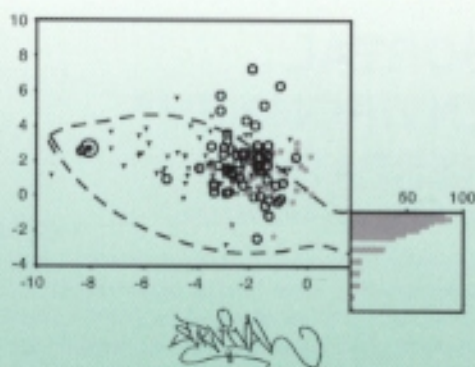


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JAAKKO MANNIO

Responses of headwater lakes to air pollution  
changes in Finland

MONOGRAPHS  
*of the*  
Boreal Environment Research

# BOREAL ENVIRONMENT RESEARCH

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MONOGRAPHS OF THE BOREAL ENVIRONMENT RESEARCH

**18**

Jaakko Mannio

**Responses of headwater lakes to air pollution changes in Finland**

Yhteenveto: Suomen latvajärvien vasteet ilmansaasteiden muutoksiin

FINNISH ENVIRONMENT INSTITUTE, FINLAND  
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*Time can create the data we need – but not the information*

### List of original publications and author's contribution

This study synthesizes the following original publications, which are referred to by their roman numerals in the text. The author's contribution is explained separately for each article. In addition, some previously unpublished results are presented.

**I** Verta M., Mannio J., Iivonen P., Hirvi J.-P., Järvinen O. & Piepponen S. 1990. Trace metals in Finnish headwater lakes – effects of acidification and airborne load. In: *Acidification in Finland* (eds. P. Kauppi, P. Anttila and K. Kenttämies), Springer-Verlag, Berlin, pp. 883–908.

**II** Mannio J., Verta, M. & Järvinen, O. 1993. Trace metal concentrations in the water of small lakes, Finland. *Applied Geochemistry Suppl.* 2: 57–59.

**III** Mannio J., Järvinen O., Tuominen R. & Verta M. 1995. Survey of trace elements in lake waters of Finnish Lapland using the ICP-MS technique. *The Science of the Total Environment* 160/161: 433–439.

**IV** Tarvainen T., Lahermo P. & Mannio J. 1997. Sources of trace metals in streams and headwater lakes in Finland. *Water, Air and Soil Pollution* 94: 1–32.

**V** Rask M., Mannio J., Forsius M., Posch M. & Vuorinen P. 1995. How many fish populations in Finland are affected by acid precipitation? *Environmental Biology of Fishes* 42: 51–63.

**VI** Mannio J. & Vuorenmaa J. 1995. Regional monitoring of lake acidification in Finland. *Water, Air and Soil Pollution* 85: 571–576.

**VII** Rask M., Raitaniemi J., Mannio J., Vuorenmaa J. & Nyberg K. 1995. Losses and recoveries of fish populations in acidified lakes of southern Finland in the last decade. *Water, Air and Soil Pollution* 85: 315–320.

**VIII** Mannio J. Recovery pattern from acidification of headwater lakes in Finland. *Water, Air and Soil Pollution* (accepted)

Author's contribution to the papers:

I J. Mannio planned and conducted the snow, water and sediment studies with M. Verta and performed all data management and data analyses concerning those sections. The paper dealing with this part was written jointly with M. Verta.

II J. Mannio performed the data analysis and wrote the paper, which was commented by M. Verta.

III J. Mannio planned the study, made the data processing and wrote the paper which was commented by M. Verta.

IV J. Mannio was responsible for the lake water data and interpretations of those results. The discussion on the sources of trace metals was written jointly by all authors.

V The paper was initiated and planned jointly by M. Rask and J. Mannio. Mannio was responsible for the pre-acidification equations for labile aluminium and organic anion concentrations and, together with M. Forsius, interpretations of past and present water quality.

VI J. Mannio was responsible for the monitoring network design and wrote the paper.

VII J. Mannio and M. Rask were initiators of the paper. Mannio was responsible for the water quality data interpretation.

VIII J. Mannio is fully responsible for this paper.

### List of abbreviations

AAS	Atomic absorption spectrophotometry
Alk	Alkalinity (Gran method)
ANC	Acid Neutralisation Capacity = $[\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+] - [\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^-]$
BC	Base cations = $[\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+]$
CLRTAP	Convention on Long-range Transboundary Air Pollution
CVAAS	Cold vapour atomic absorption spectrophotometry
EF	Enrichment factor
FGFRI	Finnish Game and Fisheries Research Institute
FLS	Finnish Lake Survey
FMI	Finnish Meteorological Institute
GFAAS	Graphite furnace atomic absorption spectrophotometry
GSF	Geological Survey of Finland
HAPRO	The Finnish Acidification Research Programme 1985–1990
HIR	Lake Hirvilampi
ICP IM	International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems
ICP Waters	International Cooperative Programme on Monitoring and Assessment of Acidification of Rivers and Lakes
ICP-MS	Inductively coupled plasma mass spectrometry
LOEL	Lowest effect level
LOI	Loss on ignition
NIVA	Norwegian Institute for Water Research
NLS	Nordic Lake Survey 1995
RMLA	Regional Monitoring of Lake Acidification
SYKE	Finnish Environment Institute
TOC	Total organic carbon
UN/ECE	United Nations Economic Commission for Europe
VK	Lake Valkea-Kotinen

## Responses of headwater lakes to air pollution changes in Finland

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*Mannio, J. 2001. Responses of headwater lakes to air pollution changes in Finland, Monographs of the Boreal Environment Research No. 18, 2001.*

The present work provides a national scale assessment of the trace metal contamination of small headwater lakes and the recent development of acidified lakes in Finland. The information is needed as a scientific basis for further actions in air pollution policy. The study is based on observations in a national monitoring network of lake acidification. Anthropogenic, atmospheric deposition is primarily responsible for the increase of Cd, Hg, Pb and As in headwater lake sediments. However, a decline of 20 to 40 % of the accumulation of these elements within the last decades was observed, indicating a relatively fast response to the decline in the atmospheric deposition, and that the accumulated stores of atmospheric trace metals in the catchment soils are not dominating the supply of trace elements to lakes. Lake water samples reflected atmospheric trace metal pollution as well, but it was not as clearly quantifiable. Acidity controls in particular the level of Cd and Zn, while organic matter (humus) controls more the level of Cr, Fe, Cu and Ni in headwater lakes. Lead, Mn and Al concentrations are affected by both these factors. Humus acts as a carrier for trace metals from catchment soils to surface waters, irrespectively of their original source. Based on comparable chemical data sets, the risks of biological effects in lakes due to trace metals are lower in Finland than in Sweden and Norway. Trace metal levels in lake waters are less critical for biota than acidity and inorganic (labile) aluminium levels. Due to acidification, there were estimated to be 2200–4400 damaged fish populations in southern and central Finland. Most of these are roach populations in lakes smaller than ten hectares. Sulphate concentrations have declined in all types of small lakes throughout Finland in the 1990s, indicating a clear response to the sulphur emission reductions. Base cation concentrations are still declining in lakes especially in southern Finland, but to a lesser extent than sulphate. There are presently no indications of elevated nitrate levels in forested headwater lakes. The increase in buffer capacity (chemical recovery) was relatively uniform throughout the country, except that the changes were not as significant statistically and by magnitude in the dilute lakes in northern Finland. Nearly 5000 headwater lakes larger than four hectares were estimated to be recovering from acidification at present. First perch population recoveries in southern Finland were observed. The monitoring and survey results presented here are an example of an approach, where both spatial and temporal data from several sources are aggregated. This facilitates the estimation of regional changes and quantifies the changes on a national scale. The consistent monitoring provides also a sound basis for further modelling of recovery processes and scenario assessment. A new challenge is the interaction of acidification/recovery processes and trace metals with possible trends in temperature and hydrology due to global climate change. This should be taken into account when assessing long-term surface water quality and developing future monitoring networks. Empirical data in space and time are needed to judge whether the emission reduction measures have been efficient.

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**Keywords:** lakes, acidification, trace metals, heavy metals, monitoring, regionalisation, sediments, water chemistry, trends, recovery, fish populations

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## 1 Introduction

### 1.1 Impacts of air pollution – from national to global problems

Human activities cause various types and amounts of pollutant emissions to the atmosphere. Atmospheric pollution was recognized to be one of the major environmental problems in many countries from the late 1970s, after scientists demonstrated that sulphur and nitrogen compounds in gases produced by burning fossil fuels were leading to increased acidification of the environment, often hundreds of kilometres from the source. Fossil fuel consumption and many industrial processes emit also a wide spectrum of trace elements and toxic organic compounds into the atmosphere, causing similar transboundary pollution concern. Anthropogenic sources comprise almost all of the atmospheric emissions of the most toxic trace elements: cadmium, lead, and well over half of mercury. During the last twenty five years acidification and airborne contamination has been one of the central issues in environmental research, and major national research programmes on these topics have been conducted in many countries in Europe and North America (Drabløs and Tollan 1980, Bernes 1986, Kauppi *et al.* 1990, RMCC 1990, NAPAP 1991).

The acidification of sensitive ecosystems occurring in industrialized regions of the northern hemisphere has been documented in a vast number of publications, and has been extensively reviewed and evaluated (*e.g.* Schindler 1988, Cowling 1989). Lake acidification is recognized as a severe environmental problem in parts of, *e.g.*, Norway (Wright and Henriksen 1978, Henriksen *et al.* 1988, Henriksen *et al.* 1989), Sweden (Bernes 1986, Forsberg and Morling 1988), Canada (Jeffries *et al.* 1986, Neary and Dillon 1988, Kelso *et al.* 1990) and the United States (Landers *et al.* 1988, Schindler *et al.* 1989, Baker *et al.* 1991). At least 100 000 lakes have been impacted in Norway, Sweden, the USA and eastern Canada (Schindler *et al.* 1989, Minns *et al.* 1990). Over the next decades, many countries in Asia, Africa and South America will probably experience major increases in the emissions of sulphur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>), very likely causing large-scale damage to sensitive aquatic and terrestrial ecosystems in these regions as well (Steinberg and Wright 1994, Galloway 1989, 1995, Rodhe *et al.* 1995, Kuylenskierna *et al.* 2001).

Airborne contamination has reached also the most remote regions of the world; mercury and persistent organic pollutants are transported globally to polar regions and alpine glaciers (Barrie *et al.* 1992, Ayotte *et al.* 1995, AMAP 1998, Landers *et al.* 1998a, Schindler 1999). The interaction between acid deposition and climate change (Wright and Schindler 1995, Schindler *et al.* 1996a) and UV-radiation (Gorham 1996, Schindler *et al.* 1996b, Yan *et al.* 1996) has gained increasing attention during the last decade.

The elucidation of the effects of acidification on the geochemical cycle of trace metals is an integral component in any assessment of the environmental risks posed by acid deposition. Many trace metals of anthropogenic origin are found in acidic deposition, and acidification can enhance the mobility of abundant elements in the Earth's crust, like Al, Mn and Fe (*e.g.* Driscoll *et al.* 1980). For metals in the biosphere, their physicochemical forms can be modified by acidification. Such changes in physicochemical form or speciation can affect metal bioavailability and toxicity to organisms (Campbell and Stokes 1985, Nelson and Campbell 1991).

### 1.2 Acidification and trace metals in Finland – a historical perspective

In Finland the first studies related to acidification were conducted in the early 1970s. Haapala (1972) noticed, that the sulphur deposition had more than doubled in southern Finland compared with earlier observations in 1955–58 (Buch 1960). Haapala *et al.* (1975) observed acidic episodes in the Kiminkijoki water course during snow melt. The first observations indicating acidification of Finnish lakes were also reported (Kenttämies 1973, 1979). During the early 1980s there was an increasing awareness of the impacts of acidic deposition in Finland. Acidification of small sensitive lakes located mainly in the southern parts of the country was documented in several studies (Tolonen and Jaakkola 1983, Kämäri 1985, Simola *et al.* 1985). First studies on the effects of atmospheric load of trace metals on small forest lakes in Finland were published in the mid 1980s (Tolonen and Jaakkola 1983, Myllymaa 1986, Myllymaa and Murtoniemi 1986, Rekolainen *et al.* 1986a,b, Tolonen *et al.* 1986, Verta *et al.* 1986). All these

studies pointed out the importance of atmospheric trace metal load on the budget of trace metals in remote lakes in Finland. Mercury load through atmospheric deposition has increased from the 1950s, and the concentration of Hg in fish in lakes outside polluted watercourses has doubled or tripled (Rekolainen *et al.* 1986a, Verta *et al.* 1986).

Monitoring of large lakes (Laaksonen and Malin 1984a,b) revealed changes in ionic composition of the lakewaters, indicating the impact of acidic deposition. Furthermore, the clear difference in precipitation chemistry between southern and northern parts of the country was documented (Järvinen and Haapala 1980), and the first comprehensive review of air quality was carried out by Kulmala *et al.* (1982). As a response to the increasing concern regarding the effects of acidic deposition the interdisciplinary 'Finnish Acidification Research Programme' (HAPRO) was conducted during 1985–1990. One of the major objectives of HAPRO was to evaluate the regional extent of acidification in Finland and to identify the areas most sensitive to the impacts of acidic deposition. To meet this objective, the programme organized surveys on emissions, compiled measurements of concentrations and deposition, assessed the sensitivity of the different regions on the basis of catchment characteristics and water quality samples, and carried out surveys to document the existing state of different ecosystems on both small and large spatial scale (Forsius *et al.* 1990a,b, Kämäri *et al.* 1991, Nuotio *et al.* 1990, Tamminen and Starr 1990, Jukola-Sulonen *et al.* 1990, Nöjd 1990).

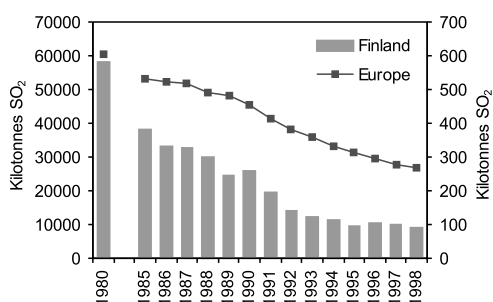
Based on a statistical lake survey, Kortelainen *et al.* (1989), Forsius *et al.* (1990a,b), Kämäri *et al.* (1991, 1993), Posch *et al.* (1993) and Forsius (1992) presented the regional estimates of the chemistry and acidification status of small lakes and critical loads of acidity for the lakes in Finland. Further development of the work led to estimates of critical loads and their exceedances on a Nordic level (Henriksen *et al.* 1990, 1992, 1998, Posch *et al.* 1997). Huttunen *et al.* (1990) indicated, based on paleolimnology, that most of the investigated acidic lakes in the southern parts of the country have been acidified recently. Monitoring results indicated a continuing acidification of small sensitive lakes located in the southern parts of the country (Roila 1992). Moreover, the first signs of groundwater acidification were observed in southern Finland (Soveri and Ahlberg 1990).

The effects of acidic deposition on the different trophic levels of small lakes were studied by a survey of 140 sensitive lakes located mainly in southern and central parts of the country (Eloranta 1990, Heitto 1990, Huttunen and Turkia 1990, Kippo-Edlund and Heitto 1990, Meriläinen and Hynynen 1990, Sarvala and Halsinaho 1990). There was, similarly, clear evidence that acidic deposition has caused declines of fish populations in sensitive lakes in southern Finland (Rask and Tuunainen 1990).

Finnish lakes are generally brown coloured due to humic substances (*e.g.*, Kortelainen 1993). Nearly 10 000 lakes (30 %) have a total organic carbon (TOC) concentration of more than 10 mg l<sup>-1</sup> (Henriksen *et al.* 1998, Mannio *et al.* 2000). The proportion is similar in Sweden, but only ca. 3 % in Norway. The flat topography and relatively humid climate have led to extensive peatland formations. Due to humic substances draining from organic-rich catchments, naturally acidic lakes are very common, especially in central Finland. Kortelainen and Mannio (1988, 1990) demonstrated that the pH in Finnish lakes was to a larger extent determined by individual catchment characteristics and high organic matter concentrations than by present atmospheric loads. The number of acidic (alkalinity ≤ 0) lakes in Finland was estimated to 4900, of which > 45 % were assumed to be naturally acidic due to high concentrations of organic matter (Forsius *et al.* 1990b). Kortelainen (1993) further clarified the role of organic acidity in acid/base status of Finnish lakes. Organic acids dominate also the acidity in small streams in central and northern Finland: organic anions exceeded sulphate concentrations in 18 out of 19 monitored headwater streams both in spring and autumn (Kortelainen and Saukkonen 1995).

### 1.3 International measures – protocols and cooperative monitoring

During the last few decades, considerable effort have been devoted to reducing atmospheric emissions of acidifying compounds in Europe and North America. International negotiations on emission reductions have been conducted under the Convention on Long-range Transboundary Air Pollution (CLRTAP, UN/ECE 1996). The first result of these negotiations was a protocol in 1985, in which the signatory states pledged a 30 % cut in



**Fig. 1.** Sulphur emissions in Europe (left axis) and Finland (right axis) in 1980 and 1985–1998 (Vestreng and Støren 2000).

sulphur emissions by 1993, compared with 1980 levels. The second sulphur protocol in 1994 is based on the principle that the difference between current sulphur deposition levels and critical loads must be reduced by 60%. It seems that the agreements are honoured, since the emissions in Europe have been approximately halved by the year 1998, from 1980 levels (Fig. 1). Protocols to reduce emissions of nitrogen oxides (1988), volatile organic compounds (1991), persistent organic compounds as well as heavy metals (1998) have been signed. The protocol on heavy metals obliges the signatories to reduce their emissions of Pb, Cd and Hg below 1990 levels by 2010. The emissions should be cut from industrial sources (iron and steel industry, non-ferrous metal industry), combustion processes (power generation, road transport) and waste incineration using best available techniques (BAT) (Table 1). The protocol requires phasing out of leaded petrol and introduces measures to lower heavy metal emissions from products like Hg in batteries, electrical components and devices, dental amalgam and other products. Other

metals with similar sources may be included in a protocol amendment at a later stage.

The signatories of the CLRTAP have agreed to cooperate on research and monitoring of the effects of major air pollutants, and a large organisational setup has been operating under this scheme. Under the Working Group of Effects, International Cooperative Programmes (ICPs) are organized to monitor and report on the status of *e.g.* forests, surface waters, field vegetation, and corrosive materials.

