TEMPORAL AND REGIONAL PATTERNS OF ATMOSPHERIC COMPONENTS AFFECTING ACIDIFICATION IN FINLAND

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ACADEMIC DISSERTATION

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Title

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Abstract

Acid deposition is caused by the anthropogenic and natural emissions of sulphur dioxide and nitrogen oxides. The main sources of the anthropogenic emissions are fossil fuel consumption and industrial processes. In this study, the atmospheric compounds affecting the acidification in Finland have been investigated from different viewpoints. The geographical distribution, temporal trends and episodicity describe the regional and temporal variations, while the exposure and modelled values illustrate the impact of the different air transport directions or emission areas.

In Finland, the SO_2 emissions and concentrations in the background areas have decreased by more than 80% since 1981. The reductions of sulphate concentrations in air and precipitation have been lower due to the dominance of the long range transport. The gas phase and particulate nitrogen compounds showed few significant trends in the 1990's. A steep decline in the atmospheric base cation deposition was discovered especially in the south-eastern part of the country.

From the Finnish perspective, the emissions of SO_2 are largest in the countries to the south as well as to the southwest and west of Finland. The frequent transport from these sectors together with the lower SO_2 emission reductions, especially in the southern sector, have contributed to the lower reductions in the sulphate concentrations. The highest sulphur dioxide and particulate sulphate concentrations in southern and central Finland originate from the sectors between south and east, while the transport is most frequent from the western sectors. Thus, the atmospheric sulphur exposure is highly affected by transport with the cleaner westerly winds, although the highest concentrations also have a remarkable effect on the mean concentration level. In the north, the transport from northeastern and northern sectors is also important for the exposure.

From the Finnish perspective, the nitrogen oxide emissions are highest in the countries in the southwestern and western sectors. There the reduction has been lower than the average in the area contributing to the deposition in Finland. The frequent transport from these areas has highly affected the Finnish concentrations and exposure.

Areas in central and especially northern Finland are highly episodic as far as the distribution of daily acid deposition factors is concerned.

ILMATIETEEN LAITOS

Tekijä

Tuija Ruoho-Airola

Nimeke

Happamoitumiseen vaikuttavien ilmaperäisten yhdisteiden ajallinen ja alueellinen vaihtelu Suomessa

Tiivistelmä

Ihmistoiminnan aiheuttamat ja luontoperäiset rikin ja typen oksidien päästöt ovat keskeinen happaman laskeuman aiheuttaja. Fossiilisten polttoaineiden poltto ja monet teollisuusprosessit ovat vuorostaan ihmistoiminnan tärkeimmät lähteet. Tässä työssä happamoitumiseen liittyviä ilmaperäisiä yhdisteitä tutkittiin useasta näkökulmasta. Maantieteellinen jakauma, trendit ja episodisuus kuvaavat alueellista ja ajallista vaihtelua, kun taas kertymä ja laskennalliset arvot osoittavat eri kulkeutumissektorien tai päästöalueiden vaikutusta.

Suomen rikkidioksidipäästöt ja pitoisuus taustailmassa on vähentynyt yli 80% vuodesta 1981. Ilman ja sadeveden sulfaattipitoisuuksien alenema on ollut pienempi johtuen kaukokulkeuman vallitsevuudesta. Ilman kaasu- ja hiukkasmaiset nitraattiyhdisteet vähenivät merkittävästi vain harvoilla mittausasemilla 1990-luvulla. Emäskationilaskeuma väheni jyrkästi erityisesti maan kaakkoisosassa.

Suomesta tarkastellen rikkidioksidipäästöt ovat suurimmat maissa, jotka sijaitsevat etelä-, lounais- ja länsisuuntaan. Vallitseva ilmavirtaus Suomeen on näistä sektoreista, mikä, erityisesti eteläsektorissa, hitaammin vähentyneiden päästöjen kanssa aiheuttaa sulfaattipitoisuuksien hitaamman alenemisen. Korkeimmat rikkidioksidi- ja ilman sulfaattipitoisuudet Etelä- ja Keski-Suomessa ovat peräisin etelän ja idän välisestä sektorista, kun taas kulkeutuminen on vallitsevaa länsisektorista. Siten puhtaammat läntiset tuulet vaikuttavat voimakkaasti ilman rikin kertymään, vaikkakin suurimmat pitoisuudet vaikuttavat merkittävästi keskipitoisuuteen. Pohjoisessa kertymään vaikuttaa myös merkittävästi kulkeutuminen koillisesta ja pohjoisesta.

Suomesta tarkastellen typen oksidien päästöt ovat korkeimmat maissa, jotka sijoittuvat lounais- ja länsisektoriin. Siellä vähenemä on ollut alempi kuin keskimäärin maissa, jotka vaikuttavat Suomen laskeumaan. Vallitseva kulkeutuminen näiltä alueilta on vaikuttanut merkittävästi Suomen pitoisuuksiin ja kertymään.

Happamaan laskeumaan vaikuttavien yhdisteiden vuorokausilaskeuma on erittäin episodimainen erityisesti maan pohjois- ja keskiosissa.

CONTENTS

PAPERS INCLUDED IN THE THESIS

This thesis consists of an introductory review part, followed by five original research publications.

I: Ruoho-Airola, T., Anttila, P. and Salmi, T., 2004: Airborne sulphur and nitrogen in Finland — trends and exposure in relation to air transport sector. Journal of Environmental Monitoring **6**, pp. 1–11.

II: Ruoho-Airola, T., Syri, S. and Nordlund, G., 1998: Acid deposition trends at the Finnish IM catchments in relation to emission reductions. Boreal Environment Research **3,** pp. 205–219.

III: Ruoho-Airola, T. and Salmi, T., 2001: Episodicity of sulphate deposition in Finland. Water, Air, and Soil Pollution **130**, pp. 529–534.

IV: Ruoho-Airola, T., Alaviippola, B., Salminen, K. and Varjoranta, R., 2003: An Investigation of base cation deposition in Finland. Boreal Environment Research **8,** pp. 83–95.

V: Ukonmaanaho, L., Starr, M. and Ruoho-Airola, T., 1998: Trends in sulphate, base cations and H^+ concentrations in precipitation and throughfall at Integrated Monitoring sites in Finland 1989–1995. Water, Air, and Soil Pollution **105**, pp. 353–363.

The author's contribution:

I T. Ruoho-Airola planned and wrote the paper, except the emissions and emission reduction section. The assessment method was developed and the calculations performed jointly with the other authors.
II The paper was planned and the results were assessed jointly by T. Ruoho-Airola, S. Syri and G. Nordlund. T. Ruoho-Airola was responsible for the manuscript coordination and the trend estimates for the observed data.
III T. Ruoho-Airola planned and wrote the paper, which was commented by T. Salmi. The data analysis was performed jointly.
IV T. Ruoho-Airola planned and wrote the paper. The regionalisation method was developed and the calculations performed jointly with the other authors.
V The paper was initiated and planned jointly by L. Ukonmaanaho, M. Starr and T. Ruoho-Airola. L. Ukonmaanaho and M. Starr wrote the first draft of the paper. T. Ruoho-Airola was responsible for the bulk precipitation.

1. INTRODUCTION

1.1. Background

The acid deposition problem can be defined as a situation in which the deposition of the acidifying compounds is higher than the level that does not cause harmful effects to humans, ecosystems or materials. The reason for acid deposition are the anthropogenic and natural emissions of sulphur dioxide and nitrogen oxides. The main sources of the anthropogenic emissions are fossil fuel consumption and industrial processes.

The harmful effects of acid deposition were recognised in e.g. the United Kingdom centuries ago, but a true understanding of this phenomenon first started to develop in the 1950's (Seinfeld and Pandis, 1998; Oden, 1968).

The atmosphere is an effective oxidizing medium, where the emitted compounds readily undergo reactions to oxidize further to sulphate and nitrate. Both gas phase and liquid phase reactions in the atmosphere are important routes to the acidic sulphate and nitrate products. The atmospheric chemistry associated with the acid deposition process, especially the part starting with nitrogen oxide, is complex. Fig. 1. shows schematically the atmospheric cycles of the sulphur and nitrogen compounds. The reactions are controlled by many factors in the atmosphere, both chemical and physical, e.g. the concentrations of the oxidising agents (O, OH, O_3), the concentration ratios of the different air pollutants, and the acidity of the liquid water associated with particles and humidity. (Seinfeld and Pandis, 1998). The oxidized sulphur and nitrogen compounds can exists either in gaseous form, bound in particles, or dissolved in rain water.
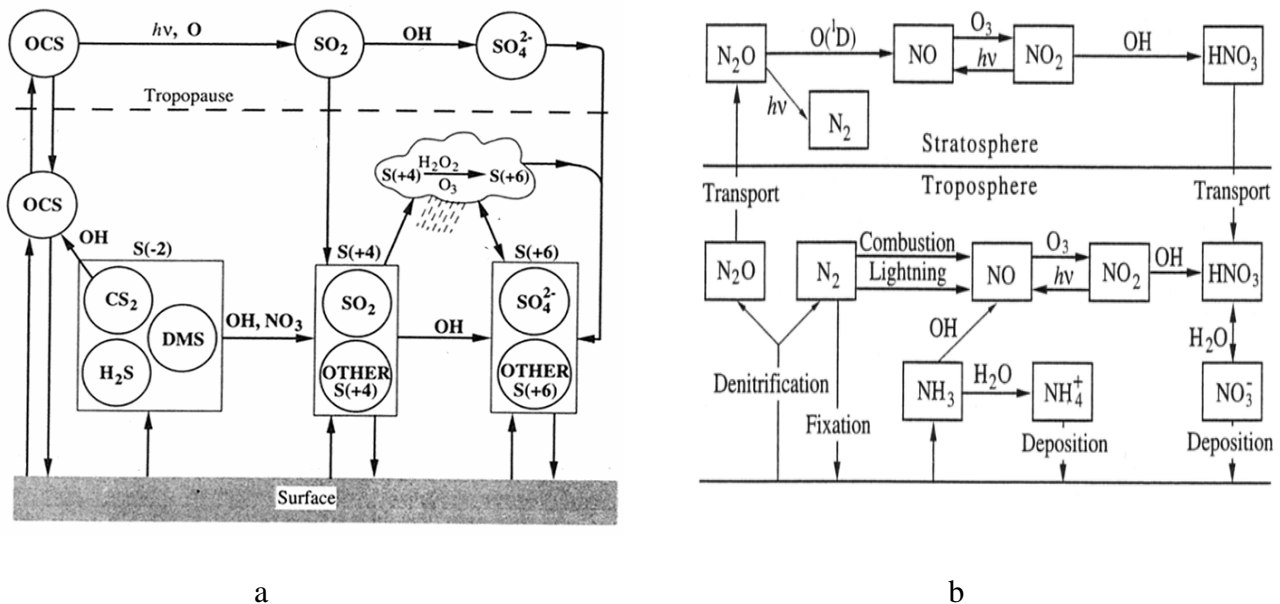
Figure 1. Atmospheric cycles of sulphur (a) and nitrogen (b) according to Seinfeld and Pandis (1998) and Berresheim et al. (1995). H_2S, DMS, CS_2 and OCS are sulfides.

The primary emitted oxides and their reaction products are transported with the air flows and simultaneously removed from the atmosphere by the dry and wet deposition processes. The dry deposition rate of the gaseous and particulate compounds is controlled by the physical and chemical characteristics of the compound, the properties of the surface and the state of the atmospheric

boundary layer. (Sehmel, 1980; Wesely and Hicks, 2000). Wet deposition is naturally highly affected by the amount of precipitation, but also the type of the aqueous phase (e.g. liquid water, snow or ice). Wet deposition removes the acid components from the atmosphere by several processes, which occur both in clouds and below clouds. The atmospheric lifetimes of sulphur dioxide (SO_2), nitrogen oxides (NO_x) and their oxidation products are of the order of a few days (Schwarz, 1979; Levine and Schwarz, 1982; Logan, 1983), thus leading to mean transport distances of 400-1200 km (Seinfeld and Pandis, 1998).

Ammonia (NH_3) and other atmospheric basic compounds, such as calcium (Ca^{2+}), sodium (Na^+), potassium (K^+) and magnesium (Mg^{2+}), neutralize part of the acidic compounds. Ammonia is highly reactive and it is removed from the atmosphere via reactions with sulphate or nitrate (Seinfeld and Pandis, 1998). Ammonium (NH_4^+) has also a potential acidifying influence if the ion is deposited in an ecosystem which is nitrogen saturated. Under such circumstances NH_4^+ will be oxidized to nitrate (NO_3^-) (Reuss and Johnson, 1986). The deposition of the alkaline metals provides the ions for neutralising the input of acidity, and they might compensate for part of the buffering capacity lost in the acid deposition. Thus, the emissions of the base compounds also play an important role in the chemistry of acid deposition.

The components NH_3/NH_4^+, SO_2/SO_4^{2-} and $NO_2/NO_3^-/HNO_3$ interact with each other in the secondary atmospheric aerosol formation resulting in differences in the formation of fine and coarse particulate matter and — due to their different sizes — in different atmospheric life times and consequently different long range transport. Furthermore, different precursor compositions will lead to different rates of aerosol formation. Sulphate and ammonium react readily and are mainly found in fine particles; they might be transported to Finland from a long distance, but also from nearby areas (Pakkanen et al., 1999). A large part of the nitrate is carried to Finland with maritime air masses in coarse particles, which deposit faster and can not be of distant origin (Kerminen et al., 1997). The formation of NH_4NO_3 in fine particles needs excess ammonia compared to sulphate (Pakkanen et al., 1999) and is favoured in cool and humid conditions (Kerminen et al., 1997). Thus, many factors, besides the primary emissions, affect the observed concentrations and trends of the compounds involved in the acid deposition process, including their relative concentrations in the atmosphere, the reversible nature of some of the reactions and the meteorological situation.

Harmful effects are caused by the acid deposition through the acidification of surface waters and the forest soil and damages to the vegetation and materials. Acidic deposition reduces the base saturation of the soil and may also in the long term reduce the pH of the soils. Acidic deposition may also lead to a decrease in the pH of the surface waters in areas where the soil has a low buffering capacity. Soil acidification may lead to the release of inorganic aluminium, known to be toxic to plant roots and to fish. Critical chemical processes occur in the soil (Reuss et al., 1987), since a major part of the air pollutants passes through the soil before entering the surface waters (Mannio, 2001).

