reliability of the model results and about the contribution of various factors to the uncertainty, statistical uncertainty analyses could be made.

One result of the integrated modelling work is the identification of factors causing uncertainty to the model output and to the assessment in general. In the modelling of impacts, these factors include e.g. uncertainty concerning effective external base cation deposition and production of cations by weathering. Similar factors causing uncertainty can be listed from the other parts of the model system, e.g. energy use forecasts, and transformation and deposition parameters.

The results of the preliminary simulations with the model system suggest that the emission reduction plans announced by various European countries are not sufficient to prevent acidification of the forest soils in Finland. If Finland alone would reduce the emissions with the maximum practical measures and the other countries would follow their present plans, the acidification would only be slightly slower. A considerable change (see Fig. 8) could be reached if all countries contributing significantly to the deposition in Finland strictly reduced their emissions.

The HAKOMA model system can be used to study the effect of various energy use and traffic scenarios and emission reduction strategies in different phases of the chain leading to acidification. These kinds of phases are, e.g. emissions, deposition, and impacts on forest soils and lakes. Also estimates of the possible extent and time scale of the impacts can be obtained. Possible critical areas which have unfavourable combinations of contributing factors can be identified from the simulation results. Integrated assessment can be used as a tool in analysing and planning the emission reduction strategies. As the model system is under development the results are preliminary and further effort is needed to improve their reliability. Work is under way to complete the model system with atmospheric models of nitrogen oxide and ammonia emissions and with the cost models of emission reductions.

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Evaluation of Finnish Sulphur Reduction Strategies for the Year 1995

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Summary

When selecting the installations which should reduce their sulphur releases to achieve internationally agreed emission reduction goals, one possible criterion is the minimization of total reduction costs when simultaneously the deposition is limited below a certain value. In this work possible sulphur emission reduction alternatives are studied for the target year 1995, with a cost optimization model connected to a medium range sulphur transport model. By varying the maximum allowed annual deposition caused by domestic sources in a range of 500 to 150 mg m^{-2}, we compared the official sulphur reduction plans to the purely optimized ones, and studied the effects of individual emission variations on the deposition distributions. We found out that if, instead of the official target (total emission reduction), we select the deposition and reduction costs as criterion where the sulphur emissions have to be reduced, we attain less expensive solutions with bigger emission reductions.

Introduction

General Background

In a Scandinavian joint co-operation study (Nilsson 1986) it was estimated that the maximum annual sulphur load the northern coniferous forests are able to bear without significant damage is 200–400 mg sulphur per m^2. Corresponding limits for lakes have not been presented. However, the critical load for them obviously cannot be higher, because many lakes in sensitive areas are already dying as a result of slightly higher deposition values. The above values have been exceeded in most parts of Finland. According to recent model calculations (Iversen et al. 1989), along the southern coast the annual deposition of long-range transported sulphur alone exceeded 1 g m^{-2} (year 1985).

Most European countries have agreed to cut the sulphur emissions by 30% from the 1980 level before 1993. In Finland this goal was set even tighter because the 1980 sulphur emissions were exceptionally high, and the 30% reduction had already been reached, mostly for other than environmental reasons. The Ministry

Kauppi et al. (Eds).
Acidification in Finland

of the Environment appointed the so-called Sulphur Committee to establish a programme for sulphur emission reduction by at least 50% from the 1980 level before the end of the century. When planning its proposals the Committee was to take into account all the technical alternatives, and compare the economic and air quality consequences of the actions. In order to support this evaluation process, a research project "Economically efficient ways for sulphur emission reductions" was set up at the Air Quality Department of the Finnish Meteorological Institute (FMI). Its work and results have been published earlier in (Hongisto et al. 1988).

The Aim of the Study

The objective of this work was to identify which Finnish installations should reduce their sulphur emissions, and by how much before the year 1995, while: (a) the domestic sulphur deposition is constrained to be below certain selected upper limits, and (b) the total reduction costs are at the same time minimized. This was done by connecting an optimization model to the medium-range sulphur transport model developed at the FMI (Nordlund et al. 1985). Thus the effects of individual emission variations on the deposition distribution could be studied.

A complete economic examination would also require knowledge of damage costs, but the available data are insufficient and inconsistent. The only economic factors considered in this study are the estimated expenditures per reduced ton of sulphur for different control measures suitable to individual installations.

This study was mainly carried out in 1986 (although it has been reported later), and at that time the air pollutant emission register of the Ministry of the Environment was under development and thus not available. Therefore the emission scenarios had to be constructed differently than is done in the HAKOMA model project (Johansson M. et al. this Vol.). Moreover, some decisions regarding the energy plant construction and process modifications had not yet been reached, which led to some differences in the calculated sulphur deposition patterns of the two projects.

Calculation Method

The Medium-Range Transport Model for Sulphur

The areal distribution of sulphur deposition was calculated by the EPAK medium range sulphur transport model (Nordlund et al. 1985). In this model concentrations near the source are assumed to follow the Gaussian plume distribution formula with an average wind direction rose. At a distance depending on meteorological stability, the vertical concentration profile is calculated with the K-theory of atmospheric diffusion, and the horizontal distribution is assumed to be uniform inside each calculation sector. The model includes the SO_2 to sulphate transformation, dry deposition as a boundary condition, and scavenging by wet deposition.

Meteorological situations are broken down into three stability classes, four wind speed classes, and three precipitation intensity classes. The deposition figures for a unit source are calculated first, using some seasonally averaged parameters. These precalculated deposition figures are then weighted for real individual sources according to the occurrence of different weather conditions, the intensity of the source and the effective release heights.

The computed elementary deposition matrices were used to calculate the unit distribution schemes for two types of reference installations in four meteorologically different areas in Finland (describing 10-year average weather situations). The sulphur deposition from sources located in different parts of Finland was calculated by replacing the actual source by the unit matrix corresponding to the source type and the meteorological zone, scaling the emissions and interpolating the calculated deposition in the selected grid. In our model, the sources are further divided into background installations with fixed emissions, and big polluting units compelled to control their discharges.

The Optimization Model

The structure of the optimization model is the following:

Let a_{ij} = the deposition of unit source i in grid point j,
p_i = the actual annual emission of installation i,
$pmax_i$ = the maximum emission of source i without reductions,
$pmin_i$ = the minimum possible emission with the selected purification system,
B_j = the maximum allowed deposition in point j,
BG_j = the deposition caused by background pollution sources,
N = the number of emission sources,
M = the number of deposition grid points,
c_i = the cost per reduced ton of sulphur for source i.

The optimization was done by simultaneously limiting the sulphur deposition and minimizing the sum of total sulphur reduction costs:

$$\sum_{i=1}^{N} [c_i * (pmax_i - p_i)] = \min! \qquad \text{when}$$

$$\sum_{i=1}^{N} [a_{ij} * p_i] \qquad \leq B_j - BG_j, \quad j = 1 \ldots M, \quad \text{and}$$

$$pmin_i < p_i < pmax_i.$$

The deposition limits cover an area of 700 × 750 km^2. However, grid points located very far beyond the Finnish borders were excluded. The distance between the grid points was basically 60 km. Near the sources the grid was tightened, so that at a distance of 20 km every installation was surrounded by grid points separated by 10–15 km. At distances closer than 20 km to the optimized sources and 10 km to the background sources, the deposition limits were not enforced. In some cases the locations of minor sources were corrected to ensure that the limitation matrix covers the area uniformly enough.

The unit costs per reduced sulphur ton c_i were calculated by converting the total investment I_i for installation i into annual costs by the annuity method, and separating the annual fixed costs CF_i and variable costs CV_i. Thus, if the real interest rate is r, the amortizing period T, and the annuity factor AN_{rT}, we have

$$AN_{rT} = [r^*(1 + r)^T]/[(1 + r)^{(T-1)} - 1], \text{ and}$$

$$c_i = AN_{rT} * I_i + CF_i + CV_i * [pmax_i - p_i], \quad \text{if } p_i < pmax_i,$$

$$c_i \quad = 0, \qquad \text{if } p_i = pmax_i.$$

The presented cost function is non-linear in the capacity factor of the installation, and discontinuous at the point where the capacity factor becomes unity and c_i drops to zero. Consequently, when examining the optimization results, one must ensure that the solution is global and not a local optimum point.

In order to compare the effect of objective function formula on the results, we used a linearized version of the model, where the objective function coefficients were constant (e.g. individual costs were directly proportional to the reduced sulphur amount), and the cost parameters were calculated using some fixed capacity, (e.g. 90%). The results of the linear and non-linear model runs were different; the former yields less expensive results, because in the linear model some sulphur reduction can be achieved without paying the whole investment cost, when the plants are operating at a low capacity factor.

The optimization was done using the MINOS optimization programming package (Murtagh et al. 1983). The installation of the optimization system into the FMI's Cyber-170/730 caused some modelling problems because the computer could not handle very large matrices. Usually linear programming matrices are very sparse; in this work the density of the matrix was almost one. Several less remarkable sources were therefore included in the fixed background load and the grid was made less dense.

Emission Scenarios

The data for the required model inputs were collected from the official statistics and reports of the Ministry of Trade and Industry and the Ministry of the Environment, from reports prepared for the Sulphur Committee, from air quality surveys of the FMI, from energy production scenarios and statistics of several private, communal and national societies or planning organizations, from energy-producing companies and from air quality announcements of individual installations made for the provincial authorities.

The 1995 sulphur emissions were estimated separately for individual point sources. Here, one point source means, e.g. all the small district or areal heating plant emissions for a specific town. The biggest polluting units were treated individually. For industrial sources we estimated the output volume and the development of unit releases and process modification possibilities. For energy-producing plants it was also necessary to estimate the building of new capacity, and the loading order of different types of power plants using alternative fuels.

For the energy-producing units, the yearly sulphur emissions $P(SO_2)$ were calculated according to the formula:

$$P(SO_2) = 2*s*k*E/th,$$

where s is the sulphur content in weight percent and th the thermal heat content (MWh/t) of the fuel; E is the used fuel amount and k is a coefficient indicating how much of the sulphur is released into the atmosphere and how much remains in the ash. The sulphur content of heavy fuel oil was staggered according to suggestions made by the Sulphur Committee: 1% maximum in the heavily polluted southern areas, 2.7% in other parts of Finland, and 3% for the large installations, in which sulphur control measures could be expected to be enforced. The sulphur content of coal was assumed to be 1%, which is somewhat higher than the average sulphur content in the coal used in Finland during the 1980's.

The base for small background source emission estimates was mainly fuel use statistics from the year 1984. These had to be extrapolated to the year 1995 by using available district heating and electricity production construction and planning schemes. Some district heating co-generating plants were assumed to produce condensed steam electricity if the plant type was suitable, and the heating load was not big enough for base load operation. The available electricity consumption estimates for the year 1995 varied between 61 TWh_e (the Ministry of Trade and Industry) and 66 TWh_e (electricity producing companies). If the difference is produced in a coal-fired power station it means about 32,400 t SO_2 yearly emission (with 2% heavy oil of S-3%). We supposed the electricity demand to be 63 TWh, which was assumed to be generated by district heating power plants (8.6 TWh), water power (12.5 TWh), import (4 TWh), industry back power installations (7.8 TWh), nuclear power (2.3 TWh), and the rest by condensed power. This means two new 500 MW_e coal and two 150 MW_e peat condensed power stations. Several new district heating plants were also included.