The reduction of acidifying compounds, especially sulphur dioxide, has been successful in Europe and in the Nordic countries in particular, during the last fifteen years. This development is clearly seen in the sulphur deposition in Finland (Kulmala *et al.* 1998). The emissions and deposition of trace metals have been decreasing along with that of sulphur and nitrogen compounds. Expensive emission reduction programs have been carried out, and more is to come: model studies estimate total costs of about 56 000 million Euros per year to further reduce European S, N and VOC emissions from the 1990 level by 2010 (Amann *et al.* 1998). It remains unclear whether current and planned emission reductions will be sufficient to meet the environmental objectives. Monitoring is needed to verify that expensive control programs actually achieve the desired results (*i.e.* restoration of healthy biotic communities in areas affected by acidic precipitation), and to determine whether emission reduction strategies require further adjustments. At best, monitoring can help to identify new emerging environmental problems.

The effects of acidification are geographically widespread, receptors are numerous, and contaminant monitoring is technically and analytically demanding; this places special needs on the monitoring activities. The demand on regionally repre-

**Table 1.** Major sources of trace elements to the atmosphere (Nriagu and Pacyna 1988, Berdowski *et al.* 1997).

Element	Combustion		Metal industry		Traffic	Waste incineration	Cement & glass industry
	Coal	Oil	Non-ferrous	Iron, steel			
Hg	X					X	
Pb			X		X	X	
Cd	X	X	X	X		X	
As	X	X	X	X			X
Zn	X		X	X			
Cu	X	X	X				
Ni		X	X	X			
Cr	X	X		X			
V	X	X					

sentative monitoring of smaller lakes is obvious, due to the continuing pressure of atmospheric (and land-use related) diffuse loading. Any monitoring network, to work optimally, should be based on a careful selection of the target media and sampling frequencies. In this case, target receptors (abiotic or biotic) suffer from long-term, often ecosystem level problems in the environment with differing tolerance and response; they include sensitive and insensitive systems and many combinations of environmental conditions. It is not possible or meaningful to monitor too many receptors, but a set of most feasible should be identified. Although many geochemical processes in these environments are reasonably well known, the biotic responses most often do not reveal directly the effects of a change in conditions, but react in a delayed manner (Dise *et al.* 1994).

#### 1.4 Requirements for monitoring atmospheric pollution of lakes

Spatial and vertical patterns of physical and chemical variables within individual lakes are major drivers of ecological processes. A more systemic view has evolved with the recognition of the key role played by interactions between lakes and their catchments and airsheds. Lakes are an integral component of the larger aquatic-terrestrial ecosystem with catchment characteristics, such as geology, land use/cover, and topography used to explain interlake variation in the chemical and trophic status of lakes (*e.g.*, Dillon and Kirchner 1975, Likens 1984, Frey 1990, Schindler *et al.* 1990, Sorrono *et al.* 1999).

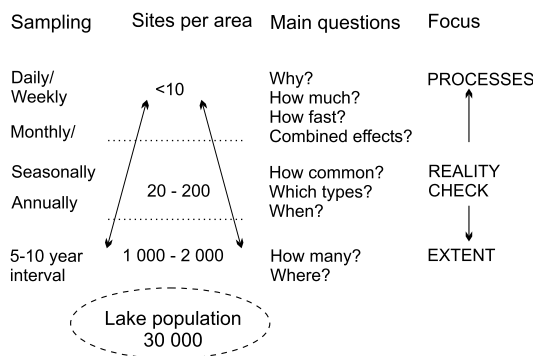
In the case of acidification, critical chemical processes occur in the soil (Reuss *et al.* 1987), since major part of the air pollutants are transferred to and pass through the soils before entering the surface waters, even in headwater lakes. The same holds true for trace metals. Four primary factors combine to determine the chemical characteristics of waters draining from forested catchments (Church 1997):

- 1) the chemical composition of incident precipitation (major ions, trace metals)
- 2) the abiotic materials (*e.g.*, metals in soil) or the biota that water contacts as it moves through the catchment
- 3) the abiotic reactivity of the materials or biotic activity of the organisms contacted

- 4) the length of contact with those materials or organisms

A key factor in this equation is the pathway that water follows through the catchment. These pathways determine the materials the water contacts and the length of that contact, and thus determine to large extent the runoff water composition. Important processes are physical (erosion and gas exchange), chemical (weathering, precipitation, cation exchange, ion sorption) and biological (uptake, respiration, decomposition, mineralization, and microbiologically mediated oxidation and reduction). Important in this context is to realize that it is the sum total of interactions (summed in different ways on different catchments, and over different times within an individual catchment) that determine the chemical composition of the runoff waters.

A monitoring programme to evaluate the environmental effect of acidic deposition on surface waters should tackle the problem in two dimensions; it can be organized in a co-ordinated and pyramidal manner (Fig. 2). At the apex of the pyramid is a small number of intensively monitored sites where sufficient information is collected from



**Fig. 2.** Schematic illustration of the pyramidal principle of aquatic effects (mainly water chemistry) of air pollutants. In Finland, the upper level consists mainly of the UN/ ECE CLRTAP Integrated Monitoring (ICP IM) programme sites. The second level in the middle is the core element of this work. It comprises of selected, acid sensitive headwater lakes distributed all over the country, including sites in the UN/ECE ICP Waters programme (NIVA 1996). The base level is represented by national lake surveys, based on statistically selected sites from a frame lake population (*e.g.*, lakes greater than 4 ha in Finland) and representing the overall status of lakes at certain point in time (modified from Mannio 2000).

relevant ecosystem components so that time-dependent dynamic models can be developed and applied to predict the future changes occurring under different deposition scenarios. Beneath the apex is a series of regional networks that employ progressively less comprehensive and frequent sampling but greater spatial coverage. Finally, the pyramid base is composed of a regional survey "network" in which a large number of sites, preferably based on statistical methods, may be sampled as infrequently as once per decade (NIVA 1996, Urquhart *et al.* 1998, Henriksen *et al.* 1998, Mannio 2000).

The regional-scale assessment of the present and future status of ecosystems depends on the continuing existence of all levels within the monitoring hierarchy. The regional monitoring/survey sites have generally been selected to be representative of the areas considered sensitive to acidic deposition. In lake-rich countries, statistical methods have been used in the monitoring/survey site selection procedure, which is the most reliable way to assure the representativeness of these sites (*e.g.* Landers *et al.* 1988, 1998b, Brooksbank *et al.* 1989, Forsius *et al.* 1990 a,b, Henriksen *et al.* 1998). The assessment of the causes and consequences of the changes in environment, requires complete and consistent water quality data sets including all major cations and anions. The frequency of sampling is dependent on the system (lake/stream), scope (spatial/temporal/ long-term/ short-term variation), expected magnitude of change, and resources available.

In regions where surface waters are universally sensitive to acidification, sites should be chosen to represent the diversity of the region (chemically, biologically and geographically). If surface waters exhibit a wide range of acid sensitivity, sites should be chosen from among the most susceptible to acidification. The aim of the site selection should be to focus primarily on sites that are likely to change in response to acid deposition, and secondarily to represent the region as a whole. Selected sites should not have a pronounced influence from local sources of pollution in the catchment that may lead to misinterpretation of chemical and biological data (*e.g.* domestic sewage, industrial waste water, agriculture, road de-icing etc.). Valuable long-term records may also be lost due to significant local changes like liming programmes and changes in forestry practices. Confidence in the future protection of the site from changes in local influences is important. National

parks and nature reserves should be considered as sampling sites.

Sufficient sites must be included to provide for statistical confidence in regional analysis of changes or trends (Young and Stoddard 1996). The number of sites should be balanced against the ability to support the monitoring on a long-term basis. Sites with long time series are preferable, if the other main criteria are met.

With regard to monitoring of the effects of atmospheric derived trace metals on aquatic ecosystems, very much the same criteria for site selection can be applied as for acidification monitoring. Indeed, much of the work on trace metal history in sediments is logically combined with paleolimnological studies (*e.g.* Norton and Kahl 1991), and catchment-scale budgets have been often co-located with other acidification studies (Schut *et al.* 1986, Dillon *et al.* 1988, LaZerte *et al.* 1989). Regional lake surveys can also reveal spatial patterns in trace metal chemistry (Skjelkvåle *et al.* 2001). Undisturbed sedimentation conditions and catchment geochemistry are important in interpreting metal stratigraphy. Seepage lakes are sometimes emphasized in sediment studies, in order to exclude the influence of catchment geochemistry.

Atmospheric, terrestrial and aquatic cycling of Hg, the synthesis of methyl-Hg and its subsequent bioaccumulation is driven by complex chemical and biological reactions involving exceedingly small quantities of Hg. Thus, monitoring Hg concentration changes in different compartments of the ecosystem does not necessarily mean that there is a change in anthropogenic load, but possibly that other environmental changes are involved (Verta 2000). In the case of mercury, perhaps more than any other metal, monitoring alone cannot reveal dose-response relationships without support from detailed research.

Representative sites for monitoring acidification and metal contamination are also suitable systems for monitoring airborne persistent organic pollutants, both chemically and biologically. Headwater lakes are ideal for, *e.g.*, calculating accumulation histories of pollutants in sediments and accumulation in biota. In paleolimnological studies the climatic and land use history can be revealed to validate (or reject) conclusions on contaminant history.

In order to link chemical changes to detectable biological effects, information of tolerance limits of carefully selected indicator species are also

needed. In many cases biota can indicate the average or worst conditions of the site more effectively than chemical monitoring. Presently, the most widely used indicator groups are invertebrates in running waters and fish and diatoms in lakes. A number of species are known to be sensitive to acid conditions and their presence/absence will indicate both current and recent past conditions. For example, molluscs are rarely found below pH 5.6, or gammarids rarely below pH 6. Numerical relationships between pH of water and species response have been developed for diatom assemblages, chrysophyte, chydorid and invertebrate communities where resolutions of 0.3 to 0.5 pH units are possible, if calibrations to local conditions are developed (Raddum and Fjellheim 1994, NIVA 1996, Hämäläinen and Huttunen 1996).

Monitoring of fish species with multimesh gill nets provides an estimate of the fish community and the relative abundance (number and biomass) of catchable fish species in a lake (Appelberg *et al.* 1995). For a single fish species, the length frequency distribution, age distribution, back calculated growth and sex ratio can be determined. Electro-fishing can be useful in lake littorals in order to complete the information obtained by gill netting. Both methods should be applied at the end of the growth season, but before the possible spawning migration.

A whole ecosystem approach, including birds, for monitoring aquatic effects has been adopted especially in Canada. Changes in waterfowl distribution and production should reflect broad-scale changes in the habitats they rely upon, with the predominant habitat change being available food resources. Hence, individual trends in species distribution and breeding success should mirror changes in populations and distributions of the fish and invertebrates they feed upon, and thus should be suitable indicators for the aquatic ecosystems under consideration (McNicol *et al.* 1995).

Site-specific, regional and even continent wide surveys and monitoring programs on air pollutant effects provide field data, which can be used to assess in detail ecosystem responses (*e.g.* Wright *et al.* 1993, Likens *et al.* 1996, Hultberg and Skeffington 1998, Henriksen *et al.* 1998, Stoddard *et al.* 1999, Skjelkvåle *et al.* 2000, Skjelkvåle *et al.*, 2001). With regards to the recovery from acidification, three different approaches can serve to shed light on the process: 1) Analysis of time series of chemical and biological data, 2) mathemati-

cal modelling, and 3) experiments involving radical reductions of deposition. Of these approaches, the first two are presently applicable under Finnish conditions. As for the third, no large-scale experimental manipulation projects have been conducted in Finland.

### 1.5 Objectives of this study

The knowledge of the risks of trace metals in sensitive upland ecosystems is much less developed and defined, than that of acidifying compounds. The transport, accumulation and effects of these metals should be known better to estimate further needs of emission reductions.

The response of ecosystems to decreasing emissions of acidifying compounds has been modelled extensively in Finland, mostly based on the critical load concept. Those estimates are primarily developed to predict long-term risks. On the other hand, there has been no comprehensive assessment of the recent development of aquatic ecosystems: biological or even chemical recovery from acidification.

The perspective of this work is on a national scale and multi annual changes; from years to decades, and even over hundreds of years in sediment profiles. The aim of this study can be divided into two themes (Fig. 3):

1. To obtain basic information on the level and changes of trace metals in Finnish headwater lakes, more specifically
  - to estimate the concentration of trace metals in headwater lakes and how they are controlled by environmental factors, in particular atmospheric deposition of trace metals, acidification, local geochemistry and ambient water quality (I–IV, this paper)
  - to elucidate how the temporal and spatial variation of these factors are reflected in lake sediment chemistry in the long term (I) and short term (this paper)
  - to assess the potential biological effects induced by atmospheric and catchment derived trace metals in headwater lakes (III, this paper)

In addition, the work aims to provide consistent and comparable data for the method development, modelling and regionalisation of effect based approaches for trace metal emission reductions in Europe.

2. Reveal the recent development and changes in

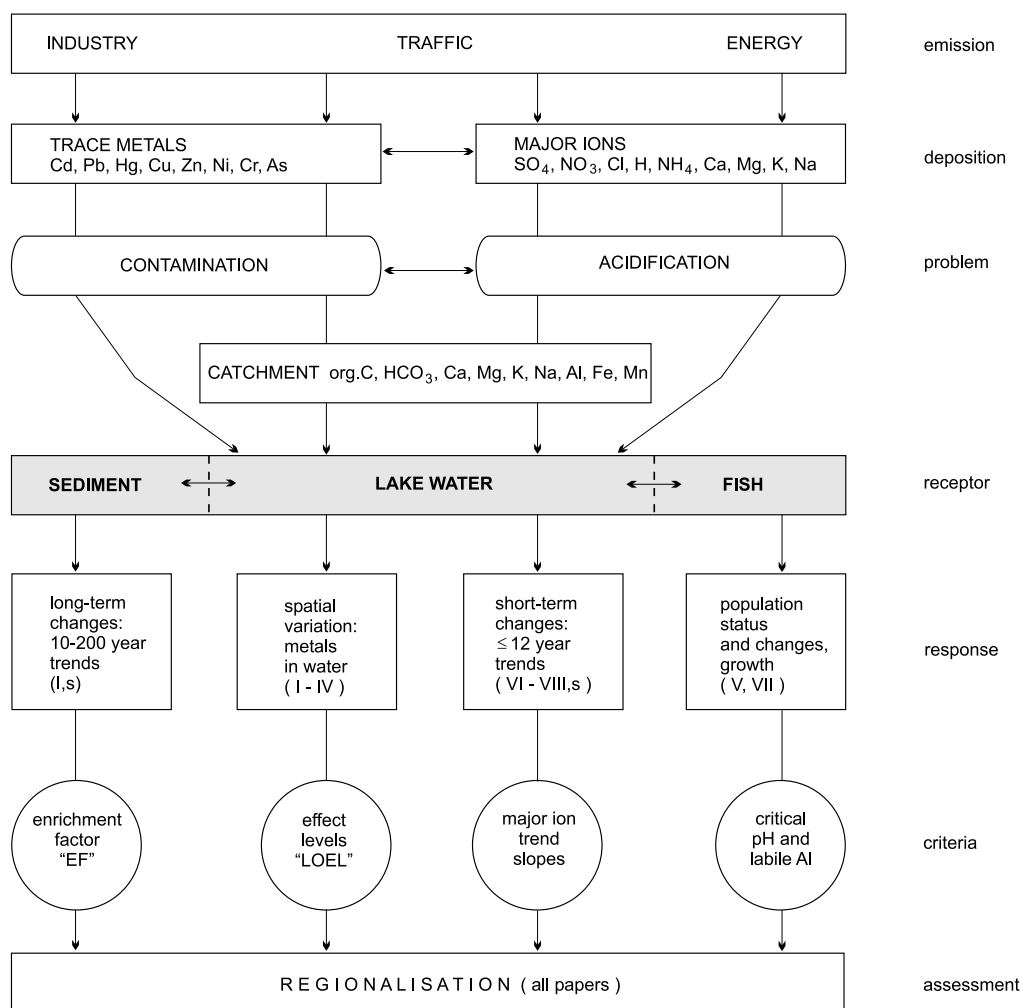


Fig. 3. The structure of this study. The Roman numerals refer to original papers I–VIII, and s to this paper.

- chemical and biological conditions in these lakes, more specifically
- to define regionally the major ion chemistry changes during the last decade in acid-sensitive headwaters (VI, VIII, this paper)
  - to show how the chemical changes can be connected to effects on fish populations on a regional level (dose/response & regionalisation) (V, VII)
  - to demonstrate how regional scale monitoring of acidification/recovery can provide data for further verification and reality checks for modeling/scenario development.

## 2 Materials and methods

### 2.1 Site selection and development of the monitoring network

The lakes comprising the core material of this study were chosen from earlier studies of acid sensitive lakes with a known chemistry and absence of direct human impact. The first national, coordinated trace metal survey in small lakes is presented in papers I and II. Initially, 259 lakes were studied for trace metals in water, 16 lakes for sediments (Table 2), and 14 lakes for trace metals in biota. The

**Table 2.** The data sets used in the studies I–VIII and in this summary.

Objectives	Sites		Years of sampling	Paper	Database/network
	n	Type			
Trace element history in lakes	16	S	1986	I	subset of RMLA
Recent devel. of trace elements	4	S	1999	this paper	subset of RMLA
Survey of trace elements in headwater lakes	259	L	1987	I, II	Prev. studies+FLS 1987
	116	L	1992	III	RMLA
	152	L	1992	IV	RMLA
Trace elements in small streams	1115	R	1990	IV	GSF
Trace elements in Finnish lakes	463	L	1995	*	NLS 1995
Fish status survey combined to National survey of lake acidification	80	L,F	1985–87	V	FGFRI
	987	L	1987	V	FLS 1987
Monitoring acidification effects on fish populations	10	L,F	1984–94	VII	subset of RMLA
Regional monitoring of lake acidification	170	L	1987–93	VI	RMLA
	163	L	1987–98	VIII	RMLA (refined)
Water quality in Finnish lakes	873	L	1995	**	FLS 1995

\*Skjelkvåle *et al.* 1999, 2001\*\* Mannio *et al.* 2000

L = lake, S = sediment core, R = stream, F= fish

Database/network, see Abbreviations

**Table 3.** Morphometric characteristics of the Regional Monitoring of Lake Acidification (RMLA) network (n=163) (from paper VIII).