1.2. International measures to solve the acid deposition problem

The long-range transport of acidifying components has been a severe environmental problem in Finland and the other Nordic countries for decades. In other parts of Europe the damage caused by acidifying compounds to natural ecosystems has likewise given rise to concern. A West-Europe wide monitoring of acid deposition was conducted in the early 1970's under the Organization for Economic Cooperation and Development (OECD). International negotiations on emission reductions resulted in the signing of the Convention on Long-range Transboundary Air Pollution (CLRTAP) under the UN Economic Commission of Europe (UN/ECE) in 1979 (UN/ECE, 1996). Under CLRTAP, the first sulphur protocol was signed in 1985; the signatories agreed to reduce the sulphur emissions to 30 % of the emissions in 1980 by 1993. A new protocol to further reduce the

sulphur emissions in Europe followed in 1994. The protocol to control the emissions of nitrogen oxides and their transboundary fluxes, signed in 1988, requested that the nitrogen oxides emissions in 1994 should not exceed those in 1987. Finally, in 1999, the Gothenburg Protocol to abate the acidification, euthrophication and the ground-level ozone was signed. This multi-pollutant/multi-effect concept makes it possible to analyse the multiple environmental impacts of the emission controls of the four pollutants considered: sulphur dioxide, nitrogen oxides, ammonia and volatile organic compounds. The second sulphur protocol and the Gothenburg Protocol are based on the critical loads concept. Critical loads are generally defined as: "a quantitative estimate of exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" (Nilsson and Grennfelt, 1988).

The signatories of the CLRTAP have agreed to cooperate in research and monitoring. In the beginning the EMEP programme focused on assessing the transboundary transport of acidification and euthrophication, later on other compounds were added to the programme. The task given to EMEP is to provide qualified scientific information on the geographical distribution and trends of the acidification. Within the EMEP programme the key variables of the acidification issue are determined both by frequent monitoring and detailed modelling. For the monitoring of the effects of the main air pollutants, the operation was conducted under the Working Group of Effects. Estimation of the critical loads of acidification and their exceedance is also a task of one of the International Cooperative Programmes under the Working Group on Effects.

The acidifying load can be transported thousands of kilometers. In order to improve the situation, one needs to know the emissions and the transboundary transport of acidification widely. Monitoring is needed to verify that the commonly agreed emission reductions lead to satisfying results regarding the acidification. The components included in the acidification chemistry have to be assessed extensively, and reliable monitoring and modelled data are needed on all those of high importance to the problem.

The international and domestic targets might be partly different, and thus domestic studies of the situation are important. For Finland, the CLTRAP has greatly contributed to improve the acidification situation from the level of the 1980's. In addition to this, the Finnish activity in this international cooperation has been intense and successful.

1.3. Acid deposition in Finland – a historical perspective

The early monitoring of the background air quality in Finland, covering many stations and a long time period, is reported to have been conducted within the international IMI network (Internationella Meteorologiska Institutet). (Kulmala et al., 1982). The monitoring was initiated by the Stockholm University in the 1950's and covered several Western European countries. In Finland, the Institute of Marine Research performed the early measurements, whereafter the activity was transferred to the Finnish Meteorological Institute in 1976.

The concern for the acidifying compounds and their harmful effects in the Nordic countries led to the establishment of the international monitoring programme LRTAP (Long-Range Transport of Air Pollutants) within the OECD Organisation in the beginning of the 1970's. Since then, the first increasing and later decreasing acid deposition has been widely studied.

In Finland the monitoring of acid deposition has been performed within several international programmes since the early 1970's: the UN ECE EMEP programme (United Nations Economic Commission for Europe, European Monitoring and Evaluation Programme) (the successor of the LRTAP programme), the WMO BAPMoN (World Meteorological Organisation Background Air Pollution Monitoring Network) and GAW (Global Atmosphere Watch) programmes, the UN ECE

IM (Integrated Monitoring) programme, the Baltic Marine Environment Protection Commission programme and, in the Arctic areas of Finland, the AMAP (Arctic Monitoring and Assessment Programme). Domestic measuring programmes for air and precipitation quality of the Finnish Meteorological Institute and the Finnish Environment Institute have supplemented the above mentioned measurements to cover the whole country. Within the UN ECE IM programme monitoring of the air quality in the forests has been performed by the Finnish Forest Research Institute. Starting in the 1970's, intensive assessments of the acid deposition in Finland have been performed, focusing on changes in the measured air concentrations and depositions and the origin of the pollutants (e.g. Järvinen and Haapala, 1980; Kulmala et al., 1982; Joffre et al., 1990; Järvinen and Vänni, 1990; Kulmala et. al., 1990; Laurila, 1990; Kulmala et al., 1998; Ukonmaanaho and Raitio, 2001).

Matematical models have been developed to simulate the transport and deposition of the acidifying compounds. The Finnish acid deposition situation has been simulated as a part of the European wide modeling by models developed in the international programmes (Simpson et al., 2003). Several studies focusing more on the Finnish perspective and the factors specifically affecting the Finnish contribution have been published (e.g. Johansson et al., 1990; Tuovinen et al., 1990; Syri et al., 1998; Hongisto, 2002 and Hongisto et al., 2002).

During the 1980's, the alarming news of the serious forest decline in Central Europe caused increased concern of the harmful effects of acid deposition in Finland, which led to the interdisciplinary Finnish Acidification Research Programme (HAPRO) during 1985-1990 (Kauppi et al., 1990). Several studies have been published on the harmful effects on water (Forsius et al., 1990; Rask and Tuunainen, 1990; Mannio, 2001), forests (Nissinen and Ilvesniemi, 1990; Ukonmaanaho and Raitio, 2001; Ukonmaanaho, 2001) and groundwater (Soveri and Ahlberg, 1990; Backman et al., 1999). In the 1990's, the harmful effects of the emissions from the Kola Peninsula were investigated in an other extensive programme, the Lapland Forest Damage project (Tikkanen and Niemelä, 1995).

In Finland, the Air Pollution Control Act and later the Environmental Protection Act have been the instruments in preventing air pollution. In addition the Council of State has issued regulations and guidelines on the air quality, the emissions, the composition of products and reductions of the use and import of products. In the 1990's, the transboundary air pollution became a subject of cooperation within the European Union, resulting in the National Emission Ceilings Directive in 2001. (Ministry of the Environment, 1989 and 2002).

1.4. Emissions of the components related to acid deposition

The emissions of sulphur dioxide, nitrogen oxides and ammonia have been officially submitted by the Parties to the Convention on Long Range Transboundary Air Pollution to the EMEP programme since 1980. The main sources of sulphur dioxide and the nitrogen oxides are the combustion of fossil fuel in power stations and industrial plants. Traffic is also a major source of nitrogen oxides, while ammonia is emitted mainly from agricultural activities. The emissions reported for the whole EMEP area have been completed and corrected, when necessary, by the EMEP MSC-W, and are available from the UNECE/EMEP gridded emission database (Webdab, 2003). The EMEP emission data base is currently probably the most complete and reliable emission survey covering the whole of Europe. The time series for 1980-2000 of the emissions in Finland and the sum of the total EMEP area (see e.g. EMEP/MSC-W, 1998) are presented in Fig. 2. (Vestreng, 2003).
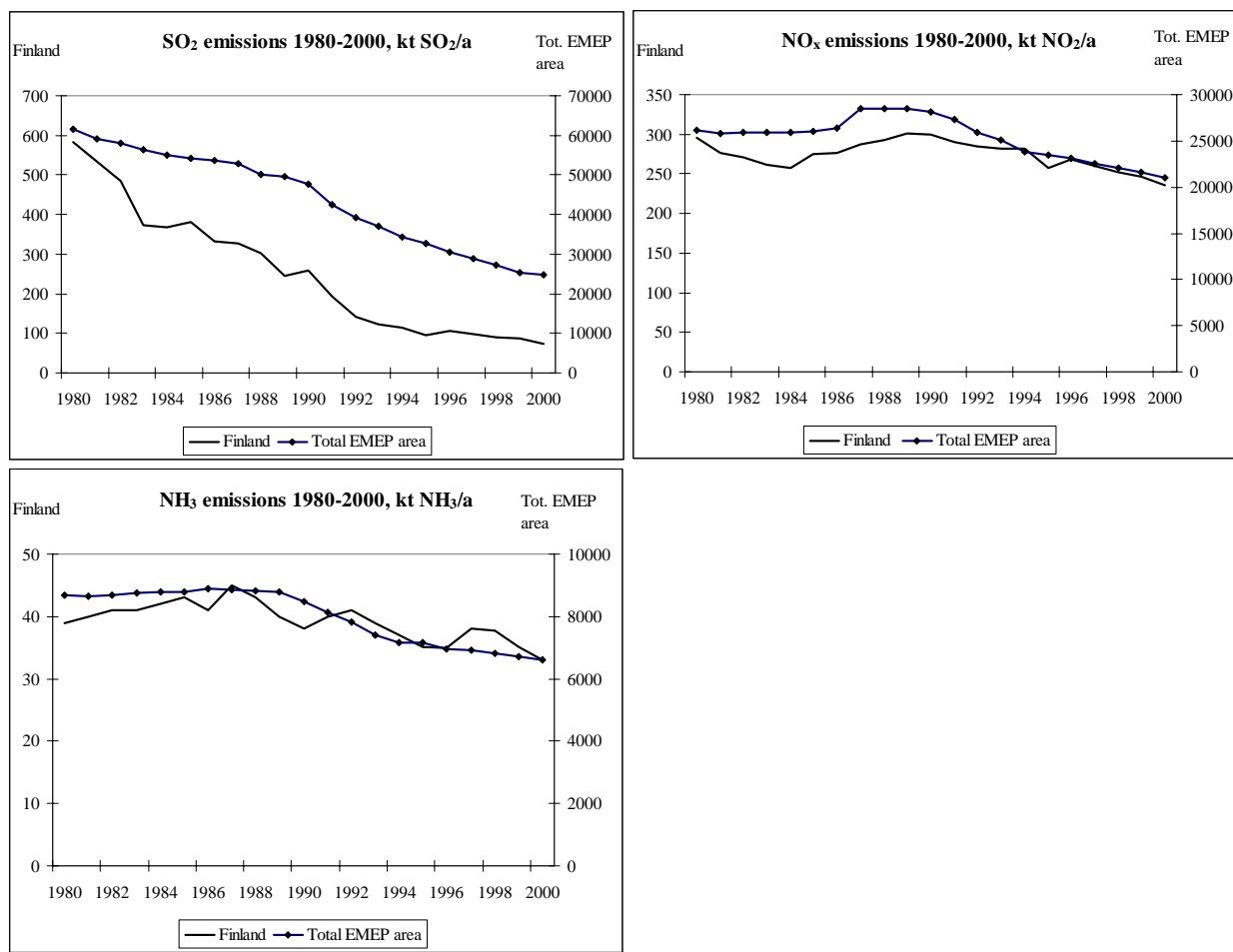
Figure. 2. Emissions of SO_2, NO_x and NH_3 in 1980-2000 in Finland and the sum of the emissions of the total EMEP area. (Vestreng, 2003)

There are few emission inventories of the base cations within the EMEP area. For calcium, inventories have been made for all sources (Lee et al., 1998) and for the anthropogenic sources (Lee and Pacyna, 1998).

In Finland, the base cation emissions were estimated for 1987 in connection with the Finnish Acidification programme HAPRO. The main sources of alkaline aerosols in Finland were soil dust, energy production, industrial processes, traffic and seawater; from the anthropogenic sources the biggest single contributors were the combustion of wood and dust emissions raised by traffic (Anttila, 1990). The high emissions of the base cations from the Estonian oil shale power plants have strongly affected the deposition in southeastern Finland (Laurila et al., 1990; Jalkanen et al., 2000; Tervahattu et al., 2002; Sofiev et al., 2003).

1.5. Objectives of this study

The concentrations of the compounds related to acid deposition in Finland are highly affected by long-range transport. Since the emissions in Europe have declined at a different pace in different countries, the origin of the air masses and the frequency of transport sectors have strongly influenced the mean concentrations and the trends. There is a need for a regional scale assessment of the updated trends and the origin of the acid deposition.

The deposition of the base cations is also an important element in determining the total deposited acidity in the critical loads approach. In the Finnish soils where the mineral content and the weathering rate are low, atmospheric deposition may be a significant source of base cations. The possible decline of the base cation deposition will partly offset the positive effect of the reductions of sulphate and nitrogen deposition. Thus, detailed knowledge of the deposition of base cations is needed for planning and implementing the international emission reduction policies.

The uneven temporal distribution of the annual acidic deposition might cause a further ecological risk to the vulnerable northern environment, which has not been thoroughly investigated.

The aim of this study was to find answers to the following questions concerning acid deposition in Finland:

- what has been the development of the geographical distribution and the temporal trends of the atmospheric components related to acid deposition during the time of the international emission reductions

- how are the changes of the European emissions reflected in the concentrations and depositions in Finland

- what is the impact of the different air transport directions on the distribution of the measured acid deposition in Finland

- how evenly is the annual load of acid deposition distributed in a temporal scale

The structure of the study is presented in Table 1.

Table 1. The aspects of the acidification issue in Finland examined in papers I-V.

Paper	Time period	Emissions	S air	S prec.	N air	N prec.	Base cations	Origin of pollutants	Trend	Other subjects
I	1981-2000	X	X	X	X	X		X	X	Exposure
II	1988-1996	X	X	X	X	X	X	X	X	Modelled values
III	1990-1998			X						Episodicity
IV	1985-1999						X		X	Regionalisation
V	1985-1995		X	X			X		X	Throughfall

2. MATERIAL AND METHODS

2.1. Measurement stations and monitoring

The ambient air and precipitation concentration measurements were performed within the background air quality monitoring network of the Finnish Meteorological Institute, except the throughfall measurements in paper V and part of the base cation concentration measurements in particles in paper IV.

The air quality monitoring network has been planned such that the results from the measuring stations would represent a larger area of the country. Most stations are situated in undisturbed background areas without nearby emission sources. However, practical details, like the frequent maintenance of the samplers, electricity etc., have limited the number of places suitable for establishing the stations. In order to investigate the temporal trends of the concentrations, the measurement station locations have been kept, as far as possible, unchanged for long periods. However, some station locations have been moved slightly due to changes in the surroundings of the stations, mostly because of increased traffic.

