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## Yhteenveto: Pienentyneen laskeuman aiheuttamat toipumisprosessit Suomen happamoituneissa järvissä

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# Contents

# 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 In addition, some previously unpublished results and figures are included in this study.

**Paper I**
Vuorenmaa, J. 2004. Long-term changes of acidifying deposition in Finland (1973-2000).
*Environmental Pollution* 128: 351-362.

**Paper II**
Forsius, M., Vuorenmaa, J., Mannio, J. and Syri, S. 2003. Recovery from acidification of Finnish lakes: regional patterns and relation to emission reduction policy. *The Science of The Total Environment* 310: 121-132.

**Paper III**
Tammi, J., Rask, M., Vuorenmaa, J., Lappalainen, A. and Vesala, S. 2004. Population responses of perch (Perca fluviatilis) and roach (Rutilus rutilus) to recovery from acidification in small Finnish lakes. *Hydrobiologia* 528: 107-122.

**Paper IV**
Vuorenmaa, J**.**, Forsius, M. and Mannio, J. 2006. Increasing trends of total organic carbon concentrations in small forest lakes in Finland from 1987 to 2003. *Science of The Total Environment* 365: 47-65.

**Paper V**
Vuorenmaa, J. and Forsius, M. 2007. Recovery of acidified Finnish lakes: trends, patterns and dependence of catchment characteristics. *Hydrology and Earth System Sciences* (in press).

**Author's contribution to the publications:**

I J. Vuorenmaa is fully responsible for this paper.

II J. Vuorenmaa was responsible for the processing and analysis of lake water and bulk deposition data. Vuorenmaa was responsible for interpretation of bulk deposition results, and jointly with M. Forsius and J. Mannio, interpretations of relationships between deposition and lake chemistry.

III J. Vuorenmaa was responsible for the water quality data and interpretation of those results.

IV The paper was initiated and planned jointly by J. Vuorenmaa and M. Forsius. Vuorenmaa made the data processing and analysis and wrote the first version of the manuscript, which was commented by M. Forsius and J. Mannio. Vuorenmaa then finalized the paper.

V J. Vuorenmaa planned the study, made the data processing and analysis and wrote the paper, which was commented by M. Forsius.

## List of abbreviations

| | |
|---|---|
| $A^-$ | Organic anion |
| AAS | Atomic absorption spectrophotometry |
| $Al_{lab}$ | Labile aluminium |
| ANC, $ANC_{CB}$ | Charge-balance Acid Neutralizing Capacity $[BC] – [SO_4^{2-} + Cl^- + NO_3^-]$ |
| $ANC_{OAA}$ | Organic acid adjusted ANC |
| AP | Acidifying potential $[SO_4^{2-}] – [Ca^{2+} + Mg^{2+}]$ |
| BC | Base cations $[Ca^{2+} + Mg^{2+} + Na^+ + K^+]$ |
| xBC | Non-marine base cations |
| CAFE | Clean Air for Europe |
| CLe | Current Legislation scenario (emissions) |
| CLTRAP | Convention on Long-Range Transboundary Air Pollution |
| $COD_{Mn}$ | Chemical oxygen demand |
| DI-pH | Diatom-inferred pH |
| DOC | Dissolved organic carbon |
| EMEP | Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe |
| FGFRI | Finnish Game and Fisheries Research Institute |
| FLS | Finnish Lake Survey |
| HAPRO | Finnish Acidification Research Programme |
| IC | Ion chromatography |
| ICP | International Cooperative Programme |
| ICP Waters | Programme on Assessment and Monitoring of Acidification of Rivers and Lakes |
| ICP Integrated Monitoring (IM) | Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems |
| MAGIC | Model of Acidification of Groundwater in Catchments |
| MFR | Maximum Feasible Reductions (emissions) |
| N | Nitrogen |
| NEC | National Emission Ceilings (EU) (emissions) |
| $NH_3$ | Ammonia (emissions) |
| NIVA | Norwegian Institute of Water Research |
| $NO_x$ | Nitrogen oxides (emissions) |
| REPRO | Recovery processes in acidified Finnish headwater lakes |
| RMLA | Regional Monitoring of Lake Acidification |
| S | Sulphur |
| SAFE | Soil Acidification in Forest Ecosystems (model) |
| SMART | Simulation Model of Acidification's Regional Trends |
| $SO_2$ | Sulphur dioxide (emissions) |
| $xSO_4$ | Non-marine sulphate |
| TOC | Total organic carbon |
| UNECE | United Nations Economic Commision of Europe |
| SYKE | Finnish Environment Institute |

# Recovery responses of acidified Finnish lakes under declining acid deposition

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The present work provides a regional-scale assessment of the changes in acidifying deposition in Finland over the past 30 years and the current pattern in the recovery of acid-sensitive lakes from acidification in relation to changes in sulphate deposition. This information is needed for documenting the ecosystem benefits of costly emission reduction policies and further actions in air pollution policy. The development of sulphate deposition in Finland reflects that of European $SO_2$ emissions. Before the 1990s, reductions in sulphur emissions in Europe had been relatively small and sulphate deposition showed no consistent trends. Due to emission reduction measures that were then taken, sulphate deposition started to clearly decline from the late 1980s. The bulk deposition of sulphate has declined 40-60% in most parts of the country during 1990-2003. The decline in sulphate deposition exceeded the decline of base cation deposition, which resulted in a decrease in acidity and acidifying potential of deposition over the 1990s. Nitrogen deposition also decreased since the late 1980s, but less than that of sulphate, and levelling off during the 1990s. Sulphate concentrations in all types of lakes throughout Finland have declined from the early 1990s. The relative decrease in lake sulphate concentrations (average 40-50%) during 1990-2003 was rather similar to the decline in sulphate deposition, indicating a direct response to the reduction in deposition. There are presently no indications of elevated nitrate concentrations in forested headwater lakes. Base cation concentrations are still declining in many lakes, especially in south Finland, but to a lesser extent than sulphate allowing buffering capacity (alkalinity) to increase. The recovery has been strongest in lakes in which sulphate has been the major acidifying agent, and recovery has been the strongest and most consistent in lakes in south Finland. The recovery of lakes in central Finland and north Finland is not as widespread and strong as observed in south. Many catchments, particularly in central Finland, have a high proportion of peatlands and therefore high TOC concentrations, and runoff-induced surges of organic acids have been an important confounding factor suppressing the recovery of pH and alkalinity in these lakes. Chemical recovery is progressing even in the most acidified lakes, but the buffering capacity of many lakes is still low and still sensitive to acidic input. Chemical recovery is resulting in biological recovery with populations of acid-sensitive fish species increasing. Increasing TOC concentrations are indicated in small forest lakes in Finland, which appear to be related to decreasing sulphate deposition and improved acid-base status of the soil. A new challenge is climate change with potential trends in temperature, precipitation and runoff, which are expected to affect future chemical and biological recovery from acidification. The potential impact of mobilization and leaching of organic acids may become particularly important in Finnish conditions. Long-term environmental monitoring has evidently shown the success of international emission abatement strategies. The importance and value of integrated monitoring approach including physical, chemical and biological variables is clearly indicated, and continuous environmental monitoring is needed as a scientific basis for further actions in air pollution policy. The effect of climate change will increase data requirements, and should be taken into account when assessing long-term surface water quality and developing future monitoring networks, due to more complex processes involved.

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Keywords: acid deposition, lakes, acidification, monitoring, trends, chemical recovery, biological recovery, TOC, organic acidity, climate change

# 1 Introduction

## 1.1 Anthropogenic sulphur and nitrogen emissions to the atmosphere and resulting acidification of environment

The substantial growth of industrialization and energy production in Europe and North America since the 1950s has caused extensive emissions of air pollutants into the atmosphere. The growing energy need has been satisfied predominantly by burning of fossil fuels, resulting in high emissions of oxidized combustion products sulphur dioxide ($SO_2$) and nitrogen oxides ($NO_x$). Along with increased industrialization, different industrial processes have largely contributed to increased $SO_2$ and $NO_x$ emissions. Agriculture has also intensified during the 20th century, and the introduction of artificial fertilizers and increased animal husbandry have caused emissions of large quantities of ammonia ($NH_3$). Acidifying sulphur and nitrogen compounds can be transported with air masses over long distances from their emission sources before deposition to the earth's surface. This long-range transboundary air pollution has caused widespread acidification of soils and waters in acid-sensitive ecosystems. International alarm about the acid rain problem, with its ecological harmful impacts, began to be raised in the late 1960s, when Swedish scientists demonstrated the relationship between sulphur emissions in continental Europe and sulphate deposition in Scandinavia and acidification of lakes (Odén 1968). Since the 1970s, acidified lakes and streams and associated damage and loss of acid-sensitive biota has been recognized as a major environmental problem in industrialized regions of the northern hemisphere. The regional-scale acidification of sensitive ecosystems in Europe and North America has been documented in a vast number of publications and has been extensively reviewed and evaluated (e.g. Schindler 1988, Cowling 1989, Rodhe *et al*. 1995). Regional lake acidification has been recognized in parts of Norway (Wright and Henriksen 1978, Henriksen *et al*. 1988, Henriksen et al. 1989), Sweden (Bernes 1986, Forsberg and Morlin 1988), Finland (Forsius *et al*. 1990a,b, Rask *et al*. 1995a), the UK (Battarbee *et al*. 1988a, Evans and Monteith 2001), 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). Over the next decades, acidification of the environment will probably develop in Asia, Africa, and Latin America where rapid industrialization is taking place. Rates of $SO_2$ and $NO_x$ emissions in these regions are increasing, and are likely to cause large-scale damage to acid-sensitive aquatic and terrestrial ecosystems they did in the northern hemisphere (e.g. Galloway 1989, 1995, Rodhe *et al*. 1995, Posch *et al*. 1996, Kuylenstierna *et al.* 2001).

## 1.2 Awareness of lake acidification in Finland

Palaeolimnological evaluations of diatom assemblages and dating of sediment cores in the 1980s showed that many acidic lakes in south Finland have been acidified recently (Huttunen *et al*. 1990). The recent acidification trend had started from about 1900, and accelerated in many lakes from the early 1960s, with abrupt decreases in pH and alkalinity (Tolonen and Jaakkola 1983, Simola *et al*. 1985, Huttunen *et al.* 1990). Modelling studies of acidification history in Finnish surface waters showed a similar development (Kämäri *et al*. 1990). The first studies related to increased sulphur deposition in Finland were conducted in the early 1970s. Haapala (1972) noticed that sulphur deposition had more than doubled in south Finland compared with observations in 1955-1958 (Buch 1960). The first acidification impacts in Finnish lakes were also reported in the 1970s (Kenttämies 1973, Kenttämies 1979), and a quantitative assessment of lake acidification in the early 1980s found that many lakes, particularly in south Finland, had lost a significant amount of their buffering capacity compared to pre-acidification levels (Kämäri 1985). Changes in fish population dynamics also indicated that severe acidification in south Finland had taken place in the 1970s (Nyberg *et al*. 1995).

The first statistically based survey of lake acidification in Finland took place in 1987 in connection with the Finnish Acidification Research Programme (HAPRO) when 987 lakes (lake area ≥0.01 km$^2$) were randomly selected (Forsius *et al.*

1990a,b). Based on this survey, Forsius *et al*. (1990b) estimated the number of acidic (Gran alkalinity ≤ 0 µeq $l^{-1}$) lakes in Finland to be 4900. A survey of lakes throughout northern Europe consisting of 5700 lakes ≥ 0.04 $km^2$ from six countries (873 lakes from Finland) was conducted in 1995 (Henriksen *et al*. 1998). Based on this survey the number of acidic (Gran alkalinity ≤ 0 µeq $l^{-1}$) lakes ≥ 0.04 $km^2$ in Finland was estimated to be 1000 (Mannio *et al*. 2000). The number of very acid-sensitive lakes (alkalinity < 20 µeq $l^{-1}$, Henriksen et al. 1988, Henriksen *et al*. 1998) was estimated to be 2700 (9% of Finnish lakes ≥ 0.04 $km^2$) (Henriksen *et al*. 1998). This proportion was lower compared to that in Sweden (13.5%) and Norway (39%). Mannio (2001a) estimated the number of Finnish lakes 0.04 to 1 $km^2$ in area susceptible to acidification to be around 5100.

The 1987 lake survey demonstrated that acidic or poorly buffered lakes were to be found throughout the country, but most commonly in south, western-central and eastern Finland (Kämäri *et al*. 1991). An extensive inventory (n=914) of small lakes during 1987-1991 demonstrated that a considerable number of acidified lakes were also to be found in north Finland. The proportions of acidic lakes (Gran alkalinity < 0 µeq $l^{-1}$) and lakes with poor buffering capacity (Gran alkalinity 0-50 µeq $l^{-1}$) in north Finland were 6 % and 19%, respectively (Kähkönen 1996). The acidity of a large number of Finnish lakes is dominated by natural organic acidity, particularly in peatland-rich regions of western and central Finland and in parts of eastern Finland and south Lapland (Kortelainen and Mannio 1990, Kähkönen 1996). Over 45% of lakes with a Gran alkalinity ≤ 0 µeq $l^{-1}$, were assumed to be naturally acidic due to high concentrations of humus matter (Forsius *et al*. 1990b). But in south Finland, where deposition of sulphur have been the largest and occurrence of peatlands is lower, minerogenic acidity commonly exceeds the catchment-derived organic acidity (Kortelainen and Mannio 1990). However, in humic lakes receiving acidic deposition, the influence of strong mineral acids is superimposed on organic acid contributions to acidity (Forsius 1989), and deposition has probably further decreased the pH in these lakes (Kämäri *et al*. 1991). Sulphate acidified clear-water lakes are found scattered throughout the country. Even in remote north Finland lakes acidified from long-range transported sulphur are found, and many fell lakes in north-eastern Lapland are affected by sulphur deposition from neighbouring Cu-Ni smelters in Kola Peninsula (Kähkönen 1996).

The effects of acidic deposition on the lake biota at different trophic levels were studied in a survey of 140 sensitive lakes located mainly in the southern and central part of the country (Eloranta 1990, Heitto 1990, Huttunen and Turkia 1990, Kippo-Edlund and Heitto 1990, Meriläinen and Hynynen 1990, Sarvala and Halsinaho 1990). Results indicated that acidification of waters had affected species composition and biodiversity of different biological communities. The damage to fish populations also has socio-economic consequences. A fish status survey in 1985-1987 reported declines and even extinction of sensitive fish species in small lakes due to anthropogenic acidification in south and central Finland (Rask and Tuunainen 1990). Rask *et al*. (1995a) estimated that the number of lakes in south and central Finland in which recent acidification has affected the growth or population structure of fish populations was estimated to be between 2200 and 4400. Out of these, the number of lakes in which fish populations have disappeared due to acid deposition was approximately 1000-2000. Almost 60% of the affected or lost populations were roach (*Rutilus rutilus*), the most sensitive of the common species in small lakes in south and central Finland, and less than 15% was European perch (*Perca fluviatilis*), the most common species. The fish status survey of Finnish lakes in connection with the Northern Europe Lake Survey in 1995 suggested that the number of lakes in which roach had been lost was 470 and 520 had affected roach stocks, and 410 lakes had affected perch stocks (Tammi *et al*. 2003a). Both fish surveys suggested that perch was not extinct in any lakes, although there were records of lost perch stocks outside the coverage of the lake size range of these studies; that is, lakes smaller than 0.01 $km^2$ (Rask and Tuunainen 1990). In north Finland, the effects of acidification on benthic invertebrates were studied in 217 small lakes and their inlet/outlet streams in 1993-1994 (Yakovlev 1999). The results suggested that both anthropogenic and natural organic acidification had had effects on the structure of benthic assemblages. Impoverished benthic fauna was found in roughly 25% of the acid and/or humic lakes in central and northern Lapland,

and attributed to decreased pH and the toxic effects of elevated aluminium (Yakovlev 1999). In a fish status and water chemistry survey carried out at 103 sites in three areas in north-eastern Lapland in 1991-1993, Lappalainen *et al.* (1995) found evidence of acid-induced damage in local minnow (*Phoxinus phoxinus*) populations in acid-sensitive low alkalinity lakes ( $< 50$ μeq $l^{-1}$) in the Vätsäri area, which has been exposed to acidic deposition from industrial emissions on the Kola Penisula.

## 1.3 Trends in European emissions of sulphur, nitrogen and base cations

### 1.3.1 Sulphur and nitrogen compounds

Total European sulphur (S) emissions exhibited a sharp increase during the 1950s and 1960s, peaking at the end of the 1970s at approximately 60 million tonnes $SO_2$ per year (Mylona 1996, Schöpp *et al.* 2003). Total European emissions of oxidised nitrogen (N) species ($NO_x$) and reduced N species ($NH_x$) experienced a corresponding increase, peaking in the late 1980s at approximately 29 and 9 million tonnes per year of $NO_2$ and $NH_3$, respectively (Vestreng and Klein 2002, Schöpp *et al.* 2003). The associated detrimental effects of acidification and transboundary air pollution led to legal international agreements to reduce emissions of $SO_2$ and $NO_x$ in Europe and North America. International negotiations on emission reductions have been conducted under the Convention on Long-Range Transboundary Air Pollution (CLRTAP), signed in 1979 under the UN Economic Commission of Europe (UNECE 1996). The first outcome of these negotiations was the 1985 Helsinki Protocol on the Reduction of Sulphur Emissions or their Transboundary Fluxes, which entered into force in 1987 in 21 ECE countries. The protocol established a standard target of a 30% reduction in national S emissions by 1993 from 1980 levels, although many countries were then exceeding 1980 levels by more than 50%. A second sulphur protocol, the 1994 Oslo Protocol on Further Reduction of Sulphur Emissions, was entered into force in 1998. It differed from the Helsinki Protocol in that it was based on an effects-based approach, the critical load concept, and current deposition levels. The principle was to reduce the difference between actual deposition and critical loads by 60%. A protocol for control of $NO_x$ emissions was signed in 1988. The latest protocols on air pollutant emission abatement strategies were the multi-effect, multi-pollutant protocol signed in Gothenburg in 1999 (UNECE 1999) and the European Commission's national emission ceilings (NEC) directive in 1999 (European Commission 1999). The Gothenburg Protocol sets emission ceilings for 2010 for four pollutants: sulphur, $NO_x$, VOCs and ammonia, and is based on the critical load concept with different requirements for different countries. If implemented, as proposed by 2010, it seeks to minimize the number of ecosystems in which the critical load is exceeded. Once the Protocol is fully implemented, Europe's sulphur emissions should be cut by at least 63%, its NOx emissions by 41%, its VOC emissions by 40% and its ammonia emissions by 17% compared to 1990 levels.

Due to national and international efforts, the acidifying emissions in Europe have substantially decreased during the past 30 years. The emissions of sulphur, nitrogen oxides and ammonia throughout Europe are provided by the EMEP project (Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe) under the LRTAP Convention. Emissions of $SO_2$ started to slightly decrease during the 1980s and due to successful implementation of emission reduction agreements, the decrease accelerated during the 1990s (Fig. 1). The total European emission reduction of $SO_2$ between 1980 and 2000 was 67%, with that between 1990 (the base year for the Gothenburg protocol) and 2000 being 48% (Lövblad *et al.* 2004). Total European emissions of N compounds exhibited a gradual decrease during the 1990s. The officially reported reduction in European $NO_x$ and $NH_3$ emissions was approximately 20-25 % between 1990 and 2000. However, in reality, the decrease for $NO_x$ has been larger, around 30%, because some sources were missing from earlier EMEP estimates (Lövblad *et al.* 2004).

Finland and the other Scandinavian countries are considered to be recipient regions, i.e. S and $NO_x$ deposition in these countries are mainly of long-range transboundary origin, primarily from central and eastern Europe. EMEP/MSC-West transport

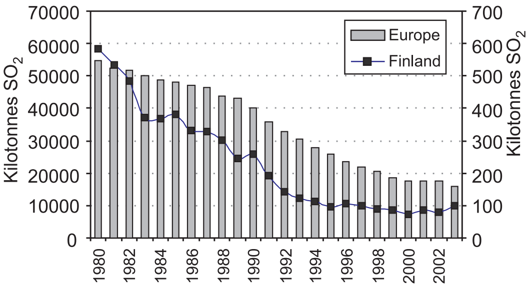

**Figure 1.** Anthropogenic sulphur emissions in Europe (left axis) and Finland (right axis) during 1980-2003 (Vestreng *et al.* 2004, 2006).

matrices have estimated the main source areas in Europe affecting acidifying deposition in Finland (e.g. Berge 1997). In 1995, approximately 11% of S deposition and 15% of $NO_x$ deposition originated from Finland's own emissions. Annual domestic emissions of S and $NO_x$ in 1985-1996 averaged 17% of S deposition and 16% of $NO_x$ deposition in Finland (EMEP/CCC and CIAM and MSC-W 2001). The contribution of Finnish emissions to total European $SO_2$ and $NO_x$ emissions in 1995 were 0.4 % and 1 %, respectively (Vestreng *et al.* 2004). The emission reductions of $SO_2$ from central and eastern Europe, which are the main source areas of deposition in Finland, have been more pronounced compared to total European $SO_2$ emission reductions, being 64 % in Russia and Baltic States, 64% in eastern-central Europe (incl. Poland, Czech Republic, Hungary, Slovakia) and 88 % in Germany (incl. former GDR) between 1990 and 2000. The reduction of Finnish $SO_2$ emissions was 87 % between 1980 and 2000 and 71 % between 1990 and 2000 (Vestreng *et al.* 2006). As for S, the emission reductions of $NO_x$ and $NH_3$ from the main source areas affecting deposition in Finland have also been more pronounced compared to total European N emission reductions, being 34% and 47% in Russia and Baltic States, 45% and 42% in eastern-central Europe (incl. Poland, Czech Republic, Hungary, Slovakia) and 36% and 15% in Germany, respectively, between 1990 and 2000. The corresponding reduction in Finnish $NO_x$ and $NH_3$ emissions were 21 % and 13 %, respectively (Vestreng *et al.* 2006).

### 1.3.2 Base cations

Base cation (BC) emissions to the atmosphere are an important component in the process of acidification and recovery. Base cations neutralize airborne acids and their deposition offsets the leaching of BC from soils that is caused by acid deposition. There is much less emission inventory data available for BCs and actual trends are not very well known (Lövblad *et al.* 2004). Of the base cations in atmospheric deposition, calcium (Ca) is by far most dominant in terms of mass, and reconciliation of the sources of Ca is the most important task in addressing base cations (Lee *et al.* 1999). An emission inventory of industrial sources of Ca emissions for Europe (base year 1990) indicated 750-800 thousand tonnes of Ca per year (Lee and Pacyna 1999). Base cations are emitted to the atmosphere from both semi-natural and anthropogenic sources (Gorham 1994). Semi-natural sources are associated with wind erosion of arid soils, marine aerosols (sea-salts), volcanic eruptions, natural forest fires and biological mobilization (pollen). Of the anthropogenic sources point-source emissions of fly ash arising from the combustion of fossil fuels in energy production and industry, and emissions from various industrial manufacturing processes are important. Non-fossil fuel (firewood) combustion and dust produced by traffic have been the most important anthropogenic sources in Finland (Anttila 1990).

There is good evidence that emissions of base cations have substantially decreased in Europe and North America during the past decades, along with the other point-source emitted substances. The observed decline in base cation concentrations in air and precipitation is attributed to a strong decline in particulate (fly ash) emissions from regional urban and industrial point sources (e.g. Hedin *et al.* 1994). In North America, there are examples that the decline in BC deposition may have partly offset the positive effect of the reduction in S and N emissions and deposition on acidification of lakes and soils in the 1990s (e.g. Stoddard *et al.* 1999).

## 1.4 Recovery from acidification

### 1.4.1 Decreasing trends in acid deposition

Due to the large decreases in emissions, acidifying sulphur and nitrogen deposition has declined over extensive areas in Europe and North America during the past decades. The emission reductions have been most successful for sulphur, and significant reductions in sulphate ($SO_4$) deposition started in

Europe and Nordic countries in the late 1980s (Barrett *et al*. 2000, Forsius *et al*. 2001, Kindbom *et al*. 2001, Moldan *et al*. 2001, Prechtel *et al*. 2001). In Finland, bulk deposition of $SO_4$ decreased throughout country by about 50-65% during the period 1981-1996 (Kulmala *et al*. 1998). The corresponding relative change for the period 1987-1996 was 40-60%, showing that the greatest decline in $SO_4$ deposition occurred during the 1990s. Parallel measurements for bulk deposition and throughfall have shown that $SO_4$ concentrations and deposition in throughfall have decreased more than those in bulk precipitation and deposition. Dry deposition of S (gaseous sulphur dioxide and particle-bound sulphate ions) is effectively intercepted by forest canopies, particularly coniferous trees, and washed off to the forest floor in subsequent rainfall. Throughfall measurements show that dry deposition of sulphate has decreased more than sulphate in wet deposition throughout Europe (Prechtel *et al*. 2001). In Finland, the decrease of $SO_4$ concentrations in throughfall has been clearly steeper than that in bulk precipitation, particularly in south Finland (Ukonmaanaho *et al*. 1998, Lindroos *et al*. 2006). Ruoho-Airola *et al*. (2004) have reported that concentrations of $SO_2$ in the air has decreased in Finland since 1981 by 85% to over 95% in most parts of the country. Sulphate concentrations in aerosols and precipitation (bulk) have declined somewhat less, but these components have declined rather evenly. The relative decrease of $SO_4$ concentrations in airborne particles was about 60% during 1981-2000, and 40-50% during 1990-2000. Corresponding decreases in bulk precipitation were about 60-75% during 1981-2000, and 40-60% during 1990-2000 (Ruoho-Airola *et al*. 2004).

Nitrogen deposition throughout Europe and in Finland has also declined since the late 1980s, but less than sulphur. The overall reduction of nitrate ($NO_3$) in bulk deposition in Finland was about 25-45% during 1987-1996. The decrease of ammonium ($NH_4$) in bulk deposition has been greater, about 40-70% during 1987-1996, but changes have been less uniform than changes for $NO_3$ (Kulmala *et al*. 1998). The overall reduction of $NO_3$ and $NH_4$ concentrations in bulk precipitation during 1990-2000 has been about 20-40% and 40-50%, respectively, (Ruoho-Airola *et al*. 2004). Concentrations of nitrogen compounds ($NO_3^-$ and $NH_4^+$) are usually lower in throughfall than in bulk deposition in Finland. Inorganic N is taken up in the canopy, reflecting the shortage of available N typical in boreal forest ecosystems (e.g. Mälkönen *et al*. 1990). Therefore long-term trends in nitrogen deposition are best shown by bulk deposition measurements.

### 1.4.2 Monitoring of acidification and recovery in surface waters

A number of monitoring programmes at both national and international levels have been established to assess the degree and regional extent of the impact of atmospheric pollution on ecosystems. The emission controls have produced widespread decreases in acidic deposition, and monitoring of expected chemical and biological recovery from acidification has been setup to important target in monitoring work. Empirical evidence is also essential for documenting the ecosystem responses of costly emission reduction investments. The signatories of the CLTRAP 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 key international bodies to monitor acidification of surface waters and catchments in Europe and North America under the UNECE CLTRAP have been the ICP Waters (Programme on Assessment and Monitoring of Acidification of Rivers and Lakes) and the ICP Integrated Monitoring (IM) (Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems) (Working Group on Effects 2004). ICP Waters was established in 1985 with 20 participating countries (18 European and USA and Canada). The chemical and site data from more than 200 catchments in 24 countries in Europe and North America are now available. ICP IM was established in 1987-1989, and network currently covers some 50 sites in 19 countries (18 European and Canada). Finland has participated actively in both these monitoring programmes. The chemical response of lake ecosystems to the deposition of acidifying compounds in Finland has been monitored also in a national program, the Regional Monitoring network of Lake Acidification (RMLA), since 1987 (Mannio 2001a,b).