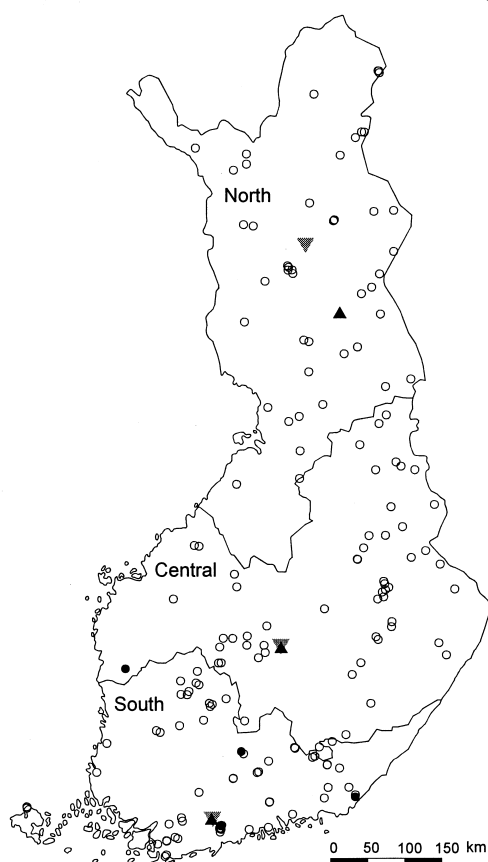
Variable	Unit	South Finland (n = 62)		Central Finland (n = 57)		North Finland (n = 44)	
		Median	Range	Median	Range	Median	Range
Lake area	ha	14.5	0.7–211	8	2–450	9	1.5–548
Catchment area	ha	91	17–2230	111	16–2100	112	18–2810
Max depth	m	8.0	1–50	6.8	1.6–22	2	1.3–18.6
Retention time	a	2.4	0.02–16	0.9	0.05–8.0	0.3	0.03–4.4
Peatland area	%	7.4	0–46	24	0–57	23	0–64
Exposed bedrock	%	7	0–51	0	0–15	0	0–78

results of trace metals in biota is discussed elsewhere (Iivonen *et al.* 1992). The lakes were generally situated in sparsely populated, forested areas at the head of a catchment basin. Some of the southernmost lakes are, however, only some 20 km from the nearest municipalities (paper I, II). All lakes were selected subjectively; 133 lakes based on previous acidification studies (Kämäri, 1985, Nuotio *et al.* 1990, Roila 1992), 100 lakes from the statistically selected population of the lake survey of 1987 (Forsius *et al.* 1990a,b) and 26 from other studies, *e.g.* mercury accumulation in fish (Mannio *et al.* 1986, Verta *et al.* 1986). The

objective of the selection was to cover the whole country, with emphasis on the headwater lakes of the most acidified and acid-sensitive, but unaffected areas. Most of the lakes occupy about 10–20 percent of the catchment. The catchments are mainly vegetated by coniferous forests or peatland, and till is the most common soil material. Ditching operations are the most common disturbance in the catchments. Cultivated land is mostly absent and in no case exceeded ten percent of the catchment area.

In 1990 the network was refined to 180 lakes for the Regional Monitoring of Lake Acidification





**Fig. 4.** RMLA lakes (○) in three regions: South (n=62), Central (n=57) and North Finland (n=44). Lakes for sediment stratigraphy studies in 1999 are marked with (●), deposition stations with (▼) and runoff stations with (▲).

(RMLA) (papers III, IV, VI), according to commonly agreed principles (NIVA 1996, Mannio 2000). At the same time, monitoring of fish populations in acidified lakes by Finnish Game and Fisheries Research Institute (FGFRI) was co-located to a subset of ca. 15 lakes of the RMLA network (paper VII, Nyberg *et al.*, manuscript). During the 1990s the network was further improved by removing less representative lakes, lakes with liming operations (ca. 10), lakes with too sparse data, geographically unnecessary dense areas, and by adding some sites to areas with no former coverage, mainly in Lapland. Presently, the monitoring network consists of 163 lakes (paper VIII), of which 133 lakes were part of the first trace metal survey in 1987 (Fig. 4, Table 2 and 3). The main difference compared to the Finnish lake population is that these lakes are more dilute and acid sensitive (Table 4). Headwater lakes can be classified to drainage lakes with an outlet, but no inlet (Wetzel 1983, Landers *et al.* 1988). In this study, a slightly broader meaning has been adopted. In the present RMLA network 28 lakes (17 %) have some small basin(s) in their catchment area, but they are, without exception, smaller than the study lake itself, and never occupy more than 10 percent of the catchment area. Seepage lakes (no inlet, no outlet) are slightly over represented in this network (>10 %), compared to the total population represented by the Finnish Lake Survey 1995 random sample (<5 %, except in Lapland). The peatland percentage (Table 3), indicating also organic carbon concentrations, reflect reasonably well the differences in different parts of

**Table 4.** Water quality of the RMLA network based on lake specific means 1987–1998 (from paper VIII).

Variable	Unit	South Finland		Central Finland		North Finland	
		Median	Range	Median	Range	Median	Range
Conductivity	mS m <sup>-1</sup>	3.0	1.4–9.4	2.1	0.7–3.8	1.3	0.7–20.6
pH		5.7	4.6–6.8	5.6	4.2–6.8	5.9	4.9–7.1
Alkalinity <sup>1)</sup>	μeq l <sup>-1</sup>	17	–35–104	26	–72–109	16	–16–141
BC*	μeq l <sup>-1</sup>	176	45–332	140	26–272	84	27–212
SO <sub>4</sub> *	μeq l <sup>-1</sup>	112	40–211	51	21–128	27	12–111
Cl	μeq l <sup>-1</sup>	39	11–121	18	6–83	14	8–46
NO <sub>3</sub>	μeq l <sup>-1</sup>	1.2	0.2–15	0.8	0.1–5.3	0.5	0.3–9.5
TOC	mg l <sup>-1</sup>	6	1.0–22	11	1.2–32	6	0.9–25
tot P	μg l <sup>-1</sup>	9	4–27	15	3–78	9	2–51
Al <sub>labile</sub>	μg l <sup>-1</sup>	19	0–207	15	0–64	6	0–56

<sup>1)</sup> Gran method

BC\*=[Ca+Mg+K+Na]\*

\* denotes non-marine concentration

the country according to Finnish Lake Survey (SYKE database, Rantakari and Kortelainen, manuscript).

## 2.2 Sampling, quality control and chemical analyses

### 2.2.1 Lake water

The trace metal surveys in lake waters (papers I–IV) were conducted with careful quality control to prevent contamination. Earlier works, especially in Sweden, had revealed that if precautions are not taken throughout the sampling procedure, contamination invalidates the results (Borg 1984). Possible sources of contamination include insufficient purity of reagents and bottles and sampling devices containing metallic parts. The development of the analytical equipment (graphite furnace AAS) enabled much lower detection limits, and made it feasible to investigate also waters receiving no direct contamination from point sources (Borg 1983, 1987, Nriagu *et al.* 1993). The bottles for trace metal analyses (125 ml polypropylene, Nalgene Labware) were kept in 10 % nitric acid for two days, followed by triple rinsing with quartz-distilled water and then put in double plastic bags for transportation. The samples were taken below the surface layer directly into the bottles, either by hand while wearing plastic gloves, or the bottle was attached to a wooden stick. Upon arrival at the laboratory, the outer plastic bag was removed. The samples were preserved at the district laboratories with 1 ml 35 % suprapur HNO<sub>3</sub> (Merck). Graphite furnace AAS was used for the determination of Cd, Cu, Pb and Ni and flame AAS for Zn. In case of an obvious contamination of the blank, all results of that district concerning that particular metal were rejected. Aluminum fractions were determined at the Norwegian Institute for Water Research according to the method of Røgeberg and Henriksen (1985).

In the second trace metal survey in fall 1992 (papers III and IV), the methods for sampling followed the same general principles as in 1987, but the procedure to prevent contamination in sampling and sample handling was developed further following a Nordic standard method. High Density Polyethylene (HDPE, Nalgene Labware, 125 ml) bottles were soaked in 7 M HNO<sub>3</sub>-solution for 3–4 days and rinsed 7 times with de-ionized water and

twice with double distilled water prepared in a quartz glass apparatus. The sampling technique was the same as in 1987, but the samples were transported to the Research Laboratory in Helsinki to minimize the possibility for contamination. The samples were preserved in the laboratory with 0.5 ml conc. HNO<sub>3</sub> (suprapur) and kept cool (+4°C). The samples were analysed by ICP-MS (Perkin-Elmer Sciex Elan 5000) for Cd, Pb, As, Cu, Cr, Ni, Zn and Al. Details of the calibration and analysis are given in paper III. The sample blank values were not subtracted from the sample values. All the freshwater samples were analysed 2–3 times, and the final result reported is the mean of these replicate values.

Throughout this study (papers I–VIII) the lake water quality variables (24 altogether) were measured with the same standard methods used by the Environment Administration (Forsius *et al.* 1990b), including pH, Gran alkalinity, conductivity and total organic carbon; Ca, Mg, K, Na with AAS; SO<sub>4</sub> and Cl with ion chromatography; NO<sub>3</sub> (or NO<sub>3</sub>+NO<sub>2</sub>) and NH<sub>4</sub> with colorimetry, and Al fractions with ion exchange (Table 5).

### 2.2.2 Snow cover

In paper I the atmospheric load of trace metals was estimated from snow samples at 48 long term ground water monitoring stations (Soveri and Ahlberg 1990). Samples were collected straight into 500 ml high density polyethylene bottles (Nalgene Labware) by scraping the wall of a dug trench (Ross and Granat 1986). The bottles were cleaned, stored and transported with the same precautions as with the lake water sample bottles. The total depth of the snowpack was sampled. The samples were kept frozen until analysis. Trace metals (Cd, Cu, Pb, Zn, Ni) were analysed using graphite furnace AAS (GFAAS). Chemical blanks were made with distilled and de-ionized water to ensure that no contamination occurred during the analysis period. Zink and Cu were abnormally high in blanks from one district, and those results were rejected.

### 2.2.3 Sediment cores

In March–April 1986 two sediment cores each were taken from the deepest points of 16 lakes (paper I) with a pistonless gravity corer (diameter 50

**Table 5.** Key variables and analysis methods used in trace element and acidification studies.

Material	Element/variable	Methods	Reference
Lake water	Cd, Cu, Pb, Zn, Ni, Mn, Fe, Al	GFAAS	I,II
Snow profile	Cd, Cu, Pb, Zn, Ni	GFAAS	I
Lake sediment cores	Cd, Pb	GFAAS	I
	Ni, Cu, Zn	ICP	I
	Hg	CVAAS	
Lake water	Cd, Cu, Pb, Zn, Ni, Cr, As, Mn, Al	ICP-MS	III, IV
Lake sediment cores	Cd, Cu, Pb, Zn, Ni, Cr, As, Mn, Fe	ICP-MS	this paper
	Hg	CVAAS	
Lake water	pH conductivity alkalinity NH <sub>4</sub> -N, NO <sub>3</sub> -N Ca, Mg, K, Na SO <sub>4</sub> , Cl, F Al fractions TOC	comb. electrode conductometry Gran plot colorimetry FAAS IC Autoanal. (PCV) IR	papers I–VIII, SYKE standard methods, ( <i>e.g.</i> Forsius <i>et al.</i> 1990b)

mm). The cores were sectioned in the field into 1.0 cm (0–10 cm) and 2.0 cm (10 cm – 30 cm) subsamples, and the two parallel samples pooled. A third core was taken from some lakes and sectioned for <sup>210</sup>Pb analysis. All cores were taken within an area of 10 m<sup>2</sup>. The samples were deep-frozen in polyethylene boxes. Nine equal volume subsamples (0–1 cm, 1–2 cm, 2–3 cm, 3–4 cm, 4–5 cm, 6–8 cm, 10–12 cm, 18–20 cm, 28–30 cm) from each core were analysed for metals. The lyophilized and homogenized samples (0.1–0.5 g) were digested with 10 ml of nitric acid (conc HNO<sub>3</sub> diluted with water 1:2) at 120 °C under pressure. Concentrations of Ni, Cu and Zn were determined by inductively coupled plasma (ICP) and concentrations of Cd and Pb by GFAAS. Mercury was determined by cold vapour AAS (CVAAS) technique after boiling 30 minutes with a mixture of conc H<sub>2</sub>SO<sub>4</sub> and fuming HNO<sub>3</sub>. The <sup>210</sup>Pb analysis was performed for nine lakes, and the accumulation history was calculated with commonly used constant rate of supply (CRS) or constant initial concentration (CIC) -methods (Robbins and Edgington 1975, Appleby and Oldfield 1978).

In March–April 1999, four lakes in southern Finland were revisited (Valkea-Kotinen, Iso-Lehmälampi, Kangasjärvi, see paper I, and Hirvilampi, Verta *et al.* 1989). Similarly to the previous study, two sediment cores each were taken from the deepest points of the lakes with a pistonless gravity corer (diameter 95 mm). This time the cores were sectioned into thinner slices, in order to detect the very latest sedimentation processes: 0.5 cm (0–2 cm), 1.0 cm (2–6 cm) and 2.0 cm (below 6 cm) subsamples. The cores were taken within an area of 10 m<sup>2</sup>. The samples were deep-frozen in glass jars. Both cores were analysed individually for trace metals, the other also for <sup>137</sup>Cs isotopes for dating recent accumulation (STUK 2000). The trace metal results are reported for the dated core. Sediments were lyophilised, homogenised and digested (Milestones Mega 1200) before the measurement with ICP-MS (Perkin Elmer Sciex Elan 6000). Nordic digestion procedure for inland sediment samples was used (250–500 mg dry sample + 5 ml conc HNO<sub>3</sub>; 2 blanks + 2 certified reference samples (ISO/CD 15586 Determination of elements)).

### 2.3 Statistical analyses

Statistical methods in papers I–IV dealing with concentrations and relations of heavy metals in different environmental compartments, consisted mainly of univariate descriptive frequency statistics, T-test between groups, correlation analyses, multivariate (stepwise) regression analyses. The metals show often non-normal distributions, which was improved with log-transformations before further analysis.

Statistical methods used in the regional monitoring of lake acidification (VI–VIII) included simple univariate descriptive statistics box-plots, Wilcoxon signed rank test and student's T-test. Kendall-Tau trend test was chosen for individual lakes 1987–1998 to examine the trend significance (paper VIII, Cluis *et al.* 1989, Mallory *et al.* 1998, McNicol *et al.* 1998). Linear regression was used in the further analysis of trend magnitude. Kruskal-Wallis and Mann-Whitney  $U$ -tests were used to test the difference between lake groups.

### 2.4 Supporting data used in the interpretation of spatial and temporal variations

The Geological Survey of Finland (GSF) has performed large scale geochemical mapping during the 1980s and 1990s (Lahermo *et al.* 1990, Koljonen 1992, Lahermo *et al.* 1996). Data of the interpolated concentrations of trace metals in till (Koljonen 1992) were used as a background variable in papers I, II and especially IV. The Finnish Forest Research Institute (FFRI) has participated in Nordic and European cooperative surveys on forest mosses since 1985 (Rühling *et al.* 1987, 1992, 1996, Kubin *et al.* 2000). Similarly to geochemical data, concentrations of metals in mosses were used to classify the lakes in groups according to comparable deposition levels (paper I and II). The Finnish Meteorological Institute (FMI) has monitored trace metal bulk deposition in four Integrated Monitoring areas since 1991 (Kulmala *et al.* 1998). The data sets are not long enough to reveal significant trends, but give a reasonable estimate of open area deposition levels of Cd, Pb, Cu and Zn in different regions in Finland. The data are compared to other estimates of metal deposition (mosses) and the accumulation in sediments.

The Finnish Environment Institute (SYKE) has

been monitoring major ion chemistry in bulk deposition since the 1970s (Haapala 1972), presently on 30 stations throughout Finland (Vuorenmaa *et al.* in print). Long-term trend data since 1982 from three selected stations in the three regions (South, Central, North Finland) of the RMLA lake network are presented here for qualitative comparison of the spatial and temporal variation of major ions (annual volume-weighted mean concentration of  $\text{SO}_4$ , base cations and  $\text{NO}_3$ ). In concordance with the deposition data, data from three SYKE small representative hydrological catchment stations (Seuna 1983), located nearby to a deposition station, are presented to illustrate the spatial and temporal variation in runoff (Fig. 4). The runoff is measured continuously by overflow weirs with water stage recorder gauges.

## 3 Results and discussion

### 3.1 Trace metals in headwater lakes

#### 3.1.1 Long-term history of trace metals in lake sediments

The studied sediment profiles, dated with  $^{210}\text{Pb}$ , showed that early anthropogenic accumulation was typical for Pb, Cd, Hg and Zn. For Pb this was evident in most cores by 1800 in southern Finland and was followed by a linear increase up to the 1970s (paper I and Verta *et al.* 1989) A prominent increase of Cd, Hg and Zn typically occurred in the 1900s and in the few cases where any marked increase in Cu, Ni or V sedimentation occurred, it was generally after 1950.

The lowest concentration of Pb in all profiles were found in the deepest analysed subsamples in southern Finland indicating that the “background level” was not reached by coring the sediment profiles of the southernmost lakes (cf. Verta and Mannio 1987). This was confirmed in the 50 cm long cores taken from the four lakes in 1999 (SYKE database). The increased atmospheric distribution of Pb in northern hemisphere already in Roman times is well documented in sediments, peat bogs and ice cores (Renberg *et al.* 1994, 2000, Shotyk *et al.* 1998, Boutron *et al.* 1994). The upward increase in concentration in sediment profiles was more than five fold with Pb in all but one lake with a maximum increase of 44-fold. With the

present knowledge of the over 2000 year long pollution history of Pb, any calculation of the enrichment factor for Pb is highly dependent on the "background" reference depth chosen. Copper and Ni had a strong intercorrelation in surface sediments, but neither of them correlated with other trace elements.

