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The 15-year report:

Assessment and monitoring of surface waters in Europe and North America; acidification and recovery, dynamic modelling and heavy metals

CONVENTION ON LONG-RANGE TRANSBOUNDARY
AIR POLLUTION

INTERNATIONAL COOPERATIVE PROGRAMME ON
ASSESSMENT AND MONITORING OF ACIDIFICATION
OF RIVERS AND LAKES

The 15-year report:
Assessment and monitoring of surface waters in Europe and North America; acidification and recovery, dynamic modelling and heavy metals

Prepared by the ICP Waters Programme Centre
Norwegian Institute for Water Research
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REPORT

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Abstract

The main aim of the ICP Waters Programme is to assess, on a regional basis, the degree and geographical extent of the impact of atmospheric pollution, in particular acidification, on surface waters. Twenty-two countries in Europe and North America participate in the programme on a regular basis. This report contains i) results from trend analysis of 189 ICP Waters sites in Europe and North America ii) an evaluation of biological response to reduced surface water acidification iii) a review of possibilities and limitations of dynamic modelling of surface waters and iv) an assessment of heavy metals in surface waters. International co-operative work to abate acidification has so far been very successful, but there is still a long way to go, and many potential set-backs. It is essential that future development of water chemistry and aquatic biota in acidified water bodies continue to be monitored in relation to further emission reductions of S and N and future effects of climate.

4 keywords, Norwegian	4 keywords, English
1. Langtransportert forurensning	1. Long-range transported air pollution
2. International overvåking	2. International monitoring
3. Forsuring av vann	3. Freshwater acidification
4. Dynamisk modellering	4. Dynamic modelling

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Preface

The International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters) was established under the Executive Body of the Convention on Long-Range Transboundary Air Pollution at its third session in Helsinki in July 1985. The Executive Body has also accepted Norway's offer to provide facilities for the Programme Centre, which has been established at the Norwegian Institute for Water Research, NIVA. A Programme subcentre is established at the Laboratory of Freshwater Ecology and Inland Fisheries at University of Bergen. The ICP Waters Programme has been led by Berit Kvæven, Norwegian Pollution Control Authority.

The work plan of the Programme includes in-depth evaluations every third year. This 15-year report summarises the results achieved so far, along the lines of the programme objectives. Focus has been on trends and regional trends in surface water chemistry, biological recovery, dynamic modeling and heavy metals.

The Programme Center aknowledge all countries that provide data to the ICP Waters database for use in the assessment work. We are also very thankful for the contribution in the discussions of an earlier version of the report that was presented at the 18th Task Force meeting in Moscow October 2002 and all the written comments to the second draft of the report. In particular we are tankful to Jim Bowman, Ireland and Rosario Mosello, Italy, who was appointed by the 18th Task Force meeting to review the final draft.

ICP Waters Programme Centre
Oslo, August 2003

Brit Lisa Skjelkvåle

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Executive summary

The recovery of surface waters from acidification is continuing. This conclusion is based on trend analysis of 189 ICP Waters sites in Europe (76) and North America (113). Sulphate concentrations are decreasing; however, nitrate shows no consistent regional pattern. Alkalinity concentrations and pH show positive tendencies in most regions. There are widespread increases in orcanic carbon throughout Europe and North America.

In general, rates of sulphate decline are smaller in surface waters than in deposition for all regions in North America and most regions in Europe. This indicates a lagged time response and may reflect the desorption of S that has accumulated in catchment soils over the past century due to atmospheric deposition.

Evidence of a biological response to reduced surface water acidification is, so far, not uniform throughout the study area. Long-term biological monitoring data show signs of recovery of invertebrates in the Scandinavian countries, while at the most acidified central Europe sites, improvements in water quality have not yet reached a level where widespread effects on biology can be detected.

Dynamic models provide an extension to critical loads by predicting the timescale of chemical recovery to emission reductions. They can also be used to determine the deposition levels required to achieve a prescribed target chemistry within a given timescale and are useful in planning further emission reductions. Methods for summarising regional model predictions are summarised and a methodology for the derivation of ‘target’ loads is proposed for use within the Convention.

The ICP Waters database contains a limited number of sites with heavy metal data. To be able to give a good picture of the general level of heavy metals in surface waters throughout Europe and North America, heavy metal data for more sites with a larger geographical cover are needed.

International cooperative work on emission reductions to abate surface water acidification has so far been very successful, but there is still a long way to go. The uncertainties in the future chemical and biological recovery mainly relate to effects of climate change and the future behaviour of nitrogen in the ecosystem..

Continuation of national monitoring programmes that submit their data to ICP Waters and the yearly chemical and biological intercalibration exercises are the most important key activities for documentations of recovery from acidification.

Summary

About the programme

The main aim of the ICP Waters Programme is to assess, on a regional basis, the degree and geographical extent of the impact of atmospheric pollution, in particular acidification, on surface waters. Twenty-two countries in Europe and North America participate in the programme on a regular basis.

ICP Waters is based on existing surface water monitoring programmes in the participating countries, implemented by voluntary contributions. The monitoring sites are generally acid sensitive and representative of low acid neutralising capacity (ANC) and low critical load levels of the distributions for all the waters surveyed in the region. The ICP site network is geographically extensive and includes long-term data series (more than 15 years) for many sites. The programme conducts yearly intercalibrations on chemistry and biology.

Trends in water chemistry

A major goal of the work of ICP Waters is to evaluate the changes in surface water chemistry in relation to emission reductions. The strongest evidence that emissions control programs are having their intended effect come from a consistent pattern of recovery (decreasing sulphate and increasing pH and alkalinity) across a large number of sites.

The most significant finding in the regional trend analysis is the almost universal decrease in sulphate concentrations in lakes and streams throughout Europe and North America. This conclusion is based on trend analysis of 189 ICP Waters sites in Europe (76) and North America (113) from six regions in Europe and six regions in North America. Only one region in this analysis failed to show a significant sulphate decrease, and this is a region (the Virginia Blue Ridge) where soil characteristics make a sulphate decrease unlikely in the short term.

Fewer than half of the ICP regions exhibited significant regional trends in nitrate. Long-term catchment responses to N deposition may occur on the time scale of centuries, rather than decades and regional declines in nitrate since ca. 1990 have to be interpreted cautiously. Over the decade of the 1990s (actually, 1900-2001), ICP sites have shown decreasing nitrate concentrations in the Adirondack Mountains, Appalachian Mountains and the Virginia Blue Ridge (all in North America), and increasing concentrations in the Alps. In all other regions, individual sites show either no change or decreasing or increasing nitrate, with no clear regional pattern.

All of the ICP regions show some tendency toward decreasing base cations. In the European regions, rates of Ca+Mg decrease are moderate (or no change), and always smaller than those for sulphate. Rates of base cation decline in North America tend to be larger than in Europe, and in some cases are in the same range as sulphate.

The decrease in sulphate and the slight increase or decrease in nitrate combined with more moderate declines in base cations, produce an expectation of recovery in alkalinity (measured), ANC (calculated) and pH. In Europe there are two regions that show significant improvement in alkalinity and ANC (Southern Nordic, East-Central Europe). One region (West-Central Europe) shows no regional increase in alkalinity despite substantial decreases in sulphate, although ANC suggests a strong recovery in this region. Three regions (UK and Ireland, Northern Nordic, Alps) show no significant changes. In North America four regions show significant improvement in alkalinity (Vermont/Quebec, Adirondacks, Appalachians and Upper Midwest), one region has no change (Virginia Blue Ridge), and the only ICP region in the current analysis exhibiting significant further acidification (Maine/Atlantic Canada). This is occurring despite significant (but small) decreases in surface water sulphate. Many of the ICP sites in this region exhibit larger decreases in base cations, than sulphate declines. Recovery in the Adirondack and Appalachian Mountains, and in the Upper

Midwest, is a new important finding as none of these regions showed significant improvement in previous regional analyses.

Two regions exhibit significant pH increase (the Southern Nordic and Adirondack regions) and both are among the top three regions in terms of alkalinity improvement. While we might expect more significant improvements in pH, it is important to recognise that pH is among the most difficult variables to measure consistently well in the laboratory. Variability in measurements makes it more difficult to detect trends.

Dissolved organic carbon (DOC) is of great interest in any analysis of surface water recovery, because it is an indicator of organic (natural) acidity. The previous ICP trends report was one of the first to note the widespread increases in DOC now being observed throughout Europe and North America. Six out of 10 ICP regions analysed in the current report exhibit significant positive slopes for DOC, and nearly all of the regional increases were significant.

Trends in sulphate in precipitation and surface water

In general, rates of sulphate decline are smaller in surface waters than in deposition for all regions in North America and most regions in Europe indicating a lagged response. This may reflect the desorption of S that has accumulated in catchment soils over the past century due to atmospheric deposition. Desorption of stored S has the effect of damping the trends in surface water sulphate and slowing the rate of decline. One exception to the pattern in North America is in the Upper Midwest region of the U.S., where most lakes are seepage lakes. In Europe, both the Alps and the UK/Ireland show approximate the same percentage change in sulphate concentrations in precipitation and surface waters indicating a very direct response of surface waters to changes in precipitation.

Trends in biological recovery

Evidence of a biological response to reduced surface water acidification is so far, not uniform throughout the study area. Signs of recovery are observed for invertebrates in the Scandinavian countries, while at the most acidified central Europe sites, improvements in water quality have not yet reached a level where widespread effects on biology can be detected. Biological recovery will occur when the water quality is sufficient to allow sensitive species to recover. Reported improvements support such a sequential process, however ecosystems may not return to an earlier stage, but will reflect the present physical, chemical and biological environment. More data collected in a uniform way with large geographical coverage are strongly needed to explore this further.

Dynamic modelling

Dynamic models provide an extension to critical loads by predicting the timescale of chemical recovery to emission reductions. They can also be used to determine the deposition levels required to achieve a prescribed target chemistry within a given timescale and so have direct utility in the formulation of further emission reductions. Dynamic models can contribute to the Convention in two important areas; firstly, they can provide an estimate of the expected surface water chemistry at any time in the future in response to the implementation of the Gothenburg Protocol (assessment of the impact of emission reductions), and secondly, they can be used to assist in the calculation (optimisation) of further emission reductions (input to the process of Integrated Assessment Modelling).

In the chain of events from the deposition of strong acids to the damage to key indicator organisms there are two major factors that can give rise to time delays. Biogeochemical processes can delay the chemical response in the catchment soils and consequently surface waters, and biological processes can further delay the response of indicator organisms, such as damage to fish. The static models to determine critical loads consider only the steady-state condition, in which the chemical and biological response to a change in deposition is complete. Dynamic models, on the other hand, attempt to estimate the time required for a new (steady) state to be achieved. This report describes the possibilities and limitations of using dynamic models to better define the limits and timescales of the recovery processes.

Four models have been identified as being widely used, documented and tested with respect to the requirement of the Convention and which are simple enough to be applied on a regional scale. Of these, the MAGIC model focuses on surface water chemistry and is generally applied at catchment scale. The model simulates soil solution chemistry and surface water chemistry to predict the annual average concentrations of the major ions in lakes and streams.

Heavy metals

The ICP Waters database contains a limited number of sites with heavy metal data, and these sites are located in relatively few countries. To be able to give a good picture of the general level of heavy metals in surface waters throughout Europe and North America, heavy metal data for more sites with a larger geographical cover are needed.

Few sites have long time series on heavy metals. Analytical methods have changed and the detection limit has generally decreased through the monitoring period for the sites with long-term trends. Both the change in method and the change in detection limit make it difficult to identify time trends in heavy metals for many sites.

It is an important task to harmonise the water quality criteria for heavy metals in different countries. At present critical limits for many heavy metals vary by more than an order of magnitude in different countries.

1. Status and findings with in the ICP Waters programme

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1.1 Programme rationale and background

Over the past 30 years acid atmospheric deposition, “acid rain”, has received considerable attention as an international environmental problem in Europe and North America. Polluted air masses containing sulphur and nitrogen compounds travel long distances, cross-national boundaries, and affect surface waters, groundwaters and forest soils in other countries. Rethinking of air pollution control strategies was necessary, including long-term monitoring of affected receptors such as rivers and lakes. The Convention on Long-range Transboundary Air Pollution (CLRTAP) went into effect in 1983 and was the first step to enforce emission reduction measures in the international sphere aiming at controlling air pollutant emissions in Europe and North America. The Working Group on Effects (WGE) has aided the Convention by developing science to support Protocols. The WGE’s six International Cooperative Programmes (on Waters, Natural Vegetation and Crops, Forests, Materials and Cultural Heritage, Integrated Monitoring, and Modelling & Mapping) and a Joint Task Force with WHO on Human Health, quantify effects on the environment through monitoring, modelling and scientific review.

The International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters) was established under the Executive Body of the Convention on Long-Range Transboundary Air Pollution (LRTAP) at its third session in Helsinki in July 1985 (EB.AIR/7, Annex/V). Canada was appointed as lead country for the first phase of the ICP Waters. The delegation from the Union of the Soviet Socialist Republics offered to support activities in the leading Programme. The Executive Body also accepted Norway’s offer to provide facilities for the Programme Centre.

The Programme Task Force has the mandate to plan and supervise activities undertaken within the ICP Waters programme. At its first meeting, held in Grafenau (Germany) on 27 April 1986, the Programme Task Force discussed the scope, objectives and general organisation of the programme and formulated a monitoring manual to be recommended to the Working Group on Effects. The aims and objectives of the programme are discussed and reviewed regularly at the yearly Task Force meetings.

The monitoring programme is designed to assess, on a regional basis, the degree and geographical extent of acidification of surface waters. The data collected provide information on dose/response relationships under different conditions and correlate changes in acidic deposition with the physical, chemical and biological status of lakes and streams (EB.AIR/W6.1./R21). As reported to the fourth session of the Executive Body, the ICP Waters is based on existing programmes in participating countries, implemented by voluntary contributions. The operational part of the programme using standardised methodologies started in 1987. At its second meeting in Oslo (14 October 1986) the Programme Task Force adopted the Programme Manual compiled by the Programme Centre in Norway based on a draft outline prepared by Canada. After finalising the Programme manual, Canada entrusted Norway to take the role as lead country in the subsequent implementation phase of the programme. This was confirmed by the

Working Group on Effects at its sixth session and reported to the Executive Body on its fifth session (EB.AIR/16, Annex/II) in December 1987.

1.2 Programme Aims and Objectives

The programme aims and objectives were discussed and reviewed at the ICP Waters 15th Task Force meeting in Pallanza, Italy October, 1999. The reviewed aims and objectives are:

Aims:

- Assess the degree and geographic extent of the impact of atmospheric pollution, in particular acidification, on surface waters;
- Collect information to evaluate dose/response relationships;
- Describe and evaluate long-term trends and variation in aquatic chemistry and biota attributable to atmospheric pollution.

Objectives:

- Maintain and develop an international network of surface water monitoring sites;
- Promote international harmonisation of monitoring practices by:
  - maintaining and updating a manual for methods and operation;
  - conducting interlaboratory quality assurance tests;
  - Compiling a centralised database with data quality control and assessment capabilities.
- Develop and/or recommend chemical and biological methods for monitoring purposes;
- Report on progress according to programme aims and short term objectives as defined in the annual work programme;
- Conduct workshops on topics of central interest to the Programme Task Force and the aquatic effects research community;
- Address water related questions in cooperation with other ICP’s

These topics are addressed in depth every 3 years in summary reports: 3-year report 1987-1989 (Wathne 1991), 6-year report 1990-1992 (Skjelkvåle et al. 1994), 9-year report 1993-1995 (Lükewille et al. 1997), 12-year report 1996-1998 (Skjelkvåle et al 2000), and 15-year report 1999-2001 (this report)

1.3 Programme Status

Table 1 summarises the participation in the different parts of the programme in the 3-year period 1999-2001. Locations of ICP sites are presented in **Figure 1**.

Table 1. *Participation in the Programme during the period 1999-2002.*

	Chemical data	Biological data	Participating in chemical intercomparison	Participating in biological intercalibration	Participation in TF meeting
Austria		•	•		
Belarus	•		•		•
Canada	•	•	•	•	•
Czech Rep.	•	•	•	•	•
Estonia	•		•	•	•
Finland	•		•	•	•
France			•	•	•
Germany	•	•	•	•	•
Hungary	•				•
Italy	•	•	•		•
Ireland	•	•	•	•	•
Latvia	•	•	•	•	•
Moldova					•
Netherlands			•		•
Norway	•	•	•	•	•
Poland	•	•	•		•
Russia			•	•	•
Slovakia		•			•
Spain		•	•		
Switzerland	•	•	•	•	•
Sweden	•	•	•	•	•
UK	•	•	•	•	•
USA	•		•		•
Total	16	13	20	13	21

In addition laboratories from Belgium, Bulgaria, the Faeroe Islands, Iceland, Lithuania, Portugal, Romania, Slovenia, India and China collaborate. Altogether 75 laboratories in 27 countries participate.

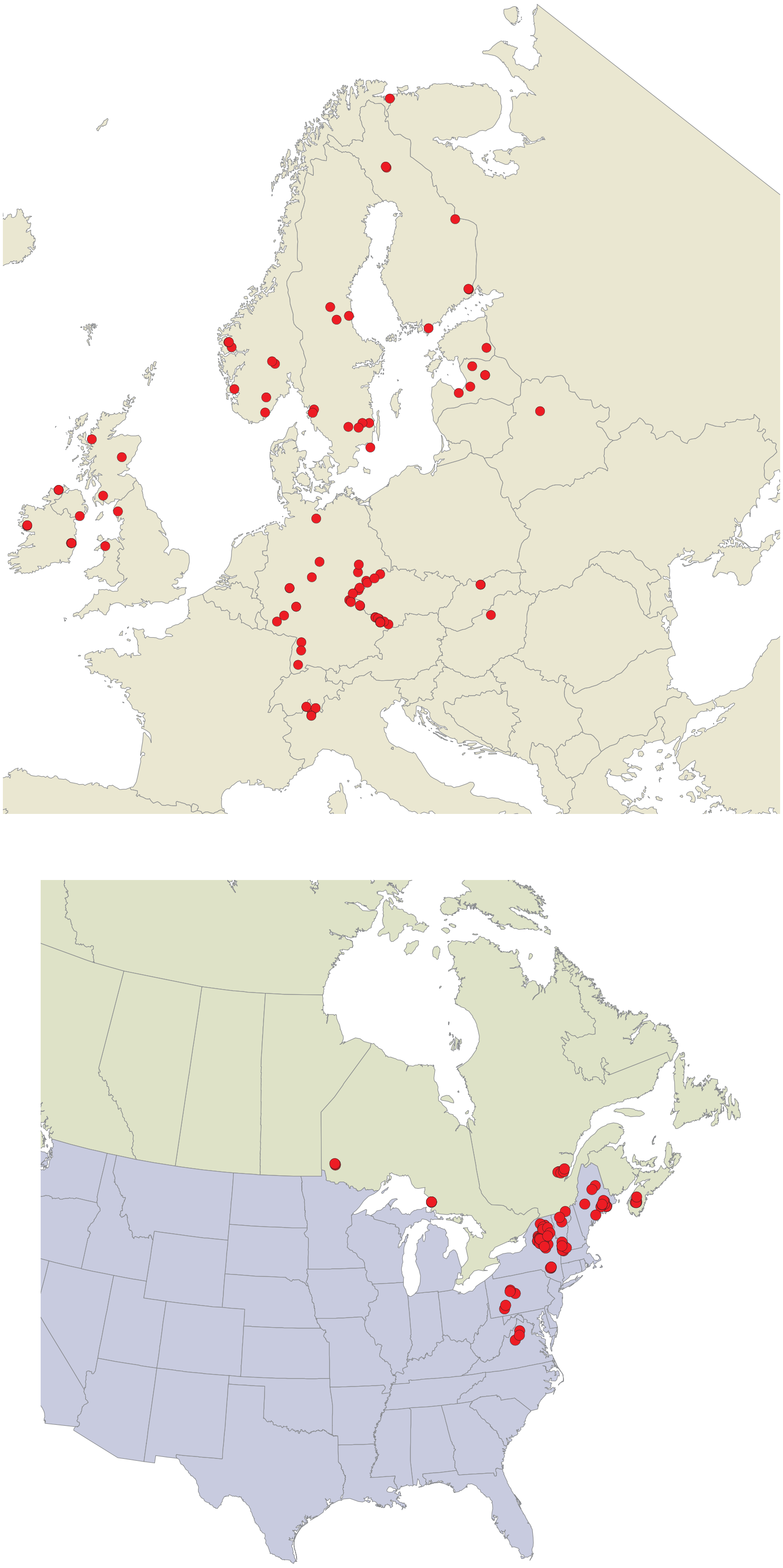

Figure 1. *Location of ICP Waters monitoring sites in Europe and North America 1999-2001.*

1.4 Previous findings within the ICP Waters programme

This section intends to give a summary of the major findings in the 15-year history of ICP waters

Representativeness of the database
The ICP Waters sites cover most of the acid-sensitive areas in Europe that receive significant acid deposition. There are no ICP sites, however, in several regions that have been or are potentially affected. Furthermore there are insufficient data from many regions in Eastern Europe to adequately assess both the risk of acidification and the sensitivity of surface waters. For North America the ICP sites cover several, but not all of the acid-sensitive regions that receive significant acid deposition, and that can be expected to show changes in response to changing levels of deposition in the future.

Many of the sites included in the ICP Waters programme are especially sensitive to acidification. They need not be representative of all surface waters in a region, but rather represent the acid-sensitive surface waters. Most of the sites appear to be well suited to monitor changes in acidification in response to changes in acid deposition. The sites are generally representative of the lower ANC, lower critical load levels of the distributions for all the waters surveyed in the region.

Trends in surface water chemistry
Trend analysis has been a major issue in each of the 3-year reports from ICP Waters. The most significant finding in the regional trend analysis, is the almost universal decrease in sulphate concentrations in lakes and streams throughout Europe and North America. In almost all cases the decreases in the 1990s are larger than in the 1980s. In the last trend with data up to 2001, only one region failed to show a significant sulphate decrease, and this is a region (the Virginia Blue Ridge) where soil characteristics make a sulphate decrease unlikely. Fewer than half of the ICP regions exhibited significant regional trends in nitrate. Regions in North America (Adirondack Mountains, Appalachian Mountains and the Virginia Blue Ridge), have decreasing nitrate concentrations during 1990-2001, while nitrate concentrations is increasing in the Alpine region of Europe in the same time period. All other regions show no clear regional pattern. All of the ICP regions show some tendency toward decreasing base cations while increases in alkalinity and ANC are found in most regions. One ICP region exhibiting significant further acidification (Maine/Atlantic Canada). This is occurring despite significant (but small) decreases in surface water sulphate. Only two regions exhibit significant pH increase and both are among the top three regions in terms of alkalinity improvement. All but one of the ICP regions analysed in the current report exhibit positive slopes for DOC, and nearly all of the regional increases were significant.

Results from the 12-year report (data up to 1999) showed that low ANC sites show the largest rates of recovery. Neither the high NO_3^- or low NO_3^- groups of sites exhibit significant trends in NO_3^- concentrations. Non-forested sites show clear and consistent signals of recovery in ANC and pH, and appropriate (relative to SO_4^{2-} trends) rates of base cation declines. Hence, the recovery we observe is, in fact, associated with declining SO_4^{2-}.

Nitrogen Leaching from ICP Waters Sites
The ICP Waters sites are evaluated with respect to status of nitrate. About 50% of the sites currently have nitrate concentrations indicative of nitrogen saturation, that is, level of nitrate above that expected in undisturbed systems not receiving significant amounts of N deposition. Due to the decrease in sulphate concentration in surface waters during the 1990's, nitrate has assumed a greater importance as an acidifying anion at the ICP sites. The data indicate no major change in N saturation at the ICP sites during the 1990s, indicating that progression to increased N saturation is a slow process with a time scale of decades. Fewer than half of the ICP regions exhibited significant regional trends in nitrate. Trend analysis up to 2001 show decrease in several regions in North America while nitrate concentrations is increasing in the Alpine region of Europe. All other regions show no clear regional pattern. Within each of the regions there are some sites with increasing or deacreasing. Some sites in central Europe show increasing trends

due to forest disturbance (harvesting or insects), while other sites in sensitive areas show decreasing trends. Despite a decline,deposition levels are still high enough for nitrate to continue to accumulate in catchment soils and run-off concentrations remain relatively unaffected. Compared with sulphur, nitrogen is much more involved in biological processes within ecosystems. Hence changes in N deposition may not always directly correlate with changes in inorganic N leaching in runoff. Besides N-deposition, the overall N-status of ecosystems, changes in climate or climate extremes and hydrology can strongly influence leaching of excess NO_3^- (and ammonium) from a catchment.

Biology - recovery

Documentation of biological response to reduced surface water acidification has so far been scattered. No large-scale biological recovery has been reported. Long-term biological monitoring data show signs of recovery of invertebrates in the Scandinavian countries, while at the most acidified central Europe sites, improvements in water quality have not yet reached a level where widespread effects on biology can be detected statistically, but positive signals of improvements in the invertebrate fauna are observed

Biological recovery after improvements of water chemistry will occur when the water quality and its envelope of fluctuations is sufficiently high to allow sensitive species to recover. There is a need to understand the sequence of steps in the ecological recovery process since all biological communities are dynamic. Ecosystems may not return to an earlier stage, but will always reflect the physical, chemical and biological environment.

Trends in biological recovery are usually assessed by the use of acidification indices. The use of multivariate statistics is a new method developed within ICP Waters to show correlation between changes in various variables (pH, Ca, ANC, TOC and time) and biology (benthic invertebrates). The method gives signals of recovery of total benthic communities, as well as changes in acidity outside the range of the acidification index. It is therefore a useful complementary method to existing use of acidification indices for invertebrates.

A workshop on Models for Biological Recovery from Acidification in a Changing Climate (Wright and Lie, 2002) held in collaboration with other research programmes examined evidence for biological recovery and factors confounding recovery, reference conditions and possibilities to predict future recovery. Recovery times (the time of observation of the first species after good water quality is obtained) for biota vary: algae 0-1 year, some sensitive invertebrates species 1-3 years, some zooplankton species 3-7 years and fish 2-20 years. Static models for biological recovery are well established, while dynamic models for biological recovery need to be developed further through cooperation between biologists, chemists and modellers.

Critical limits for biology

Critical limits of ANC based on ivertebrates are suggested for different regions of Europe. In areas with originally high pH (6.0-8.0) and high Ca-concentrations (e.g., southern Sweden, Germany and the Vosges Mountains of France) a critical ANC limit of 50 µeq/L is proposed. In areas where fauna is adapted to water with low conductivity, low pH (5.5 - 6.5) and low calcium concentrations (e.g., Ireland, UK and Norway), ANC values should be 20 µeq/L to protect invertebrates. In the high Alps and Pyrenees a limit of about ANC 30 µeq/L is suggested.

Heavy metals

The ICP Waters database contains a limited number of sites with heavy metal data, and these sites are located in relatively few countries. To be able to give a good picture of the general level of heavy metals in surface waters throughout Europe and North America, heavy metal data for more sites with a larger geographical cover are needed. Few sites have long time series on heavy metals. The analytical methods have changed and the detection limit has generally decreased through the monitoring period for the sites with long-term trends. Both the change in method and the change in detection limit make it difficult to identify time trends in heavy metals for many sites.

ICP Waters arranged a workshop March 2002 in Lillehammer, Norway, to reviewed the present knowledge and understanding in three areas: Critical limits, monitoring methods and dose/response relationships with modelling. The workshop encouraged further review of existing data and information, including active cooperation with other bodies, EU research programmes and national research. It was noted that effect based approach to the control of heavy metals in surface waters requires further development. Defining critical loads for individual heavy metals need not necessarily be the final step in the process. Additional methods may also prove to be advantageous. ICP Waters was encouraged to act as a facilitator in providing data and information for development of critical limits for heavy metals in aquatic ecosystems. This implies activity from national focal points.

Implications for the Assessment of Critical Loads

An assessment of the status for critical load and critical load exceedances, using the methods described in the mapping manual (UN/ECE 1996) showed that at 46% of the European ICP Waters sites the critical loads of acidity is less than 50 $meq/m^2/yr$, and 68% of the sites have critical loads less than 100 $meq/m^2/yr$. The corresponding figures for the North American sites are 40% and 75%, respectively. The results indicated that many of the selected ICP Waters sites are sensitive to acidification. This raises the question whether the sensitivity of the surface waters has been underestimated in large parts of Europe, and that in several of the EMEP-grid cells the low percentiles would be even lower if critical loads for surface waters had been included.

Dynamic modelling

Dynamic models provide an extension to critical loads by predicting the timescale of chemical recovery to emission reductions. Just as the damage to biota is delayed beyond the onset of acid deposition, so the recovery from acidification will also be delayed. ICP Waters has made a report on possibilities and limitations in dynamic modelling of surface waters. Four models have been identified as being widely used documented and tested with respect to the requirement of the Convention and which are simple enough to be applied on a regional scale. Of these, the MAGIC model focuses on surface water chemistry and is generally applied at catchment scale.