In most cases, the process emissions also included the sulphur releases from the industry back power production. The estimates for industrial boilers are based on air quality reports made for local authorities by the companies themselves. When calculating the maximum potential process emissions, many sulphur-reducing control measures or process modifications were known to take place by the end of the 1980's in any case; hence, their costs were not included in the model. After these reductions the specific emissions for the pulp industry were mostly under 6.5 t SO_2 per ton of product, and in some cases under 3 t SO_2 t^{-1} of pulp. For some industry boilers we assumed that the increased natural gas use cuts down almost all the emissions. For other industrial process emissions we used mainly estimates published in the series of the Ministry of the Environment.

For most of the installations fuel changes towards cleaner or domestic energy sources were assumed to take place, at least in some scale. The use of heavy oil as supporting material in combustion was also restricted to 1–10%, depending on the boiler and the primary fuel type.

Since the considered time range was less than 10 years, we built only one emission scenario which is the upper limit of the emissions. In the model the total domestic sulphur emission estimate for the year 1995 varies between 110,000–375,000 t SO_2, of which 41,000–303,000 t SO_2 comes from the optimized sources. The lower figure gives the emission amount attainable if all reductions taken into the optimization are used, the upper limit gives the emissions without any preventive actions. The Sulphur Committee's emission potential estimate for the year 1993 without any extensive reduction measures is 335,000–365,000 t SO_2 with 2.4/0.8% oil/coal sulphur content, and 365,000–455,000 t for 3/1.2% oil/coal S-content (Rikkitoimikunnan mietintö 1986). Our model estimate of 375,000 t fits within these limits. It is possible that all the sources are not included in our calculations, e.g. the areal distribution of heavy fuel oil use, estimated to cause 90,000 t SO_2 yearly emissions by the Sulphur Committee, was not known exactly, and the light fuel and diesel oil use (20,000 t SO_2 1993) was not included either.

Sulphur Reduction Techniques and Costs

Sulphur emission reductions were assumed to be achieved by fuel switching, process modifications to cycle and purify collected gases, or by flue gas desulphurization techniques. For industrial processes the costs were estimated from gas purification costs of general combustion, and scaled according to the pollutant emission amounts; furthermore, the gas collection system costs were added.

For most of the installations the costs correspond to the semi-wet scrubbers. In some of the cost alternatives cheaper but less efficient injection methods and fluidized bed burners were used. Some typical examples of the cost structure assumed for different types of units are shown in Table 1 and Fig. 1.

Optimization Alternatives

Because optimization models are quite a rough approximation of the reality, numerical answers alone cannot give exact solutions to the imposed real problems. Optimization models are best suited to "what-if" types of problems: e.g. comparison of different alternatives, or sensitivity analysis done by changing the initial conditions. We have constructed two main optimization alternatives: free optimization, case A, and Sulphur Committee restricted, case B. The Sulphur Committee suggested the control measures using an average marginal cost curve, in case B we take also the maximum permitted deposition as a limit. We optimize only domestic emission control alternatives, which means that the long-range transported sulphur load is not included in the deposition limits. The alternatives are:

Table 1. Cost structure for some typical installations

I = investment cost, Mmk (Finnish Marks, 4.5 Fmk ≈1 $)
F = other fixed costs, Mmk y^{-1}
FXy = total fixed costs, Mmk y^{-1}, calculated with r = 8%, T = 15y
VA = variable costs per reduced 1000 t of SO_2
MAX = maximum reduction amount, 1000 t of SO_2
MC1 = marginal reduction cost, mk per 1000 t SO_2, 100% operating capacity
MC2 = same as MCl with 90% capacity factor
MC3 = same as MCl with 50% capacity factor
HDS = semi-wet scrubber cost structure
SCT = sulphur committee alternative cost structure

Plant	I Mmk	F Mmky^{-1}	FXy Mmky^{-1}	VA kmkt^{-1}	MAX 1000t	MC1 mkt^{-1}	MC2 mkt^{-1}	MC3 mkt^{-1}
1, HDS	90	3.5	14.1	1.15	8.55	2790	2970	4430
2, HDS	380	12.0	56.4	1.15	30.6	2990	3200	4840
2, SCT	220	5.6	31.3	1.00	30.6	2020	2140	3050
3, SCT	205	6.7	30.7	1.15	18.0	2850	3040	4560
4, SCT	60	2.4	9.4	1.00	2.7	4490	4880	7980
5, HDS	50	1.9	7.7	1.15	3.4	3410	3670	5680
5, SCT	35	1.0	5.1	1.00	3.4	2490	2650	3980
6, SCT	60	2.4	9.4	1.50	2.6	5060	5460	8630
7, SCT	150	5.1	22.6	1.50	9.6	3860	4120	6213

Plant 1: old coal using district heating plant; 2: old coal using condensation (power generating) plant; 3: same as plant 2, new plant; 4: peat using district heating plant; 5: fluidized bed district heating plant; 6: small pulp process plant; 7: large pulp process plant.

A Free optimization case study:

A1 background emissions were not included; just semi-wet scrubbing techniques allowed, cost parameters r = 8%, T = 15 y, deposition in all grid points limited to 300–>100 mg S m^{-2}, run step 10 mg m^{-2}.

A2 background emissions were included in the deposition limits; the control techniques and costs in optimizations as suggested by the Sulphur Committee. Deposition limited to 500–>150 mg S m^{-2}, 50 mg m^{-2} run steps. r = 5%, T = 20 v.

A3 Same as A2, but with r = 8%, T = 15 y.

B Emission restrictions proposed by the Sulphur Committee.

B1 same as A1, except that individual plant emissions are restricted both by the deposition limits and according to the programme likely to be proposed by the Sulphur Committee.

B2 parameters as in A2, plant emission limitations as in B1.

B3 parameters as in A3, plant emission limitations as in B1.

The lower deposition limit for the different computer runs came from the feasibility criteria: all the variables must be kept within the boundaries. By free optimization we mean a case in which the upper limits are the potential maximum emissions, and the lower limits correspond to conditions where all possible sulphur reduction steps included in the model have been taken. In case B, the directives supposed to be issued by the Sulphur Committee were used to limit the emissions of the individual plants. Thus, we can estimate the changes in the costs and emission patterns when the decision-making criterion is changed from total emission reduction to deposition limits.

Results

Emission Control Measures in Different Establishments

If the sulphur deposition from domestic sources in the free optimization case A2 is constrained below a limit of 500 mg m^{-2} per year, the sulphur emissions have to be reduced by 28,000 t SO_2, i.e. a 7.5% reduction of the maximum emission. The sources where the control measures have to be taken first are in the capital city area, at Naantali oil refinery plant, at Kemira plants in Siilinjärvi and in Kokkola, and at the newly planned coal condensation power plant in Pori. These installations are not the biggest emitters in Finland, but they are located in heavily polluted areas where the background deposition is already higher. Here also the meteorological situation orders the selection criteria: if a second polluting unit is situated close to the optimized one downwind in the dominant wind direction, the deposition is not limited in the most polluted area because the minimum grid distance to the emission source was 20 km. This explains why the huge emissions of the Inkoo power plant near the capital city were not among the first to be cut. The tendency of the model to select the smaller plants first also stems from the shape of the objective function. If the load only needs to be reduced by a small amount, the marginal costs of a big desulphurization unit not utilized at full capacity are higher than the costs of a small unit, because the investment is paid in full, regardless of the capacity factor.

For a deposition limit of 400 mg m^{-2}, the above-mentioned Inkoo emissions must be reduced, this is required also at the other refinery plant located near

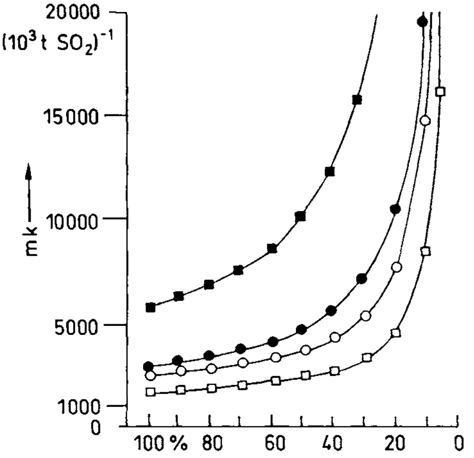

Fig. 1. The value of the cost function for some example installation types as a function of the plant operation factor. *Full squares* pulp industry power plant, r = 8%, T = 15 y, semi-wet scrubber (SWC). *Circles* big coal condensation plant (BCP) with SWC, 8%, 15 y (full circles), 5%, 20 y (open circles), *open squares* BCP with WFAC, 5%, 20 y.

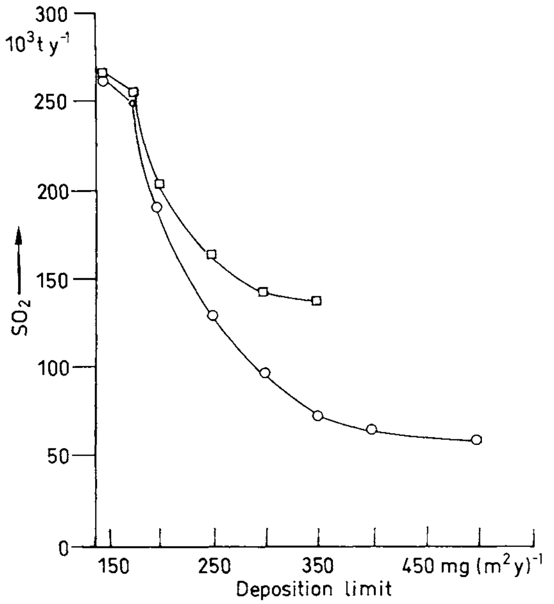

Fig. 2. The emission reduction required for certain deposition limits. Sulphur Committee techniques and costs. *Circles* free optimization case, *squares* Sulphur Committee limits

Porvoo. The sulphur emission reductions as a function of the deposition limit are shown in Fig. 2. Most of the desulphurization measures are done when deposition is imposed to be under 300 mg m^{-2}.

The sulphur reduction programme would also have changed if the foreign background had been taken into account. But the long-range transported load for the year 1995, after control measures of 30–50% in the different countries, was not unanimously accepted. According to available general figures it would have imparted stricter restrictions to installations in southern Finland.

The total sulphur reductions in the free optimization and Sulphur Committee restricted cases are represented in Fig. 2.

Development of Sulphur Reduction Costs

The costs of the emission control installations were estimated at a time when there were no functioning sulphur reduction devices in Finland, so the Finnish cost estimates were somewhat low compared to the realized cost in other countries. While making emission scenarios for the year 1995, some fuel changes to, e.g. natural gas or domestic energy sources, as well as some process modifications already under construction were assumed to be carried out in any case, and the costs for these measures were not included into the estimates.

The change of the interest rate or amortizing period altered very seldom the optimized solution. The fixed costs were 25–85% of the total costs while the cost calculation parameter dependent part was 65–75% of it when the plant was operating at full capacity. The model decisions were made when the plants were operating at their minimum capacity which was enough for the deposition limit. At a particular location, where the deposition limit was exceeded, the nearest polluting units usually had very different cost structures. Different types of units have very individual investments, so that the unit type rather than the cost parameters determined the installation which must reduce its emissions. It is also noteworthy that although optimum measures in a critical load area were selected according to economic criteria among the nearest installations, the source density and intensity in heavily loaded areas was more important in constructing sulphur reduction programmes than any economic parameters.

The total annual cost development as a function of emission reduction amount for different deposition limit requirements is represented in Fig. 3A and B. In the free optimization cases the solution was 200–250 Mmk less expensive than for the Sulphur Committee restriction case. With an annual total of 500 Mmk one can achieve an emission reduction of over 200,000 t SO_2 in the free optimization case A2, while in the restricted case B2 the emission reduction is about 35,000 t SO_2 smaller. In the former case the maximum deposition was less than 200 mg m^{-2}, in the latter case about 250 mg m^{-2}. Thus it can be said that with the same costs one could reach bigger emission restrictions and smaller deposition than suggested by the Sulphur Committee. With very strict deposition limits the results were about the same. The domestic small source background was quite important in the cost figures: for a 300 mg m^{-2} deposition limit with the inclusion of background value, the additional annual cost was 90 Mmk, for a limit of 150 mg m^{-2} the expenses increased from 535 Mmk to 840 Mmk (cases A1 and A3).