When analysing intercorrelation of trace metals in surface (0–5 cm) and deep (18–30 cm) sediments, clear differences in trace metal behaviour was evident (paper I). In deep sediments trace metals had only few intercorrelation (Zn–Cd;  $r = 0.60$ , Zn–Cu;  $r = 0.60$ ). The metals showing highest anthropogenic enrichment (Pb, Cd, Hg) were normally strongly intercorrelated in surface sediments and also correlated with sediment organic matter, possibly reflecting their affinity to biota and humus in the water column, and their subsequent sedimentation with organic material.

The recent gross accumulation rates of trace metals can be compared with the calculated background accumulation rates (conc. in deep sediment  $\times$  accumulation rate) and further calculate the anthropogenic accumulation as the difference between these two estimates (Verta *et al.* 1989). The share of anthropogenic accumulation in sediments varied from 74 to 97 % for Pb, from 62 to 91 % for Cd, from 70 to 89 % for Hg and from 39 to 91 % for Zn in southern and central Finland. For Cu and Ni the variation in the anthropogenic share was much larger between different lakes ranging from 0 to 84 % for Cu and from 0 to 75 % for Ni. Because only slight or no disturbances have occurred in the catchment areas of the lakes, most of the anthropogenic trace metal accumulation into sediments is through atmospheric transport or as a result of increased leaching from the catchment due to acidification and subsequent sedimentation in lakes. The reasons for the large variation between metals and regions is further discussed in the next sections.

### **3.1.2 Geographical differences in the accumulation of metals in sediments**

Sediment surface concentrations of Pb, Cd and Hg had a clear regional pattern showing higher concentrations in southern Finland than in northern Finland. The concentrations of these three elements were also much lower in the two northernmost lakes than in the other lakes. These observa-

tions are in concordance with other regional studies in Nordic countries (Johansson 1989, Rognerud and Fjeld 1993). Zink also had somewhat higher concentrations in the south than in the north. On the contrary, Cu and Ni did not show any regional differences in surface sediments, suggesting dominance of local geochemical influence. If significant geological sources for the trace elements existed, these should be reflected as elevated concentrations in the deeper layers as well, with minimal vertical gradients. Indeed, regional differences (southern vs. northern lakes) were not found in the deep sediments (18–30 cm), except for higher concentrations of Zn in the north. This indicates a relatively similar distribution of the geochemical signal in the preindustrial sediments in southern and northern lakes.

The enrichment factor (EF) (*e.g.* Rognerud and Fjeld 1993, 2001) can be used to compare lakes with different geochemical and deposition histories. It is a useful tool for geographical comparison between studies, since the ratio is insensitive to differences, *e.g.*, in sediment focussing and sample digestion. The enrichment factor is calculated as the ratio between the modern (0 to 2–5 cm in this study) and historical (20–30 cm, or >150 yr) concentrations. Accordingly, EF 2 means that the modern concentration is twofold the historical. The increase in concentration in sediment profiles was more than five fold with Pb. Most of Cd, Hg and Zn profiles showed EFs between 2 and 10. Half of the EF values for Cu were less than 2 and in only three lakes EF values of 2 for Ni were exceeded. Clearly higher EF values were found in the southern part of the country, with the exception of Cu, Ni and Cr (Table 6).

It is interesting, that in the southern regions Norwegian EF values for Pb, Cd and Hg are lower than those in Finland and Sweden, in spite of higher or similar concentration level in lake water (Skjelkvåle *et al.* 2001). This could be related to the differences in the sedimentation process in lakes with different trophic status. Norwegian lakes are more dilute and oligotrophic, less humic (Henriksen *et al.* 1998), and the mechanisms for metal scavenging to sediments could be less favourable.

Although not as pronounced as in South Finland, anthropogenic signals of trace metals are evident in northern Finland as well (paper I, Mannio *et al.* 1997). The results of various regional studies are compared using the enrichment factors (Table

**Table 6.** Comparison of average enrichment factors (EF) of different metals and arsenic in Fennoscandian lake sediments. The Norwegian values with a range are means of three subregions. The range in northern Finland is based on individual lakes (n=5).

	Pb	Cd	Hg	As	Zn	Cu	Ni	Cr	Ref.
Southern Finland	18	8	6.3	4.6	6	1.9	1.7	1.5	I, (As, Cr this study)
Southern Sweden	>10	10	5	..	5	2	..	..	Johansson (1989)
Southern Norway	3–7	2–4	2–4	..	..	..	1–2	..	Rognerud and Fjeld (1993)
Northern Finland	5–10	2–5	2	3	<2	<2	1–3	<2	I, Mannio <i>et al.</i> (1997)
Northern Sweden	~2	~2	~2	..	~1	~1	..	..	Johansson <i>et al.</i> (1995)
Northern Norway	2–3	..	1–3	..	<1	<1	1	..	Rognerud <i>et al.</i> (1998)
Norway	6.2	2.0	2.6	3.9	1.3	1.3	1.1	1.1	Rognerud and Fjeld (2001)

6). Typical EF-values in northern Finland (Lapland) were; for Pb 5–10, for As 3 and for Hg 2. Cadmium had a high EF in three surface sediments (ca. 5). Nickel (EF ca. 3) was high in two lakes near the border in NE Lapland, less than 50 km away from a Russian nickel smelter. Chromium and Cu did not show EF values over 2. Similar values have been reported from northern Scandinavia (Johansson *et al.*, 1995, Skotvold *et al.* 1997, Rognerud *et al.* 1998).

### 3.1.3 Atmospheric deposition of trace metals in recent decades

The duration of permanent snow cover before sampling in winter 1986–1987 varied from 90 days in southern Finland to 202 days in northern Finland, and the deposition values thus represent a mean of 3 months to nearly 7 months. Three short melting periods occurred during the winter in southern Finland during which a decrease of 10 to 20 % of the thickness of the snow cover took place. The water content of the snowpack, however, increased even in southern Finland to late March, and no increase in the runoff from small catchments occurred.

Concentrations of Pb and Cd correlated significantly with SO<sub>4</sub> and NO<sub>3</sub> in the snowpack, but those of Zn, Cu and Ni did not. Only half of the intercorrelation between trace metals in the snowpack were significant ( $p < 0.05$ ). These were Pb–Cd, Pb–Cu, Zn–Cd, Zn–Ni and Cu–Ni. Aluminum correlated with most trace metals, possibly because the areas susceptible for soil drift are mostly the same that receive high amounts of atmospheric transported trace metals. These intercorrelation were remarkably lower than those be-

tween Pb, Cd, Zn, and SO<sub>4</sub> reported by Ross and Granat (1985) in northern Sweden. They concluded on the basis of good correlations that the deposition of these metals is primarily due to long-range transport of anthropogenic emissions from the European continent. This was also concluded by Rühling *et al.* (1987) from a decreasing concentration gradient of these metals in mosses in Scandinavia from south to north. The appearance of atmospheric pollution from some local emission sources of heavy metals both in mosses and in the snowpack is unavoidable and makes the differentiation between different sources difficult.

The primary emission sources of Pb to the atmosphere are automobile exhausts, whereas Cd, Zn and Cu are released by metal smelting and refining, and Ni by oil combustion and smelting (Nriagu and Pacyna 1988). Sulphur is predominantly released by burning of fossil fuels and nitrogen compounds by automobile exhausts. Intercorrelation of trace elements in deposition may thus not indicate the same source or transport, but reflect that most of the emissions of these compounds are concentrated in the same areas both in central Europe and in southern Scandinavia (paper I).

Trace metal concentrations in mosses (*Hylocomium splendens*, Berg *et al.* 1995, *Pleurozium schreberi*, Rühling *et al.* 1996) have been compared to bulk deposition estimates with good correlation even in background stations. Regression equations have been developed successfully to convert the moss data to deposition estimates of *e.g.* Pb, Cd, As, Cu, V, and Zn (Berg *et al.* 1995). There are differences in the metal accumulation to the two different species, but they are relatively minor for strongly adsorbed elements, *e.g.* Pb and Cd. For the qualitative purposes, the moss data 1985–1995 are used as a measure of the

**Table 7.** Comparison of recent deposition estimates ( $\text{mg m}^{-2}\text{a}^{-1}$  except Cd  $\mu\text{g m}^{-2}\text{a}^{-1}$ ) of trace elements in Finland. Snow results from paper I (mean), moss from Rühling *et al.* 1992 (median concentration converted to deposition according to Berg *et al.* 1995), bulk deposition from Kulmala *et al.* 1998 (range of annual mean). The geographical areas are not identical in different data sets.

	Pb	Cd	Cu	Ni	Zn
<b>Southern Finland</b>					
snow cover 1987	1.3	20	0.5	0.4	1.7
moss survey 1990	2	60	1	0.5	5
bulk depos.1991–96	0.8–2	16–25	0.4–1.3	..	1.5–2.9
<b>Northern Finland</b>					
snow cover 1987	0.7	11	0.3	0.14	1.3
moss survey 1990	1.5	40	1	0.5	2.5
bulk depos.1991–96	0.1–1	5–18	0.4–1.6	..	0.4–1.7

level and changes of the recent metal deposition history in Finland. Trace metal bulk deposition data from background areas in Finland are available for ca. last ten years; from two coastal stations starting 1989 and four Integrated Monitoring stations from 1991 (Kulmala *et al.* 1998). A comparison of the recent deposition level estimated from snow, moss and bulk deposition is presented in Table 7. The rough deposition estimate from snow cover in 1987 falls within the range of the deposition stations in 1990s, with the exception of Cu in northern Finland. In general, the level of bulk deposition is slightly lower than that based on moss in 1990. This could be due to the difference in sampling period, or simply due to natural distribution differences between two stations and a regional grid network.

The metal concentrations in moss in Sweden peaked during the 1970s (or early 1980s), approximately at the same time as the sulphur deposition

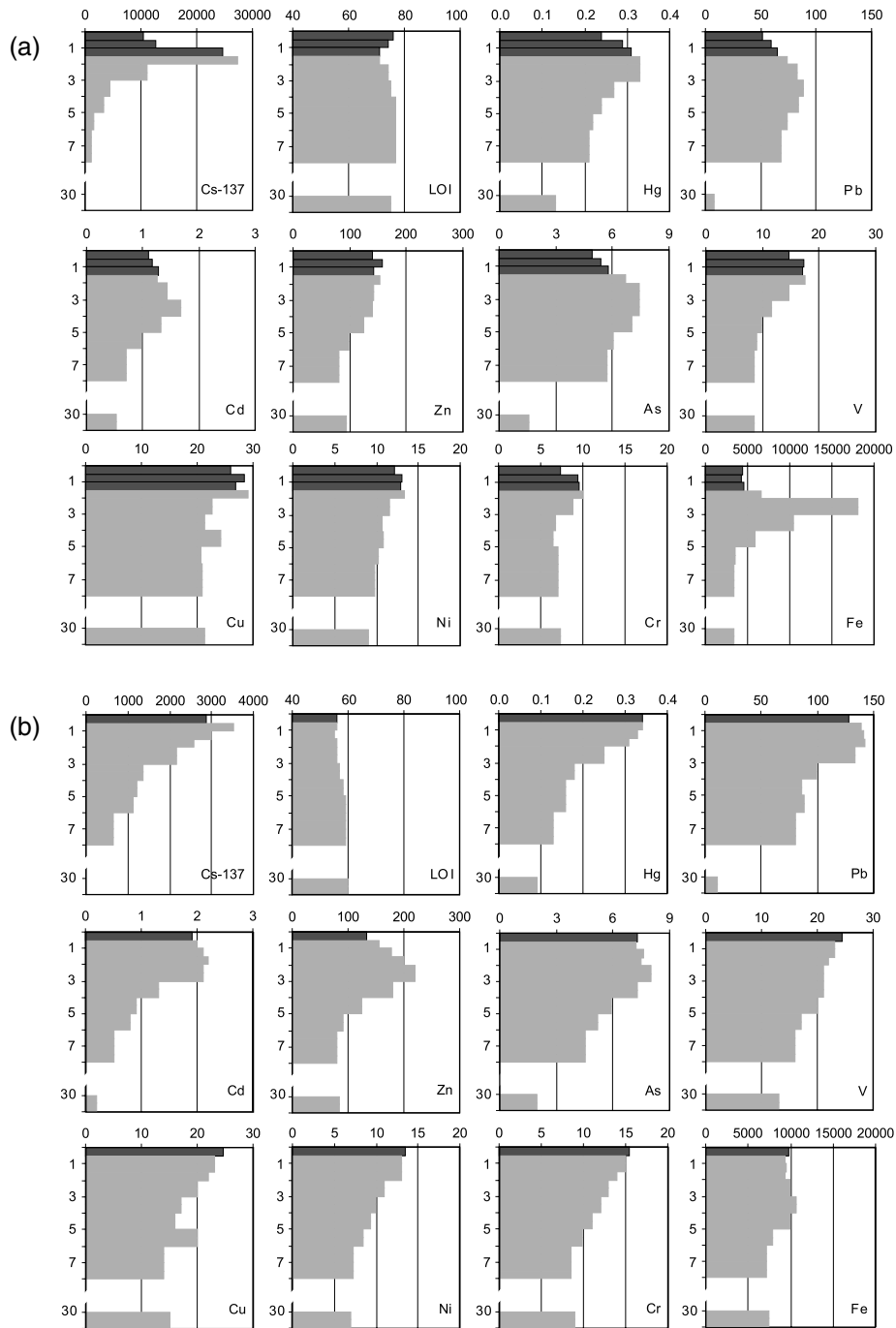
was highest (Gydesen *et al.* 1983). The atmospheric loading of the most widespread and toxic metals, Pb, Hg and Cd has decreased considerably during last 20–25 years (Rühling *et al.* 1987, 1996). The deposition trend of at least the long-range transported metals Cd, Pb has probably been similar in Finland as well (Kubin *et al.* 2000).

### 3.1.4 Recent changes in the metal accumulation to lake sediments

Four lakes with a known sediment stratigraphy from the 1980s (I, Verta *et al.* 1989) were resampled in 1999 to evaluate the present metal accumulation in comparison to the decades with highest atmospheric load. The assumption is that there have been substantial reductions in deposition, which should be reflected in the sediments (Table 8, Fig. 5). Such changes may be masked and

**Table 8.** Semi-quantitative comparison of recent decrease of trace element concentration and deposition in Finland. Sediment is from this study, forest moss from Kubin *et al.* (2000), bulk deposition from Kulmala *et al.* (1998). Symbols: --- = 40–80 %; -- = 20–40 %; - = 10–20 %; 0 = <10 %, .. = missing value

Element	Lake sediment (Valkea-Kotinen) <1986–99	Forest moss whole of Finland 1985–1995	Bulk deposition (Haapasaari, SE Finland) 1989–1995
Pb	---	---	---
Cd	--	---	---
Hg	--	..	..
As	--	..	..
V	-	---	..
Zn	-	0	..
Cu	-	-	..
Ni	0	-	..
Cr	--	0	..



**Fig. 5.** Trace element concentrations ( $\mu\text{g g}^{-1}$  dry weight),  $^{137}\text{Cs}$  activity ( $\text{Bq kg}^{-1}$  dw.) and organic matter (LOI, loss on ignition, %) in recent sediments of (a) Lake Valkea-Kotinen (VK) and (b) Lake Hirvilampi (HIR). The dark area represents recent sedimentation after 1986, based on  $^{137}\text{Cs}$  dating. The continuous stratigraphy (0–8 cm) represents ca. 50 years in VK and considerably more in HIR. The lower reference layer (30–31 cm) represents pre-industrial background, except for Pb.



delayed by at least two factors affecting the metal transport in the catchment and lake: continuing leaching processes from the metal-enriched organic surface soils, and the lag in the sediment focussing to the deepest part of the basin. However, there were signs of declining Pb already in these sediment cores in the 1980s, relatively soon after major emission reductions (Verta and Mannio 1987). According to the Nordic moss surveys, between 1985–95 the largest declines in concentration levels, 50 to 60 %, have been for Pb, Cd and V (Kubin *et al.* 2000). Slight decreases (<15 %) were observed for Cu and Ni, and no change for Zn and Cr (Table 8). Trends in bulk deposition are reported only from Haapasaari station in southeastern corner of Finland, and the declines are notable; 80 % for both Cd and Pb.

The recent development in the sediments is illustrated in Fig. 5a–b with two acidic lakes, one with high (Lake Valkea-Kotinen, TOC > 10 mg l<sup>-1</sup>, in Evo, 130 km north of Helsinki) and one with low humus content (Hirvilampi, TOC < 5 mg l<sup>-1</sup>, in Ylämaa, southeastern corner of Finland). They have typical background concentrations (Table 5 in paper I) of trace elements in the sediment, reflecting their catchment geology. Due to differences in trophic status, basin formation and organic content, the gross accumulation of material is higher in the humic Lake Valkea-Kotinen (VK) (33 g m<sup>-2</sup> a<sup>-1</sup>) compared to Lake Hirvilampi (HIR) (10 g m<sup>-2</sup> a<sup>-1</sup>). Both values are in the lowest range reported for this kind of lakes in Finland.

The <sup>137</sup>Cs activity suggests a 1.5 cm depth as a reference level for post 1986 accumulation for VK and only 0.5 cm for HIR. Therefore, the development is better displayed in the core from VK. The continuous profile of 8 cm for VK, displayed in Fig. 5a, corresponds approximately to the last 50 years, extrapolated from the <sup>137</sup>Cs and the former <sup>210</sup>Pb -profiles. No changes of the accumulation rate is assumed for the last decades, since the whole catchment has been protected from land-use activities. The organic material content of the profiles (LOI) is also vertically uniform. The <sup>137</sup>Cs profile for HIR shows that some postdepositional mixing has occurred. The probable reason for this is bioturbation, although diffusion and porewater movement are also possible in a very porous matrix (water content 95 % in these sediments). This, in addition to the low sedimentation rate, suggests that any recent changes (<10 yr) in the sediment cores of this type of lake is difficult to demonstrate

in a quantitative way. The earlier sediment survey revealed that four cores out of the 18 had some mixing problems based on the <sup>210</sup>Pb or <sup>137</sup>Cs profiles. In the present study, only Lake Valkea-Kotinen showed excellent, undisturbed stratigraphy.

In Valkea-Kotinen, assuming the 1.5 cm net accumulation after 1986, Pb maximum concentration match with the earlier core (Verta *et al.* 1989), thus supporting the dating result. The concentration of the elements Pb, Hg, Cd and As show presently 60 to 80 % of their maximum values in VK. This is a clear indication of decreasing accumulation of these metals in the sediments, due to lower atmospheric loading and catchment supply. The anthropogenic increase of Cd through time is clear, but the recent changes are still difficult to quantify in the sediments.