Sulphate deposition has been the major driving force in the anthropogenic acidification of surface waters in the Nordic Countries (Skjelkvåle *et al*. 2001a) and elsewhere in Europe (Prechtel *et al*. 2001, Wright *et al*. 2005). Following the general decreasing trends in S deposition, recovery from acidification of sensitive surface waters, indicated by decreasing concentrations of sulphate and a subsequent increase in alkalinity, has been observed in many parts of Europe and North America during the 1990s (Stoddard *et al*. 1999, Evans *et al*. 2001, Skjeklvåle *et al*. 2005). Increase in alkalinity, however, has been more common in Europe than in North America (e.g. Stoddard *et al*. 1999, Skjeklvåle *et al*. 2005).

The regional increase in alkalinity connected with sulphate decline in Finnish lakes was first observed in the early 1990s (Mannio and Vuorenmaa 1995). The monitoring period was too short to show reliable statistical trends, but the comparison of the years 1987 and 1993 revealed that sulphate was decreased and alkalinity and pH increased in most of the RMLA lakes. The first statistical trend assessment of RMLA lakes for the period 1987-1998 showed clear evidence on regional chemical recovery of acid-sensitive lakes in Finland (Mannio 2001a,b). Sulphate concentrations were significantly declined in 60% of the lakes in north Finland and by up to 80% of the lakes in central and south Finland. Base cation concentrations were also declined, but to a lesser extent than sulphate, allowing buffering capacity (alkalinity) to increase. Alkalinity significantly increased in 55% of the RMLA lakes in south, and in 25% of the lakes in central and north Finland. Although lakes have exhibited a strong response to declining sulphate deposition overall, hydrology-induced surges in organic acidity and consequent decrease in alkalinity have been observed in several monitoring lakes in some years (Mannio 2001a). This highlights the importance of catchment characteristics and climatic and hydrological variability in affecting the recovery process.

Biological monitoring of acidified lakes in Finland has primarily been that of fish abundance and population structure. The results showed that European perch had recovered in the early 1990s in south Finland, which had experienced poor reproduction periods and populations close to extinction in many acidified lakes in the 1970s and 1980s (Nyberg *et al*. 1995, Rask *et al*. 1995b). The recovery of perch populations continued in later years (Nyberg *et al*. 2001). The recovery of roach, which is a more acid-sensitive species, has been less clear. However, in a few acidic lakes that were inhabited by sparse roach populations during 1985-1995, some reproduction had observed in the late 1990s (Nyberg *et al*. 2001). Minnow populations in lakes in north-eastern Finland in the Vätsäri area have experienced recovery during the 2000s along with decreased $SO_2$ emissions from the smelters on the Kola Peninsula (Tammi *et al*. 2003b, Lappalainen *et al*. 2007).

### 1.4.3 Increasing trend in DOC concentrations in acid-sensitive surface waters

At the same time as $SO_4$ concentrations and alkalinity in lakes and streams have respectively decreased and increased during the 1990s, dissolved organic carbon (DOC) concentrations have increased in glaciated, acid-sensitive landscapes across substantial areas of northern and central Europe and eastern North America (Evans and Monteith 2001, Skjelkvåle *et al*. 2001a, Stoddard *et al*. 2003, Worrall *et al*. 2004, Evans *et al*. 2005, Skjelkvåle *et al*. 2005, Monteith *et al*. 2007a). In Scandinavia, the increasing trend in total organic carbon (TOC) concentrations have been detected in many lakes in Norway and Sweden, but in Finland there was very little indication of this phenomenon at that time (Skjelkvåle *et al*. 2001a, Mannio 2001a). The widespread increase in DOC concentrations indicates a widespread environmental change and various explanations have been put forward to explain it. These explanations have included an increase in temperature (Freeman *et al*. 2001, Hejzlar *et al*. 2003), changes in hydrological regimes (Tranvik and Jansson 2002, Hejzlar *et al*. 2003), increasing atmospheric $CO_2$ concentrations (Freeman *et al*. 2004), airborne nitrogen enrichment of soils (Findlay 2005), and decreasing sulphur deposition (Stoddard *et al*. 2003, Evans *et al*. 2005, Evans *et al*. 2006, Monteith *et al*. 2007a). If the decline in sulphur deposition is causing the increase in DOC concentrations, then the increasing DOC trend in surface waters is integral to recovery from acidification.

## 1.5 Objectives of this study

The substantial reduction in emissions of acidifying air pollutants has resulted in decrease in acid deposition, and clear signs of recovery from acidification in sensitive surface waters have been observed in Finland and in large areas in Europe and North America during the 1990s. Therefore it is important consider whether a regional-scale decrease in acid deposition will continue to decline and chemical recovery of acid-sensitive Finnish lakes will progress in the 2000s. Despite substantial decreases in sulphur deposition and a statistically significant decline in sulphate concentrations in all types of lakes in Finland, a significant increase in alkalinity has so far been observed in only a number of the acidified lakes. Whilst this may be due to lag effects, it is apparent that a number of factors other than decreasing sulphate concentrations have an effect on recovery. Catchment characteristics can be expected to play an important role in chemical recovery of Finnish lakes. Along with improved water chemistry, the recovery of acid-sensitive fish populations in acidified lakes in south Finland was indicated during the 1990s. It is therefore important to determine if chemical conditions in the formerly most acidified lakes have returned to levels that would result in regional-scale biological recovery of fish populations. Given the concern about widespread increase in DOC concentrations in remote lakes and streams, it would be important to establish if this phenomenon is indicated in Finnish lakes and whether it is related to decreasing sulphate deposition.

Against this background, the key aims of this study were to:

- Evaluate the changes of acidifying deposition in Finland over the period 1973-2003 and examine the relationship to lake chemistry (I-V, this study).
- Analyze the regional trends in water chemistry for acid-sensitive headwater lakes over the period 1990-2003 (V) and examine the later changes in water chemistry of selected acidified lakes (this study).
- Identify important catchment characteristics and hydrological patterns affecting the recovery of alkalinity in lakes (V, this study).
- Identify water chemistry changes that underlie the recovery of fish populations from acidification (III).
- Evaluate total organic carbon (TOC) concentrations in small forest lakes for possible long-term trends, and identify the role of potential drivers, particularly that of S deposition (IV).

# 2 Materials and methods

## 2.1 Monitoring of acidification

### 2.1.1 Regional monitoring of lake acidification (RMLA)

The national monitoring of lake acidification in Finland started in 1979 with 28 small forest lakes (Roila 1992). The monitoring network was extended in 1987 in connection with the national survey of lake acidification by subjectively chosen lakes from the survey lake population. The objective of the selection was to cover the whole country, with emphasis on the remote headwater lakes of the most acidified and acid-sensitive areas. The network was refined and extended in 1990 to better cover the whole country, to improve representation of humic lakes within the selected set of lakes, and to fulfil commonly agreed criterions for monitoring of air pollution impacts and responses for deposition changes in lakes (NIVA 1996, Mannio 2000). In 1990, the concept of the Regional Monitoring of Lake Acidification (RMLA) was also adopted as the monitoring strategy for acid-sensitive lakes in Finland. This approach is based on assessment of water chemistry characteristics and trends using three geographical regions: South (39% of the monitoring lakes), Central (36%) and North Finland (25%) (Fig. 2 in V). These regions were identified on the basis of the long-range transboundary air pollution gradients in atmospheric deposition and lake chemistry (Mannio and Vuorenmaa 1995, Mannio 2001a,b). The monitoring of fish populations by Finnish Game and Fisheries Research Institute (FGFRI) was carried out on a subset of 15 acidified lakes from the RMLA network (Rask *et al*. 1995b, Nyberg *et al*. 2001).

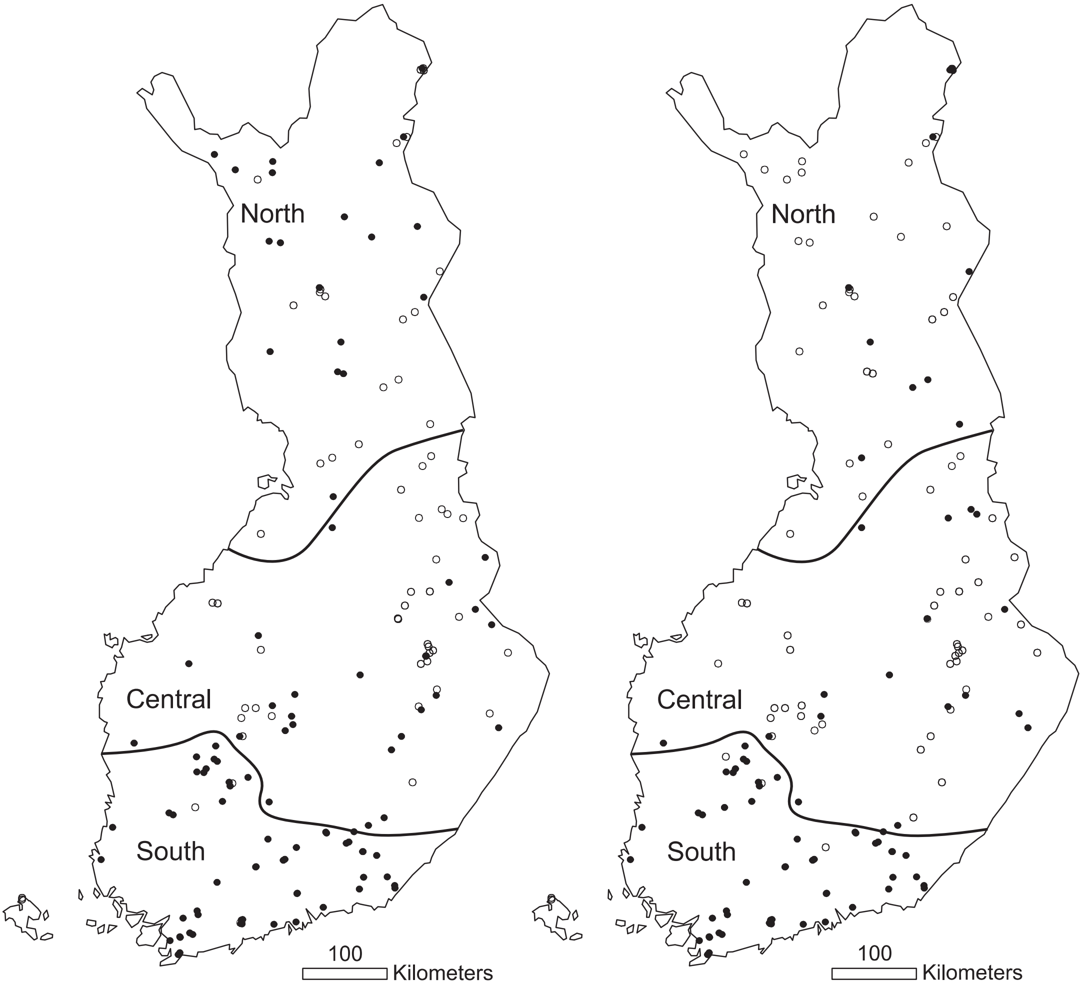

**Figure 2.** Location of the RMLA lakes (n=157) and trends in Gran alkalinity (left) and median xSO$_4$ to A$^-$ ratio (right) over the period 1990-2003. For alkalinity solid circle (•) indicates a significant ($p < 0.05$) increasing trend (Kendall-τ) and open circle (○) indicates no trend. For xSO$_4$ : A$^-$, solid circle (•) indicates median xSO$_4$ ≥ A$^-$ and open circle (○) xSO$_4$ < A$^-$. Solid lines define the boundaries between the south, central and north Finland regions (from paper V).

**Table 1.** The data sets used in studies I-V and this summary(s).

| Objectives | Sites |  | Study period | Database / network | Paper |
|---|---|---|---|---|---|
|  | Type | n |  |  |  |
| Monitoring of bulk deposition | B | 17-19 | 1973-2003 | National monitoring network of bulk deposition (SYKE) | I, s |
| Regional monitoring of lake acidification | L | 163 | 1990-1999 | RMLA | II |
|  | L | 157 | 1990-2003 | RMLA | V, s |
|  | L | 6 | 1985-2006 | subset of RMLA | s |
| Recovery of fish populations from acidification | L, F | 21 | 1987-2002 | subset of RMLA | III |
|  | L, F | 9 | 1987 and 2001/2002 | subset of REPRO | III |
| Trends of TOC concentrations in lakes | L | 10 | 1987-2003 | subset of RMLA | IV |
|  | L, R | 3 | 1987-2003 | subset of ICP IM sites | IV |
| Water quality in Finnish lakes | L | 874 | 1995 | FLS 1995 | s |

B= bulk deposition, L=lake, R=stream, F=fish
Database/network, see Abbreviations

The RMLA network in 1990 consisted of 180 lakes. During the 1990s some less representative lakes (lakes with liming operations, lakes with too sparse data and lakes located geographically unnecessary dense areas) were dropped from the monitoring network. Reciprocally, some lakes were added to network in areas with sparse coverage, mainly in Lapland. In this study, the total number of RMLA lakes varied between 157-163 (Table 1).

The monitoring lakes are small (median area= 0.1 km$^2$) headwater or seepage lakes, which have been shown to be good indicators of air pollution impacts. The RMLA lakes have been chosen to form an "early warning" system (Mannio and Vuorenmaa 1995, Mannio 2001a), and they are more sensitive to acidification than the lake population as a whole (Table 3). Some 75% of the RMLA lakes had no upstream lake, 20% classified as a drainage lakes having < 5 % upstream lake area in the catchments. The catchments in which lakes were located had low catchment-to-lake area ratio. The land cover is mainly forested (78% of the catchments had no agriculture and only 4% of the catchments had a agriculture area > 3 %). The lakes are acid-sensitive with low base cation concentrations, low alkalinity and pH and, in some lakes, elevated labile aluminium concentrations (Mannio and Vuorenmaa 1995, Mannio 2001a). The catchments have not been exposed to direct human impact except some forestry practices forest drainage being the most important. The RMLA monitoring network is described in detail in Mannio (2001a).

### 2.1.2 Bulk deposition

The national monitoring network for bulk deposition in Finland was launched in the Finnish Environment Institute (SYKE) during 1971-1972 (Haapala 1972). The monitoring network was distributed throughout the whole country and from 1973 annual monitoring data has been available continuously from 49 stations. At the beginning, the purpose of the bulk deposition monitoring was to complete mass balance calculations of small drainage basins with information on atmospheric deposition inputs. Particular attention was paid to the contribution of deposition on lake eutrophication but acidification aspects became increasingly important. Earlier studies on long-term deposition changes at stations of SYKE have been reported for the period 1971-1988 (Järvinen and Vänni 1990).

The number of monitoring stations in the network was reduced in 1998 to 29 measuring stations by removing less representative stations, stations with high local agricultural impact or stations located geographically unnecessary dense areas. Out of these 29 stations, data from 17-19 selected stations was used to assess changes of acidifying deposition in Finland in 1973-2003 (Fig. 3, Table 1, paper I, this study). The monitoring stations are distributed throughout the whole country and most are located in rural background areas with no significant nearby point emissions, thus providing a representative basis for assessing gradients and changes in deposition. The monitoring procedure, observation sites, comparability of the results over the study period and data quality assessment are described in detail in Järvinen and Vänni (1990), Vuorenmaa *et al.* (2001), and in the paper I.

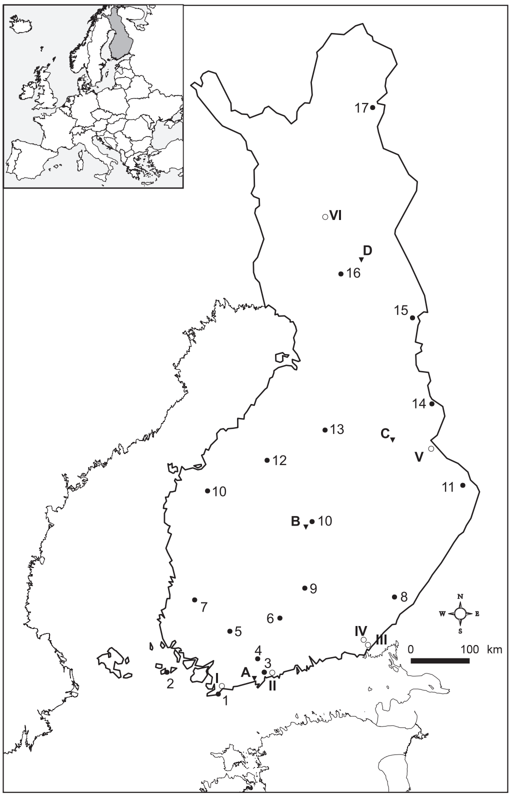

**Figure 3.** Location of the deposition monitoring stations (•, 1-17), seasonally sampled lakes (○, I-VI) and runoff measurement stations (▼, A-D) used in this study. The numbers of deposition stations refer to those in Tables 4 and 5, the Roman numbers refer to those in Figure 12, and letters A-D refer to those in Figure 13.

## 2.2 Sampling and chemical analysis

### 2.2.1 Lake water

In papers II, III and V, a water sample from each RMLA lake was taken from either the middle of the lake (1 m depth) or at the outlet once a year during the autumn thermal overturn phase (from early September in the north to mid November in the south). This autumnal sampling strategy is considered representative for long-term monitoring of conservative acidification ions (Mannio 2001a,b). In paper IV, long-term changes in total organic carbon (TOC) concentrations in 13 acid-sensitive forest lakes were evaluated. These 13 lakes had been more intensively monitored from the mid-1980s. Ten of the lakes have been monitored under national (RMLA) and UNECE ICP Waters monitoring programmes, and three lakes have been monitored under the UNECE ICP Integrated Monitoring Programme (ICP IM) (Forsius *et al.* 2001). Samples from these 10 lakes were taken during the thermal winter stratification (February-March in south Finland, April in north Finland), two samples during the spring flow (April-May in south, May-June in north), one sample during thermal summer stratification (August) and two samples during the autumn thermal overturn (September-November). The IM lakes were subject to more frequent sampling, comprising 8-12 samples per year. All the results used in papers II-V and in this study all refer to samples taken at 1 m depth.

Throughout this study (papers II-V) the lake water quality variables (24 altogether) were measured with the standard methods used by the Environmental Administration and included pH, Gran alkalinity, total organic carbon (TOC), Ca, Mg, Na, K, $SO_4$, Cl, $NO_3$-N, $NH_4$-N, chemical oxygen demand ($COD_{Mn}$) and aluminium fractions (Table 2).

### 2.2.2 Bulk deposition

Bulk precipitation samples were collected in open areas and analyzed on a monthly basis. All the analyses were carried out in the laboratory of the Finnish Environment Institute using standardized methods for pH, Ca, Mg, Na, K, $SO_4$, Cl, $NO_3$-N and $NH_4$-N. The analytical methods are given in Table 2, and are described in detail in Järvinen and Vänni (1990) and Vuorenmaa *et al.* (2001). The montly amount of precipitation for calculation of bulk deposition in the monitoring sites was measured with separate meteorological precipitation gauges by SYKE and the Finnish Meteorological Institute.

**Table 2.** Key chemical variables and methods of analysis used in studies I-V and this summary (s).

| Material | Variable | Methods | Reference |
|---|---|---|---|
| Precipitation | pH | potentiometric | paper I,<br>SYKE standard methods |
| | Ca, Mg, Na, K | AAS | |
| | $SO_4$ | nephelometric, IC | |
| | Cl | titrimetric, potentiometric, IC | |
| | $NO_3$-N, $NH_4$-N | colorimetry | |
| Lake water | pH | potentiometric | Papers II-V,<br>SYKE standard methods |
| | Alkalinity | Gran plot | |
| | Ca, Mg, Na, K | AAS | |
| | $SO_4$ | nephelometric, IC | |
| | Cl, | titrimetric, potentiometric, IC | |
| | F | IC | |
| | $NO_3$-N, $NH_4$-N | colorimetry | |
| | Al fractions | Autoanal. (PVC) | |
| | $COD_{Mn}$ | titrimetric, potentiometric | |
| | TOC | IR | |

## 2.3 Statistical methods

The deposition data used for the trend analysis were either annual precipitation-weighted mean concentrations or annual bulk deposition values. A significant ($p < 0.05$) monotonic increasing or decreasing trend for individual sites was tested for using the non-parametric Kendall tau trend test. The annual change, i.e. slope of the linear trend, was calculated using linear regression (paper I) or the Theil-Sen slope estimator (this study), which is equivalent to the Sen slope estimator (Sen 1968). The relative change of deposition (as a percentage) was calculated for sulphate using Theil-Sen slope estimator extracted from the annual values, assuming a linear trend over the length of the study period (this study). The total change was then related to the value of the first year of the fitted trend line equation. The method presented is based on the assumption of a linear trend. If the slope in the downward trend is larger at the beginning, the method may overestimate the total relative change of annual values. A detailed description of the method is given in Kulmala *et al.* (1998).

Statistical trend analysis methods used for lake chemistry consisted of non-parametric Kendall tau test for lakes with autumn samples only (papers II, III, V), and non-parametric seasonal Kendall test (Hirch *et al.* 1982) for seasonally sampled lakes (paper IV). The rate of change, i.e. slope of the trend, was calculated using linear regression (papers II, III) or the Theil-Sen slope estimator (papers IV, V). The relative total change for sulphate concentrations was calculated with the similar method used for deposition and precipitation chemistry (this study). Measures of central tendency of variable were calculated and interdependence was evaluated using correlation analysis and stepwise multiple regression analysis (paper IV). The discriminant analysis, using logistic regression, was used to find variables that best differentiated between prior determined classes: those having a statistically significant increase ($p < 0.05$) in alkalinity (recovering) and those having no significant increase (non-recovering) (paper V). Logistic regression is frequently used as a non-parametric alternative of classical discriminant analysis (Press and Wilson 1978, Tabachnick and Fidell 1996). The Wilcoxon rank-sum (Mann-Whitney) test was also used to compare these two unpaired groups (paper V).

In papers I, II and V, lake and deposition data were assessed by a regional approach. For this analysis the lakes and deposition measuring sites were divided into three geographical regions: south,

**Table 3.** Characteristics (median values) of the lake monitoring network (RMLA, n=157) and of the Finnish Lake Survey (FLS, n=577) in 1995. Only FLS lakes < 100 ha are included in the comparison.

| Variable | | Total country | | South | | Central | | North | |
|---|---|---|---|---|---|---|---|---|---|
| | | FLS | RMLA | FLS | RMLA | FLS | RMLA | FLS | RMLA |
| Number of sites | | 577 | 157 | 134 | 61 | 263 | 57 | 180 | 39 |
| Lake | ha | 10 | 10 | 11 | 15 | 10 | 8 | 9 | 9 |
| Catchment | ha | 192 | 109 | 193 | 89 | 192 | 111 | 189 | 115 |
| Peatland | % | 12 | 12 | 6 | 7 | 14 | 24 | 19 | 22 |
| | | | | | | | | | |
| Conductivity | mS m$^{-1}$ | 3.1 | 2.0 | 4.1 | 2.7 | 3.2 | 1.9 | 2.5 | 1.2 |
| Gran alkalinity | µeq l$^{-1}$ | 110 | 21 | 105 | 19 | 100 | 32 | 120 | 13 |
| pH | | 6.6 | 5.9 | 6.4 | 5.9 | 6.5 | 5.9 | 6.8 | 5.95 |
| $xSO_4$ | µeq l$^{-1}$ | 64 | 60 | 121 | 111 | 70 | 46 | 34 | 31 |
| xBC | µeq l$^{-1}$ | 245 | 131 | 308 | 164 | 247 | 136 | 206 | 69 |
| $ANC_{CB}$ | µeq l$^{-1}$ | 173 | 63 | 171 | 59 | 177 | 85 | 171 | 40 |
| $Al_{lab}$ | µg l$^{-1}$ | 10 | 10 | 10 | 10 | 10 | 10 | 5 | 5 |
| TOC | mg l$^{-1}$ | 8.1 | 6.4 | 10.1 | 5.2 | 9.7 | 8.7 | 5.6 | 5 |
| Tot P | µg l$^{-1}$ | 14 | 10 | 16 | 8 | 16 | 14 | 8 | 7 |

central and north Finland. In order to determine deposition changes with respect to first protocol on the reduction of sulphur emissions in 1985 (Helsinki Protocol) and implementation of international emission reduction agreements (CLRTAP), the study period 1973-2000 in paper I was divided into two time periods: 1973-1985 and 1986-2000. In this study, the changes of deposition are presented for the period 1986-2003.

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

The Finnish Environment Institute has carried out hydrological monitoring in a network of small drainage basins throughout Finland (Seuna 1983, Vuorenmaa *et al*. 2002). The runoff data from 4-5 forested catchments were used to illustrate spatial and temporal changes and variation in hydrological conditions (Fig. 3, papers IV-V, this study). Runoff was measured continuously by overflow weirs fitted with water stage recorder gauges.

# 3 Results and discussion

## 3.1 Acidifying deposition in Finland

### 3.1.1 Regional gradients of deposition

The deposition of sulphur (S) is greatest in south Finland, where both deposition from Finland's own emissions and the load of transboundary air pollution are highest. The bulk deposition of non-marine sulphate ($xSO_4$) (i.e. anthropogenic sulphate) is clearly highest in the southernmost part of country, decreasing gradually towards the north (Table 4, Fig. 4, paper I). The mean bulk deposition of $xSO_4$ in south Finland (stations 1-9) during 1986-2003 was, on average, 1.6-fold higher compared to central Finland (stations 10-15) and 2.3-fold higher compared to north Finland (stations 16-17). The mean annual (1986-2003) bulk deposition of $xSO_4$ at stations in south Finland varied between 27 and 46 meq m$^{-2}$ a$^{-1}$ (0.5-0.7 g S m$^{-2}$ a$^{-1}$), from 18 to 25 meq m$^{-2}$ a$^{-1}$ (0.3-0.4 g S m$^{-2}$ a$^{-1}$) in central Finland and, from 11 to 18 meq m$^{-2}$ a$^{-1}$ (0.2-0.3 g S m$^{-2}$ a$^{-1}$) in north Finland. Besides longer distances from major emission sources and consequently lower air pollution loads, the gradient in bulk deposition between south and north Finland is attributable to lower precipitation amounts in the north (paper I).

Open area bulk deposition measurements do not provide measure of the total deposition load to forest ecosystems. Throughfall deposition measurements have shown that coniferous forest canopies in particular capture significant amounts of dry deposition increasing total deposition (wet + dry) of S to the forest floor. Ukonmaanaho and Starr (2002) have reported that the total deposition of $SO_4$ in coniferous stands in south Finland during 1989-1997 was, on average, 1.7-fold higher compared to bulk deposition and 1.2-fold higher compared to bulk deposition in central Finland. In northernmost Finland, the total $SO_4$ deposition was, on average, 1.9-fold higher compared to bulk deposition. Similarly, concentrations of $SO_4$ in throughfall in south Finland were, on average, 2.6-fold higher, and 1.6-1.8-fold higher in central and north Finland compared to bulk precipitation. Lindroos *et al.* (2006) have reported about 2-fold higher $SO_4$ deposition in the throughfall in south Finland compared to bulk deposition during 1996-2003. In north Finland, the dry deposition of sulphur dominates due to the lower precipitation and may account for about 80% of total deposition (Tuovinen *et al.* 1993). Sulphur total deposition in south Finland was, on average, 1.6-fold higher compared to central Finland and 2.6-fold higher compared to north Finland during 1989-1997 (Ukonmaanaho and Starr 2002), showing that proportionally the differences in total S deposition gradients are relatively similar than that in bulk deposition.