The stations operate according to different air quality monitoring programmes. Fig. 3. lists the programmes and the stations included in 1998, when all the stations covered in this study where in operation. The abbreviations used for the programmes are the following: EMEP for the Co-operative Programme for Monitoring and Evaluation of the Long-Range transmission of Air Pollutants in Europe, co-ordinated by the UN/ECE; IM for the International Co-operative Programme Integrated Monitoring, co-ordinated by the UN/ECE; GAW for Global Atmosphere Watch, co-ordinated by the World Meteorological Organization; HELCOM for the Baltic Marine Environment Protection Commission; national stations for the national programme to supplement the others in order to cover the whole country. The stations on the map are grouped to represent different areas of the country when the results are discussed. The following abbreviations of the areas are later used in the text: SW for southwestern Finland, SE for southeastern Finland, C for central Finland, SL for southern Lapland, and NL for northern Lapland.

Four of the stations are located in a marine environment. The stations Utö (SW), Guttorp (SW) and Hailuoto (C) are located on Baltic Sea islands, while Virolahti (SE) is on the coast of the Gulf of Finland. Utö is situated on a rocky outer island, the surroundings of the other marine stations are sparsely populated agricultural areas with forests and fields. All other stations are inland stations, Virolahti and Ähtäri in sparsely populated agricultural areas, surrounded by forests and fields, and the other stations in mostly forested environments. The stations are situated from 4 to 375 m above the sea level, most stations lower than 200 m a.s.l.. The stations measuring precipitation have been presented in detail, including maps and descriptions of the surroundings, in the combined report of the Finnish Environment Institute and the Finnish Meteorological Institute (Vuorenmaa et al., 2001). The catchment areas of the IM programme have been presented in detail in Bergström et al. (1995).

In the beginning of the study period gaseous SO_2 was sampled by the H_2O_2 absorption method at all stations. Since 1989 an open-face filter pack with a NaOH impregnated Whatman 40 filter has been used at the EMEP stations. Particulate SO_4^{2-} is sampled on a Whatman 40 filter installed in front of the SO_2 sampling. The sum of the gaseous HNO_3 and particulate NO_3^- is sampled by the same filter pack as the sulphur compounds. Sampling artifacts due to the evaporation of fine particulate nitrate from the first filter and recollection on the impregnated filter (Pakkanen et al., 1999) make the separation of these compounds by a simple aerosol filter pack unreliable. For the sum of the
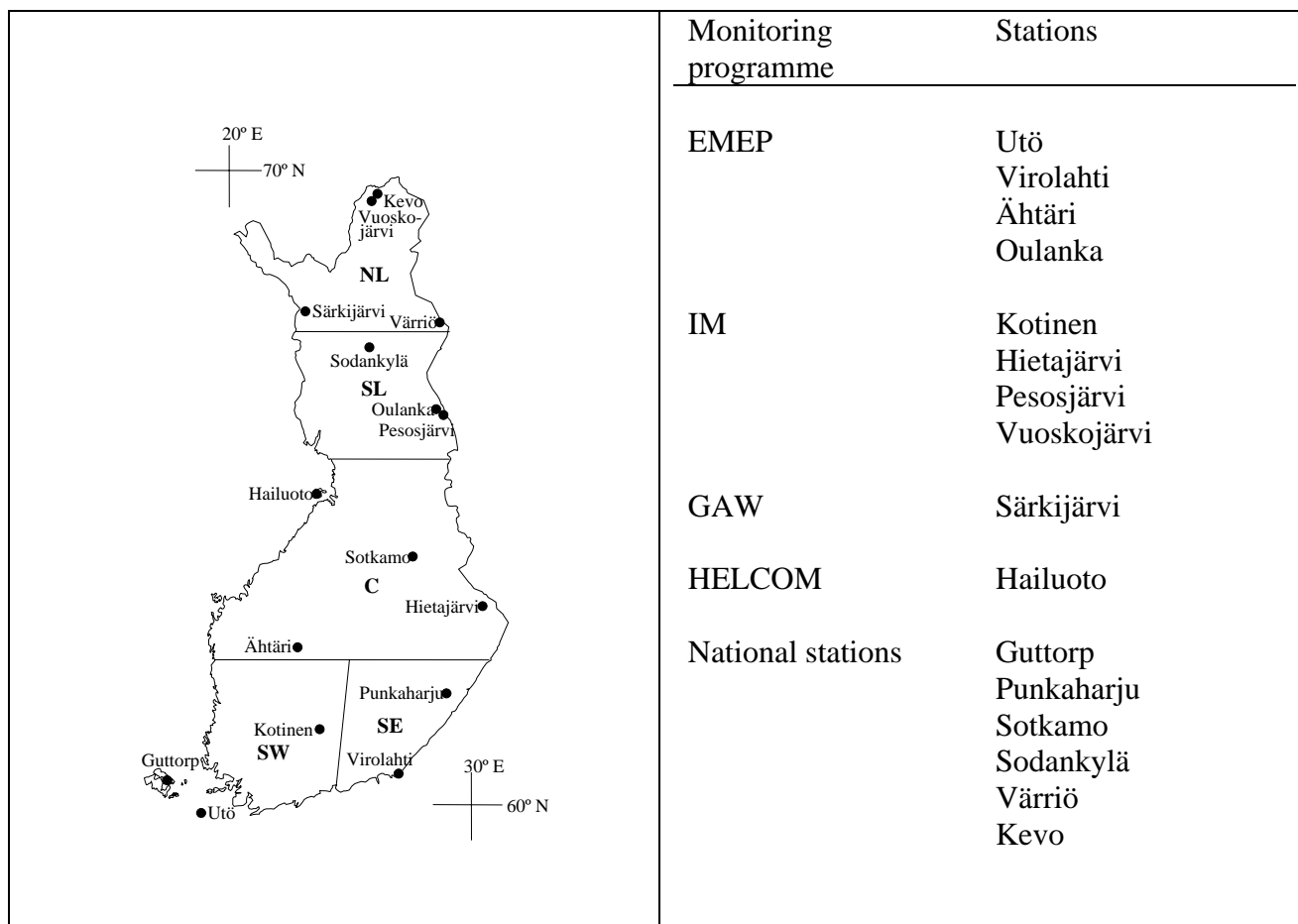
Monitoring programme	Stations
EMEP	Utö
	Virolahti
	Ähtäri
	Oulanka
IM	Kotinen
	Hietajärvi
	Pesosjärvi
	Vuoskojärvi
GAW	Särkijärvi
HELCOM	Hailuoto
National stations	Guttorp
	Punkaharju
	Sotkamo
	Sodankylä
	Värriö
	Kevo

Figure 3. Location of the background stations in 1998 and a list of stations in the different monitoring programmes.

NH$_3$ and particulate NH$_4^+$, a second filter line is used with a (COOH)$_2$ impregnated Whatman 40 filter. For the deposition samples, the stations have been equipped with NILU-type bulk deposition samplers.

The analysis is performed at the Air Chemistry Laboratory of the Finnish Meteorological Institute (FINAS accredited laboratory TO97, 9.5.1997). More detailed specifications for the accredited test methods are given in the annual Air Quality Reports (e.g. Leinonen, 2000). At the end of the study period, all compounds were analysed by ion chromatography, the particles and gases after H$_2$O extraction. In the beginning of the monitoring other methods were used: X-ray fluorescence for atmospheric SO$_4^{2-}$ (until 1987), the spectrophotometric Thorin method for SO$_4^{2-}$ in precipitation (until 1984) and SO$_2$ (until 1989), and the indophenol blue method for the ammonium compounds (until 1992 in precipitation and 1995 in air). The base cation concentrations were analysed by atomic absorption spectrophotometry until 1992, whereafter ion chromatography has been used. The NO$_2$ concentration has been monitored by the automated Saltzman method and a chemiluminescence monitor (since 1996). The sampling frequencies used for the components at different stations vary substantially: from continuous, in the case of NO$_2$, to daily at the EMEP stations, and from weekly to monthly at the other stations.

The sampling and the analysis of the samples in the laboratory as well as the quality control of the whole chain have been carried out using the best possible practices according to the guidelines given by the EMEP CCC (Chemical Co-ordinating Centre) (EMEP/CCC, 1996) and ICP IM (Environment Data Centre, 1993). The sampling and analysis methods and changes performed

during the monitoring period have been described in detail in the annual reports of the Finnish Meteorological Institute ranging from 1985 to 2000 (Leinonen, 2001), and in the report on the time trends in concentrations until 1996 (Kulmala et al., 1998).

The troughfall measurements referred to in paper V have been performed by the Finnish Forest Research Institute at the IM stations. The methods used have followed the guidelines of the programme (Environment Data Centre, 1993), the measuring areas and the monitoring methods have been described in detail in Ukonmaanaho and Starr (1995).

The airborne concentrations of base cations, referred to in paper IV, have mainly been analysed during projects of short duration. However, for the stations Punkaharju and Kevo data was available for a longer time period 1989–1999, excluding the years 1993 and 1994. The methods used in the projects to obtain the airborne concentrations are described in detail in Paatero et al. (2001) and Ricard et al. (2002).

2.2. Statistics and assessment methods

2.2.1. Trend calculations

The basic data for the trend analysis were either the monthly or the annual weighted concentrations in precipitation or the concentrations of the gas and aerosol components in air. The existence of a monotonic increasing or decreasing trend was tested with the nonparametric Mann-Kendall test (Gilbert, 1987), followed by the estimate for the slope of a linear trend, calculated with the nonparametric Sen's method (Gilbert, 1987; Sen, 1968) (paper I) or with the nonparametric Seasonal-Kendall –test (Gilbert, 1987; Hirsch et al., 1982; Driscoll et al., 1995) (papers II and V). Both tests for the trend are based on ranks within the time series. Sen's slope estimator is the median of the slopes calculated from all pairs of values in the data series. In cases with a downward trend, when the slope is larger at the beginning, the method may overestimate the total relative change of annual values. A detailed description of the method is given in Salmi et al. (2002).

2.2.2. Impact of the different air transport directions

The origin of the pollutants and the transport directions contributing to the results were studied using back-trajectories and synoptic weather maps. The exposure values are time-weighted airborne concentrations classified according to the air transport sector. The rates of the transboundary and domestic sulphur and nitrogen depositions at the IM stations were calculated with the DAIQUIRI model, the method is described in 2.2.4

The sectors contributing to the gaseous and particulate sulphur and nitrogen compounds were calculated by means of 2-dimensional 925 hPa trajectories describing the transport route of each 24-hour sample. The trajectories were obtained from the EMEP/MSC-W (EMEP, 2003). They were based on meteorological data from the Numerical Weather Predicition models, LAM150 for 1985-1996 and PARLAM-PS for 1997–2000, both developed at the Norwegian Meteorological Institute. The transport routes were calculated by tracking the air parcel every 2 hours for 96 hours backwards in time, 4 times per day along modelled wind fields. The area around the arrival point was divided into 8 equal sectors. The criterion for the allocation of the trajectories of a particular arrival day to a specific sector was that at least 50% of their given positions during transport were found within that sector. If this criterion was not fulfilled, the sector for that day was set undetermined. The accumulated exposure hours of atmospheric sulphur and nitrogen from different sectors were calculated by multiplying the sector mean concentration by the number of days with transport from the corresponding sector. The sum was further multiplied by 24 hours/day to give the unit of exposure, mg h m^{-3}.

The meteorological characteristic of the episodes in paper III were studied using synoptic weather maps, and air trajectories calculated by the TRADOS model of the Finnish Meteorological Institute (Valkama and Rossi, 1992). The weather maps gave a general view of the meteorological features during the episodes. With trajectories calculated backwards in time, an indication of the origin of the deposited pollutant was obtained.

2.2.3. Episodicity

The number of episodic daily sulphate depositions was calculated from values which exceeded the annual median value of the station by a factor of 10. The numbers of episode days were counted. Differences between the stations were tested with the non-parametric Kruskal-Wallis test (Conover, 1980). To ensure that the difference in episodicity between the stations was not caused by coincidence, the calculations were repeated after setting the limit for an episode day at 8, 9, 11 and 12 times the annual median deposition at the stations.

2.2.4. Model calculations with the DAIQUIRI model

In paper II, the deposition in the IM catchments was also estimated by the regional deposition model DAIQUIRI in order to evaluate the extent to which long-term changes in deposition at the IM stations are caused by domestic emission reductions and the extent to which they are due to reduction measures abroad. DAIQUIRI has been developed at the Finnish Environmental Institute in collaboration with the Finnish Meteorological Institute (Syri et al., 1998; Kangas and Syri, 2002), and its construction enables the determination of the contributions of individual emission sources or regions to the total deposition.

DAIQUIRI employs the transfer matrix concept, in which the annual transport has been calculated using more detailed models and the results expressed as two-dimensional matrices, each matrix cell describing the annual amount of deposition caused by a unit source located in the centerpoint of the matrix. These matrices are then used to depict the deposition fields caused by all the individual emission sources, and the total deposition is obtained as the sum of all the deposition fields caused by individual emission sources within the calculation domain and the long-range transported deposition.

The mesoscale sulphur transport matrices represent ten year- averaged weather conditions, and separate matrix sets have been generated for four climatological regions in Finland. The transport matrices of sulphur and nitrogen have a resolution of about 14 km and 30 km, respectively. The deposition from outside the DAIQUIRI calculation region was taken from the annual sulphur, nitrogen oxides and ammonia transport matrices of the EMEP/MSC-W ROOT150 model (Barrett and Berge, 1996). The sulphur transport matrix scheme is described in more detail in Johansson et al. (1990) and the nitrogen transfer matrix system in Syri et al. (1998).

2.2.5. Base cation deposition estimates

The inverse distance weighting (IDW) interpolation method was used for the deposition field calculations in paper IV. Wet deposition was calculated by multiplying the annual bulk concentration field by the precipitation field. Dry deposition was estimated from the seasonal mean airborne concentration fields and the dry deposition velocities for two seasons and two land use classes.