There are no earlier data reported on As (or Cr) stratigraphy in headwater lakes in Finland. The profiles show an enrichment factor of over 3 for As in these lakes. This is a relatively high value, since As has been considered to be controlled very much by local geochemistry (Lahermo *et al.* 1996, paper IV). Arsenic may interact with iron in redox processes, thus moving vertically in sediments (DeVitre *et al.* 1991), but this would not explain the significant enrichment factor (signal to noise ratio) in these profiles.

All these recent changes are less obvious in the HIR profile, for which the smaller sedimentation rate and mixing are probably the main causes. Another factor may be the higher present deposition rate of metals. Hirvilampi is situated in the southeastern corner of Finland, receiving transboundary pollution from the St Petersburg area. This is also indicated in the regional moss analysis for at least As, Cd and V (Rühling *et al.* 1996).

Copper, Ni and Cr have a small anthropogenic signal (EF <2) in most Finnish headwater lakes in background areas. In HIR, there is a doubling of the concentration in comparison to the background, indicating possibly higher former deposition levels due to the more industrialised regions in Russia. However, the recent moss surveys do not indicate particularly elevated concentrations in the southeastern corner of Finland (Rühling 1996, Kubin *et al.* 2000). The apparent constant increase may be caused by bioturbation or physical mixing of the surface layers, as the Cs profile suggests.

The Zn profile in HIR is typical for recently acidified lakes; the sedimentation process is prob-

ably reduced due to acidic water column (*e.g.* Norton 1984, Renberg 1985) or there is a post-depositional migration in the sediment (Carignan and Tessier 1985). Vanadium is dispersed in the environment from fossil fuel combustion. The earlier rise and recently started decline are similar to Hg in Valkea-Kotinen. Iron species are able to migrate diagenetically in the sediment. When the iron content forms a substantial part (> 15 %) of the total sum of constituents of the dry sediment, it can have an effect on the concentration of other elements (Norton 1984, Cornwell 1986). There is a subsurface maximum of Fe in VK, but the concentration level is so low (<2 %), that it is unlikely it has affected other profiles. The profiles of Mn and Al were vertically uniform in both lakes.

An important implication from this data is that the sedimentation of Pb, Cd, Hg and As seems to react relatively fast to decreased atmospheric loading. Only part of the element flux to the lake enters directly via the lake surface. In the case of Valkea-Kotinen, the lake to catchment ratio is 1:5. Calculations show, that soils in Sweden have accumulated large amounts of these elements during this century (Johansson *et al.* 1995). If there were a continuous supply from this pool in the catchment, the sedimentation rate of these elements in the lake would most likely not have changed substantially. Recent calculations of metal (Cd, Cu, Pb, Zn, Ni) budgets in the VK catchment suggests, that the direct deposition of Pb and Cd onto the lake surface is of the same order of magnitude as the supply from the catchment (Ukonmaanaho *et al.* in print). For Pb this is in line with earlier observations suggesting strong retention in the soil, but for Cd, a much larger part has been estimated to enter the lake from the catchment (Borg and Johansson 1989, LaZerte *et al.* 1989). The retention of the total atmospheric load (bulk+throughfall) of Pb, Cd, Cu and Zn was over 77 % at VK (Ukonmaanaho *et al.* in print), and most of the retention took part in the terrestrial catchment. Only a relatively small fraction, 3–26 % was accounted for lake sedimentation. While the sedimentation or concentration of a metal in sediment does not directly reflect the conditions in the lake water, the data suggests, that the trace metal loading to headwater lakes is reduced proportionally to decreases in deposition.

### 3.1.5 Geographic variation and other factors affecting the concentration of trace metals in lake waters

The concentrations of Zn, Cd and Ni in water decreased northwards parallel to the pattern of atmospheric deposition, a distribution commonly observed in Fennoscandia (Henriksen and Wright 1978, Borg 1987, Mannio and Verta 1987). A comparison of lake water chemistry data with metal concentration in moss (Rühling *et al.* 1987) showed that the average concentration of Cd, Cu, Pb, Zn and Ni were higher in water, in areas where the regional concentration of the same metal was higher in moss (paper I).

The order of concentration of the trace metals in lake water was: Fe > Al > Mn > Zn > Cu-Ni > Pb > Cd, the same order as in similar Swedish lakes (Borg 1983, 1987) and in a pilot study in Finland (Mannio and Verta 1987). The concentration levels are similar to those of Swedish studies but lower than in those from the southern Norwegian survey in 1974–75 (Henriksen and Wright 1978).

It appears not possible to distinguish quantitatively the influence of acidification from the increased atmospheric loading of trace metals without detailed catchment studies (*e.g.* Nelson and Campbell 1991). In papers I and II, an attempt was made to minimize the regional differences in metal loading by grouping the lakes according to concentrations of the metals in moss. The grouping suggested that acidity and/or acidification is the primary factor determining the lake metal concentration. For Zn, Cd and Pb the pH value explains the variation from 15 to 42 %, depending on the region. Other variables (lake area, percent exposed bedrock, TOC) explain only 4 to 9 % of the variation.

The terrestrial input of dissolved humic substances from the catchment is an important carrier of metals to small lakes located in forested areas (*e.g.* Borg and Johansson 1989), because of their metal complexing abilities (*e.g.* Beneš *et al.* 1976, Reuter and Perdue 1977, Mantoura *et al.* 1978). The concentrations of the mainly land-derived metals Al, Fe, and Mn are strongly dependent on TOC, as well as on acidity. The concentrations of Cu and Ni in lake waters are more dependent on TOC than those of Cd, Zn and Pb. These relationships were found to be similar to, but statistically more significant in this study, than those reported

in previous studies in Sweden (Borg 1983, 1987) and Finland (Mannio and Verta 1987), because of a much larger data set (papers I and II).

The concentration of Cu, Ni and to some extent Mn and Zn in lake water is correlated to their concentration in till material (paper II). However, in the stepwise regression analysis, only the explained variation of Cu in water is significantly ( $P < 0.01$ ) enhanced by introducing Cu concentration in till into the equation. Also other catchment characteristics, such as the area of peatland, exposed bedrock, catchment to lake area ratio, are correlated to metal concentrations; however, the co-linearity with water quality parameters (most significantly pH and TOC) is usually so strong that other catchment characteristics do not improve the degree of explanation of the models.

In paper IV the emphasis was on possible regional geochemical signals that might be reflected in the concentrations of the elements. The lakes with highest As concentrations were found in an area with greenstones and arsenic-rich black schists. The same lakes have high Cu concentrations, which evidently are derived from the Cu-rich greenstones of the catchment. The high Cu concentration of streams and lakes in the industrialized region of the southwest coast are due to several anthropogenic sources.

The highest concentrations of Cr occur in brown water lakes (and streams) rich in humic substances (TOC), while Mn and Zn concentrations are controlled by acidity, with a tendency to be elevated in low-pH waters. The high Ni concentrations in lakes in southwestern Finland are probably due to anthropogenic input, while Ni anomalies in stream and lake water in eastern Finland are correlated with high Ni contents of glacial till. There is no connection of Pb concentrations in lakes and till parent material. Based on the high atmospheric deposition level and anthropogenic signal in sediments, the Pb concentrations in lakes are mainly of airborne anthropogenic origin. However, the pattern is not clearly increasing towards south, and most likely the concentration in an individual lake is controlled largely by humic substances.

For various reasons, none of the studies before 1992 provided information on the regional concentration levels of some of these trace elements in Finnish Lapland. In paper III, data of Cd, Pb, As and Cr concentrations in small lakes in Lapland were presented for the first time, including a com-

parison with other areas in Finland. The survey was designed as a pilot project for the new ICP-MS equipment. The extremely low concentration level of trace metals set special demands on sampling, sample handling and analysing. ICP-MS was a relatively new method for multi-element analysis in 1992, and is ideally suited to the analysis of waters, because the majority of elements can be detected below the  $0.1 \mu\text{g l}^{-1}$  level. An important aspect of that survey was that very small concentrations of trace elements can be measured with high accuracy and repeatability.

The median values of the metals in Lapland were (in  $\mu\text{g l}^{-1}$ ): Cd 0.02, As 0.17, Cr 0.24, Ni 0.25, Pb 0.25, Cu 0.28, Zn 1.84 and Al 63. These values are similar to the concentrations in northern Sweden and comparable values have also been reported in other high latitude lakes (Schut *et al.* 1986, Stephenson and Mackie 1988, Traaen *et al.* 1991, Nriagu *et al.* 1993), bogs (Urban *et al.* 1987) and groundwaters (Ledin *et al.* 1989).

Although the study lakes in Lapland were situated relatively far from point sources of trace metal pollution, the effects of an acidic environment in enhancing trace element mobility can be seen. The elements Cd, Zn and As correlated significantly with the acidity of the lake water. When considering the whole country, Pb and Al also correlated similarly. This study is in accordance with earlier results, but suggests further that of the potentially airborne elements, Cr concentration is also dependent on the organic carbon content.

The results of the lake water surveys in papers I–IV are consistent with the observations of intensive catchment budget and lysimeter studies (Aastrup *et al.* 1995, Ukonmaanaho *et al.* in print). The mobility of many elements increases in acidic environments. Soil acidification enhances the transport of originally airborne metals. In humic waters, elevated concentrations of especially land-derived metals are to be expected. Due to their complexing ability and their acidity, humic substances can also transport metals, which in other conditions would be retained in the soils of the catchment. Acidity and the concentration of organic carbon reflect several characteristics of the lake and its surroundings and are therefore major variables in determining the fate of metals in lake ecosystems.

The pattern of atmospheric deposition is reflected in the concentrations of Cd, As, Cu, Zn and Ni in headwater lakes, but land-use and the natural

distribution of metals in the overburden as well as water acidity and the amount of humic substances influence the distribution of trace metals in both lakes and streams (paper IV). Thus the regional distribution of trace metals in headwater lakes cannot be used alone in estimating the contribution of anthropogenic atmospheric deposition to metal anomalies in Finnish surface waters.

### 3.1.6 Potential effects of trace metals on lake biota

In order to assess the risk of metals to aquatic organisms one should have knowledge of the speciation of the metals to which the organisms are exposed to. In the present study only aluminium speciation was determined. Thus, the estimation of the potential risk of heavy metals is based on total concentrations. Another aspect is the seasonal fluctuation of the concentrations of heavy metals. In order to estimate the risk of the elements to aquatic biota, one should know the range/magnitude of the elevated concentrations and the duration of the event. There is very limited information on this fluctuation both in Finland (*e.g.* Ukonmaanaho *et al.* 1998) and elsewhere (Nelson and Campbell 1991). Since the focus in papers I–IV was on the regional occurrence of the metals, an estimate of the risks can be based, with caution, on the distribution of trace metals in spatially large data sets (Lydersen and Löfgren 2000). These distributions will then be compared to published critical limits for aquatic biota (Alm *et al.* 1999).

The concentrations of the trace metals in headwater lakes in 1995 are compared to the levels in the statistically selected set of 464 lakes in Finland (Fig. 6) included in the Nordic lake survey (Skjelkvåle *et al.* 1999, Skjelkvåle *et al.* 2001). In general, the concentrations are comparable and the levels of different elements between these two data sets do not differ substantially. There is a difference in two important aspects: one is the lower pH level in headwaters, and the other is the higher lake to catchment area ratio. Consequently, headwaters do receive atmospheric deposition more directly, both on the lake surface and via catchment. The median concentrations suggest that both Pb and Zn are elevated in headwaters in comparison to the general lake population. The Cd level is probably higher as well, but the complete distribution is not known due to relatively high detection limit (0.03

$\mu\text{g l}^{-1}$ ). This elevated median level could be explained both by the more direct influence of the headwaters by the atmospheric deposition, and the lower pH of these systems. The geochemical signal for Cd and Pb is low, as the sediment studies have shown, and the potential for acid induced mobility for Zn (and Cd) is high.

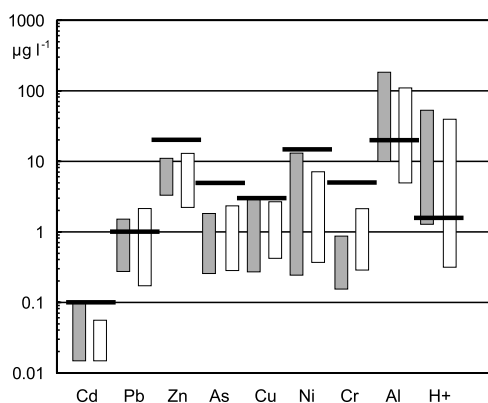
In contrast, Cu, Ni and Cr all have higher median concentrations in the general lake population. This indicates that the elements with more pronounced influence in the catchment geochemistry reach generally higher concentration levels in lakes not exclusively in the upland catchments.

In both of these data sets, very few observations, mostly for Cd and Pb, reached the lowest effect level (LOEL) or critical limit established for Swedish surface/natural waters (Alm *et al.* 1999) based on extensive scientific assessment (*e.g.* Lithner 1989). These observations represent ca. 2 % for Pb, and ca. 0.1 % for Cd in the lake population represented by the survey. Only one Cd and one Pb observation (out of 143) in headwater lakes reached the critical limit. No violations for other metals were detected in headwaters, and only 0.3 to 0.5 percent for Zn, Cu and Ni in the general lake population (Fig. 6).

The number of lakes exceeding the critical limit for these elements in Norway and Sweden is higher than in Finland (Skjelkvåle *et al.* 2001). Lead showed exceedances of 6 to 7 percent of the lakes in those countries. Correspondingly, Cd levels were exceeded in ca. 3.5 percent of lakes. The exceedances were concentrated in the southernmost area, especially in Norway, and in the southwestern area of Sweden. A strong intercorrelation existed between these elements, indicating an atmospheric source as an explanation for the distribution of these elements in lakes. Such a clear generalization cannot be drawn from the Finnish data. There are no regional elevated levels, except for Cd on the southern coast (Fig. 6 in paper IV). The Pb levels in Finnish lakes follow merely pH and the organic carbon content, as do Cu, Ni and especially Cr (paper III).

Two variables differ with respect to the critical limit: labile Al and pH (as hydrogen ion) are exceeding their critical limit in considerable number of lakes in both data sets (Fig. 6). Approximately half of the headwater lakes have a pH value considered harmful for sensitive fish species (section 3.2.1).

The autumn overturn, when these lakes were



**Fig 6.** Trace element and hydrogen ion concentrations in the RMLA network lakes ( $n=143$ , dark bars) and in the general lake population of the Finnish Lake Survey ( $n=463$ , white bars) in autumn 1995 in comparison to "lowest effect level" (LOEL, Alm *et al.* 1999) (median = lower end of bar, 99.5 percentile=upper end of bar, LOEL=vertical line)

sampled, is probably suitable of describing the annual average concentration level of the element. The most critical time of elevated metal concentrations is in spring, when accumulated contaminants are released from the snow cover during the melting period and entering lakes in runoff. There are, however, very little published data on the concentrations of heavy metals in different seasons in Scandinavian lake/surface waters. In Finland, seasonal fluctuation of the concentrations have been measured in four lakes in the network of the ICP IM (Ukonmaanaho *et al.* 1998). Three years' observations (ca. 20 samples per year in each lake and outlet stream) indicate, that the 95<sup>th</sup> percentile concentrations are regularly 3–5 times higher than the medians.

Another possible way of estimating the potential risk to biota is to look at the concentrations in snowpack (paper I): Pb, Cd and Cu concentrations in snow have been violating the critical limit for surface waters; would it be possible to transfer these into critical concentrations in water? Most likely not, if we consider the whole lake, since the theoretical residence times in these lakes are typically in the range of 0.5 to 2 years. Local effects on littoral fauna could be possible, but there is no way to estimate that kind of a risk on a regional scale.

Neither of these approaches can answer to questions of concentrations and exposure time in the littoral areas or in the uppermost layer under ice-cover. There are observations from lakes with short residence times, that melt water can form thick layers under the ice cover (Salonen *et al.* 1984, Arvola *et al.* 1990).

In any case, the risk of spring snowmelt metals causing damage to aquatic biota has diminished during the 1990s with the reduced deposition of trace metals (Kulmala *et al.* 1998). This does not apply directly to elements derived solely from the catchment, like aluminium, which is discussed in the next section 3.2.1. Nevertheless, if the acidity of the snowcover is reduced, the capability of meltwaters to transport aluminium ions to surface waters is reduced as well (Laudon *et al.* manuscript).

### 3.2 Acidification status and trends in headwater lakes in 1987–1998

#### 3.2.1 Effects of acidification on fish populations

Based on the statistical lake chemistry survey in 1987 (Forsius *et al.* 1990a) and the fish status survey (Rask and Tuunainen 1990, Tuunainen *et al.* 1991), the status of aquatic ecosystems with respect to acidification was reasonably well understood. The number and distribution of fish populations and the history and present degree of acidification could be estimated, and the responses of the species were derived from laboratory and field observations. This enabled an exercise to combine these sets and estimate the number of lost and affected fish populations in southern and central parts of the country (paper V).

The number of acidified lakes in Finland was first estimated by Forsius *et al.* (1990a). A method estimating the original pH and Al concentration was developed in connection to the derivation of critical loads (Forsius *et al.* 1992, Posch *et al.* 1993), and used in paper V. Due to the high concentration of organic carbon in Finnish lakes (median  $14 \text{ mg l}^{-1}$  in these lakes) many of the presently acidic lakes were acid already in pre-industrial times according to the model, as the paleolimnological studies also suggested (Huttunen *et al.* 1990). For example, the proportion of lakes with pH <5.5 were 26 percent in 1987, but

were already 19 percent in pre-industrial times, even when a low background sulphate concentration is assumed. Due to the organic acidity, many of the presently acidic lakes probably never had populations of the sensitive species, like roach. Therefore, only those lakes were considered 'affected' or 'extinct' where the pre-acidification pH and Al values did not violate critical values.

The fish status survey showed that a considerable number of small lakes suffered from damage to fish populations due to acidification. Out of the eighty lakes, twenty-one had affected fish populations, mostly roach and perch. Roach catches from 12 lakes with a pH level 5 to 6 consisted of a low amount of mainly larger roaches, suggesting acidification effects. Four of these populations were considered to be close to extinction. According to information from local fishers, at least five roach populations had already disappeared in recent years or decades from the more acidic lakes. Four perch populations were close to extinction and additional five affected. Details of this classification are described in paper V.