The deposition of N compounds exhibits a similar geographical gradient as that of sulphur, decreasing from south to north Finland (Table 4, paper I). Bulk deposition contains rather equal amounts of ammonium-nitrogen ($NH_4$-N) and nitrate-nitrogen ($NO_3$-N). The mean annual (1986-2003) bulk deposition of $NO_3$-N varied between 15 and 26 meq $m^{-2}$ $a^{-1}$ (0.21-0.37 g N $m^{-2}$ $a^{-1}$) in south Finland, 10 and 14 meq $m^{-2}$ $a^{-1}$ (0.14-0.20 g N $m^{-2}$ $a^{-1}$) in central Finland, and between 4 and 10 meq $m^{-2}$ $a^{-1}$ (0.06-0.14 g N $m^{-2}$ $a^{-1}$) in north Finland. Correspondingly, the bulk deposition of $NH_4$-N in south Finland varied between 13 and 28 meq $m^{-2}$ $a^{-1}$ (0.19-0.40 g N $m^{-2}$ $a^{-1}$), between 10 and 21 meq $m^{-2}$ $a^{-1}$ (0.14-0.30 g N $m^{-2}$ $a^{-1}$) in central Finland, and between 4 and 9 meq $m^{-2}$ $a^{-1}$ ( 0.06-0.13 g N $m^{-2}$ $a^{-1}$) in north Finland. The influence of local sources is more pronounced for $NH_4$ than for $NO_3$, and somewhat higher values for $NH_4$ are found in parts of south and central Finland where there is more agricultural land use.

Non-marine base cation (xBC) deposition is also decreasing from south to north Finland (Table 4, paper I, Ruoho-Airola *et al.* 2003). Higher xBC deposition in parts of south Finland is partly related to the pronounced impact of alkaline fly ash emissions from Estonia and Russia (Anttila 1990, Jalkanen *et al.* 2000). Calcium is the main contributing ion in BC deposition on the basis of charge equivalents, comprising, on average, 64 % in south, 61 % in central and 57 % in north Finland (paper I). Brydges and Summers (1989) have defined the concept of 'acidifying potential' (AP) as the effective amount of acid delivered to a terrestrial or aquatic ecosystem calculated as $(SO_4^{2-}) - (Ca^{2+} + Mg^{2+})$. This formula is based on the assumption that $Ca^{2+}$ and $Mg^{2+}$ are the most important cations neutralizing $SO_4^{2-}$ acidity. If the nitrogen is taken up by the soil/vegetation system, then the amount of hydrogen ions ($H^+$) in precipitation, which has to be neutralized by the surface waters, is defined by the AP. In this study xAP deposition was calculated from non-marine fractions of $xSO_4$ and x(Ca + Mg). The acidifying potential (xAP) of deposition is highest in south Finland. Although the deposition of x(Ca+Mg) is also the highest there, the input of $xSO_4$ exceeds that of x(Ca + Mg) more than compared to central and north Finland. The acidifying effect of deposition (AP) can also be considered as residual $H^+$, which is reflected as higher $H^+$ deposition and lower pH in precipitation in south Finland (Table 4, paper I).

Historically, Finland has been exposed to lower sulphur deposition compared to levels in central Europe, south Norway and south Sweden. Model-calculated total deposition of sulphur in 1980, when European S emissions were at their highest, was > 4000 mg S $m^{-2}$ in central Europe (Lövblad *et al.* 2004). Southern parts of Norway, Sweden and Finland received total S deposition loads of 1000-2000 mg S $m^{-2}$, increasing to 2000-3000 mg S $m^{-2}$ for the southernmost areas of Norway and Sweden. In 2000, the total S deposition in south Norway and south Sweden was estimated to be 500-1000 mg S $m^{-2}$, and < 500 mg S $m^{-2}$ in south Finland (Lövblad *et al.* 2004). The lower deposition levels in south Finland have probably resulted in lower accumulation and

**Table 4.** Mean annual precipitation (mm $a^{-1}$), bulk deposition (meq $m^{-2}$ $a^{-1}$) and concentrations (µeq $l^{-1}$) in bulk precipitation of $xSO_4$, acidifying potential xAP=($xSO_4$) – x(Ca + Mg), x(Ca + Mg), $NO_3$-N, $NH_4$-N and $H^+$ at the studied deposition monitoring sites in 1986-2003.

| Station | Precipita-tion | | $xSO_4$ | xAP | x(Ca+Mg) | $NO_3$-N | $NH_4$-N | $H^+$ | | $xSO_4$ | xAP | x(Ca+Mg) | $NO_3$-N | $NH_4$-N | $H^+$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | mm $a^{-1}$ | | meq $m^{-2}$ $a^{-1}$ | | | | | | | µeq $l^{-1}$ | | | | | |
| 1 Tvärminne | 620 | | 36.6 | 21.7 | 14.9 | 23.6 | 19.1 | 20.2 | | 58.7 | 34.6 | 24.1 | 38.3 | 30.9 | 32.2 |
| 2 Korppoo | 649 | | 32.7 | 22.2 | 10.5 | 21.5 | 18.7 | 19.3 | | 50.3 | 33.8 | 16.5 | 33.2 | 28.8 | 29.6 |
| 3 Espoo | 740 | | 45.9 | 27.6 | 18.3 | 26.2 | 27.6 | 19.1 | | 61.2 | 36.4 | 24.9 | 35.5 | 37.0 | 25.3 |
| 4 Vihti | 639 | | 37.3 | 25.9 | 11.4 | 23.3 | 26.6 | 18.3 | | 58.5 | 40.4 | 18.1 | 36.5 | 41.7 | 28.3 |
| 5 Jokioinen | 615 | | 29.6 | 18.4 | 11.3 | 16.9 | 18.5 | 12.6 | | 47.9 | 29.7 | 18.1 | 27.4 | 30.0 | 20.2 |
| 6 Lammi | 635 | | 26.7 | 16.8 | 10.0 | 16.1 | 15.0 | 13.0 | | 42.0 | 26.4 | 15.6 | 25.3 | 23.7 | 20.5 |
| 7 Peipohja | 616 | | 29.0 | 17.2 | 11.9 | 18.5 | 17.5 | 15.4 | | 47.4 | 28.1 | 19.3 | 30.1 | 28.5 | 24.9 |
| 8 Kotaniemi | 611 | | 31.4 | 16.8 | 14.6 | 17.0 | 16.3 | 11.8 | | 51.7 | 27.6 | 24.1 | 27.9 | 26.8 | 19.4 |
| 9 Sysmä | 611 | | 26.8 | 16.1 | 10.7 | 14.9 | 13.2 | 13.9 | | 43.2 | 26.0 | 17.2 | 24.2 | 21.4 | 22.6 |
| 10 Laukaa | 577 | | 24.7 | 17.0 | 7.6 | 12.8 | 20.9 | 7.6 | | 42.1 | 29.0 | 13.2 | 22.0 | 36.1 | 13.0 |
| 11 Naarva | 697 | | 23.7 | 14.5 | 9.2 | 13.0 | 10.7 | 13.0 | | 34.0 | 20.7 | 13.3 | 18.8 | 15.4 | 18.5 |
| 12 Lestijärvi | 603 | | 19.9 | 13.0 | 6.8 | 13.6 | 20.2 | 7.1 | | 33.2 | 21.7 | 11.5 | 22.8 | 33.8 | 11.7 |
| 13 Viitamäki | 647 | | 19.7 | 12.2 | 7.5 | 11.2 | 10.1 | 9.1 | | 30.3 | 18.9 | 11.5 | 17.3 | 15.6 | 14.1 |
| 14 Kuhmo | 598 | | 20.9 | 14.2 | 6.7 | 12.9 | 14.4 | 9.9 | | 34.6 | 23.5 | 11.1 | 21.5 | 23.8 | 16.4 |
| 15 Kurvinen | 631 | | 18.1 | 11.9 | 6.2 | 10.2 | 10.5 | 9.0 | | 28.9 | 18.9 | 9.9 | 16.3 | 16.8 | 14.4 |
| 16 Juotas | 555 | | 17.7 | 13.8 | 4.0 | 10.2 | 9.4 | 11.3 | | 32.6 | 25.2 | 7.4 | 18.7 | 17.0 | 21.2 |
| 17 Nellim | 480 | | 10.9 | 7.9 | 3.0 | 4.0 | 3.7 | 5.5 | | 23.0 | 16.6 | 6.3 | 8.5 | 7.5 | 11.7 |

lower soil pools of $SO_4$ compared to most affected areas in south Norway and Sweden.

### 3.1.2 Deposition trends

#### 3.1.2.1 Sulphur

Bulk deposition of $xSO_4$ in south, central and north Finland showed no consistent trend over 1973-1985, and there were no marked differences in mean deposition load between the 1970s (1973-1980) and 1980s (1981-1990). Sulphate concentrations in bulk precipitation have slightly declined since the 1970s, particularly in south Finland. This trend during the 1970s and 1980s was disappearing in the deposition load records, which may be due to higher precipitation amount in the 1980s compared to the 1970s with strong correlation between precipitation and deposition during these decades (Fig. 5, paper I). Estimates of European $SO_2$ emissions with a time step of five years were approximately 55, 57 and 54 million tonnes in the years 1970, 1975 and 1980, respectively (Mylona 1996). EMEP European emissions for the period 1981-1990 (excluding emissions from international shipping and natural sources) averaged 47 million tonnes $SO_2$ per year, but declined from 52 million tonnes of $SO_2$ in 1981 to 40 million tonnes of $SO_2$ in 1990 (Vestreng *et al.* 2006). The historical inventory of $SO_2$ emissions involves many uncertainties relating to the availability of data and derivation methods (Mylona 1996, Schöpp *et al.* 2003). European $SO_2$ emission estimates for the 1970s are for five year periods, and the inter-annual variation is unknown. Nevertheless, it is likely that changes in $SO_2$ emissions in Europe between the 1970s and 1980s were relatively small, which explains the relative small changes in sulphate deposition in Finland. Long-term bulk deposition and concentration records from Sweden and Norway show small changes in $xSO_4$ during the 1970s, but a slight decline during the 1980s (Wilander 2001, Moldan *et al.* 2001). The variation in deposition trends and the weak responses to slight reduction of total S emissions suggest different meteorological and emission regimes in Europe in the 1970s and 1980s.

Due to the successful implementation of S emission reduction measures in Europe, bulk deposition of $xSO_4$ culminated in the late 1980s, followed by a substantial decline during the 1990s (Table 5, Fig. 4, Paper I). Both deposition loads and concentrations in precipitation have significantly ($p < 0.05$) declined between 1986-2003 at all studied monitoring stations, the relative decrease being about 45% in northernmost Finland and 60-70 % in south and central Finland. The decrease was strongest during the late 1980s and early 1990s, with the relative decrease between 1990-2003 being slightly lower (40-60 % in south and central Finland and 20% in the northernmost Finland, Fig. 6a-b). Ruoho-Airola *et al.* (2004) have also reported on substantial (40-60%) reduction in sulphate concentrations in bulk precipitation throughout the Finland over the period 1990-2000. A clear decline in $xSO_4$ deposition, starting mainly in the late 1980s, has also been reported from other Nordic countries (Sweden, Norway) as well as for wide areas in Europe (Barrett *et al.* 2000, Forsius *et al.* 2001, Kindbom *et al.* 2001, Moldan *et al.* 2001, Prechtel *et al.* 2001). Domestic emissions of S and in areas of eastern and central Europe which are the main source areas affecting sulphate deposition in Finland, exhibited rapid decline (60-90 %) from 1990 to 2000 (Vestreng *et al.* 2006).

The reductions of S emissions are closely followed by those of deposition, particularly in south Finland, which shows the strongest emission reduction responses in deposition. The median annual change in $xSO_4$ deposition during 1986-2000 was $-2.37$ meq $m^{-2}$ $a^{-1}$ in south Finland, $-1.56$ meq $m^{-2}$ $a^{-1}$ in central Finland and $-0.79$ meq $m^{-2}$ $a^{-1}$ in north Finland (paper I). During the 1986-2003 period, the median slopes for the trend in $xSO_4$ deposition and concentrations in precipitation was $-1.89$ meq $m^{-2}$ $a^{-1}$ and $-2.75$ µeq $l^{-1}$ $a^{-1}$ in south Finland (stations 1-9), and $-1.22$ meq $m^{-2}$ $a^{-1}$ and $-1.78$ µeq $l^{-1}$ $a^{-1}$ in central Finland (stations 10-15), respectively. In north Finland (stations 16 and 17) the slope of the trends varied between $-0.85$ and $-0.37$ meq $m^{-2}$ $a^{-1}$ for deposition and between $-2.16$ and $-0.81$ µeq $l^{-1}$ $a^{-1}$ for concentrations (Table 5). As discussed above, the decrease of sulphate deposition was strongest during the late 1980s and early 1990s, and the slopes for both deposition and concentrations were steeper between 1986-2003 compared to the period 1990-2003, particularly in south Finland (Fig. 6c-d). Throughfall measurements also indicate a substantial reduction in sulphate in dry deposition, being the

**Table 5.** Trend slopes (Theil-Sen) in bulk deposition (meq $m^{-2}$ $a^{-1}$) and concentrations in bulk precipitation (µeq $l^{-1}$ $a^{-1}$) of $xSO_4$, acidifying potential $xAP=(xSO_4) - x(Ca + Mg)$, x(Ca + Mg), $NO_3$-N, $NH_4$-N and $H^+$ at the studied deposition monitoring sites for the period 1986-2003. Statistically significant trend (Kendall-τ, $p < 0.05$) is denoted with an asterisk (*).

| Station | $xSO_4$ | xAP | x(Ca+Mg) | $NO_3$-N | $NH_4$-N | $H^+$ | $xSO_4$ | xAP | x(Ca+Mg) | $NO_3$-N | $NH_4$-N | $H^+$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | meq $m^{-2}$ $a^{-1}$ | | | | | | µeq $l^{-1}$ $a^{-1}$ | | | | | |
| 1 Tvärminne | -2.26* | -1.31* | -0.76* | -0.73* | -0.70* | -1.27* | -2.84* | -1.74* | -1.14* | -0.79* | -0.82* | -1.57* |
| 2 Korppoo | -2.05* | -1.43* | -0.47* | -0.67* | -1.00* | -1.27* | -2.61* | -2.17* | -0.51 | -0.88* | -1.36* | -2.03* |
| 3 Espoo | -2.86* | -2.36* | -0.67 | -0.84* | -1.22* | -2.14* | -2.75* | -2.83* | -0.63 | -0.82* | -0.88* | -2.04* |
| 4 Vihti | -2.57* | -1.77* | -0.62* | -0.83* | -1.11* | -1.23* | -3.61* | -2.82* | -0.62 | -0.87* | -1.52* | -2.14* |
| 5 Jokioinen | -1.89* | -1.53* | -0.31 | -0.59* | -0.48* | -1.40* | -2.70* | -2.43* | -0.25 | -0.72* | -0.59* | -2.06* |
| 6 Lammi | -1.68* | -1.29* | -0.51* | -0.57* | -0.66* | -1.20* | -2.65* | -1.95* | -0.62* | -0.89* | -1.01* | -1.65* |
| 7 Peipohja | -1.83* | -1.18* | -0.53* | -0.73* | -0.22 | -1.52* | -2.75* | -2.14* | -0.97* | -1.14* | -0.18 | -2.65* |
| 8 Kotaniemi | -1.77* | -1.35* | -0.48 | -0.24 | -0.53* | -0.91* | -2.98* | -2.09* | -0.68 | -0.33 | -1.04* | -1.48* |
| 9 Sysmä | -1.79* | -1.00* | -0.80* | -0.39* | -0.43* | -1.03* | -2.64* | -1.45* | -1.19* | -0.58* | -0.67* | -1.69* |
| 10 Laukaa | -1.75* | -1.37* | -0.46* | -0.34* | -0.54* | -0.83* | -2.90* | -2.16* | -0.65* | -0.51* | -0.69 | -1.33* |
| 11 Naarva | -1.24* | -1.06* | -0.06 | -0.31* | -0.40* | -1.00* | -1.62* | -1.52* | -0.09 | -0.41 | -0.56* | -1.26* |
| 12 Lestijärvi | -1.20* | -0.94* | -0.22* | -0.29* | -0.35 | -0.67* | -1.94* | -1.45* | -0.40* | -0.50 | -0.62 | -1.25* |
| 13 Viitamäki | -0.98* | -0.70* | -0.22 | -0.27* | -0.10 | -0.82* | -1.55* | -1.15* | -0.31 | -0.44* | -0.12 | -1.22* |
| 14 Kuhmo | -1.40* | -0.91* | -0.38* | -0.68* | -1.01* | -0.81* | -2.00* | -1.42* | -0.56* | -0.93* | -1.50* | -1.25* |
| 15 Kurvinen | -0.90* | -0.90* | -0.04 | -0.25* | -0.56* | -0.91* | -1.59* | -1.49* | -0.17 | -0.50* | -1.02* | -1.50* |
| 16 Juotas | -0.85* | -0.63* | -0.17* | -0.17 | -0.04 | -0.95* | -2.16* | -1.47* | -0.44* | -0.45* | -0.31 | -1.96* |
| 17 Nellim | -0.37* | -0.30* | -0.11 | -0.01 | 0.10 | -0.38* | -0.81* | -0.74* | -0.26 | -0.08 | 0.15 | -0.83* |

strongest in south Finland (Ukonmaanaho *et al.* 1998, Ukonmaanaho and Starr 2002). The absolute decline in sulphate concentrations in throughfall has been greater than that in bulk precipitation in Finland (Ukonmaanaho *et al.* 1998) and in many other areas of Europe (e.g. Prechtel *et al.* 2001). This indicates that absolute decline in total deposition of sulphur has been stronger than the decline shown by bulk deposition.

### 3.1.2.2 Nitrogen compounds

Nitrate deposition in Finland increased between the periods 1973-1980 and 1981-1990, particularly in south and central Finland. Mean annual $NO_3$ deposition was 25% higher in the 1980s compared to the 1970s (paper I). At all stations the trend slopes in 1973-1985 were increasing and in 60% of stations in south and central Finland the trend was significant whereas in north Finland no significant trends were detected. The median slope of the trend for 1973-1985 varied from 0.09 meq $m^{-2}$ $a^{-1}$ in north Finland to 0.53 meq $m^{-2}$ $a^{-1}$ in south Finland. Ammonium deposition from the 1970s to 1980s also increased in south and central Finland, but at a lower rate than $NO_3$ deposition. At nearly all the stations, the $NH_4$ trend slopes for 1973-1985 were positive, but rarely significant. Ammonium contamination from local agricultural emissions, degradation, and qualitative deficiencies in the sample collection procedure in the preliminary years of monitoring may have caused 'noise' in time trends (paper I).

Nitrogen deposition culminated in the late 1980s (Fig. 5, Paper I). $NO_3$ concentrations in bulk precipitation decreased by 30-40% in south Finland, by 20-40% in central Finland and by 20-30% in north Finland over the period 1988-2000. The decreases in $NH_4$ deposition were larger, being 40-50% in south Finland, 30-50% in central Finland and 30% in north Finland (paper I). Nitrogen deposition at nearly all stations showed negative trend slopes in 1986-2000/2003, and the trend was significant ($p < 0.05$) for about 70-80% of the stations. Nitrogen deposition showed the strongest decrease in south Finland. The median slope of the trend for $NO_3$-N during 1986-2000 was –0.60 meq $m^{-2}$ $a^{-1}$ in south Finland, –0.45 meq $m^{-2}$ $a^{-1}$ in central Finland and –0.11 meq $m^{-2}$ $a^{-1}$ in north Finland. The corresponding decline in $NH_4$-N deposition was –0.62 meq $m^{-2}$ $a^{-1}$ both in south and central Finland and –0.08 meq $m^{-2}$ $a^{-1}$ in north Finland. The median slope of the trend for $NO_3$-N deposition and concentrations in precipitation for the period 1986-2003 was –0.67 meq $m^{-2}$ $a^{-1}$ and –0.82 µeq $l^{-1}$ $a^{-1}$ in south Finland (stations 1-9), and –0.30 meq $m^{-2}$ $a^{-1}$ and –0.50 µeq

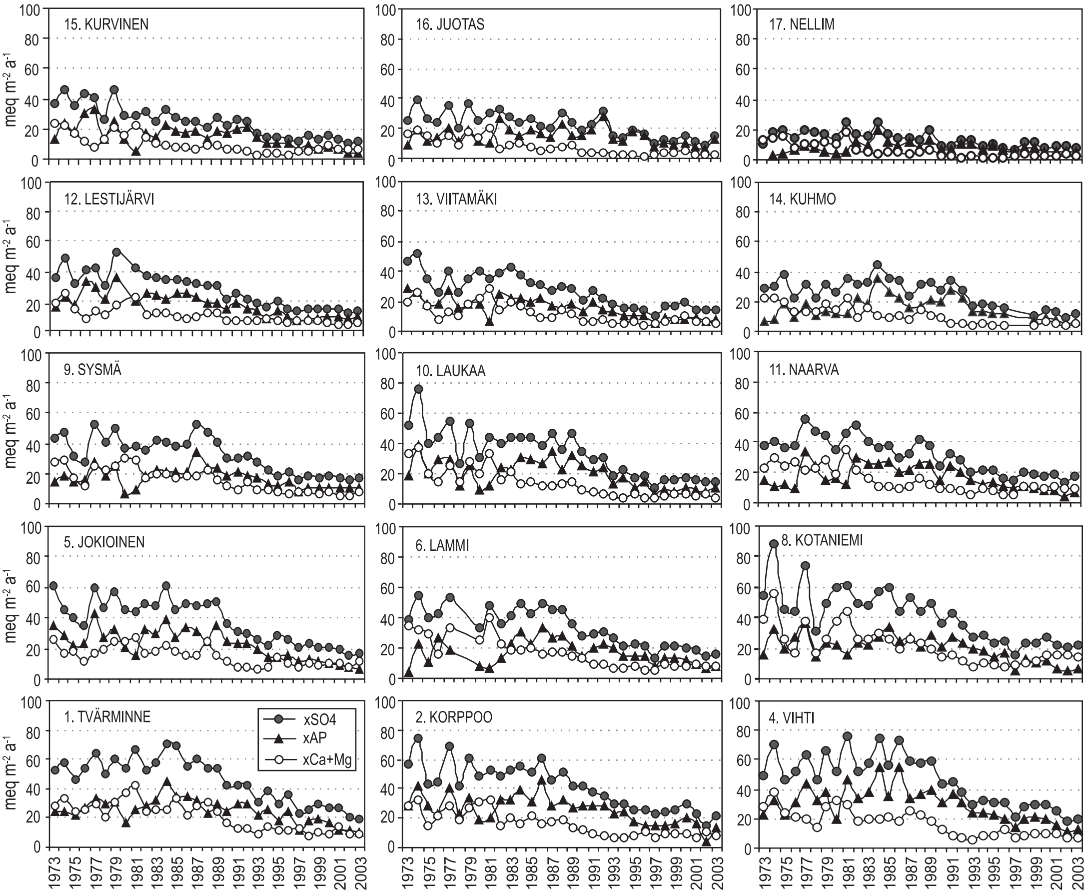

**Figure 4.** Annual bulk deposition of $xSO_4$ (●), acidifying potential $xAP=(xSO_4) - x(Ca + Mg)$ (▲), and x(Ca + Mg) (○) at monitoring stations for the period 1973-2003. The numbers of the stations refer to those in Table 4 and 5.

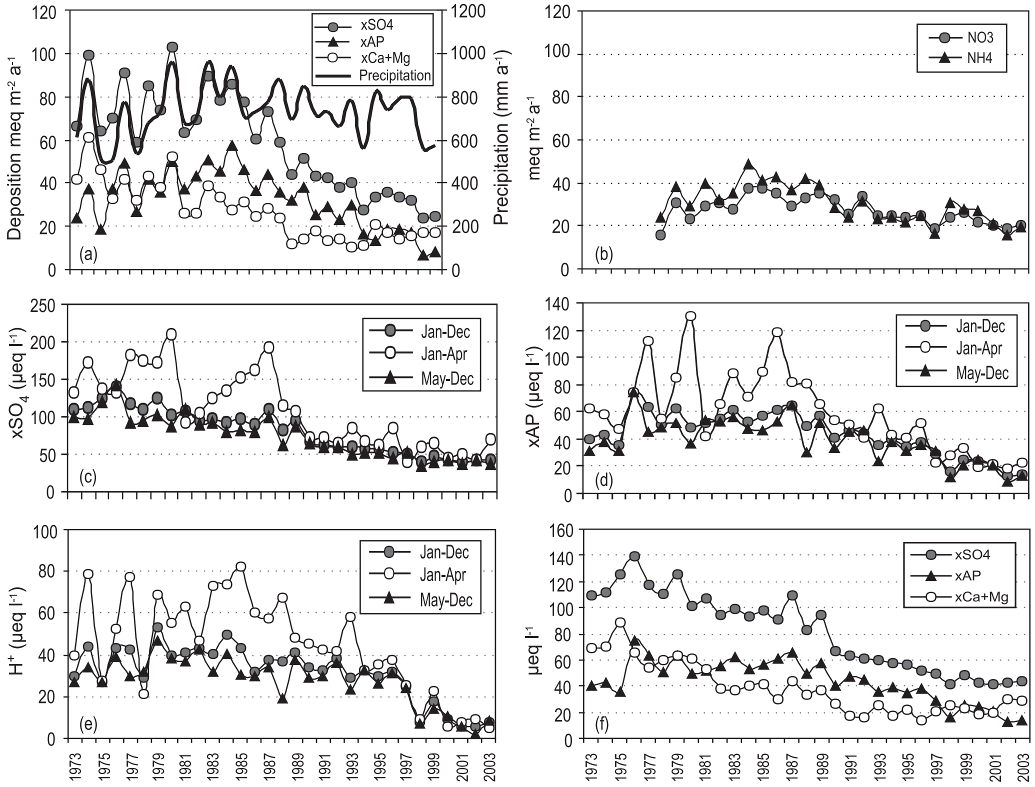

**Figure 5.** Bulk deposition at the Espoo monitoring station during the period 1973-2003 for (a) annual $xSO_4$, acidifying potential $xAP=(xSO_4) - x(Ca + Mg)$, $x(Ca + Mg)$, (b) annual $NO_3$-N and $NH_4$-N; Seasonal (c) $xSO_4$, (d) xAP and (e) $H^+$ concentrations; and (f) mean annual concentrations for $xSO_4$, xAP and x(Ca + Mg). Annual precipitation amount is shown in (a).

l$^{-1}$ a$^{-1}$ in central Finland (stations 10-15), respectively. In north Finland (stations 16 and 17) the slopes of the trend varied between –0.17 and –0.01 meq m$^{-2}$ a$^{-1}$ (deposition) and –0.45 and –0.08 µeq l$^{-1}$ a$^{-1}$ (concentrations) (Table 5). The median slope of the trend for $NH_4$-N deposition and concentrations in precipitation for the period 1986-2003 was –0.66 meq m$^{-2}$ a$^{-1}$ and –0.88 µeq l$^{-1}$ a$^{-1}$ in south Finland, and –0.47 meq m$^{-2}$ a$^{-1}$ and –0.65 µeq l$^{-1}$ a$^{-1}$ in central Finland, respectively. In north Finland (stations 16 and 17), the slopes of the trend varied between –0.04 and 0.10 meq m$^{-2}$ a$^{-1}$ (deposition) and –0.31 and 0.15 µeq l$^{-1}$ a$^{-1}$ (concentrations). The decrease in $NH_4$ concentrations and deposition loads was somewhat greater compared to $NO_3$. This trend may be influenced by a larger reduction in $NH_3$ emissions in eastern-central Europe and by reductions of sulphur dioxide. A substantial part of ammonium can be deposited as ammonium sulphate formed from the interaction of ammonia with sulphur dioxide in the atmosphere, and reduced $SO_2$ emissions may have resulted in a reduced rate of reaction of $NH_3$ to $NH_4$ and decreased co-deposition of ammonium and sulphate (De Schrijver *et al.* 1998, Horváth and Sutton 1998).