The annual mean concentration of the base cations in precipitation was interpolated by the IDW method to a 5 km x 5 km grid. The annual precipitation field was likewise interpolated by the IDW method from the observations at the 416 meteorological stations. A wet deposition estimate was

calculated to each grid node by multiplying the concentration value by the amount of precipitation. The weight factor related to the distance between the location of interest and the observation point was proportional to the second power of the distance.

Dry deposition was estimated by a combination of interpolated seasonal airborne concentrations and seasonal dry deposition velocities for different land use classes. The deposition velocities used in Norway were applied in this investigation and are given in paper IV (Table 2) (Tørseth and Semb, 1998). The EMEP land use classification in a 50 km x 50 km grid by Sandnes (1995) was used. The division of the land use was, however, made only into two classes, one for forest and one for other areas.

3. RESULTS AND DISCUSSION

3.1. Emission reductions

The atmospheric sulphur and nitrogen concentrations in Finland are not only a result of the national emissions but also affected by the European wide emissions and their changes. Changes in the emissions of sulphur dioxide and the nitrogen compounds in areas relevant to the deposition in Finland are shown in Table 2. The emissions have been published by Vestreng (2003).

Table 2. Emission reductions of sulphur dioxide, nitrogen oxides and ammonia in Finland and selected European countries. Reductions are given for the periods 1981-2000 and 1990-2000.

Emission area	Emission reduction	
	Period 1981-2000,%	Period 1990-2000,%
SO$_2$		
Finland	86	72
Kola Peninsula	73	57
Russia (Kola Peninsula excluded)	72	57
Countries to the south of Finland	63	56
Countries to the southwest and west of Finland	78	68
Total	**73**	**62**
NO$_2$		
Finland	15	21
Kola Peninsula	-33	36
Russia (Kola Peninsula excluded)	39	35
Countries to the south of Finland	44	43
Countries to the southwest and west of Finland	28	27
Total	**33**	**32**
NH$_3$		
Finland	17	13
Kola Peninsula	negligible	negligible
Russia	45	45
Countries to the south of Finland	45	42
Countries to the southwest and west of Finland	11	9
Total	**28**	**35**

The reduction of the Finnish SO$_2$ emissions in 1981-2000 was 86%. First the reduction rate was steep, after 1995 the emissions have been more uniform. In the 1990's the emissions declined by 72%. The Finnish emission reduction was much higher than the mean emissions reduction in the

twenty five European countries contributing most to the deposition of oxidized sulphur in Finland. The emissions have decreased most in countries to the southwest and west of Finland, whereas the likewise high emissions in the southern sector have declined less.

The sulphur and oxidized nitrogen emissions originating from the shipping in the Baltic Sea, which are not included in Table 2, were estimated to contribute 6 % and 10 %, respectively, to the deposition in Finland (Johnson et al., 2000). The ship emissions are based on estimates for the year 1990 and no update has been made. During recent decades, there has been a significant increase in maritime traffic, specifically in container vessel traffic. The traffic in the Baltic area has not only increased, but the nature of the traffic has also changed rapidly. Today, many of the shipping routes consist of frequent traffic, where fast ships are running between seaports on a fixed timetable (Rytkönen et al., 2002). Since the emissions of SO_2 and NO_x from the shipping in the Baltic Sea are the only sectors with a substantial, recent increase, and the prognosis for the Baltic Sea area shows an annual growth rate of 2-4 % for cargo and a small growth rate for passenger traffic (Rytkönen et al. 2002), an update of the emission estimate is needed.

The total reduction of the Finnish NO_x emissions during the whole period 1981-2000 was 15%. If the 1990's are considered separately the emissions decline was 21%. This is much less than the average reduction in the area contributing to the nitrogen deposition in Finland. From the Finnish perspective, however, the nitrogen dioxide emissions are highest in the countries in the southwestern and western sectors, where the reduction has also been lower than the average in the area contributing to the deposition in Finland.

The reduction of the Finnish annual ammonia emissions during 1981–2000 has been 17%. If the 1990's are considered separately the emissions decline was 13%. The ammonia emissions in other countries have declined most, by 45%, in the east and southeast sectors and in the south. The largest emissions, from the Finnish perspective, are in countries in the southwestern and western sectors, where the reduction has also been lower than elsewhere. However, for ammonium the uncertainties in emission estimates are large (Erisman et al., 2003).

3.2. Geographical distribution of the compounds

There are large regional variations in the deposition of acidifying compounds in Finland, with the highest concentrations and deposition values measured mostly in the southern or southeastern part of the country. The concentrations are gradually decreasing northwards. The deposition of components which are mainly of sea salt origin, Na^+ and Mg^{2+}, increase again in the far north in the vicinity of the Arctic Ocean.

The annual mean concentrations of the components related to the acid deposition are given in Figures 4 and 5 for the years 1982, 1990 and 1999 (Ruoho-Airola and Leinonen, 1994; Kulmala et al., 1998; Leinonen, 2000), as an example of the geographical distribution and change in the time series over the period investigated in this study. The stations have been arranged along the abscissa from south to north to represent different areas of the country (see Fig. 3.). The precipitation amount and the concentration of components in bulk deposition are presented in Fig. 4 and the air components in Fig. 5.

Almost all of the highest concentrations have been measured in the southern, eastern and southeastern parts of the country in 1982. The vicinity of the high emissions of sulphur dioxide of the Kola Peninsula is evident in the sulphur dioxide concentration in Kevo in the far north: in 1999 the level there exceeded the value typical for the other remote Nordic stations. At the Virolahti station, local agricultural emissions might have increased the concentration of total ammonium in air to values higher than typical for the area. The same is true for the nitrogen dioxide
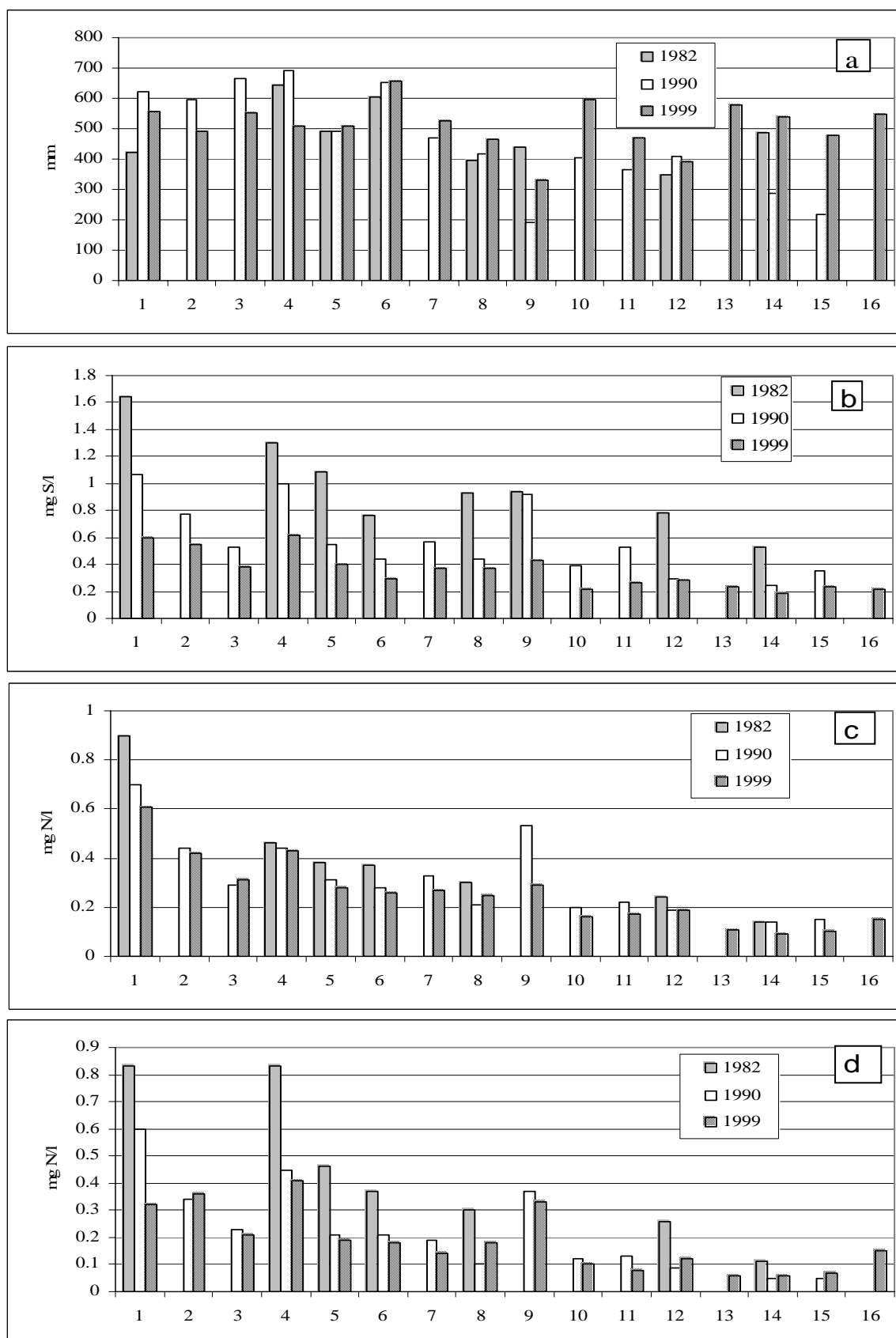
Figure 4. Geographical distribution of the precipitation amount (a) and the annual mean concentration in precipitation of sulphate (b), nitrate (c), and ammonium (d) in different years. Station numbers: 1 Utö, 2 Guttorp, 3 Kotinen, 4 Virolahti, 5 Punkaharju, 6 Ähtäri, 7 Hietajärvi, 8 Sotkamo, 9 Hailuoto, 10 Oulanka, 11 Pesosjärvi, 12 Sodankylä, 13 Värriö, 14 Kevo, 15 Vuoskojärvi, 16 Särkijärvi.
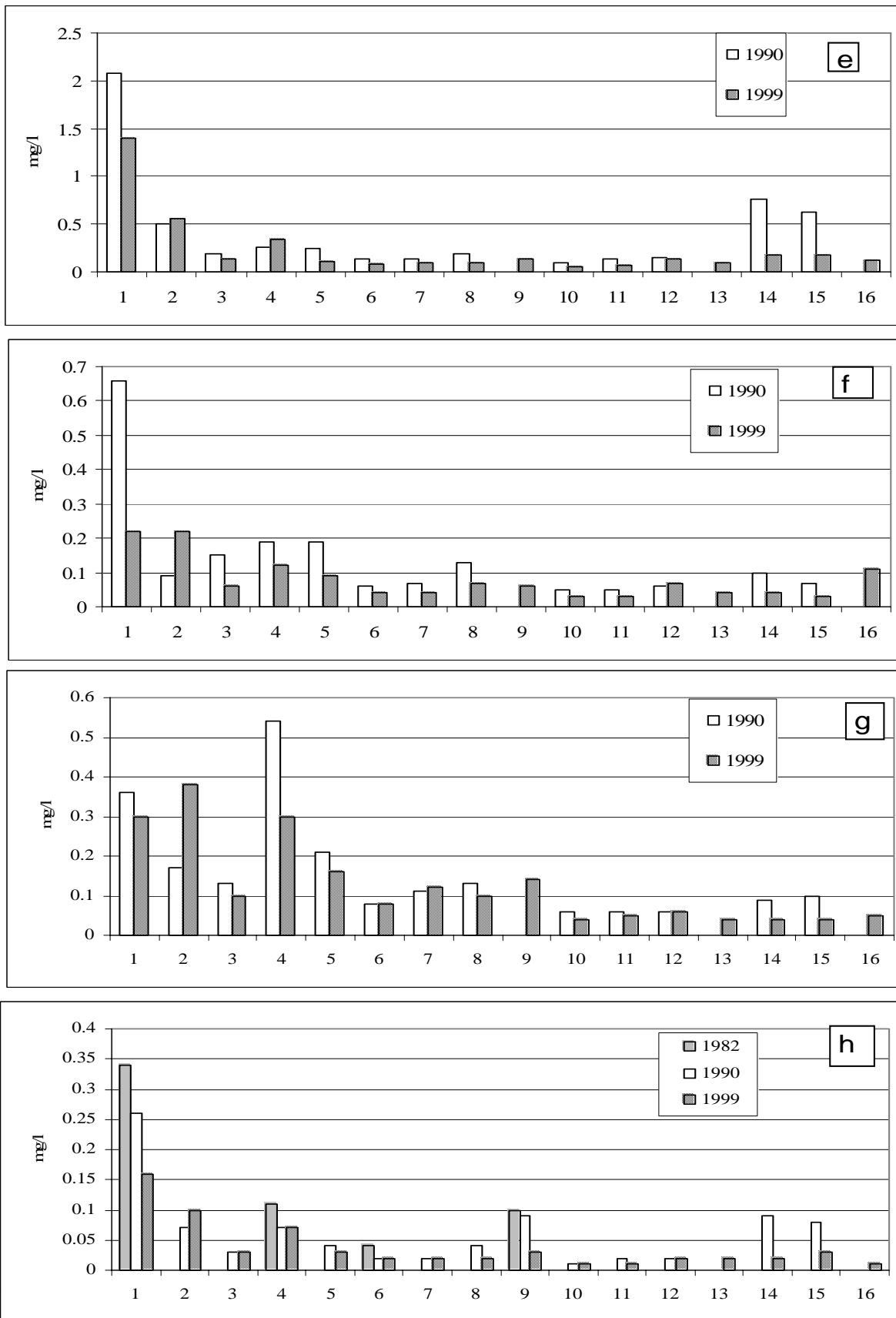
Figure 4 continued. Annual mean concentration in precipitation of sodium (e), potassium (f), calcium (g), and magnesium (h).
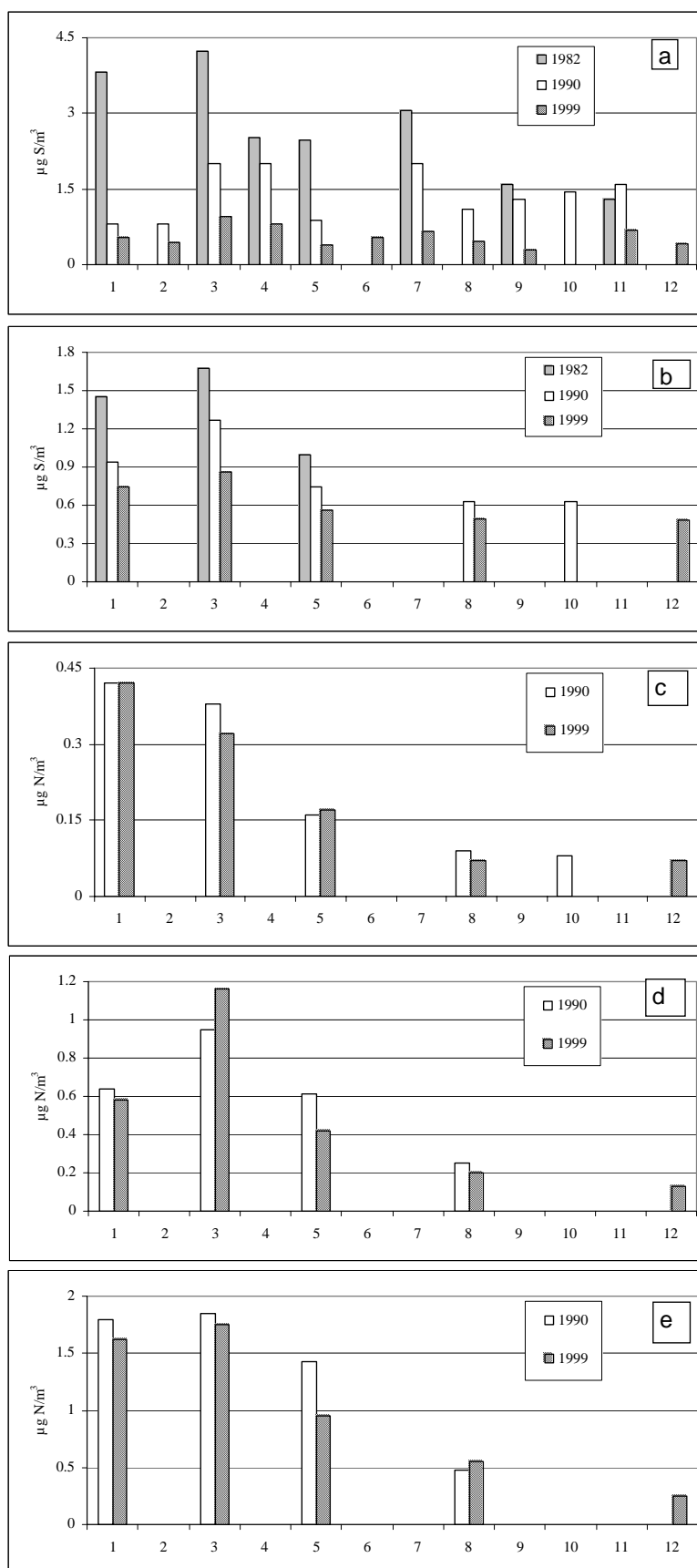
Figure 5. Geographical distribution of the mean annual concentration in air of sulphur dioxide (a), sulphate (b), total nitrate (c), total ammonium (d), and nitrogen dioxide (e) in different years. Station numbers: 1 Utö, 2 Guttorp, 3 Virolahti, 4 Punkaharju, 5 Ähtäri, 6 Hietajärvi, 7 Sotkamo, 8 Oulanka, 9 Sodankylä, 10 Värriö, 11 Kevo, 12 Särkijärvi.