Quality control

The programme conducts yearly chemical and biological intercalibrations.

The number of participating laboratories in the chemical intercomparison have increased from 9 in 1987 to 72laboratories in 26 countries in the 15th chemical intercomparison in 2001. The investigated variables are pH, conductivity, HCO_3^- (alkalinity), NO_3^- $+NO_2^-$, Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, K^+, Al, reactive Al, non-labile Al, DOC and COD-Mn. From 2001 Fe, Mn, Cd, Pb, Cu, Ni and Zn is included. The intercomparison confirm that the results are generally compatible between laboratories.

Sixteen laboratories have participated in six or more intercomparisons from 1987-2000. These laboratories were selected for evaluation of possible trends in their performance based on the intercomparison results reported. No clear performance trend for this group of laboratories was found. A probable reason may be that nearly all of these laboratories have been well established for many years, and thus the participation in intercomparisons will have only minor effects on their analytical quality.

Intercalibration of invertabrate fauna started in 1993 and has been conducted 5 times up to 2001. About 5-7 labs participate each time and up to now 13 different labs has participated in the intercalibration. The biological intercalibration has proved that the methods suggested in the Programme Manual are reliable and suitable to assess the effects of acidification on aquatic fauna.

1.5 Future work

The results from the ICP Waters Programme clearly show that surface waters respond to changes in atmospheric deposition. Surface waters are much more responsive than either soils or terrestrial vegetation to changes in long-range transported acid deposition. Lakes and rivers also have the advantage that they integrate response over the entire catchment area. The ICP site network is geographically extensive and includes long-term data series (> 15 years) for more than 1000sites. The network is thus well poised to document changes that result from implementation of the protocols.

Future trends in recovery from acidification may be influenced by a number of confounding factors. Climate is widely believed to be undergoing long-term change, and the direction and degree of this change may significantly influence the behaviour of both terrestrial and aquatic ecosystems. The extent of N retention in the future, and consequently the future influence of N on surface water acidification, therefore represents a key uncertainty in future recovery from acidification. Continuation of the national monitoring programmes that submit their data to ICP Waters and the yearly chemical and biological intercalibration exercises are the most important key activities in future work.

Mapping critical loads for acidifying components is a key activity within the Convention work. Dynamic models provide an extension to critical loads by predicting the timescale of chemical recovery to emission reductions. Dynamic models can also be used to determine the deposition levels required to achieve a prescribed target chemistry within a given timescale and so have direct utility in the formulation of further emission reductions. ICP Waters will use the expertise within the ICP Waters network to support the modelling work under the Convention and assess the possibilities for using dynamic modelling for surface waters in Europe and North America.

Future work should also include dynamic biological responses in the recovery process. The widespread improvement in surface water quality during the past 15-20 years should give rise to biological recovery. Yet there are relatively few documented examples of biological recovery. The explanation may be found in the dynamic nature of biological response but also a lack of appropriate long-term monitoring data. ICP Waters will explore the possibilities of developing biological response models for use in assessing recovery from acidification.

Heavy metals (in particular lead, cadmium and mercury) and POPs (persistent organic pollutants) from long-range transport have not received the same attention in monitoring programmes as acidifying components. In the future ICP Waters plan to undertake an assessment of existing data for POPs (both chemical and biological) as well as make recommendations for monitoring, development of appropriate dose-response relationships and participate in work on effect based approaches for POPs and heavy metals.

1.6 Aim of the 15-year report

The aim of the 15-year report is to provide an overall synthesis and assessment of information on water chemistry and biology accumulated in the ICP Waters Programme within the last 3 years (1999-2001)

- **Status and findings** within the ICP Waters programme (Chapter 1)
- **Water chemistry -**Trends in surface water chemistry 1990-2001 (Chapter 2)
- **Biology -** Is biological recovery from acidification lacking? (Chapter 3)
- **Dynamic modelling -** Dynamic Modelling of Surface Waters: Impact of emission reduction - possibilities and limitations (Chapter 4)
- **Heavy metals -** Heavy metals in surface waters; results from ICP Waters (Chapter 5)

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2. Trends in surface water chemistry 1990-2001

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2.1 General overview of trend analysis

One of the most valuable uses of data from the ICP Waters program is evaluation of long-term trends. Trend analyses have been conducted previously on ICP Waters data and have provided important indications of the geographic extent of acidification and recovery of lakes and streams (Lükewille et al. 1997, Newell and Skjelkvåle 1997, Skjelkvåle et al. 1994, Stoddard et al. 1999, Skjelkvåle et al. 2000). In this 15-year report, we report trends from 189 ICP Waters monitoring sites for the 12-year period 1990-2001. This period is one in which all of the regions covered by the ICP monitoring sites have experienced substantial reductions in sulphur deposition (Stoddard *et al.* 2003, Barrett *et al.* 2000), and this can be expected to be reflected in trends in surface water SO_4^{2-} concentrations and acidity (pH and alkalinity).

The 9-year report suggested that many regions had shown early signs of recovery during the 1980s, but that the rate of recovery appears to have accelerated during the 1990s. Within Europe, however, a degree of spatial heterogeneity has been evident, with the clearest evidence of recovery from parts of Scandinavia where deposition changes have been large.

Our analysis of surface water response to changing deposition focuses on the key variables that play major roles in acidification and recovery:

1) **SO_4^{2-}** and **NO_3^-**, the acid anions of acidic deposition. Trends in the concentrations of these anions reflect recent trends in deposition (especially SO_4^{2-}) and in ecosystem response to long-term deposition (e.g., NO_3^-).
2) **Base cations -** $\Sigma(Ca^{2+} + Mg^{2+})$**,** which are mobilised by weathering reactions and cation exchange that neutralise acids in watersheds. Base cations will respond indirectly to changes in SO_4^{2-} and NO_3^-
3) **Acidity,** including **pH**, **measured (Gran) alkalinity** and **calculated ANC**, which reflects the outcome of interactions between changing concentrations of acid anions and base cations.

4) Concentrations of **Dissolved Organic Carbon** (DOC) or alternatively **Total Organic Carbon (TOC)**, as a surrogate for organic acidity. Organic acids are often natural, sources of acidity in surface waters.

Both SO_4^{2-} and base cation concentrations were sea-salt corrected prior to analysis, and the analysis of pH were made on values transformed to H^+ concentrations.

As in the 12-year report, we again present the trends for each individual site, as well as aggregated trends organised by regions. While it is important to know how individual sites in various countries are responding to decreased atmospheric deposition, the strongest evidence that emissions control programs are having their intended effect comes from a consistent pattern of recovery (decreasing SO_4^{2-} and increasing pH and ANC) across a large number of sites; the regional trend analysis is intended to test for these large-scale patterns.

2.2 ICP Sites Chosen for Trend Analysis

Sites in the ICP Waters database exhibit a wide range of sampling frequencies, completeness of chemistry, and length of record. In order to make a meaningful comparison of trends among these sites, it is necessary to impose a minimum set of requirements for inclusion of data. We chose to focus the current analysis on:

- sites where data are available for at least 7 out of the 12 years.
- sites that had all of the variables that would have a direct response to changes in atmospheric deposition (i.e., sulphate, nitrate and base cations), and at least one of the two indicators of recovery (i.e., pH and ANC).
- sites sensitive to acidification (ANC < 200 µeq/L)
- sites with undisturbed catchments
- sites with no major source of sulphate in catchment soils

The results of this selection process are summarised in Appendix A. 189 sites had sufficient data for trend analysis. In addition we have run trend analysis on SO_4^{2-} for nine sites considered insensitive to acidification.

Table 2. Number of sites for trend analysis in each country. A total of 189 sites have sufficient data for trend analysis.

Europe	# sites
Belarus	0
Czech Rep.	6
Estonia	0
Finland	7
Germany	24
Hungary	0
Italy	6
Ireland	3
Latvia	0
Norway	9
Poland	2
Russia	0
Slovakia	0
Switzerland	0
Sweden	10
UK	6
Total	73

North America	# sites
Canada	16
USA	100
Total	116

2.3 Quality assurance of data

Standardisation of sample collection and analytical methodologies are addressed in the latest version of the ICP Waters Programme Manual (1996). Aspects of site selection, water chemistry/biological monitoring and data handling are also described in detail in the manual.

Three levels of quality control of water chemistry data can be distinguished: in-laboratory controls in individual countries, between-laboratory controls and quality control of data reported to the National Focal Points and to the Programme Centre at NIVA. The last step does not focus on the physical-chemical analysis of single parameters in the laboratory, but is a more technical procedure including:

- looking for outliers
- tests for continuity in time series
- calculation ionic balance

2.4 Statistical Methods Used for Trend Analyses

Numerous statistical techniques are available to analyse trends in time series like those presented here. In the two previous ICP Waters reports on assessment of trends we have used the Seasonal Kendall test (SKT) (Hirsch *et al.* 1982, Hirsch and Slack 1984). This method deals well with censored data, and with data collected at irregular intervals with marked seasonality (Loftis and Taylor 1989). The regional analyses we present in this report depend on the ability to calculate a robust estimator of slope for each site. Rather than utilising a Zen estimator of slope, as is often done with the SKT, we chose simple linear regression (SLR) to calculate a trend slope for each monitoring site.

Two sided t-tests for the null hypothesis that the slope equals zero, i.e. no trend is present, have been calculated for each site, and the null hypothesis is rejected for p-values below 0.05. There are both seasonal patterns and strong serial correlations present in the data, but this only reduces the power of the tests and does not introduce bias or inflate the significance levels. Even though these tests are valid if each site is considered separately, the overall significance level will be inflated when all the tests are taken into account, and the risk of making a small number of false rejections of the null hypothesis will inevitably become very high. Because of this, the t-tests have been employed mainly as a screening device, and do not allow any conclusions about the exact number of sites that have increasing or decreasing trends. However, they can be used to give approximate numbers. If each test is regarded as a Bernoulli trial with a success probability of 0.05, the probability for making 14 or more false rejections of the null hypothesis when 189 tests are made is below 0.03. For a large number of the sites, the actual significance level is much lower than 0.05, so the actual number of false rejections at this level is likely to be lower than 14.

While the significance of individual tests conducted with SLR are highly questionable, the slopes calculated for multiple sites within a region represent a distribution of results, which can in turn be examined and analysed for patterns. Within each region, we test for a significant regional trend by calculating confidence limits about the median value in the slope distribution, and whether these confidence limits include zero. For a distribution in which all of the slopes are negative, for example, the median value would be significantly less than zero, indicating a significant regional downward trend.

2.5 Results of trend analysis

2.5.1 General trends 1990-2001

189 sites are used for trend analysis; of these 73 are European and 116 are from North America. The results of the trend analysis for the single sites and the calculated slopes are presented in Appendix D and are summarised in **Table 3**. In this section we describe only the overall pattern in the results, while a discussion of the trends is included in next section on regional trends.

Most sites (85%) show significant decreasing trends in non-marine SO_4^{2-}, while only a few sites (2%) show a significant increasing trend.

Few sites show significant trends in nitrate concentrations (21% decreasing, 7% show increasing trends), while the majority of sites (70%) show no significant trend. These results confirm the conclusion from the 12-year report, that there is no clear picture with regard to trends in NO_3^-.

The majority of the trends for base cations (Ca+Mg) (62%) show significant decrease, while only some few sites (5%) show significant increasing trends. As for SO_4^{2-}, the decrease in base cations is a pronounced pattern in the ICP Waters sites.

Alkalinity shows increasing trends at 31% of the sites while significant decrease is found in 14% of the sites. ANC is only calculated for European sites, and the results can therefore not be directly compared with alkalinity. ANC shows a strong tendency for increase (recovery from acidification) in 46% of the European sites, with only 8% show decrease (further acidification).

There is a weak signal in the data for pH with 24 % showing decrease in H^+ (increase in pH) and 6% show increase. However, most sites show no significant trend in H^+. pH is among the most difficult variables to measure well in the laboratory (Hovind 2002). Variability in measurements makes it more difficult to detect trends.

Some sites have data for DOC, some TOC, and some have both. A few have no reported values. In the results presented here, we have used DOC, or TOC if DOC data do not exist. Many sites show increase in DOC (38%), while only 2% show significant decrease.

Table 3. Results of trend analysis for 189 ICP Waters sites for the period 1990-2001. Significance level is $p<0.05$.

	SO_4	NO_3	Ca+Mg	Alkalinity	ANC	H^+	DOC/TOC
Europe							
Increasing	**1**	**10**	**9**	**26**	**37**	**6**	**31**
No trend	9	40	24	36	34	36	27
Decreasing	**63**	**23**	**40**	**17**	**2**	**31**	**2**
North America							
Increasing	**3**	**4**	**1**	**32**	**4**	**6**	**36**
No trend	16	95	38	75	7	95	78
Decreasing	**97**	**17**	**77**	**9**	**5**	**15**	**2**
Total no of sites in trend analysis	**189**	**189**	**189**	**185**	**89**	**189**	**176**
Total no of increasing trends	**4**	**14**	**10**	**58**	**41**	**12**	**67**
Total no of no trends	25	135	62	101	41	131	105
Total no of decreasing trends	**160**	**40**	**117**	**26**	**7**	**46**	**4**
% increasing trends	**2**	**7**	**5**	**31**	**46**	**6**	**38**
% no trends	13	72	33	55	46	70	60
% decreasing trends	**85**	**21**	**62**	**14**	**8**	**24**	**2**

2.5.2 Regional trends

The strongest evidence that emissions control programs are having their intended effect is a consistent pattern of recovery (decreasing SO_4^{2-} and increasing pH and alkalinity) across a large number of sites. For this reason, we are again reporting trends for aggregations of ICP sites. The sites are grouped into geographic regions based on similar acid-sensitivity (e.g., similar geology, soil characteristics) and rates of deposition. In some cases, in order to reach sufficient sample sizes (i.e., number of sites), we have grouped sites into regions that are more heterogeneous than would be ideal. For example, the “Upper Midwest” region of the U.S. and Canada includes sites in central Ontario (the Turkey Lakes area), western Ontario (Experimental Lakes Area), northern Michigan and northern Wisconsin. While there are certainly many similarities in the geology of these areas, they comprise a very large geographic area with different climate and rate of change of atmospheric deposition. The list of regions on which we report is therefore based on both scientific and pragmatic decisions resulting from availability of data.

Table 4. Regions in Europe and North America and number of sites in each region

	Region	No of sites in region
Europe	Alps	6
	East Central Europe	20
	Northern Nordic	7
	Southern Nordic	19
	U.K. and Ireland	9
	West Central Europe	12
North America	Adirondacks	48
	Appalachian Plateau	9
	Maine and Atlantic Canada	18
	Vermont and Quebec	15
	Upper Midwest	23
	Virginia Blue ridge	3

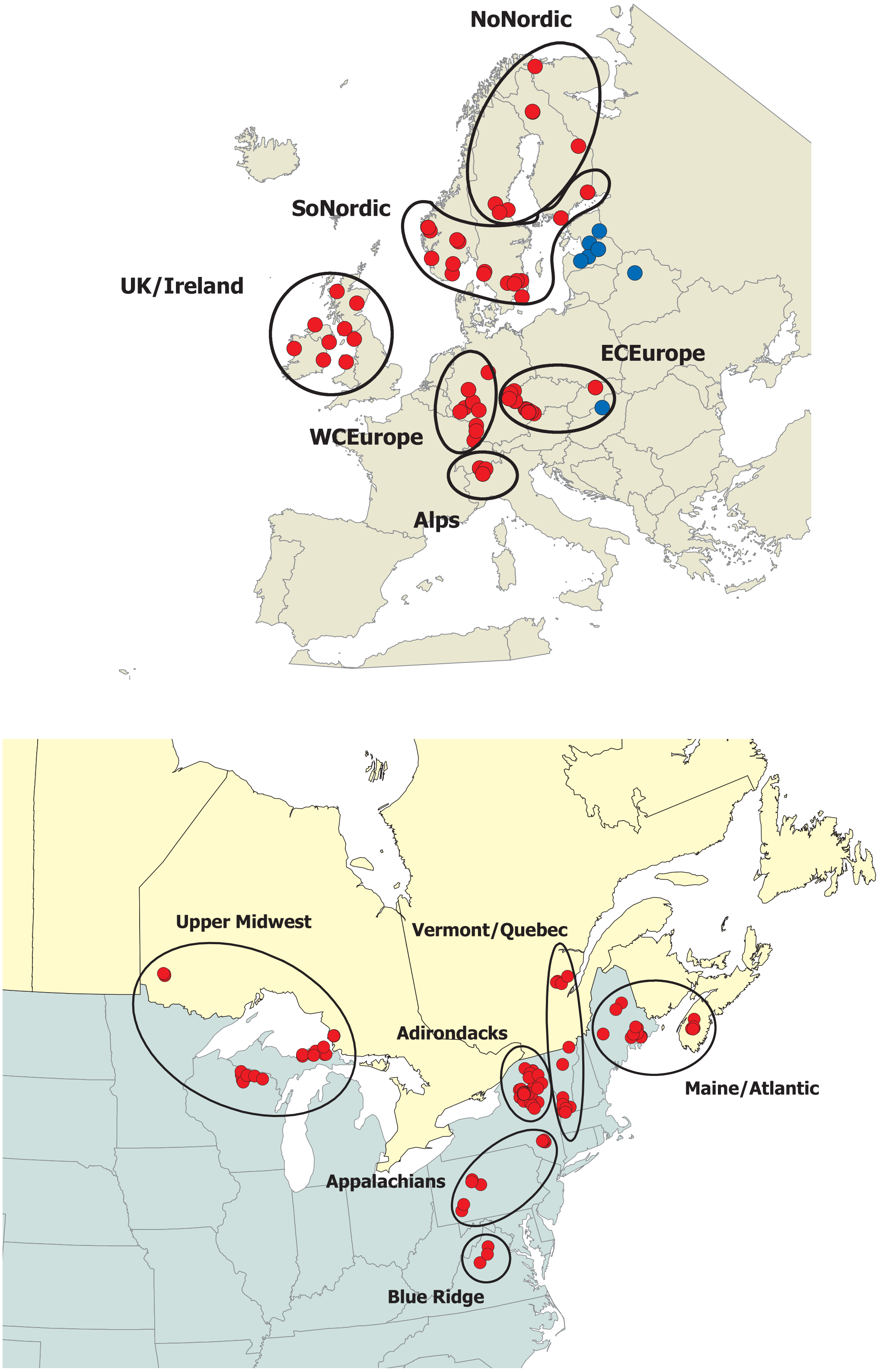

Figure 2. Map showing location of ICP Waters sites used for trend analysis in this report and outline of geographical regions. Red dotes are sites included in the trend analysis, while the blue dots are sites with trend analysis only for sulphate.

Table 5. Regional trend results for ICP Waters sites for the period 1990-2001. Values are median slopes, and 90% confidence intervals of trend tests on all sites in each region. Units for sulphate, nitrate, base cations [Ca^{2+} + Mg^{2+}], Gran alkalinity, ANC and hydrogen are µeq/L/year. Units for DOC are mg/L/year. Shading indicates significant trends.

		N	**SO_4^{2-}**				**NO_3^-**			
Region	Continent		**Median**	Lower CI	Upper CI	p	**Median**	Lower CI	Upper CI	p
Alps	Europe	6	**-1.80**	-4.44	-1.30	<.01	**+0.52**	0.14	2.65	<.01
East Central Europe	Europe	20	**-3.91**	-7.80	-2.39	<.01	**-0.87**	-2.86	0.09	n.s.
Northern Nordic	Europe	7	**-1.68**	-2.79	-0.15	<.01	**+0.00**	-0.18	0.09	n.s.
Southern Nordic	Europe	19	**-6.75**	-7.28	-1.55	<.01	**-0.05**	-0.21	0.05	n.s.
UK/Ireland	Europe	9	**-1.45**	-2.36	-0.61	<.01	**+0.02**	-0.32	0.57	n.s.
West Central Europe	Europe	12	**-3.95**	-9.50	-0.82	<.05	**-1.00**	-2.49	0.60	n.s.
Maine/Atlantic Canada	North America	17	**-1.02**	-1.12	-0.55	<.01	**+0.00**	-0.08	0.04	n.s.
Vermont/Quebec	North America	16	**-2.20**	-2.88	-1.93	<.01	**-0.20**	-0.31	0.15	n.s.
Adirondacks	North America	48	**-2.26**	-2.52	-1.72	<.01	**-0.47**	-0.91	-0.25	<.01
Appalachian Plateau	North America	9	**-2.27**	-3.48	-1.35	<.05	**-1.37**	-2.44	-0.14	<.01
Upper Midwest	North America	23	**-2.47**	-3.71	-1.69	<.01	**+0.02**	-0.06	0.06	n.s.
Virginia Blue Ridge	North America	3	**+0.35**	-0.03	0.55	n.s.	**-1.36**	-2.23	-0.65	<.01

			H^+				**Gran Alk**			
Region	Continent		**Median**	Lower CI	Upper CI	p	**Median**	Lower CI	Upper CI	p
Alps	Europe	6	**+0.00**	-0.12	0.01	n.s.	**-1.30**	-2.91	3.01	n.s.
East Central Europe	Europe	16	**-0.13**	-0.70	0.00	n.s.	**+1.19**	0.36	3.99	<0.05
Northern Nordic	Europe	7	**-0.07**	-0.67	0.02	n.s.	**+0.72**	-2.12	1.81	n.s.
Southern Nordic	Europe	19	**-0.16**	-0.34	-0.03	<.01	**+1.32**	0.66	2.94	<.05
UK/Ireland	Europe	9	**-0.29**	-0.57	0.01	n.s.	**+0.00**	-0.00	0.51	n.s.
West Central Europe	Europe	12	**+0.02**	-2.53	0.23	n.s.	**+0.01**	-9.04	6.49	n.s.
Maine/Atlantic Canada	North America	17	**+0.00**	-0.01	0.08	n.s.	**-0.82**	-1.16	-0.07	<.05
Vermont/Quebec	North America	16	**-0.05**	-0.20	0.03	n.s.	**+0.86**	0.19	1.09	<.05
Adirondacks	North America	48	**-0.19**	-0.39	-0.06	<.01	**+1.03**	0.67	1.31	<.01
Appalachian Plateau	North America	9	**-0.08**	-0.17	-0.01	n.s.	**+0.79**	0.16	1.40	<.05
Upper Midwest	North America	23	**-0.01**	-0.12	0.01	n.s.	**+0.90**	0.32	2.06	<.01
Virginia Blue Ridge	North America	3	**-0.00**	-0.07	0.00	n.s.	**+0.06**	-1.23	2.12	n.s.

			ANC				**Ca+Mg**			
Region	Continent		**Median**	Lower CI	Upper CI	p	**Median**	Lower CI	Upper CI	p
Alps	Europe	6	**-0.02**	-0.67	1.62	n.s.	**-1.35**	-2.56	2.15	n.s.
East Central Europe	Europe	20	**+2.55**	1.06	7.42	<.01	**-2.26**	-4.81	-0.49	<.05
Northern Nordic	Europe	7	**+0.26**	-1.24	2.28	n.s.	**-0.76**	-2.28	0.00	n.s.
Southern Nordic	Europe	19	**+3.30**	1.80	4.85	<.01	**-1.78**	-3.38	0.44	n.s.
Uk/Ireland	Europe	9	**+0.33**	-1.35	5.92	n.s.	**-0.19**	-1.62	3.01	n.s.
West Central Europe	Europe	12	**+6.02**	2.93	13.75	<.01	**-2.49**	-6.66	3.41	n.s.
Maine/Atlantic Canada	North America	17	**--**	--	--	--	**-0.62**	-2.16	-0.29	<.01
Vermont/Quebec	North America	16	**--**	--	--	--	**-1.40**	-1.80	-1.03	<.01
Adirondacks	North America	48	**--**	--	--	--	**-2.29**	-2.50	-1.59	<.01
Appalachian Plateau	North America	9	**--**	--	--	--	**-2.97**	-7.10	-1.78	<.01
Upper Midwest	North America	23	**--**	--	--	--	**-1.80**	-3.10	-1.01	<.01
Virginia Blue Ridge	North America	3	**--**	--	--	--	**-0.58**	-1.60	-0.04	<.05

			DOC			
Region	Continent		**Median**	Lower CI	Upper CI	p
Alps	Europe	0	**--**	--	--	--
East Central Europe	Europe	17	**+0.06**	-0.04	0.11	n.s.
Northern Nordic	Europe	7	**+0.05**	0.04	0.14	<.01
Southern Nordic	Europe	18	**+0.08**	0.02	0.16	<.01
Uk/Ireland	Europe	6	**+0.13**	0.08	0.20	<.01
West Central Europe	Europe	12	**+0.03**	-0.03	0.15	n.s.
Maine/Atlantic Canada	North America	17	**+0.04**	-0.03	0.10	n.s.
Vermont/Quebec	North America	16	**+0.06**	0.03	0.18	<.01
Adirondacks	North America	48	**+0.06**	0.02	0.09	<.01
Appalachian Plateau	North America	9	**+0.03**	-0.04	0.15	n.s.
Upper Midwest	North America	23	**+0.06**	0.03	0.11	<.01
Virginia Blue Ridge	North America	3	**-0.04**	-0.07	-0.02	<.05

Trends in sulphate by region

The most significant finding in this regional trend analysis, as in others conducted on earlier data (Stoddard et al. 1999, Skjelkvåle et al. 2001a), is the almost universal decrease in sulphate concentrations in lakes and streams throughout Europe and North America (**Table 5**, **Figure 3**). Only one region in this analysis failed to show a significant SO_4^{2-} decrease, and this is a region (the Virginia Blue Ridge) where soil characteristics make a SO_4^{2-} decrease unlikely (Cosby et al. 1986, Church et al. 1990). Although the number of ICP sites located in this region is small (n=3), they follow the pattern illustrated by a more comprehensive assessment of streams in the region (Stoddard et al. 2003). Sulphur-adsorbing soils typical of the Southern Blue Ridge exert a strong control on atmospherically-deposited SO_4^{2-}, and produce small but significant increases in surface water SO_4^{2-}, even during a time of decreasing rates of acidic deposition.

In Europe, regional rates of SO_4^{2-} decline ranged from ca. -1 µeq/L/yr in the U.K. and Ireland and the Northern Nordic region, to more than -6 µeq/L/yr in the Southern Nordic region. Rates in central Europe were intermediate, with both East- and West-Central Europe exhibiting regional SO_4^{2-} declines of ca. -4 µeq/L/yr. All of these changes represent ecologically significant declines in this acid anion, and are consistent with declines in rates of S deposition in Europe (see below).

Previous regional trend analyses of ICP data did not find decreases in SO_4^{2-} in the UK and Ireland, but the addition of data from the late 1990s and 2000s leads to a highly significant, though modest, rates of SO_4^{2-} decline (**Table 5**)

In North America, rates of SO_4^{2-} decline ranged from ca. -1 µeq/L/yr in the region with the lowest rates of S deposition (Maine and Atlantic Canada), to more than -2 µeq/L/yr in the Adirondack Mountains, Appalachian Mountains, and the Upper Midwest (U.S. and Canada). In an analysis of recent trends in both surface waters and deposition (Stoddard et al. 2003), conclude that lake and stream concentrations of SO_4^{2-} are declining more slowly than those in deposition, probably as a result of desorption of soil-stored sulphur.

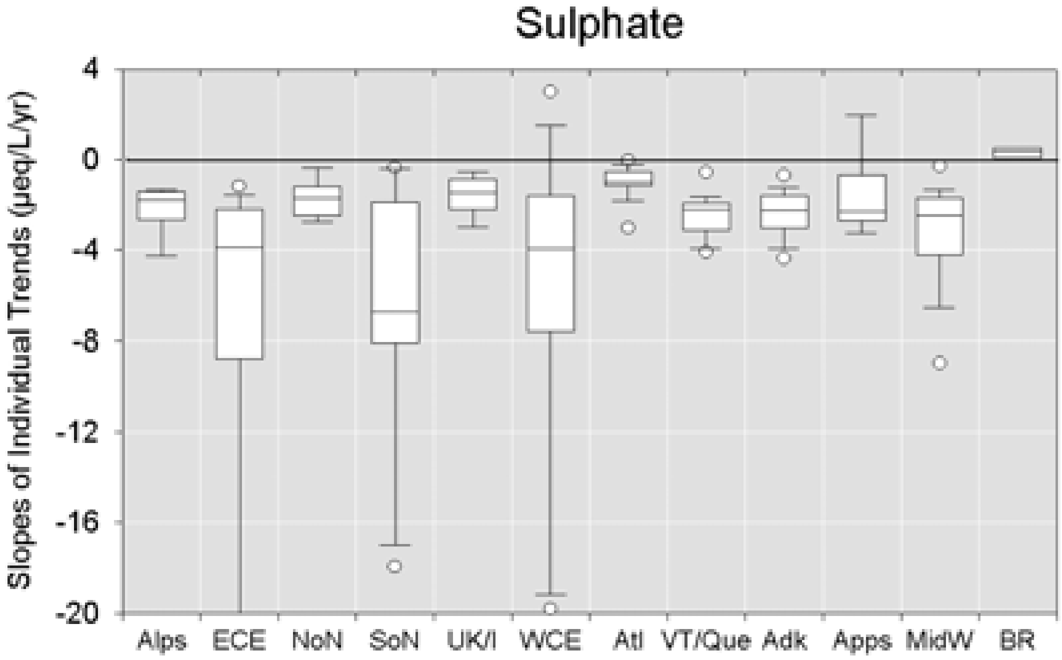

Figure 3. Distributions of slopes for SO_4^{2-} trends in ICP regions in Europe and North America. Each box shows the range (25th to 75th percentiles, with line at median) of slopes; confidence intervals indicate 10th and 90th percentiles; dots indicate 5th and 95th percentiles. Significance of regional trend is indicated by preponderance of slope values (e.g., 95%) either above or below zero. Abbreviated region names are: ECE=East-Central Europe; NoN=Northern Nordic; SoN=Southern Nordic; UK/I=United Kingdom and Ireland; WCE=West-Central Europe; Atl=Maine and Atlantic Canada; VT/Que=Vermont and Quebec; Adk=Adirondack Mountains; Apps=Appalachian Plateau; MidW=Upper Midwestern U.S. and Canada; BR=Virginia Blue Ridge.