Nitrogen deposition trends in Finland parallel those of European N emissions; increasing until the late 1980s and then declining during the 1990s. At the Espoo monitoring station in southern Finland, $NO_3$ and $NH_4$ deposition has declined by 40-50% since the late 1980s (Fig. 5). However, after the culmination in the late 1980s, trends in nitrogen deposition and concentrations appeared to be levelling off from the early 1990s (Fig. 5, paper I). Statistically significant declines in N deposition in Europe during the 1990s are rare (Wright *et al.* 2001). After the largest decrease in N emissions during the period from the late 1980s to the early

1990s, the decline of N emissions has been small. N wet deposition is rather strongly influenced by variations in meteorological conditions, such as precipitation, producing large year-to-year variation in deposition. This "noise" in the record means that any decrease in N in bulk precipitation must be relatively large before deposition trends become statistically significant. This probably explains why significant trends in N deposition in Europe during the 1990s have not been detected (Wright *et al*. 2001). Ruoho-Airola *et al*. (2004) reported significant downward trends in nitrogen concentrations in precipitation in Finland during 1981-2000. During the 1990-2000 period only a few significant trends for nitrate were found, and those for ammonium were also weaker. This is interpreted as an indication of minor domestic and European emission reductions and fluctuation of the concentrations during the 1990s.

#### 3.1.2.3 Base cations

The deposition of base cations has declined since the early 1970s (Fig. 4, paper I). Between the periods 1973-1980 and 1981-1990 the mean annual deposition of non-marine base cations (xBC) declined by 10%, 18% and 26% in south, central and north Finland, respectively (paper I). xBC deposition exhibited a negative trend at about 80% of the stations in 1973-1985, but trends were rarely significant. The decline in xBC deposition, although relatively weak, is in agreement with declining particulate emissions and the decrease in deposition of base cations in large areas in Europe in the 1970s and 1980s (Hedin *et al*. 1994). Similarly, decreasing BC deposition in Finland over 1973-1988 is also reported by Laurila (1990). The median slope of the trends for all stations in 1973-1985 was –0.41 meq $m^{-2}$ $a^{-1}$ in south Finland, –0.65 meq $m^{-2}$ $a^{-1}$ in central Finland and –0.54 meq $m^{-2}$ $a^{-1}$ in north Finland.

A strong decline in xBC deposition occurred in the 1990s, with a 50-60% reduction in mean annual deposition between the periods 1981-1990 and 1991-2000. The decline for calcium was 55-68% and for magnesium was 37-63% in the different regions between the 1980s and 1990s (paper I). The median annual change over 1986-2000 was the greatest in south Finland (–0.95 meq $m^{-2}$ $a^{-1}$) compared to central (–0.77 meq $m^{-2}$ $a^{-1}$) and north (–0.47 meq $m^{-2}$ $a^{-1}$) Finland. Trends in deposition and concentrations of x(Ca + Mg) in 1986-2003 show similar declines (Table 5). The xBC decline was strongly associated with a simultaneous decline in $xSO_4$ from the late 1980s, and was equivalent to 40-60% of the concurrent $xSO_4$ deposition decline. The decline in xBC deposition was dominated by xCa. The median annual change of xCa between 1986 and 2000 accounted for 87% of xBC deposition changes in south Finland, for 64% in central Finland and for 62% in north Finland (paper I).

The decrease in xBC deposition in Finland fits the general point-source emission reductions of substances in Europe, contributing to a decline in xBC emissions and deposition along with those of other pollutants. The decrease in xBC deposition, particularly in south Finland, can also be related to major reductions of alkaline emissions from Estonia and Russia in the 1990s (Jalkanen *et al*. 2000). However, the decrease in base cation deposition in bulk deposition (paper I, Ruoho-Airola *et al*. 2003) and throughfall (Ukonmaanaho and Starr 2002) appears to be levelling out.

#### 3.1.2.4 Acidifying potential and hydrogen ion

The acidifying potential (xAP) of deposition exhibited a slight increase between the 1970s and 1980s in all three regions and 80% of the stations showed an increasing trend slope in 1973-1985, being significant ($p < 0.05$) in about 30% of the stations (paper I). The increase in xAP is due to a greater decline in x(Ca + Mg) deposition than that of $xSO_4$. The change in xAP is reflected by an increase in hydrogen ion ($H^+$) deposition, and increasing trend slopes for $H^+$ deposition were found at 80% of the stations, although rarely significant. Similarly, increasing acidity in deposition (defined as increasing AP and $H^+$) in Finland over 1973-1988 is also reported by Laurila (1990). The acidifying potential in deposition was highest during the 1980s. However, during the period 1986-2000 xAP decreased, being significant at 80% of the stations. Trends in $H^+$ showed a significant decline over the same period at all stations. During the period 1986-2003, the trends in xAP deposition and concentrations in precipitation are significantly decreasing at all stations (Table 5, Fig. 4). The decrease in xAP and $H^+$ ion deposition over the 1990s was due to a greater decrease in $SO_4$ than BCs. The mean annual xAP of deposition in the

1990s was about 40% lower in south and central Finland and 20 % lower in north Finland compared to the 1980s (paper I).

### 3.1.3 Seasonal changes in deposition

Besides long-term changes in deposition load and concentrations, there have been seasonal changes in concentrations. Mean annual seasonal concentrations of $xSO_4$, xAP and $H^+$ for the winter period (January-April) and the summer/autumn period (May-December) for the Espoo monitoring station located near Helsinki, are presented in Figure 5. The station has therefore been exposed to both local urban emissions and long-range transboundary air pollution. The concentrations of $xSO_4$ and acidity in precipitation during the winter time were clearly higher during the 1970s and 1980s compared to summer/autumn period, but this difference diminished during the 1990s.

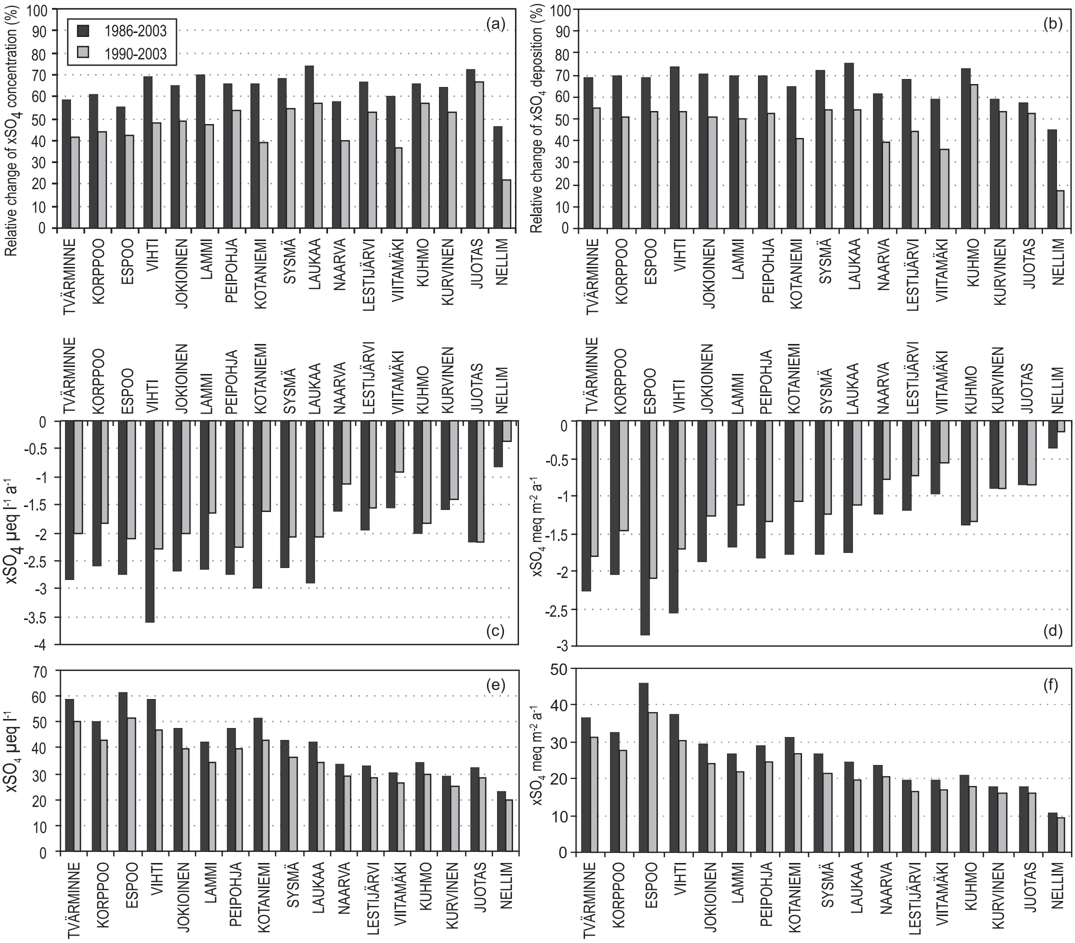

**Figure 6.** Relative change in $xSO_4$ concentrations in precipitation (a) and $xSO_4$ bulk deposition (b); annual change (Theil-Sen slope) in $xSO_4$ concentrations in precipitation (c) and $xSO_4$ bulk deposition (d); mean annual $xSO_4$ concentration in precipitation (e) and mean annual $xSO_4$ bulk deposition at monitoring stations for the periods 1986-2003 (black bars) and 1990-2003 (grey bars). The monitoring stations are sorted by latitude of station.

## 3.2 Recovery of Finnish lakes from acidification

### 3.2.1 Regional water chemistry of RMLA lakes

Finland is situated in north Europe and spans ten degrees of latitude (from 60ºN to 70ºN) resulting in wide environmental gradients, particularly in atmospheric deposition. This has contributed to geographical gradients in concentrations of major ions in small headwater lakes along with gradients in deposition chemistry. Lake water sulphate concentrations are the greatest in south Finland and decrease gradually towards the north (Fig. 7 and 9a). Base cation concentrations are also higher in south Finland. This pattern reflects the deposition pattern, but a significant cause of this gradient, however, is probably due to the more intense weathering and ion-exchange from the thicker and better buffered soils in south Finland (Kämäri *et al*. 1991). Greater sulphate deposition in the south also increases leaching of BC in runoff (e.g. Kortelainen *et al*. 1989).

Since the RMLA lakes have been selected from a population of acid lakes, Gran alkalinity and pH exhibit only small differences between the regions. Nevertheless, the charge-balance ANC ($ANC_{CB}$) is somewhat higher in central Finland due to higher base cation to sulphate ratios. $ANC_{CB}$ is an alternative chemical measure to describe the acid-base status and buffering capacity of water (Reuss and Johnson 1986), and is defined as the equivalent sum of base cations minus the equivalent sum of strong mineral acid anions: $(Ca + Mg + Na + K) - (SO_4 + NO_3 + Cl)$. In north Finland, ion concentrations in lakes are low, particularly that of BC, contributing to low $ANC_{CB}$ and alkalinity. The low ionic strength of the lake water is due to both low loads of air pollution and low weathering rate of the minerals due to cold climate and acidic geochemical characteristics of the bedrock. Inherently acid-sensitive catchments with low buffering capacity are characteristic of many parts of Finnish Lapland (Kähkönen 1996). Labile aluminium concentrations ($Al_{lab}$) are highest in south Finland but elevated concentrations are also found in lakes in central Finland (Table 6, Fig. 7, paper V). Lake water nitrate concentrations were low in comparison to those in other Nordic countries and Central Europe (Skjelkvåle *et al*., 2001b). During the autumn overturn in the dormant season, 90% of the lakes in all regions have median $NO_3$-N concentration < 2 µeq $l^{-1}$ (< 28 µg $l^{-1}$). Nitrate concentrations were lowest in north Finland. TOC concentrations are the highest in the lakes of central Finland, where proportion of peatlands in the catchments is the highest (Table 6). Although the proportion of peatlands in the catchment area in north Finland is also high, TOC concentrations are low compared to central Finland. The colder climate and consequently longer soil frost period, lower primary production and decomposition, coupled with thinner soil and peat deposits are likely to result in lower levels organic carbon leaching to the lakes (Kortelainen 1993b).

The non-marine sulphate to organic anion ratio ($xSO_4:A^-$) was > 1 in 92% of the lakes in south Finland (Fig. 2 in V, paper V), indicating that minerogenic acidity exceeds catchment-derived organic acidity due to greater sulphur deposition and lower amount of peatlands in the catchments (Table 6). Sulphate concentrations exceeded organic anion concentrations in only 30% of the lakes in central and north Finland, indicating that the sulphate deposition acidity is superimposed on a significant amount of organic acidity in these regions.

### 3.2.2 Regional trends of acidification in RMLA lakes in 1990-2003

In glaciated areas of Scandinavia, soils are generally young and thin, have a low cation exchange capacity and little retention of deposited sulphate. Sulphate is normally a “mobile anion” in glaciated terrain, i.e. nearly all sulphate in deposition is transported through the catchment (e.g. Henriksen *et al*. 1998). Surface waters in these acid-sensitive areas are poorly buffered against acid deposition and prone to rapid acidification. Conversely, when acid deposition decreases, they can be expected to show relatively fast recovery (Skjelkvåle *et al*. 2003). The reduction of sulphate deposition since the late 1980s has resulted in a clear decrease of $xSO_4$ concentrations in all types of small lakes throughout Finland. Concentrations have significantly decreased in 93% of the RMLA lakes over the period 1990-2003. Regionally, a significant decreasing trend in $xSO_4$ concentrations was detected in 98% of lakes in south Finland, 95% of lakes in central Finland and 82 % of lakes in north Finland (Fig. 8 in V). The slopes of the trend exhibit a geographical pattern, being steepest

**Table 6.** Percentiles (25, median 50 and 75%) of the catchment characteristics, concentrations and trend slopes (Theil-Sen) for the RMLA lakes in 1990-2003.

| Variable | Unit | South Finland (n=61) | | | | Central Finland (n=57) | | | | North Finland (n=39) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 25% | Median | 75% | | 25% | Median | 75% | | 25% | Median | 75% |
| Lake | ha | 6 | 15 | 31 | | 4 | 8 | 22 | | 3 | 9 | 24 |
| Catchment | ha | 53 | 89 | 248 | | 58 | 111 | 254 | | 63 | 115 | 220 |
| Catchm./Lake | | 4.7 | 6.6 | 10 | | 5.8 | 9.8 | 18.2 | | 6.1 | 10.8 | 18 |
| Exp. bedrock | % | 1 | 6 | 21 | | 0 | 0 | 1 | | 0 | 0 | 0 |
| Peatland | % | 4 | 7 | 12 | | 13 | 24 | 37 | | 6 | 22 | 43 |
| Retention time | year | 0.9 | 2.6 | 3.9 | | 0.4 | 0.9 | 1.9 | | 0.1 | 0.3 | 0.7 |
| max depth | m | 4.2 | 8.4 | 13.6 | | 4.0 | 6.8 | 9.1 | | 2 | 2 | 3.9 |
| | | | | | | | | | | | | |
| pH | | 5.40 | 5.85 | 6.20 | | 5.30 | 5.75 | 6.15 | | 5.63 | 5.90 | 6.35 |
| Alkalinity | µeq l$^{-1}$ | 9 | 25 | 53 | | 3 | 32 | 49 | | 5 | 18 | 34 |
| xBC | µeq l$^{-1}$ | 128 | 166 | 222 | | 101 | 138 | 186 | | 42 | 59 | 93 |
| $xSO_4$ | µeq l$^{-1}$ | 83 | 103 | 123 | | 34 | 43 | 64 | | 17 | 25 | 36 |
| $ANC_{CB}$ | µeq l$^{-1}$ | 32 | 65 | 96 | | 48 | 89 | 131 | | 15 | 43 | 67 |
| TOC | mg l$^{-1}$ | 4.0 | 5.4 | 9.5 | | 5.8 | 9.9 | 15.0 | | 3.8 | 5.2 | 8.1 |
| $NO_3$-N | µeq l$^{-1}$ | 0.46 | 0.79 | 1.36 | | 0.36 | 0.64 | 0.96 | | 0.36 | 0.36 | 0.43 |
| Al lab | µg l$^{-1}$ | <10 | 10 | 40 | | <10 | 10 | 20 | | <10 | <10 | 10 |
| $xSO_4 / A^-$ | | 1.3 | 2.3 | 3.9 | | 0.4 | 0.6 | 1.5 | | 0.3 | 0.5 | 1.1 |
| | | | | | | | | | | | | |
| $H^+$ | µeq l$^{-1}$ a$^{-1}$ | -0.19 | -0.05 | -0.01 | | -0.13 | -0.03 | 0.00 | | -0.04 | -0.01 | 0.00 |
| Alkalinity | µeq l$^{-1}$ a$^{-1}$ | 1.50 | 1.89 | 2.75 | | 0.44 | 1.00 | 1.75 | | 0.79 | 1.05 | 1.50 |
| xBC | µeq l$^{-1}$ a$^{-1}$ | -1.99 | -0.97 | -0.40 | | -1.50 | -0.63 | 0.14 | | -1.41 | -0.74 | -0.06 |
| $xSO_4$ | µeq l$^{-1}$ a$^{-1}$ | -5.54 | -4.12 | -2.79 | | -2.39 | -1.80 | -1.53 | | -1.79 | -1.42 | -0.85 |
| $ANC_{CB}$ | µeq l$^{-1}$ a$^{-1}$ | 1.57 | 2.44 | 4.04 | | 0.33 | 1.10 | 2.12 | | 0.05 | 0.65 | 1.12 |
| TOC | mg l$^{-1}$ a$^{-1}$ | 0.00 | 0.04 | 0.11 | | -0.08 | 0.00 | 0.05 | | -0.08 | 0.02 | 0.08 |

for lakes in south Finland having highest initial $xSO_4$ concentrations, and decreasing gradually towards the north with decreasing concentration levels (Fig. 9a-b, Table 6). The median slope for $xSO_4$ is –4.1 µeq l$^{-1}$ a$^{-1}$ in south Finland, –1.8 µeq l$^{-1}$ a$^{-1}$ in central Finland and –1.4 µeq l$^{-1}$ a$^{-1}$ in north Finland. This pattern is to a large extent due to the S deposition pattern (Fig. 6c-f). The slope of the trend in lake $xSO_4$ concentrations is steeper than that in bulk precipitation particularly in south Finland. This may be because the absolute decline in the total deposition (wet + dry) of sulphur has been larger than that of bulk deposition, and the decline in total S deposition has been the greatest in south. In addition to the pattern of sulphate deposition, soil modifies the leaching of sulphate to runoff and lake water. The catchments in south have less peatlands and more mineral soils, and retention of deposited sulphate may therefore be lower in these catchments. Sulphate retention can be quantitatively important in peatlands and in catchments with peaty soils (Forsius *et al.* 1995), and a high proportion of peatland in the catchment can contribute to lower concentrations of sulphate and lower rate of decline in lake concentrations (paper IV). Within all regions, $xSO_4$ concentrations in lakes correlate negatively and significantly ($p < 0.05$) with the proportion of peatland and with lake water TOC concentrations, indicating retention by peat soils. However, both the proportion of peatland and TOC concentrations correlate poorly with the trend slopes of lake water $xSO_4$ within all regions and, in general,

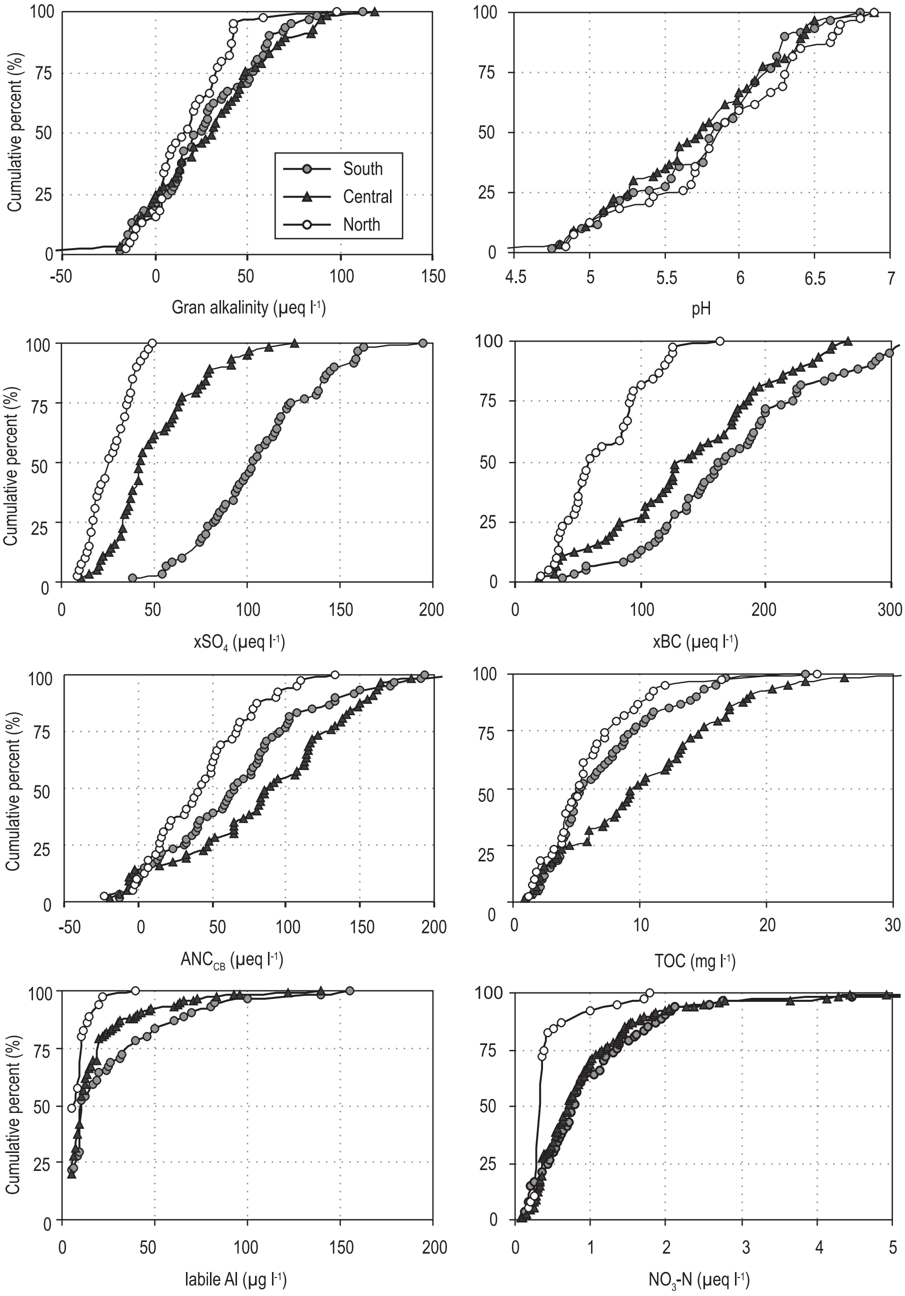

**Figure 7.** Cumulative percent distribution for Gran alkalinity, pH, $xSO_4$, xBC, $ANC_{CB}$, TOC, labile Al and $NO_3$-N concentrations in lakes in south (•), central (▲) and north (○) Finland. The values are medians for the period 1990-2003 (from paper V, except labile Al and $NO_3$-N).

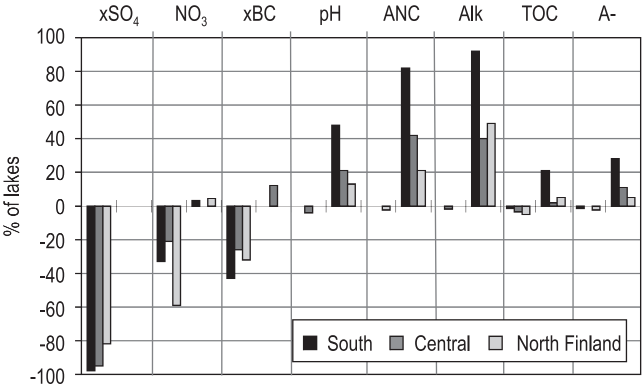

**Figure 8.** Percent of RMLA lakes (n=157) in south, central and north Finland showing significant increasing or decreasing trends (Kendall-τ, $p < 0.05$) of key water quality variables for the period 1990-2003 (from paper V).

the effect of peat soils for buffering sulphate trends can be considered to be less significant in RMLA lakes. Water retention time in RMLA lakes in south Finland is longer than in lakes in other regions (Table 6). Longer retention time may enable in-lake processes, and this may has influenced the biogeochemical processes contributing to steeper decline of sulphate in lakes in south.

Lake acidification monitoring programme have generally sort to establish a relationship between trends in sulphate deposition and trends in sulphate concentrations in surface waters. However, it is difficult to compare absolute changes in $xSO_4$ concentrations in surface waters and bulk deposition because of dry deposition and evaporative concentration resulting in higher $SO_4$ concentrations in surface waters than in precipitation (Skjelkvåle *et al.* 2005, paper II). Assuming that dry deposition has declined proportionally at the same rate as bulk (wet) deposition (see Section 1.4.1) and that no changes in rates of evaporation have occurred over time, the percent change in $SO_4$ in surface waters and precipitation, however, should be relatively similar. The mean relative decrease in sulphate concentrations in lakes between 1990-2003 was 41% (range 18-76%) in south Finland, 43% (range 10-101%) in central Finland and 51% (range 15-92%) in north Finland (Fig. 9a and c). There is a relatively good correlation between percentage change and concentration level in lakes such that lakes with the highest $SO_4$ concentrations show the lowest percentage change and lakes with lowest $SO_4$ concentrations show the highest percentage change. In general, the percentage change in lake water $xSO_4$ increases from south to north (Fig. 9a). The relative decline in lake water $xSO_4$ concentrations is, on an average, rather similar to the relative decline in $xSO_4$ deposition. With some exceptions in the north Finland, the percentage change in both bulk precipitation and deposition during 1990-2003 varied between 40-60% (Fig. 6b). However, about 40-50% of the lakes in south and central Finland and 25% of lakes in north Finland have experienced a percentage decline in $xSO_4$ concentrations less than 40% (a minimum level in relative decrease of deposition) (Fig. 9c). This pattern in lakes can be explained by gradients of initial concentration levels, but it may also be related to a lagged response in the most affected areas in south Finland and in parts of central Finland. This may reflect the desorption of sulphur (or sulphur mineralization from organic soils) that had accumulated in the soil over the past century due to atmospheric deposition, thereby decreasing the rate of decline in lake sulphate concentrations. The high number of lakes showing statistically significant decline in sulphate concentrations (and high increase of buffering capacity), however, suggest that the decline in the lake water $SO_4$ concentrations has not essentially decreased due to sulphur desorption from the soil. Sulphate deposition and lake water $xSO_4$ concentrations both decline steeply until 1998 and then their decline slows down (Fig. 4 and 12). This could be also an indication that the $SO_4$ pattern of lakes is to a large extent driven by very recent depositional processes.