concentration, which is affected by the emissions of traffic, especially during the later years of monitoring.

The precipitation amount greatly influences the wet deposition. In Finland the rain amount is lower at the island stations and in Lapland. There are large interannual variations in the precipitation amounts, but no clear trend. The gradient for the compounds is clear: the concentrations decrease along the predominant air flow from the southwest to the northeast (Drebs et al., 2002). The transboundary contaminants, which contribute more to the concentration, deposit during the transport and less new emissions are added from the domestic sources. The phenomenon is especially nicely evident in the nitrate in precipitation and the total nitrogen concentration in air.

The concentrations of both sulphate and ammonium in precipitation have declined in 1999 to less than a half of the 1982 levels, whereas the nitrate concentration has decreased only slightly. Likewise, the sulphur in air has declined also in the 1990's, but for the nitrogen compounds no clear trend is evident.

3. 3. Trends

3.3.1. Sulphur compounds

For the period 1981–2000, the trend of all sulphur compounds was highly significant at all measurement stations. The decline of the sulphur dioxide concentration since 1981 was dramatic, from 85% to over 95% in all areas of the country except northern Lapland, where a reduction of 65% has taken place. The impact of the large and slowly declining emissions from the Kola Peninsula is at least partly to be blamed for this lower reduction — 90 % of the sulphur deposition in the far north of Finland originated outside the country in 1987–1995. The slope estimate of sulphur dioxide is more uncertain than that of the other sulphur compounds because of its non-linear time series. However, it gives a rough indication of the relative total change.

Fig. 6. shows a graphical presentation of the annual mean values of the sulphur compounds in Virolahti, the Sen's estimate with confidence limits and the residuals calculated by the MAKESENS template, (Salmi et al., 2002), which was used in this work for testing the trends and estimating the slopes. The concentrations of sulphate in particles and precipitation have declined rather evenly since 1981. The downward trends of sulphate in particles and in precipitation were about 60% and 60–75%, respectively. The size of the slope estimate is largest in the south and southeast and decreases northwards showing that the reductions of sulphate concentrations have been the greatest in southern and southeastern Finland where the concentrations have been the highest. The deposition of sulphate in northern Finland is of highly episodic character — a few long-range transport episodes often dominate the annual deposition. This is understandable, because the effect of meteorology, especially the wind direction, increases with increasing distance to the heavy emission sources in Finland and elsewhere in Europe: looking from the station, the sector in which the pollution sources are located is narrower. Thus, coincidental meteorological factors strongly impact the annual mean concentration of oxidized sulphate in this area of Finland, and a decade might not be long enough to detect a trend.

In the 1990's, the concentrations of the sulphur compounds continued to decline even if the significance of the trend was lower. The shorter time period, with fewer annual values in the test, partly reduced the significance of the result. The downward trend of sulphur dioxide was 50-80% in the 1990's. Guttorp in the southwest is the only station outside the northern Lapland where the SO_2 concentration has hardly declined during the 1990's and shows no significant trend. This is explained by the increased exposure from the east and southeast with higher concentrations of SO_2. For the total monitoring period for Guttorp (1985–1999), the downward trend of SO_2 was highly

significant, with a total reduction of 79%. In the 1990's, sulphate in particles declined in all areas of the country by 40-50% and sulphate in precipitation 25-60%. At the northernmost stations there was no trend for the sulphate concentration in precipitation.
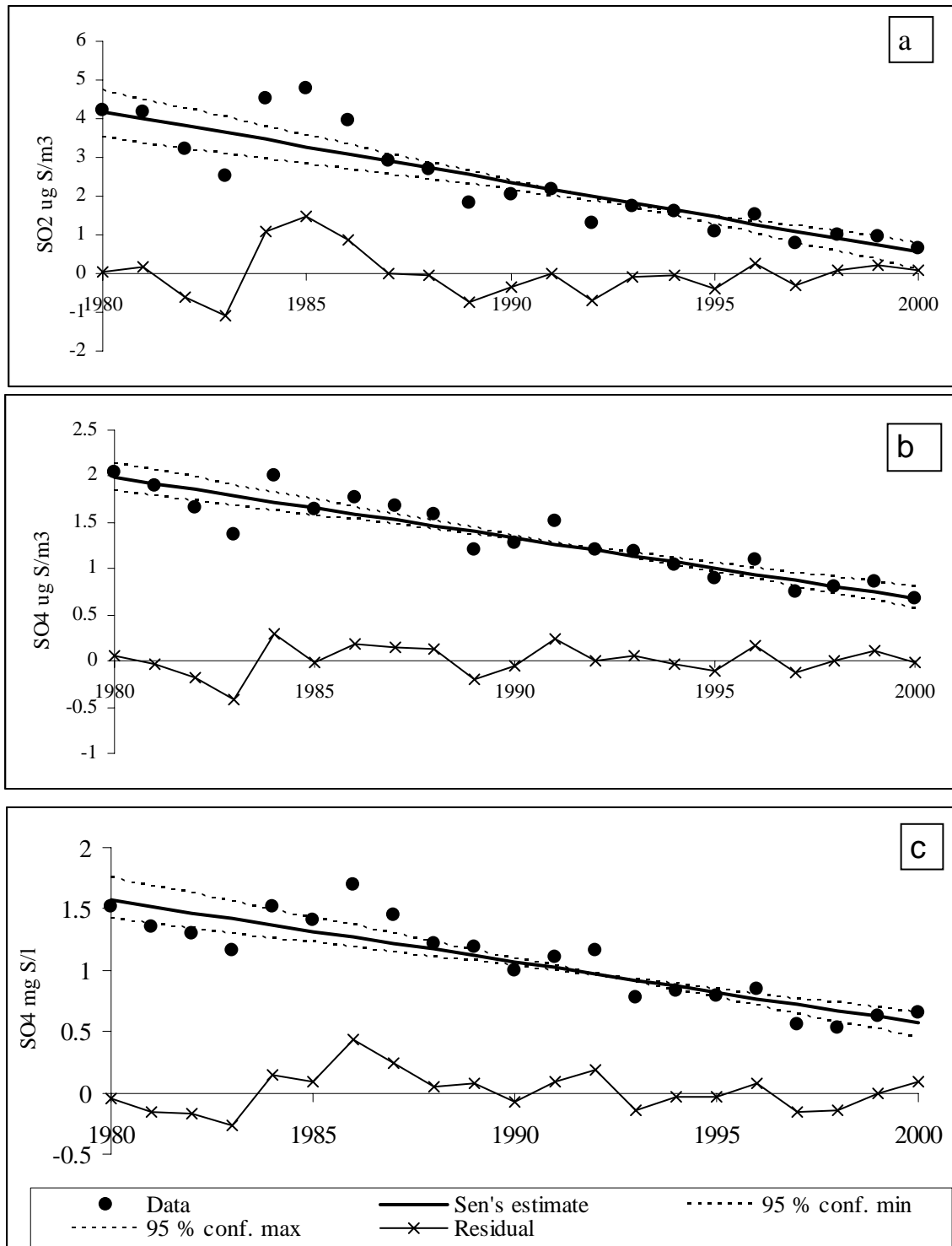

Figure 6. The trends of sulphur dioxide (a), sulphate in particles (b) and sulphate in precipitation (c) at the Virolahti station in 1980-2000. Sen's estimate for the trend with 95% confidence limits is also given.

The sulphate concentrations in both bulk precipitation and throughfall at the IM stations in 1989-1995 have significant (p<0.05) negative linear trends at all catchments except Vuoskojärvi (where the slope estimates were not significantly different from zero). Furthermore, the size of the slope estimate decreases northwards; showing that the reductions in sulphate concentrations have been the greatest in southern Finland where the concentrations have been the highest. Since bulk throughfall includes a fraction of dry deposition that is not included in the bulk precipitation, the steeper decline in the sulphate concentrations registered for throughfall is presumably due to a proportionally greater reduction in the dry deposition of sulphur than wet.

Sulphur dioxide emissions have declined strongly in all emission areas contributing to the long-range transport to Finland (see Table 2). The domestic emissions in Finland have declined most, the level in 2000 being about 1/8 of the 1981 level, which contributes positively on the sulphur dioxide trend. However, the trends of the sulphate compounds are lower than those of sulphur dioxide, which is partly explained by the slower cut down of the large emissions in the important southern sector. The sulphate concentrations in air and precipitation all over the country have, roughly speaking, declined approximately as much as the mean of the sulphur dioxide emissions in Table 2. Fig. 7 illustrates the rate of decline of the different sulphur species in Ähtäri. The 1980 value has been taken as an initial year to which the values of the later years have been compared.
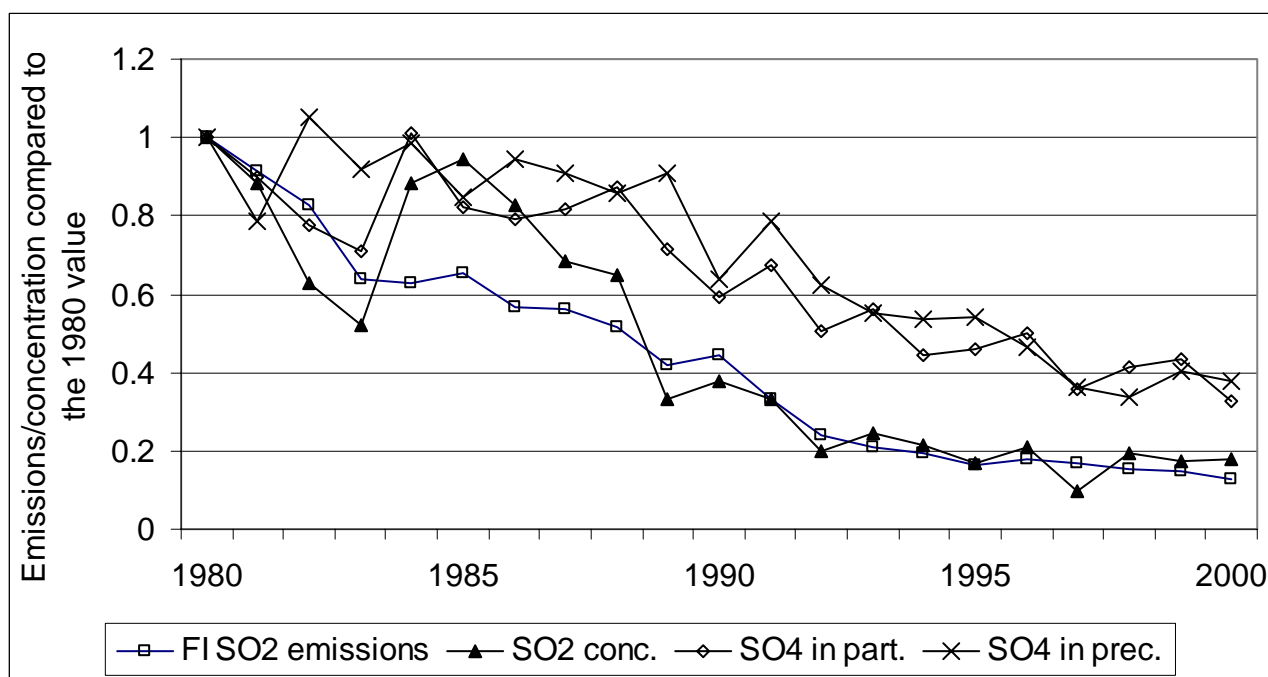

Figure 7. Decline of the Finnish SO_2 emissions, the SO_2 concentration in air and the SO_4^{2-} concentration in particles and precipitation in Ähtäri. The annual values are compared to the 1980 value.