Trends in sulphate in sites not sensitive to acidification (Baltic region and Hungary)

Some of the ICP Waters sites are regarded as insensitive to acidification (ANC > 200 μeq/L). However, we wanted to see if the general decrease in sulphate that are observed in acid sensitive sites also are found in these sites (**Table 6**). Only three of the eight sites show significant trends, and of these one is increasing and two are decreasing. It is difficult to interpret this pattern. These sites are obviously influenced by local sources of sulphate in the catchment, either from natural conditions (geology) or anthropogenic input (agriculture).

Table 6. Trend slopes of SO_4 is sites not sensitive to acidification. Significant slopes indicated in bold. Mean ANC (1999-2001) are also given.

		Trend slope SO_4^{2-} μeq/L/yr	P	N	ANC μeq/L
Belarus	BY01	28.9	0.07	41	2691
Estonia	EE01	-5.0	0.06	58	3889
Hungary	HU01	116.0	0.09	24	761
Latvia	LV01	-9.0	0.05	40	2724
	LV02	**-11.2**	0.01	62	3780
	LV03	-9.0	0.58	72	3464
	LV04	**-13.1**	0.00	95	2884
	LV05	**32.0**	0.00	40	362

Trends in nitrate by region

Fewer than half of the ICP regions exhibited significant regional trends in NO_3^- (**Table 5**), and only the Alps region showed a significant increase. Regional declines in NO_3^- since ca. 1990 have been noted elsewhere (Stoddard et al. 1999, Skjelkvåle et al. 2001a), and need to be interpreted cautiously. The time period of data analysed in the current ICP report, and in previous reports, is on the order of a decade. While decadal trends in ions undergoing incremental and consistent changes (i.e., SO_4^{2-}) can be validly interpreted as a recovery from acidic deposition, they may not represent true long-term changes for ions as temporally variable as NO_3^-. Both mathematical (Aber and Driscoll 1997) and conceptual (Stoddard 1994, Wright et al. 2001) models of nitrogen suggest that long-term catchment responses to N deposition may occur on the time scale of centuries, rather than decades. Several large scale analyses of NO_3^- data suggest the strong spatial patterns observed, with the highest NO_3^- concentrations occurring in regions of highest N deposition, can only be explained by long-term accumulation and eventual leakage of atmospherically-deposited NO_3^- from catchment soils and vegetation (Dise and Wright 1995, Stoddard et al. 2001). A recent comprehensive assessment of North American data has shown that these spatial patterns are evident in forest foliage, soils and surface waters (Aber *et al.* 2003), and concludes that many of the trends reported for lake and stream NO_3^- may represent only the short-term variation in a large-scale and long-term increase in NO_3^- due to nitrogen saturation.

Over the 12-year period 1990-2001, ICP sites show decreasing NO_3^- concentrations in the Adirondack Mountains, Appalachian Mountains and the Virginia Blue Ridge (all in North America), and increasing concentrations in the Alps. In all other regions there is no individual clear pattern (**Figure 4**). Within each of the regions there are some sites with increasing or deacreasing. Some sites in Central Europe (DE08, DE17, DE27 and CZ04) show increasing trends due to forest disturbance (harvesting or insects), while other sites in sensitive areas show decreasing trends. Vesely *et al.* (2002) have showed that NO_3 in streamwaters with pH less than or equal to 6 in Czech Republic have decreased up to 60% between 1984-86 and 1996-2000. This is greater than the decrease of N emission in central Europe of about 35% in the same period. Extensive regional decrease of NO_3 is surprising and is probably described for the first time. The difference in NO_3 concentrations between the two periods was probably enhanced by (a) an increase of mineralisation of forest floor in the mid-1980s and (b) by higher uptake of N in the late-1990s (Vesely *et al.* 2002).

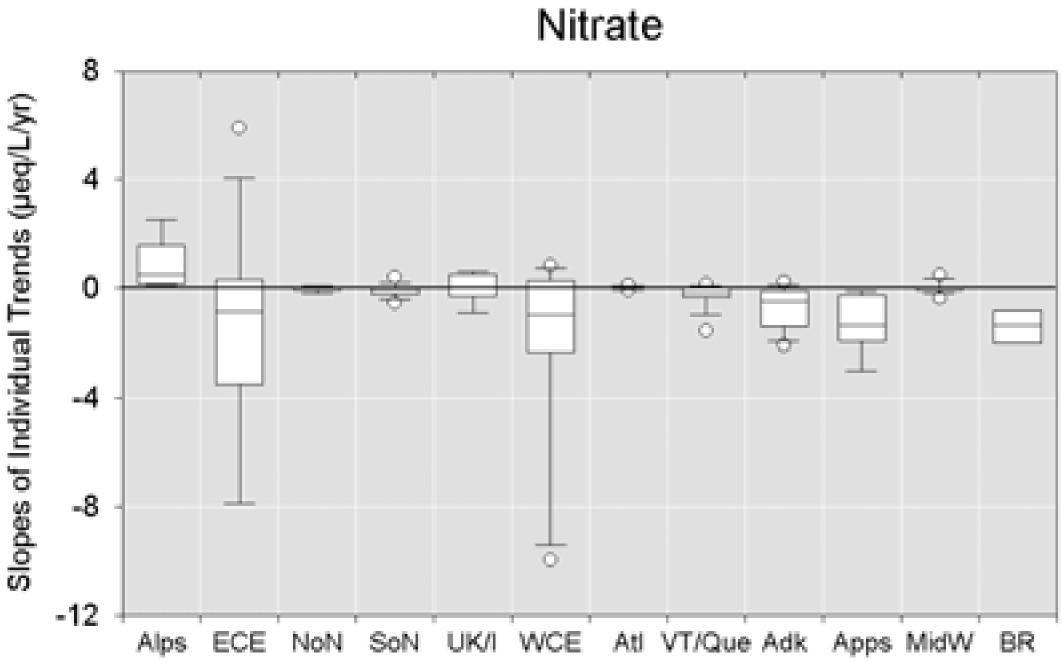

Figure 4. Distributions of slopes for NO_3^- trends in ICP regions in Europe and North America. Interpretation of boxes and whiskers, as well as region names, are as in **Figure 3**.

Trends in base cations by region

One of the expected responses of catchments to decreasing SO_4^{2-} is a decrease in base cation concentrations (Galloway et al. 1983). In this report, we use the sum of calcium and magnesium (Ca+Mg) as a surrogate for total base cations, because these cations are the most quantitatively important at the majority of acid sensitive monitoring sites, and because they exert the most control over alkalinity (Stoddard et al. 2003). As expected, all of the ICP regions show tendency toward decreasing Ca+Mg (**Figure 5**). One of the key findings of earlier regional assessments (Stoddard et al. 1999, Skjelkvåle et al. 2001a) is the larger-than-expected decreases in Ca+Mg in some regions, particularly in North America. When rates of Ca+Mg decline are equal, or nearly equal, to rates of SO_4^{2-} and NO_3^- decline, then recovery (increasing alkalinity and pH) is prevented.

In the European regions, rates of Ca+Mg decrease are often zero, and always smaller than those for SO_4^{2-} (**Table 5**, **Figure 5**). Rates of Ca+Mg decline in North America tend to be larger than in Europe, and in some cases are in the same range as SO_4^{2-} declines (but see discussion of Gran alkalinity, below).

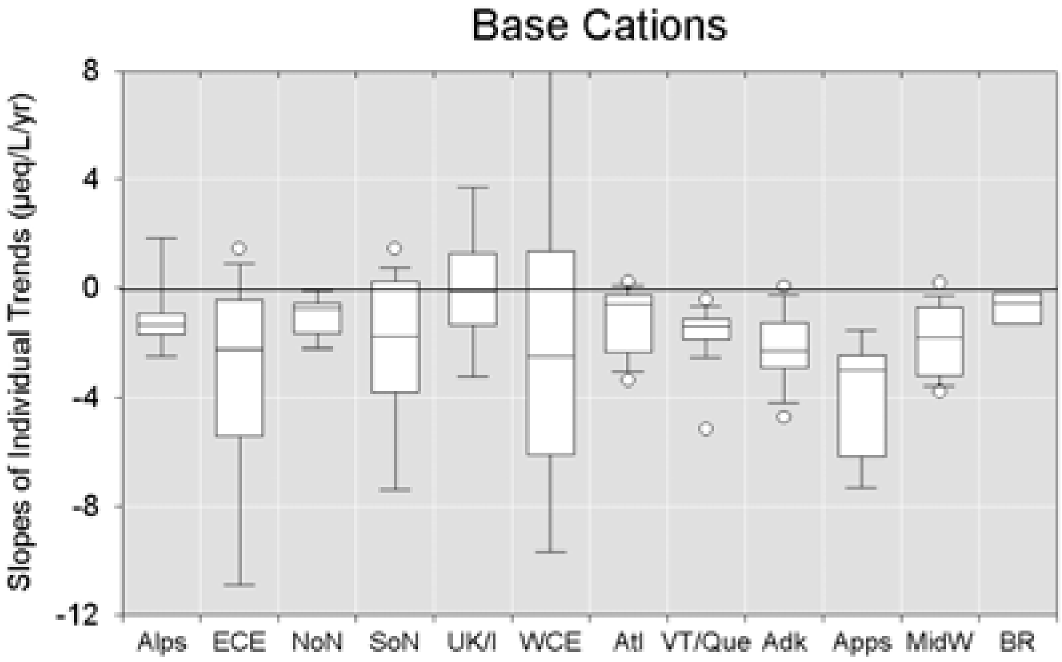

Figure 5. Distributions of slopes for base cation (Ca+Mg) trends in ICP regions in Europe and North America. Interpretation of boxes and whiskers, as well as region names, are as in **Figure 3**.

Trends in alkalinity and ANC by region

Because SO_4^{2-} is declining regionally in almost all ICP regions, and NO_3^- is either declining or unchanged in all but one region, we expect to see increases in the key indicators of recovery from acidification, Gran alkalinity (measured), ANC (calculated) and pH (decline in H^+). Gran alkalinity is a measured variable that indicates the water's ability to buffer acidic inputs. ANC (acid neutralising capacity) is a calculated surrogate for alkalinity. ANC is defined as the equivalent sum of base cations minus the equivalent sum of strong acid anions. The decrease in sulphate and the slight increase or decrease in NO_3^- combined with more moderate declines in base cations, produce an expectation of recovery in alkalinity (and ANC).

In the Alps, SO_4^{2-} is declining at a median rate of -1.8 µeq/L/yr. Combined with a median increase in NO_3^- of +0.5 µeq/L/yr, the Alps exhibit an overall change in acid anion concentrations of -1.3 µeq/L/yr, which is almost exactly the median change in base cations for this region (-1.35 µeq/L/yr). As a result, there is no increase in alkalinity in the Alps, and no significant recovery is discernible in the data (**Table 5**, **Figure 6**).

In East-Central Europe, the decline in $SO_4^{2-}$is -3.9 µeq/L/yr, considerably larger than the decline in base cations for this region (-2.3 µeq/L/yr) (NO_3^- did not change significantly). The observed significant increase in Gran alkalinity of +1.2 µeq/L/yr is consistent with these changes in SO_4^{2-} and Ca+Mg (**Table 5**, **Figure 6**), and represents significant recovery at sites in Poland, the Czech Republic, and eastern parts of Germany. A handful of sites in this region do not report gran alkalinity values (n=16), but a total of 20 sites have sufficient data to calculate ANC. Trends in ANC suggest a faster rate of recovery (+2.6 µeq/L/yr) for the region (**Table 5**, **Figure 7**), with 75% of the sites exhibiting increasing ANC.

In the more remote Northern Nordic areas, rates of deposition have historically been lower than in the rest of Europe; as a result, acidification is much less severe, and rates of recovery are not expected to be large. Despite significant declines in SO_4^{2-} of -1.7 µeq/L/yr in this region. Alkalinity shows no trend (**Table 5**, **Figure 6**).

By contrast, the Southern Nordic region has experienced high rates of acidic deposition, especially in past decades, and significant surface water acidification (e.g., Henriksen et al. 1988, Kämäri et al. 1991, Skjelkvåle et al. 2001b). Recovery in the southern portions of Norway, Sweden and Finland have been observed since ca. 1990 (Stoddard et al. 1999, Skjelkvåle et al. 2001b), and continue into the 2000s (**Table 5**). During the period 1990-2001, this region experienced large decreases in surface water SO_4^{2-}, no change in NO_3^-, and increases in Gran alkalinity of +1.3 µeq/L/yr (**Table 5**). More than 75% of ICP sites in the Southern Nordic region exhibited upward trends in Gran alkalinity, and all sites exhibited upward trends in ANC (**Figure 7**).

The modest decreases in surface water SO_4^{2-} at ICP sites in the UK and Ireland, combined with small and insignificant decreases in Ca+Mg, are apparently not sufficient to produce significant change in Gran alkalinity (**Table 5**, **Figure 6**) or ANC (**Figure 7**).

In West-Central Europe, no regional increase in Gran alkalinity is observed (**Table 5**) despite substantial decreases in SO_4^{2-}. Curiously, calculated ANC suggests a strong recovery in this region (**Table 5**, **Figure 7**) while measured Gran alkalinity does not. There were many large inconsistencies between the slopes in alkalinity and ANC at single sites in this region, which make it difficult to conclude with any confidence that recovery is occurring. Certainly, the relatively close balance between SO_4^{2-} trends (-3.9 µeq/L/yr) and base cation trends (-2.5 µeq/L/yr) make an overall change in ANC of +6 µeq/L/yr (**Table 5**) unlikely.

In North America four regions show significant improvement in Gran alkalinity (Vermont/Quebec, Adirondacks, Appalachians and Upper Midwest), one region with no change (Virginia Blue Ridge), and the only ICP region in the current analysis exhibiting significant further acidification (Maine/Atlantic Canada). Recovery in the Adirondack and Appalachian mountains, and in the Upper Midwest, is an important finding because none of these regions showed significant improvement in previous regional analyses (e.g., (Stoddard et al. 1999, Skjelkvåle et al. 2001a). All of these regions exhibit upward alkalinity trends that began in the early- to mid-1990s, and in all cases 75% or more of the individual sites have positive trend slopes (**Figure 6**). In the Adirondacks, in particular, recent widespread recovery has received much attention, and includes increasing Gran alkalinity and pH, as well as significant decreases in toxic aluminium (Driscoll *et al.* 2003, Stoddard et al. 2003). Evaluation of the changing pattern of chemical trends observed in Canadian lakes over the past ten years shows that there has been a gradual shift from "no response" to "recovery" although the degree of recovery is still clearly at a very early stage (Jeffries *et al.* 2003).

The Virginia Blue Ridge region is not experiencing, nor is it expected to experience, decreasing SO_4^{2-} concentrations. As a result, there is no expectation that Gran alkalinity will increase in the immediate future; the current analysis indicates there has been no significant change in alkalinity during 1990-2001 (**Table 5**).

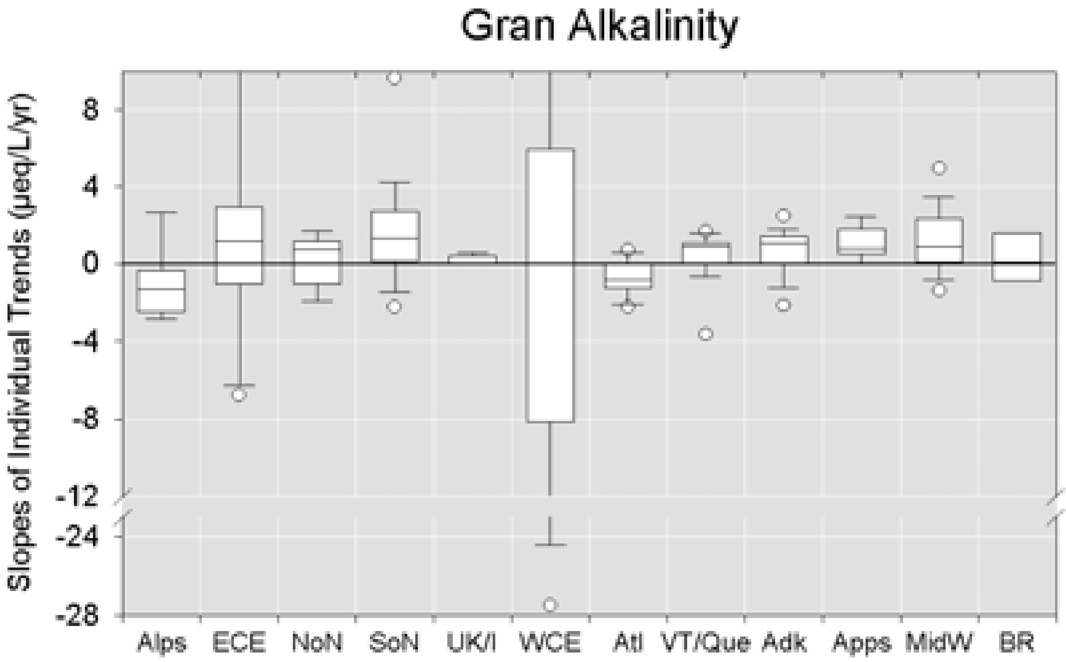

Figure 6. Distributions of slopes for Gran alkalinity trends in ICP regions in Europe and North America. Interpretation of boxes and whiskers, as well as region names, are as in **Figure 3**.

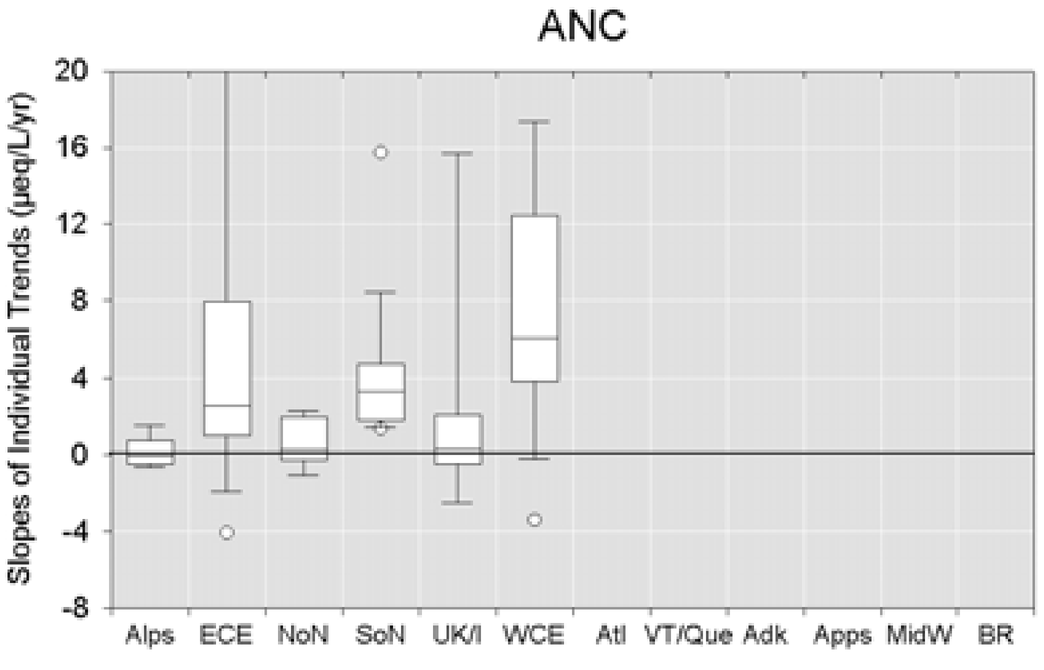

Figure 7. Distributions of slopes for calculated ANC trends in ICP regions in Europe and North America. Interpretation of boxes and whiskers, as well as region names, are as in **Figure 3**. (ANC values were not calculated for the North American regions.)

The region of Maine and Atlantic Canada is the only ICP region where significant acidification has occurred during the 1990s and early 2000s. This is despite significant (but small) decreases in surface water SO_4^{2-}. While it is not immediately obvious in the median trend slopes presented in **Table 5**, many of the ICP sites in this region have larger decreases in base cations (see **Figure 5**, where roughly half of the sites show downward trends of the magnitude -1 to -3 µeq/L/yr), than SO_4^{2-} (**Figure 3**, with nearly all slopes in the -0.5 to -1.5 µeq/L/yr range). This somewhat extreme base cation behaviour has been noted previously in other regions now undergoing recovery (e.g., Kirchner and Lydersen 1995, Lawrence et al. 1999, Couture, 1995, Jeffries *et al.* 2002), and still has no accepted geochemical explanation. It appears currently to be preventing recovery in Maine and Atlantic Canada.

Trends in pH by region

Chemical recovery of surface waters involves a combination of changes towards a more natural historical, chemical composition. Included in these changes are decreases in SO_4^{2-} and potentially NO_3^- (in regions where NO_3^- has been a significant agent of acidification in the past), and increases in alkalinity and pH. Of these changes, increases in pH are perhaps the most biologically relevant due to the relation between low pH and high concentrations of toxic aluminium. In the current assessment we analyse trends in hydrogen ion (calculated from pH measurements). An increase in pH implies a decrease in hydrogen ion concentration. Only two of the regions exhibit significant H^+ declines (the Southern Nordic and Adirondack regions) (**Table 5**, **Figure 8**). (The decrease in H^+ in UK/Ireland is not significant, possible due to the low number of sites n=9). Both are among the top three regions in terms of Gran alkalinity improvement. pH is among the most difficult variables to measure well in the laboratory and variability in measurements makes it more difficult to detect trends. A longer data record might overcome inherent variability in the data, and lead to a conclusion of increasing pH in additional regions.

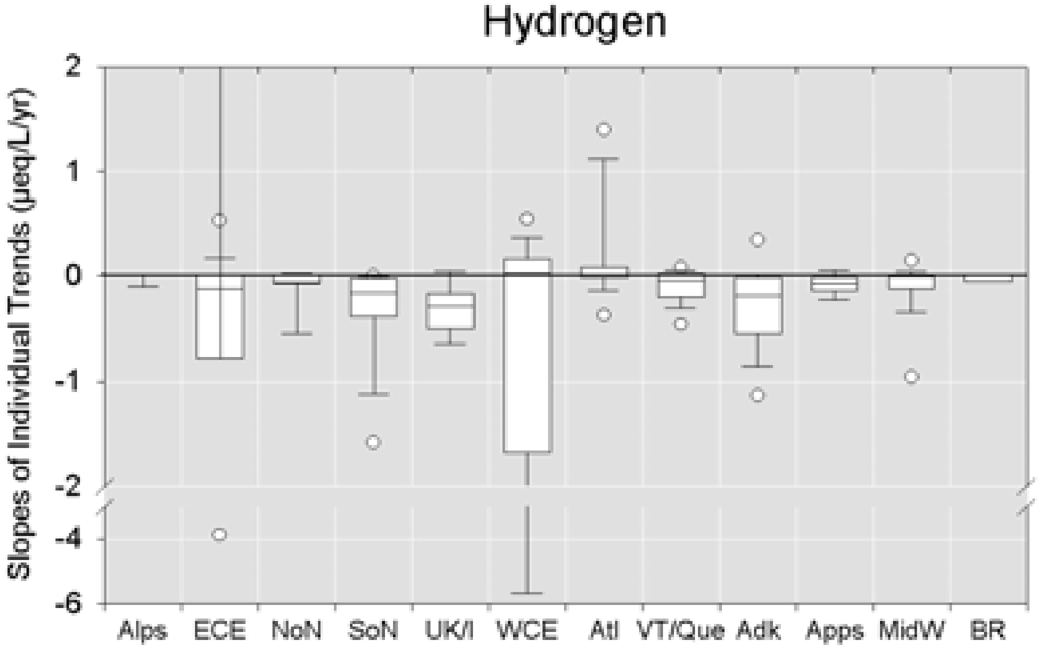

Figure 8. Distributions of slopes for hydrogen ion trends in ICP regions in Europe and North America. Interpretation of boxes and whiskers, as well as region names, are as in **Figure 3**. Increasing pH (an indicator of recovery) is the same as decreasing H^+.

Trends in DOC by region

Dissolved organic carbon (DOC) is of great interest in any analysis of surface water recovery, because it is an indicator of natural organic acidity (Driscoll et al. 1989). The previous ICP trends report (Skjelkvåle et al. 2000) was one of the first to note the widespread increases in DOC now being observed throughout Europe and North America. Six of the 10 ICP regions analysed exhibit positive slopes for DOC (**Table 5**). Increasing DOC at ICP sites indicates that concentrations of organic acids are rising. The explanaition for this is further discussed in chapter 2.7.

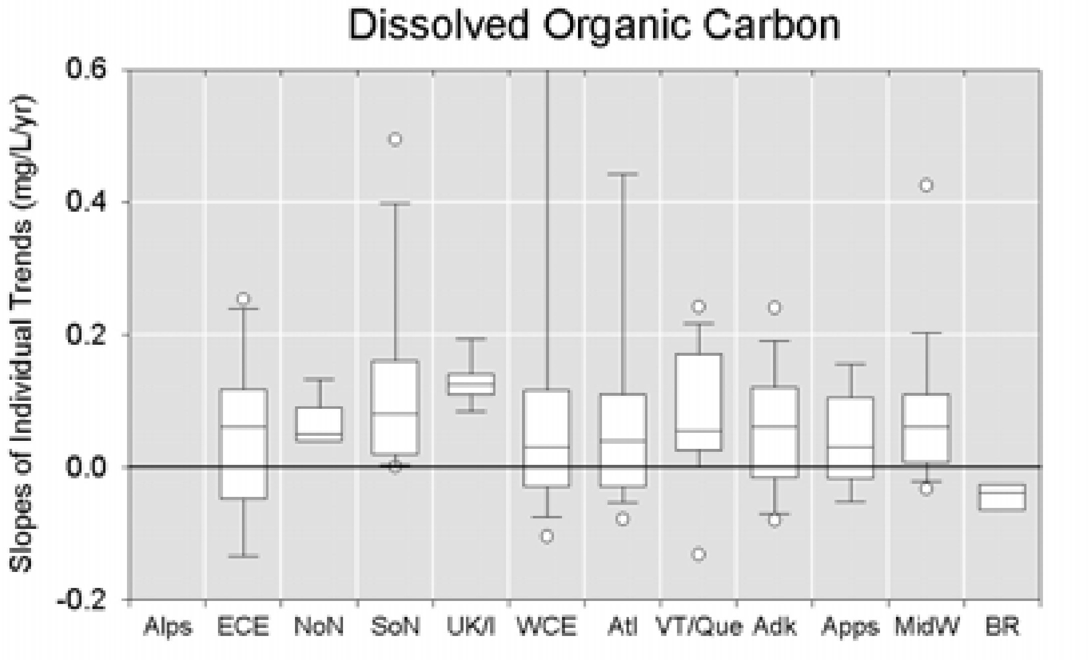

Figure 9. Distributions of slopes for trends in dissolved organic carbon in ICP regions in Europe and North America. Interpretation of boxes and whiskers, as well as region names, are as in **Figure 3**. Increasing DOC is an indicator of the increased importance of organic acids in the acid/base chemistry of ICP sites.

2.6 Confounding factors in future recovery of water chemistry

The uncertainties in future chemical recovery mainly relate to the effects of climate change and the future behaviour of nitrogen in the ecosystem. Four major climate-related confounding factors that may influence the chemical and biological recovery process are: i) increased frequency and severity of sea-salt episodes; ii) increased frequency and severity of drought and increased rainfall; ii) increased turnover of organic carbon; iv) increased mineralisation of nitrogen. An additional confounding factor may be internal alkalinity production in lakes.

The recovery may also be delayed by reasons that are already discussed in the text, such as decrease in base cations due to decrease in deposition or reduced release of base cations from the soils, or increase in sulphate in runoff water despite reduced deposition due to leakage of old sulphate stored in the catchments.