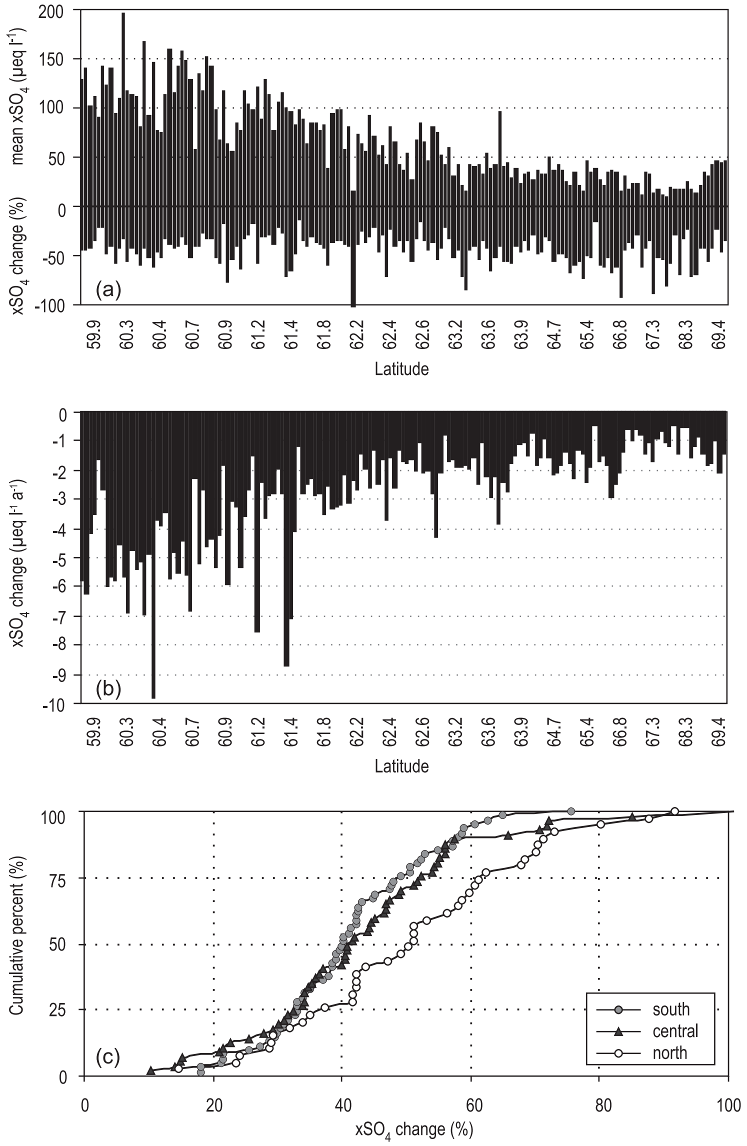

**Figure 9.** Mean annual concentrations of (a) $xSO_4$ (positive y-axis) and relative change of $xSO_4$ concentrations (negative y-axis), and (b) annual change (Theil-Sen slope) of $xSO_4$ in RMLA lakes for the period 1990-2003 by latitude of lake. Cumulative percent distributions for relative change of $xSO_4$ concentrations in 1990-2003 in lakes in south (•), central (▲) and north (○) Finland are shown in (c).

The trend slopes in lake water xBC concentrations were decreasing for most lakes, but to a lesser extent than those of sulphate and some lakes exhibited even a significant increase in xBC concentrations (Fig. 8 and 10 in paper V). Over the period 1990-2003 xBC concentrations have been decreasing in about 80% of the lakes, but only in 10% of the lakes was the decline in xBC concentrations steeper than that of $xSO_4$. A statistically significant decreasing trend in xBC concentrations was found for 23 to 43% of the lakes, depending on the region (Fig. 8 in V). The decrease in xBC concentrations has been the steepest in south Finland. The median annual change in xBC concentrations was –0.97 µeq $l^{-1}$ $a^{-1}$ in south Finland, –0.63 µeq $l^{-1}$ $a^{-1}$ in central Finland and –0.74 µeq $l^{-1}$ $a^{-1}$ in north Finland. One of the expected response of catchments to decreasing runoff water sulphate is a decrease in base cation concentrations (Galloway *et al*. 1983). As sulphate anions move through the catchment, equivalent concentrations of cations, primarily base cations, are also transported. Larger loss of sulphate from the catchments in south Finland may have decreased BC pools of the watersheds (Mannio 2001b). As with sulphate deposition, the decrease in base cation deposition has been the steepest in south Finland. In both cases, the supply of base cations to the lake is reduced due to the smaller amount of mobile sulphate anion. According to Mannio (2001b), the slope of xBC concentration trend for Finnish lakes is steeper for lakes in catchments having less peatlands, more exposed bedrock and longer water retention times, characteristics which are typical for headwater lakes in south Finland (Table 6).

The less steep decline in lake water xBC concentrations compared to that of $\text{xSO}_4$ has allowed the buffering capacity to increase in lakes. The lakes in south Finland have experienced the greatest increase in alkalinity and $\text{ANC}_{\text{CB}}$ compared to those in central and north Finland. Gran alkalinity and $\text{ANC}_{\text{CB}}$ have significantly increased in 92% and 82% of the lakes in south Finland, in 40% and 42% of the lakes in central Finland and in 49% and 21% of the lakes in north Finland during 1990-2003 (Fig. 8 in paper V). The median slope for Gran alkalinity and $\text{ANC}_{\text{CB}}$ is 1.9 µeq $l^{-1}$ $a^{-1}$ and 2.4 µeq $l^{-1}$ $a^{-1}$ south Finland, 1.0 µeq $l^{-1}$ $a^{-1}$ and 1.1 µeq $l^{-1}$ $a^{-1}$ in central Finland and 1.1 µeq $l^{-1}$ $a^{-1}$ and 0.7 µeq $l^{-1}$ $a^{-1}$ in north Finland, respectively. Acidification of lakes in south Finland has mainly occurred through sulphur deposition and therefore the decrease in sulphur deposition that has taken place has directly resulted in an increase in alkalinity of the lakes. The increasing alkalinity of lakes in north Finland are not so directly related to changes in $\text{ANC}_{\text{CB}}$. The lakes in north Finland tend to be small headwater or seepage lakes with low ionic strength (xBC < 100 µeq $l^{-1}$) and have had only modest impacts from air pollutants. Variation in hydrological regimes can cause pronounced inter-annual variation in ion concentrations, causing 'noise' in time series (Skjelkvåle *et al*. 2006). For the lakes in south Finland, all the slopes of alkalinity and $\text{ANC}_{\text{CB}}$ for the 1990-2003 period were increasing. For lakes in central Finland the corresponding figures were 84% and 88%, and lakes in north Finland, 97% and 82%. This may indicate that regional-scale recovery might be a more common phenomenon than shown by the statistically significant results alone. The RMLA lakes are representative of the approximate 5100 lakes in Finland of size 4-100 ha. Based on

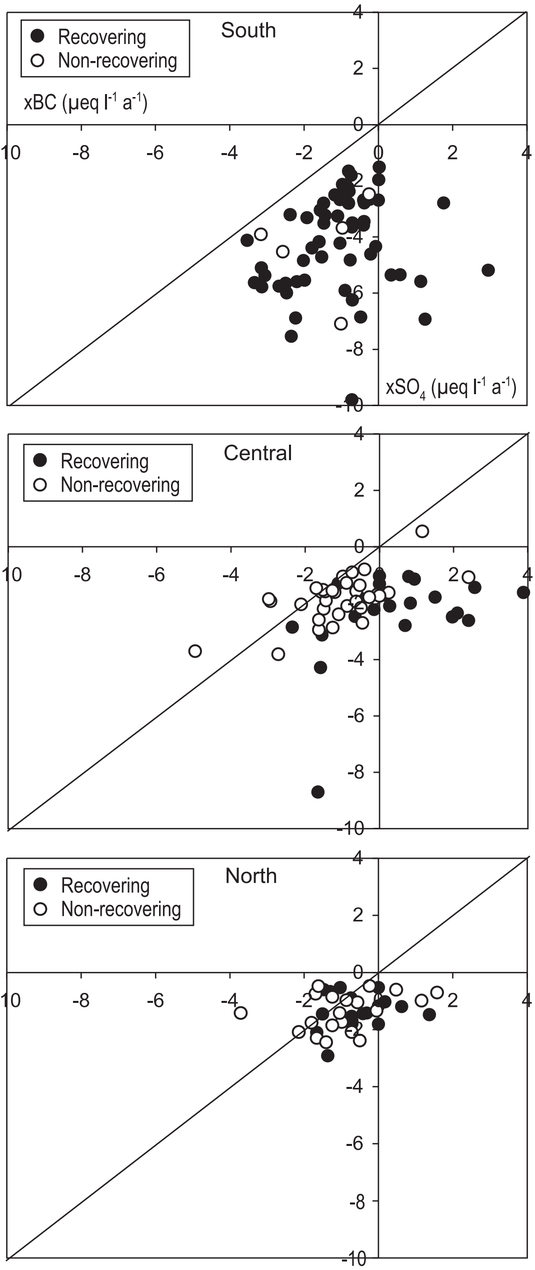

**Figure 10.** Relationships between annual change (Theil-Sen slope) of $\text{xSO}_4$ and xBC concentrations in south, central and north Finland for the period 1990-2003. Lakes with significant increase in alkalinity (• = recovering) or with no trend (○ = non-recovering) are indicated (from paper V).

the coherence of the trend slopes of the RMLA lakes one can calculate that nearly 5000 headwater lakes larger than four hectares are recovering from acidification (Mannio 2001a, paper II).

Particularly with respect to biological effects, it is of interest to evaluate how very acid-sensitive lakes, which have lost, or nearly so, their buffering capacity, are recovering. A chemical threshold value of 20 μeq $l^{-1}$ for calculated charge-balance ANC ($ANC_{CB}$) and measured alkalinity has been used to define very acid-sensitive lakes where there is potential damage of sensitive fish species (Henriksen *et al*. 1988, 1998, Tammi *et al*. 2003a, paper III). $ANC_{CB}$ is independent of the effects of variations in organic acid concentrations, and therefore can be used as an indicator of effects of acid deposition and minerogenic acidity. In humic lakes, measured Gran alkalinity is also affected by the presence of natural organic acids. A three year (1990-1992) annual average value in lake was used to describe the initial chemical conditions prior to improvement in water quality. Out of 157 RMLA lakes, 42 (18 in south, 11 in central and 13 in north Finland) were acidified to $ANC_{CB}$ <20 μeq $l^{-1}$ and 87 out of 157 lakes (33 in south, 29 in central and 25 in north Finland) were acidified to Gran alkalinity <20 μeq $l^{-1}$ in 1990-1992. Some of the lakes had $ANC_{CB}$ (n=26) and Gran alkalinity (n=43) < 0 μeq $l^{-1}$. The lakes with low $ANC_{CB}$ are predominantly clear-water lakes (mean TOC 3.5 mg $l^{-1}$ in 1990-92) whereas in lakes with low alkalinity, significant levels of organic acids may also be present (mean TOC 8.0 mg $l^{-1}$ in 1990-92). Annual average $ANC_{CB}$ and Gran alkalinity values for the period 2001-2003 have increased > 0 compared to the early 1990s in 70% and 60% of the lakes. In 31% and 38% of the lakes, $ANC_{CB}$ and Gran alkalinity has increased ≥ 20 μeq $l^{-1}$, respectively (Fig. 11). Most (about 50-80%) of the lakes where this increase has taken place are in south Finland. These results show that chemical recovery is progressing even in the most acidified lakes, but the buffering capacity of many lakes is still low and still sensitive to acidic episodes and any future increase in acid deposition.

The strengthening of alkalinity was not very clearly reflected in acidity (pH). However, the autumnal sampling strategy used in this study is not optimal to reveal changes in pH. Acidity varies during the year due to acidic snowmelt waters in spring and natural organic acid episodes during high runoff periods in autumn, and pH is also influenced by biological activity. In addition, both aluminium and organic acid buffering may delay changes in pH in most acidified systems. A significant increasing trend in pH during 1990-2003 was detected in 30% of all the lakes, and pH had significantly increased in about half of the lakes in south Finland (Fig. 8 in V). A similar significant increase in lake water pH has also been observed in southern parts of Sweden and Norway, where, in general, chemical recovery has been most strongest compared to other parts of the countries (Skjelkvåle *et al*. 2005).

Low pH is associated with high concentrations of labile aluminium, and a decrease in acidity is reflected in decreasing labile aluminium concentrations in formerly most acidic but now recovering lakes (paper V). The decrease has been substantial in south Finland, where, in some lakes, $Al_{lab}$ concentrations > 200 μg $l^{-1}$ occurred in the early 1990s. The median concentration of $Al_{lab}$ in the study lakes in 1992 was 40 μg $l^{-1}$ but 10 μg $l^{-1}$ in 2003. A subset of the most acidified RMLA lakes in south Finland have shown that elevated concentrations of $Al_{lab}$ in these lakes in 1987 (80-160 μg $l^{-1}$) have decreased in 2001-2002 to a level 20-60 μg $l^{-1}$ (paper III).

Studies in Finland have suggested that nitrate plays only a minor role in the acidity status of lakes (Mannio 2001a). From this study, there are no indications of elevated nitrate levels in forested Finnish lakes, and decreased nitrogen deposition has decreased concentrations in lakes (Paper II and V). The ratio of $NO_3$: ($NO_3$ + $xSO_4$) provides an index of the influence of $NO_3$ on chronic acidification status (Traaen and Stoddard 1995, Curtis *et al*. 2005). A value of 0.5 indicates an equal influence on surface water acidification for both $NO_3$ and $xSO_4$, while larger values would indicate a greater influence of $NO_3$. Kaste *et al*. (2007) suggested that ratio < 0.1 indicates a minor role, and 0.1-0.25 a moderate role of nitrate in the acidification. Based on annual values for the RMLA lakes in 2001-2003, the median ratio is 0.007 for lakes in south Finland, 0.01 in lakes in central Finland and 0.009 in north Finland. The 95% percentile of this ratio was 0.08 in south Finland, 0.07 in central Finland and 0.12 in north Finland. Nitrate concentrations in lakes are very much dependent on temperature-driven biological activity, and there are high inter-annual variations

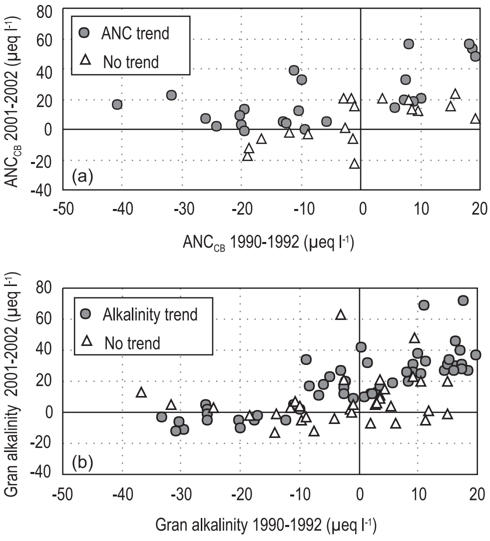

**Figure 11.** Mean annual concentration of (a) $ANC_{CB}$ for the period 1990-1992 vs. $ANC_{CB}$ for the period 2001-2003 and mean annual concentration of (b) Gran alkalinity for the period 1990-1992 vs. Gran alkalinity for the period 2001-2003. Only those lakes with mean $ANC_{CB}$ and Gran alkalinity values < 20 µeq l$^{-1}$ for the period 1990-1992 are included. Lakes with a significant increasing trend ($p < 0.05$) (•) or no trend (▵) for the period 1990-2003 are indicated.

in lake concentrations. Statistical trend analysis for nitrate using samples from autumn only is therefore sensitive to outliers. According to the Kendall-test, nitrate concentrations were significantly decreased in 20-60% of the lakes in 1990-2003 (Fig. 8 in V), and in 70-80% of the lakes decreasing trend slope was observed, depending on the region. Seasonally monitored lakes in Finland show no or decreasing trends in $NO_3$ concentrations (Forsius *et al.* 2001, Kleemola and Forsius 2006).

Although nitrogen has played a minor role in the acidification in the past, its relative importance is increasing because N emissions have decreased much less than sulphur emissions. On a molar basis, the deposition of N compounds ($NO_3$-N + $NH_4$-N) has exceeded $xSO_4$ deposition during the 1990s, and in recent years $NO_3$-N deposition in Finland has been at approximately the same level as $xSO_4$ (paper I, Fig. 5). In contrast to sulphur, nitrogen deposition is usually retained in boreal terrestrial ecosystems; typically < 10% is leached in runoff, mostly as $NO_3$. Nitrate is a strong acid anion and so can acidify soil and water like $SO_4$ (Wright *et al.* 2005). The role of nitrate as an acidifying agent may increase, when continued high nitrogen deposition may result in N-saturation of terrestrial ecosystems, and excess $NO_3$ leach to surface waters (e.g. Aber *et al.* 1989, Dise and Wright 1995, Macdonald *et al.* 2002). During the past 20-30 years, there are no signs of widespread regional increases in nitrate concentrations in sensitive freshwaters in Europe. However, nitrogen continues to accumulate in catchment soils and vegetation. N-saturation may thus require many decades to occur, at least at levels of N deposition typical for Europe (Wright *et al.* 2001). Analysis of from many sites indicate that a combination of N deposition and ecosystem enrichment, expressed by the C:N ratio of the soil organic layer, can predict nitrate leaching in European forests (e.g. Gundersen *et al.* 1998, Dise *et al.* 1998, MacDonald *et al.* 2002). A similar assessment has been done for North American catchments (Aber *et al.* 2003), indicating a link between N deposition and N status of forest ecosystems.

Empirical data from forested ecosystems in Europe show a clear relationship between N deposition and N loss (e.g. Dise and Wright 1995, Wright *et al.* 2001, MacDonald *et al.* 2002). These data indicate that very little $NO_3$ leaching occurs at N deposition below 9-10 kg ha$^{-1}$ a$^{-1}$, leaching can occur at intermediate deposition 10-25 kg ha$^{-1}$ a$^{-1}$, and significant leaching occurs at sites receiving deposition more than 25 kg ha$^{-1}$ a$^{-1}$. In southern Finland, which receives highest N deposition in the country (stations 1-4, Table 4), the long-term (1986-2003) annual average N deposition ($NO_3$ + $NH_4$) varied between 6-7 kg ha$^{-1}$ a$^{-1}$ and present deposition levels are lower than in the late 1980s. This suggest also that so far there is a little deposition-driven risk for elevated $NO_3$ leaching in Finnish forest lakes.

A regional-scale study of trends in acid-sensitive regions of Scandinavia, west-central and east-central Europe, UK and North America showed that sulphate concentrations have declined practically in all regions during the period 1990-2001 (Skjelkvåle *et al.* 2005). Base cation concentrations are also declining, but rates of decline are mostly smaller than those for $xSO_4$. This has resulted in improvement of in at least one indicator of chemical recovery: Gran alkalinity (measured), $ANC_{CB}$ (calculated) and pH. Some exceptions are UK and Ireland, and some regions in North America, where recovery has so far been limited, or even showing continuing acidification. During the period 1990-2001, the southern parts of Norway, Sweden and Finland experienced largest observed decreases in surface water $xSO_4$ (-6.8 µeq $l^{-1}$ $a^{-1}$) and strongly increasing Gran alkalinity (1.7 µeq $l^{-1}$ $a^{-1}$). Generally, the observed regional estimates for sulphate and alkalinity in southern Scandinavia are comparable to that in south Finland (Table 6).

The long-term monitoring data provide evidence that the chemical recovery of Finnish acid-sensitive lakes in the 1990s is continuing in the 2000s. A significant decreasing trend in lake water $xSO_4$ concentrations and increasing trend in alkalinity and pH occurred in 75%, 27% and 12% of the monitoring lakes during 1990-1999, respectively (paper II), whereas sulphate concentrations have significantly decreased in 93% of the lakes and alkalinity and pH had increased in 60% and 30% of the lakes by 2003, respectively (paper V). Compared to the period 1990-1999 (paper II), the decrease of the trend slopes in base cation concentrations up to 2003 had slowed down, which confirm the continued positive trends in $ANC_{CB}$ and alkalinity. Skjelkvåle *et al.* (2006) have reported chemical trends of key acidification variables for the Euro-Arctic Barents region (i.e., the northern part of Finland, Sweden, Norway and the Kola Peninsula of the Russia) for the period 1990-2004. The method for trend analysis was similar (non-parametric Mann-Kendall test) as used in this study. The analysis of 35 RMLA lakes from Finnish Lapland showed significant increase in Gran alkalinity in 70% of the lakes and significant decrease in $xSO_4$ in 86% of the lakes.

The changes of water chemistry in 6 lakes with seasonal water quality sampling during 1985-2006 are shown in Figure 12. These lakes are acid-sensitive clear-water lakes (mean TOC 1.5 –5.8 mg $l^{-1}$) and are considered to indicate the changes in acid-base status of soil and water in the anthropogenic strongly acidified headwater lake population. In most of the lakes, water chemistry has shown severe recent acidification during the 1980s, and single measurements of pH for some of these acid lakes from the late 1970s were < 5. As mentioned in Section 1.2, acidification of the lakes in south Finland accelerated in the 1960s and severe acid-induced changes in fish populations took place in the 1970s. The fish studies in 1988 showed still very deteriorated water conditions in recently acidified lakes indicated by very little changes in the populations of perch and continuing deteriorating of roach populations (Rask and Tuunainen 1990).

All the 6 lakes show relative similar pattern of recovery in water chemistry (Fig. 12). Sulphate concentrations started to decline in the early 1990s. Base cation concentrations have also declined in most lakes, but less than sulphate, and since the late 1990s concentrations of xBC (on a molar basis) are equal or slightly higher than those of $xSO_4$. This has allowed $ANC_{CB}$ and Gran alkalinity (bicarbonate) to increase. Weak acid-anion bicarbonate ($HCO_3^-$) is the most important anion buffering clear-water lakes, and its production and export in soils is expected to increase when acid deposition and leaching of sulphate decreases and soil pH increases. The decrease in sulphate concentrations has resulted in increasing pH since the late 1990s, which is correlated with decreasing labile aluminium concentrations (Fig. 12). Noteworthy has been the decrease in intensity and severity of episodic acidification during the springtime. Acidifying air pollutants accumulated in the snowpack are released in snowmelt waters causing a sharp decrease in pH and alkalinity, and increase in concentrations of toxic labile aluminium in surface waters (e.g. Davies *et al.* 1992, Wigington *et al.* 1992, 1996). Such episodes in water chemistry are detrimental to acid-sensitive aquatic biota (Baker *et al.* 1996). Although depressions in pH and alkalinity in spring flood are commonly attributed to acidic deposition effects, in remote areas with lower deposition, episodic acidification in spring can be largely related to natural conditions such as base-flow dilution and leaching of organic acids (e.g. Ivarsson and Jansson 1995, Laudon and Bishop 1999, Laudon *et al.* 1999). However, the decline of acid deposition has resulted in a decrease in anthropogenically driven springtime episodic acidification events in remote areas (Laudon and Bishop 2002, Laudon and Hemond 2002, Laudon *et al.* 2002). The depression of pH and alkalinity and increase in labile aluminium in springtime during the 1980s and in the 1990s can be detected in acidified RMLA lakes, but this episodic acidification has become less severe during the past 10 years (Fig. 12). Thus the marked decrease in acidity and $xSO_4$ concentrations in winter time deposition (Fig. 5, see Section 3.1.3) has resulted in decreases in springtime acidification peaks: increases in pH and alkalinity and decreases in labile aluminium concentrations.

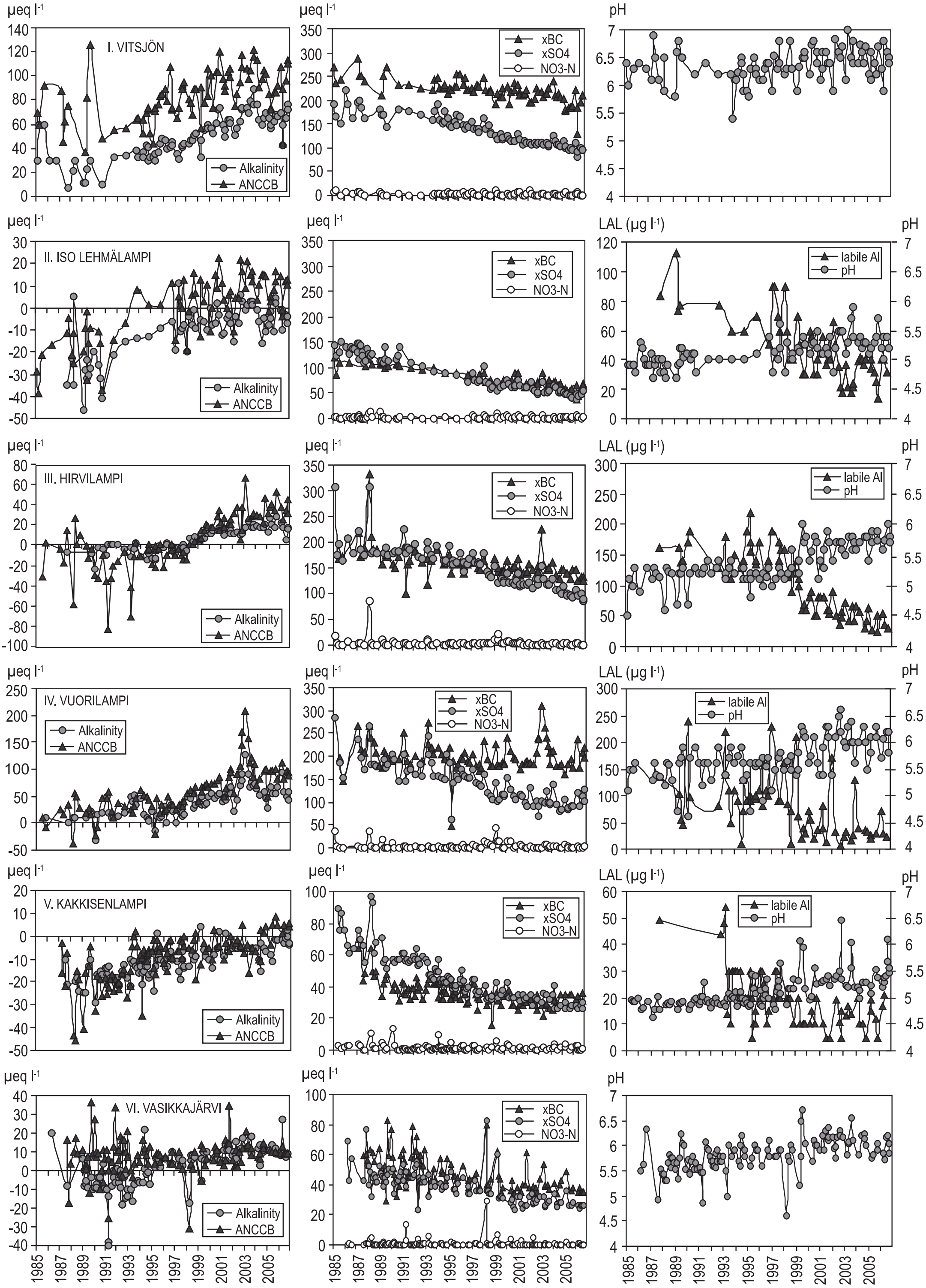

**Figure 12.** Time series of key chemical acidification parameters for 6 seasonally monitored RMLA lakes for the period 1985-2006. The lakes are chosen from seasonally monitored lake group to represent the pattern of recovery in sulphate acidified, clear-water lakes (mean TOC 1.5 – 5.8 mg l-1).