Similar changing chemical transformation processes involved in wet and dry deposition have been reported in Germany and the United Kingdom. The emission decreases there were accompanied by a much larger decrease in the concentration of sulphur dioxide, compared to the decline in the concentration of sulphate in aerosols or precipitation (Fricke and Beilke, 1992; Borrell et al., 1997; NEGTAP, 2001). Thus, the contribution of the wet deposition to total sulphur deposition has increased. Important contributors to the non-linearity are the limited supply of oxidants in the atmosphere and cloud processes, mainly cloud formation but possibly also cloud chemistry (Borrell et al., 1977). In UK, the non-linearity has been reported to originate from a change in the canopy resistance to dry deposition, when the ratio of NH_4^+ to the sulphur compounds changes (NEGTAP,

2001). This has increased the dry deposition velocity of SO_2 with time. An enhancement in sulphate in air arriving from the Atlantic Ocean, largely caused by shipping but possibly also by an increased contribution from the North American sources are further reasons for the non-linearity (NEGTAP, 2001). Grennfelt et al. (1994) have pointed out that a reduction in precursor emissions of a particular pollutant may influence the transport distance of other pollutants. If NO_x or organic emissions are reduced, lower amounts of oxidants are formed, and thus less SO_2 will undergo oxidation increasing the transport distance of SO_2 (Borrell et al., 1997).

3.3.2. Nitrogen compounds

Both the Finnish and European NO_x emissions have decreased only modestly since 1981. Consequently, at many stations the concentrations of the oxidized nitrogen compounds in air and precipitation have declined only slightly, or not at all. The estimates of the trends for the nitrogen compounds in Virolahti are presented in Fig. 8.

For the gas phase and particulate nitrogen compounds, the measurements covered the 1990's. The statistical test gave few significant trends: the sum of nitrate and nitric acid declined by around 30% at stations in the southeast and in southern Lapland, and the sum of ammonia and ammonium decreased by 50% in the southern part of central Finland. The significance of the ammonium trend was, however, very high ($p<0.001$). No significant trend was detected for nitrogen dioxide. The test accepts the missing values in the time series of nitrogen dioxide, but they weaken the test and might prevent exposing trends with weak significance. Further, the change in the monitoring method of nitrogen dioxide in 1996 increased the uncertainty in the calculation of the trend over that period. On the other hand, the result of no trend illustrates well the modest reduction of the domestic nitrogen dioxide emissions, which highly affect the concentration.

According to the statistical test, the downward trend of the concentration of nitrate in precipitation during 1981–2000 was highly significant at most stations in the south and at Ähtäri (C) in the southern part of central Finland. At these stations the total decline per period reached 40%. At Virolahti (SE), in the southeastern corner of Finland, the concentration has undergone a rather low total reduction of 20%. The reason might be different transport routes from areas with slower emissions reductions. Finally, the significance of the trend was lower in the areas in the north, but the calculated total reduction was almost as high as in the south. For 1990–2000 the calculations resulted in only very few significant trends, indicating minor domestic and European emission reductions and a fluctuation of the concentrations.

The ammonium concentration in precipitation has declined significantly between 1981 and 2000. The statistical test gave as high probabilities for the existence of trends as for the sulphur compounds. Also the total reductions follow very regularly those of sulphate, with only slightly lower values. The overall reduction of ammonium in precipitation during 1981-2000 was around 60% in the southern and central parts of the country, and 80% in the north. In the 1990's, there was a downward trend of ammonium in precipitation at two of the three stations in the southwest and in the southern part of central Finland (reduction ca. 40%). In the southeast the decline did not continue. The deposition of the nitrogen compounds declined significantly at the southern IM stations during 1988-1996.

The time series of total ammonium in air in Virolahti (Fig. 8d) shows a turning point in 1995. The test does not give a significant trend for the whole period of measurements and if divided into two parts of the time series are too short for testing. Additional values are thus needed to assure the possible increase of concentration after 1995.
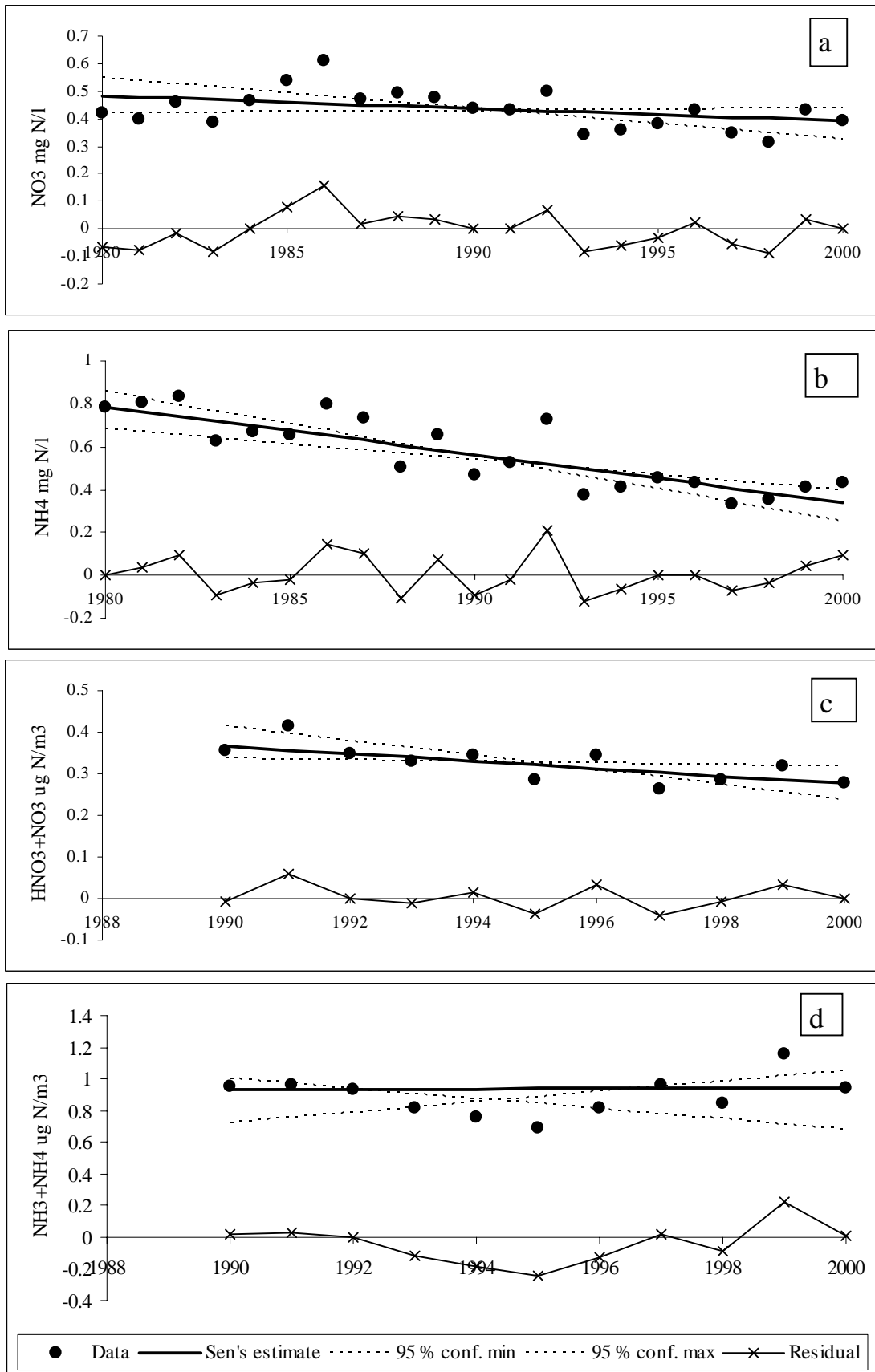
Figure 8. The trend of nitrate (a) and ammonium (b) in precipitation in 1980-2000 and total nitrate (c) and total ammonium (d) in air in 1990-2000 at the Virolahti station. Sen's estimate for the trend with 95% confidence limits is also given.

3.3.3. Base cations

The concentrations of the base cations in precipitation and in particles have declined in large areas of Finland during the studies conducted. The sum of the base cations in precipitation decreased by 15-35% between the years 1989 and 2000. The decline was most remarkable in the calcium concentration: both the total concentration and the share of the non-sea-salt (nss) calcium decreased significantly in other parts of the country except for the northernmost area (Ruoho-Airola and Salminen, 2003). For the other base cations, significant downward trends were found for some of the stations.

The changes in the base cation deposition are particularly interesting in comparison to the deposition of acidifying components. In the southern and central Finland the sulphur deposition decreased rapidly during the monitoring period. At stations in the southeast, a marked decline in the base cation deposition in bulk precipitation was observed as well. This cuts off part of the positive effect of the reduced sulphur deposition. At the stations in other parts of the country, the sulphur deposition reduced much more than the base cation deposition. In the south-western station as well as in the far north, no clear long-term change in the base cation deposition could be detected. Fig. 9 illustrates the weighted moving average time series of the sulphate and base cation bulk deposition.
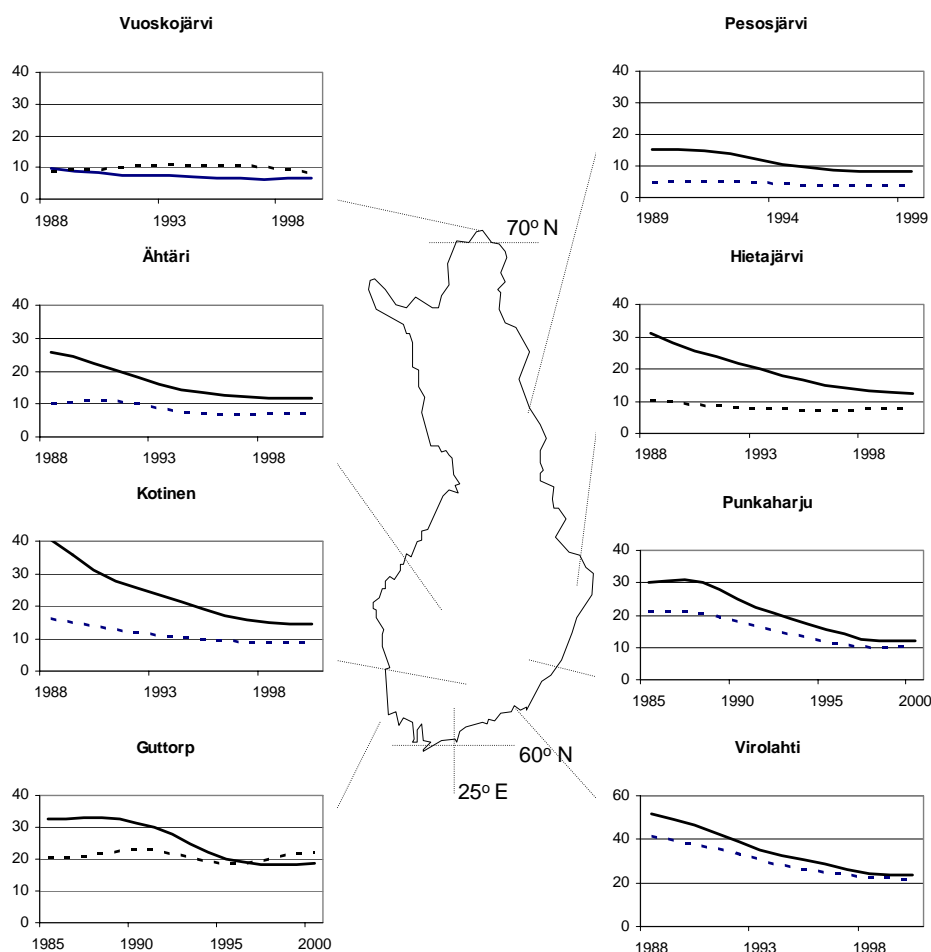

Figure 9. Gaussian smoothing curves showing the trends in sulphate (solid line) and the sum of the base cation (dashed line) deposition in bulk precipitation at stations in different parts of the country (unit meq m^{-2}).

The sum of base cation deposition in bulk precipitation levelled off at about 20 meq m^{-2} at stations in the southeast. At the station in the southwest, the deposition fluctuated around the same value. At all other stations the bulk base cation deposition reached the level of 5-10 meq m^{-2}.

3.4. Impact of the different air transport directions

The origin of the pollution has been studied in three of the papers. The sectoral distributions of the gas phase and particulate sulphur and nitrogen compounds in paper I illustrate roughly the relative importance of different transport directions to the dry deposition of sulphur and nitrogen in Finland. The origin of the selected high daily wet depositions of sulphate is discussed in paper III. Finally, the origin of the acidifying deposition at the IM stations was calculated with the DAIQUIRI model in paper II. The modeled values include both the dry and wet the deposition.

3.4.1. Dry deposition

Daily concentrations of gas phase and particulate sulphur and nitrogen components together with the estimates of air transport routes enable a sectoral examination of the pollution exposure. The sectoral exposure is the sum of the daily loads arriving from a specific sector over the time period assessed. The accumulated annual exposure would be the sum of the summer and winter exposures in all eight sectors plus the approximately 30% of the daily exposure values that could not be classified to a specific transport sector. The sectoral distributions in Fig. 10 illustrate roughly the relative importance of different transport directions to the sulphur dry deposition in Finland even if absolute dry deposition values can not be calculated. In summer, the gaseous and particulate sulphur influenced the total sulphur exposure with rather equal weights. In the winter exposure, the weight of gaseous sulphur was about two thirds.