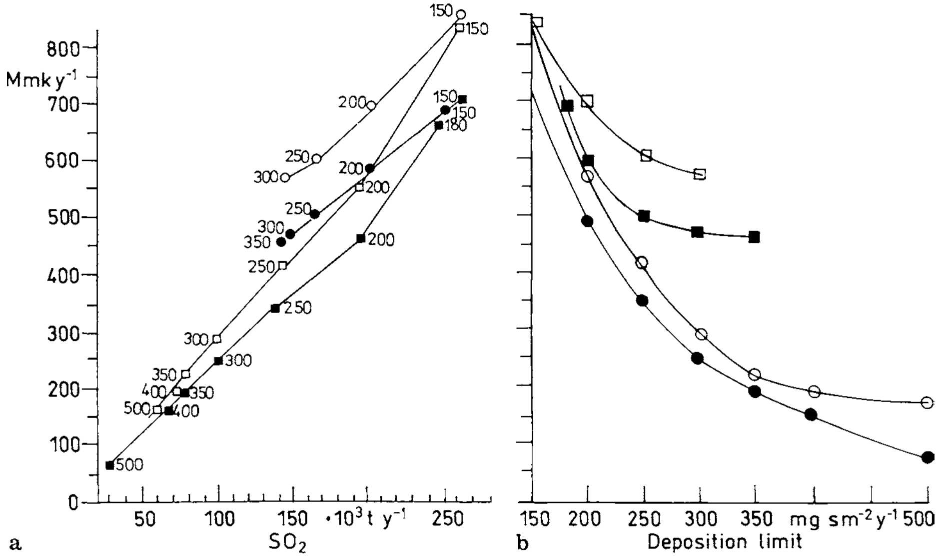

Fig. 3a, b. Annual desulphurization costs as a function of the emission reduction amount and the deposition limit, Mmk y^{-1}. **a** *Circles* Sulphur Committee limits (SCL), *squares* free optimization (FO), **b** *Circles* FO, *squares* SCL, 8%, 15 y (more expensive), 5%, 20 y (less expensive) cost parameters.

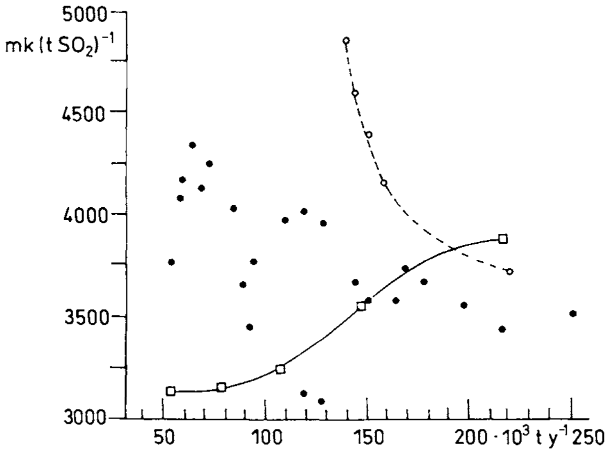

Fig. 4. Average desulphurization costs mk per reduced ton of SO_2 in optimal cases. Small installations background not included. *Squares* linearized model, *open circles* SCL, *full circles* FO, 8%, 15 y.

In Fig. 4 we present the average unit cost variation for the case studies. For the sake of comparison we also show the unit cost structure in a case where the installations are used with fixed capacity, describing the results of the linearized model. In this case the average cost increases with the tightened deposition limits and more expensive installations, which seems a reasonable contradiction to the non-linear version. But the costs given by the linear version are not correct: in the solutions the optimized reductions cannot be restricted to correspond to the average cost of the installations in the cost function unless one uses mixed integer programming. In the non-linear model results, one can observe the average capacity factors of different solutions: when the deposition limit is filled with a partial use of desulphurization installation, the model does not increase the costs further by using the installation by more than the minimum action level. Every additional reduced ton increases the cost function. At stricter limits, when some more expensive purification installations are required by the model, the utilizing factor of the earlier built installations increases so that the average cost per reduced ton decreases. Here we see that in defining the solution the boundary conditions are stronger than the optimizing criteria. The model proposes some costly installations already in the less heavily restricted cases, especially in the Sulphur Committee cases.

The Deposition Figures

In Figs. 5 and 6, sulphur deposition caused by domestic emissions is shown for the year 1995, in both the free optimization and the Sulphur Committee restricted cases. One can say, that when imposing the Sulphur Committee restrictions on the plants taken into the optimization, the sulphur deposition exceeds the lower critical level for forests in many locations. Even in a case where all the possible reductions were made this value (200 mg S m^{-2}) was exceeded in some places. But we had only about 50 biggest emitters as optimized variables in the model, and this number has to be increased in order to obtain lower deposition patterns. If we keep in mind that all the domestic sulphur sources were probably not in the emission statistics, and that at the south coast the transported load alone is more than twice the upper critical limit, the situation seems more pessimistic.

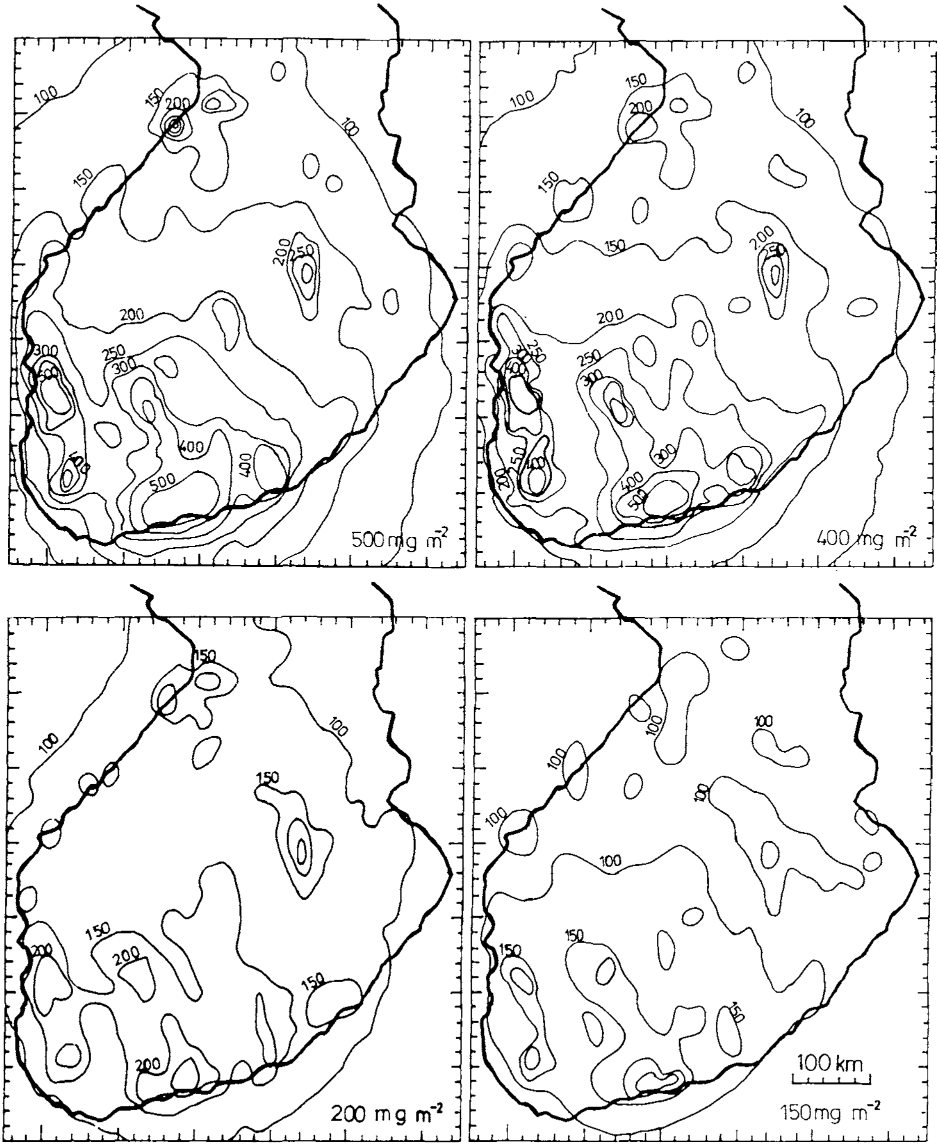

Fig. 5. Annual sulphur deposition, mg S m^{-2}. Free optimization case A2. Deposition limit at the *corner* of the figures

Discussion

We conclude that optimization techniques described in this paper offer a means to obtain more emission reductions and lower maximum depositions with the same investment than proposed by the official reduction programme. One can argue that instead of using just percent reductions as targets it would be reasonable to take also the deposition distribution into account, because a majority of the population

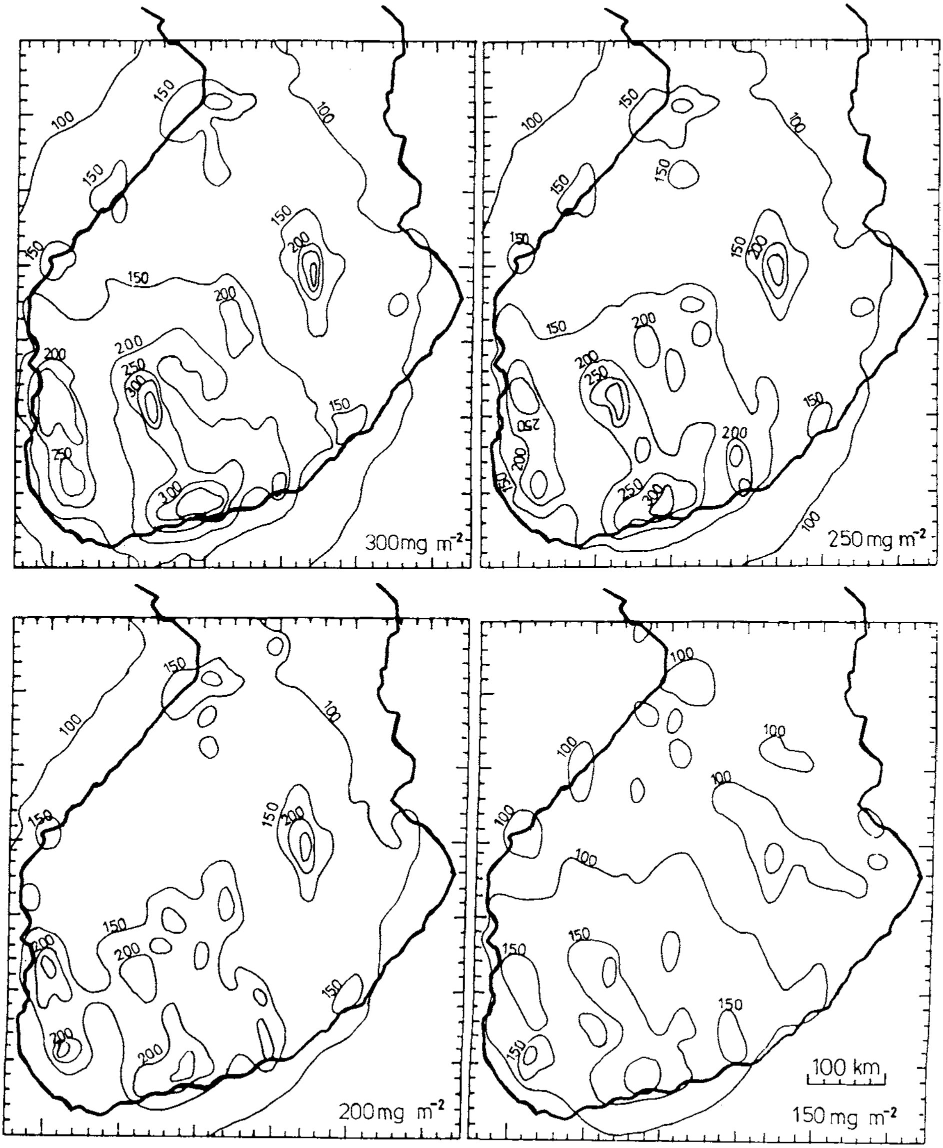

Fig. 6. Annual sulphur deposition, mg S m^{-2}. Sulphur Committee restriction case B2. Deposition limit in the *corner* of the figures

lives in the area where the pollutants are emitted. However, the deposition maximum cannot be the only criterion because there is a danger that the pollutants just spread over a wider area.