Sea-salt episodes

The “sea-salt effect” in surface waters (Wiklander 1975) is important in areas receiving substantial inputs of marine sea-salts as well as acid deposition, in particular coastal areas in Norway, the UK, Ireland, the US and Canada (e.g. Heath et al. 1992, Hindar et al. 1994, Langan 1989). The sea-salt effect may temporarily increase the acidity of the runoff by ion-exchange of Na^+ from sea-salts with Al^{3+} and H^+ in the catchment soil.

The North Atlantic Oscillation (NAO) Index (Bjerknes 1964) describes the large-scale weather systems in the north Atlantic Ocean which influence weather patterns in Europe, particularly in winter. The NAO index can be correlated to sea-salt episodes in near-coastal surface waters in the UK and Norway. The NAO may lead to cyclical patterns of aluminium and acidity in runoff on a decadal timescale (Evans et al. 2001, Hindar et al. 2002). These cyclical changes are effectively superimposed on, and may obscure, long-term trends in acidity associated with changing acid deposition. In addition, recent climate forecasts (Hulme et al. 2002) predict a dramatic increase in the NAO Index over the next 80 years, implying that warm, westerly conditions in winter may become more prevalent. A greater frequency and intensity of sea-salt episodes may therefore be expected in coastal surface waters.

Hydrological changes

Water table or lake level draw-down due to drought allows wetland soils and littoral zone sediments to dry thereby producing conditions where previously-reduced S species are oxidised. When the systems re-wet, export of the resulting mobile sulphate produce occasions of episodic acidification when H^+ was an important co-exported cation, and extended periods of elevated sulphate (relative to pre-drought levels) when calcium was typically the compensating cation.

Drought has particularly influenced sulphate-export from some lakes in Ontario, Canada where reduction and storage of sulphate in wetlands, and subsequent re-oxidation and release, have been shown to have a major impact on runoff water quality and hence recovery trends (Dillon and LaZerte 1992, Dillon et al. 1997, Yan et al. 2003, Jeffries et al. 2003,). In the UK, large flushes of sulphate were widely observed in streams following a drought in 1995, e.g. (Harriman et al. 2001) and in Norway following a summer drought in 1976 (Cristophersen *et al.* 1980).

Analysis of UK monitoring data show that the dominating confounding factor for recovery is a dilution effect resulting from increased rainfall and changes in flow path. Many climate scenarios suggests substantial changes in rainfall.

In effect, these climate-regulated S retention and releases represent ‘noise’ within an overall recovery trend. Release of stored S will delay recovery where pools are large. Additionally, sulphate flushes following droughts (particularly if these become more severe due to climatic change) may continue to generate acidic episodes in future, despite improvements in baseline water quality.

These drought-driven episodes can both be more extreme or frequent in future climate scenarios and may in the same way as sea-salt episodes contribute to delay both chemical and biological recovery in surface waters.

Increased content of organic carbon in lakes

The regional trends of increasing organic carbon, recorded during the current period have also been observed in earlier monitoring and documented from the UK (Evans and Monteith 2001), the Nordic countries (Skjelkvåle et al. 2001b) elsewhere in Europe (Skjelkvåle et al. 2001a), and in the US (Stoddard and Kahl 2002, Stoddard et al. 2003), while the picture is less straightforward in Canada (Jeffries et al. 2003).

These increases may be coupled to warmer climate, particularly to elevated summer temperatures (Freeman et al. 2001), due to increases in decomposition rates in soils, especially in peatlands (e.g. Tranvik and Jansson 2002, Evans et al. 2002). If changes are temperature-driven, a warmer future climate may lead to further increases in DOC concentrations, with complex consequences for surface waters; these include increased organic acidity, increased buffering of changes in pH, increased complexation with Al (lowering of toxicity), increased water coloration, and decreased visible light and UV-B penetration within the water column.

While increased organic acidity may delay chemical recovery from acidification in surface waters, the other factors may influence biological recovery.

Future behaviour of nitrogen

The 1999 Gothenburg protocol (UNECE 1999) is based on the precautionary principle in that it assumes that all N-deposition over a certain catchment-specific threshold value will leach out in runoff water in the future (Henriksen and Posch 2001). This leakage is the potential contribution of N to acidification. Today most catchments retain far more N than this hypothesis would suggest. At present, there is very limited evidence of this occurrence in Europe or North America (Couture 1995, Jeffries et al. 2002, this report). Replacement of declining sulphate export by increasing nitrate export as occurs in ecosystems that are approaching N saturation will nullify acidification recovery. The extent of N retention in the future, and consequently the future influence of N on surface water acidification, therefore represents a key uncertainty in future recovery from acidification.

Additional uncertainties with regard to N processes relate to the influence of climate (short and long-term) on nitrate leaching, which may alter the long-term trend, or simply add ‘noise’ to the anthropogenic signal. Because internal ecosystem cycling of N greatly exceeds system inputs and outputs, any disturbance of this cycle has the potential to completely obscure the relationship between N deposition and runoff.

In the UK, large pulses of nitrate have been observed in surface waters following severe winters possibly as a result of soil freezing (Monteith et al. 2000). This is also shown from the US (Mitchell et al. 1996). The frequency of such pulses may be expected to change in future in response to altered climate. Results from the CLIMEX project (Wright and Jenkins 2001), where ambient air and soil temperature was increased over three years, show increased leaching of inorganic N, probably due to increased mineralization and nitrification rates in the soils.

Continued high deposition of nitrogen should tend to increase N saturation and give increased nitrate concentrations in runoff, thereby delaying recovery due to reductions in S-emissions. Increased temperature due to climate change may increase nitrate in runoff and thereby also contribute to delay in recovery. The role of nitrogen in both acidification and recovery continues to deserve additional research.

Internal alkalinity production

Factors that affect internal alkalinity generating processes may profoundly influence lake acidification or recovery. The importance of internal alkalinity generation in lakes generally increases with the water replenishment time and is of significance for lakes with residence time > 3 years. Typically the most important processes underlying internal alkalinity generation include sulphate reduction, denitrification, ion exchange at the water-sediment interface, and DOC degradation. Whole-lake acidification studies conducted at the Experimental Lakes Area (ELA) in northwestern Ontario, Canada have indicated that internal alkalinity generation can be impaired such that the pH trajectory during recovery differs from the acidification trajectory (Jeffries 1997). At a minimum there is a lag in the pH recovery relative to the sulphate decline, and a significant likelihood that the chemical condition of the lakes is proceeding to a different state than the original. Impairment of internal alkalinity generation also appears to depend partly on the severity of the acidification. For example, reducing the pH below 5, as was the case in one ELA experiment impaired the lake’s internal alkalinity generation, while lowering the pH to only 5.1 in another experiment did not. The impairment of a lake's biogeochemical ability to internally buffer acids means that the efficiency of acidifying inputs is greater during the recovery period than it was during acidification.

Factors accelerating recovery

In the same way as some processes confound recovery from acidification, other factors related to global climate change may also accelerate the recovery process. Here we mention some few known factors, but we dont intend to give a full review of all possible accelerating factors.

Vesely et al (2003 in press) have shown that the 10% of the decrease in Al in Czech lakes from 1984-1999 can be explained by increase in avearge annual temperature. The inverse relationship between Al solubility and temperature caused lower Al mobilization in soil horizons and/or enhanced precipitation of Al in the lakes at higher temperature but otherwise similar conditions. Consequently, the recent period of warmer years and mild winters significantly contributed to the trend of decreasing Al in lakes recovering from acidification.

An increased release of base cations due to enhanced weathering rate induced by climate warming can accelerate the recovery (Sommaruga-Wögrath *et al.* 1997). Temperature changes affect snowpack dynamics in mountain areas determining depth and duration of the snow cover and extent of the area subject to weathering in the different periods of the year.

Episodic deposition of Saharan dust can neutralize the acidic input associated with atmospheric deposition (Loÿe-Pilot *et al.* 1986). This factor may be particularly important in the alpine and subalpine areas.

2.7 Do trends in deposition translate into trends in surface waters?

A major goal of the work of ICP Waters is to evaluate the changes in surface water chemistry in relation to reductions in emission and deposition of S and N.

It is difficult to compare absolute changes in sulphate concentrations in surface waters and deposition, because of the effects of dry deposition and evapotranspiration. Both dry deposition and the evaporative concentration of ions in surface waters cause sulphate concentrations in lakes and streams to be higher than in deposition. Higher concentrations lead to larger rates of change for sulphate concentrations in surface waters than in deposition. The percent change, however, should be relatively similar, assuming that dry deposition declines at the same rate as wet deposition, and that no changes in rates of evapotranspiration have occurred over time. There is a relatively good correlation between percentage change and concentration level, which means that sites with low concentrations of sulphate show high percentage of change and sites with high concentrations of sulphate show low percentage change. This will influence the comparison between regions, but the comparison between change in deposition and surface waters in the same region is unaffected.

We therefore present a comparison of percent change in sulphate in precipitation and surface waters for each of the regions. Precipitation data are from EMEP Coordination Centre for Chemistry (CCC).

In general, rates of sulphate decline are smaller in surface waters than in deposition for all regions in North America and most regions in Europe (**Figure 10**) indicating a lagged response. This may reflect the desorption of S that has accumulated in catchment soils over the past century due to atmospheric deposition. Desorption of stored S has the effect of damping the trends in surface water sulphate and slowing the rate of decline. One exception to the pattern in North America is in the Upper Midwest region of the U.S. (**Figure 10**), where most lakes are seepage lakes. Here, the soils play only a minor role in controlling sulphate concentrations, and declines in lake sulphate concentrations reflect a recovery from the drought that affected this area in the late 1980s and early 1990s (Stoddard *et al.* 2003). Currently, this recovery from drought is producing declines in sulphate larger than would be predicted from rates of decline in atmospheric deposition. In Europe, both the Alps and the UK/Ireland regions show approximately same percentage change in precipitation and surface waters indicating a very direct response on surface waters to changes in precipitation.

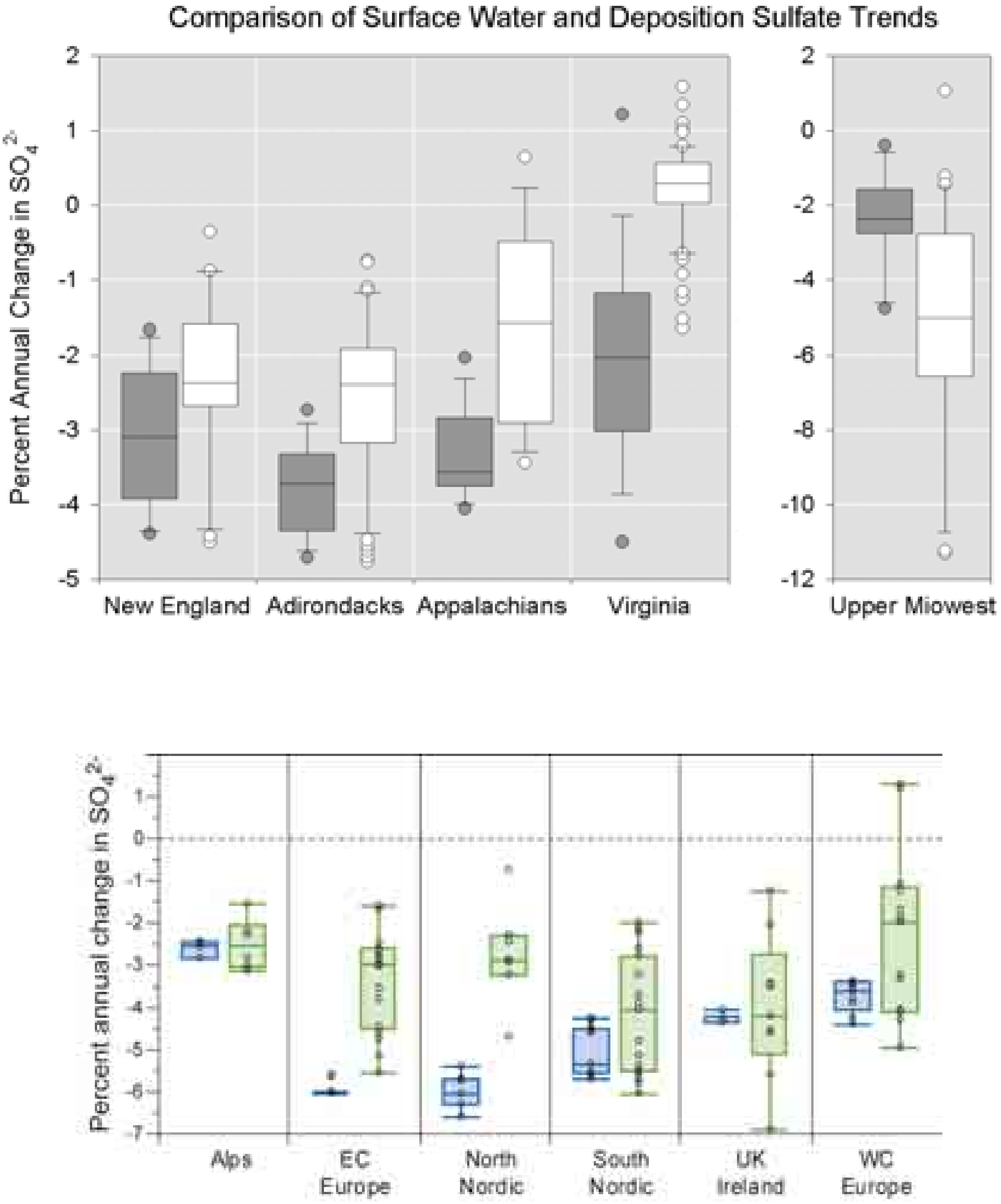

Figure 10. Comparison of trend slopes for SO_4^{2-} in precipitation (left box) and SO_4^{2-} in surface waters (right box) for the period 1990-2000 in acid sensitive regions of the USA and in Europe. Wet deposition concentrations for U.S. are from the National Atmospheric Deposition Program (NADP) (from Stoddard et al. 2003), and for Europe from EMEP CCC. Each box shows the range (25th to 75th percentiles, with line at median) of slopes; confidence intervals indicate 10th and 90th percentiles; dots indicate 5th and 95th percentiles. Significance of regional trend is indicated by preponderance of slope values (e.g., 95%) either above or below zero.

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3. Is biology failing to recover from acidification?

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During the last decades a significant reduction in sulphur emissions has taken place both in Europe and North America (Stoddard et al. 1999, Skjelkvåle et al. 2003) pointed out that significant large scale recovery is documented for improvement in water chemistry, while such data are lacking for biology. The aim of this review is to look behind these statements and evaluate the reason for "the lack" of biological recovery. Focus will be on the most important factors determining the biological recovery in different regions and what should be expected in relation to the recovered chemical status. Some important issues identified at the ICP Waters sponsored Workshop on Models for Biological Recovery from Acidification in a Changing Climate (Wrigt and Lie, 2002) sponsored by ICP Waters are listed below.

- Improvements in water chemistry have not yet reached the level necessary for acid sensitive species to recover (recovery can not start before water quality is suitable).
- Episodes of acid water connected with snowmelt, sea-salt deposition etc. will prevent stable recovery and result in multiple recolonisations (an on/off situation for sensitive species)
- Bottlenecks arise due to problems of dispersal of sensitive species (arrival factors)
- Bottlenecks arise due to interactions and competition with other species (survival factors of the sensitive species)
- Dispersal mechanisms are affected by stream and lake characteristics such as size, morphology, distance from refugia, etc.
- Dispersal and recolonisation are dependent on life cycle and behaviour (resting eggs, flying insects, size etc.)

There is difficulty in defining biological recovery. Is it reversal of acidification to a pre-acidic species assemblage, or the development of a community reflecting the chemical and physical environment at the moment? The recovery pathways will be affected by global warming, sea-salt episodes, droughts, changing hydrology etc. and these must be evaluated to understand the recovery.

Water chemistry data consist of measured chemical concentrations, exact numbers where the detection limits determine the significance level of the analyses. Biological data are often less accurate and do not have the same possibility to detect small changes.

3.1 Status of chemical recovery

Stoddard et al. 1999 have suggested that many regions showed early signs of recovery in water chemistry during the 1980s, but that the rate of recovery appears to have accelerated during the 1990s. Generally, thin soils have low cation exchange capacity and little retention of deposited sulphur. This is typical for large areas in Scandinavia and some high mountain areas in Europe. Lakes and rivers in these areas are therefore poorly buffered against acid deposition, and will undergo rapid acidification. When deposition decreases, they are also expected to show relatively fast recovery (Skjelkvåle et al. 2003). On the other hand, lakes and surface waters in areas with deep and older soils have a higher buffering capacity and sulphur retention, and they become acidified more slowly. These localities are likely to recover slowly due to release of stored sulphur. Chemical recovery in such areas is likely to be slow (Prechtel et al. 2001).

Other factors have also been shown to obscure chemical recovery. In the UK, cyclical variations in the deposition of sea-salts appear to have masked recovery trends during the early part of the 1990s (Evans et al. 2001). In US, there are examples of strong decreases in base cation deposition that have offset the decline in sulphate, and thereby reduced the magnitude of recovery or even contributed to further acidification (Stoddard et al. 1999).

Overall, the extent of chemical recovery from acidification in Europe varies over time, between regions, and between sites within regions, depending on a range of factors. These are the magnitude of deposition change, catchment characteristics, land management, and the role of so-called ‘confounding factors’ (Skjelkvåle et al. 2003). In general there is clear evidence that reduced S deposition has led, or will ultimately lead, to significant improvements in the chemical status of acidified surface waters throughout Europe.

3.2 Status of biological recovery

Biological recovery was documented during the 1990’s in running waters in watersheds in south-western Norway by increased acidification indexes as well as reappearance of acid sensitive species (SFT 2001, Raddum et al. 2001). The data have been analysed by multivariate statistical analyses to test if the improvements also can be detected as changes in the abundance of invertebrates. The method used is described in detail in Skjelkvåle et al. 2000). Several of the localities in the Norwegian monitoring network showed significant recovery of the macrobenthic communities over time, corresponding to improvements in water chemistry (Halvorsen *et al.* 2002). Based on material from Sweden, Halvorsen (op cit.) demonstrated that recovery is occurring in both highly acidified and slightly acidified lakes, but generally biological recovery is less pronounced in Swedish lakes. The multivariate methods show, however, that they can detect biological changes outside the range of the acidification index.

In the UK, evidence for biological recovery is limited, but individual sites showing chemical improvements also show shifts from acidophilous to acid-sensitive invertebrate assemblages (Monteith and Evans 2001, Tipping et al. 2002). In Germany only very few examples of biological recovery exists (Bauer in Wright and Lie, 2002). This is, however, in accordance with the lack of recovery in water chemistry in central Europe (Alewell et al. 2001). In Canada, biological recovery varies in lakes surrounding the large nickel smelter at Sudbury, Ontario where sulphur emmissions have declined by more than 90% over the last 30 years. The recovery has occurred among insects as well as zooplankton **(**Snucins et al. 2001, Yan *et al.* 2003), but lack of recovery is also common. In conclusion, reports of biological recovery are therefore more scattered than water chemical recovery.

3.3 Magnitude of water chemical - versus biological recovery

Lakes in high mountain areas in Scandinavia with thin soil cover, such as those monitored in Norway, can become rapidly acidified, but recover quickly as well. Improvements in the water chemistry (Skjelkvåle et al. 2003) and in the biological communities (Raddum et al. 2001, SFT 2002) occur quickly in response to reduced input (**Figure 11**, **Figure 12**). The recovery is also traced by multivariate analysis of invertebrate data from such areas (**Figure 13**) (Halvorsen et al. 2002).

In regions with deeper and older soils acidification of surface waters is slower due to high retention of sulphur and cation exchange. Acidified lakes and streams in such areas also recover more slowly (central Europe, UK, parts of Sweden) (Skjelkvåle op cit.). The scattered and often lack of biological recovery is mostly associated to these regions. The immediate conclusion based on these observations is that the sensitive biology has responded in accordance with the critical limits of the species but that the changes in water quality are low in most cases. Recovery of sensitive species is stepwise and not smooth like in water chemistry. The changes in chemistry must therefore be substantial before bilogical recovery can occur. The scarce biological recovery in areas with deeper soils is as expected in relation to chemical recovery.

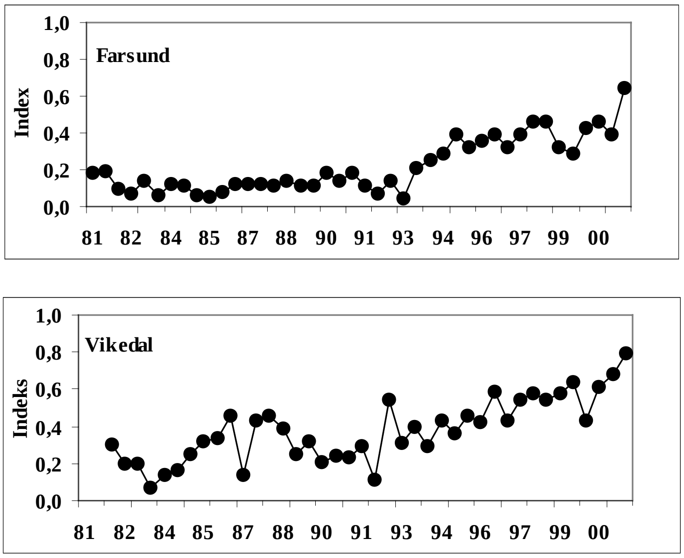


Figure 11. Acidification index for invertebrates in streams in two catchments in southern Norway during the period 1981 to 2001. An index of 0 indicates acidophilic fauna assemblage, while an index of 1 indicates normal, undamaged assemblage.

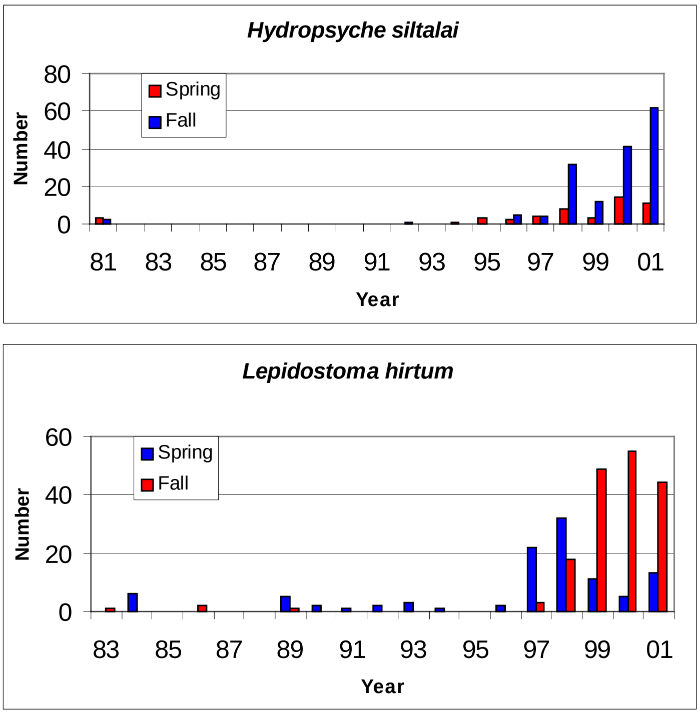


Figure 12. Biological recovery of two moderately acid-sensitive invertebrate species in two acidified sites in southern and western Norway. The major improvement in water quality with regard to acidification started about 1990. Upper panel: The development of the acid sensitive species *H. siltalai* in the Farsund area, southern Norway. Lower panel: Development of the acid sensitive species *L. hirtum* in Nausta, western Norway (SFT 2002).

The magnitude of chemical recovery for areas in southern Norway can be illustrated by using the model of Hindar and Wright 2002) for estimating chemistry in lakes prior to acidification.

As example we use one of the lakes in the Farsund area, where a significant chemical recovery has occurred. The estimated pH of the lake was 6.3 prior to acidification. At present the pH is 5.3-5.4 during turnover in autumn. In the early eighties the pH was approximately 4.7 for that period. The moderately sensitive species *H. siltalai* (**Figure 12**) which has a critical limit of about pH 5, was absent in the 1980s, but recovered during the 1990s. Very sensitive species, with critical limit of pH 5.5, are not yet present in stable populations, but have appeared from time to time after 1995 (**Figure 13**) which corresponds with better water quality during summer. In this locality the biological response has been very fast and the sensitive fauna reflect the chemical status more or less immediately. The chemical recovery, however, seems still to be far from the ideal target which should be pH > 6. The chemical recovery has only commenced but is far from complete. The biology has recovered in accordance with the chemical environment and is also in an early stage since populations of very sensitive species are still mostly absent.

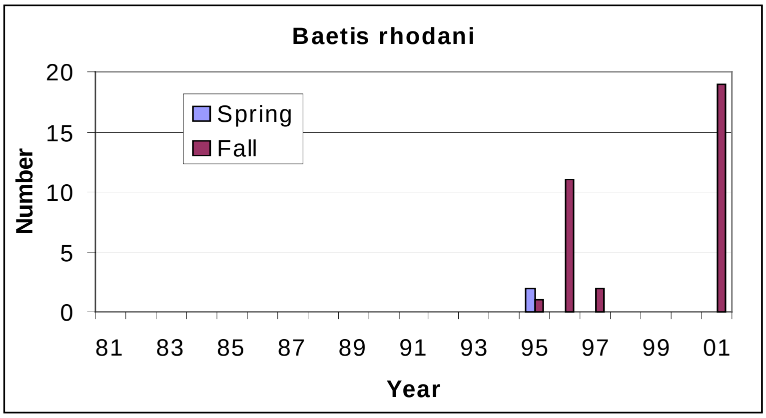


Figure 13. Occurrence of the very acid sensitive mayfly-species *B. rhodani* in Farsund.

3.4 Episodes of acid water

The water chemistry is subjected to a number of episodes with low pH and poor water quality. The reason for this is snowmelt, sea-salt deposition, droughts etc. The recovery of water chemistry is therefore not a smooth line, but highly variable. Significant improvements in pH is illustrated for unlimed parts in River Audna in southern Norway (**Figure 14**) and Trodøla (Nausta watershed) in western Norway (**Figure 15**). The significant chemical improvements measured as mean values are of low relevance as long as the severity of the episodes exceeds the critical limits of sensitive species. **Figure 18** illustrates how annual variations in sea-salt episodes affect both water chemistry and biology. A stable recovery of sensitive species can first take place when the episodes do not harm or wipe out the species. At present the recovery in water quality does not prevent damaging episodes and multiple recolonisations of sensitive biota will occur (**Figure 13**). This seems to be the case in many Norwegian watersheds, demonstrating that the chemical recovery so far is not sufficient to establish a diverse acid-sensitive community. When describing chemical recovery it is important to evaluate the variability in the improvements and its relevance for the biota.

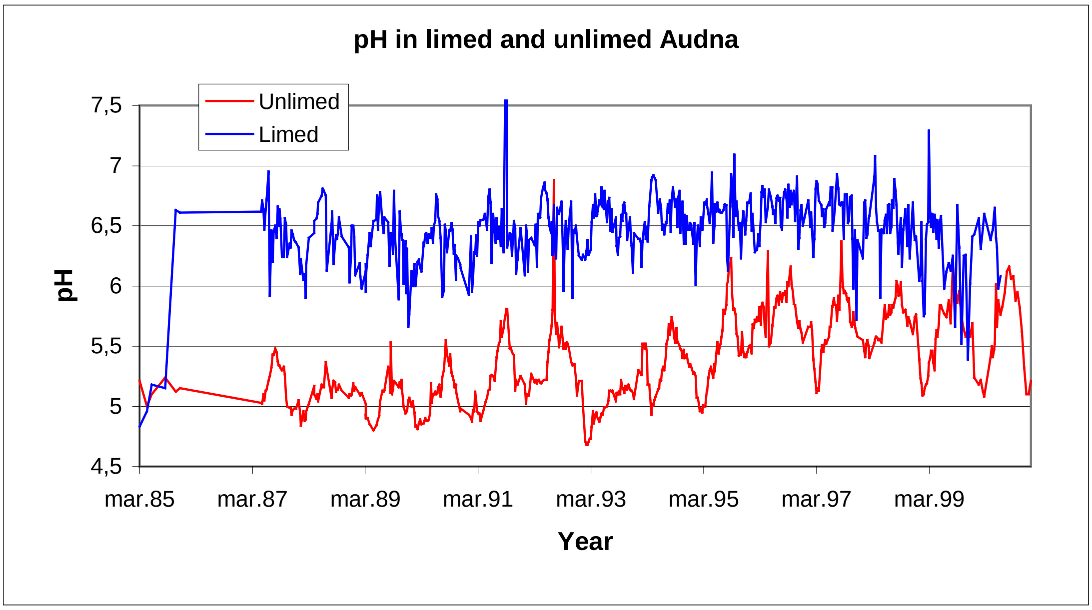


Figure 14. pH in limed and unlimed River Audna, southern Norway during the period spring 1985 – 2000.