The highest concentrations of sulphur dioxide and sulphate in the particles have been found in air masses arriving from the east, southeast and south (Fig. 10 a-d.). The most frequent transport sector has been west (Fig. 10 e). Thus, transport from the southwest and west sectors has dominated the sulphur exposure during the summer months. In winter, all sectors towards the south have been important to the sulphur exposure. In Fig. 10 f, the mean annual exposure for the total sulphur in air in Virolahti has been summed up from the seasonal exposures. At the southern Lapland station Oulanka, the effect of the north and northeast sectors has also been remarkable. Remarkable for the sulphur exposure in Finland is the change in the weight of the transport sectors in the 1990's: the exposure from west and south has still declined, whereas the transport from north and east has turned to a slight increase during the last decade.

At Virolahti, the mean concentrations of SO$_2$ in air masses arriving from the east, southeast and south sectors were elevated compared to air from the other sectors during the whole period investigated. Although transport from these sectors was not very frequent, its weight in the wintertime exposure – and dry deposition – has been and is still evident. The differences between the seasons are in line with the large-scale meteorological observations in southeastern Finland: in summer the southwesterly flow dominates and the effect of the elevated concentrations of sulphur dioxide in the southeastern air masses evens out, while in winter there is no remarkable difference between the southwesterly, southerly and southeasterly winds (Drebs et al., 2002).

The total atmospheric nitrate accumulated strongly with transport by the southwesterly and westerly winds with air masses arriving from sectors where the NO$_2$ emissions were the largest. The rather small changes in the exposure patterns during 1991–2000 reflected the minor reductions of the NO$_x$ emissions. The pattern of exposure of the total atmospheric ammonium greatly resembled the corresponding distribution for particulate sulphate; the transport from southwest peaked during summer and the transport from west, southwest and south dominated during winter. Also with
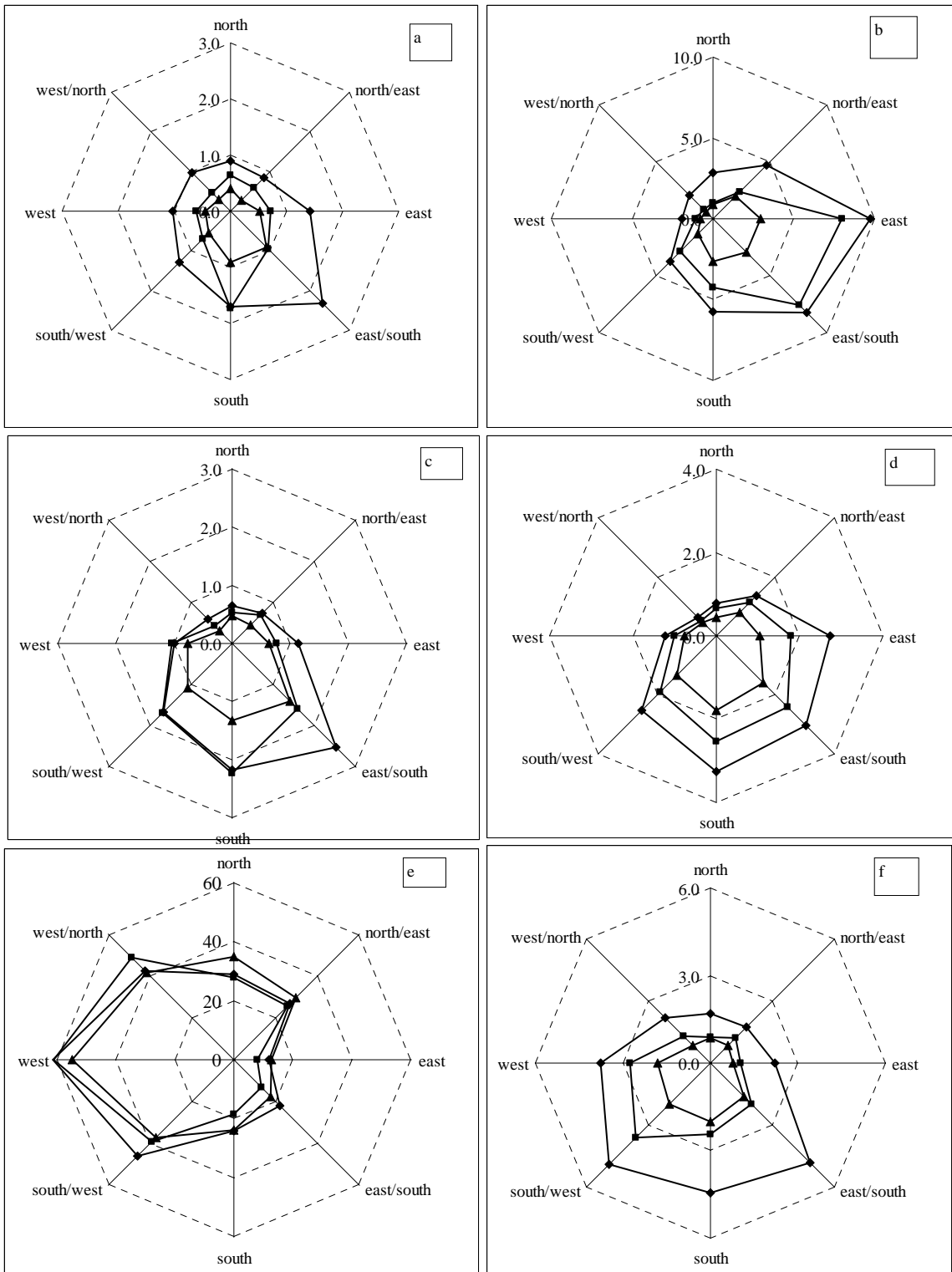
Figure 10. Five year mean concentrations of sulphur dioxide (a for summer, b for winter) and sulphate in particles (c for summer, d for winter), the frequency of the transport sectors (e) and the exposure of total atmospheric sulphur (f) classified according to the air mass transport sector arriving at the Virolahti station. Units: μg S/ m^{-3} for concentrations, days for frequency and mg h S m^{-3} for exposure. Symbols: solid diamond for mean values in 1986-1990, solid square for mean values in 1991-1995, and solid triangle for mean values in 1996-2000.

regard to the nitrogen exposure, there seems to have been a slight transition towards an increased eastern and northern contribution, even if the total exposure was mostly affected by transport from the southern and western sectors.

3.4.2. Wet deposition

Daily precipitation samples enable also the classification of the wet deposition according to air transport sectors. The method of defining the transport sector based on air mass trajectories is not always suitable for the calculation of the accumulated wet deposition, because the rain might have lasted for only a short period while the transport sector is set for 24 hours.

Fig. 11 shows as an example the accumulated sulphate deposition in bulk precipitation classified according to air transport sectors in Ähtäri in 1999. The worst 20 days, accounting for 50% of the annual sulphate deposition in precipitation, were assessed. For 6 of the days no constant transport sector could be set. The most important transport sector was definitely the southwest. However, a closer investigation of the transport sectors with weather maps would improve the reliability of the results.
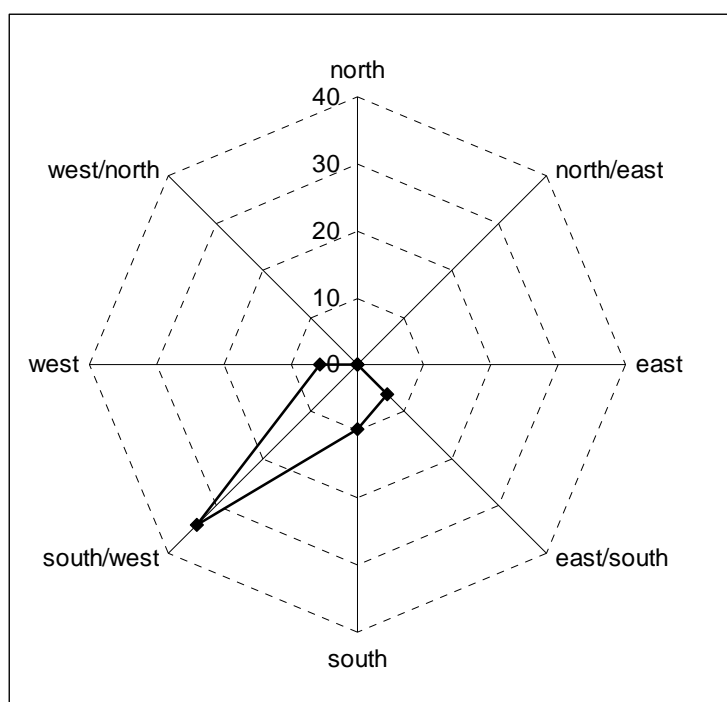

Figure 11. Sulphate bulk deposition accumulated during transport from different sectors in Ähtäri in 1999, mg S m^{-2}.

The estimated probable origin of the wet deposition of sulphate during the episode days in paper III was based on weather maps and backward air trajectories. Most of the episodes occurred in northern Finland. A great number of episode cases was related to transport from the eastern Europe sector (the Baltic Countries, the Russian Federation), which is partly due to a relatively large amount of cases in which the trajectories passed over Estonia and the St. Petersburg area. Many cases were tracked also to the eastern central Europe (Poland, Czech Republic, Slovakia). The large sulphur emissions on the Kola Peninsula were responsible for causing a sulphate wet deposition episode in rather few cases.

3.4.3. Calculated values

Estimated with the DAIQUIRI model, the sulphur dry and wet deposition derived from sources outside of Finland has dropped from 510 mg S m^{-2} per year to 340 mg S m^{-2} per year at Kotinen in 1987-95. The share of deposition of domestic origin has decreased from 230 mg S m^{-2} per year to 70 mg S m^{-2} per year. At the northern stations, Pesosjärvi and Vuoskojärvi, the model calculations indicate that more than 90 % of the sulphur deposition originates from outside of Finland. In northernmost Finland, domestic emissions seem to have little influence on the deposition level, whereas in southern Finland the dramatic decline of the Finnish emissions has significantly contributed to the decrease of the total deposition level.

According to the DAIQUIRI model calculations, the NO_X deposition of domestic origin was of the order of 30 % at Kotinen, and the effect of domestic emissions decreases when moving northwards being only a couple of percent at Vuoskojärvi. The distribution between domestic and imported ammonia deposition is very similar to the nitrate deposition throughout the country.

3.5. Episodicity

A large proportion of the annual acid deposition is accumulated in a few days: the worst 5 days at the Finnish background stations can bring up to 20–30 % of the annual bulk sulphate, nitrate, ammonium and calcium load (Paper III; Walden et al., 1999; Leinonen et al., 2000; Ruoho-Airola et al., 2001). In central and northern Finland there were significantly more episode days than in the south. The episodes can not be completely explained by the high precipitation amounts: the mean sulphate concentration in episodic rain was higher than the annual mean concentration. The episodicity of the acid deposition has been discussed also in 3.2.

Nordlund (1981) discussed the episodicity of sulphur dioxide: more than 50% of the daily concentration values were less than half of the annual mean of the station, and in about 10% of the cases they were higher than two times the yearly mean.

3.6. Comparison to other results

In a number of papers covering investigations in Europe and North America since the 1980's strongly declining concentrations and deposition of the atmospheric sulphur compounds and smaller changes in the nitrogen compounds in precipitation have been found. Kulmala et al. (1998) have extensively investigated the air quality trends at the Finnish background stations for a time period ending in 1996. In the EMEP programme, a declining sulphur trend has been observed in other areas of the programme except the Balkans, Iberia and part of Britain, while fewer trends were found for the nitrogen compounds (Barrett et al., 2000). Moldan et al. (2001) have calculated a significant downward trend for the sulphur concentration in precipitation at Scandinavian background stations in the 1980's and 1990's. The sulphate deposition has decreased by 30 to 60% whereas the inorganic nitrogen deposition has shown little change until the mid-1990's (Moldan et al., 2001). Forsius et al. (2001) have assessed the trends of the ICP IM precipitation data for 22 stations across Europe for the period 1988/89–1998. Statistically significant downward trends of SO_4^{2-}, NO_3^- and NH_4^+ have been observed at 50% of the stations, but the changes of sulphur have been found to be larger than the changes of the nitrogen compounds, calculated as equivalents.

Similar results have been reported based on monitoring covering many other western and central European countries (e.g. Tørseth et al., 2001; Kindbom et al., 2001; Irwin et al., 2002; Zimmermann et al., 2003; Arends et al., 1997; Tsakovski et al., 2000). In North America, several studies show that the sulphur concentrations in air and precipitation were highest in the 1980's and have

decreased since then. In contrast, the nitrate concentrations generally have not changed as much (e.g. Lynch et al., 2000; Hicks et al., 2002; Holland et al., 1999; Shannon, 1999).

The presented sectoral exposure estimates are in line with the calculations by the EMEP model of average export from other countries to Finland in 1985-1996; the largest foreign contribution to the sulphur deposition comes from Russia, Germany and Poland. The largest foreign contribution to the oxidised nitrogen deposition is from Germany, Sweden and Poland, and to the reduced nitrogen deposition from Russia, Germany and Poland (Tarrasón and Schaug, 2000). The early model calculations did not cover separate emissions of the shipping. In 2000, the largest foreign contributors were mainly the same, but the Baltic Sea traffic was estimated to be a significant source of sulphur and oxidized nitrogen deposition. The largest import of sulphur deposition in 2000 was estimated to originate in Russia, followed by Poland and the Baltic Sea. With regard to the oxidized nitrogen the main foreign contributors were Russia, Germany and the Baltic Sea, and for reduced nitrogen Germany, Poland and Russia (Tarrasón et al., 2003)

The EMEP MSC-W calculates annually the source-receptor matrices for the acidifying compounds. These matrices estimate the transport of substances between the various countries. Table 3 shows the origin of the acid deposition in Finland and the transport of the Finnish emissions for 1998. The countries have been classified in categories according to their geographical locations. Other in the table means marine areas and areas that could not be attributed in the calculations.

Table 3. The origin and the transport of the acidifying compounds to and from Finland in 1998. (Statistics Finland, 2000).