The results given by the model are only rough estimates, both for the desulphurization installation choices and their costs. The optimization and distribution models are quite simple and we have made many generalizations in assessing the emissions, costs and other parameters for the year 1995. The evaluation of the sulphur dispersion model is done in Nordlund et al. (1985), and the calculated wet deposition is later compared to measurements in a close vicinity of the Inkoo power station (Nordlund et al. 1988). According to the evaluation close to the sources, the sulphur is not washed out as SO_2 as effectively as modelled, so in the distances of our calculations the wet deposition is slightly underestimated.

The optimality concept itself is very questionable when one is concerned with environmental problems. Optimality in the computer simulations only meant the finding of a maximally economically effective solution when some restrictions were active. One can argue a lot on what the environmentally acceptable models could be. If one wants to continue this work it is necessary also to include the economic damages caused by pollutants in the model or build a multi-goal programming model.

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Amount, Quality and Utilization of Flue Gas Desulphurization (FGD) Wastes in Finland

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Summary

Ashes and desulphurization wastes can be an environmental problem in the future, as they form in large amounts, their quality may vary and possibilities for their utilization are poor. Simple forms of utilization are then required, and possible environmental impacts of these applications should be determined. The amount of wastes to be developed in Finland is reviewed and their quality with regard to environmental aspects and ways of utilization are discussed.

Introduction

FGD wastes are derived from coal-fired power/heat stations in Finland. The first desulphurization plant was commissioned in 1987. The plant operates with the wet-dry method using slaked lime as reagent. Fluidized-bed technique with limestone addition had been commissioned in Finland already earlier. Desulphurization methods have been developed in Finland by Tampella Corp. (Lifac, dry limestone injection), Outokumpu Corp. (Sulfred, regenerative producing elemental sulphur), Rauma-Repola Corp. (potassium sulphate), and A. Ahlstrom Corp. (fluidized-bed).

Quantity of desulphurization wastes in Finland

Present Amount of FGD Wastes

The amount of coal used for power and heat production totalled 4.0 Mt in 1987 (Energy Statistics 1987). Major consumption sites are given in Table 1. The amount of sulphur dioxide emissions from coal firing was about 66,000 t a^{-1} (Hupa et al. 1988).

The amount of desulphurization wastes in Finland was about 60,000 t in 1988. Half of the amount was disposed of and the other half was used in landfilling and road embankments on an experimental scale. These wastes were produced by one wet-dry process (30,000 t a^{-1}) and a number of small fluidized-bed (FBC) units

Kauppi et al. (Eds).
Acidification in Finland

Table 1. Major coal consumption sites in Finland (1987)

Consumption site	Coal consumption (t a^{-1})
1. Helsinki	1,250,000
2. Inkoo	690,000
3. Naantali	360,000
4. Espoo	250,000
5. Kristiinankaupunki	210,000
6. Lahti	200,000
7. Vantaa	170,000
8. Vaasa	120,000
9. Hämeenlinna	70,000
10. Pori	60,000
11. Kotka	35,000
12. Kokkola	35,000
13. Jyväskylä	20,000
14. Turku	20,000
Total	3,490,000

with limestone injection. Although the amount is small for the time being, it will rapidly increase in the near future. The present production of fly ash is about 550,000 t a^{-1}, and 60% of it is utilized by the cement and concrete industries.

Amount of Desulphurization Wastes by the Year 2000

The use of coal is expected to increase in Finland from the present level of about 5.7 million t a^{-1} in 1987 to 11.2 million t a^{-1} by the year 2000 (IEA 1989). If this is realized, and supposing that the emission standards of at least the present level are applied to all coal-fired plants, except for small (< 50 MW) ones, the amount of desulphurization wastes will amount to 1.3–1.5 million t a^{-1}. In addition, different kinds of ash will form about 1.2 million t a^{-1} (Table 2).

A crucial factor affecting the amount of wastes is whether the pre-separation of fly ash is included in the process or not. This is of interest for two reasons. Firstly,

Table 2. Estimated amounts of different FGD wastes from coal fired power plants in Finland

Type of waste	Amount of waste t a^{-1} 1987	1993	2000
Fluidized bed comb. ash	15,000	74,000	72,000
Gypsum	–	115,000	189,000
Wet/dry	30	333,000	550,000
Dry inj.	20	393,000	519,000
Elem. sulphur	–	–	4,000
Ash	500,000	665,000	1,178,000
Total	565,000	1,580,000	2,508,000

if the ash is not separated, it will mix with the desulphurization products and double or triple its amount depending on ash content and the degree and method of desulphurization. In addition, if the fly ash is not separated in the process, it cannot be used for conventional purposes, i.e. mixed with cement and concrete.

If the production of the cement and concrete industries, which are the main utilizers of fly ash today, does not increase, there should be no problems in the availability of fly ash. The disposal of increased amount of fly ash in the future may, however, become a problem.

Environmental Characteristics of FGD Wastes

The following types of waste and FGD products will likely be produced in Finland in the future:

- waste of the wet-dry method,
- waste of the dry additive method,
- waste of the fluidized-bed method,
- gypsum,
- products of regenerative methods (sulphur/sulphuric acid).

The major components of the leachate studied were calcium, sulphate, chloride and nitrite/nitrate (only in the wastes from wet-dry process). The amount of toxic metals leached was usually $< 1 \text{ mg l}^{-1}$. The metals analyzed were selected according to earlier studies in Sweden and Denmark (Nilsson 1987, Hjelmar et al. 1986). The smallest values were measured for fluidized bed ash.

The granulation of the wastes from the wet-dry process and the addition of cement did not reduce leaching of substances.

The results of the shaking tests were in conformity with those of the column test (Wahlström et al. 1989). Some metals like Cr and Mo appeared in higher concentrations in the leachate from the column test (mixture of waste from the wet-dry process) or in the leachate from the shaking test (fluidized-bed ash). On the other hand, highly toxic substances like Hg remained below the detection limit.

The leachates from desulphurization wastes were alkaline or neutral. The leachate will probably remain alkaline or neutral for a very long time due to the high calcium content of the wastes. The pH values for the leachates from the columns were lower than those for the leachates from shaking tests, probably due to channelling.

The maximum concentrations of substances leached from desulphurization wastes and reference material are summarized in Table 3. The high concentration of chlorine in the wet-dry FGD sample is due to seawater used in lime slaking. The shaking test was carried out according to Lundgren (1986), in which a relatively low liquid/solid ratio (L/S) is applied and the procedure is repeated with a fresh solvent. The column test was carried out with a 20-cm diameter column using acidified water (Ranta et al. 1989).

Table 3. Maximum concentrations from different FGD leachates using shaking (s)[a] and column (c)[b] tests

Sample	Wet-dry with 65% fly ash[c]	Wet-dry with 65% fly ash[d]	Fluidized-bed combustion[e]	FBC[f]	Moraine reference[g]
Test	c	c	s	c	s
pH	12.4	11.2–11.7	10.4	7.6–12.0	6.7
NO_2 mg l^{-1}	82	780	–	< 1	
NO_3	390	84	–	< 0.5	
SO_4	910	180	2400	2500	–
F	–	–	0.4	0.2	
Cl	10,000	2200	200	320	
Ca	4,700	1300	530	640	2.0
As mg l^{-1}	0.018	0.026	0.020	0.011	< 0.002
Ba	1.48	0.25	0.30	0.2	< 0.23
Cd	0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.001
Cr	0.78	0.80	0.12	0.017	< 0.003
Cu	0.006	0.01	0.02	0.04	< 0.02
Mo	0.78	1.53	0.13	0.028	< 0.005
Ni	< 0.01	< 0.01	–	< 0.01	< 0.01
Pb	0.003	0.002	–	0.006	< 0.01
Zn	0.05	0.008	0.019	0.07	0.08

[a] Shaking test (Lundgren 1986, Wahlström 1988).
[b] Column test (according to Ranta et al. 1989).
[c] Liquid/solid ratio 0.7, 3 days' storage.
[d] Liquid/solid ratio 0.5–1.
[e] Liquid/solid ratio 0.34, 3 days' storage.
[f] Liquid/solid ratio 0–0.5.
[g] Liquid/solid ratio 0.8.

The amount of arsenic, chromium and molybdenum leached from the waste of the wet-dry process was higher than that from the reference materials (only moraine is given in Table 3). No significant difference was observed in the contents of the other elements between the waste and reference materials. The amount of As leached from the expanded clay sample (0.11 mg l^{-1}) as well as the amount of Zn leached from the piece of red brick (0.14 mg l^{-1}) was even higher than that leached from desulphurization wastes.

Although the results indicate that the amount of leachate was usually not higher than that of the reference materials, it should be borne in mind that the amount of dissoluble metals in the desulphurization waste is dependent on the type of the fuel used. In addition, the samples studied contained enough fly ash to affect a pozzolanic reaction which results in stabilization of heavy metals (Rademaker and Wiegers 1987). The leachable metals' origin mainly from fly ash, and its quality and quantity, determine the quality and quantity of leachate if no stabilization occurs. For this reason, the desulphurization wastes from other types of fuel are different. The origin of ash should be known when disposed of or utilized, and clearly detrimental wastes should be subjected to special treatment.

Utilization of FGD Wastes

In the dry additive and fluidized-bed methods the fly ash is totally mixed in the final product, and consequently, cannot be utilized in conventional objects of use. Gypsum can, as is well-known, be used for replacing natural gypsum in the building material industry. Waste from wet-dry techniques has been of no use so far. On the other hand, products from regenerative techniques, especially in the form of elemental sulphur, are relatively easy to utilize. Some characteristics of different FGD techniques and wastes are summarized in Table 4.

In many cases the quality of waste is sufficient for these uses, but there is no specific market for their utilization. The waste must therefore be disposed or placed in buffer storage.

Part of desulphurization wastes, for example gypsum, elemental sulphur, etc., will be suitable for utilization. However, the use of gypsum is limited (total use today 200,000 t a^{-1}) in Finland. In pilot experiments the most promising use for sulphite fly ash mixtures was in road embankments. However, because of the large quantity of this type of waste that will be produced, it is advisable to store these wastes in buffers before their utilization. This results in problems, for example, as the utilization of the natural puzzolanity of the material is not possible in all respects.

The utilization of desulphurization wastes has been insignificant so far. Except for gypsum and pure chemicals, it is not easy to find ways of utilization for them even in the future, the dumping of wastes being hence the primary alternative, which cannot, however, be considered advisable.

In geotechnical applications the use in road embankments is promising. Properties of significance are
- sufficient strength,
- water impermeability.