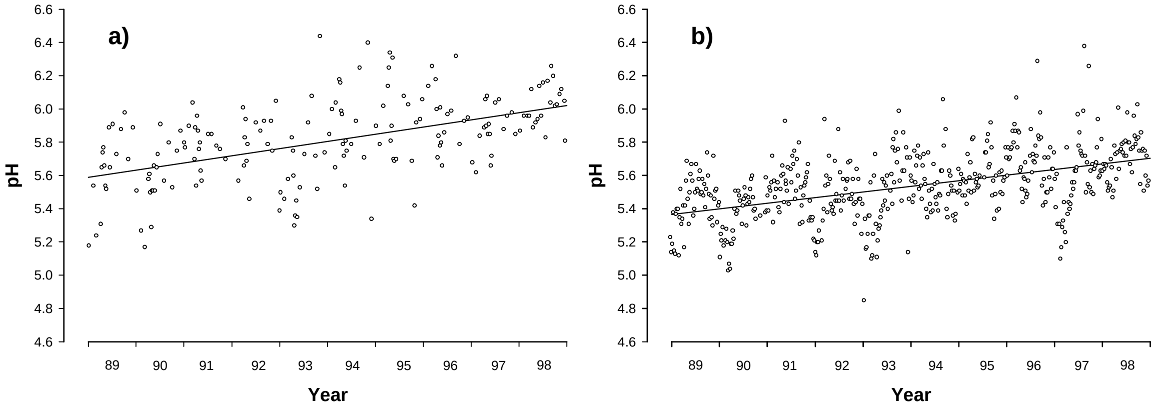


Figure 15. Regressions of all of the pH measurements on time from 1989 to 1998 in the Nausta river, western Norway. **a)** - the main river Nausta at locality 11. **b)** - the tributary Trodøla at locality 7 (from Halvorsen *et al.* 2003)

3.5 Factors connected to arrival, survival and dispersal

Reappearance of extinct sensitive species in a chemically-recovered locality will vary depending on type of organism. Zooplankton can develop from resting eggs in the sediment. Winged insects can easily be transported through air, but distance to source locality, flying ability, longevity and dispersal behaviour will be important. In running water downstream drift will be an additional important dispersal mechanism from a source locality.

Biotic recovery in lakes takes longer time and is less predictable than recovery in rivers (Yan *et al.* 2003, Raddum and Fjellheim 2003). Competition and predation effects, especially on zooplankton in lakes from fish and invertebrate predators, make it difficult to evaluate recovery. In running water fish predation on invertebrates is relatively low and can seldom be measured. Both fish and sensitive invertebrates increase in parallel in River Audna after liming (Raddum and Fjellheim 2003) (**Figure 16**). Arrival and dispersal have been studied in River Audna, southern Norway, where the water quality become acceptable for most acid sensitive species immediately after liming. Reappearance of sensitive species took from 2 - 10 years in the limed River Audna. After arrival the different sensitive species dispersed to the whole limed stretch within 5 years (**Figure 16**) (Raddum and Fjellheim 2003).

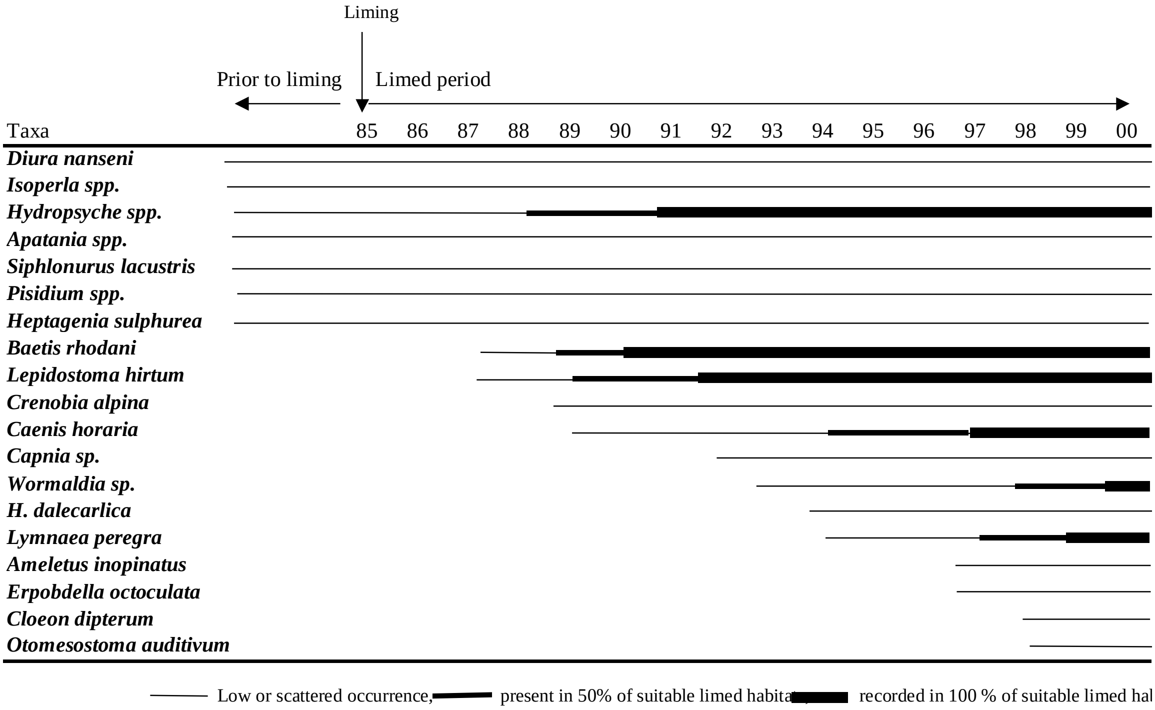


Figure 16. Summary of the development of sensitive taxa in limed River Audna after 15 years of liming.

Liming gives an indication of the expected recovery of invertebrates in response to fully recovered water chemistry. The chemical situation between the limed and unlimed part of River Audna also gives an illustration of the status of the chemical recovery in unlimed parts of River Audna (**Figure 14**). The recovery of sensitive species in this part is about 1/3 compared with the number in the limed part after 15 years of liming (**Figure 17**). This is another example indicating that the recovery in water chemistry is not yet sufficient for recovery of the most sensitive invertebrates.

3.6 Conclusion

There is no lack of biological recovery after improvements of water chemistry. When the water quality is good enough sensitive fauna recover, but the sequence of steps in the ecological recovery process is insufficiently understood since all biological communities are of dynamic nature. This implies that an ecological system can not return to an earlier stage, but always will reflect the surrounding physical, chemical and biological environment. “Lack of recovery” may simply be the manifestation that species composition may move in different directions in different localities after improvements in water quality.

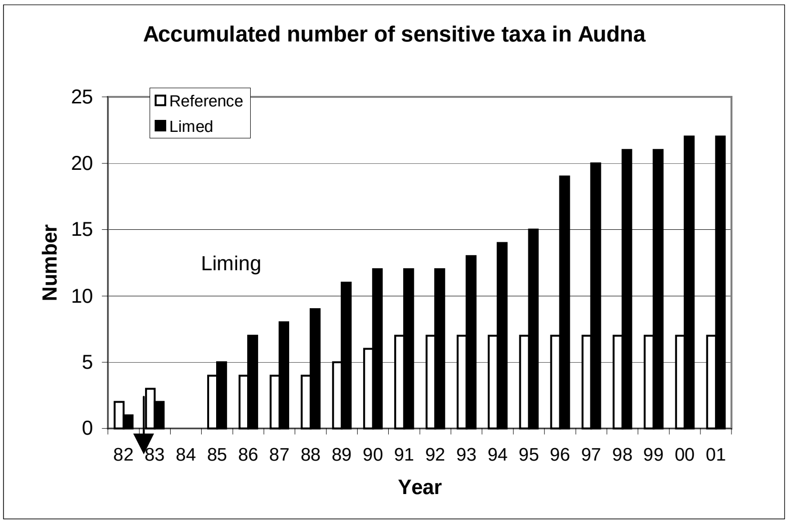
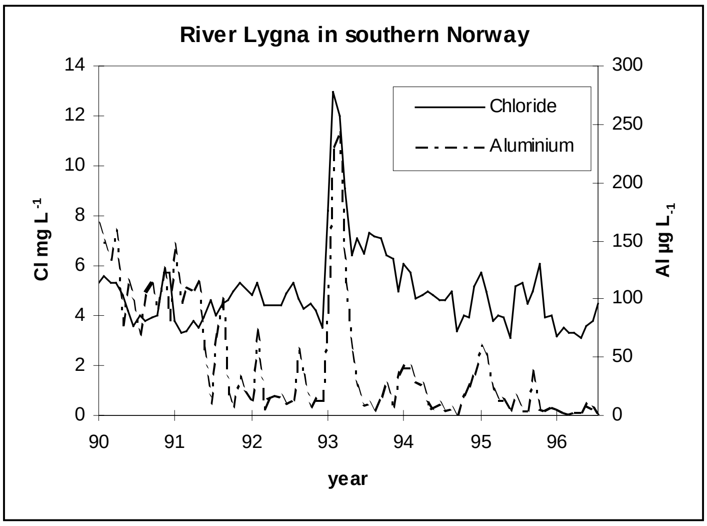


Figure 17. Accumulated number of sensitive taxa recorded in limed and unlimed sites in River Audna, Southern Norway.



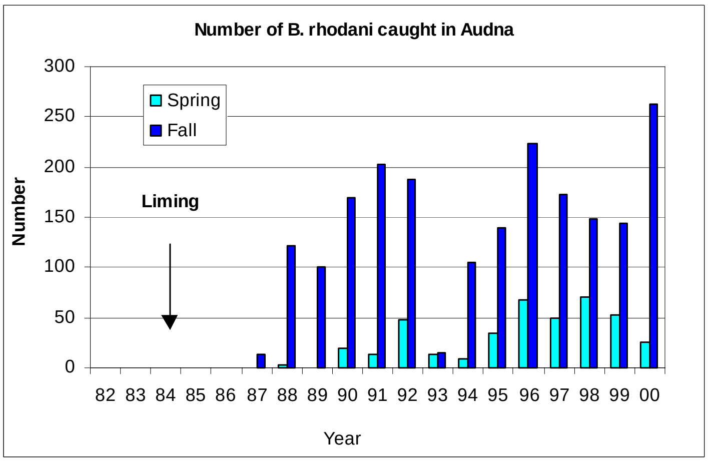


Figure 18. Effects on water chemistry and biology of a winter storm with high transport of sea-salt 1993 in southern Norway. Upper panel shows chloride and inorganic aluminium in River Lygna from 1990 to 1996. The decrease in Al from 1990 to 1993 is due to chemical recovery in this river, while the peak in 1993 is due to the sea-salt episode. Bottom panel shows effect of the seasalt episode on biota (number of caught *Baetis Rhodani*) in the neighbouring river Audna. River Audna is limed from 1985. From Skjelkvåle et al. 2003).

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4. Dynamic Modelling of Surface Waters: Impact of emission reduction - possibilities and limitations

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The link between the emission of oxides of sulphur and nitrogen and reduced nitrogen to the atmosphere and the acidification of soils and surface waters is now well established and understood. The impact of the chemical changes on biota is also sufficiently understood such that chemical targets aimed at protecting both aquatic and terrestrial biota have been established to form the basis of international agreements on emission reductions within the UNECE and EU. The link between deposition of acidic pollutants and the loss of or damage to biota, however, is not immediate.

Just as the damage to biota was delayed beyond the onset of acid deposition, so the recovery from acidification will also be delayed. In the chain of events from the deposition of strong acids to the damage to key indicator organisms there are two major factors that can give rise to time delays. Biogeochemical processes can delay the chemical response in the catchment soils and consequently surface waters and biological processes can further delay the response of indicator organisms, such as damage to fish. The static models to determine critical loads consider only the steady-state condition, in which the chemical and biological response to a change in deposition is complete. Dynamic models, on the other hand, attempt to estimate the time required for a new (steady) state to be achieved. This report describes the possibilities and limitations of using dynamic models to better define the limits and timescales of the recovery processes.

With critical loads, i.e. in the steady-state situation, only two cases can be distinguished when comparing them to deposition: (1) the deposition is below (and or equal to) critical loads, i.e. does not exceed critical loads, and (2) the deposition is greater than critical loads, i.e. there is critical load exceedance. In the first case there is no (apparent) problem, i.e. no reduction in deposition is deemed necessary. In the second case there is, by definition, an increased risk of damage to the ecosystem, and therefore the deposition should be reduced. A critical load serves as a warning as long as there is exceedance, since it tells that deposition should be reduced. However, it is often assumed that acidification of soils and surface waters is fully reversible and that reducing deposition to (or below) critical loads immediately removes the risk of ‘harmful effects’, i.e. the chemical parameter (e.g. the [ANC]-limit) that links the critical load to the biological effect(s), immediately attains a non-critical (‘safe’) value and that there is immediate biological recovery as well. The removal of the risk of further damage, however, does not necessarily imply that recovery will occur. In addition, the reaction to changes in deposition is delayed by (finite) buffers, such as the cation exchange capacity (CEC) in catchment soils. These buffers can delay the attainment of a critical chemical parameter and it might take decades or even centuries, before a (new) equilibrium (steady state) is reached. These finite buffers are not included in the critical load formulation, since they do not influence the steady state, but only the time to reach it. It is also likely that the desirable or critical chemical target will be achieved prior to a new steady state and so the concept of equilibrium in the long term becomes irrelevant. Dynamic models, therefore, are needed if we wish to estimate the times involved in attaining a certain chemical state in response to given deposition scenarios, e.g., the consequences of ‘gap closures’ in emission reduction negotiations. In addition to the delay in chemical recovery, there is likely to be a further delay before the ‘original’ biological state is reached, i.e. even if the chemical criterion is met (e.g. [ANC]>0), it will take time before full biological recovery is achieved as a result of the dispersion characteristics of the species, for example. On the other hand, the possibility remains that the original biological status will not be recovered but this possibility is common to both critical load and dynamic approaches.

The possible development of a chemical and biological variable in response to a ‘typical’ temporal deposition pattern can be summarised into five stages (**Figure 19**):

Stage 1: Deposition was and is below the critical load (CL) and the chemical and biological variables do not violate their respective criteria. As long as deposition stays below the CL, this is the ‘ideal’ situation.

Stage 2: Deposition is above the CL, but (chemical and) biological criteria are not violated because there is a time delay before this happens. No damage is likely to occur at this stage, therefore, despite exceedance of the CL. The time between the first exceedance of the CL and first violation of the biological criterion (the first occurrence of actual damage) is termed the *Damage Delay Time* (DDT=t_3–t_1).

Stage 3: The deposition is above the CL and both the chemical and biological criteria are violated. Measures (emission reduction) have to be taken to avoid a (further) deterioration of the ecosystem status.

Stage 4: Deposition is below the CL, but the (chemical and) biological criteria are still violated and thus recovery has not yet occurred. The time between the first non-exceedance of the CL and the subsequent non-violation of both criteria is termed the *Recovery Delay Time* (RDT=t_6–t_4).

Stage 5: Deposition is below the CL and both criteria are no longer violated. This stage is similar to Stage 1 and only at this stage can the ecosystem be considered to have recovered.

Stages 2 and 4 can each be further subdivided into two sub-stages: Chemical delay times (DDT_c=t_2–t_1 and RDT_c=t_5–t_4; dark grey in Figure 1) and (additional) biological delay times (DDT_b=t_3–t_2 and RDT_b=t_6–t_5; light grey). Very often, due to the lack of operational biological response models, damage and recovery delay times mostly refer to chemical recovery alone and this is used as a surrogate for overall recovery.

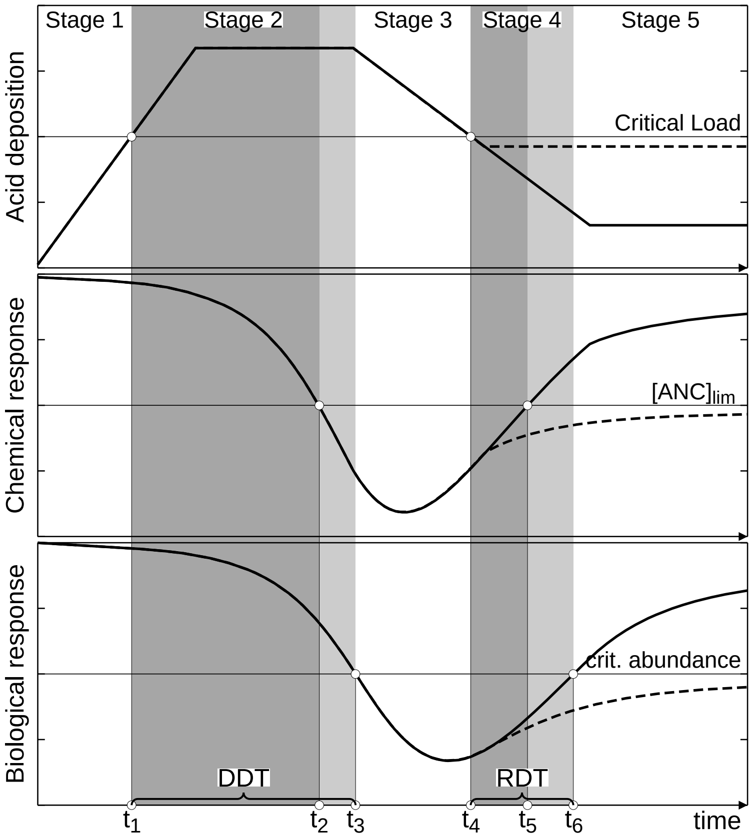

***Figure 19.** 'Typical' past and future development of the acid deposition affects on a lake chemical variable (ANC concentration) and the corresponding biological response in comparison to the critical values of those variables and the critical load derived from them. The delay between the (non-) exceedance of the critical load, the (non-) violation of the critical chemical criterion and the crossing of the critical biological response is indicated in grey shades, highlighting the Damage Delay Time (DDT) and the Recovery Delay Time (RDT) of the system. If deposition is reduced only to the critical load, recovery takes much longer (dashed lines).*

The speed of recovery also depends on the extent of the deposition reduction (**Figure 19**). If deposition is reduced to (or just below) the critical load only, chemical and biological recovery might take a very long time (see dashed lines in **Figure 19**). The determination of delay times (DDT and RDT) as a function of the deposition reductions is an important task of dynamic modelling since these strongly influence target loads and are helpful to assess the likely chemical response of freshwaters to an agreed emission reduction within a given timescale. These delay times are new quantitative information which is complementary to the critical loads concept. Modelling of DDT and RDT allows assessment of deposition scenarios which are, from a critical loads point of view, equal but which may have very different biological consequences.

Dynamic models have a key role to play in the review of the latest (Gothenburg) Protocol for emission reductions and can provide a new effects driven basis to underpin any further negotiations in the future. They can be applied to determine the timing of ecosystem recovery in response to the Gothenburg Protocol and their capabilities in this respect are documented in this report. Models can be used to predict recovery from acidification of soils and surface waters since it is not possible to de-couple the soil and water system with respect to chemistry, but this report is focused only on surface waters as model outputs. Dynamic models for assessing soil responses are fully documented elsewhere (Posch *et al*. 2002).

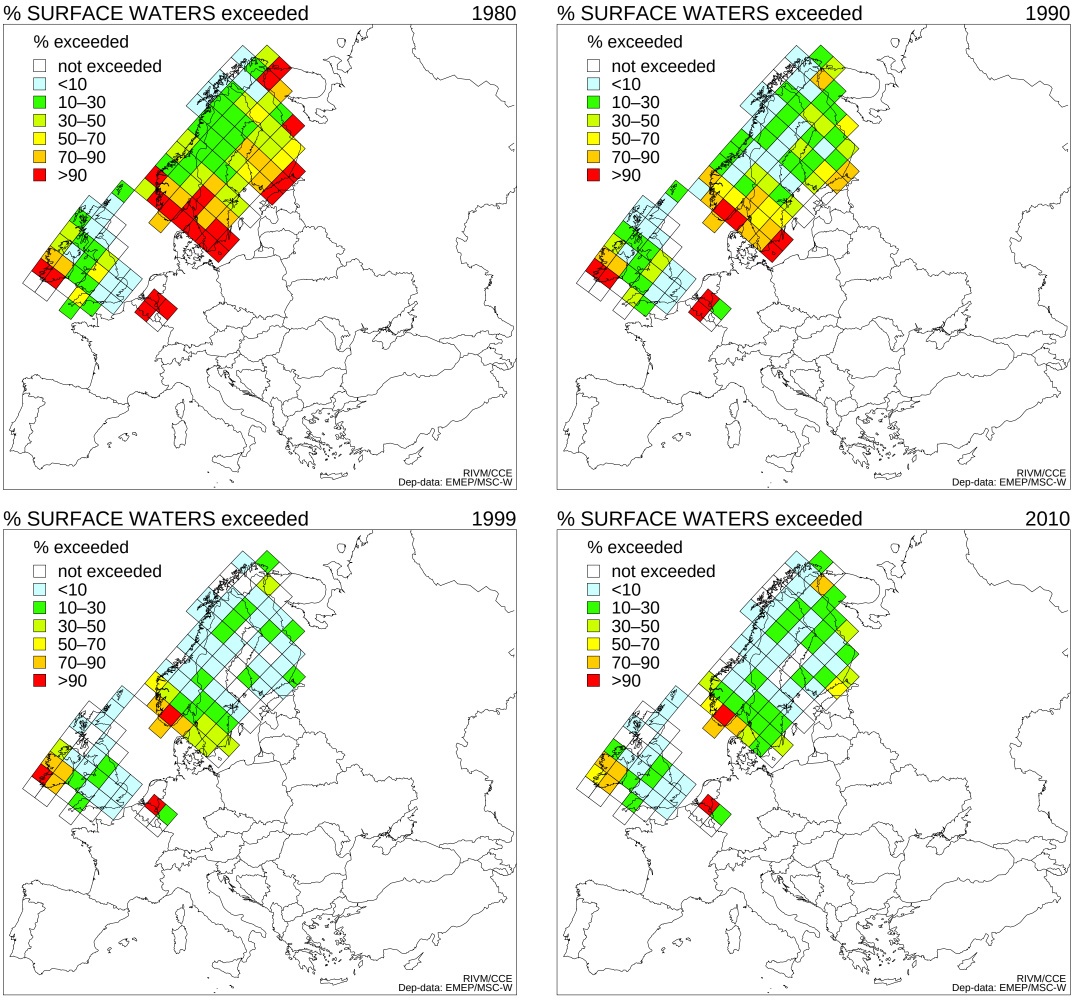

Figure 20. *Surface water critical load exceedances at EMEP grid scale, 1980 (maximum deposition) to 2010 (assuming implementation of the Gothenburg Protocol). Dynamic modelling is appropriate in almost all squares for which data was reported to the CCE.*

Dynamic model applications are to a certain extent limited by the availability of suitable data to describe the physico-chemical characteristics of surface waters and their terrestrial catchment areas, especially soil chemistry. Given this requirement, it is clear that the focus of dynamic model applications should be on areas that are considered to be acidified or acid ‘sensitive’. This makes sense within the framework of the Convention since emissions across Europe are declining and will continue to decline into the foreseeable future under the Gothenburg Protocol and so the speed of recovery from acidification is the key question. An attempt to identify acid sensitive regions has been initiated by the Joint Expert Group on Dynamic Modelling (UNECE 2002) and this implies a wider extent of the problem (**Table 7**) than might be inferred from an analysis of critical load exceedances (**Figure 20**).

4.1 Dynamic Models of Surface Waters

Four models have been identified as being widely used, documented and tested with respect to the requirement of the Convention (Posch *et al*. 2002) and which are simple enough to be applied on a regional scale; SAFE (Warfvinge *et al*. 1993), SMART (De Vries *et al*. 1989), VSD (Posch and Reinds 2003) and MAGIC (Cosby *et al*. 1985a). An overview of the first three models, all of which are effectively plot scale soil models is given in Posch *et al*. (2002). The MAGIC model, however, focuses on surface water chemistry and is generally applied at catchment scale. The catchment implicitly modelled by MAGIC is defined by the location of the surface water sampling point and can, therefore, vary considerably in size. A key difference, therefore, is that weathering rates must be calibrated from surface water and soil chemistry data rather than estimated empirically or from mineralogy (e.g. using PROFILE; Warvfinge and Sverdrup 1992).

4.1.1 The MAGIC Model

MAGIC (**M**odel of **A**cidification of **G**roundwater **I**n **C**atchments) is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on soils and surface water chemistry (Cosby *et al*. 1985a,b,c, 1986). The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of the major ions in lakes and streams. MAGIC represents the catchment with aggregated, uniform soil compartments (one or two) and a surface water compartment that can be either a lake or a stream. MAGIC consists of (1) a section in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving sulphate adsorption, cation exchange, dissolution-precipitation-speciation of aluminium and dissolution-speciation of inorganic and organic carbon, and (2) a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering inputs, net uptake in biomass and losses to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change in surface water acidity thus depend both of flux factors and the inherent characteristics of the affected soils.

The soil layers can be arranged vertically or horizontally to represent important vertical or horizontal flowpaths through the soils. If a lake is simulated, seasonal stratification of the lake can be implemented. Time steps are monthly or yearly. Time series inputs to the model include annual or monthly estimates of (1) deposition of ions from the atmosphere (wet plus dry deposition; (2) discharge volumes and flow routing within the catchment; (3) biological production, removal and transformation of ions; (4) internal sources and sinks of ions from weathering or precipitation reactions; and (5) climate data. Constant parameters in the model include physical and chemical characteristics of the soils and surface waters, and thermodynamic constants. The model is calibrated using observed values of surface water and soil chemistry for a specific period.

MAGIC has been modified and extended several times from the original version of 1984. In particular, organic acids have been added to the model (version 5; Cosby *et al*. 1995) and most recently nitrogen processes have been added (version 7; Cosby *et al*. 2001).

The MAGIC model has been extensively applied and tested over a 17-year period at many sites and in many regions around the world (Cosby *et al*. 2001). Overall, the model has proven to be robust, reliable and useful in a variety of scientific and environmental management activities (Ferrier *et al*. 1995, Jenkins *et al.* 1998, Cosby *et al*, 1995, Wright *et al*. 1998).

***Table 7.** Acid sensitive regions receiving significant inputs of acid deposition identified by the UNECE Joint Expert Group on Dynamic Modelling and the current status of dynamic modelling (UNECE 2002)*

Region	**Country**	**ICP Waters Sites**	**Soil data**	**Modelling**	**Comments (project/contact)**
Fenno-Scandian shield	Norway	YES	YES	YES	RECOVER:2010 + national project + EMERGE
	Sweden	YES	YES	YES	RECOVER:2010 + national project
	Finland	YES	YES	YES	NMR - project
	Russian Federation - Kola	YES	NO	?	
	Russian Federation - Karelia	NO	?	NO	
Upland areas in the British Isles	Scotland	YES	YES	YES	RECOVER:2010 + national project + EMERGE
	Wales	YES	YES	YES	RECOVER:2010 + national project
	Northern England	YES	YES	YES	RECOVER:2010 + national project
	Ireland	YES	NO	NO	
Lowland Heaths/Forests	SE England	NO	YES	NO	
	Denmark	NO	YES	NO	
	Germany – northern	YES	YES	YES	RECOVER:2010 + national project
	Netherlands	YES	?	?	
	Belgium	NO		NO	
Mid-European Forests	France – Vosges	NO	?	NO	
	Belgium – Ardennes	NO	?	NO	
	Germany – Black Forest, Harz Mountains	YES	YES	YES	RECOVER:2010 + national project
	Germany – Bavarian Forest, Mittelgebirge	YES	YES	YES	RECOVER:2010 + national project
	Czech Republic	YES	YES	YES	RECOVER:2010 + national project
Pyrenees	Spain	YES	YES	YES	EMERGE
	France	YES	?	?	
Alps	Italy	YES	YES	YES	RECOVER:2010 + EMERGE
	Switzerland	YES	NO	NO	
	Austria	YES	NO	NO	
Tatras	Slovakia	NO	YES	YES	RECOVER: 2010 + EMERGE
	Poland	YES	?	YES	
S. Europe	Bulgaria	NO	?	NO	

4.1.2 List of required data

The data requirement to run MAGIC must be spatially and temporally averaged (or ‘lumped’) to represent the whole catchment area (divided into one or several soils and waters compartments) and the time step of the model (annual or monthly). If physical and chemical data are available at only one point in the catchment or from one point in time, it must be assumed that this is representative of the whole catchment at that time step. Any uncertainty in these data and in the representativeness is incorporated into the model and the prediction must be interpreted accordingly. The minimum data requirement is given below:

Hydrological parameters:

- Annual runoff (m/yr)
- Annual precipitation volume (m/yr)

Soil parameters:

- Soil depth (m)
- Porosity (%)
- Bulk density (kg/m^3)
- CEC (meq/kg)
- SO_4 maximum adsorption capacity (meq/kg)
- SO_4 half-saturation coefficient (meq/m^3)
- Dissociation constant for aluminium hydroxide solid phase, K_{Al} (log_{10})
- Temperature (annual average) (^oC)
- pCO_2 (%)
- Organic acids (mmol C/m^3)
- Dissociation constants for organic acids (pK)
- Nitrification (% of input)

Surface water parameters:

- Retention time (Yr)
- Relative area (%)
- Temperature (annual average) (^oC)
- Dissociation constant for aluminium hydroxide solid phase, K_{Al} (log_{10})
- pCO_2 (%)
- Organic acids (mmol C/m^3)
- Dissociation constants for organic acids (pK)
- Nitrification (% of input)

Surface water/soil chemistry in calibration year (i.e. 2001):

- Concentration of major ions (Ca, Mg, Na, K, NH_4, SO_4, Cl, NO_3) (meq/m^3)
- Soil exchangeable base cations (Ca, Mg, Na, K) (meq/kg)

Deposition parameters in calibration year (i.e. 2001):

- Concentration of major ions (Ca, Mg, Na, K, NH_4, SO_4, Cl, NO_3)
- Time sequence of change in:
  - deposition concentration
  - dry deposition factors for each ion (= total deposition/wet deposition)

The historical sequences of changing deposition of sulphur and nitrogen are usually derived from estimates made by EMEP (Mylona 1993). These historical ‘trajectories’ at the scale of the EMEP grid are usually modified at a site or regional scale to incorporate more detailed measurements or estimates, particularly in more recent years. Further updated deposition histories for the EMEP grid are currently being derived by the CCE/IIASA (Posch, *et al.* 2003).