The occurrence of the key species, perch and roach, indicated that populations might be affected at pH levels <5.5 and <6.5, respectively, but unaffected populations are still found. This is because of other factors than acidity (*e.g.* aluminum, calcium and organic matter) affects biological responses. Labile aluminum appeared to be decisive for perch populations, since this species can tolerate practically the entire pH range found in Finnish lakes, if Al concentrations are small, like in some seepage lakes in esker formations. The observations on the importance of aluminum are in line with many other studies (*e.g.* Baker and Scofield 1982, Brown 1983, Henriksen *et al.* 1984, Vuorinen *et al.* 1990).

A comparison with values obtained from laboratory exposures of newly hatched perch and roach to waters with different pH and aluminum concentrations suggested that the level for effects varies from pH 4.8 and  $Al_{lab} >150 \mu\text{g l}^{-1}$  (perch extinct) to pH <5.8 and  $Al_{lab} >20 \mu\text{g l}^{-1}$  (roach affected). These values are in accordance with values reported from other Nordic countries (Hultberg 1988, Polèo *et al.* 1997, Lydersen and Löfgren 2000) for the same species. For the other species in the Finnish survey, critical levels of perch were used for pike and ruffe, and roach values for burbot.

An important point is that the critical limits are

derived from lakes where population changes had already taken place. The population responses caused by disturbances in reproduction must have developed earlier, most probably at a lower degree of acidification.

Another important feature is the size of the affected lakes. The surface area of the lakes with damaged roach populations is on the average much smaller than the area of the studied lakes in general. As much as 85 % of the lakes with extinct roach populations are smaller than 10 ha, and more than 30 % smaller than 4 ha (Fig. 6 in paper V). This has an important implication for any estimate of biological damage in small Finnish lakes. When reporting a number of lakes fulfilling certain criteria, one should define the 'frame population' in question (Landers *et al.* 1988, Forsius *et al.* 1990a). This caveat applies probably to other Nordic lakes as well, since the smallest area of studied lakes in the 1995 cooperative survey was set at 4 hectares.

Finally, the numbers of affected lakes were calculated from the frequencies of their occurrence in lakes, *e.g.* perch 94 % and roach 61 %. The total number of extinct populations of the five species in lakes above 1 ha ranged between 1000 and 2000, and additional 1200–2400 was affected. The number of affected populations is probably closer to the lower figure; the high figure is calculated assuming strong acidification based on low original  $SO_4$  and labile Al concentration.

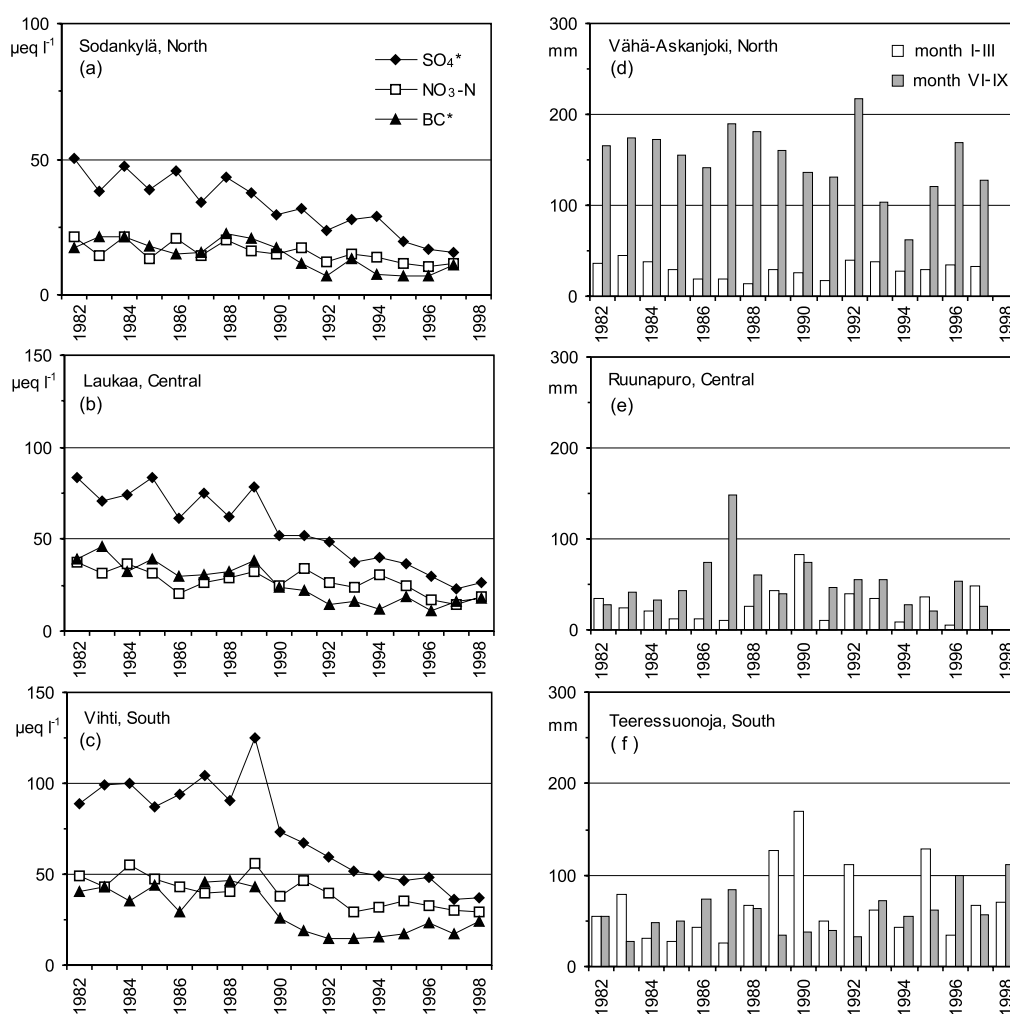
In comparison, a recent estimate of fish damages in Finnish lakes based on postal questionnaire targeted to lakes in 1995 Finnish Lake Survey ( $\geq 4$  ha), suggested 470 lost and 520 threatened populations of roach, and 410 threatened perch populations (Rask *et al.* 2000, Tammi *et al.* manuscript). The numbers are fairly comparable to those in paper V, considering the entirely different approaches used. The same Nordic assessment in Norway ends up with 5100 lost and 5800 reduced populations of brown trout, which is the most common and most affected species. In Sweden, 1200 populations of brown trout, 1100 roach and 1100 perch populations are estimated to be lost (Rask *et al.* 2000, Tammi *et al.* manuscript). Even if we take into account the lower total number of lakes in Finland, these figures suggest that the magnitude of the effects of acidification on fish populations is clearly lower in Finland than in Sweden and Norway.

### 3.2.2 First signs of chemical recovery and response of fish populations

The deposition of acidifying compounds has declined in Finland significantly, sulphate with 40–60 % in most parts of the country during the period 1987–1996, to the present level of  $0.5 \text{ g S m}^{-2} \text{ a}^{-1}$  in the southern part and  $0.1 \text{ g S m}^{-2} \text{ a}^{-1}$  in the northern part of the country. Nitrogen ( $\text{NO}_3 + \text{NH}_4$ ) deposition has declined less, and is presently at a similar level as S deposition; from  $0.6 \text{ g N m}^{-2} \text{ a}^{-1}$  in

southern to  $0.15 \text{ g N m}^{-2} \text{ a}^{-1}$  in northern Finland. The acidity of deposition, however, has not declined as strongly, largely due to declines in base cation deposition (Kulmala *et al.*, 1998). The temporal development of major ions in bulk precipitation in different parts of Finland is presented in Fig. 7 a–c.

The regional increase in alkalinity connected with sulphate decline in Finnish lakes was first observed in papers VI and VII. The monitoring period was too short to show clear statistical trends,



**Fig 7.** Sulphate, nitrate and base cations in precipitation (a–c) as annual mean volume-weighted concentration. Winter and summer runoff in small hydrological catchments (d–f). The sites (see fig.4) are chosen from monitoring networks of the Finnish Environment Institute to represent the general pattern of deposition and runoff in the three geographical areas starting five years before RMLA lake observations.

but a comparison of the years 1987 and 1993 revealed significant differences in sulphate, base cation (lower in 1993), pH and alkalinity (higher in 1993).

The test-fishing of twenty monitored lakes in 1988 showed very little changes in the populations of perch, and the decrease of roach populations continued (Rask and Tuunainen 1990). In 1992, the first positive changes in the status of perch were recorded in several lakes (paper VII); successful reproduction resulting in higher catches and more normal population structure, and decreased growth due to increased competition. At the same time, regional monitoring of lake acidification (paper VI, VII) indicated improved conditions in water quality.

At the turn of the decade (1990) there were only few lakes with seasonal water quality sampling. Considering the importance of conditions during spring runoff period for the reproduction of spring-spawning species, data of pH and labile Al concentrations would help to assess the critical conditions. On a regional scale, monitoring spring events in a coherent way for a set of lakes is difficult logistically, due to the limited access to the lake and the short melting period. It was, therefore, decided to avoid the logistic difficulties of spring-time sampling, and to concentrate the efforts on fish populations as a 'continuous' monitoring element. Thus, the conclusions about the improved chemical conditions for perch are based to some extent on indirect evidence. Based on autumnal sampling, an increase in the level of buffer capacity (in some cases pH) indicates improved overall conditions (paper VI, Nyberg *et al.* 1995), which should be reflected in spring time as well. Additionally, decrease in the load of acidic substances in the snow cover ameliorates the conditions in runoff waters during spring melt (Laudon *et al.* manuscript).

Other factors than a decreasing acid load may have affected the occurrence of suitable conditions for the reproduction of perch after 1988. During the late 1980s and early 1990s there were several warm years, which may have ameliorated the conditions for successful perch reproduction. Increased temperatures during the growing season are known to be beneficial to percid fishes in boreal waters, resulting in both strong year-classes and increased growth (Koli *et al.* 1985). In 1989 the autumn was dry, resulting in a low water table in the spring melting period in 1990. Permafrost was weak during that winter, allowing melting wa-

ters to percolate through soils, which could result in less acid input to the lakes in spring. Mild winters in 1989, 1990 and 1992 resulted in higher than normal runoff (Fig. 7 f), and consequently lower spring melt runoff (paper VII).

In paper VII it was concluded that the water quality improvements were not sufficient for a successful roach population reproduction. Later, based on continuing monitoring of the same lakes, the situation has improved for roach as well (Nyberg *et al.*, manuscript). During the 1990s successful reproduction has taken place in two study lakes, resulting in intraspecific competition and decrease of the mean weight of roach.

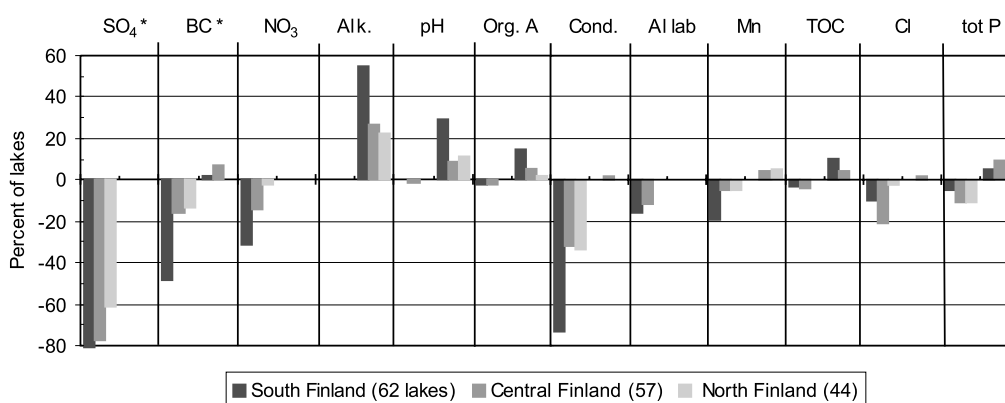
It is interesting, that the positive signs in fish populations were detected at the same time, or in some cases even earlier than the measured chemical changes. Thus, species like perch with good tolerance and adaptation ability, seem to react fast to improved conditions, if previous poor conditions have not led to its extinction. This observation underlines the necessity of monitoring environmental changes by integrating information from several different sources: physical, chemical and biological variables. This is possible and preferable also in cases, where the original setup is not designed in a truly integrated manner (SYKE 1998, NIVA 1996).

### 3.2.3 Recent changes in the chemistry of acid sensitive lakes

The environmental responses to emission reductions should be detectable over large regions. Ideally, one would like to know how the populations of lakes (or streams) that are exposed to reduced atmospheric deposition are changing through time; that is, we would like to have information on regional trends in the chemistry of lakes. Stoddard *et al.* (1998a) as well as Urquhart *et al.* (1998) define the regional trend as the central tendency in *change per unit time for the population of interest*, e.g. the median (or mean) change among all of the lakes in a region. Although the methods for detecting and combining regional trends may differ, this is in general the way regional trends were reported in papers VI and VIII for Finnish lakes.

The trends in the ionic composition of lake waters are strongest in southern Finland, which could be due to combined effect of the largest declines in S deposition and highest initial concentration lev-

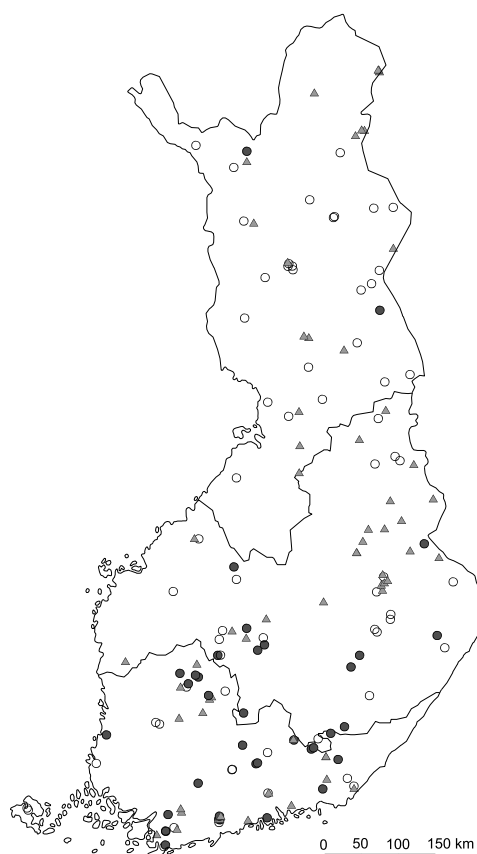




**Fig. 8.** Percent of RMLA lakes (n=163) in southern, central and northern Finland showing significant trends (Kendall-t,  $p < 0.05$ ) of key water quality variables in 1987–1998.

els of major ions. Up to 81 % of the lakes in South and Central Finland show a statistically significant decline in sulphate. The corresponding values in the northern group (61 %, 27 lakes) indicate a decrease in the long-range transported fraction of sulphur (Figs. 8 and 9). It is notable that no significant positive trends were detected for sulphate. The median slope of the trend for  $\text{SO}_4$  was  $-3.3 \mu\text{eq l}^{-1} \text{a}^{-1}$  in South,  $-1.9 \mu\text{eq l}^{-1} \text{a}^{-1}$  in Central and  $-1.1 \mu\text{eq l}^{-1} \text{a}^{-1}$  in North Finland (paper VIII). These trends are in line with the aggregated trends from seasonally monitored sites across Nordic Countries (Table 9, Stoddard *et al.* 1999).

The base cation (BC) concentrations are declining, especially in southern Finland, where every second lake shows a significant downward trend (Fig. 8, paper VIII). There are at least three possible reasons for this. First of all, reduced acidic input will decrease the BC concentration in runoff due to decreased release from soil exchange sites. Secondly, there are observations of a declining deposition of base cations (Hedin *et al.* 1994, Kulmala *et al.* 1998). The third possibility is cation depletion of the catchments (Likens *et al.* 1996, Lawrence *et al.* 1999). In all cases, the supply of BC to the lake is reduced due to the smaller amount of the mobile anion  $\text{SO}_4^{2-}$ . Both trend significance and slope analysis suggests, that the BC decline is smaller than that of sulphate, which is the most important prerequisite for any alkalinity increase. For the Finnish data set, this condition applies generally for all regions, although some outliers exist (Fig. 10a).



**Fig. 9.** Significant positive alkalinity trends (●), significant negative sulphate trends (▲) and no trend (○) in 163 RMLA lakes 1987–1998 (Kendall-t,  $p < 0.01$ ).

**Table 9.** Comparison of trend slopes ( $\mu\text{eq l}^{-1} \text{a}^{-1}$ ) in regional monitoring networks of surface water acidification.