If the strength is sufficiently high, even savings can be achieved as a smaller

Table 4. Summary of process factors

Waste type	Fly ash proportion %	Sulphur removal %	Calcium sulphur ratio	Possibilities for utilization
Wet-dry	~ 30	~ 90	~ 1.3	∓
Limestone inj.	~ 100	~ 60	~ 2	∓
Fluidized-bed combustion	~ 100	~ 80	2.4	∓
Gypsum	1–3	~ 95	1.1	±
Regenerative	~ 0	~ 90	~ 1	+

∓ Uncertain or limited.
± Good, amount being a limiting factor.
+ Good.

quantity of the base course. If the product is almost impermeable to water, the environmental impacts are eliminated very efficiently.

The street construction tests were carried out with fly ash (FBC with limestone). The material was easier to handle at the generation site than the stabilisate and was not as sensitive to water. However, the composition of the material was very inhomogeneous, mainly due to inadequate intermediate buffer, which resulted in great variations in density. It can be concluded from the tests that it is fairly easy to construct a stabile embankment from the fly ash of fluidized-bed combustion. In high-class street constructions the use is hampered by variations in the material properties.

Other forms of utilization are also possible. The most promising concrete-technical application seems to be the so-called soil-most concrete, in which the proportion of desulphurization waste could be high, hundreds of kg m^{-3}. The product of the wet-dry method could also be used for manufacturing concrete, but there will be problems in maintaining homogeneous quality as well as in availability and costs, i.e. competitiveness with conventional raw materials for the building industry.

Conclusions

The amount of desulphurization wastes will grow significantly also in Finland by the year 2000, when these wastes will no doubt be a significant environmental problem, if sensible ways of utilization are not found for them.

The most likely user of this waste, the building material industry, is not short of raw materials, and hence will only utilize a portion of the waste produced. The biggest potential application, i.e. use in geotechnical applications, requires a good availability and quality of products and, further, no detrimental impacts on the environment. Although the environmental impacts could be mastered efficiently, there is so far no technology available that would make FGD wastes economically competitive with conventional materials in geotechnical applications. However, they could be used, technically, in large amounts in secondary geotechnical applications.

From an environmental point of view the desulphurization wastes will produce leachates with elevated concentrations of salts for a very long time. The salts, mainly sulphites and sulphates, but also nitrite and nitrate, can be detrimental to man.

The leaching to toxic metals was quite insignificant except for Cr and Mo. Compared to the reference materials, no significant difference was observed for many metals.

The desulphurization waste cannot, however, be disposed or used as substitutes without restrictions. Special attention has to be focused on the leaching of salts and nitrate and nitrite. The leachate from a deposit can affect the ground water quality in the surroundings of the deposit. The environmental impacts have to be evaluated from case to case regarding the characteristics of the environment and the origin of the waste concerned.

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Economic Impacts of Western European Air Pollution on the Finnish Forest Sector

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Summary

This chapter reports on the effects of Western European novel forest damage on the Finnish forest sector. A model revised from the global forest sector model developed at IIASA (International Institute of Applied Systems Analysis) is used in the analysis. Five different air pollution scenarios are compared to a base case scenario with no forest damage. The main result of the analysis is that impacts in the forest sector as a whole are slow and the market mechanism efficiently smoothens the impact of changes in timber supply caused by forest damage. Except in the case of really catastrophic and widespread forest dieback, harvests and forest industry production in Finland are affected only to a minor extent. Indirect linkages of international forest product markets may, however, cause unexpected long-term impacts.

Introduction

Scope of the Study

This chapter deals with the economic effects of Western European forest damage on the Finnish forest industries. "Western Europe" is here defined as a region which covers other Western European countries than Finland and Sweden. These two countries are the principal European export suppliers of forest industry products in the area. Although in the long run, possible domestic forest damage may have a serious effect on the Finnish economy, this topic is not discussed here.

When we use the term "forest damage" we mean "novel" forest damage, i.e. geographically widespread and chronic forest decline (see e.g. Metz 1988). The main causes of novel damage are harmful substances in the air.

Finland and the Western European Forest Product Market

Finland is more dependent on forest industries than any other developed country in the world. Therefore, the economic consequences – as well as indirect consequences – of forest decline in other countries are probably more distinct than in other Western countries.

Kauppi et al. (Eds).
Acidification in Finland

At present, 40% of Finland's export earnings is derived from wood-based industries. As for export regions, Western Europe is by far the most important area. It comprises over two-thirds of the export value of the Finnish forest industry.

Imports of Western European forest sector products to Finland have traditionally been insignificant and contain practically no forest industry products. Roundwood imports from Western Europe have slightly increased in recent years, being 0.2 million m^3 or 3% of the total import.

According to the most recent European Timber Trends and Prospects Study ETTS IV (1986), Western Europe will remain a major net importing area of forest industry products. This means that in the future Western Europe will also be a major export region for Finland's forest industries. This conclusion is based on the assumption that forest decline will not substantially increase the production of the Western European forest industries.

For Europe as a whole, the annual demand for forest products, converted into a removals equivivalent, is expected to be between 20 and 35 million m^3 higher than supply by the year 2000 (European . . . 1986). This "gap" is accounted for, to a significant extent (about 50%), by two countries, the FRG and Italy. Thus, the development of the domestic markets of these two countries will no doubt influence the supply/demand balance for all of Western Europe. This statement also applies to the effects of forest decline, especially in the FRG.

Use of a Model in the Analysis

There is currently no widespread consensus on the magnitude of air pollution damage to forests. Consequently, several alternative assumptions on the extent of the damage must be used when analysing the impacts of air pollution on the forest sector. This kind of sensitivity analysis is very laborious without a formal tool, because the number of scenarios to be analysed should be relatively high. Therefore, we have chosen to use a computer model as such a tool.

The analysis of the economic impacts of forest decline assumes a well-established procedure. The changing timber supply caused by forest damage must be linked to timber markets. Furthermore, timber markets must be linked to the processing of the timber into products. The demand for these products requires an analysis of consumption and its major determinants, such as economic activity and consumer behaviour. And finally, the analysis should include the trade flows of both roundwood and industrial products. Consequently, a global forest sector model is needed for the analysis.

The construction of a global, or at least a European forest sector model, is a substantial undertaking. Fortunately, such models are in existence. In 1985 the Forest Sector Project of the International Institute for Applied Systems Analysis (IIASA) completed a comprehensive global model, GTM (Global Trade Model), to analyse policies relating to forestry and forest industry (Kallio et al. 1987). Among the scenarios developed by the IIASA project was an "Acid Rain Scenario" which illustrated the potential economic effects of prolonged atmospheric pollution.

In addition to this single scenario, a series of scenario runs was made with the IIASA model after the determination of the Forest Sector Project (Dykstra and Kallio 1987). These nine scenarios illustrated pollution impacts on Western Europe as a whole. The effects on individual countries were not analysed.

As for product assortment and regional distribution, the IIASA model is a global compromise. It does not always serve well the objectives of an individual country. Therefore, it was decided to build a "tailored" version of the model for Finnish purposes, and at the same time, update the IIASA model (Seppälä and Seppälä 1987). This new model was used as a tool in the analysis described in this work. The model is discussed in more detail in Section 3.1.

Forest Damage in Western Europe

Nature of the Damage

Forest damage caused by air pollution is not the only damage which can influence the health and productivity of the forest. In fact,these other causes, such as forest fires, storms, and insect damage, have so far affected the forest sector much more than so-called novel damages.

As for the consequences to timber markets, forest damage can be divided into two classes (cf. European . . . 1986; Ovaskainen 1987):

1. Damage causing short-term impacts. This damage may affect the timing of the availability of the wood for the market, but not the long-term productivity of the site. Insect epidemics and storms are examples of this category. The novel forest damage also may cause these short-term impacts through sanitary cuttings.
2. Damage causing long-term impacts. This damage may affect the productivity of the site, increment rates, and hence the volume of the long-term wood supply. Most of the damage in this category is novel forest damage, and the impact comes mainly through the soil.

It is not always easy to separate these two categories. For example, forest fires have a short-term effect by destroying standing timber, but in some countries, as in the Mediterranean region, it may cause the deterioration of a forest ecosystem over a long period of time. In other areas, such as northern countries, fire may improve site quality for several tree generations.

Damage Situation

There are several uncertainties involved in measuring the extent of forest damage in Western European countries. Different methods have been used in different countries. Usually national surveys measure the percent of trees affected. The limits of damage classes vary between regions, which makes international comparisons laborious. In Central Europe, trees are considered to be damaged if they have lost at least 10% of their needles or leaves; in Nordic countries the corresponding limit is 20%. Whatever these alternating limits are, the central point remains, how does the damage affect wood supply?

Although it is difficult enough to get comparable figures on the present damage situation, it is even more difficult to evaluate the progression of damage over time, both in the past and in the future. This is one of the main reasons why sensitivity analysis is needed to test and compare different assumptions on the magnitude of forest damage.

The forest damage attributed to air pollution does not affect all European forests equally. Based on the 1988 estimates, the share of coniferous trees which had lost 10% or more of their needles varied in Western European countries from 20% in northern Italy to 71% in Czechoslovakia (Forest damage . . . 1989). The corresponding shares in the FRG and Finland were 49 and 40% respectively.

As for the recent development over time, the increase in the proportion of damaged trees since the mid-1980's has been very minor in most regions. In some countries (e.g. Switzerland and the FRG) and in some tree species (mostly coniferous) the share of damaged trees has even decreased (Waldschadenserhebung 1988).

Consequences of Forest Decline

From the Finnish point of view, the economic impact of the Western European forest decline is significant if it affects Finland's foreign trade of forest sector products, i.e. roundwood and industrial goods. Although every possible effort is likely to be made to prevent sanitary felling from causing a rise in total removals, an increase in timber supply may occur. The increased supply will materialize either as increased industrial production or as increased exports of roundwood – or both. If the increase in supply is noticeable, a fall in timber price may follow. On the other hand, harvesting costs may rise due to accelerated cuttings.

Up to the late 1980's it has been possible, in most cases, to adjust normal fellings to increased sanitary cuttings. Consequently, there has been no significant market disruption at the European or national level due to oversupply, so far. The market situation is, however, in this respect unclear, as separate statistics are usually not kept on sanitary fellings. Based on an estimate made for ETTS IV, 3–4% of the European total fellings was attributed wholly or partially to pollution damage in 1984 (European . . . 1986).

Research into the suitability of damaged wood as raw material indicates that sawn timber from damaged trees can be used without restriction (e.g. Becker 1987). Pulpwood from damaged trees is, however, attacked sooner by damaging organisms than wood from non-effected trees. It has been shown that if the wood is not allowed to dry out, it can be used as raw material for most industrial purposes. Once allowed to dry out, the wood is often only suitable for fuelwood (European . . . 1986).

In the long run, the growing stock and increment may be reduced as a result of novel forest damage. This will decrease timber supply and increase the anticipated gap between demand and supply in Western Europe. A rise of timber price will follow, not only because of reducing supply, but also due to the increase in timber production costs.

For Finland, the key question concerning the European forest damage is how the wood processing industry in Western Europe can absorb the changes of timber supply. First, the industry should adjust itself to an increasing supply by new capacity, and then later to a decreasing supply by reducing capacity.

The Model

Structure of the Model

The model used in this study is a partial economic market equilibrium model cast in the framework suggested by Samuelson (1952). It is solved as a nonlinear programming model, with linear constraints and a partially nonlinear objective function (Kallio et al. 1987).

In any time period, the model finds the market equilibrium solution for 16 forest-product categories in 18 regions, which make up the whole world (for product categories and regions, see Appendix). No consideration is made for any possible influence on future time periods. The model is then advanced to the next time period, and a new market equilibrium solution for that time period is computed.