Emitter	Origin of the deposition in Finland, % of total			Receiver	Transport of emissions of Finnish origin, % of total		
	SO_2–S	NO_X–N	NH_3–N		SO_2–S	NO_X–N	NH_3–N
Finland	17	29	53	Finland	46	25	62
Western Europe	13	23	19	Western Europe	9	7	7
Russia	29	9	5	Russia	16	14	12
Baltic States	7	4	8	Baltic States	3	2	1
Other Eastern Europe	17	7	15	Other Eastern Europe	1	2	0
Others	16	27	0	Others	25	49	18

In 1998, the estimated total deposition in Finland of sulphur, oxidised nitrogen and reduced nitrogen were 140 ktonnes S, 68 ktonnes N and 38 ktonnes N, respectively (Tarrasón and Schaug, 2000). The emissions are given in Fig. 2. Finland is a net importer of sulphur: from the 1998 deposition only 1/6 was of domestic origin, but almost half of its emissions deposited on the Finnish territory. For the nitrogen deposition, the domestic sources contributed 33-50%. The main part of the Finish ammonium emissions was estimated to remain in Finland. Remarkable in Table 3 is the quite high share of the category of marine and unattributed areas.

The sectoral exposure estimates at Oulanka (SL) confirm the earlier estimates by Tuovinen et al. (1993) that in summer the total accumulated dry deposition there was dominated by transport from north and northeast, while in winter the influence of the southern sectors increased. At Sevettijärvi in northern Lapland in the vicinity of the Kola Peninsula emission sources, transport from east and northeast was dominant for SO_2 and transport from southwest for SO_4^{2-}, when the exposure was averaged over a two year period (Virkkula et al., 1995).

Ryaboshapko et al. (1998) estimated, for the year 1985, that the emissions of the former Soviet Union (FSU) sources contributed highly to the sulphur and nitrate wet deposition in the eastern and northern parts of Finland. According to the estimate, the contributions of the FSU emissions to the sulphur and nitrate wet deposition were about 50% and 25%, respectively.

Hedin et al. (1994) reported on steep declines in the atmospheric base cation deposition in several areas of Europe and North America. The depositions in paper IV were approximately at the same level as in Sweden (Lövblad et al., 2000) and Norway (Tørseth and Semb, 1998). Laurila (1990) discussed the wet deposition trends of Mg^{2+} in the 70's and 80's at three stations in the southeast, southwest and central Finland. The concentration of Mg^{2+} in precipitation decreased generally at all stations. In the southeast of Finland, an increase was detected when the wind direction during the precipitation was from the south, which reflected the increasing emissions of the Estonian oil shale power plants. In addition, the highest calcium concentrations were measured there during southerly winds (Anttila, 1990).

4. METHODOLOGICAL UNCERTAINTES

4.1. Uncertainty of the monitoring data

The accuracy, precision and detection limits of the monitoring data of the Finnish Meteorological Institute used in this study have been controlled through the whole chain of measurements by means of field blanks, control samples and split samples. The EMEP CCC routinely tests the data quality by intercomparisons, which are performed annually for the chemical analysis and every now and then for the sampling methods. According to the EMEP CCC quality assessment (EMEP CCC, 2003), the quality of the Finnish measurements of precipitation and air quality at the four EMEP stations has been high during the whole measuring period. All these data are classified in the best A class (uncertainty within ±10%), except the NO_2 data, which are classified in class C (uncertainty within ±30%). The detection limit of nitrogen dioxide is rather high compared to the low background concentrations at the stations, which leads to a higher uncertainty in the concentration.

The ammonium concentration in precipitation, especially in the north, might contain a larger uncertainty than the values obtained for the other compounds. Firstly, ammonium is usually transported for shorter distances than nitrate (Tarrason, 1997), and possible local and regional sources, such as agriculture, have a relatively larger effect on the concentration. Secondly, the concentration, especially in the north, is so low that even minor ammonia sources may have weakened the reliability of the time series. Finally, the ammonium concentration in the samples is contaminated more easily than the other compounds. This may have occurred in the beginning of the monitoring period in spite of the careful data checking, which would lead to too high annual mean values.

4.2. Methodological constrains

The network of stations monitoring long time environmental phenomena is always a compromise between an ideal set up of numerous stations with an extensive programme at representative locations and the practical resources. The important thing is that the critical factors affecting the whole process of monitoring are under control and that the quality of the data is controlled through the whole chain.

For accurate estimates, the wet deposition should be measured as wet-only deposition. The calculations for wet deposition in this work were based on results from open bulk samplers, which

collected also a part of the dry deposition. However, according to Swedish parallel wet and bulk measurements for five years at four rural stations, the difference was only approximately 10% as a mean value (Lövblad et al., 2000).

There are missing values in the time series. In addition, the enormous data set of nearly 100 000 values analysed in this work contains erroneous values, in spite of the careful checking over the whole monitoring chain. However, the effect of these errors and limitations on the results obtained might not be very large, because the non-parametric trend tests used in this work are not sensitive to missing values or occasional high values (Gilbert, 1987). Mean values for 5 years were used, when studying the accumulated exposure for the atmospheric sulphur and nitrogen compounds. This has reduced the impact of individual errors on the results.

As the trend calculations in paper II were based on only bulk deposition measurements, a change in the ratio between the dry and wet deposition of the compounds might explain part of the different behaviour of the emissions and deposition.

The sectoral distributions in paper I illustrate roughly the relative importance of different transport directions to the sulphur and nitrogen dry deposition in Finland even if absolute dry deposition values or specific source areas could not be defined. It can be assumed that nearby sources and the background concentration found everywhere maintain a low basic value for all compounds in all of the sectors, especially during low wind velocities. However, the monitoring stations have been located far from any larger local sources. Thus, it can be supposed that the differences between the sectors originate mainly from loads transported from outside the immediate surroundings of the station, which can be separated rather well with the classification method used in the study. The criterion for the allocation of the trajectories of a particular arrival day to a specific sector was that at least 50% of their given positions during transport were found within that sector. This makes the selection of the right transport sector uncertain, even if great many positions for one day were checked before the sector definition: 4 trajectories per day were calculated by tracking the air parcel every 2 hours for 96 hours backwards in time for each of the trajectories.

In this study only part of the exposure of the acid deposition could be allocated to its transport directions and source areas. The analysis covered fairly well the dry deposition, but for the wet deposition only exemplifying calculations on the transport sectors were given and a further assessment is needed.

The base cation regionalization is based on rather few measuring points and has been calculated for only one year. For the wet deposition maps, the precipitation observations of the 416 meteorological stations were utilised. Especially, the estimate of the dry deposition of the base cations was of more tentative nature because of few stations and the use of fixed seasonal deposition velocities. On the other hand, the maps do not attemp to describe the variation of deposition in detail but rather with five magnitude classes and only a few isolines.

The throughfall measurements in paper V did not cover the winter periods before 1994. In order to maintain comparability between the four different catchments and the results achieved by the bulk deposition and the throughfall method, the trend calculations covered only the months common to both measurements and all areas. Thus the trends express rather the change in the summer period. The test may be used for monthly values even though there are seasonal cycles and missing values.

The modeled values for the depositions and the origin of the pollutants obtained by the DAIQUIRI model represent a more statistical approach to the problem, while the measurements describe the situation from the local meteorological point of view. Thus, the results with the two methods might differ when compared. A detailed analysis of the uncertainties of the model is given in Syri (2001).

The study includes results based on different types of assessment methods. Thus, the development of the acid deposition in Finland has been examined from different points of view. Even if the applied methods contain constrains, the achieved results support each other and lead to a general outcome concerning the problem.

5. SUMMARY AND CONCLUSIONS

The geography and the climate have preserved Finland from an even higher sulphur load than what actually occurred. The highest sulphur dioxide and particulate sulphate concentrations in the southern and central Finland originate from the sectors between south and east, while transport is most frequent from the western sectors. Thus, the atmospheric sulphur exposure is highly affected by transport with the cleaner western winds, although the highest concentrations also have a remarkable effect on the mean concentration level. In the north, the transport from northeastern and northern sectors is also important for the exposure. Remarkable for the sulphur exposure is the change in the weight of the transport sectors in the 1990's: exposure from the west and south has still declined, whereas transport from the north and east has turned to a slight increase.

In Finland, the SO_2 emissions and concentrations in the background areas have decreased more than 80% since 1981. For sulphate concentrations in air and precipitation, the reductions have been lower due to the dominance of the long range transport. From the Finnish perspective, the emissions of SO_2 are largest in the countries to the south as well as to the southwest and west of Finland. The frequent transport from these sectors together with the lower SO_2 emission reductions, especially in the southern sector, have contributed to the lower reductions of the sulphate concentrations. In southeastern Finland, the decline of the SO_2 concentration started later than in the other parts of the country, because of the larger contribution of southeastern transport from areas with slower emission reductions. In the northernmost part of the country no significant downward trend could be detected in the 1990's for sulphate in precipitation, and the reduction of the SO_2 concentration since 1981 was lower than elsewhere in the country.

For the gas phase and particulate nitrogen compounds there were few significant trends in the 1990's. No significant trend was detected for nitrogen dioxide. In the south, the concentration of nitrate in precipitation has decreased during 1981–2000. However, the concentration of ammonium in precipitation has decreased significantly during 1981–2000, by more than the Finnish and European NH_3 emissions. The monitoring of the background concentrations of the nitrogen compounds should be continued all over the country in order to verify possible changes in their time series.

From the Finnish perspective, the nitrogen oxide emissions are highest in the countries in the southwestern and western sectors. There the reduction has been lower than the average in the area contributing to the deposition in Finland. The frequent transport from these areas has highly affected the Finnish concentrations and exposure. Lately there seems to have been a slight transition towards an increased eastern and northern contribution. So, contrary to the case of the sulphur exposure, the geography and the climate of Finland have rather aggravated the problem of the nitrogen exposure.

A steep decline in the atmospheric base cation deposition in Finland was discovered especially in the south-eastern part of the country. Part of the positive effect of the reduced acid deposition in Finland is thus lost. For the wet deposition, the largest decrease in the base cation deposition occurred in southeastern Finland. Further studies are needed to evaluate whether the decreased base

cation emission from the southern shore of the Gulf of Finland has negative effects on the Finnish ecosystems.

The proportion of domestic origin out of the total acid deposition decreases northwards: for sulphate, nitrate and ammonium the deposition of domestic origin is of the order of one third of the total in the south, and only a few percent in the northernmost area. Thus, international measures are still important in reducing the transboundary acid deposition in Finland.

The daily acid deposition in central and especially northern Finland is highly episodic. It seems that the massive decrease of sulphur emissions has not changed this situation. Within the CLRTAP the accepted load of acid deposition is defined by means of the exceedence of the critical load to the environment. The annual total deposition of the compounds is used in the calculations. Thus it would be necessary to ascertain if the episodicity of acid deposition causes an additional ecological stress and, if so, to include episodicity in the calculations.

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Annex 1.

Review of the papers

Paper I

The paper presents the concentration trends for the period 1981–2000 and the accumulated exposure to sulphur and nitrogen compounds from different transport sectors for the period 1986–2000 in Finland. The concentrations of all sulphur compounds have declined significantly, by more than 60%, throughout the country during 1981–2000; in the 1990's significant trends were detected in all time series except sulphate in precipitation at the northernmost stations. The largest decline has taken place already before 1991 and during winter. From the Finnish perspective, the emissions of SO_2 are largest in the countries to the south and southwest to west of Finland. The frequent transport from these sectors together with the smaller SO_2 emission reduction, especially in the southern sector, has contributed to the lower reductions of the sulphate concentrations. The concentration of nitrate in precipitation has reduced by 20–40% and that of ammonium in precipitation by more than 50% during 1981–2000. However, in the 1990's, not many significant monotonic downward trends were obtained for the concentrations of the nitrogen compounds in air and precipitation. Transport from the western and southwestern sectors dominated the sulphur exposure during summer, while in winter all the southward sectors were important. The nitrogen exposure was mainly dominated by transport from sectors between west and south, but lately a slight shift towards increased transport from the sectors ranging from the north to the south-east appears possible.

Paper II

The effects of transboundary air pollutants on the deposition levels and the precipitation concentrations were studied within the UN/ECE Integrated Monitoring Programme in 1988–1995 at four Finnish background stations. A monotonic decreasing trend was detected for the concentration and deposition of sulphate, nitrate, ammonium and potassium in bulk precipitation at the southern stations. Farther to the north, fewer compounds showed a significant reduction. The origin of the acidifying deposition was estimated. The proportion of domestic sulphur and nitrogen deposition decreased when moving northwards. For sulphur in the south, the reduction reflected rather well the reduction of sulphur emissions in Finland and elsewhere in Europe. The downward trend of the nitrogen compounds throughout the country seems to be due to international emission reductions.

Paper III

The paper discusses the episodicity of the sulphur bulk deposition from daily measurements in the 1990's. A large proportion of the annual acid deposition is accumulated in a few days: the worst 5 days at the Finnish background stations can bring 20–30 % of the annual bulk sulphate load. In the central and northern Finland there were significantly more episode days than in the south. A new definition for an episode, based on the exceedance of the annual median value, was introduced. The episodes cannot be completely explained by high precipitation amounts: the mean sulphate concentration in episodic rain was higher than the annual mean concentration. The episodes were mostly imported: the air mass arriving at the station had passed over areas with high emissions outside Finland.

Paper IV

In the paper, deposition maps of the base cations Na^+, K^+, Ca^{2+} and Mg^{2+} were estimated for 1998 for Finland using measurement data for precipitation and air quality. The highest deposition for all compounds was measured near the southern coast, and it gradually decreased northwards. The deposition of Na^+ and Mg^{2+} increased again in the far north, in the vicinity of the Arctic Ocean. During the last decade the sum of the base cation concentrations in bulk precipitation as well as the sum of the non-sea-salt fraction decreased by approximately 15–35% in all areas in Finland. An especially large reduction occurred in the southeastern part of Finland, where the wet deposition of base cations decreased almost as much as the wet deposition of sulphur.

Paper V

The paper presents temporal trends of sulphate, base cation ($Ca^{2+}+ Mg^{2+}+ K^+$), and H^+ ion concentrations in bulk precipitation and throughfall samples collected over a seven year period (1989-95) in four forested catchments in Finland. The sulphate and H^+ ion concentrations in bulk precipitation and throughfall both showed negative linear trends, which were significant for the 3 southernmost catchments. The decline was greater for throughfall than for bulk precipitation, indicating a proportionally greater reduction in dry deposition than wet. The reported reduction in sulphur emissions over the study period has resulted in a significant reduction in the acidity and sulphate concentration of bulk precipitation, and this reduction has also been reflected in the throughfall concentrations.