Region	Time scale	n of sites	SO <sub>4</sub>	BC	Alk/ANC	Reference
South Finland	87–98	62	-3.3	-2.5	+1.7	paperVIII
Central Finland	87–98	57	-1.9	-0.7	+1.8	paperVIII
North Finland	87–98	44	-1.1	-0.7	+1.4	paperVIII
Sweden	83–97	137	-2	-2	+1	Wilander and Lundin 2000
South Norway	86–95	254	-2	-0.5	+2	Skjelkvåle <i>et al.</i> 1998
Nordic countries	90–95	33	-3.1	0	+2.1	Stoddard <i>et al.</i> 1999
UK	90–95	18	0	+2.4	+1.5	Stoddard <i>et al.</i> 1999
Nordic/UK	89–98	24	-2.1	-1.0	+2.4	Skjelkvåle <i>et al.</i> 2000
Germany	89–98	34	-2.9	-2.1	+1.1	Skjelkvåle <i>et al.</i> 2000
Adirondack, N.Y.	82–94	13	-1.8	-2.0	-0.5	Stoddard <i>et al.</i> 1998b
Vermont/Maine	82–94	23	-1.6	-0.7	+0.8	Stoddard <i>et al.</i> 1998b
Sudbury, Ontario	83–95	155	-5.2	-3.4	+0.3	Mallory <i>et al.</i> 1998
E. North America	89–98	22	-2.4	-2.5	+0.1	Skjelkvåle <i>et al.</i> 2000

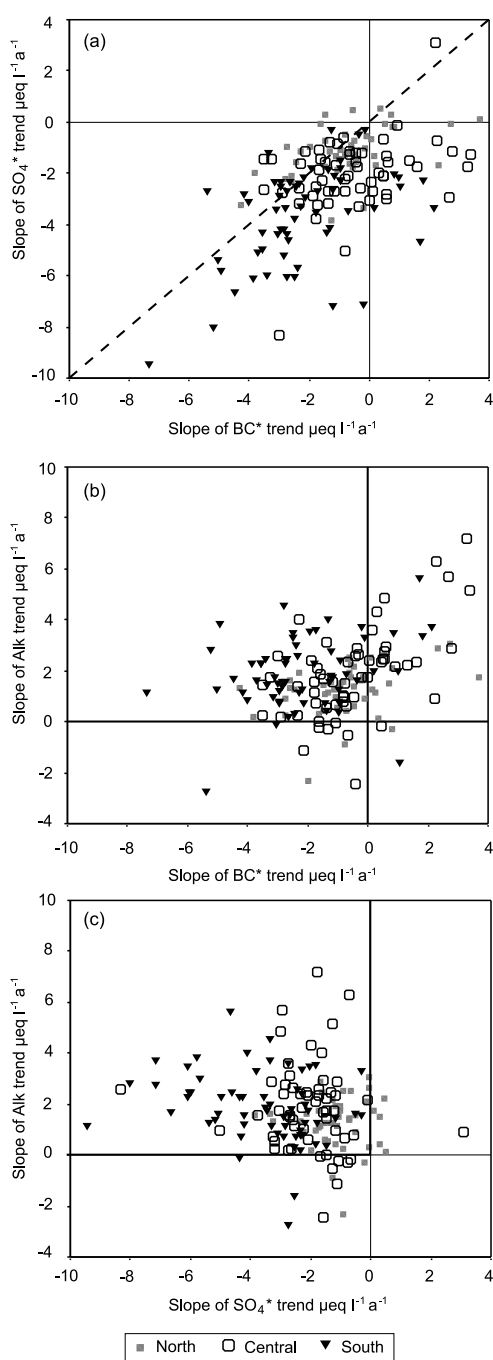
The downward trend for BC is strongest for lakes with a low peatland percentage, high exposed bedrock percentage and long retention time (Table III in paper VIII). These characteristics are strongly correlated, and typical for the upland lakes in southern Finland. In Central Finland a smaller SO<sub>4</sub> decline, but even smaller BC decline than in South Finland, results in a similar median alkalinity trend,  $+1.75 \mu\text{eq l}^{-1} \text{a}^{-1}$  (Fig. 10b). This outcome may have several reasons. In Central Finland there could be: 1) a better supply of BC from catchments with a) more organic soils, b) higher catchment to lake ratio, 2) inherently finer soil texture and better cation exchange capacity 3) smaller BC decline in deposition (Fig. 7b–c). A further quantification of the role of these factors requires more site-specific information on deposition as well as on the catchment properties and processes. There is one additional, climate-driven possibility (Schindler *et al.* 1996a), where base cations may be diluted more in southern Finland due to increasing summer runoffs (Fig. 7e–f). In Central Finland almost the opposite is observed, a slightly declining summer runoff throughout the 1990's (although the missing runoff for 1998 was high).

Generally, the observed trend in alkalinity is comparable to regional estimates in Nordic countries ( $1.3 \mu\text{eq l}^{-1} \text{a}^{-1}$  in 1990–95, Stoddard *et al.* 1999). The similarity in the slopes of SO<sub>4</sub>, BC and alkalinity in this data compared to seasonal sampling can be taken as indirect evidence that autumnal sampling is reasonably representative for long-

term monitoring of these ions. Autumn overturn has been proposed as the index time for yearly sampling for long-term monitoring purposes. It allows to reduce three terms of variance: 1) within the lake (circulation period) 2) year-to-year and 3) lake-to-lake (several weeks time window allows the lakes to be sampled in similar conditions).

It is noticeable that no statistically significant negative alkalinity trends were detected (Fig. 8). The strengthening of the buffer capacity is, however, in an early stage and not very clearly reflected in the pH-level (paper VIII). The general increase of lake water pH with ca. 0.2 units per decade in these autumn observations is probably not representative for the whole year. However, when the acidic deposition is lowered, it is expected that the acid surges caused by snow melt waters are less severe and may result in considerable improvements in springtime pH.

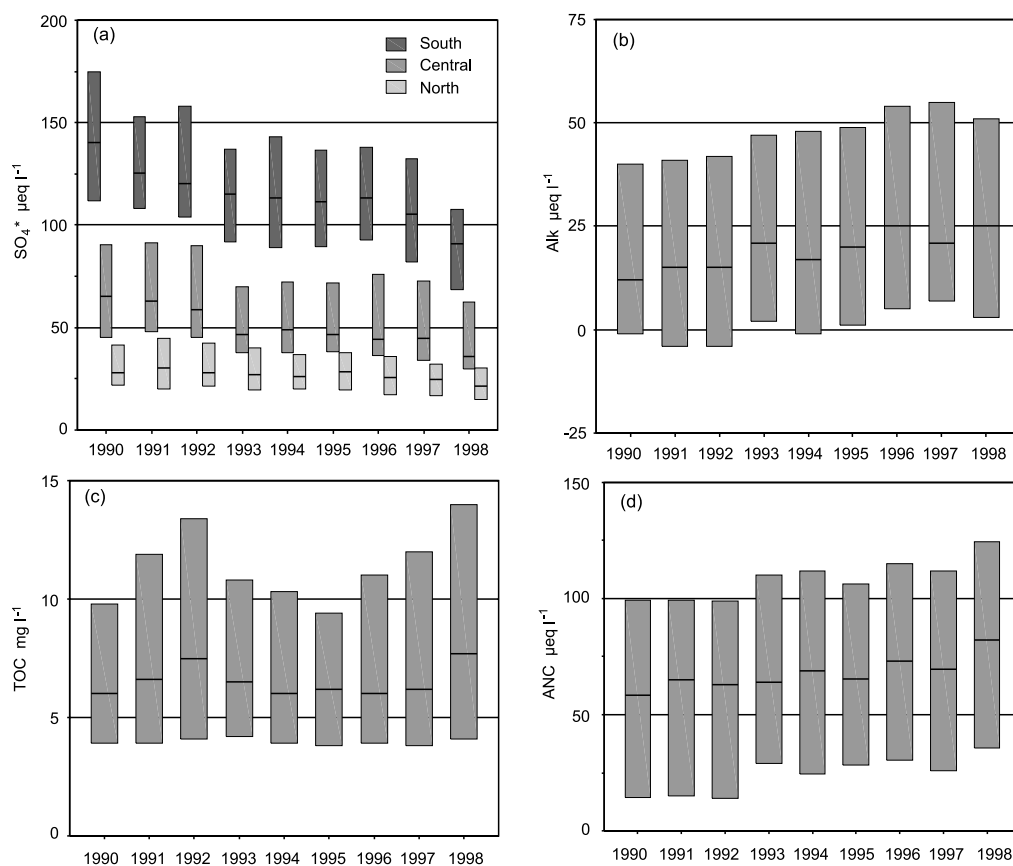
The nitrate concentrations in upland lakes in Finland are low in comparison to other monitored sites in Nordic countries or Central Europe (Traaen and Stoddard 1995). According to the North European Lake Survey, ca. 4 % of the lakes had autumnal NO<sub>3</sub> concentration above  $10 \mu\text{eq l}^{-1}$  in Finland, 8 % in Norway, nearly 30 % in Scotland and 50 % in Wales (Henriksen *et al.* 1998). In lowland areas, large part of the NO<sub>3</sub> is derived from agricultural activities and point sources. Three sites of the ICP Waters Programme in the southeastern corner of Finland are sampled seasonally, and they rarely exceed  $10 \mu\text{eq NO}_3\text{-N l}^{-1}$ ,



**Fig. 10.** Relationships between trend slopes (linear regression) of (a) sulphate and base cations, (b) alkalinity and base cations and (c) sulphate and alkalinity in RMLA lakes between 1987–1998.

even during spring snow melt. These lakes are all in the Stage 0 or 1 in Stoddard's nitrogen saturation classification (Stoddard 1994). At Stage 0, nitrogen concentrations are negligible due to strong ecosystem retention (biological uptake). At Stage 1, N supply exceeds demand during winter but catchments remain N-limited during summer, so that runoff concentrations vary seasonally, from near zero during summer to maxima in late winter and early spring. In Stage 2 saturation occurs when catchments cease to be N-limited at any time, causing summer minima to rise above detection limits. There are no seasonally monitored lakes in Finland showing this, but some small catchments have shown indications of N-saturation (Lepistö 1995). The trend analysis for  $\text{NO}_3$ , using slopes from autumn only, is too sensitive to outliers to be performed with the RMLA lakes. Several lakes in southern Finland show significant negative trend according to the Kendall-test, but these should be interpreted with caution (Fig. 8). The  $\text{NO}_3$  concentration is very much dependent on temperature, and therefore sensitive to annual and lake-to-lake variation. Based on the general deposition development in Europe, as well as on other trend analyses (Stoddard *et al.* 1999, Skjelkvåle *et al.* 2000), there are much fewer significant trends for  $\text{NO}_3$  to be expected than for  $\text{SO}_4$ , BC or alkalinity.

There is very little indication of significant long-term changes in organic carbon (TOC) concentration. Median trends in RMLA range from  $+0.03$  in South to  $-0.06 \text{ mg l}^{-1} \text{ a}^{-1}$  in Central Finland (paper VIII), with relatively few significant trends (10 % of lakes in southern Finland) (Fig. 8). The rate of change is below 1 % of the TOC concentration in most cases, and is not likely to be detected as statistically significant. Increasing trends have been detected in some recent trend analyses of similar regional data sets in Canada (*e.g.* Bouchard 1997) and especially in UK (Monteith and Evans 2000). International monitoring data show an increasing regional trend of TOC by  $+0.04 \text{ mg l}^{-1} \text{ a}^{-1}$  in Nordic countries between 1989–1998 (Skjelkvåle *et al.*, 2000). Organic carbon concentration in lakes is normally positively correlated with precipitation and increases during wet periods when the groundwater table is high and surficial runoff through organic horizon predominates. The regional-scale trend detection capability is very sensitive to the relative magnitude of the year-to-year coherent variation. This pattern is often caused by regional scale factors affecting



**Fig. 11.** Boxplots of middle quartiles (25–75 %, line= median ) of (a) sulphate, (b) alkalinity, (c) total organic carbon and (d) ANC in 113 RMLA lakes with no missing data (South= 52, Central= 35, North=26 lakes).

in a consistent way, such as climate (wet/dry years). This is reflected in TOC variation, and the 'error' introduced to trends is more random than fixed effect -type (Urquhart *et al.* 1998).

Neither positive nor negative trend implies a constant trend; either could display curvature, as long as the directional dominance continues. Nevertheless, when a trend exists, a linear trend exists (Urquhart *et al.* 1998). Not unexpectedly, the RMLA data show non-linearity for all major ions, including  $\text{SO}_4$ . The inter-annual or coherent variation (Magnuson *et al.* 1990) in RMLA lakes can be examined using box plots (Fig 11). In evaluating these annual data from groups of lakes it should be remembered the variation in retention time in lakes as well as various dynamic catchment processes.

However, there are features that could be linked to hypotheses on geochemical processes. The  $\text{SO}_4$  decline appears to be stepwise in all three regions, most clearly in southern Finland. After a steady decline in the beginning of 1990's, there is a plateau in mid 90's, and a second decline after 1996 (Fig 11a). Reasons for this could be deposition changes, hydrological conditions, possible sulphur stores in the catchment, or a combination of these factors. On a regional level, it is difficult to combine quantitatively observations from deposition and lake water networks, but both qualitative (Skjelkvåle *et al.* 1994) and illustrative approaches (*e.g.* Stoddard *et al.* 1998b) have been reported. There seems to be a small plateau in  $\text{SO}_4$  concentration in bulk deposition in 1994–96 in both the

southern and central stations (Fig. 7a–b). This could be an indication, that the  $\text{SO}_4$  level of these lakes is to a large extent driven by very recent depositional processes. Jeffries *et al.* (1995) have reported year-to-year reflection in lake  $\text{SO}_4$  concentration and deposition of  $\text{SO}_4$  in two lake regions in southeastern Canada.

It is difficult to see corresponding connection between summer runoff data preceding the observed autumnal  $\text{SO}_4$  concentrations, but some features may have strengthened the lag-period in lake  $\text{SO}_4$  trend in mid 1990s (Fig. 7d–e). In southern and central Finland there was a dry summer in 1994, which could have led to low groundwater table and re-oxidation of stored sulphur in the catchment, especially in organic layers (DeVito *et al.* 1999). In the following years 1995–98, increasing summer runoff could have mobilised  $\text{SO}_4$  from the catchments, as reported from Ontario (Jeffries *et al.* 1995, Dillon *et al.* 1997, Mallory *et al.* 1998) and Midwestern US (Webster and Brezonik 1995). On the other hand, there were dry summers from 1989 to 1992 in South Finland as well, and the lake  $\text{SO}_4$  level declined steadily, also in 1993 with a higher summer runoff. The lack of knowledge on the details of the differences in soil conditions, sulphur storage and extremity of dry periods between Mid North America and Finland hampers further comparison between these regions. However, the rate of decline in lake  $\text{SO}_4$  concentration ( $-2$  to  $-3 \mu\text{eq l}^{-1} \text{a}^{-1}$ ) is much slower than that in bulk precipitation ( $-4$  to  $-6 \mu\text{eq l}^{-1} \text{a}^{-1}$ ) (Fig. 7), indicating continuing  $\text{SO}_4$  transport from the catchment. Continued deposition of sulphur increases the pool of adsorbed  $\text{SO}_4$  in the soil. When deposition falls, the adsorbed  $\text{SO}_4$  begins to be leached, with the result that improvements in runoff chemistry are also delayed. Moreover, the quantity of organically bound sulphur pool in soils is much larger than the inorganic, adsorbed on minerals. Net changes of this organic sulphur pool are normally small, but even small changes could have major consequences for the sulphur budget (Warfvinge *et al.* 1999). The group of lakes in central-eastern Finland have the highest peatland percentage, but show also a significant downward  $\text{SO}_4$  trend (Fig. 9). The data from 1990s do not suggest that the re-oxidation of sulphur in peatland would be increasing, but this process could become more important, if summer temperatures and the frequency of dry periods would increase along climate change (Parrý 2000).

The variation in summer runoff is clearly reflected in the interannual TOC values (Fig. 11c). The exceptionally wet summer of 1992 in northern Finland dominates the TOC distribution of that year. After 1995, the TOC level has increased corresponding to increased runoff in 1996 and especially 1998 (Figs. 11c and 7). The interannual variation of  $\text{SO}_4$  and TOC reflects directly on alkalinity values (Fig. 11b). The suppressing effect of organic acidity is observed in 1992 and 1997–98, whereas the steady  $\text{SO}_4$ -level affects alkalinities in 1994–95. The development of ANC (Fig. 11d) is not affected by TOC changes, reflecting more directly  $\text{SO}_4$  changes. ANC has been proposed as an integrating single criterion in assessing biological damage of acidification (Henriksen *et al.* 1992, Bulger *et al.* 1993, Lien *et al.* 1996, Lydersen and Löfgren 2000). It has the potential to be a stable variable in regional trend detection of recovery as well. The hydrological signal affecting TOC and consequently alkalinity, is omitted in ANC. It is also based on the same analytical measurements in different countries, providing compatibility for regional assessment. The only drawback is the probability of error in combining at least seven different analytical measurement.

Site specific analyses of acidification/recovery trends for lakes and streams have been reported throughout 1990s for many regions (Clair *et al.* 1995, Driscoll *et al.* 1995, Jeffries *et al.* 1995, Couture 1995, Evans and Jenkins 2000). The obvious reason for the increased reporting is that most of the monitoring sites and networks have been established during the 1980s, and the ability to detect any significant changes needs five years of observations at a minimum (Urquhart *et al.* 1998). Additionally, many areas did not experience major changes in deposition before the emission reductions in the late 1980s.

Several studies of trends on a regional level in lake rich, acid sensitive regions in Scandinavia and North America have been published recently (Wilander 1997, Bouchard 1997, McNicol *et al.* 1998, Mallory *et al.* 1998, Stoddard *et al.* 1998a,b, 1999, Skjelkvåle *et al.* 1998, Wilander and Lundin 2000) (Table 9). Practically all regions show recent  $\text{SO}_4$  declines and most regions BC declines, whereas alkalinity increase is much more common in Europe than in North America (Stoddard *et al.* 1999).

The areas showing heterogeneous trends and less than expected recoveries (Stoddard *et al.*

1998a,b, Mallory *et al.* 1998) are mostly regions that have experienced long-term elevated deposition of acidifying compounds (Adirondack, Sudbury) and probably impaired soil conditions, lowered BC pool and cation exchange capacity, so that the prerequisites for recovery process are not yet met. In this respect, Finnish headwater lakes show relatively coherent behaviour in major ion chemistry and good pre-conditions for recovery.

### 3.2.4 Regional estimates of lakes recovering from acidification in Finland

As presented in 3.2.3,  $\text{SO}_4$  concentrations have declined in all types of small lakes throughout Finland in the 1990s, indicating a clear response to the S emission reductions. Base cation concentrations are still declining in lake water and deposition, especially in southern Finland, but to a lesser extent than  $\text{SO}_4$  concentration (Kulmala *et al.* 1998). This allows an increase of the buffering capacity, which is significant in every third lake in this monitoring network. The data suggest, that the initial recovery from lake acidification in Finland is a regional phenomenon (paper VIII). The regional estimation of the recovery of fish populations is still premature, but for the water quality improvement an example can be given. The extrapolation of the trend results from a (subjective) judgement sample into regional level has at least two prerequisites (Stoddard *et al.* 1998a): 1) The sample should represent the (sub)population in question 2) The trend behaviour should be consistent within each subpopulation.

The extrapolation can be based on the knowledge of the overall rate of change in each subpopulation (from RMLA) and the size of similar subpopulation from the Finnish Lake Survey 1995 (SYKE databases, Mannio *et al.* 2000). This information may be combined to estimate the rate of change in Finnish headwater lakes as a whole.