The global forest sector is sufficiently complex that none of its individual components can be analysed in isolation. Therefore, accounting numerous complex linkages requires formal analytical models of the various forest-sector components for each region of the world. This has been done in the model by linking four component models for each of the 18 regions. These component models (modules) include a model of timber supply, a model of processing industries, a model of product demand and a model of trade among regions to account for the spatial aspects.

The solution for a given time period indicates the annual quantity of logs and pulpwood removals for the next 5-year period, the quantity of logs and pulpwood to be traded between regions or converted into products within each region, the quantity of final products to be produced within each region, and quantity of final products to be traded among regions.

The dual solution indicates the marginal prices of both raw materials and final products. Information from the solution for a particular period is used to project timber growing stock, processing costs and capacities, and other relevant factors for the subsequent period. The solution/updating sequence is repeated until the model's time horizon (in this case six periods or 25 years) has been reached.

Base Scenario Assumptions

The model has been designed as a policy analysis tool, not as a forecasting model. This kind of policy analysis model attempts to show how such variables as production levels or prices are likely to change in response to alternative decisions made by, e.g., governments or industry. The results of a particular scenario run are therefore likely to be presented as deviations from results obtained for a base scenario, rather than reporting absolute numerical values.

For this reason, the base scenario is aimed at representing a future development which is based on a satisfactorily neutral set of assumptions. Thus, it will provide a useful basis against which alternative scenarios can be measured.

The world's forests, the forest products industry and consumers of forest products are inevitably affected by many decisions or changes that occur outside the forest sector. Such key exogenous variables that influence projections made by the model are economic growth, income and price elasticities, population growth, exchange rates and tariffs.

For most variables, we assume that their future development will roughly correspond to their past development; except in the case of economic and population growth where we assume the growth rate to be slightly lower than that of the 1960's and 1970's. Growth rates in income per capita are assumed to decline as real income per capita rises.

The base scenario assumes that there will be no substantial change in forest growth rates, forest area, or mortality rates due to atmospheric pollution or climatic change during the period 1985–2010.

Base Scenario Projections

The projections of the base scenario serve as a reference for air pollution scenarios. Therefore, the main results of the base scenario run are first summarized. In addition to Finland and Western Europe, we also refer to the development of the North American forest sector because of its important role in the world trade of forest products.

Roundwood Products

The development of annual removals in Finland shows no increase before the late 1990's, after which removals increase by about 1%/year. The share of coniferous logs in the total removals steadily decreases at the expense of coniferous pulpwood.

In spite of the very modest increase in cuttings, Finland's share of total removals in Western European countries does not diminish because cuttings in Western Europe will also remain below the sustained yield.

The reason for the modest growth of removals in Western Europe, despite the increasing industrial use of wood, is a growth in wood imports. During the 25-year period, imports increase by over 400% and in total exceeds 60 million m^3 in 2010.

Finnish and Western European roundwood imports originate from the USSR, and for Western Europe also from other Eastern European countries. Japanese wood imports from North America decrease and will be replaced by increased imports from the Soviet Union.

The increasing role of the USSR and Eastern European countries in the world trade of roundwood in the model results is mainly based on the exogenous assumptions of the base scenario. Production of both timber and end products is assumed to be determined exogenously rather than as a result of market forces. This assumption results from a surplus of wood production with respect to domestic consumption.

Final Products

Sawn wood production in Finland will remain approximately at its present level until the mid-1990's, after which it will start to increase, slowly reaching an annual level of about 9 million m^3. After 2000, sawn wood exports from Finland will be mainly directed outside Western Europe because of the increasing self-sufficiency in the area.

With respect to particle and fibre boards, the Finnish producers are mainly domestic suppliers. However, in printing and writing papers, especially in wood-containing grades, Finland will play a dominant role in Western European markets. The rapid growth of production and export will result in a market share of over 50% of the consumption in Western Europe by the year 2000.

Newsprint production in Finland, and also other Nordic countries, will decline. Imports from Nordic countries to Western Europe will be replaced by imports from Canada. Changes in the Western European production of newsprint will be marginal.

The relative importance of North America increases globally in other paper and board production. Imports of this group from eastern USA to Western Europe will increase, whereas Nordic countries will lose market shares in these grades.

As a result of slow growth of market pulp production (1%/year) net exports of pulp from Finland will terminate and turn to net imports in the late 1990's.

Prices

The prices computed by the model are international market-clearing prices, rather than domestic ones. Finland is a price taker in international forest industry product markets. End product prices therefore generally follow price developments in Western Europe.

In the base scenario, real prices of end products only increase very slowly. This is the case especially in paper products and in coniferous sawn wood. Prices of construction panels and nonconiferous sawn wood increase more rapidly. They are, however, of minor importance to the Finnish forest industries as a whole.

The price of coniferous white pulp increases much more than that of paper products, especially in Finland and in North America. This is because of the steady increase in the price of coniferous pulpwood. This again is due to the slow growth of the supply of coniferous pulp. Technical development in woodpulp-saving technology in papermaking diminishes, however, the cost pressure on paper production.

The price trend of coniferous logs in western and northern Europe is declining. Price differences of industrial wood between western and northern Europe and North America tend to diminish.

Air Pollution Scenarios

Assumptions

The "Acid Rain Scenario" was one of the original demonstrations developed to test the capabilities of the IIASA global model, GTM, as a tool for policy analysis (Kallio et al. 1987). This "original" acid rain scenario was also developed to illustrate some of the potential effects of prolonged air pollution on the forest sector in Western Europe. It considered two major effects on forests of air pollution: an increase in tree mortality, and the reduction in the rate of forest growth.

In the study on hand, the basic problem and assumptions are, in principal, similar to the original acid rain scenario. The emphasis here is on the potential economic consequences that forest damage in Central Europe may cause to the Finnish forest sector.

In Finland, two-thirds of the total export value of forest products originates from Western Europe. Consequently, changes in the forest sector in Western Europe directly affect the development of the Finnish forest sector. There are, however, a large number of world trade linkages in forest products that result in a world-wide reallocation of resources in the forest sector, although a change takes place only in one region. Therefore, countries outside Europe are included in the analysis.

We now summarize the assumptions used in the scenarios. Differences with respect to the IIASA acid rain scenario are briefly noted.

1. Only the forests of Western Europe (excluding Finland and Sweden) are assumed to be affected significantly by atmospheric pollution. Thus, the acid rain in Eastern Europe, the Soviet Union, as well as in Sweden and Finland, neither increases fellings nor decreases increment. The interpretation of our assumption is that sanitation fellings fully substitute normal harvests in Eastern Europe, the Soviet Union, Finland and Sweden (see Kallio et al. 1987).
2. Sanitation harvests are assumed to increase the supply of timber in Western Europe after 1990. It is assumed that salvage harvests caused by an increase in forest dieback are a temporary effect with a duration of 10 or 20 years depending on the scenario.

Sanitation harvests represent trees that would not otherwise have been harvested during the period concerned. The corresponding increase in timber supply is modelled by shifting short run roundwood supply curves to the right. This means that the fraction of removals attributable to sanitation harvests is treated as an inelastic part of timber supply.

The level of removals is, however, unlikely to increase by the same percentage as the supply curve shifts. Increasing the timber supply implies that roundwood prices will also fall, unless the demand curve is at the same time shifted correspondingly to the right. As a result, some of the undamaged timber that would otherwise have been harvested during the period concerned will be held for future harvests.

In the original acid rain scenario, the effect of forest dieback increased timber supply between 1985 and 1995 (Kallio et al. 1987). In our scenarios, the increase in the supply of timber starts only in 1990. This is because there have been no clear signs of an increase in removals caused by sanitation harvests in Western Europe since 1985 (Air Pollution . . . 1989).

3. The decrease of forest growth due to pollution is assumed to have begun in 1985. The growth is measured as a percentage of growing stock volume. The reduction in growth rates is assumed to be a long-term phenomenon lasting the whole projection horizon. The reduction is assumed to change linearly over time, reaching its maximum value in 2010, and remaining constant thereafter.
4. The dieback effect in these scenarios concerns only coniferous timber. The reason is that air pollution normally effects the vitality of coniferous trees more severely than nonconiferous tree species. Coniferous timber is also much more strategic for the Finnish forest sector than nonconiferous timber.
5. In the scenario assumptions, no distinction is made between the quality of timber removed in sanitation harvests and the quality of timber removed in normal harvests. The validity of this assumption depends, at least in part, on whether trees can be harvested soon enough after death.

Table 1 summarizes the scenario assumptions. The growth parameter in each scenario shows the growth rate of trees in 2010 compared to the base. The mortality parameter illustrates the multiplier when the supply curve is shifted to

Table 1. Scenario assumptions in terms of growth and mortality parameters

Scenario	Growth parameter	Mortality parameter	Duration of sanitation harvests
1 (base)	1.00	1.00	
2	0.67	1.20	1990–2000
3	0.50	1.00	
4	1.00	2.00	1990–2000
5	1.00	2.00	1990–2010

the right compared to the base. The duration of sanitation harvests indicates the time period when the supply curves is shifted to the right.

Parameter values in scenario 2 are the same as in the IIASA acid rain scenario (Kallio et. al 1987). The mortality effect, however, is valid only for coniferous timber and the growth effect materializes gradually, starting from zero in 1985 and reaching 0.67 in 2010. These assumptions soften the effect of air pollution on the forest sector compared to the IIASA acid rain scenario.

Main Results

Objectives of the Analysis

The main purpose of this chapter is to undertake a sensitivity analysis of the potential economic impacts of air pollution damage of Western European forests on the Finnish forest sector. These impacts, however, are only a part of a worldwide mechanism by which forest sector markets adjust to a new equilibrium. Therefore, we must also study global trade flows and other international development paths to obtain an idea of the impacts of damage as a whole.

One of the major difficulties in analysing and reporting the results of a complex model is the tremendous quantity of output, which makes the interpretation of the scenarios very complicated. Therefore, instead of providing detailed tables of results, we use graphical presentation whenever possible. In Figs. 1–8 and 10–13, the base case scenario always equals 100, and scenarios 2–5 are expressed as index numbers in relation to the base.