### 3.2.3 Biological responses to chemical recovery of Finnish lakes

The biological survey of 140 lakes carried out as a part of the HAPRO project between 1984-1988 showed acidification-induced effects on fish (Rask and Tuunainen 1990), macrozoobenthos (Meriläinen and Hynynen 1990) and littoral periphytic diatoms (Eloranta 1990). For fish, these effects were mainly observed in reproduction, which resulted in decreased number of young fish and declining populations dominated by old and large individuals. In extreme cases extinction was observed. Increased growth rates of perch (*Perca fluviatilis*) were observed in some highly acidic lakes where the population, and consequently, food competition declined (Raitaniemi *et al*. 1988). Sometimes the death of adult fish has been recorded (Rask and Tuunainen 1990). For benthic invertebrates, acidification induced decreases in the number of benthic species has been detected, especially in the littoral zone of lakes, whereas no significant changes in the biomass or number of animals appeared. Many acid-sensitive species, especially among the snails, mayflies and small mussels, were found, by means of which it was possible to evaluate the stage of acidification of a lake. The presence of these species was closely related to the acid peak that occurs after snowmelt (Meriläinen and Hynynen 1990). The structure and number of species of littoral periphytic diatom communities were found to differ with respect to water pH and alkalinity (Eloranta 1990). Acidophilic and acidobiontic taxa dominated in lakes with zero or negative alkalinity (and low pH), whereas in less acidified lakes the communities had higher species richness and the relative proportions of neutrophilic and alkaliphilic taxa were higher. The prevailing acidity conditions (pH) could be inferred from diatom assemblages.

The ultimate goal of reducing emissions is to enable biological recovery, including the return of sensitive species that have been eliminated during the course of acidification. According to Gunn and Sandøy (2003) "...biological recovery occurs when a number of key organisms have resumed their role in an ecological system by re-establishing a viable population". In Finnish lakes, the present trends in chemical variables that have direct toxic effects on biota (primarily pH and labile aluminium) are moving towards levels tolerable for acid-sensitive species. Similar trends are taking place for variables that ameliorate some of the toxic effects (primarily base cations, and particularly calcium). These trends suggest that biological recovery is possible or expected. The first positive biological changes in acidified Finnish lakes were detected for fish (perch populations) in the early 1990s (Nyberg *et al*. 1995, Rask *et al*. 1995b). In order to examine whether widespread chemical recovery has been accompanied by biological recovery, a project: 'recovery processes in acidified Finnish headwater lakes (REPRO)' was conducted in 2001-2003. A subset of 30 lakes from the 140 headwater lakes collected during the HAPRO project were re-sampled for chemical parameters and resurveyed for fish (paper III), macrozoobenthos (Hynynen and Meriläinen 2005) and littoral periphytic diatoms (Eloranta and Kwandrans 2005, Kwandrans 2007). For benthic invertebrates, palaeolimnological samples were also taken in order to assess whether subfossil chironomids have value in the monitoring of long-term changes in the degree of acidity in small forest lakes (Hynynen and Meriläinen 2005). The 30 study lakes are located in south and central Finland and most of them (21) belong to RMLA network and so had chemical data available in 1987 and from 1990 onwards.

The water quality showed critical acidified conditions for fish in 19 out of 30 study lakes in the late 1980s (paper III). The critical minimum limit value of alkalinity for perch (0 μeq $l^{-1}$), as given by three-year average (1987, 1990, 1991) values, did not occur in 13 of the lakes. The alkalinity level of 6 of the lakes was between 0 μeq $l^{-1}$ and the critical minimum limit value for roach, 20 μeq $l^{-1}$. The effect of low pH and consequently elevated labile aluminium concentrations is detrimental to acid-sensitive fish populations (Hultberg 1988, Rask *et al*. 1995a). As described earlier, concentrations of labile aluminium in most acidified study lakes in 1987 were 80-160 μg $l^{-1}$, the level of which fish populations are strongly affected (perch affected/extinct, roach extinct) (Rask *et al*. 1995a). By the early 2000s, alkalinity was increased in all of the study lakes, being below 0 μeq $l^{-1}$ in 6 lakes and between 0 μeq $l^{-1}$ and 20 μeq $l^{-1}$ in 5 lakes (three-year average 2000-2002 values). The labile aluminium had decreased to 20-60 μg $l^{-1}$ (paper III). The resurvey of the fish populations showed that increases in alkalinity and decreases in labile aluminium concentrations resulted in increase in the recruitment of perch. As described earlier, the concentrations of $xSO_4$ and acidity in precipitation during the wintertime (January-April) were higher during the 1970s and 1980s compared to other seasons, but these acidic episodes had mitigated during the 1990s (Fig. 5). This positive development has resulted in improvements in springtime water quality including increased pH and decreased toxic aluminium concentrations (Fig. 12), which are pre-requisite for surviving of fish eggs and larvae (Driscoll *et al*. 1980, Baker and Schofield 1982, Tuunainen *et al*. 1991). A decrease in mean weight of the sampled fish indicated an increase of the number of young and small year classes and the growth rate of perch decreased due to an increase in the population density (paper III). Recovery of the more sensitive roach has not been so evident, but a slight strengthening of the populations in less acidic lakes has taken place. In the two most acidified lakes, in which the roach populations were at a critical state during the HAPRO-sampling period, the roach populations had subsequently disappeared. The critical water conditions and increase of the perch populations may be affected the recovery patterns of roach populations in these lakes. However, some reproduction for roach has been reported in the late 1990s for some acidic lakes that were inhabited by sparse roach populations during the 1985-1995 (Nyberg *et al*. 2001).

It is interesting that clear recovery of perch populations in Finnish lakes was detected in the early 1990s, at the same time or in some cases even earlier than the measured chemical changes. Thus, other factors than a decreased acid deposition may have affected the occurrence of suitable conditions for the reproduction of perch at that time. Rask *et al*. (1995b) suggested that favourable thermal conditions, such as warm springs and growing seasons and the mild winters of 1989, 1990 and 1992, may have had a beneficial impact on the reproduction of perch. Higher temperatures during the growing season in boreal waters may produce strong year-classes and promote growth (Hokanson 1977, Koli *et al*. 1985). In addition, the autumn of 1989 was dry, resulting in low water tables in spring 1990. Permafrost was weak during that winter, allowing melting waters to percolate through soils, resulting in less acid input to the lakes in spring. The mild winters and thin snow cover in 1991 and 1992 may also have contributed to the weaker acidic pulse during the spring melt runoff.

Acid-sensitive and moderately acid-sensitive benthic invertebrate species showed a slight recovery in the formerly most acidic (pH ≤5.5) but now recovered lakes (Hynynen and Meriläinen 2005). The most significant factors correlating to the response of benthic communities were increased pH and decreased labile aluminium concentration of the lakes. The results revealed that a recovery is progressing in acid-impacted lakes, but evidently more time is needed for a distinct recovery of acid-sensitive benthic species to take place. Palaeolimnological chironomid analysis revealed structural similarity between the present and pristine chironomid assemblages. This implies that no major changes in chironomid communities of these acidic lakes have occurred during the past centuries (Hynynen and Meriläinen 2005).

Comparison of diatom-inferred lake water pH (DI-pH) between the HAPRO-period and the resurvey results clearly indicated an increase in pH and alkalinity (Kwandrans 2007). Littoral diatoms indicated the most clear positive pH-change (median increase 0.5-0.75 pH units) in the lakes in south Finland, where empirical evidence of chemical recovery has been the strongest. In central Finland both negative and positive DI-pH changes were found. Many lakes in central Finland and some lakes in south Finland did not show clear changes in diatom communities. These lakes tended to be naturally acid due to high humus concentrations and organic acidity and some had even lower pH than in the 1980s indicating the sensitivity to pH changes due to low alkalinity (low ionic strength water with high humus content and acid mineral soils). In north Finland, the acidity of some lakes was associated solely to organic acidity and no changes in diatom communities were recorded (Kwandrans 2007). Palaeolimnological studies on diatom assemblages in the north Finland have also concluded that there is no evidence of altered diatom assemblages due to acidification (Korhola *et al*. 1999, Sorvari *et al*. 2002).

Studies elsewhere in affected areas have shown that biota can respond relatively rapid to improved water quality due to reductions in S emissions, such as had occurred in the region of Sudbury, Ontario, Canada, during the 1980s (e.g. Keller *et al*. 1992). The first documented observations of recovery from acidification in surface waters due to declined S deposition in Europe were from Scottish lakes in the early 1980s, and the recovery was partly inferred by changes in diatom assemblages (Battarbee *et al*. 1988b). Biological recovery of littoral invertebrates since the mid-1980s (Warfvinge and Bertills 2000) and of perch populations in the early 1990s (Ek *et al*. 1995) were detected in Sweden. The studies from Europe and North America suggest that while biological recovery is taking place as a consequence of the improvements in water quality, there are many acid-damaged lakes with no clear biological recovery and for many sensitive species recovery may take decades (e.g. Gunn and Sandøy 2003, Skjelkvåle *et al*. 2003). Thus far in Europe, reports of biological recovery are scattered and documentation of large-scale biological recovery is limited compared to chemical recovery (e.g. Wright and Lie 2002, Skjelkvåle *et al*. 2003). The biological recovery or biological changes due to improvements in water chemistry is difficult to predict because of the complex interaction between the many physical, chemical and biological variables involved (Keller *et al*. 1999). The importance and value of integrated monitoring approach including physical, chemical and biological variables is clearly indicated (SYKE 1998, NIVA 1996).

## 3.3 Regional patterns of chemical recovery and dependence on catchment characteristics

As presented in Section 3.2.2, the regional-scale trend assessment for the period 1990-2003 showed the strongest acidification recovery of lakes in south Finland with a good correlation between trends of $xSO_4$ and alkalinity, whereas in central and north Finland this correlation in lakes was weaker. Many lakes in central and north have been exposed to modest or low load of sulphur deposition and were, therefore, expected to show less drastic recovery (alkalinity) responses. However, sulphate in both lake concentrations and deposition exhibit significant decrease in these regions. Despite lower S deposition in north Finland, many acid-sensitive lakes there were subjected to anthropogenic acidification during the 1980s, but showing now clear recovery along with decreasing S deposition (Fig. 12, Tammi *et al*. 2003b, Vuorenmaa *et al*. 2005, Lappalainen *et al*. 2007). Therefore, other factors than an acid deposition pattern may have contributed to the weaker recovery pattern in lakes in central and north Finland.

The recovery of lakes from deposition induced acidification can be expected to show different paths. In spite of declining acid deposition, a variety of factors can be involved in delaying the recovery of lakes. It is well known that in spite of declining acid deposition, depletion of base cation supply and diminished buffering capacity in damaged acid-sensitive soils may continue over many years due to chronic soil acidification. Desorption and leaching of sulphate from large soil pools built up during decades of high atmospheric deposition (e.g. Fölster *et al*. 2003), leaching of nitrogen from the N-saturated soils (e.g. Wright *et al*. 2005), and in-lake processes causing impaired in-lake buffering (Baker and Brezonik 1988) can delay recovery. Climate-related factors may also potentially confound chemical and biological recovery. Skjelkvåle *et al*. (2003) identified sea-salt episodes, in which the acidity of runoff may increase by cation-exchange of aluminium and hydrogen-ion in soil by marine Na, particularly in Atlantic regions; the drought-induced re-oxidation of previously stored (reduced) sulphur in wetlands and release of sulphate during runoff; the increased turnover of organic carbon (organic acidity); and, the increased mineralization and leaching of nitrate controlled by climatic variations.

Dry summers can lead to low groundwater table levels, and may result in re-oxidation of stored sulphur in the catchment, especially in organic layers (DeVito *et al*. 1999). Mannio (2001a) suggested that re-oxidation of S due to dry summer in 1994, and increasing summer runoff in 1995-1998 could have mobilized $SO_4$ from the catchment, and may have caused some plateau in sulphate trends in RMLA lakes in the mid-1990s. However, this mechanism, and the desorption and leaching of sulphate from soil pools (see Section 3.2.2), are considered to have played only a minor role in buffering of $SO_4$ and chemical recovery trends in RMLA lakes. Thus far, there are also little evidence of increased leaching of nitrate from soils and elevated N concentrations in Finnish acid-sensitive forest lakes (see Section 3.2.2). Based on the monitoring results of chloride in the RMLA lakes, sea-salt effect is quantitatively unimportant on changes of acidity (SYKE, unpublished data).

The headwater lakes receive most of their water via runoff and only a small portion of their water directly via precipitation. Runoff and its quality are therefore largely affected by catchment and soil characteristics. The lake water is subsequently affected by in-lake processes. In this study the role of catchment characteristics in the recovery responses of lakes is emphasized (paper V). The lakes within south, central and north Finland were divided into two group: those having a statistically significant ($p < 0.05$) increase in Gran alkalinity (recovering) during 1990-2003 and those having no significant increase (non-recovering). These two groups (recovering and non-recovering) were tested if they were significantly different in terms of catchment characteristics and other chemical parameters (paper V). Trend of Gran alkalinity is suitable measure of acidification recovery, since Gran alkalinity provides a measure of the buffering capacity of waters, and the most important anions in buffering systems of natural waters are primarily bicarbonate (carbonate system). However, Gran alkalinity in humic lakes is significantly affected by the presence of natural organic acids, but the influence of strong mineral acids is superimposed on organic acid contributions to acidity. Organic acids make humic lakes more sensitive to acid deposition than clear-water lakes, for lakes with the same base cation concentration (Brakke *et al*. 1987), and acid deposition has further decreased pH and alkalinity in many natural acid humic lakes in Finland (Kämäri *et al*. 1991).

The chemical recovery of lakes has clearly taken place in south Finland, and in only a few study lakes significant increase in alkalinity was not detected. The proportions of recovering lakes and non-recovering lakes were in south 92% and 8%, central 40% and 60% and north Finland 49% and 51%, respectively. Discriminant analysis using logistic regression allows rather unequal sample sizes, but in the case of south Finland high difference may lead to insufficient data for comparison of lake populations (paper V).

The non-recovering lakes in all three regions were found to have a lower median pH, alkalinity and in south Finland higher labile aluminium concentrations compared to recovering lakes. Using discriminant analysis (paper V) higher median TOC concentrations in south and central Finland and lower xBC concentrations in south and lower $xSO_4$ in central Finland distinguished the non-recovering lakes from recovering lake group. In north Finland higher median $xSO_4$ concentrations in non-recovering lakes best revealed differences between the two groups of lakes. For the magnitude of the trends, i.e. slopes, a discriminatory effect was found only in lakes in central Finland, associated with base cations and sulphate, with more downward trends and steeper slopes for xBC, and gentler decreases for $xSO_4$ in the non-recovering lakes. The catchment characteristic that best revealed the differences between the two groups of lakes in south and central Finland was proportions of peatland in the catchment. In south Finland, the proportion of exposed bedrock also distinguished between the lake groups. In central Finland, non-recovering lakes have also shorter median water retention time than recovering lakes. In north Finland, none of the catchment characteristics distinguished between the recovering and non-recovering lakes.

The acid-sensitive catchments in south Finland were characterized by exposed bedrock whereas occurrence of exposed bedrock in the catchments in central and north Finland was low. The non-recovering lakes in south Finland have a higher median proportion of exposed bedrock and somewhat lower lake water median xBC concentrations compared to the recovering lakes (Table 7), thus characterizing very acid-sensitive properties in these catchments with poor base cations supply and low neutralization properties. The bedrock and soil in acid-sensitive areas e.g. in south Finland are composed of granite or other acidic siliceous rocks, and overburden usually consists of thin soil layers and coarse soil types such as till, sand and gravel (Kämäri 1986, Nuotio *et al*. 1990, Huttunen *et al*. 1990). The slightly steeper median decrease in xBC concentrations may have resulted in the smaller increases in $ANC_{CB}$ in the non-recovering lakes. However, the median $ANC_{CB}$ of the non-recovering lakes was higher than that of the recovering lakes and trend slopes for $ANC_{CB}$ are increasing, being significant in 40% of the non-recovering lakes. Thus, other factors than acid-sensitive geochemical properties of landscape have also buffered the increasing trend in alkalinity.

Peatland cover was important in distinguishing the non-recovering lakes in south and central Finland, and indicated by higher median TOC concentrations. In central Finland the difference in proportion of peatland cover is clear (median 14% in recovering lakes and 32% in non-recovering lakes), whereas in south Finland percentile distributions showed very similar proportion of peatland cover in both lake groups (Table 7). The large difference in TOC concentrations between the lake groups in south Finland (median 5.3 mg $l^{-1}$ in recovering and 14.5 mg $l^{-1}$ in non-recovering lakes) suggest that it is the presence of peatland that is as important as the amount of peatland cover. Peatlands, even in catchments with low peatland coverage, are mainly located in the riparian zone of the lakes, where it can modify the runoff and lake water chemistry (Schiff *et al*. 1998).

Hydrology-induced variation in TOC/organic acids may reflect directly on alkalinity values and can suppress the recovery trend in lakes (Mannio 2001a). In the pH range 4-7, a significant fraction of organic acids can be considered strong and have a large influence on pH and alkalinity (e.g. Brakke *et al*. 1987, Munson and Gherini 1993, Kortelainen 1993a). Kortelainen (1993a) has shown that the Gran alkalinity of Finnish lakes is lowered by 5.3 µeq $l^{-1}$ for each mg $l^{-1}$ of TOC on average. On the other hand, weak organic acids buffer against strong mineral acids in acid humic lakes (e.g. Hrůska *et al*. 1999, 2003). The average buffering capacity provided by organic anions in the Finnish lakes was estimated to be 1.6-1.9 µeq $l^{-1}$ for each mg $l^{-1}$ of TOC (Kortelainen 1993a, Roila *et al*. 1994). The contribution of organic alkalinity is emphasized in high TOC lakes with relatively low pH, due to reduced or exhausted bicarbonate alkalinity in such waters. Overall, only a limited fraction of organic anions contributes to buffering capacity in Finnish lakes. The fraction of organic anions contributing to the buffering capacity represented about 16% of the median organic acidity contribution in Finnish lakes and organic carbon is more important source than a buffer of acidity (Kortelainen 1993a).

Organic acidity derived from the peatland is an important contributor to acidity in non-recovering humic lakes. In paper V, the lowering effect of strong organic acid fraction on acid-neutralizing capacity was estimated using the method described by Lydersen *et al*. (2004), in which a modified expression for $ANC_{CB}$, the strong organic acid adjusted ANC ($ANC_{OAA}$) in which permanent anionic charge from strong organic acids, is included. The level of 'original' $ANC_{CB}$, which behaves conservatively to changes in TOC concentrations (e.g. Neal *et al*. 1999), is higher, but the $ANC_{OAA}$ is lower in non-recovering lakes than in recovering lakes in south Finland. Subtracting strong organic acid adjusted ANC ($ANC_{OAA}$) from original charge-balance ANC ($ANC_{CB}$), the median difference ($ANC_{CB} – ANC_{OAA}$) is larger in non-recovering lakes than in recovering lakes in central Finland. Similarly, taking into account the acidifying effect of organic anions to the sensitivity concept in the humic waters by inclusion of $A^-$ ($xBC – A^-$), the non-recovering lakes are more susceptible to acid input than the recovering lakes (Table 7) (Forsius 1989). $ANC_{OAA}$ was better correlated with Gran alkalinity than with $ANC_{CB}$, particularly in the non-recovering lakes in central Finland, and temporal changes in alkalinity coincided well with changes in $ANC_{OAA}$. The inter-annual variation in TOC was reflected in pH and alkalinity values in non-recovering lakes in all regions. TOC concentrations in lakes showed a high increase in the early 1990s and in 1998 (and 2001 in south) when summer/autumn runoff were high (Fig. 13, paper IV), and alkalinity, pH and $ANC_{OAA}$ showed a steep decline (paper V). Nonetheless, after the TOC/organic acid surges, alkalinity tends to increase. In the non-recovering lakes, all those in south Finland, 75% in central Finland and 95% in north Finland showed an increasing trend slope in alkalinity. This may indicate that chemical recovery from anthropogenic acidification is progressing also in non-recovering lakes, but that runoff-related organic acid surges produces 'noise' within an overall recovery trend. The lakes with a decreasing trend slope of alkalinity are mostly small (median 4 ha) seepage lakes with short water retention time (median 0.4 yr), acidic conditions (median Gran alkalinity 5 µeq $l^{-1}$), high humus content (median TOC 11 mg $l^{-1}$) and a low sulphate to organic anion ratio (median 0.4). In these lakes, alkalinity

**Table 7.** Percentiles (25, median 50 and 75%) of the catchment characteristics, trend slopes (Theil-Sen) and concentrations for the recovering and non-recovering RMLA lakes (from paper V).

| Variable | Unit | South Finland (n=61) | | | | | | Central Finland (n=57) | | | | | | North Finland (n=39) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Recovering (n=56) | | | Non-recovering (n=5) | | | Recovering (n=23) | | | Non-recovering (n=34) | | | Recovering (n=19) | | | Non-recovering (n=20) | | |
| | | 25% | 50% | 75% | 25% | 50% | 75% | 25% | 50% | 75% | 25% | 50% | 75% | 25% | 50% | 75% | 25% | 50% | 75% |
| Lake | ha | 7 | 16 | 36 | 2 | 4 | 29 | 5 | 10 | 43 | 4 | 7 | 15 | 4 | 9 | 24 | 3 | 10 | 27 |
| Catchment | ha | 54 | 92 | 306 | 28 | 62 | 175 | 53 | 111 | 256 | 58 | 113 | 254 | 76 | 115 | 183 | 47 | 112 | 284 |
| Catchm./Lake | | 4.6 | 6.4 | 8.4 | 12.5 | 15.5 | 16.3 | 4.3 | 7.5 | 13 | 6.5 | 13.9 | 22 | 6.0 | 11.3 | 17 | 7.2 | 10.4 | 18.2 |
| Exp. bedrock | % | 0.5 | 5 | 16 | 10 | 29 | 30 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 |
| Peatland | % | 4 | 8 | 12 | 4 | 7 | 15 | 4 | 14 | 25 | 23 | 32 | 42 | 8 | 21 | 50 | 3 | 22 | 35 |
| Retention time | year | 1 | 3 | 4 | 0.2 | 0.9 | 1.2 | 0.6 | 1.6 | 3.5 | 0.3 | 0.8 | 1.1 | 0.1 | 0.2 | 0.7 | 0.1 | 0.3 | 0.7 |
| max depth | m | 4.3 | 8.8 | 13.7 | 2.5 | 6.0 | 12 | 5.4 | 8.5 | 10.1 | 3.4 | 5.6 | 8.6 | 2.0 | 2.0 | 3.0 | 2 | 2 | 4 |
| pH | pHunit a$^{-1}$ | 0.004 | 0.020 | 0.033 | 0.000 | 0.005 | 0.017 | 0.000 | 0.020 | 0.047 | 0.000 | 0.000 | 0.017 | 0.000 | 0.000 | 0.015 | 0.000 | 0.000 | 0.013 |
| $H^+$ | µeq l$^{-1}$ a$^{-1}$ | -0.20 | -0.05 | -0.01 | -0.19 | -0.02 | 0.00 | -0.14 | -0.05 | 0.00 | -0.13 | -0.02 | 0.00 | -0.03 | -0.02 | -0.003 | -0.14 | -0.004 | 0.000 |
| Alkalinity | µeq l$^{-1}$ a$^{-1}$ | 1.50 | 1.95 | 2.91 | 1.28 | 1.50 | 1.55 | 1.18 | 2.00 | 3.14 | -0.33 | 0.50 | 1.00 | 1.12 | 1.38 | 1.72 | 0.62 | 0.80 | 0.97 |
| xBC | µeq l$^{-1}$ a$^{-1}$ | -1.96 | -0.91 | -0.39 | -2.58 | -1.01 | -0.97 | -1.11 | 0.14 | 1.50 | -1.57 | -1.04 | -0.46 | -1.30 | -0.72 | 0.00 | -1.64 | -1.01 | -0.37 |
| $xSO_4$ | µeq l$^{-1}$ a$^{-1}$ | -5.56 | -4.14 | -2.79 | -4.52 | -3.91 | -3.68 | -2.61 | -2.00 | -1.44 | -2.16 | -1.76 | -1.53 | -1.68 | -1.44 | -0.90 | -1.97 | -1.38 | -0.80 |
| $ANC_{CB}$ | µeq l$^{-1}$ a$^{-1}$ | 1.73 | 2.62 | 4.09 | 1.48 | 1.50 | 2.41 | 1.10 | 2.32 | 4.00 | 0.15 | 0.73 | 1.40 | 0.52 | 0.90 | 1.33 | 0.00 | 0.49 | 0.82 |
| $ANC_{OAA}$ | µeq l$^{-1}$ a$^{-1}$ | 1.77 | 2.53 | 3.70 | 1.48 | 1.95 | 2.29 | 1.13 | 2.21 | 3.88 | 0.29 | 0.70 | 1.55 | 0.36 | 0.66 | 1.15 | 0.01 | 0.42 | 1.02 |
| $A^-$ | µeq l$^{-1}$ a$^{-1}$ | 0.20 | 0.51 | 1.16 | -0.44 | -0.36 | 1.50 | -0.47 | 0.36 | 0.59 | -1.04 | -0.39 | 0.35 | -0.75 | 0.35 | 0.94 | -0.56 | -0.12 | 0.34 |
| TOC | mg l$^{-1}$ a$^{-1}$ | 0.01 | 0.04 | 0.10 | -0.08 | 0.01 | 0.11 | -0.05 | 0.02 | 0.08 | -0.15 | -0.03 | 0.04 | -0.09 | 0.03 | 0.11 | -0.07 | -0.01 | 0.04 |
| pH | | 5.5 | 5.9 | 6.2 | 5.3 | 5.6 | 5.8 | 5.7 | 5.9 | 6.4 | 5.1 | 5.5 | 6.1 | 5.8 | 6.0 | 6.3 | 5.1 | 5.8 | 6.4 |
| Alkalinity | µeq l$^{-1}$ | 8 | 27 | 54 | 14 | 21 | 21 | 21 | 36 | 58 | -2 | 18 | 49 | 8 | 21 | 32 | -3 | 5 | 35 |
| xBC | µeq l$^{-1}$ | 125 | 170 | 223 | 138 | 161 | 168 | 78 | 167 | 203 | 101 | 126 | 176 | 50 | 64 | 91 | 35 | 58 | 97 |
| $xSO_4$ | µeq l$^{-1}$ | 85 | 106 | 134 | 74 | 79 | 99 | 42 | 61 | 79 | 32 | 39 | 49 | 16 | 19 | 34 | 21 | 32 | 38 |
| $ANC_{CB}$ | µeq l$^{-1}$ | 32 | 62 | 97 | 67 | 78 | 82 | 32 | 105 | 138 | 52 | 87 | 121 | 31 | 49 | 67 | 7 | 30 | 66 |
| $ANC_{OAA}$ | µeq l$^{-1}$ | 13 | 43 | 71 | 28 | 31 | 34 | 22 | 61 | 100 | 19 | 40 | 86 | 8 | 26 | 43 | -8 | 8 | 41 |
| $A^-$ | µeq l$^{-1}$ | 29 | 40 | 69 | 83 | 105 | 117 | 24 | 55 | 95 | 58 | 90 | 128 | 31 | 44 | 67 | 20 | 35 | 53 |
| TOC | mg l$^{-1}$ | 3.9 | 5.3 | 8.8 | 11 | 14.5 | 15 | 3.1 | 7.3 | 12.2 | 8.0 | 12.6 | 16.2 | 4.1 | 5.5 | 8.1 | 2.8 | 4.8 | 7.7 |
| $NO_3$-N | µeq l$^{-1}$ | 0.43 | 0.77 | 1.38 | 0.54 | 0.57 | 1.44 | 0.36 | 0.50 | 0.86 | 0.43 | 0.71 | 1.00 | 0.36 | 0.36 | 0.36 | 0.36 | 0.36 | 0.81 |
| Al lab | µg l$^{-1}$ | <10 | 10 | 40 | 24 | 25 | 32 | <10 | 10 | 20 | <10 | 10 | 20 | <10 | <10 | <10 | <10 | 10 | 11 |
| $xSO_4 / A^-$ | | 1.46 | 2.38 | 3.91 | 0.58 | 0.61 | 1.21 | 0.44 | 0.97 | 2.28 | 0.34 | 0.45 | 0.86 | 0.33 | 0.43 | 0.64 | 0.36 | 0.82 | 1.94 |
| $A^- / xBC$ | | 0.19 | 0.27 | 0.39 | 0.50 | 0.53 | 0.72 | 0.21 | 0.37 | 0.56 | 0.50 | 0.75 | 0.88 | 0.51 | 0.75 | 0.88 | 0.38 | 0.69 | 0.95 |
| $xSO_4 / xBC$ | | 0.53 | 0.63 | 0.76 | 0.46 | 0.47 | 0.60 | 0.28 | 0.37 | 0.55 | 0.24 | 0.34 | 0.41 | 0.21 | 0.30 | 0.45 | 0.27 | 0.48 | 0.79 |
| $(xBC)-(A^-)$ | µeq l$^{-1}$ | 86 | 113 | 163 | 43 | 87 | 97 | 59 | 71 | 104 | 9 | 26 | 73 | 10 | 22 | 41 | 2 | 19 | 48 |

variation and trends can be affected by such runoff-induced organic acid episodes. Davies *et al*. (1992) have reviewed several studies, that have shown that natural acidification caused by organic acid surges significantly depress surface water pH and alkalinity during high runoff events. Kortelainen and Saukkonen (1995) demonstrated in central and north Finland that organic acids dominate headwater stream acidity, and pH depression during the spring melt and autumn runoff was dominantly driven by organic acids. The important role of organic acidity in the depressions of pH and alkalinity in streams during spring floods has also reported from north Sweden (e.g. Laudon *et al*. 1999). Similarly, acid episodes caused by rainstorms and associated outwash of organic acids from forest soils can be the most important source of acidity underlying steep depressions of pH and alkalinity in late summer and autumn in streams in the central-northern Sweden (Jansson and Ivarsson 1994). A recent study of acid-sensitive lakes in the UK has indicated that the decreasing trend in acid anion concentrations was considerably larger than the decreasing trend in base cation and proton concentrations. Contrary to the expected response to net less acidity, no significant chemical recovery in terms of increasing alkalinity was found, which may be partly connected to the increase in DOC concentrations (de Wit *et al*. 2007).