More detailed data is desirable to describe:

- dry deposition flux
- uptake to plant biomass in soil and water
- in-lake processes (stratification, sedimentation etc)
- forest growth history

These data, if available, can improve the model performance against observations and serve to increase confidence in model predictions. In addition to the data required to parameterise the model, information is also required to enable model calibration.

4.1.3 Model Calibration

The calibration of MAGIC is a sequential process whereby firstly the input and output of those ions assumed to act conservatively in the catchment are balanced (usually only Cl); next, the anion concentrations in surface waters are matched by adjusting catchment net retention (of N) and soil adsorption (of S) if appropriate. Thirdly, the four individual major base cation concentration in the stream and on the soil solid phase (expressed as a percentage of cation exchange capacity) are matched by adjusting the cation exchange selectivity coefficients and the base cation weathering rates. Finally, surface water pH, Al and organic anion concentrations are matched by adjusting the aluminium solubility coefficient and total organic acid concentration in surface water.

The first step is achieved through comparison of the present day wet (or bulk) deposition concentration of Cl, the rainfall amount (which together provide the input flux), the surface water concentration of Cl and the runoff (which together provide the output flux). In most cases the input based on wet deposition only is less than the output and it is assumed that the extra Cl is deposited as a dry deposition of sea-salt that is not represented by the wet deposition concentration. This extra Cl is added as a neutral salt by also adding base cations in their sea-salt ratio to the deposition flux. Similarly, there is a need to estimate the dry deposition of S if the measurements are not available. In catchments where the net output flux of SO_4 is greater than the input flux at present day, a similar calculation is performed assuming this to represent dry deposition of SO_2 and also assuming no S adsorption within the catchment.

Observed inputs of N are usually much higher than observed N concentrations in surface waters. Indeed, NH_4 concentrations are usually zero. For calibration, nitrification of NH_4 is set such that simulated concentrations of NH_4 match observed. Then net catchment retention required to match the observed NO_3 concentration in the surface water is calculated. This percentage retention is usually assumed to be constant throughout the model simulation. For SO_4, if surface water data is available for only one point in time the adsorption parameters (Maximum adsorption capacity = E_{mx} and Half-saturation constant = C) if required, must be estimated from soils data. For regions with geologically ‘young’ soils, SO_4 adsorption is generally small. For the applications with long time-series the C and E_{mx} can be calibrated to match the observed trend in surface water SO_4 given an observed trend in SO_4 deposition.

The base cation calibration follows an iterative process whereby the base cation selectivity coefficients are set, values are chosen for base cation weathering, the model is run from some background, pre-acidification condition, the simulated values of base cations in soil and surface waters are compared with observed. This process is repeated, adjusting the selectivities and weathering rates until the observed target concentrations are achieved. If time-series data are available further adjustment may be undertaken to match trends. This part of the calibration procedure can be undertaken automatically using an appropriate numerical optimisation procedure.

This calibration procedure is performed to determine the catchment weathering rate of base cation and the initial fraction of base cations held on the soil solid phase (cf ion exchange selectivities). These parameters can be estimated or measured but given that they vary greatly in space across the catchment and during the year in response to other factors, notably soil moisture in the case of weathering, their calibration provides pragmatic values. In any case, comparison of calibrated weathering rates from MAGIC with those estimated using other weathering models or catchment mass-balance studies show an acceptable consistency (Warfvinge *et al.* 1992).

4.1.4 Model Output

The basic model output (Figure 3) provides a reconstruction of the key chemical variables from a historical or background condition which represents a pre-acidification condition to the present day under assumed (up to c.1970) and measured (c.1970 to present) emission/deposition levels. This pre-acidification condition also potentially provides the ultimate target for the future chemistry of the water, i.e. it is not possible to achieve better conditions than were present prior to the onset of acidic deposition by merely reducing the acid deposition in the future. The timing and magnitude of the historical acidification response at any given site, indicated by the ANC (**Figure 21**) is determined mainly by the flux of S and N deposition over time, as reflected by the change in surface water SO_4 concentration (**Figure 21**) and the capability of the catchment soils to buffer the strong acids with base cations from weathering and the soil exchange complex, reflected by the Ca concentrations (**Figure 21**).

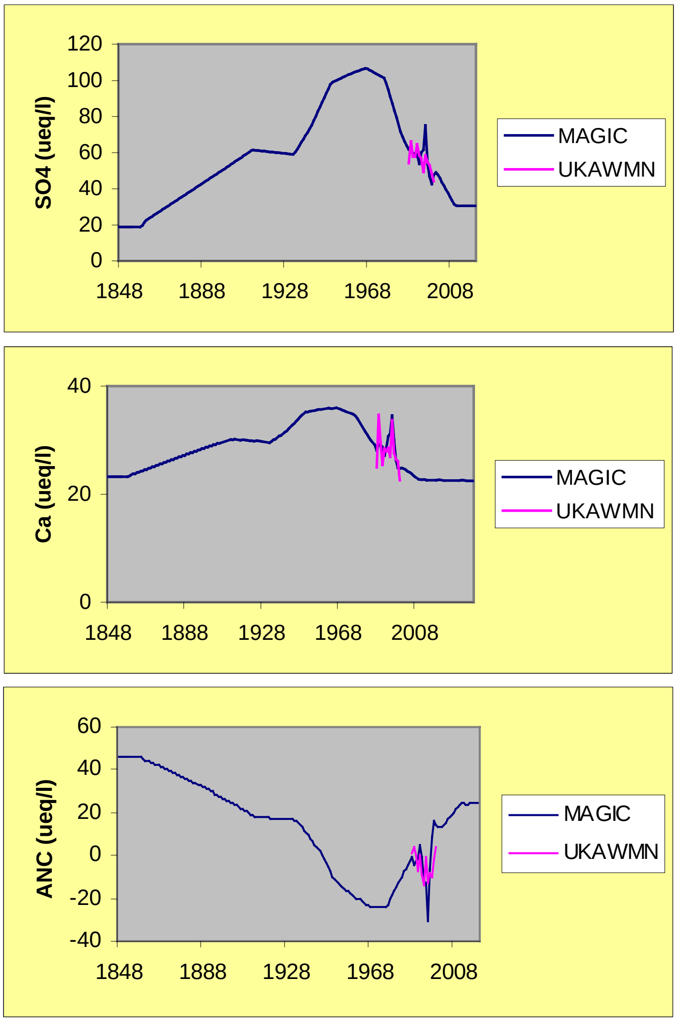

Figure 21. *The MAGIC model applied to Lochnagar, NE Scotland, driven using the historical (1848-1986) S deposition from EMEP (Mylona 1993), observed S deposition at the site (1986-2000) and modelling deposition in response to the Gothenburg Protocol (2000-2020). Also shown are the observed annual mean surface water concentrations (1988-2000) from the UK Acid Waters Monitoring Network.*

Beyond the present day, the model is driven forward under some assumptions regarding the deposition of strong acids from the atmosphere. Assuming the emission reductions agreed under the Gothenburg Protocol are achieved by 2010, the model predicts a rapid recovery of water chemistry (**Figure 21**) in response but a much slower response thereafter as emissions are assumed to remain constant at that level beyond 2010. In most acid sensitive regions of Europe, water chemistry data is available to describe the current status of many surface waters and so the model can be calibrated to multiple sites (typically in order of tens to hundreds of sites) and thereby enable this question to be asked at a regional scale.

4.1.5 Model Testing

Clearly, the future predictions from a model are subject to uncertainties in the data used in the processes represented within the model and the mathematical representation of those processes. The degree to which the model fits against observations, therefore, indicates the confidence with which we can interpret those predictions. Dynamic models of surface water chemistry have key advantages over soil models in that they can be tested against three independent data sources: historical pH trends inferred from diatom reconstructions; long time-series data of direct measurements; and, data from ecosystem manipulation experiments.

Comparison with Observed Data

Deposition and water chemistry time-series data are available for many sites covering 10-30 years (e.g Stoddard *et al.* 1999, Moldan *et al.* 2001, Evans and Monteith 2001, Evans *et al.* 2001a). These data provide the opportunity to compare the model simulation for the last decade or so against observations to ensure that the model is capable of capturing the dynamics of the system (**Figure 22**). At nearly all sites across Europe the past two decades have seen a marked reduction in S deposition and so the observations of water chemistry reflect recovery from acidification and the model can closely match observed trends (**Figure 22**). The MAGIC model has been tested at many sites spanning a range of environments, deposition levels and deposition reductions and matched the observations well in all cases (e.g. Jenkins and Cullen 2001, Hruška *et al.* 2002, Jenkins *et al.* 2003).

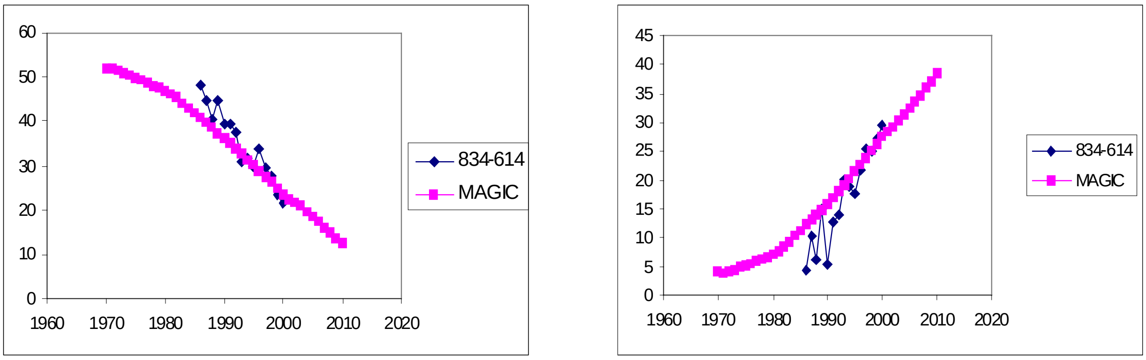

Figure 22. *Comparison of MAGIC simulated SO_4 (left) and ANC (right) and observed annual mean chemistry at Stavsvaten, S Norway. The model simulation beyond 2000 is driven assuming implementation of the Gothenburg Protocol.*

Comparison with Experimental Data

Since the mid-1980s, a number of whole ecosystem manipulation experiments have been undertaken to assess the acidification and recovery process. Whilst these experiments necessarily accelerate the rate of change in the ecosystem by significantly changing the input of S and N relative to the slower changes in response to emissions increase and reduction, they offer a unique test for the dynamic models. The processes operating to produce the surface water chemistry in the manipulated catchments are the same as those operating under ambient conditions and so the dynamic models should be capable of reproducing the observations. At the roof covered catchment experiment in Sweden (Gårdsjön), the MAGIC model successfully reproduced (**Figure 23**) the effects of 'clean rain' treatment (Beier *et al.* 2003). Similar successful applications of the model to experimental catchment manipulations have been undertaken at Risdalsheia (Norway) and Klosterhede (Denmark) (Beier *et al.* 1995). The MAGIC model also captured the acidification response induced by addition of S and N at catchments in Norway (Sogndal) (Cosby *et al.* 1995). Further detailed comparisons between the

MAGIC model and experimental data have been undertaken by Moldan *et al*. (1998) and Wright *et al*. (1998).

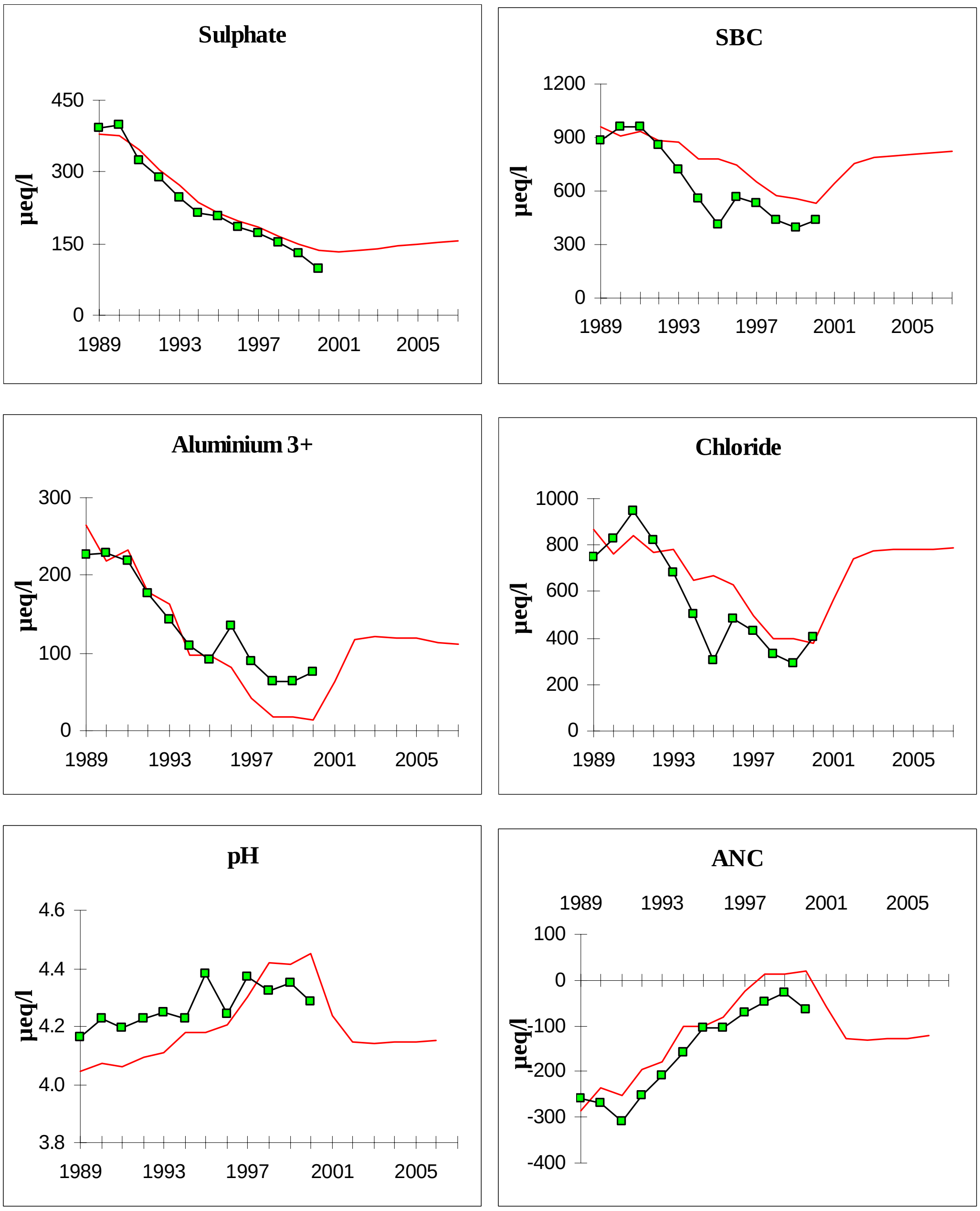

Figure 23. *Measured and predicted pH and concentrations of sulphate, aluminium, sum of base cation, chloride and ANC at the Gårdsjon experimental roof catchment (after Beier et al. 2003). The observations (squares) and MAGIC predict (solid line) represent annual means.*

Comparison with Diatom Reconstructions

A key method by which the long-term acidification of surface waters has been demonstrated is the reconstruction of surface water pH based on diatom assemblages from lake sediment cores (Battarbee *et al*. 1990). There have been several attempts to compare these pH reconstructions with the historical simulated pH change from dynamic models (Jenkins *et al* 1990, Wright *et al*. 1986). The similarity in the predicted and reconstructed timing of pH change and the background pH inferred from both techniques has generally been found to be good. Recently both the diatom reconstructions and the dynamic models have been changed to incorporate new processes and data; there remains a reasonable match between the two techniques (**Figure 24**).

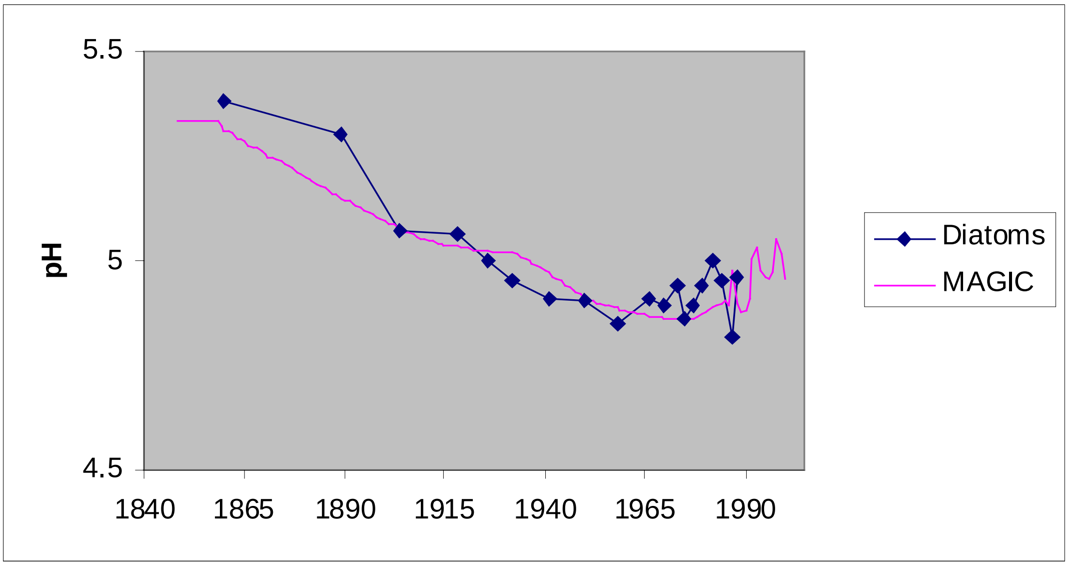

Figure 24. *A comparison of the diatom pH reconstruction and MAGIC model pH simulation at the Round Loch of Glenhead, SW Scotland, UK.*

4.2 The Contribution of Dynamic Modelling of Surface Waters to the Work under the Convention

Dynamic models can contribute to the Convention in two important areas; firstly, they can provide an estimate of the expected surface water chemistry at any time in the future in response to the implementation of the Gothenburg Protocol (assessment of the impact of emission reductions) and secondly, they can be used to assist in the calculation (optimisation) of further emission reductions (input to the process of Integrated Assessment Modelling).

Regional assessment of surface water response to the implementation of the Gothenburg Protocol has been conducted under the EU RECOVER:2010 project (Ferrier *et al*. 2001) as well as numerous national studies (e.g. Evans *et al.* 2001b) for Southern Norway, Southern Sweden, Galloway, Wales and the Pennines in the UK, Central Germany, Northern Italy and the Czech Republic. Regional modelling produces a time series output (e.g. **Figure 21**) for each of the sites under consideration and these can be summarised to provide regional responses through time (**Figure 25**). Presented in this form, however, only regional questions can be addressed and the model applications lose their spatial resolution. Clearly, it is possible to summarise the regional output and still maintain the spatial distribution of the data in map form. In the simplest form the regional assessment can take the form of maps (**Figure 26**). These show the chemistry of the region at any given time and provide an indication of the areas within the wider region which require more detailed assessment possibly with a view to further emission reductions or management intervention such as liming. This is potentially very useful with respect to sites of special scientific interest or special conservation areas such as those identified under the EU Habitats Directive.

A more quantitative summary of the regional response to deposition reductions can be provided using the same "time slice" data from the model predictions but presented as frequency distributions (**Figure 27**) or cumulative frequency distributions (**Figure 28**). These provide a clear quantification of how the mean ANC has changed across the region in response to the change in SO_4 and also, perhaps more importantly, provide an estimate of the percentage of surface waters in the region which do not reach the specified target ANC within a given timescale. This “tail” of the distribution is potentially of most significance since it represents the most acidified sites (**Figure 29**).

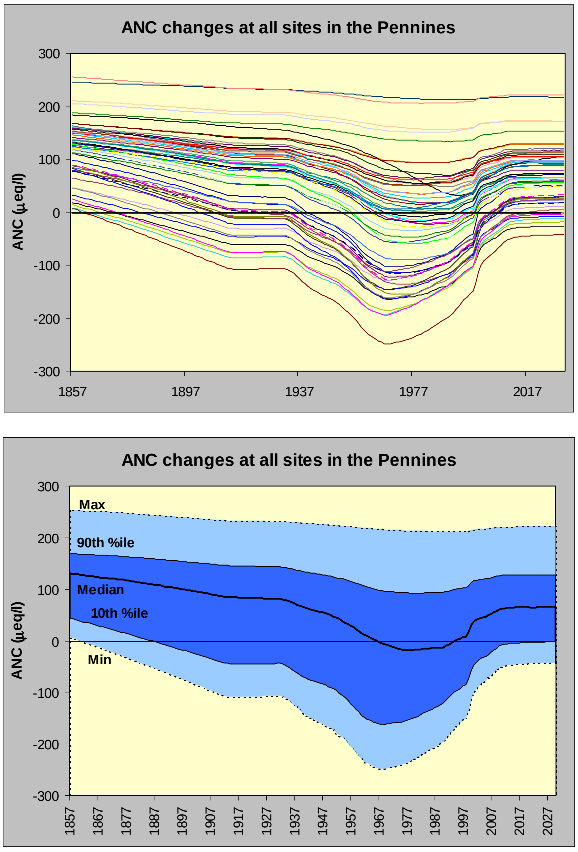

Figure 25. *Time series output from MAGIC for many sites in a region (left) which can be summarised to provide regional statistics through time (right).*

Most crucially then, dynamic models are currently capable of providing an assessment of the implications of achieving the emission reductions agreed under the Gothenburg Protocol. They are capable of addressing the question of whether the current agreements promote an appropriate response in surface water chemistry within a given timeframe and in helping to identify regions where further reductions might be required to achieve the specified target chemistry at some specified time. If it is determined that further emission reductions are required and desirable, the models can be put to a further use, that is, to determine the level of deposition that must be met within a certain time to reach the specified target chemistry within a specified time. This capability provides a clear advantage over the concept of critical loads in that these provide the deposition required to reach the specified target chemistry at some un-specified time in the future when the aquatic system has reached an equilibrium with the deposition chemistry. This is likely to take several decades or even hundreds of years. The link between the dynamic model approach and the critical loads is clear, however, in that if the model is run with the calculated critical load it will be possible to specify the time required to reach the chemistry target. Conversely, if the target year in which the specified chemistry is required is set to several hundred years from present, the calculated deposition required in the dynamic model to meet that target should approximate closely to the critical load. In the context of management and policy making, however, such long time scales (typically required for recovery of soils) are difficult to accommodate in current legislative plans and so the use of dynamic models for surface waters is crucial in providing the reductions required over a timescale of a few decades.

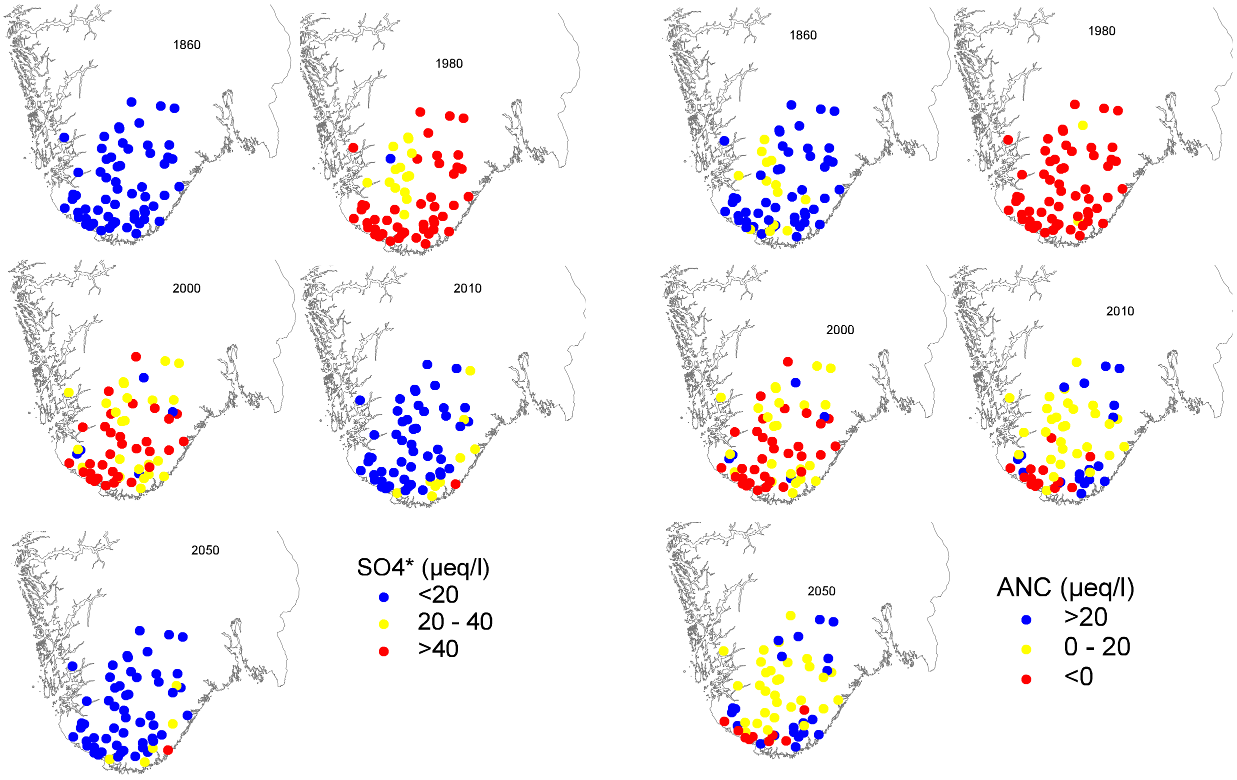

Figure 26. *The MAGIC model applied regionally in S Norway. The left panels show the modelled excess sulphate concentrations in lakes; the right panels the modelled ANC in lakes.*

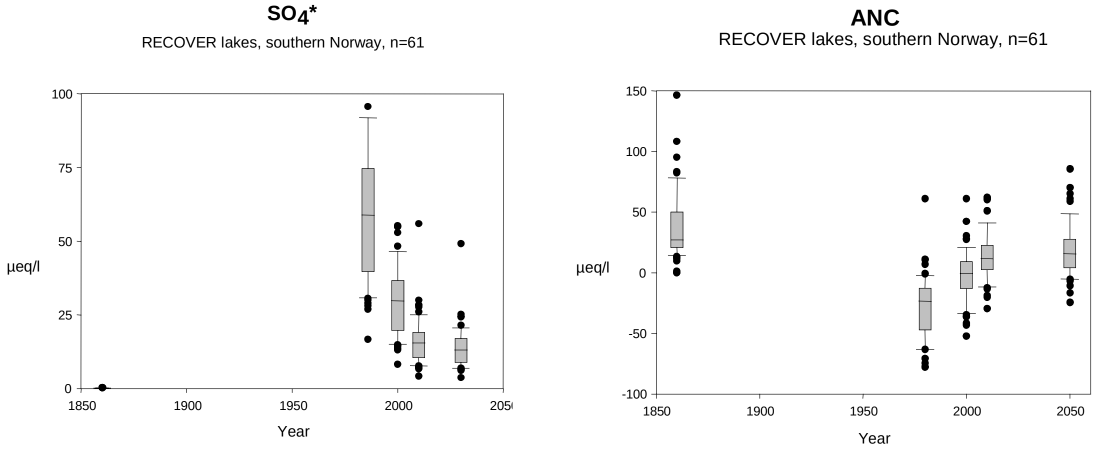

Figure 27. *Frequency distributions from MAGIC model simulations for S Norway. Deposition to 2010 assumes implementation of the Gothenburg Protocol and held constant thereafter to 2050.*

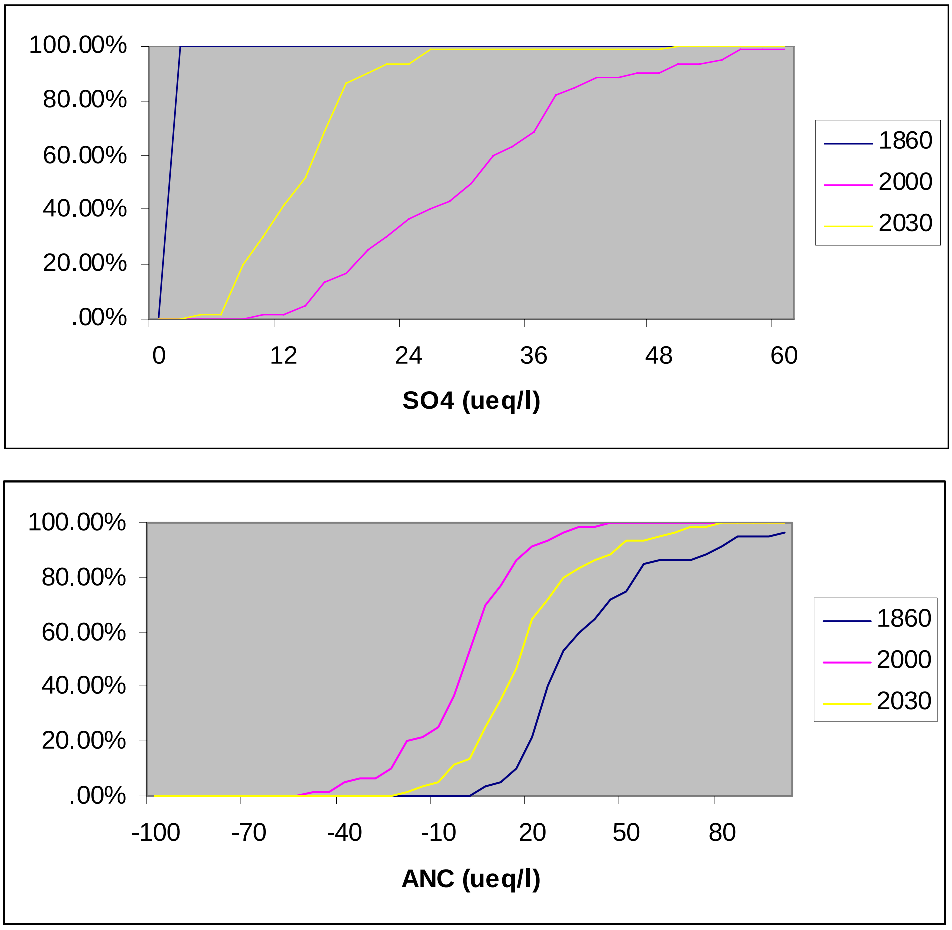

Figure 28. *Cumulative frequency distribution of SO_4 (upper) and ANC (lower) from the regional MAGIC application in S Norway.*

Outputs from dynamic models can be summarised and presented as a logical extension to the critical loads approach already used in the Integrated Assessment process. For example, in the same way in which the critical loads of S and N are represented as a function for input to the Integrated Assessment Models (**Figure 30**), the deposition required to achieve a given chemistry within a specified time can be calculated from the dynamic models and expressed as a target load function (TLF) (**Figure 30**). At every combination of S and N deposition on the target load function, a target ANC will be reached in the specified target year. The only difference between the TLF and the critical load function (CLF) being the concept of time to reach the target chemistry since for the CLF, the time to reach the chemical target is infinite. Note that the shape of both the CLF and TLF are similar, the ‘shelf’ at low N deposition representing the long-term capability of the system to utilise N, but the TLF will always be lower than the CLF. For a target chemistry to be reached in the very long term (infinite timescale) the TLF and CLF are the same.