Timber Harvests

Figures 1 and 2 show the alternative developments of industrial coniferous timber harvests in Western Europe. Especially for coniferous logs, timber removals change only very modestly as a result of changes in timber supply. The effect on timber harvests in Finland is even smaller, but in an opposite direction (Figs. 3

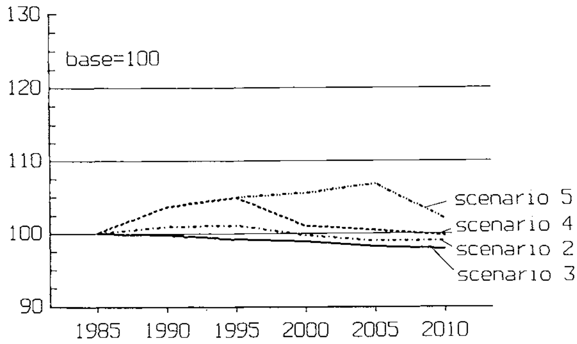

Fig. 1. Harvests of coniferous logs in Western Europe, base scenario = 100

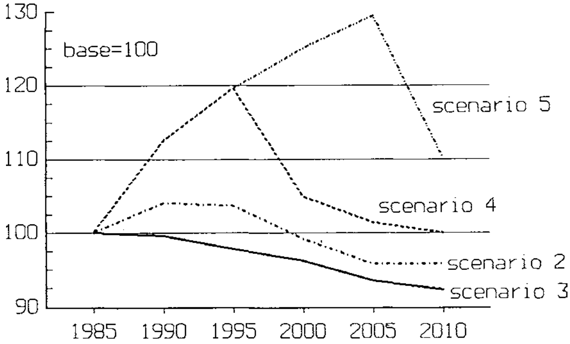

Fig. 2. Harvests of coniferous pulpwood in Western Europe, base scenario = 100

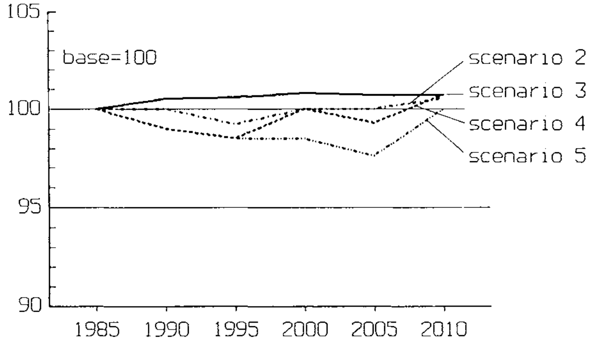

Fig. 3. Harvests of coniferous logs in Finland, base scenario = 100

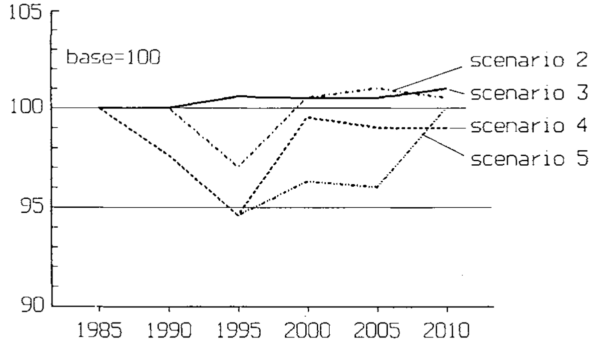

Fig. 4. Harvests of coniferous pulpwood in Finland, base scenario = 100

and 4). This is because of increased industrial production in Western Europe and increased wood imports to Finland.

The limited increase in removals is mainly due to the substitution of sanitation harvests for some "normal" harvest. In scenario 2, where coniferous timber supply is increased by 20% due to the mortality effect, Western European coniferous timber removals are only 3% more in 1995 than in the base scenario. The modest increase of removals in scenario 2 is also partly explained by decreasing timber growth: 87% compared to the base by 1995.

In scenario 2, sanitation harvests due to increased tree mortality are assumed to have been terminated by 2000. After this, the impact of decreased forest growth begins to appear in timber removals. Because of the slow dynamic adaptation of the forests, total coniferous harvests decrease only 2% by year 2010 compared to the base.

Scenarios 3–5 also indicate the slow adaptation of timber harvests to changes in supply. A 100% increase in coniferous timber supply increases timber removals only by 10% during a 10 year period. When the same increase in timber supply lasts another 10-year period (scenario 5), the increase in removals is 17% at the end of the whole period.

The slow change of removals is also seen when timber growth decreases. Scenario 3 shows that, as a result of a 50% decrease in timber growth, removals are diminished by only 5% after a 25-year period.

Production

Changes in timber supply bring changes in timber prices and thus changes in consumption of both intermediate and end products. In scenarios 2–5, the changes in consumption are marginal. Thus, changes in the industrial production are also small. Changes in production of coniferous sawn wood and paper and board in Western Europe and Finland relative to the base scenario are presented in Figs. 5–8.

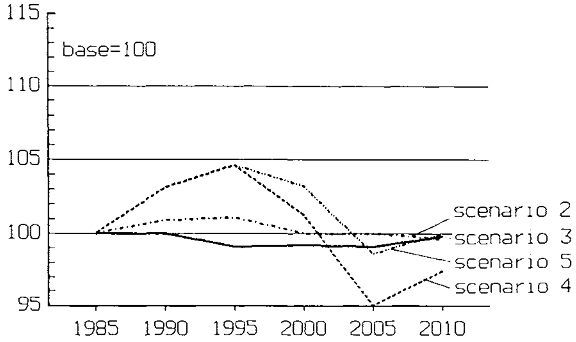

Fig. 5. Production of coniferous sawn wood in Western Europe, base scenario = 100

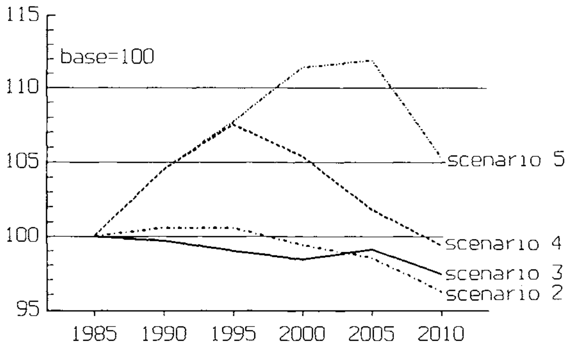

Fig. 6. Production of paper and board in Western Europe, base scenario = 100

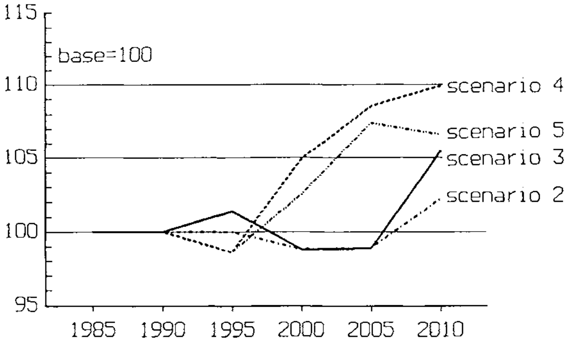

Fig. 7. Production of coniferous sawn wood in Finland, base scenario = 100

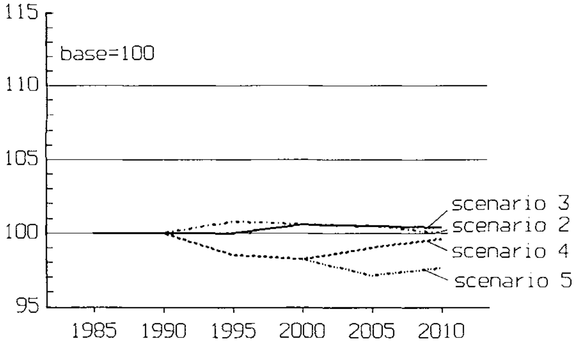

Fig. 8. Production of paper and board in Finland, base scenario = 100

Patterns of Market Adjustment

The main result of this study is that the forest sector as a whole reacts slowly to, and smoothens, the changes in timber supply caused by forest damage. One reason for this is the inertia effects of investments and trade. The patterns of market adjustment are depicted in Fig. 9.

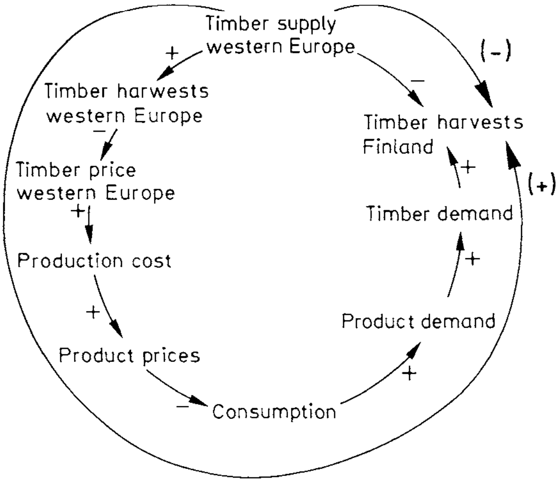

Fig. 9. An example of patterns of market adjustment. Positive correlation between causal relations is marked with + and negative correlation with –

Usually, only direct linkages are observed. In this case, it would mean that increase (decrease) in timber supply in Western Europe decreases (increases) harvests in Finland. This is because of increased (decreased) industrial production in Western Europe and increased (decreased) wood import to Finland. In addition to this direct linkage, there are also several indirect linkages. One of these produces a positive overall correlation between changes in timber supply in Western Europe and changes in harvests in Finland. This linkage is described in Fig. 9 and can be interpreted as follows.

Changes in timber supply in Western Europe result in changes in timber harvests, which produces changes in wood prices. This leads to changes in production costs and end product prices. These changes influence consumption. Changes in consumption affect product and timber demand, and finally timber harvests in Finland.

To obtain a more concrete impression of the pattern of change described above, one of the scenarios will be studied in more detail. We chose scenario 5 (Table 1), because it produces the largest differences in comparison to the base scenario. The changes in harvests and production by regions in year 2000 are summarized in Table 2. In 2000, the sanitation harvests in Western Europe caused by forest damage are assumed to have lasted for 10 years. Changes of prices in Western Europe and Finland and changes of production in North America (USA and Canada) relative to the base scenario for selected products are presented in Figs. 10–13.

By 2000, a 100% shift of the supply curve of coniferous timber will have increased coniferous harvests in Western Europe by 12.7 million m^3 or 14% compared to the base scenario. The increase in world timber consumption as a result of decreased timber prices, however, is marginal (3.9 million m^3).

The increase in harvests and production of the forest industry in Western Europe results in a reduction in imports to the area and hence a decrease in the production of other regions. In absolute terms, the major decrease in harvests is experienced in North America (4.9 million m^3), i.e. only 1% of the total coniferous harvests in the region. In Finland and Sweden, combined harvests decrease by 1.9 million m^3 or 2.7% of their total coniferous harvests.

Table 2. Changes in coniferous timber harvests, production of coniferous sawn wood and total paper and board by regions in year 2000 in scenario 5 compared to the base scenario

	Coniferous harvest (million m^3)	Coniferous sawn wood production (million m^3)	Paper and board production (million tons)
Western Europe	+12.7	+1.2	+3.6
Finland	−1.0	+0.2	−0.3
Sweden	−0.9	−1.0	−0.7
North America	−4.9	−2.2	−2.3
Latin America	−1.5	+0.1	−0.2
Rest of world	−0.5	+2.6	−0.1

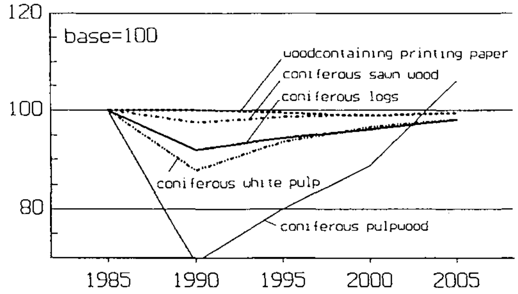

Fig. 10. Product prices in Western Europe in scenario 5, base scenario = 100

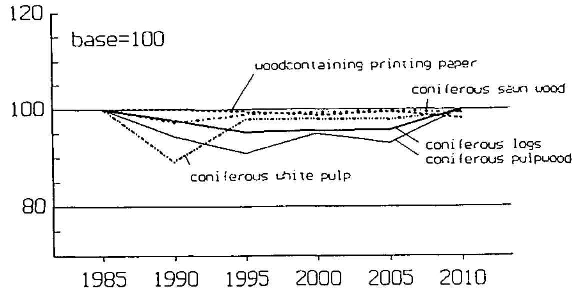

Fig. 11. Product prices in Finland in scenario 5, base scenario = 100

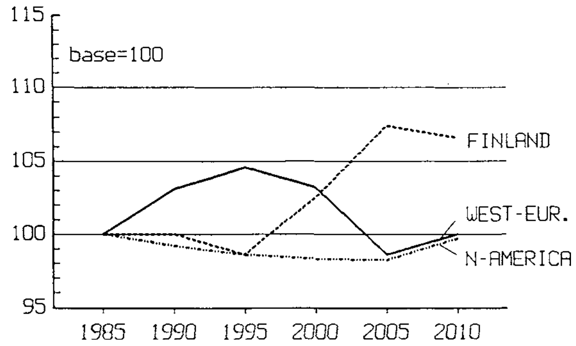

Fig. 12. Production of coniferous sawn wood in Western Europe, Finland and North America in scenario 5, base scenario = 100

The results of this scenario indicate that, as for harvests in a single exporting country, the effects of increased timber supply in Western Europe are by no means crucial. To better understand the reason for this, the resultant simultaneous changes in production and trade, product by product and region by region, are now demonstrated.