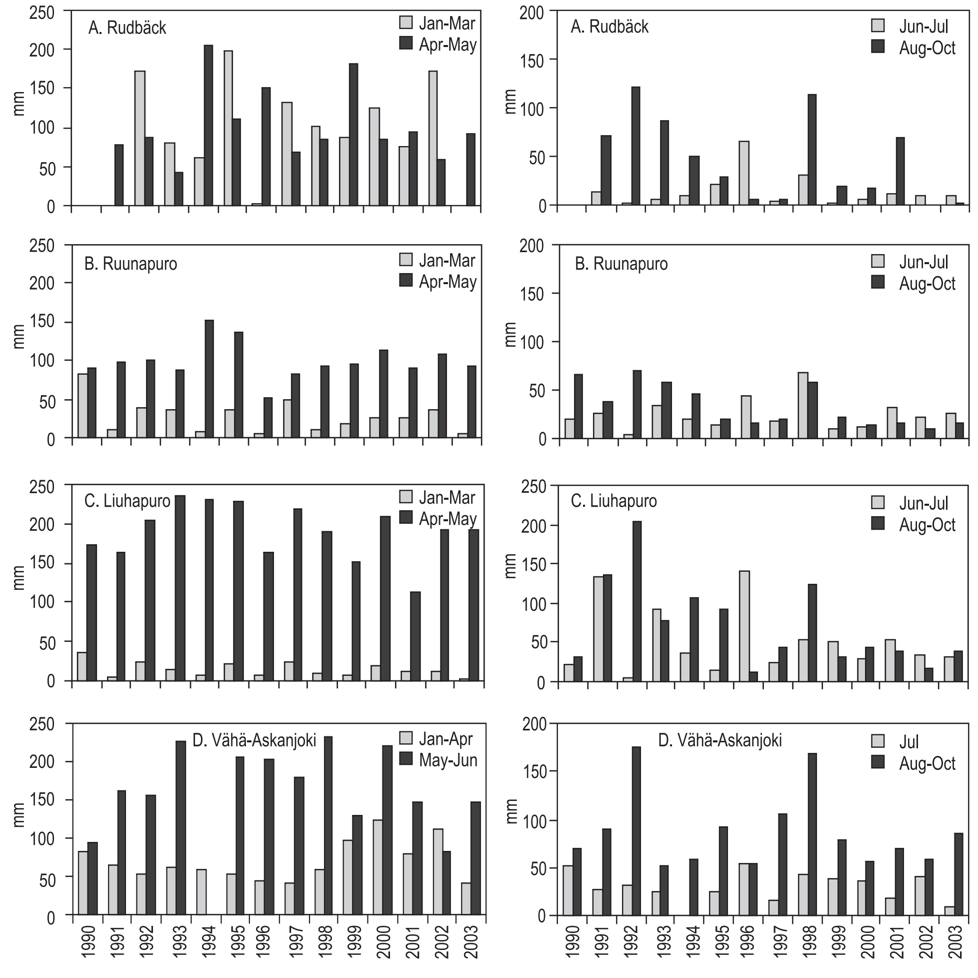

**Figure 13.** Time series for seasonal sums of runoff at runoff measurement sites A-D: winter flow (grey bars) (January – March for sites A-C, January – April for site D) and spring flow (black bars) (April – May for sites A-C and May – June for site D) in left column, summer flow (grey bars) (June – July for sites A-C and July for site D) and autumn flow (black bars) (August – October for sites A-D) in right column.

The important role of organic acidity in alkalinity pattern can be seen in the lakes in central Finland. Most of the recovering lakes are located in the southern part of the central Finland region, whereas most of the non-recovering lakes are clustered in the northern part of central Finland (Fig. 2 in V, paper V). Lakes in the southern part of central Finland exhibited both higher $xSO_4$ concentrations and steeper decline in concentrations than the lakes in the northern part, which is due to greater sulphate deposition and probably somewhat higher decline of total S deposition in southern part. The recovering lakes also have lower proportion of peatland in the catchment, and $xSO_4$ to $A^-$ ratio appeared to be higher for these lakes compared to non-recovering lakes (Table 7). Sulphate derived acidity has been more important acidifying agent in recovering lakes than in non-recovering lakes, and the decreased deposition of S has directly caused an increase in buffering capacity of recovering lakes. Sulphate-dominated recovering lakes are also found in northern part of the central region. For example, Lake Kakkisenlampi, which is acidified clear-water lake with low initial TOC concentrations (mean 1987-1993 1.8 mg $l^{-1}$) and very acid-sensitive chemical properties (xBC < 50 µeq $l^{-1}$), shows a clear recovery responses along with decreasing $xSO_4$ concentrations (Fig. 12, paper IV). The non-recovering lakes, which are clustered mostly in the northern part, have more peatland cover in their catchments and a higher contribution of organic acids to the acid-base status and acidity. They were also somewhat more acidic compared to recovering lakes, and sensitive to runoff-induced organic acid surges. Forest ditching and draining of peatlands have been common in central Finland, and had been carried out in 65% of the study catchments there, and in 82% of the catchments in the non-recovering lake group (39% in the recovering lakes) (paper V). The role of ditching on organic acid surges and alkalinity patterns in RMLA lakes was not studied in this study. In general, the channelization may intensify the water flow and organic acid pulses during rainfalls.

The leaching of organic acidity is also important to the acidity of low-ionic strength and poorly buffered lakes in north Finland (Kähkönen 1996). Non-recovering lakes are found scattered in the region, and vulnerability to acidification varies greatly, even between neighbouring catchments (Fig. 2 in V, paper V). In very low ionic strength lakes, high precipitation and discharge may dilute runoff and lake water, but also increase the export of organic acidity from peatlands to the lakes, and resulting in the variation in changes in acid-base status and buffering capacity observed. The ANC estimates suggest a large drop in buffering capacity of non-recovering lakes when organic acidity is included ($ANC_{OAA}$) (Table 7). However, the proportion of peatland cover was similar between the non-recovering and recovering lake groups, and TOC concentrations are similar in both lake groups. $xSO_4$ concentrations were higher and decline in xBC concentrations steeper in the non-recovering lake group, and these lakes have lower $ANC_{CB}$ values (Table 7, paper V). The area of peatland, based on topographic maps, may not be the best measure of the effect organic soils in the catchment. The influence of mineral soils with acid-sensitive characteristics i.e. probably lower BC supplies may therefore be more important in the non-recovering lakes than expected on the basis of peatland area estimates.

Lake water retention time distinguished between the recovering and non-recovering lakes only in central Finland. In the non-recovering lakes water retention time was low (median < 1 yr) due to lower depth, water volume and higher runoff in the northern part of central Finland (Table 7, paper V). Longer reaction time between runoff water and soil, and longer water retention time are considered to favour recovery from acidification (Baker and Brezonik 1988, Nuotio *et al*. 1990, Schindler *et al*. 1996), whereas in conditions of high discharge and short retention time in the catchment, runoff water can be more diluted and less buffered. The water chemistry in shallow scour lakes draining large, boggy watersheds can be largely affected by runoff induced dilution (Clair 1992). Also in-lake generation of alkalinity is less in lakes having short water retention time (Baker and Brezonik 1988).

While organic acid surges result in short-term fluctuations in alkalinity, it is the pool of base cations in the soil and the trend in base cations flow that determine the long-term development in alkalinity. The magnitude of the trend in xBC concentrations did distinguish between the recovering and non-recovering lake groups in central Finland. In most of the recovering lakes, xBC concentrations are slightly increasing (Fig. 10 in V), suggesting a good buffering capacity of soils in the catchments and they have not been subjected to strong acidification. In addition, the decline in xBC deposition that levelled off over the 1990s, may have contributed to positive lake water xBC pattern. A significant increase in $ANC_{CB}$ was detected in 80% of the recovering lakes. In contrast, the median xBC concentrations were lower in the non-recovering lakes than in the recovering lakes (Table 7), and the decreases in concentrations in the non-recovering lakes were more steeper over the study period, and little change in $ANC_{CB}$ are observed. A significant increase in $ANC_{CB}$ was found in 20% of the non-recovering lakes. Base cation deposition decreases towards the north (Table 4, paper I), but the decrease in BC deposition also becomes gentler moving northwards (Ruoho-Airola *et al.* 2003). It is expected that the supply of base cations to the lake is reduced due to the decrease of sulphate in runoff, but acid-sensitive catchment characteristics may have caused xBC concentrations not to increase in the same way as in the recovering lakes. The location of the non-recovering lakes coincides well with the areas identified as acid-sensitive based on geochemical properties of bedrock and soil, runoff and relief (Kämäri 1986, Lahermo *et al.* 1996) and BC weathering rates (Johansson and Tarvainen 1997). These characteristics may have largely defined the low inherent supplies of base cations resulted in lower lake water xBC concentrations and steeper downward trends for xBC in these lakes.

The proportion of peatland in the catchment may also have controlled the leaching of base cations in central Finland. Finér *et al.* (2004) studied BC export on 40 unmanaged forested catchments throughout Finland, and concluded that the concentrations and export of BC in streams flowing out from catchments with more fertile forest site types were higher than those from less fertile ones, which had more mires and their topography was flat. The catchments with high proportion of peatland retain base cations and sulphate more effectively than mineral soils (Kortelainen and Saukkonen 1995).

## 3.4 Increased organic carbon concentrations in surface waters

### 3.4.1 Trends of total organic carbon (TOC) concentrations in remote Finnish lakes

In this study (paper IV), increasing trends in total organic carbon (TOC) concentrations in remote Finnish lakes are indicated. TOC trends in 13 of the seasonally monitored acid-sensitive forest lakes throughout the Finland, with minimal direct human impact in their catchment, were analysed over the period 1987-2003. A significant increasing trend was found in 10 of the lakes, and 12 of the lakes showed a significant increase in organic anion concentrations. In most of the lakes, the trends were highly significant ($p < 0.001$). Examples of the time-series in TOC concentrations and chemical oxygen demand ($COD_{Mn}$) (indicative of the mass of humus material present) for an acidified lake in south Finland (Vuorilampi) and in central-eastern Finland (Kakkisenlampi), in which the increase in $TOC/COD_{Mn}$ during the past 10-15 years has been one of the strongest are presented in Figure 14. Studies for organic carbon have been mostly connected to dissolved organic carbon, but DOC in Finnish surface waters constitutes 94% of TOC on average, and therefore TOC values can be considered to be essentially equivalent to DOC (Mattsson *et al.* 2005). Based on the records of autumn samples only, increasing trend slopes for TOC and organic anions were found in 85% of the lakes in south Finland, and were significant in 21% (TOC) and 28% ($A^-$) of the lakes (paper V). For the central and north Finland regions, increasing trend slopes for TOC concentrations were found for 50-60% of the lakes, but the trends were rarely significant. But it has to be remembered that the sampling is only once a year (autumn), which may not be optimal measure for detecting long-term trends in organic carbon because the effect of other seasons on potential trends ( e.g. high-flow springs) is omitted.

Increasing trends in TOC or organic anion concentrations were detected in different types of acid-sensitive lakes/catchments, in both clear-water lakes and humic lakes, in lakes with different catchment and surface areas and in lakes with different water retention times (paper IV). Water retention time is known to govern in-lake processes and DOC retention in lakes (Curtis and

Schindler 1997, Schindler *et al.* 1992, 1997). These catchment characteristics significantly affect TOC concentrations in Finnish lakes (Kortelainen 1993b, Rantakari *et al.* 2004). There were indications that the largest annual increases in TOC concentrations have occurred in lakes with the largest initial concentrations. This pattern is repeated in several studies, suggesting that magnitude of TOC or DOC trends generally increase with increasing proportion of peatland/organic carbon stores in the catchment (Worrall *et al.* 2004, Evans *et al.* 2005, Monteith *et al.* 2007b). Evans *et al.* (2005) argued that the strong positive correlation between the rate in annual DOC increase and initial DOC concentrations found in UK surface waters implies similar proportional increases between the sites across the country, which may indicate a driving mechanism operating consistently at the same spatial scale. Although the number of lakes in this study (paper IV) is small, the fairly coherent trend in TOC concentrations shown by almost all catchments indicates a large-scale causal factor.

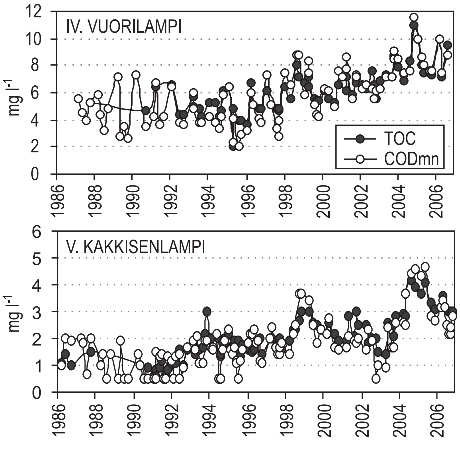

**Figure 14.** Time series of total organic carbon (TOC) and chemical oxygen demand ($COD_{Mn}$) in two seasonally monitored RMLA lakes for the period 1986-2006.

### 3.4.2 The effect of runoff on TOC trends

The leaching of organic matter is strongly dependent on hydrological and meteorological conditions and fluctuations in temperature and runoff may largely modify the decomposition and release of organic carbon from soils to the water courses, also in Finnish conditions (e.g. Holmberg *et al.* 2006). Therefore the trends in monthly and annual runoff in the studied regions were analysed. Although there was high inter-annual differences in total annual and seasonal flows, there was little evidence of a consistent overall increase in the volume of discharge in studied areas over the time span covered by TOC concentration increase (paper IV). Neither runoff nor air temperature did explain the variation in TOC concentrations and neither annual nor monthly temperatures over the period 1987-2003 showed any temporal trends. Monteith *et al.* (2007a) in an assessment of over 500 lakes and rivers throughout Europe and North America did not find any correlation between regional patterns of temperature and DOC trends. Finnish studies found no evidence of a consistent trend in water discharge during the past 20 years (Hyvärinen 2003, Räike *et al.* 2003, Granlund *et al.* 2005). The observed long-term increases in TOC concentrations (paper IV) cannot therefore be driven by long-term changes in runoff. However, a more complex relationship between TOC leaching and runoff is not excluded. For example, following the dry years 1996 and 1997 there was an apparent increase in TOC concentrations in most lakes in 1998 with very high summer and autumn runoff. Elevated TOC concentrations persisted into the early 2000s despite lower runoff. Watts *et al.* (2001) have noted enhanced levels of water color after droughts, and recovery of color levels from these episodes may persist for several years. Further work is required to elucidate the role of hydrological conditions and temperature patterns on TOC trends.

### 3.4.3 The effect of decreased acid deposition on TOC trends

Several studies have proposed that the observed increase in surface water DOC concentrations observed throughout Europe and North America is related to the decline in sulphur deposition and, in some Atlantic regions, changes in sea-salt deposition (Stoddard *et al.* 2003, Evans *et al.* 2005, Evans *et al.* 2006, Monteith *et al.* 2007a). In this study, decreasing S deposition, associated mineral acid input and improved acid-base status of the soil appear to be driving the mobilisation of TOC observed in Finnish acid-sensitive lakes. Thus inverse relationship between the annual change in TOC (and organic anion) concentrations and $xSO_4$

concentrations in lakes is found (paper IV); the larger the initial $xSO_4$ concentrations (probably in lakes exposed to highest S deposition), the larger the decrease in $xSO_4$ and the increase in TOC concentrations per year. However, this pattern is not so clear in those catchments having a high peatland cover and strong retention of sulphate. A positive and slightly stronger correlation was detected between changes in TOC (and organic anion) concentrations and $ANC_{CB}$ changes. Although changes in sulphate have been incorporated into the $ANC_{CB}$ model, a better correlation with $ANC_{CB}$ than with $xSO_4$ may suggest that changed acid-base status in soils better explains the TOC increase than the changes of sulphate alone (Fig. 15, paper IV). The correlations of TOC (and organic anion) concentrations with those of pH, alkalinity, $xSO_4$ and $ANC_{CB}$ were the strongest in the acidified lakes, but which now show clear changes in these variables. Monteith *et al.* (2007a) found that the response of DOC to changing acid anion ($SO_4$ and Cl) concentrations has been the greatest in the most acid-sensitive systems, and concluded, through an appraisal of different drivers, that changes in the chemistry of atmospheric deposition provide the only regionally consistent explanation for widespread upward trends in surface water DOC concentrations.

Atmospheric deposition can affect the release of DOC from soils through at least two mechanisms: by changing the pH of soil, and by changing the ionic strength of the soil solution. Elevated acid deposition decreases the pH in base-poor soil, which decreases the solubility of DOC and leading to a decrease in organic acids in soil and surface waters. But when the strong acid input is reduced, the pH of the soil and solubility of DOC increases and leading to a increase in organic acids (Krug and Frink 1983). Although that proposed process – inverse relationship between mineral acidity and organic acidity controlling surface water acidification – is quantitatively less important than originally predicted by Krug and Frink (1983), DOC solubility has been linked to pH in a number of laboratory (de Wit *et al.* 2001, Clarke *et al.* 2006) and field (Vogt *et al.* 1994) studies. Secondly, a number of studies have shown that increasing the ionic strength of the soil solution reduces the rate of DOC release from the soil (Tipping and Hurley 1988, Evans Jr *et al.* 1988, Vance and David 1989).

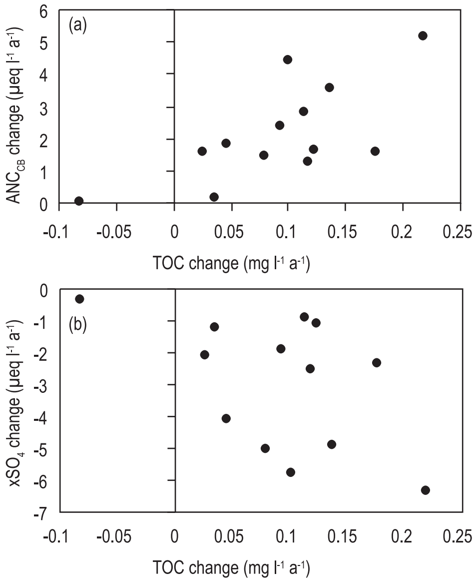

**Figure 15.** Relationship between annual change (Theil-Sen slope) in lake water TOC and (a) trend slope in lake water $ANC_{CB}$ and (b) trend slope in lake water $xSO_4$ in 13 seasonally monitored RMLA lakes for the period 1987-2003 (from paper IV).

Decreasing atmospheric deposition reduces ionic strength of the soil solution and thereby should lead to an increasing DOC release from the soil. Since decreasing atmospheric deposition reduces both soil acidity and soil solution ionic strength, it is difficult to separate the role of soil pH and ionic strength effects on DOC solubility. However, both of these mechanisms are suggested to driven mainly by decreasing sulphate deposition (Monteith *et al.* 2007a), emphasized in this study.

In addition to these two mechanisms affecting DOC concentrations/fluxes, the increase in DOC/organic anion may be related to cation-anion balance (paper IV). Based on the cation-exchange theory (Reuss and Johnson 1986), a decrease in the concentrations of strong acid anions, such as sulphate, must be compensated for either by an increase in the concentration of another anion such as organic anions or by a decrease in cation concentrations. Although base cations in recovering lakes have declined, the decrease is less than the $SO_4$ concentrations (paper V). Bicarbonate (alkalinity) concentrations have increased but are still very low or non-existent in many acid lakes that show clear increase in TOC. This implies that some proportion of the decreasing sulphate concentrations has been balanced by an increase in organic anions.

It must be pointed out that the study period 1987-2003 covers the time period when both chemical recovery from acidification and increasing trends of TOC concentrations have taken place. Therefore there is a risk that trend in any acidification parameter can, to some extent, correlate with TOC without a reliable causative relationship. The mechanisms operating in the background of regional long-term increase of DOC concentrations are still not fully understood (Roulet and Moore 2006), and more work are needed to integrate the research into pollutant and hydrometeorological impacts and elucidate the relative significance of the various drivers and complex consequences for surface waters.

## 3.5 Future scenarios for recovery from acidification

Long-term monitoring data, such used in this study, give empirical evidence as to how sensitive ecosystems have reacted to reduced inputs of acid deposition. Substantial reductions in the deposition of acidifying substances (primarily sulphur) and recovery of sensitive ecosystems have occurred in Finland and in wide areas of Europe, and following recent emission reduction agreements, these trends are likely to continue. The question arises as to how ecosystems will react to continuing declining emissions and deposition in the future. Several process-oriented dynamic models, such as MAGIC (Cosby *et al*. 1985, 2001), SAFE (Warfinge *et al*. 1993) and SMART (De Vries *et al*. 1989) have been developed and used extensively on both site-specific and regional scales to predict changes in soil and surface water chemistry. Posch *et al*. (2003) used the SMART dynamic acidification model to estimate the potential for continued recovery of the subset of 36 RMLA lakes in Finland. The study lakes were located mostly in south Finland. The model was used to simulate soil and water chemistry until 2030 under 'a current legislation scenario' resulting from implementing current European emission reduction agreements, assuming both the implementation of the 1999 Gothenburg Protocol of the LRTAP Convention as well as the NEC Directive (Schöpp *et al.* 2003). The results indicated that soil in most of the catchments would show very little change in base saturation, whereas the positive trends in lake ANC and the negative trends in lake sulphate concentrations would continue into the future, albeit at a slower pace. They also predicted that during 2010-30 all the study lakes will have reached a positive ANC, a pre-requisite for the recovery of fish populations. In a later study, Posch *et al*. (2007) used the MAGIC model to predict the response of 163 Finnish RMLA lake catchments to future acidic deposition and climatic change scenarios. Future deposition (S and N) was assumed to follow current European emission reduction policies (Cle, CAFE) and a scenario based on maximum (technologically) feasible reductions (MFR). Based on a larger and spatially more representative data set compared to earlier study (Posch *et al*. 2003), four lakes were estimated to have a negative ANC in 2030 and 28 to have ANC < 20 μeq $l^{-1}$. Simulations suggested that only the MFR emission reduction scenario would result in significant recovery of soils and surface waters from acidification, and would bring back water quality close to pre-acidification values. The MFR scenario showed significant recovery potential: ANC increased by 10.18 μeq $l^{-1}$, pH by 0.28 units and percent base saturation by 3.35 % (Posch *et al*. 2007). Wright *et al.* (2005) applied the MAGIC and SMART models to twelve acid-sensitive surface water regions in Europe. Assuming that the Gothenburg protocol and other current legislation will be implemented by 2010, as agreed, the model results indicated that recovery will continue and that by 2016 most waters will meet the threshold value of ANC > 20 μeq $l^{-1}$. However, even after complete implementation of the emission reduction agreements, acidification with commensurate adverse biological effects will continue to be a significant problem in southern Norway, southern Sweden, the Pennines in the UK, the Tatra Mountains (Slovakia), and the Italian Alps. In each of these regions more than 5 % of the lakes will not meet the ANC criterion to protect sensitive aquatic organisms.

Environmental factors other than acid deposition – so called 'confounding factors' – are expected to affect future chemical and biological recovery from acidification in freshwaters in response to reduced acid deposition (de Wit *et al*. 2007). Confounding factors are essentially related to climate change.

There is a high probability that, over the next decades, climate will change and have a large impacts on water chemistry and freshwater biology (e.g. Wright and Jenkins 2001, Skjelkvåle *et al.* 2003, Wright *et al.* 2006). Changes in temperature, precipitation and runoff pattern, and storminess can all affect surface water chemistry directly as well as indirectly through changes in vegetation and soils.

Climate change may increase the mobilization and export of DOC and organic acidity to surface waters, which in turn may delay recovery from acidification (e.g. Evans 2005, Holmberg *et al.* 2006, Wright *et al.* 2006, Posch *et al.* 2007). In a sensitivity analysis, Wright *et al.* (2006) modelled an approximately 50% increase in organic acid concentrations ramped from 2000 to 2030 due to climate change. Model trials indicated that increased DOC concentrations would be one of the important climate-induced factors affecting the chemical recovery trends of surface waters in the future. If the gradual decline in the sulphur deposition is one of the main drivers underlying the increased DOC concentrations, the progressing chemical recovery of acidified surface waters may thus be offset by increases in organic acidity.