Clearly and implicitly, at a currently acidified site the deposition reduction required to reach a specified target within 15 years will be greater than that required to reach the same target over a longer timescale. This is because the deposition flux over the whole period (i.e. integral under the deposition curve over time) is largely responsible for the chemistry predicted for a given year (**Figure 31**). Assuming that costs increase with greater reduction of N and S, this implies, therefore, that there is an increased cost associated with selecting a more immediate ecosystem recovery. Additionally, it is also clear that the deposition reduction required to reach a less stringent water chemistry target (for example ANC=0 ueq/l) over the same timescale will be less than for the more stringent target (for example, ANC=30 ueq/l) (**Figure 32**). Again, the economic implication is that the stricter the target chemistry, the larger emission reductions required and the higher the cost. It should be noted that the slopes of the TLFs under different target years and target chemistry will vary from site to site as a function of the buffering capacity of the soils (weathering rate, soil exchangeable base cations) the deposition (historical and current) and the predicted level of future deposition.

The specification of the TLF from a dynamic model requires one further set of assumptions regarding the timing of further emission reductions. For example, the start and end years of the required reductions must be specified since any delay in emission reduction and the time period over which they are achieved will affect the position of the TLF (**Figure 33**).

In terms of achieving an optimal solution to emission reduction, therefore, the policy maker needs to make key decisions regarding: (i) the target chemistry required to protect the chosen biological receptor (target chemistry) (note also that this will also influence the critical load); (ii) the year in which the target chemistry is required (target year); (iii) the year in which emission reductions will start to be implemented (implementation year); and (iv) the year in which the emission reduction must be completed (completion year). Clearly, the regional TLF is constructed for use by the IAM will incorporate the result of these four assumptions. In effect, therefore, there is a possibility to 'optimise' these four assumptions/decisions prior to application of the IAM.

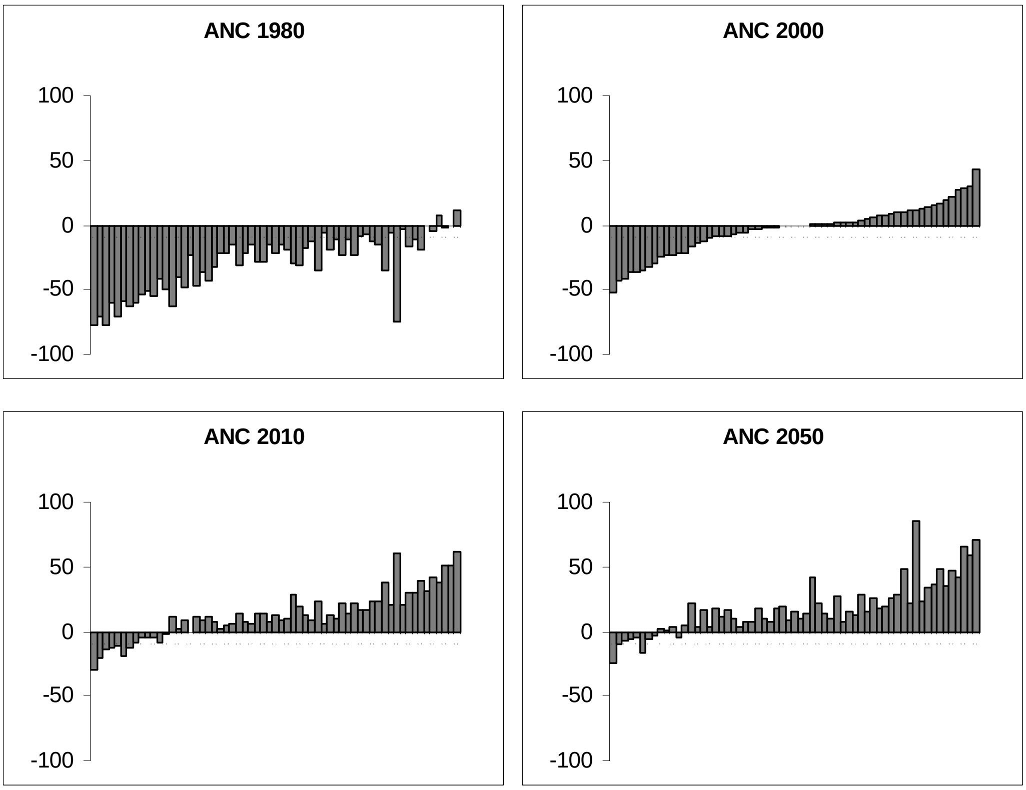

Figure 29. *Ranked change plots over time from the regional MAGIC application to S Norway.*

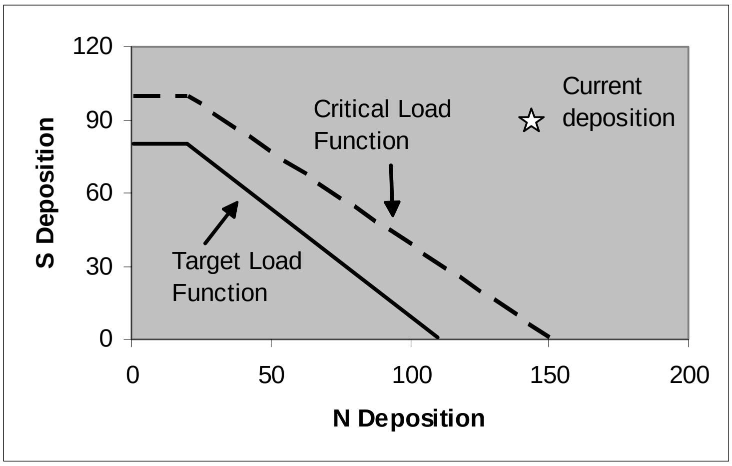

Figure 30. *The critical load function (upper) as constructed and used by the Integrated Assessment Models for calculation of optimal deposition reduction scenarios. Emission reductions must be achieved at some future time to achieve the target chemistry at some (unknown) point in the future. The target load function is essentially the same* <u>*but*</u> *the timing of emission reductions must be specified to achieved the specified chemistry in a given year.*

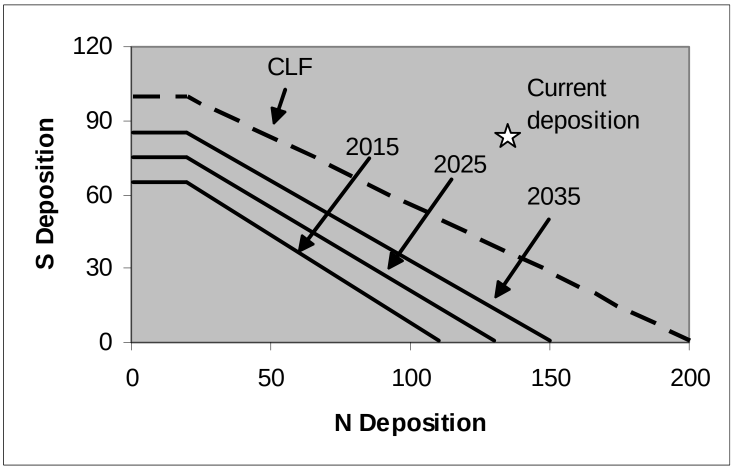

Figure 31. *The effect of different target years on the target load function for a given target chemistry at an individual site.*

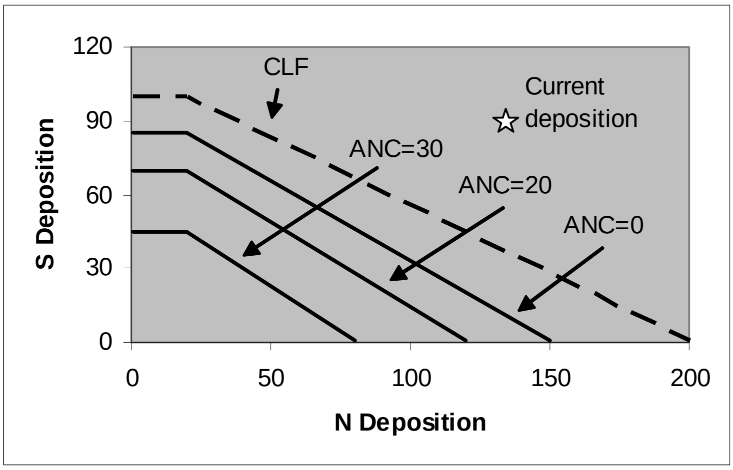

Figure 32. *The effect of different target chemistry on the target load function for a given target year at an individual site.*

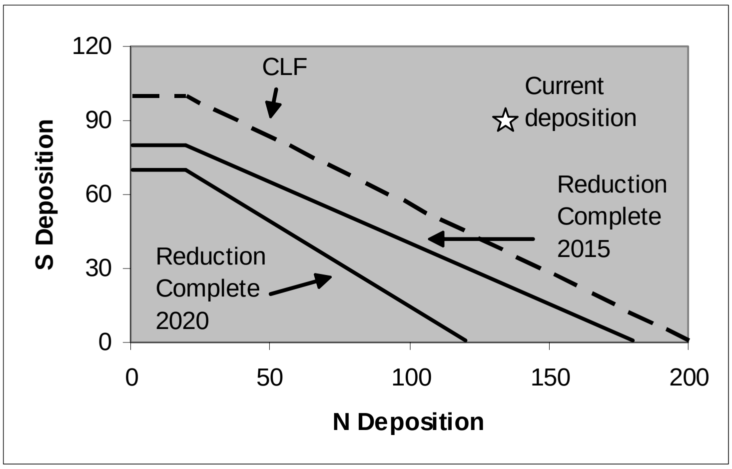

Figure 33. *The effect of different years of implementation of the emission reductions to meet the specified target chemistry in 2025 at a site. The two cases shown here represent the reductions beginning in 2010 and being completed by 2015 and 2010.*

These target load functions can be accumulated for all of the sites within a given region and analysed to provide a regional TLF which represents the combination of S and N deposition required to achieve the target chemistry at all sites within that region or some percentage of them (**Figure 34**). This ‘minimum’ regional TLF may be further constrained by the current deposition of N and S on the basis that it is unlikely that increased emission of either pollutant will be acceptable. This methodology can also be developed to incorporate the “gap closure” concept used in the IAMs for the development of the Gothenburg Protocol.

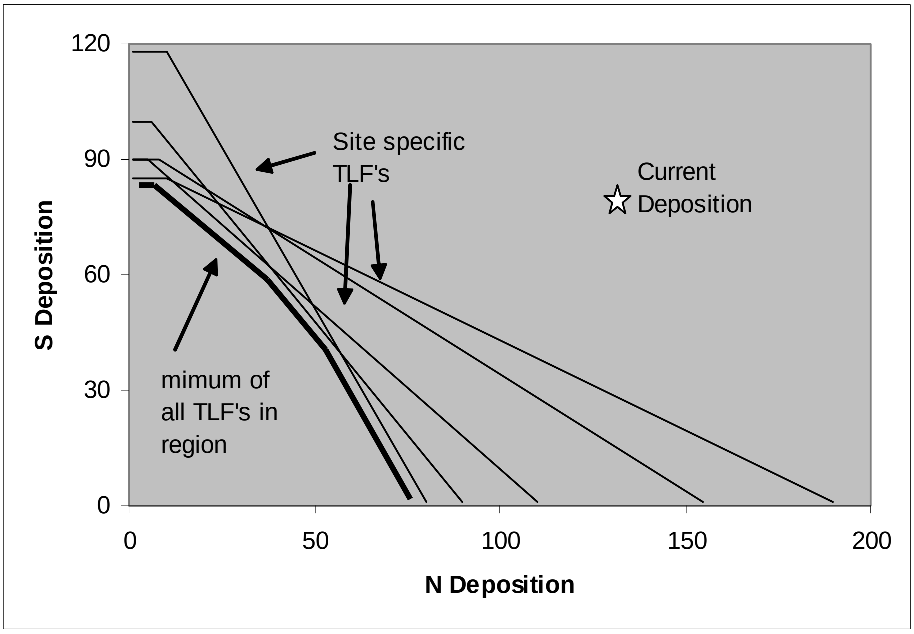

Figure 34. *Calculation of a regional target load function. This would also represent a method for calculating the TLF within grid squares for a given target year, target chemistry (ANC) and emission reduction implementation and completion years.*

4.3 Future Developments

The MAGIC model is currently capable of wide application across acid sensitive areas of Europe in support of the objectives of the Convention. There still exists, however, a requirement for further developments with respect to the model, its interpretation and its application. These developments are required in the near future if the full potential of dynamic models are to be realised within the timescale of the Convention, i.e. the forthcoming review of the Gothenburg Protocol as scheduled by the Working Group on Effects medium term strategy.

4.3.1 Model Uncertainties

There are uncertainties related in the application of all mathematical models. Different types of uncertainties exist depending on the model, its application and the information available for running the model. One way of grouping uncertainties is to consider them according to whether they can be quantified. This provides three groups: technical uncertainties; methodological uncertainties; and, epistemological uncertainties (Funtowicz and Ravetz, 1990). The latter group are, by definition, impossible to quantify and difficult to include in model applications. Such uncertainties relate to the fact that unforeseen events may occur to cause model predictions that do not match reality. Such events are not included in the models (if they were, these are no longer epistemological uncertainties) and are only imaginable to a limited extent. Accordingly, epistemological uncertainties are not discussed further.

Technical uncertainties in dynamic modelling of surface waters are related to estimation of model inputs and parameters from observed data and relate mainly to measurement errors and variability in both time and space. These can in principle be quantified if enough measurements are available and hence it may be possible to quantify the uncertainty in model predictions (Larssen et al. 2003). The representativity of available data used for modelling is important for the overall uncertainty in model predictions. The natural variation in, for example, deposition or runoff composition throughout a year may be substantial and the uncertainty in model prediction will typically increase with decreased sampling frequency. Similarly, the spatial variability, especially in soil data, results in increasing uncertainty in predictions as the spatial resolution of the sampling decreases. Hence, for regional model applications, the uncertainty in predictions will increase due to decreased resolution. The technical uncertainties in model outputs can be summarised and presented as probability distributions (**Figure 35**).

The methodological uncertainties are more difficult to assess and can only partly be quantified. This group of uncertainties relates to the fact that models are necessarily simplifications of nature and that important processes may be excluded or inappropriately described in the model. Examples of factors giving methodological uncertainties in dynamic modelling of freshwaters are nitrogen dynamics, the role of organic matter and climate impacts including sea salt events (Ferrier et al. 2001). The lack of scientific understanding is an important factor for this group of uncertainties, in particular the current lack of understanding of the controls on N leakage from the terrestrial to the aquatic system has been intensively studied, but remain is a major source of uncertainty in model predictions.

Episodic impacts from sea salt episodes are important in delaying recovery from acidification in areas located relatively close to the sea. Severe storms have been shown to kill aquatic biota due to sea salt induced acidification peaks (Hindar et al. 1994). Models can reproduce such events, but the likely frequency and magnitude of such events in the future is not known. A practical approach to address this is to repeat the observed frequency of sea salt deposition into the future and in this way illustrate the importance and magnitude of such events relative to the predicted general trend. In this way the importance of naturally extreme years in combination with reduced anthropogenic deposition can be shown (**Figure 36**).

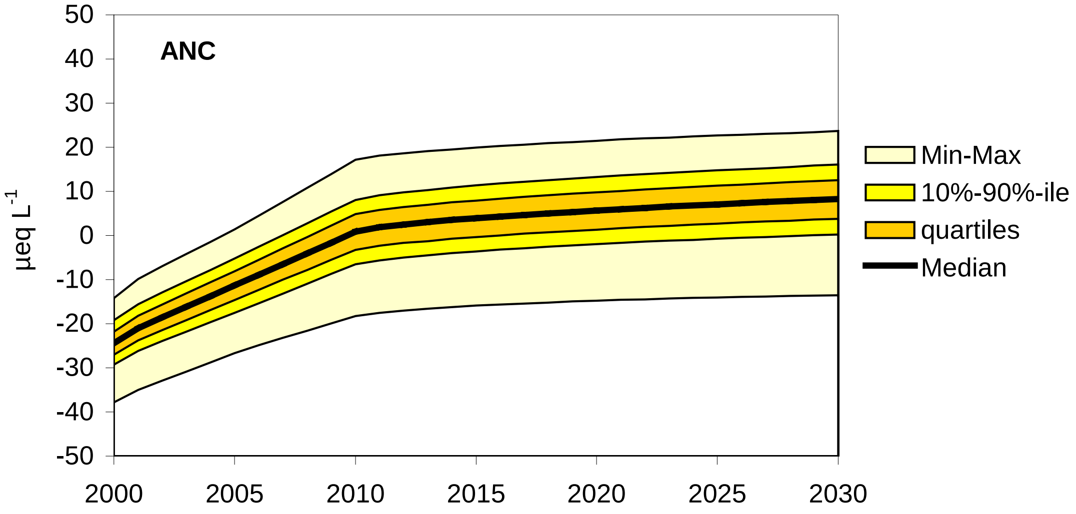

Figure 35. *The technical uncertainties in model predictions can be calculated and presented as probability distributions over time. This example show the probability distribution for ANC into the future at Birkenes (S. Norway), given implementation of the Gothenburg protocol and taking technical uncertainties into account in the model inputs and parameter estimates (Larssen et al. 2003).*

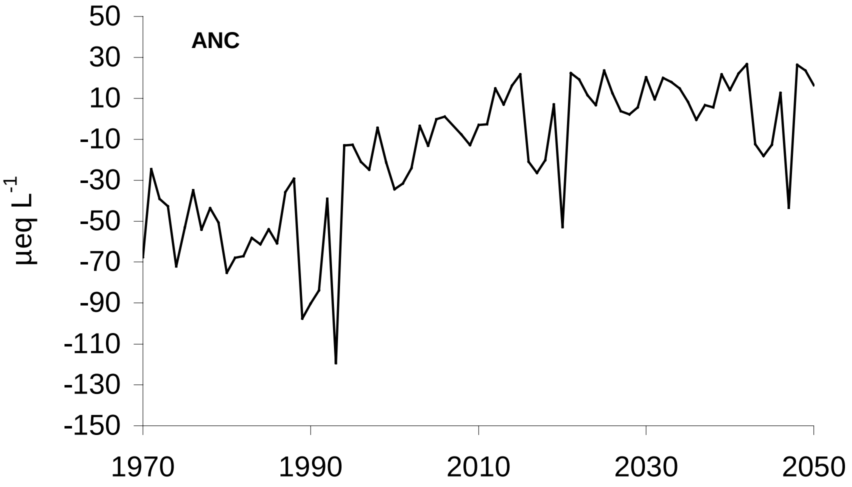

Figure 36. *Illustration of the response in ANC at Birkenes (S. Norway) when taking the variation in sea salt deposition into account in combination with decreased sulphur and nitrogen deposition under the Gothenburg protocol. The observed sea salt deposition frequency for the period 1973-2000 is repeated into the future (Larssen et al. 2002).*

As the deposition of S decreases in Europe, the relative importance of N increases since the reduction of N emission is comparatively very small. Most semi-natural terrestrial systems, however, are N-limited and the vegetation and soils retain most of the N deposited with only a very small flux to surface waters in most areas. Nevertheless, where NO_3 is observed in surface water, this acts as a strong acid anion to promote increased acidity and decreased ANC. The question that remains to be answered is what controls the degree of N leakage in the long term? A 'worst case' assumption is that when N deposition exceeds the uptake requirement of the vegetation and microbial biomass in the soil, or when root damage caused by acidification reduces the N uptake capacity, N leakage to surface waters increases (Aber *et al*. 1989; Stoddard 1994). This saturation and breakthrough response is further strengthened by observations of C/N ratios and soilwater NO_3 at forested sites across Europe within the NITREX project (Gundersen *et al*. 1998a). In this respect, an empirical relationship between soil litter layer C/N ratio and NO_3 (**Figure 37**) leakage from the terrestrial system has been established (Gundersen et al. 1998b). There currently exists, however, little empirical evidence of changes in surface water NO_3 concentrations over time to support the concept of N saturation (Wright *et al*. 2001). At Lange Bramke, central Germany, for example (**Figure 38**) streamwater NO_3 concentrations rose steadily through the 1980s but have since declined again indicating that climatic influences may have been responsible. The potential for climate induced changes in N dynamics has been demonstrated from catchment manipulation studies (e.g. Wright and Jenkins, 2001). This does not mean, however, that N saturation does not occur in the long-term but perhaps indicates that the process takes a very long time (several decades).

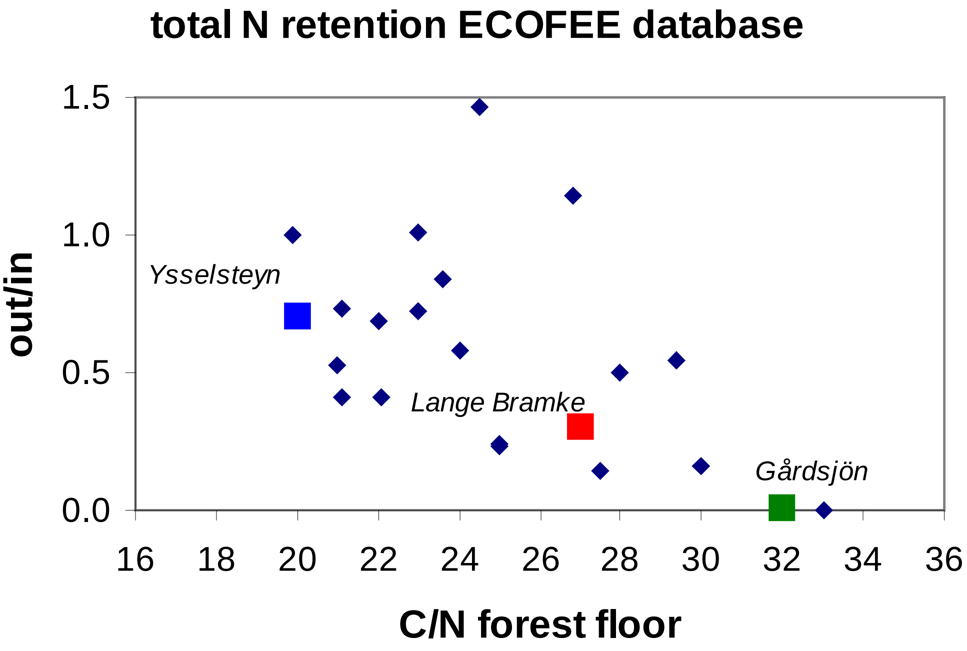

Figure 37. *The observed relationship between C/N of the forest floor and NO_3 input/output flux for sites across Europe (Gundersen et al. 1998a).*

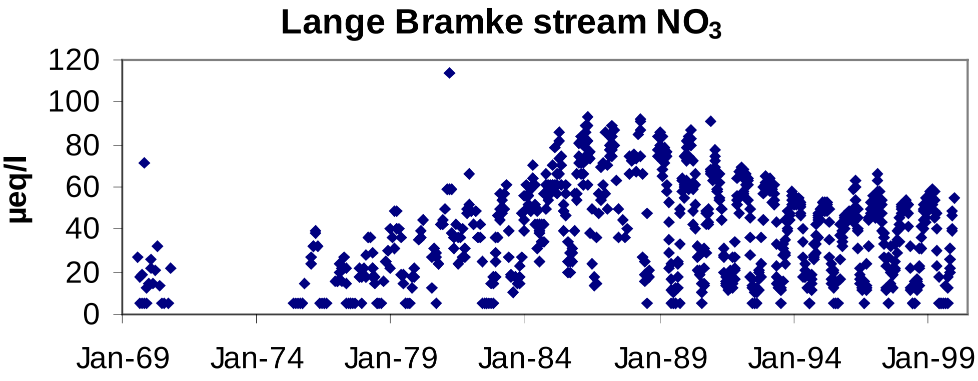

Figure 38. *Long-term changes in stream NO_3 concentration at Lange Bramke, Germany (Wright et al. 2001).*

In terms of critical loads, the steady state FAB model (Henriksen and Posch 2001) embraces the concept of N-saturation and assumes that at some point in the future, the terrestrial system will be incapable of immobilising incoming N other than some small fraction that is required for net plant uptake, lost to denitrification or immobilised as soil builds up in the long-term. In this case, the derived critical load incorporates a maximum level of N leakage and hence NO_3 concentration. This N saturation concept has also been incorporated into MAGIC by assuming the relationship between C/N in soils and NO_3 concentration in water (**Figure 37**) to be a time dependent process (Cosby *et al*. 2001). Given the lack of observed time-series data describing increased NO_3 concentrations in surface waters, however, it is also possible to model N dynamics by calculating the current proportion of N immobilised in the terrestrial system and assuming this to remain constant into the future, irrespective of N deposition changes. Clearly, the result of this assumption is that NO_3 concentration decreases proportionally with decreased N deposition and this may be considered a 'best case'. The net effect of these 'best' and 'worst' cases on the model predictions in the longer term (**Figure 39**) and under the Gothenburg Protocol reductions in N and S are not appreciable with respect to ANC over a time-scale of c.30 years (Jenkins and Cullen 2001, Jenkins *et al.* 2001). Beyond this, however, NO_3 leakage could have a significant impact on the acidification status as the proportion of N retained declines even under constant N deposition.

A more detailed analysis of the uncertainty related to N dynamics and the impact of episodic sea-salt inputs in relation to uncertainty in data for calibration and parameterisation has been undertaken at Birkenes, Norway (Larssen *et al*. 2002) and is summarised in Jenkins *et al.* (2003).