The regional interpretation of trends has been

shown to be extremely difficult, if the prerequisite of the trend coherence is not met (Stoddard *et al.* 1998a). However, the relatively good consistency in the trends of the key variables  $\text{SO}_4$ , BC and alkalinity allow an attempt to regionalise the results in Finland. On the other hand, there is no statistical evidence, that the trend distribution in the whole lake population would be similar to that in the judgement sample, because the sample is not derived statistically from the original frame population. Therefore, only some rough numbers of lakes behaving in a coherent way may be estimated. The number of significant negative  $\text{SO}_4$  trends and the total lack of positive trends suggests, that the decline in small Finnish lakes is nearly universal for the time period 1987–1998.

The number of lakes recovering presently is estimated on the basis of the following criteria:

- 30 % of the judgement lakes are showing a significant increase in alkalinity (Kendall- $t$  trend test)
- 90 % have a positive alkalinity trend based on linear regression, but no specified rate of change (slope) is assumed from the linear regressions
- from the probability sample of the Finnish Lake Survey, subpopulation (essentially) similar to the judgement sample is defined based on the following key variables:
  - lake type: headwater or seepage
  - lake area: 4–100 ha
  - field percent: < 5 % of the catchment area
  - alkalinity:  $\leq 60 \mu\text{eq l}^{-1}$

There were 125 lakes out of 873 in the FLS data fulfilling these criteria. The comparison of key variables in the two populations is presented in Table 10. These groups are similar enough for making conservative extrapolations. The 125 lakes are distributed in the three RMLA regions as follows: 35 (40 % of the probability sample) in the South, 56 (20 %) in the Central and 34 (17 %) in the North. This is transformed into population esti-

**Table 10.** Median lake characteristics in RMLA network and a subset of 125 headwater and seepage lakes of the Finnish Lake Survey (FLS) in 1995 (selection criteria: lake area <100 ha, field percentage <5 %, alkalinity  $\leq 60 \mu\text{eq l}^{-1}$ ).

	TOC $\text{mg l}^{-1}$	pH	Alk. $\mu\text{eq l}^{-1}$	BC	$\text{SO}_4^*$	P-tot $\mu\text{g l}^{-1}$	Area ha	Catchment ha	Peat %
RMLA	7.1	5.8	18	137	63	10	10	108	14
FLS	7.8	5.9	30	144	50	13	9	120	17

mates by multiplying the total number of lakes in these strata (4–10 ha and 10–100 ha, Mannio *et al.* 2000) with the calculated percentages:

South	0.40 x 1 300
Central	0.20 x 12 200
North	0.17 x 12 500
Finland	5 100

Out of these 5100 lakes, 30 % are expected to show statistically significant trends based on the judgement sample. However, based on linear regression nearly 90 % have increasing alkalinity. Based on these assumptions and data, the total number of acid sensitive, small headwater lakes in forested areas presently recovering from acidification is estimated at 4500. This number would be higher, perhaps more than double, if we include even smaller lakes (1 to 4 hectares) in the estimate. In principal, these smaller lakes may behave, in spite of their dilute and acid character, relatively similar to these larger lakes.

#### 4 Conclusions

Headwater lakes are susceptible to inputs of pollutants and reflect the changes in the atmospheric load. The present work provides a national scale assessment of the trace metal contamination of small headwater lakes and the recent development of acidified lakes in Finland. This type of information on both these subjects is needed as a scientific basis for further actions in air pollution policy. We need empirical data in space and time to judge whether the emission reduction measures have been efficient. This is an important aspect in dealing with the effects of a widespread problem. Spatial knowledge of impacts is necessary to advance our scientific understanding, but perhaps more urgently, to address society's needs for sustainable and healthy aquatic ecosystems.

The historical development of trace metal pollution in Finnish headwater lake sediments is presented. The anthropogenic proportion of the total metal accumulation in sediments was estimated from 62 to 95 % for Cd, Hg and Pb. It is atmospheric deposition which is responsible for this development. Generally, As and Zn were also elevated due to air pollution. The atmospheric signal for other elements (Cu, Ni and Cr) was lower and highly variable, depending on local geochemistry. Based on one lake only, a decline of 20 to 40 % in

trace metal accumulation within the last decades was observed in the sediments for most atmospheric and toxic elements (Pb, Hg, Cd, As). This has two connected implications: 1) the decline in the atmospheric deposition is reflected relatively fast in the metal accumulation in sediments, and 2) the accumulated stores of atmospheric trace metals in the catchment soils are not dominating the supply of trace elements to lakes.

Lake waters reflected atmospheric trace metal pollution as well, but it was not as clearly quantifiable. There was a general northwards decreasing pattern for concentrations of several metals (Cd, Zn, Ni, As), but the atmospheric signal was difficult to separate from other factors, mainly acidification and natural catchment acidity. Acidity controls in particular the level of Cd and Zn, while organic matter, often derived from peatland, controls more the level of Cr, Fe, Cu and Ni in headwater lakes. Concentrations of Pb, Mn and Al are affected by both these factors. Outside polluted regions, catchment properties and soil geochemistry determine trace metal levels. Humic substances act as carriers for trace metals from catchment soils to surface waters, irrespectively of their original source.

Headwater lakes usually have higher concentrations of Pb, Cd, Zn and Al than other types of lakes. Highest Cd and Zn concentrations were found in acidic upland lakes near the southern coast of Finland. However, regions with consistently elevated concentrations of Pb, Cd and Zn, that would suggest a risk of biological damage, were not found. Based on comparable chemical data sets, the risks of biological effects in lakes due to trace metals are lower in Finland than in Sweden and Norway. Trace metal levels in lake waters are less critical for biota than acidity and inorganic (labile) aluminium levels. Due to acidification, there are 2200–4400 damaged fish populations in southern and central Finland. Most of these are roach populations in lakes smaller than ten hectares.

Sulphate concentrations have declined in all types of small lakes throughout Finland in the 1990s, indicating a clear response to the sulphur emission reductions. In southern and central Finland, sulphate concentrations have declined one third during the 1990s. There are presently no indications of elevated nitrate levels in forested headwater lakes. Base cation concentrations are still declining in lakes especially in southern Finland, but to a lesser extent than sulphate. This al-

lows the buffer capacity to increase, which is significant in a third of the monitored lakes. The median trend slopes of sulphate, base cations and alkalinity in Finland were comparable to those reported in Sweden and Norway. However, the factors behind different rates of change in individual lakes need further analysis. The similarity in the major ion trend slopes in this data compared to seasonal sampling can be taken as indirect evidence that autumnal sampling is reasonably representative for long-term monitoring of these ions.

The chemical recovery was relatively uniform throughout the country, except that the changes were not as significant statistically and by magnitude in the dilute lakes in northern Finland. Based on the coherence of the trends, nearly 5000 headwater lakes larger than four hectares were estimated to be recovering from acidification at present. The chemical conditions were found to be improving throughout Finland, and first perch population recoveries in southern Finland were observed. The successful reproduction started simultaneously with chemical improvement of the lake water and favourable hydrological and thermal conditions, suggesting an important role of climate in determining biological responses.

The monitoring and survey results presented here are an example of a three-dimensional approach, where spatial and temporal data from several sources are aggregated. This facilitates the estimation of regional changes and quantifies the changes on national scale. The combination of chemical and biological (fish) data is important for the further development of dose-response functions. The consistent monitoring provides also sound basis for further modelling of recovery processes and scenario assessment.

As abiotic factors improve, the ecosystems will move towards recovery, but significant lags in biotic responses may be involved or irreversible changes have occurred. At present, there is some information to estimate the implication of this development on fish populations. The observations on re-colonisation of perch and recently on roach as well, give a promising indication of the biological recovery process. However, we know very little about the present status and changes of other biological communities in small Finnish lakes. In the sense of biodiversity, we don't know if our small lakes are healthy or not. The biological status in a defined, representative set of lakes from the HAPRO-project should be re-surveyed. The

fish monitoring has served as a 'continuous' monitoring element in the regional headwater lake network. The next logical task in acidification dose/response assessment is to assess biological data from different regions (several countries) to, *e.g.*, verify the critical limits used.

The chemical recovery of acidified surface waters has been relatively rapid during the last ten years in Nordic countries. In forthcoming analyses, factors behind different responses in different lake types may be better understood by combining and grouping already existing data. Both site-specific and regional analyses are needed to reveal the effects of short-term hydrological variation as well as soil and vegetation characteristics influencing, *e.g.*, sulphate retention, nitrogen saturation and mercury transformations. It seems evident that in the future the role of nitrogen will be more in focus than that of sulphur, and mercury more than other trace elements. This will increase data requirements, due to the more complex processes involved.

Another new challenge is the interaction of acidification/recovery processes and trace metals with possible trends in temperature and hydrology due to global climate change. Climatic variation modifies hydrologic patterns, formation, decomposition and transport of organic matter, and may have unpredictable effects on both trace metal distribution and speciation as well as acidification status of the aquatic environment. This should be taken into account when assessing long-term surface water quality and developing future monitoring networks.

## Yhteenveto

Ilman kautta ympäristöön leviävien happamoittavien päästöjen määrää on onnistuttu vähentämään 1980-luvun puolivälin jälkeen tehokkailla rajoitustoimilla sekä Keski-Euroopassa että erityisesti Pohjoismaissa. Tämä kehitys näkyy selvästi esimerkiksi rikkiyhdisteiden laskeuman vähenemisenä. Muuttuvan laskeuman vaikutusta metsämaihin ja järviin on Suomessa mallinnettu ns. kriittisten kuormitusten avulla, jotka ennustavat lähinnä pitkän aikavälin riskejä. Mitattua tietoa ekosysteemin mahdollisesta toipumisesta tai edes kemiallisesta palautumisesta on sitä vastoin julkaistu vähän. Rikki- ja hiukkaspäästöjen ohella on myös vähenetty haitallisten raskasmetallien päästöjä. Näiden



ilmaperäisten raskasmetallien esiintymisestä ja mahdollisista vaikutuksista Suomessa on ollut vähän tietoa. Kalliita investointeja on tehty päästöjen vähentämiseksi, mutta toimenpiteiden mahdollisista suhteellisen nopeista vaikutuksista on vain vähän tietoa jatkotoimenpiteiden ohjaamiseksi.

Vesistöalueiden ylimpänä sijaitsevat latvajärvet ovat herkkiä ilmansaasteiden vaikutuksille ja heijastavat ilmaperäisen kuormituksen muutoksia. Tässä työssä esitetään arvio Suomen pienten latvajärvien happamoitumisen viimeaikaisesta kehittymisestä ja raskasmetallien esiintymisestä näissä järvissä perustaksi ilmansuojelupolitiikan päätöksenteossa. Päästövähennysten riittävyyden arvioimiseksi tarvitaan mittauksiin perustuvaa tietoa, jonka tulee olla sekä ajallisesti että maantieteellisesti kattavaa.

Aineistona tutkimuksessa oli järvien happamoitumisen kansallinen seurantaverkosto, jossa tarkasteltiin veden kemiallisia muutoksia 1987–1998 (163 järveä), kalaston muutoksia (10 järveä), metallien kertymistä pohjakerrostumiin (16 järveä) ja raskasmetallien alueellista esiintymistä (152–259 järveä). Arvioiden laajentamiseksi Suomen järvien kokonaisjoukkoon käytettiin laskennassa lisäksi kahden valtakunnallisen vedenlaatu-kartoituksen (873 ja 987 järveä) ja kalastokartoituksen (80 järveä) tuloksia.

Työssä esitetään tyyppisimpien ilman kautta kulkeutuvien raskasmetallien (Hg, Cd, Pb, Zn, Cu, Ni, Cr) ja arseenin (As) kertymishistoria järvien pohjakerrostumuissa. Ihmisen toiminnan aiheuttama ilmaperäinen kuormitus vastaa 62–95 % elohopean, kadmiumin ja lyijyn kokonaiskertymästä. Myös valtaosa arseenin ja sinkin kertymisestä johtuu samasta syystä. Muiden metallien kertyminen vaihteli enemmän paikallisten geokemiallisten olosuhteiden mukaan. Ympäristön kannalta haitallisimpien aineiden (Hg, Pb, Cd ja As) kertyminen on vähentynyt kahden viime vuosikymmenen aikana 20–40 %. Arvio perustuu yksittäisen järven tuloksiin, mutta siitä voidaan päätellä, että ilmaperäisen kuormituksen väheneminen heijastuu metallien kertymiseen suhteellisen nopeasti. Tämä viittaa myös siihen, ettei maaperään jatkuvasti kertyneiden metallivarastojen aiheuttama kuormitus järveen peitä suoran ilmakehän kuormituksen muutosta.

Järvien veden laatu heijasti myös ilmaperäistä metallikuormaa, muttei yhtä selkeästi kuin pohjakerrostumat. Useiden metallien (Cd, Zn, Ni, As) pitoisuus oli korkein Etelä-Suomessa ja väheni pohjoisessa. Ilmaperäistä osuutta oli kuitenkin vai-

kea erottaa luontaisen happamuuden ja happamoitumisen vaikutuksista. Happamuus säätelee erityisesti kadmiumin ja sinkin pitoisuutta, kun taas lähinnä turvemailta peräisin oleva humus säätelee pääasiassa kromin, raudan kuparin ja nikkelin pitoisuutta. Lyijyn, mangaanin ja alumiinin pitoisuus riippuu molemmista edellämainituista tekijöistä. Tausta-alueilla järven valuma-alueen ominaisuudet ja geokemia säätelevät metallien pitoisuutta. Humus toimii metallien kuljettajana valuma-alueelta järveen, riippumatta metallin alkuperästä.

Latvajärvissä on korkeammat lyijy-, kadmium-, sinkki- ja alumiinipitoisuudet kuin pienjärvissä keskimäärin. Korkeimmat kadmium- ja sinkkipitoisuudet esiintyvät Etelä-Suomen karuilla, happamalla ylänköalueilla. Kuitenkaan sellaisia alueita ei löytynyt, joilla esiintyisi yleisesti eliöille haitallisen rajan ylittäviä lyijy-, kadmium- tai sinkkipitoisuuksia. Vertailukelpoisten järviaineistojen perusteella raskasmetallien muodostama riski vesieliöille on Suomessa pienempi kuin Ruotsissa ja Norjassa. Raskasmetalleja ja arsenia suurempi riski vesieliöstölle on happamuus ja sen aiheuttama kohonnut alumiinin pitoisuus. Happamoituminen on vaurioittanut Etelä- ja Keski-Suomessa 2200–4400 kalakantaa. Useimmat näistä ovat särkikantoja pienissä, alle 10 hehtaarin järvissä.

Järvien sulfaattipitoisuus on vähentynyt kairakentyyppisissä pienjärvissä 1990-luvulla, mikä osoittaa rikin päästövähennysten vaikuttaneen nopeasti. Etelä- ja Keski-Suomessa sulfaattipitoisuus on vähentynyt kolmanneksella 1990-luvun aikana. Tällä hetkellä ei ole merkkejä kohooneista ilmaperäisistä nitraattipitoisuuksista latvajärvillä. Emäskationien (Ca, Mg, K, Na) pitoisuus on myös alentunut, mutta vähemmän kuin sulfaatin. Tämä on edellytyksenä puskurikyvyn eli alkaliniteetin kasvulle, joka on tilastollisesti merkitsevää kolmasosalla tutkitusta järvistä. Sulfaatin, emäskationien ja alkaliniteetin keskimääräinen muutos latvajärvissä on ollut 1990-luvulla Suomessa samaa tasoa kuin Ruotsissa ja Norjassa. Kuitenkin yksittäisten järvien muutosten taustalla olevat syyt vaativat lisäselvitystä. Järvien kemialliset olosuhteet parantavat koko maan alueella, joskin muutos oli pienempi Pohjois-Suomen järvissä. Muutosten yhdenmukaisuuden perusteella voidaan arvioida, että tällä hetkellä lähes 5000 järveä Suomessa on toipumassa happamoitumisesta.

Tässä tutkimuksessa havaittiin ensimmäiset merkit ahvenkantojen elpymisestä Etelä-Suomessa

jo 1990-luvun alkupuolella. Ahventen lisääntyminen havaittiin yhtäaikaaisesti järvien kemiallisen toipumisen kanssa, mutta jaksolle osui myös suotuisia leutoja talvia ja lämpimiä kesä. Tämä viittaa myös ilmasto-olojen merkitykseen biologisia vasteita tarkasteltaessa. Tällä hetkellä tiedetään erittäin vähän muiden eliöryhmien kuin kalojen nykytilasta happamoituneissa järvissä. Jotta saisimme käsityksen vesiekosysteemien toipumisprosesseista, tulisi eri eliöryhmiä tutkia uudelleen aiemmin tutkituissa, happamoituneissa järvissä. Tällä edistettäisiin myös pienjävien biodiversiteetin tuntemusta.

Työssä esitetty seuranta- ja kartoitusaineistojen yhdistäminen mahdollistaa muutosten arvioinnin alueellisesti ja järvien lukumäärinä. Kemiallisen ja biologisen tiedon avulla voidaan kehittää edelleen annos-vaste -funktioita. Jatkuva seuranta toimii myös lähtötietona ja verifiointiaineistona toipumisprosessin ennustemalleissa.

Ilmansaasteiden vaikutusten jatkotutkimuksissa tarvitaan sekä valuma-aluekohtaista että alueellista analyysiä, jotta voidaan selvittää hydrologian, maaperän ja kasvillisuuden vaikutusta esimerkiksi sulfaatin pidättymiseen ja typen kyllästymiseen maaperässä sekä elohopean olomuotojen muutoksiin ympäristön eri osissa. Tämä tulee aiheuttamaan kerättävälle tiedolle lisävaatimuksia, sillä nämä prosessit ja niiden aiheuttamat vasteet ovat monimutkaisia.

Uusi haaste tulee olemaan ilmastonmuutoksen aiheuttama vaihtelu lämpötiloissa ja hydrologiassa ja näiden vuorovaikutus happamoitumis/toipumisprosessiin ja metallien kiertoon ekosysteemissä. Ilmastonmuutos vaikuttaa hydrologisiin prosesseihin sekä orgaanisen aineen muodostumiseen, hajoamiseen ja kulkeutumiseen. Tällä voi olla ennalta arvaamattomia vaikutuksia sekä raskasmetallien kulkeutumiseen että esiintymismuotoon mutta myös vesistöjen toipumiseen happamoitumisesta. Tämä tulee ottaa huomioon arvioitaessa pintavesien tilan pitkän ajan muutoksia ja kehitettäessä tulvavastuksen seurantaverkostoja.

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Jaakko Mannio

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