Another of the confounding factors are the retention and loss of N and S. Predicted increases in temperature and precipitation may be expected to increase nitrate leaching to surface waters. Experiments have shown that increased temperature can accelerate mineralization rates of soil organic matter, with subsequent release of $NO_3$ to runoff (van Breemen *et al.* 1998, Wright and Jenkins 2001). Re-oxidation of reduced sulphur stored in wetlands due to climate-induced drought events and a release of sulphate upon rewetting of system have been shown to generate acidic episodes in runoff water subsequently delaying the recovery of Canadian lakes from acidification (e.g. Dillon and LaZerte 1992, Dillon *et al.* 1997, Jeffries *et al.* 2003). In the UK, large flushes of sulphate were widely observed in streams following a drought in 1995 (Harriman *et al.* 2001). Immobilization and re-mineralization of S within soil organic matter have also been shown to be important in European soils (Alewell 2001). The oxidation of stored sulphur is important also the in coastal area in western Finland, where soils contain large amounts of old marine sulphur deposits. These acid sulphate soils can release large amounts of sulphate and aluminium to the water courses due to climate-induced drought-rewetting cycles, which combined with very low pH, have resulted in deterioration of the aquatic biota including sudden fish kills in many streams (Åström *et al.* 2005). If the frequency of severe droughts will increase due to climate change, these types of sulphate flushes following droughts may continue to generate acidic episodes in the future, at least in soils where S pools are large.

Studies on remote acid-sensitive high-alpine lakes have shown that temperature effects, rather than acid deposition, appear to dominate changes in acidity and other water chemistry (Sommaruga-Wögrath *et al.* 1997, Koinig *et al.* 1998). Factors related to increasing temperature, such as enhanced weathering, decreased duration of snow and ice cover and changes in in-lake processes have a large influence on physico-chemical conditions, particularly to pH, and biota in lakes. Temperature changes may largely determine changes in pH, and potential climate warming can mitigate or even compensate for the anticipated effects of acid deposition in high-alpine lakes. However, global warming would cause additional stress to sensitive alpine ecosystems.

# 4 Conclusions

Sulphate deposition has been the major driving force in the anthropogenic acidification of lakes in Finland as well as in other acid-sensitive ecosystems in Europe. National and international efforts resulted in emission control programmes for $SO_2$. Empirical evidence based on long-term environmental monitoring programmes is essential for documenting the ecosystem benefits of costly emission reduction policies. The present work provides a regional-scale assessment of the changes in acidifying deposition in Finland over the past 30 years and the current pattern in the recovery of acid-sensitive lakes from acidification in relation to changes in sulphate deposition.

The development of sulphate deposition in Finland over the past 30 years reflects that of European sulphur emissions. Before the 1990s, reductions in $SO_2$ emissions in Europe had been relatively small and sulphate deposition showed no consistent trends. Due to international and national emission reduction measures that were then taken, sulphate deposition started to clearly decline from the late 1980s. Both the deposition load and concentrations of sulphate in precipitation have now significantly declined over the period 1986-2003, the relative decrease has been 45% in the northernmost Finland and 60-70% in south and central Finland. The decrease in sulphate deposition was the strongest during the late 1980s and early 1990s, and the decline during the 1990-2003 period was slightly lower, being 40-60% in most parts of the country. The deposition of sulphur and nitrogen from both Finland's own emissions and transboundary transported air pollution are in the south Finland highest, and it is this region that has also shown strongest emission reduction responses in deposition. The decline of sulphate deposition exceeded the decline of base cations resulting in a decrease in acidity and acidifying potential of deposition during the 1990s. Nitrogen (nitrate and ammonium) deposition has also decreased, but less than that of sulphur. Between 1988-2000 the bulk deposition of nitrogen has declined by 30-50% in south Finland, 20-50% in central Finland and 20-30% in north Finland. But most of the decline took place during the late 1980s and early 1990s and trends in nitrogen deposition and concentrations had levelled off during the 1990s. Deposition of N compounds has exceeded the sulphate deposition during the 1990s, and in the recent years nitrate deposition in Finland has been at approximately the same level as sulphate.

Sulphate concentrations in lakes throughout Finland and off all types started to decline from the early 1990s. A significant decrease over the period 1990-2003 was detected in 93% of the study lakes, and concentrations have declined by an average of 40% in south and central Finland and by 50% in north Finland. This suggests a direct response to the reductions in sulphate deposition. In general, the relative decline in lake water sulphate increases from south to north Finland. This suggests that the recovery response to reduced sulphate deposition in south Finland and in parts of central Finland was being dampened by desorption and leaching of sulphate from pools of sulphur in the soil that had built up over several decades of high atmospheric deposition. However, this is considered to have played only a minor role in buffering of $SO_4$ and chemical recovery trends in lakes. Thus far, there are no indications of elevated nitrate concentrations in Finnish headwater forest lakes. Nitrate concentrations are decreasing in most of the study lakes, and nitrate plays only a minor role as an acidifying agent in Finnish lakes.

Base cation concentrations are still declining in many lakes, especially in south Finland, but to a lesser extent than sulphate. Following a steeper decline during the 1990s, the decrease in base cation concentrations have now slowed down and is actually increasing in some lakes. The less steep decline in lake water base cation concentrations compared to that of sulphate indicates improved acid-base status of soils and has led to increased buffering capacity of the lakes. Lake water alkalinity has significantly increased by 60% of the study lakes. The increase in pH in lakes is less common than the increase in alkalinity, but pH has increased the most in most affected areas in south Finland. Accompanying the increases in pH, concentrations of labile aluminium are decreasing in the formerly most acidified lakes. Episodic acidification during spring floods has become less severe, including increases in pH and decreases in toxic aluminium concentrations in springtime water quality, which are pre-requisite for recovery of acid-sensitive biota. There is thus strong empirical evidence that chemical recovery detected in the 1990s is continuing in the 2000s.

The chemical recovery of lakes from acidification has been the strongest and most consistent in south Finland. Sulphate has been the major acidifying agent in lakes in south, and over 90% of the lakes monitored showed significant increase in alkalinity along with decreased lake sulphate concentrations. A few study lakes in south Finland, which had not experienced a significant increase in alkalinity, were characterized by acid-sensitive properties of catchments with low BC concentrations and high TOC (organic acidity) concentrations in the lake derived from surrounding peat soils. Episodic summer and autumn runoff events have produced organic acid surges to the lake delaying pH and alkalinity increase in lakes. The recovery of lakes in central Finland is not as strong and widespread as observed in south, but the pattern is similar. Chemical recovery was the strongest in lakes in which sulphate had been the major acidifying agent. Lakes showing no significant increase in alkalinity are mostly located to the north-eastern part of central Finland, and are in catchments with a high proportion of peatland, have high concentrations of TOC and organic anion had been the major acid anion in lakes. Runoff-induced surges of organic acid have been an important confounding factor suppressing the recovery of pH and alkalinity in these lakes. Non-recovering lakes are also located in areas identified as acid-sensitive based on geochemical properties of bedrock and soil. The lakes in north Finland have been exposed to the lowest deposition loads, and severity of anthropogenic acidification and subsequent recovery was not as large as further south. The role of regionally declining sulphate deposition on lake recovery was less than local factors and the spatial pattern of recovery was considerably more varied than in south and central Finland. Runoff-induced organic acid surges and dilution of ion concentrations probably account for the variation in $\mathrm{ANC_{CB}}$ and alkalinity in these low ionic strength lakes.

In summary, there is clear evidence of continuing large-scale chemical recovery of lakes from anthropogenic acidification in Finland. Increases in TOC in some lakes, related to surges in leaching, is reducing the increase in alkalinity but not preventing it. Chemical recovery is progressing even in the most acidified lakes, but the buffering capacity of many lakes is still low and still sensitive to acidic episodes and any future increase in acid deposition. Further reduction in sulphur emissions are needed for the concentration of base cations, $\mathrm{ANC_{CB}}$ and alkalinity to increase in the acid-sensitive lakes.

The chemical recovery of Finnish lakes is clearly resulting in biological recovery, the ultimate intention of emission abatement policy. Increases in pH and alkalinity, and decreases in labile aluminium concentrations towards levels tolerable for acid-sensitive species are mainly responsible for this positive development. Perch, which has good tolerance and adaptation ability, is responding to most to improved water quality conditions. For more acid-sensitive species, like roach, recovery will depend on further improvement of water conditions.

Increasing TOC concentrations, as observed in Scandinavia, UK and North America is also indicated in small forest lakes in Finland. The increase in TOC concentrations appears to be related to the recovery from acidification, i.e. decreasing sulphate deposition and improved acid-base status of the soil, rather than other proposed mechanisms such as increasing temperature and changes in runoff. However, these different factors act simultaneously and in complex ways, and the relative significance of each can be expected to vary between sites and regions. Clearly, more work is needed to elucidate the complex interactions between changing air pollution and climate change in order to determine the effect on in surface waters.

Model calculations suggest that if the 1999 Gothenburg multi-effect, multi-pollutant protocol and other current legislation will be implemented as agreed, recovery of soils and surface waters from acidification in Finland would continue, allowing widespread recovery of acid-sensitive aquatic biota. Although the decrease in acid deposition is expected to continue, environmental factors other than acid deposition are expected to affect the future chemical and biological recovery from acidification. Changes in temperature, precipitation and runoff pattern, can all affect surface water chemistry, both directly and indirectly through changes in vegetation and soils. The potential impact on the mobilization and export of DOC and organic acidity may become particularly important in Finnish conditions because of the large stores of organic matter in boreal forest soils.

Long-term environmental monitoring has evidently shown the success of international emission abatement strategies; a widespread recovery of sensitive surface waters from acidification has taken place in Europe and North America. The importance and value of integrated monitoring approach including physical, chemical and biological variables is clearly indicated, and persistent environmental monitoring is needed as a scientific basis for further actions in air pollution policy.

The effects of climate change, and potential nitrogen saturation of terrestrial ecosystems as well, will increase data requirements, and should be taken into account when assessing long-term surface water quality and developing future monitoring networks, due to more complex processes involved.

# Yhteenveto

Ilman epäpuhtauslaskeuma havaittiin vakavaksi uhaksi ympäristölle Euroopassa 1960-luvun lopussa, kun tutkijat osoittivat rikki- ja typpiyhdisteiden ilmapäästöjen aiheuttavan laaja-alaisesti maaperän ja vesistöjen happamoitumista. Keski- ja Itä-Euroopan suurilta teollisuusalueilta ilmansaasteet voivat kulkeutua ilmakehässä jopa tuhansia kilometrejä ennen laskeutumistaan maahan, ja erityisesti rikkilaskeuma on aiheuttanut järvien ja jokien happamoitumista herkissä ekosysteemeissä laajoilla alueilla Eurooppaa, varsinkin Skandinavian maissa. Rikkilaskeuma on Suomessa vakavasti happamoittanut pieniä ja karuja metsäjärviä jo 1960- ja 1970-luvuilla erityisesti Etelä-Suomessa, mutta laskeumaperäisesti happamoituneita järviä esiintyy koko maassa aina pohjoisimpia alueita myöten.

Kansainvälisten päästövähennystoimenpiteiden ansiosta rikkipäästöjen määrää Euroopassa on pystytty tehokkaasti vähentämään 1980-luvun puolivälin jälkeen. Typpiyhdisteiden päästöjä on myös pystytty alentamaan, mutta vähemmän kuin rikillä. Päästövähennykset ovat selvästi pienentäneet happaman laskeuman kuormitusta ympäristöön, mikä on ilmennyt selkeinä merkkeinä happamoitumisherkkien vesistöjen toipumiskehityksestä Suomessa sekä muualla Euroopassa 1990-luvun aikana. Ilmansaasteiden päästöjen vähentämiseksi on tehty, ja tehdään edelleen kalliita investointeja, ja vähennyksien vaikutuksia seurataan kansallisin sekä laajoin kansainvälisin ympäristön tilan seurantaohjelmin. Toimenpiteiden riittävyyden arvioimiseksi tarvitaan jatkuvaa mittauksiin perustuvaa tietoa ilmansuojelupolitiikan päätöksenteon tueksi ja jatkotoimenpiteiden ohjaamiseksi.

Tässä työssä esitetään rikki- ja typpilaskeuman kehitys Suomessa viimeisen 30 vuoden ajalta, ja arvioidaan happamoituneiden metsäjärvien kemiallista ja biologista toipumiskehitystä suhteessa laskeuman kemian muutoksiin. Laskeuman tutkimuksen aineistona oli koko maan kattava, pääosin ilman laadun seurannan tausta-alueilla toimiva laskeuman kansallinen seurantaverkko (19 mitta-usasemaa). Järvien tutkimuksen aineistona oli järvien happamoitumisen kansallinen seurantaverkko, missä tarkasteltiin vesikemian alueellisia trendejä (Etelä-, Keski- ja Pohjois-Suomi) 1990-2003 (157 järveä), yksittäisten intensiiviseurannassa olevien järvien kemiallisia muutoksia 1985-2006 (6 järveä), sekä vesikemiallisten muutosten yhteyttä kalaston biologiseen toipumiseen happamoituneissa järvissä (30 järveä). Alkaliniteetin eli veden puskurikyvyn kasvu on ollut heikkoa osassa happamoituneissa järvissä, joten tutkimuksessa lisäksi arvioitiin valuma-aluetekijöiden ja hydrologisten vaihteluiden vaikutusta toipumiskehitykseen. Orgaanisen hiilen pitoisuuksien kasvua on havaittu happamoitumisherkkien alueiden pintavesissä laajalti eri puolilla Eurooppaa ja Pohjois-Amerikkaa kuluneen parin vuosikymmenen aikana. Eräänä hypoteesina kasvutrendeihin on esitetty sulfaattilaskeuman sekä maaperän happamuuden vähentymisestä aiheutunut orgaanisen hiilen liukoisuuden kasvu maaperässä. Tässä työssä arvioidaan siten myös orgaanisen hiilen (TOC) pitoisuuksien pitkäaikaismuutoksia Suomen järvissä (13 järveä) ja pitoisuuksien mahdollisen kasvutrendin yhteyttä vähentyneeseen sulfaattilaskeumaan.

Sulfaattilaskeumassa ei esiintynyt merkittäviä muutoksia 1970- ja 1980-lukujen aikana, kunnes sulfaattipitoisuudet sadevedessä ja sulfaattilaskeuma taittuivat selvään laskuun 1980-luvun lopusta. Sulfaattilaskeuma on vähentynyt koko maassa vuodesta 1990 noin 40-60%. Typpilaskeuma (nitraatti ja ammonium) on myös vähentynyt, mutta vähennys on ollut pienempi kuin rikillä, noin 20-50%. Typpilaskeuma on ylittänyt rikkilaskeuman 1990-luvun aikana, ja viime vuosina nitraattilaskeuma on ollut samansuuruinen sulfaattilaskeuman kanssa. Emäskationien (Ca, Mg, Na, K) laskeuma on vähentynyt 1970- ja 1980-luvuilta, mutta 1990-luvun aikana lasku on tasaantunut. Sulfaattilaskeuma on vähentynyt emäskationilaskeumaa jyrkemmin minkä seurauksena sadeveden happamuus ja laskeuman happamoittamispotentiaali on pienentynyt. Rikin ja typen laskeumat ovat alentuneet voimakkaimmin Etelä-Suomessa, missä laskeumakuormitus Suomen omista päästöistä ja muualta Euroopasta tulleesta kaukokulkeumasta on ollut korkein ja siten myös päästövähennysten vaikutukset ovat olleet suurimmat.

Järvien sulfaattipitoisuudet ovat alentuneet kaiken tyyppisissä järvissä koko maan alueella 1990-luvun alusta lähtien osoittaen päästörajoitusten alkaneen vaikuttaa Suomessa varsin nopeasti. Sulfaattipitoisuuksissa on tilastollisesti merkitsevä lasku noin 90% tutkituista järvistä, ja pitoisuudet ovat pienentyneet vuodesta 1990 keskimäärin 40-50% eli suhteellisesti saman suuruisesti kuin laskeumassa. Tällä hetkellä ei ole merkkejä kohonneista laskeumaperäisistä nitraattipitoisuuksista metsäalueiden latvajärvissä. Emäskationien pitoisuudet järvissä ovat pienentyneet sulfaattia vähemmän, osoittaen puskurikyvyn (alkaliniteetti) paranemista maaperässä ja järvissä, ja 60% tutkituista järvistä alkaliniteetissa on merkitsevä kasvu. Kevätaikaiset lumen sulamisvesien mukana tulevat happamuusepisodit – pH:n ja alkaliniteetin voimakas lasku ja liukoisen alumiinin nousu – ovat myös lieventyneet 1990-luvun puolivälin jälkeen. Järvien toipumiskehitys on ollut voimakkainta Etelä-Suomessa, missä hapan rikkilaskeuma on ollut suurin ja sen vähentyminen on ollut voimakkainta. Etelä-Suomessa noin 90% tutkimusjärvistä alkaliniteetilla ja 50% tutkimusjärvistä pH:ssa on merkitsevä kasvu. Keski- ja Pohjois-Suomen järvissä kemiallinen toipuminen ei ole ollut yhtä vahva ja yhdenmukainen. Happamoituneiden järvien vesikemiallinen toipuminen edistyy hyvin, mutta monet järvet kärsivät edelleen alhaisesta pH:sta ja puskurikyvystä, ja ovat siten yhä herkkiä happamuusepisodeille. Happamoituneimmissa järvissä puskurikyvyn palautuminen voi kestää vuosikymmeniä, ja kemiallisten olosuhteiden parantuminen vesistöissä vaatii rikin ja typen aktiivista päästövähennyspolitiikkaa myös tulevaisuudessa.

Vesikemiallisen toipumiskehityksen myötä myös kalaston biologinen toipuminen edistyy. Alkaliniteetin ja pH:n kasvu ja eliöille myrkyllisen alumiinin pitoisuuden lasku ovat johtaneet ahvenkantojen elpymiseen 1990-luvun aikana ja menestymiseen aiemmin hyvin happamoituneissa mutta nyt vesikemiallisesti toipuvissa järvissä. Ahvenkantojen elpymistä on myös voinut edistää leudot talvet ja lämpimät kesät, mikä viittaa myös ilmasto-olosuhteiden merkitykseen biologisia vasteita tarkasteltaessa. Happamoitumiselle herkemmän särjen osalta toipuminen on ollut heikompaa. Toipumista on hidastanut särjelle yhä kriittiset vesikemialliset olosuhteet. Vesikemiallinen toipumisen on havaittu edistävän biologista toipumista myös muissa eliöryhmissä. Happamuudelle herkät pohjaeläinlajit alkavat palautumaan vesikemiallisesti toipuviin järviin. Myös kasviplanktonin piileväyhteisöissä havaitut pitkäaikaismuutokset ovat ilmentäneet veden happamuuden pienentymistä aiemmin happamista elinolosuhteista kärsineiden lajien nyt runsastuessa eliöyhteisöissä. Monissa järvissä happamuus on yhä kriittisellä tasolla herkimmille eliöryhmille, ja herkimpien lajien merkittävä palautuminen voi kestää pitkään, jopa vuosikymmeniä. Vesien biologisesta toipumisesta – sen nykytilasta, laajuudesta ja eri eliöryhmien vaikutuksista/vasteista – on Suomessa kuin myös muualla Euroopassa selvästi vähemmän tietoa kuin kemiallisesta toipumisesta. Biologiseen toipumiseen vaikuttavat vesikemiallisten muutosten lisäksi monet monimutkaiset vuorovaikutussuhteet fysikaalisten, kemiallisten ja biologisten tekijöiden välillä. Ilmansuojelupolitiikan erityisenä tavoitteena on edistää vesien happamoitumisesta kärsineiden eliöyhteisöjen palautumista. Vesiekosysteemien toipumisprosessien arviointiin nyt ja tulevaisuudessa tarvitaan jatkuvaa yhdennettyä fysikaalis-kemiallista ja biologista seurantaa.

Etelä- ja Keski-Suomessa voimakkaimmin toipuvat järvet ovat kirkasvetisiä sulfaattilaskeuman happamoittavia järviä, joissa alkaliniteetti on selvässä kasvussa rikkilaskeuman pienentymisen myötä. Sen sijaan alkaliniteetti on kasvanut heikommin turvemaavaltaisten valuma-alueiden ruskeavetisissä humusjärvissä, joissa orgaanisten happojen merkitys järven happamuudelle on merkittävä, tai jopa suurempi kuin laskeumaperäisten vahvojen mineraalihappojen. Alkaliniteetin ei ole havaittu olevan laskussa humusjärvissä, mutta korkeat syysvalunnat ovat aiheuttaneet suuria orgaanisen happamuuden episodeja kuluttaen puskurikykyä ja hidastaen alkaliniteetin nousutrendiä. Etelä- ja Keski-Suomen tutkimusjärvet, joissa alkaliniteetin kasvu on ollut heikompaa, esiintyvät lisäksi alueilla joissa maa- ja kallioperän ominaisuuksista johtuen emäskationien varastot ovat pienemmät sekä vapautuminen maaperästä on heikompaa. Valuma-alue on siten erityisen herkkä happaman laskeuman vaikutuksille, mikä on voinut osaltaan vaikuttaa puskurikyvyn hitaampaan palautumiseen järvissä. Pohjois-Suomessa sulfaattilaskeuma on ollut pienempi ja veden laadun muutokset ovat olleet vähäisempiä kuin kuormitetuimmilla alueilla, vaikkakin järvien sulfaattipitoisuudet ovat merkitsevässä laskussa myös pohjoisessa. Ilmastollisista sekä maaperän geologisista ominaisuuksista johtuen monet Pohjois-Suomen pienet järvet ovat luontaisesti kemiallisilta ominaisuuksiltaan laimeita eli ionipitoisuudet ovat alhaisia. Valuntahuiput lisäävät orgaanisten happojen huuhtoutumista maaperästä, ja vähäionisissa vesissä korkat valunnat aiheuttavat myös ionipitoisuuksien laimentumista, jotka pienissäkin määrin voivat muuttaa veden happo-emästasapainoa ja siten vaikuttaa puskurikykyyn, aiheuttaen vaihtelua alkaliniteetin trendissä. Lähes kaikissa tutkimusjärvissä koko maan alueella sulfaattipitoisuudet ovat selvässä laskussa ja mahdollisella sulfaatin mobilisoitumisella maaperässä desorption tai rikin hapetusreaktioiden kautta ei havaittu olevan merkittävää heikentävää vaikutusta järvien kemialliseen toipumiseen. Metsäisten valuma-alueiden ominaispiirre Suomessa on hapan podsolimaa ja runsas soiden osuus, ja monet metsäjärvet ovat alkujaan luontaisesti happamia, vaikka näissäkin järvissä sulfaattilaskeuma on vielä lisännyt veden happamuutta. Ilmaperäisen laskeuman pienentyessä minerogeeninen happamoituminen on selvästi vähentymässä Suomen järvissä, mutta hydrologiset vaihtelut ja orgaanisten happojen huuhtoumat ovat tärkeä puskurikyvyn toipumista vaimentava tekijä happamissa humusjärvissä.

Laajoilla alueilla Eurooppaa ja Pohjois-Amerikkaa happamoitumisherkissä pintavesissä havaittu orgaanisen hiilen pitoisuuksien kasvutrendi havaittiin tässä tutkimuksessa myös Suomessa. Latvavesistöalueilla sijaitsevissa pienissä metsäjärvissä orgaanisen hiilen pitoisuudet ovat kasvaneet voimakkaimmin niillä valuma-alueilla ja järvissä, joissa sulfaattipitoisuus on laskenut ja puskurikyky on kasvanut voimakkaimmin. Valunnan pitkäaikaismuutoksien ei havaittu selittävän orgaanisen hiilen pitoisuuksien kasvua. Tulokset viittaavat siihen että vähentynyt rikkilaskeuma ja maaperän toipumisprosessit happamoitumisesta olisivat lisänneet orgaanisen hiilen huuhtoutumista vesistöihin happamoitumisherkillä valuma-alueilla Suomessa. Orgaanisen hiilen pitoisuuksien kasvutrendeihin on kuitenkin esitetty vahvana hypoteesina ilmaston muuttuminen, josta tärkeimpinä selittäjinä lämpötilan kasvuun ja valunnan muutoksiin liittyvät prosessit. Mahdollisesti orgaanisen hiilen pitoisuuksien kasvu on seurausta usean tekijän yhteisvaikutuksesta, ja eri tekijöiden suhteellinen vaikutus voi vaihdella alueittain. Orgaanisen hiilen kasvuun liittyvien prosessien selvittäminen tarvitsee ilmansaasteiden ja ilmastotekijöiden vaikutusten integroitua tutkimusta.

Pitkäaikainen veden laadun seuranta on osoittanut että herkät pintavedet ovat toipumassa happamoitumisesta Suomessa. Ennustemallit ovat arvioinneet tämän positiivisen kehityksen jatkuvan myös tulevaisuudessa, mikäli kansainvälisissä sopimuksissa ja EU:n päästökattodirektiivissä asetetut päästörajoitukset rikille ja typelle toimeenpannaan täysimääräisesti. Merkittävänä tulevaisuuden haastena happamoitumisen toipumiskehityksessä tulee kuitenkin olemaan typpilaskeuma, joka nykyisin on rikkilaskeumaa suurempi. Vuosikymmenien aikana typpilaskeuma kertyy maaperään ja kasvillisuuteen, ja voi johtaa typen kyllästymiseen maaperässä ja lisääntyneeseen nitraatin huuhtoutumiseen vesistöihin. Toinen merkittävä haaste on ilmastonmuutos, jonka on arvioitu tulevina vuosikymmeninä aiheuttavan merkittäviä vaikutuksia happamoitumisen toipumiskehitykseen. Muutokset lämpötilassa ja hydrologiassa vaikuttavat useisiin prosesseihin kuten typen mineralisaatioon, sulfaatin pidättymisprosesseihin sekä orgaanisen aineksen hajoamiseen maaperässä, ja aineiden kulkeutumiseen vesistöihin. Mahdollisesti lisääntyvä orgaanisen aineksen huuhtouma johtaa orgaanisen happamuuden kasvuun vesistöissä, minkä on arvioitu olevan yksi tärkeimmistä ilmastonmuutoksen aiheuttamista vaikutuksista pintavesien toipumiskehitykseen happamoitumisesta tulevaisuudessa.

Ympäristön tilan seuranta on osoittanut kansainvälisen ilmansuojelupolitiikan vaikuttaneen merkittävästi happamoittavien päästöjen vähentymiseen ja ympäristön toipumiseen happamoitumisesta. Vaikka kehitys on menossa hyvään suuntaan, vesistöjen happamoitumisongelmaa ei ole kuitenkaan kokonaan ratkaistu, ja pitkäjänteistä ympäristön tilan seurantaa on jatkettava edelleenkin. Tulevaisuuden ilmastonmuutos tulee todennäköisesti aiheuttamaan happamoitumisen seurannalle ja tutkimukselle lisävaatimuksia, sillä monet ilmastonmuutoksen aiheuttamista prosesseista ja niiden aiheuttamaista vasteista ekosysteemeissä ovat monimutkaisia, ja nämä tulee ottaa huomioon arvioitaessa pintavesien tilan pitkän ajan muutoksia ja kehitettäessä tulevaisuuden seurantaverkostoja.

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