The slow growth of sawn wood demand, compared to pulp and paper demand, as well as minor substitution between sawn wood and nonwood construction materials in Western Europe, are the main reasons why harvests of logs change more slowly than those of pulpwood. There is no worldwide reduction in trade of coniferous logs by 2000 in this scenario. The only change is that 0.8 million m^3 of

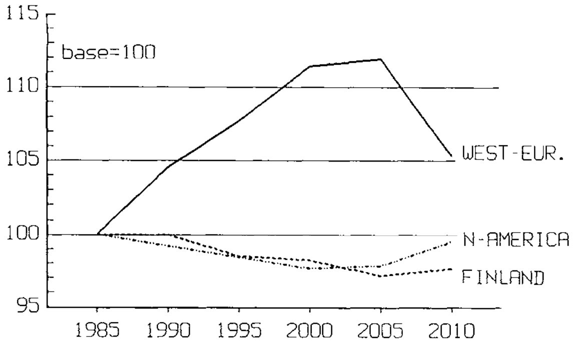

Fig. 13. Production of paper and board in Western Europe, Finland and North America in scenario 5, base scenario = 100

log exports from the USSR is relocated mainly to Finland. As a result, the price of coniferous logs in Finland goes down, and Finland is able to maintain its market share of sawn wood in Western Europe, where as other exporters to Western Europe lose their market shares.

World trade in coniferous pulpwood decreases by 1.4 million m^3 as a result of reduction in imports to Western Europe. Again, the reduction of imports from the USSR is relocated to Finland. The net import flow from Sweden starting in year 2000 in the base scenario turns to modest export from Western Europe to Sweden. These changes indicate that sanitation harvests in Western Europe tend to decrease timber removals in Nordic countries. As we will soon show, this is to a great extent absorbed by product markets.

A good demonstration of dynamic, indirect linkages can be found from the world markets of coniferous sawn wood. Although there are only minor trade flows of coniferous sawn wood from North America to Western Europe, the production of coniferous sawn wood in the USA and Canada decreases in this scenario by 2.4 million m^3. This is twice the amount of respective production increases in Western Europe.

The reason for this is mainly the reaction of the Japanese forest industries. The decrease of sawn wood export from the Soviet Union to Western Europe (0.9 million m^3) is partially substituted by exports to Japan (0.6 million m^3). At the same time production of coniferous sawn wood in Japan increases to 2.8 million m^3, resulting in a decrease of imports from North America (western Canada) by 3.2 million m^3. Looking at only direct linkages this seems to make no sense.

The answer can be found when the situation in the pulp and paper sector is studied simultaneously with the sawn wood sector. According to the base scenario, Western Europe and Japan have deficits in roundwood and in the supply of intermediate forest products. In Japan, the deficit is worst in coniferous pulpwood. Consequently, in the base scenario the Japanese forest industries have used in the base scenario a part of its log consumption for pulping during the period

1990–2000 (during which the price of coniferous pulpwood in Japan equals that of coniferous logs).

Based on increased harvests and industrial production in Western Europe, there is greater coniferous pulp capacity available in the world market. Thus, Japan increases its import of pulp and invests in sawmilling capacity to process the logs released from pulping. The reduction of coniferous sawn wood exports from western Canada to Japan changes trade flows inside North America such that the decrease in production is evenly distributed between different parts of North America. It must also be noted that the main part of the increase in pulp imports to Japan originate from the USA and Canada. This is because the increase of European pulp production decreases pulp import from North America to Europe thereby forcing the USA and Canada to find new export markets.

Total paper production in Western Europe increases 3.6 million tons or 11% compared to the base scenario. Newsprint production increases 40% (1.2 million tons), wood-containing printing and writing papers 25% (0.7 million tons) and other paper and board 7% (1.6 million tons). Because Canada is a major exporter of newsprint and the USA a major exporter of other paper and board to Western Europe, their trade and production are also diminished most. The 2.3 million ton decrease in the total paper production of the USA and Canada means only 2% of their paper production, where as the 1.0 million ton decrease of the paper production of Finland and Sweden means a 4.5% reduction.

Discussion

The results of the analysis indicate that the impacts of forest damage by air pollution are evident in the timber supply and forest-product markets. These impacts primarily affect Western Europe and, except in extreme cases, other regions only to a minor extent. This is mainly because of the smoothening effect of forest-product markets.

Only catastrophic forest dieback or essential changes in cutting behaviour, as a result of regulatory forest policy for example, might have a crucial effect on the Finnish forest sector. Indirect linkages of international forest-product markets may cause unexpected developments also in Finland.

Main results of the analysis are summarized as follows:

1. A short-term increase in timber supply through sanitation harvests will increase timber harvests in Western Europe much less than the amount of sanitation harvests suggest. The relative modest increment in harvests is mainly due to the substitution of sanitation harvests for "normal" harvest.

   Furthermore, the decrease of roundwood imports reduces the effect of increased salvage supply on forest industry production in Western Europe. The adjusting effects of the international markets for forest products dampen the effects in other regions. The increased consumption of forest products caused by lower timber and product prices also helps to absorb the increasing industrial production.

Indirect linkages, however, may result in unexpected developments in the Finnish forest sector. For example, sawn wood production increases as a result of the relocation of coniferous sawlog exports from the USSR to Finland instead of Western Europe.

2. A gradual long-term reduction in the rate of forest growth will reduce timber harvests and forest industry production much less than the reduction in the growth rate suggests. A 50% reduction of forest growth during a period from 1985 to 2010 in Western Europe will reduce harvests in the region by less than 10% in 2010 compared to the base scenario. The decrease in forest industry production is even smaller. Sawn wood and panel production will diminish about 1%, pulp production about 10% and paper and board production less than 5%.

   The effect on the Finnish forest sector is marginal. For example, the reduction of paper production is insignificant, because its production in Western Europe diminishes most in other paper and board categories of which the USA is a major importer.
3. The market mechanism plays a major role in absorbing the effects of potential forest damage in Western Europe on other regions. The forest sector as a whole reacts slowly to, and smoothens, the changes in timber supply. Inertia is also present, especially in investments and trade. Changes in timber supply change wood prices, which cause changes in consumption. Finally, changes in harvests and production in one region are absorbed by a large number of often intrigately linked changes in production, consumption and trade in other regions.

To a certain extent, the main results presented above contradict a common belief that Western European forest damage will substantially decrease cuttings and disturb roundwood markets in Finland. Because of the uncertainty concerning the future, we do not know which of the alternatives will be true, if any. The common belief is not based on scientific investigation. Although the results of this work are so based, the model runs are dependent on the structure and parameter values of the model employed. Some of the assumptions used in model runs can be questioned.

In the model, we have assumed that sanitation harvests concern only coniferous timber. The main reason for this is that forest damage in Western Europe has so far been discovered mainly in coniferous species. The neglect of nonconiferous timber can be defended by the fact that their share is not more than 18% of the growing stock in Finland.

Furthermore, Western European broad-leaved trees are not very competitive for the timber quality. As for logs, in Finland birch is used mainly for plywood production, and the Finnish birch plywood is so superior that the danger of increasing Western European competition does not exist. As for pulpwood, there is a chronic shortage of nonconiferous pulpwood in the Finnish forest industry, and this tree assortment is the most important item in roundwood imports. Therefore, any increase in imports is warmly welcomed by the industry if the wood quality satisfies requirements.

In the model, the decrease of the growth rate of trees due to soil acidification is assumed to be gradual and advance rather slowly. There are strong opinions (e.g. Hari et al. 1987) that the reduction is sudden. This alternative was studied by Dykstra and Kallio (1987), and their result was that roundwood markets react very slowly even to a drastic and sudden drop in growth rates. Furthermore, it must be remembered that most Western European forests are overaged and overstocked, and in the 10–20 year time horizon there is a silvicultural need for increased cuttings regardless of growth rates (Kuusela 1987).

We have assumed that wood supply in Eastern Europe and in the Soviet Union, as well as in Finland and Sweden, is not affected by sanitation harvests nor reduced timber growth rates. It is, however, assumed exogenously that the Eastern Block will increase its timber supply by 15% from 1985 to 2010. This can at least partly be interpreted as a result of forest dieback in some centrally planned countries. For reasons of organization and the weak logistics of timber harvesting as well as difficulties in rapidly expanding the industrial capacity, it may be difficult for the Eastern Block countries to increase their cuttings more than is considered necessary for exporting timber in order to earn hard currency.

As for Finland and Sweden, it is very probable that sanitation harvests can easily substitute for normal harvests, because timber-harvesting logistics is well established. So far, the growth rates have increased, not decreased, and concerning the structure of forests, cuttings should increase during the next 10–20 year period, even though the growth rates would decrease.

In the model, the dynamic aspects of timber supply are handled by shifting a short run marginal cost curve through time in response to changes in the level of timber inventory. This procedure does not, however, account for any intertemporal conditions of market equilibrium. As a consequence, reduced future growth affects only future prices and not current ones. A Hotelling-type specification (see Hotelling 1932) of the timber supply component would produce immediate increases in current prices: producers would shift production from current years into future years to take advantage of the higher prices anticipated in the future.

In the short run, this process would tend, at least in part, to smooth out the price effects and to sharpen the quantity effects. In the long run it might, however, as well smoothen the quantity effect, as indicated by Ovaskainen (1987).

There are also some other critical assumptions that may affect the results of model runs, such as those for price elasticities, the quality of timber removed in sanitation harvests and the exclusion of combined effects with other variables (exchange rates, production cost structures, etc.). The most important feature concerning the results of this study is, however, the structure of the basic model, especially those parts which create inertia in the behaviour of the model.

An advantage of this kind of study is that it is comparative in nature. This means that air pollution alternatives are compared to a base case scenario, and hence only the deviations from the base are analysed. This smoothens the possible errors in assumptions and in the structure of the model. We are, therefore on the rather safe side when we repeat our main conclusion from this study that air pollution damage in Western Europe will have only a minor effect on the Finnish forest sector during the next 25-year period.

Appendix

Product Categories:

1. Coniferous logs
2. Nonconiferous logs
3. Coniferous pulpwood and chips
4. Nonconiferous pulpwood and chips
5. Fuelwood
6. Coniferous sawn wood
7. Nonconiferous sawn wood
8. Veneer and plywood
9. Composition panels
10. Coniferous white pulp
11. Nonconiferous white pulp
12. Newsprint
13. Wood-containing printing and writing paper
14. Wood-free printing and writing paper
15. Other paper and board
16. Recycled paper

Regions:

1. Western Canada
2. Eastern Canada
3. Western USA
4. Eastern USA
5. Brazil
6. Chile
7. Rest of Latin America
8. Finland
9. Sweden
10. Rest of Western Europe
11. USSR
12. Eastern Europe
13. Africa
14. China
15. Japan
16. Southeast Asia
17. Australia-New Zealand
18. Rest of the World

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The main research report of the Finnish Acidification Research Programme (HAPRO), designed to support research in this field between 1985 and 1990 with a total budget of about 50 million FIM (about 11 million USD), is the most complete presentation available on the acidic deposition issue in Finland.

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