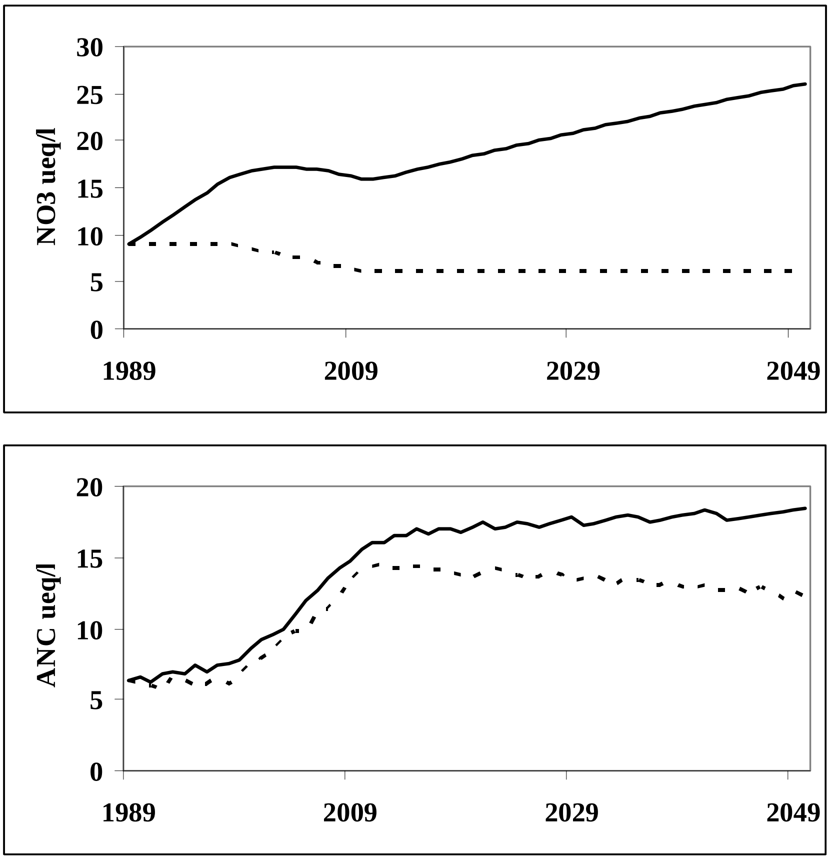

Figure 39. *MAGIC predicted NO_3 (top) and ANC (bottom) at Lochnagar, Scotland, assuming a best case N leakage (dotted line) and a worst case (solid line) (see Jenkins et al. 2001).*

4.3.2 Inclusion of Biological Responses

With respect to biological status, the link between surface water ANC and brown trout population has been established in Norway (Lien *et al*. 1992; ***Figure 40***). This relationship is derived from chemistry and fish population status data of the Norwegian 1000-lake survey (Henriksen *et al*. 1989). Lakes with ANC < 20 μeq l^{-1} generally had damaged fish populations and most lakes with ANC < 0 were barren of fish. On this basis, a simple probability algorithm has been incorporated into MAGIC to link a given ANC with three categories of brown trout status; healthy, sparse and extinct (Wright *et al.* 1994). A comparison of the MAGIC output and historical information on fish catch from Loch Riecawr in Galloway, Scotland (Harriman *et al*. 2001) demonstrates the utility of this approach (**Figure 41**), whereby the predicted decline in the probability of a healthy fish population correlates closely with the historical fish catch record (Helliwell and Juggins 2002). More work is clearly required to relate the probability of fish status to population numbers but the utility of the approach with respect to target loads for emission reduction is clear.

From the relationship detailed by Lien *et al.* (1996) it is also possible to define critical 'target' ANC concentrations to summarise the regional response of brown trout to emission reduction scenarios on a static basis. In simple terms, for example, it is possible to define ANC < 0 as being an unacceptable chemistry with brown trout essentially absent; ANC 0 to 20 as being intermediate with the brown trout population 'at risk'; and ANC > 20 where the chemistry is acceptable as a healthy population is expected. The predicted chemistry for a region can then be used to represent biological status at any point in time. For the S. Norwegian lakes (e.g **Figure 26 - Figure 29**), for example, this information can be readily summarised to represent the consequences of the Gothenburg Protocol implementation over the next 50 years (**Figure 42**).

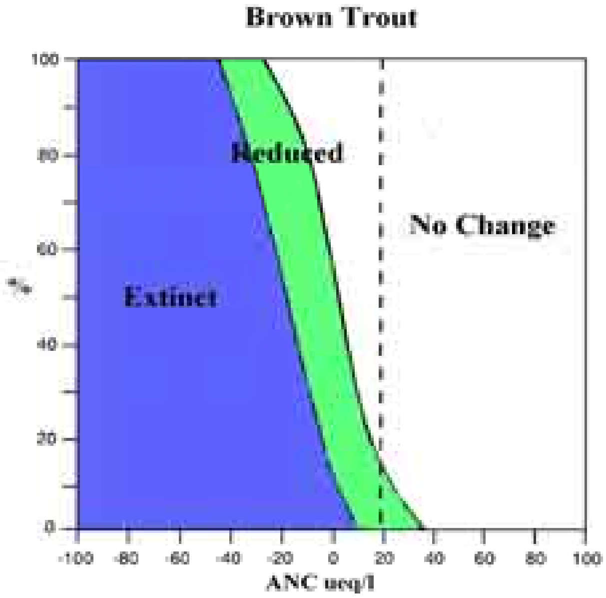

Figure 40. *The observed relationship between brown trout status and surface water ANC at 827 sites in Norway (from Lien et al. 1996).*

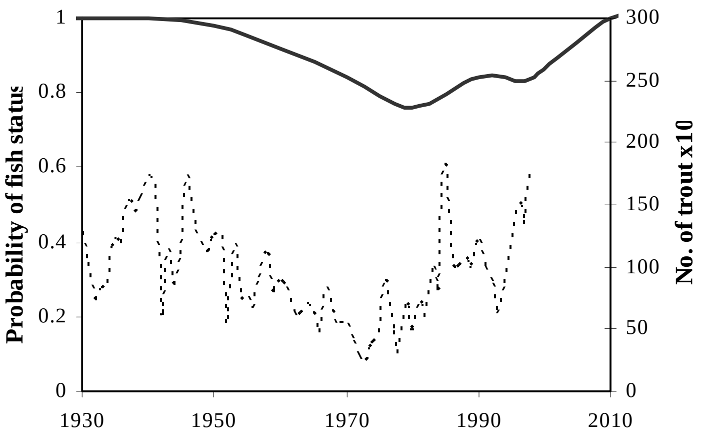

Figure 41. *Comparison of MAGIC predicted probability of healthy brown trout population (Helliwell and Juggins 2002) and observed fish catch (Harriman et al. 2001) at Loch Riecawr, Galloway, Scotland.*

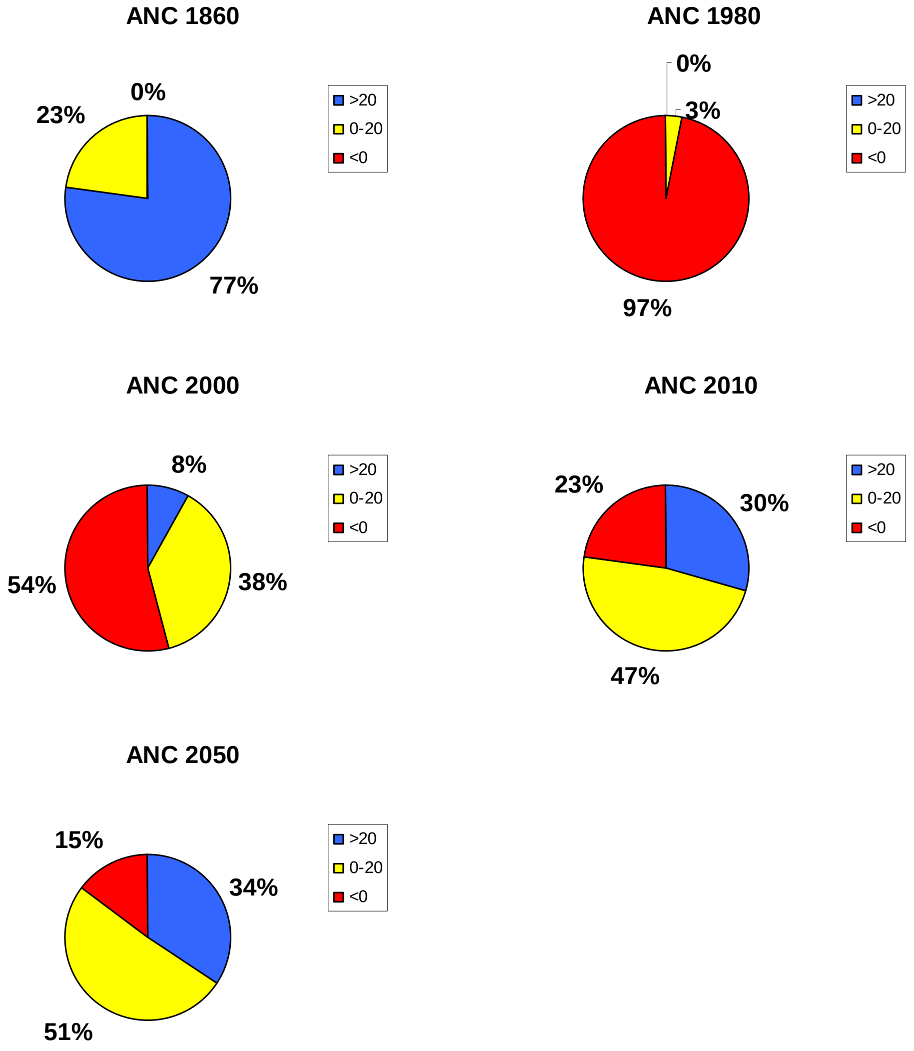

Figure 42. *The predicted surface water status in S Norway lakes prior to acidification, at peak deposition, present day and into the future assuming full implementation of the Gothenburg Protocol by 2010. ANC < 0 implies an extinct brown trout population; ANC 0-20 implies a population 'at risk'; and ANC > 20 implies a viable population.*

The widespread improvement in surface water quality during the past 15-20 years should give rise to biological recovery. Thus far, however, there are relatively few documented examples of biological recovery. The reason might be lags in biological response but also a lack of appropriate long-term monitoring data.

The time lag to biological recovery can be divided into two parts. The first is the lag for return of extirpated species. The second is for sensitive species to achieve densities and distributions typical of undamaged lakes and rivers. For some species of macroinvertebrates and fish the second is longer than the first. The lag times for return of fish depend on connections to source populations. If the lake or river is isolated from sources of colonisers, the return of fish will depend on stocking (at least if we want them to return within a timescale of a hundred years or so). Stocking means that the fish can return as soon as chemistry recovers, essentially a lag time of zero. Most of the other taxa (algae, macroinvertebrates and zooplankton) are more mobile and many species will return without human intervention.

Once the chemical threshold is reached, lag times for common, widely distributed species might be:

1. Algae: 1-2 years
2. Macroinvertebrates: 1-3 years in streams (for first appearance of sensitive species; normal populations 5-10 years). 1-10 years in lakes.
3. Zooplankton: 1 year (species with resting stages in the sediments) - >10 years (for whole communities).
4. Fish: 2-20 years.

Biological recovery following liming of acidified waters gives a good indication of the potential lag times involved in biological recovery (**Figure 43**). For example, during the 15 years following liming of the River Audna, southern Norway, the reappearance of sensitive species of invertebrates required 1-10 years, depending on such factors as the proximity of refuge populations and the life cycles and dispersal mechanisms of the various species (Raddum and Fjellheim, 2003).

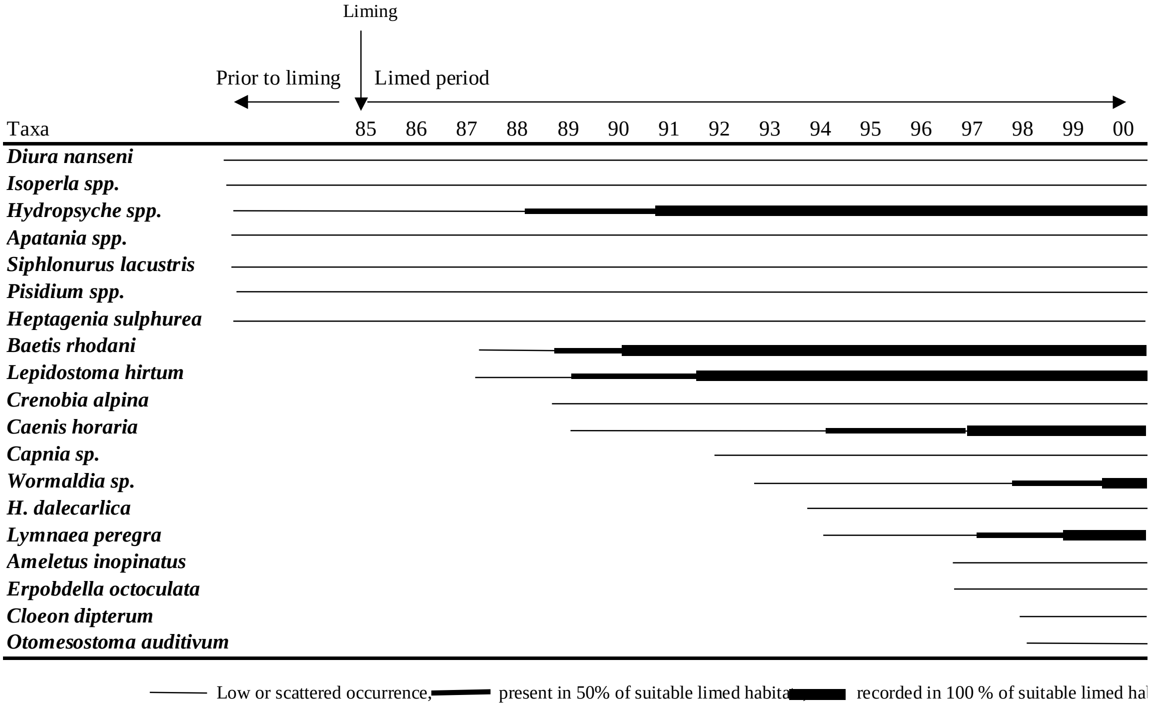

Figure 43. Summary of the development of sensitive taxa of invertebrates in the River Audna during the 15 years following liming (from Raddum and Fjellheim, 2003).

4.3.3 Wider Application in Europe

The application of MAGIC to those areas of Europe where surface waters are considered to be acid sensitive (Table 1) depends primarily on the availability of soil and surface water chemistry data with which to parameterise and calibrate the model. The role of the ICPs (Forests, Mapping and Modelling, Waters and Integrated Monitoring) is crucial to providing this information. Furthermore, each ICP is often represented by a different Institution as the National Focal Point and it is not always the NFCs who are best placed for undertaking the modelling work. It is clear that each country needs to enforce integration of data and expertise if they are to undertake a site-specific or regional modelling exercise. There also exists a number of European scale databases which may provide data for new parameterisation. These include:

Soils: The Soil Geographical Data Base of Europe (SGDBE) is now available (in digital form) on a scale 1:1,000,000. Apart from the map, which uses the FAO soil classification, it also contains pedo-transfer rules, a soil profile analytical database and a database of hydraulic properties (European Soil Bureau 1999).

Land use/land cover: The most detailed European database is the CORINE land use database. However, CORINE does not (yet) cover the whole of Europe (mostly EU countries). A pan-European land cover map/database is the one prepared by the PELCOM project (Mücher *et al*. 2000). Another European land use/cover database, used also by EMEP/MSC-W, is held at the Stockholm Environment Institute (SEI) in York (www2.york.ac.uk/inst/sei/fsheets). A short comparison of these three European databases can be found in De Smet and Hettelingh (2001).

Deposition: Present (and more recent past) deposition fields of S and N covering Europe can be obtained from EMEP/MSC-W (www.emep.int). Historical depositions, mostly based on work by EMEP and IIASA, are available from Posch *et al*. (2003).

Obviously, none of these databases contains the information (input data) in the form needed to run dynamic models. But they often do contain information which can be used in conjunction with so-called (pedo-)transfer functions to get an estimate of the desired input data. Examples of such transfer function can be found in the Mapping Manual (UBA 1996) and in Posch *et al*. (2002).

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5. Heavy metals in surface waters; results from ICP Waters

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In 1999 (12-year report) ICP Waters made an assessment of heavy metals (HM) in surface waters based on data we held in the Programme database (Skjelkvåle *et al.* 1999). The ICP Waters database contains only a small number of sites with heavy metal data, and these sites are located in relatively few countries. Data on heavy metals are reported from fewer sites in each of these countries than major solutes. To be able to give a good picture of the general level of heavy metals in surface waters throughout Europe and North America, heavy metal data for more sites with a larger geographical cover are needed. Some Focal Centres reported that there exist data on heavy metals from additional rivers. These sites are not likely to be suitable for monitoring the effects of air-transported heavy metals to surface waters due to significant inputs from local sources in the catchment.

The report concluded that heavy metals are much more influenced by local pollution sources and human activities in the catchments, than the acidification components (sulphate, nitrate, pH) and that selection of sites for monitoring the effects on HM from air-transported pollution must be made with care.

Few sites have long time series of data for heavy metals. Analytical methods have changed and the detection limit has generally decreased through the monitoring period for the sites with long-term trends. Both the change in method and the change in detection limit make it difficult to identify time trends in heavy metals for many sites.

Heavy metal data in the ICP Waters database has been analysed with different analytical methods and analytical precision. All the laboratories reporting data to ICP Waters participate in national and international intercalibrations. To be able to compare the data within the programme it is of great importance to conduct intercalibration of analysis of heavy metals for improvements of results.

Based on the results from the 12-year report the ICP Waters programme decided to arrange a workshop on heavy metals in aquatic ecosystems to look more closely into the possibilities and problems related to heavy metals in surface waters from long-range transported air pollution.

Here we give a short summary of the Workshop and an update of HM data now held in the ICP Waters database.

5.1 Heavy metals Workshop 2002

The workshop on Heavy Metals (Pb, Cd and Hg) in Surface Waters; Monitoring and Biological Impact." March 18-20, 2002, Lillehammer, Norway, is a contribution from ICP Waters to the ongoing work under 1998 Århus Protocol on Heavy Metals (UN/ECE, 1998) under the UN/ECE Convention on Long-Range Transboundary Air Pollution (Skjelkvåle and Ulstein, 2002).

The 1998 Århus protocol on Heavy Metals targets three particularly harmful metals: Cd, Pb and Hg. According to one of the basic obligations, Parties will have to reduce their emissions for these three metals below their levels in 1990 (or an alternative year between 1985 and 1995). In the protocol there is also a request for looking at the possibility of an effects based approach to setting reduction targets for the purpose of formulating future optimised control strategies which also take into account economic and technological factors.

The effect-based approach, including critical limits and calculation of critical loads, has been a subject on a series of workshop arranged by ICP Modelling and Mapping. Looking at the major conclusions and recommendations from these workshops we see that there has been a development in the understanding Pb, Cd and Hg in aquatic ecosystems.

Bad Harzburg 1997 (Umweltbundesamt, 1998)

- Critical limit for Hg should be defined in terms of the concentration in fish.
- Critical limit for Cd should be defined in terms of the total dissolved concentrations
- For Pb it was recommended that the present water quality criteria should be refined
- Calculations of Critical Loads for Cd and Pb appear feasible
- Steady-state modelling of Cd and Pb has potential problems, because certain key processes will never reach steady-state
- Methods for calculating Critical Loads for Hg are not available at present, but possible ways to proceed have been identified

Schwerin 1998 (Umweltbundesamt, 1999)

- Available Critical Limits vary widely, with most not based on biological effects and expressed as total concentrations
- Existing Critical Limits were found inadequate for Critical Loads calculations (in particular for soils)
- There is a need to map Critical Loads for waters
- Modelling Hg is now possible
- Candidate models for Pb and Cd are now ready for testing

Bratislava 2000 (urlík *et al.* 2000)

- Recommended critical limits for metals in soils, and also suggested limits for waters.
- In tight cooperation with the work in the workshops, several manuals for calculating critical loads for aquatic ecosystems were made (de Vries *et al.* 1998, de Vries *et al.* 2001).
- In 2002 the first call for data on Critical Loads on heavy metals for soils and surface waters was submitted. This submission of data was voluntary. The first report on modelling and mapping of critical loads and levels for cadmium and lead in Europe was published in 2002 (Hettelingh et. al 2002).

Lillehammer 2002 (Skjelkvåle and Ulstein, 2002)

The major aim of the Heavy Metal Workshop at Lillehammer was to**:**

- Agree on monitoring and analytical methods
- Contribute and participate in the ongoing discussions on Critical Limits and Critical Loads for heavy metals in surface waters

The opening presentations at the workshop showed that numerous national and international activities and research programmes, monitoring, regional and national surveys, intensive studies and experiments, have substantially increased present knowledge over the last years on the effect of long-range transport of heavy metals on aquatic ecosystems, including concentration levels, spatial variability, trends in time, effects on the biota (bioavailability, biomagnification, bioaccumulation) and modelling.

The workshop reviewed the present knowledge and understanding in three areas,

(i) Critical limits
(ii) Monitoring methods
(iii) Dose/response, relationships and modelling thereof

The workshop encouraged further review of existing data and information, including active cooperation with other bodies, EU research programmes and national research. ICP Waters should make full use of information in other programmes and vice versa.

Effect-based approach to the control of heavy metals in surface waters requires further development. Defining critical loads for individual heavy metals need not necessarily be a final step in the process. Additional methods may also prove to be advantageous.

ICP Waters was encouraged to act as a facilitator in providing data and information for development of critical limits for heavy metals in aquatic ecosystems. This implies activity from national focal points.

ICP Waters should revise and update the Programme manual and continue intercomparisons on heavy metals.

5.2 Heavy metals in the ICP Waters database 2002

Eleven countries have reported data on heavy metals to the Programme centre during the last 3 years (1999-2001). Of these, 11 have submitted data on Cu and Zn, 9 on Pb, 8 on Cd and 6 on Ni. This is a slight increase from the last assessment in 1999.

Mean values for Pb, Cd, Zn, Cu and Ni for the period 1999-2001 are listed in Appendix B. In calculating mean values, all values under detection limit are given the value of 2/5 of the detection limit. In some cases where the detection limit changed (to a lower value) within the 3-year period, only the latest observations are used.

The detection limit varies from very low values in Sweden and Finland to very high values in Hungary. In Germany, the laboratories analysing heavy metals operate with different detection limits.

5.3 Long-term trends in heavy metals

The methods for analysing heavy metals have changed and improved over the last years. In recent years the ICP-MS method has increasingly become the standard and has resulted in major improvement in detection limits for many metals. Both the change in method and the change in detection limit make it difficult to identify time trends in heavy metals for most sites. In addition, monitoring of heavy metals in many countries is a relatively new activity. Hence, we have not considered it appropriate to perform trend tests on the data but perform a visual judgement of data plots. The plots are also limited to the last 10 years.

In the ICP Waters database, some sites from Germany, the Czech Republic, Latvia and Sweden have long time-series and high quality data. Further, Canada has several long time series on zinc.

Trends for two sites in Germany and the Czech Republic are shown (**Figure 44** and **Figure 45**). The German site (DE03) illustrates the changes in decrease in detection limit. The detection limit for Pb changes from 2 µg/L to 0.2 µg/L after 1992. The detection limit for Cd changes from 0.3 µg/L prior to 1991, to 0.2 µg/L through 1992 and then to 0.04 µg/L subsequently. The Czech site shows a clear decline in Pb, Cd and Zn over the last 10 years, while the German site shows no clear trends. The decrease in zinc and cadmium in the Czech sites is due to a combination of deposition decrease with the pH increase; lead decrease due to deposition decrease (Vesely and Majer, 1996). The Swedish and Latvian sites show no clear trends, as illustrated by site SE01 (**Figure 46**) and site LV02 (**Figure 47**). The zinc data from Canada (CA01 - CA04, **Figure 48**) show no obvious time trends but have conspicuous short term spring peaks, often exceeding 100 µg/l, with maximum values up to 400 µg/l. The peaks may be connected to the early stage of snowmelt, but there is no known local source for this pollution (D. Jeffries pers.com.).

Lake erné (CZ01) in Czech Republic

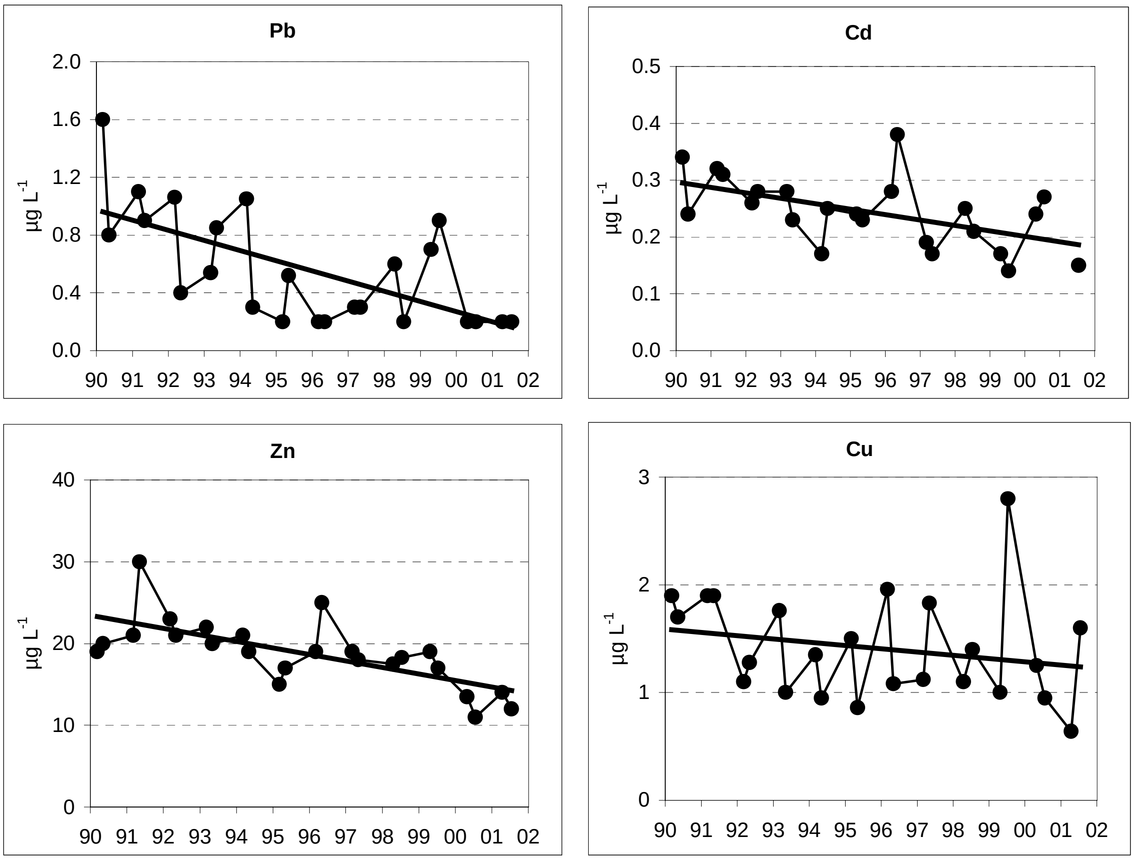

Figure 44. Trends in Pb, Cd, Zn and Cu for Lake erné (CZ01) in Czech Republic. $P<0.001$ for Pb, Cd and Zn and $p<0.05$ for Cu.

Due to the low number of sites with heavy metals data and because of the shortcomings in the data (short series, changes in analytical methods), it is presently not possible to do an analysis of long-term trends in heavy metals on a regional scale, in a manner similar as for acidification. There are several reasons for the lack of such data. Most countries prioritise monitoring of heavy metals mainly in problem areas were there are known local sources of pollution (industry, mining activity). Hence, the monitoring of long-range transported metals in surface waters is absent or limited to spot tests without a systematic sampling or occasional regional surveys (e.g. Nordic Survey, Skjelkvåle *et al.* 2001). It is also difficult to distinguish the local geological contribution of metals from long-range transported metals, particularly if deposition data are not available. In addition, trace metal behaviour is complex due to differences in partitioning between water and solids in the water, which in addition sharply changes with pH (Vesely et al 2001). Probably the most severe polluting heavy metal by long range transport is mercury. Since surface waters are not suitable for monitoring mercury, long-range transported heavy metals are often analysed in lake sediments, fish or mosses.

Intensive monitoring of heavy metals in surface waters may, however, reveal surprising and potential harmful concentrations of heavy metals, as shown by the Canadian zinc data above. Only high frequency of sampling will reveal such concentration peaks. Low frequency of sampling with an occasional sample during a peak would probably be mistaken as an outlayer due to contamination of the sample or analytical error.

Elberndorfer Bach (DE03) in Germany

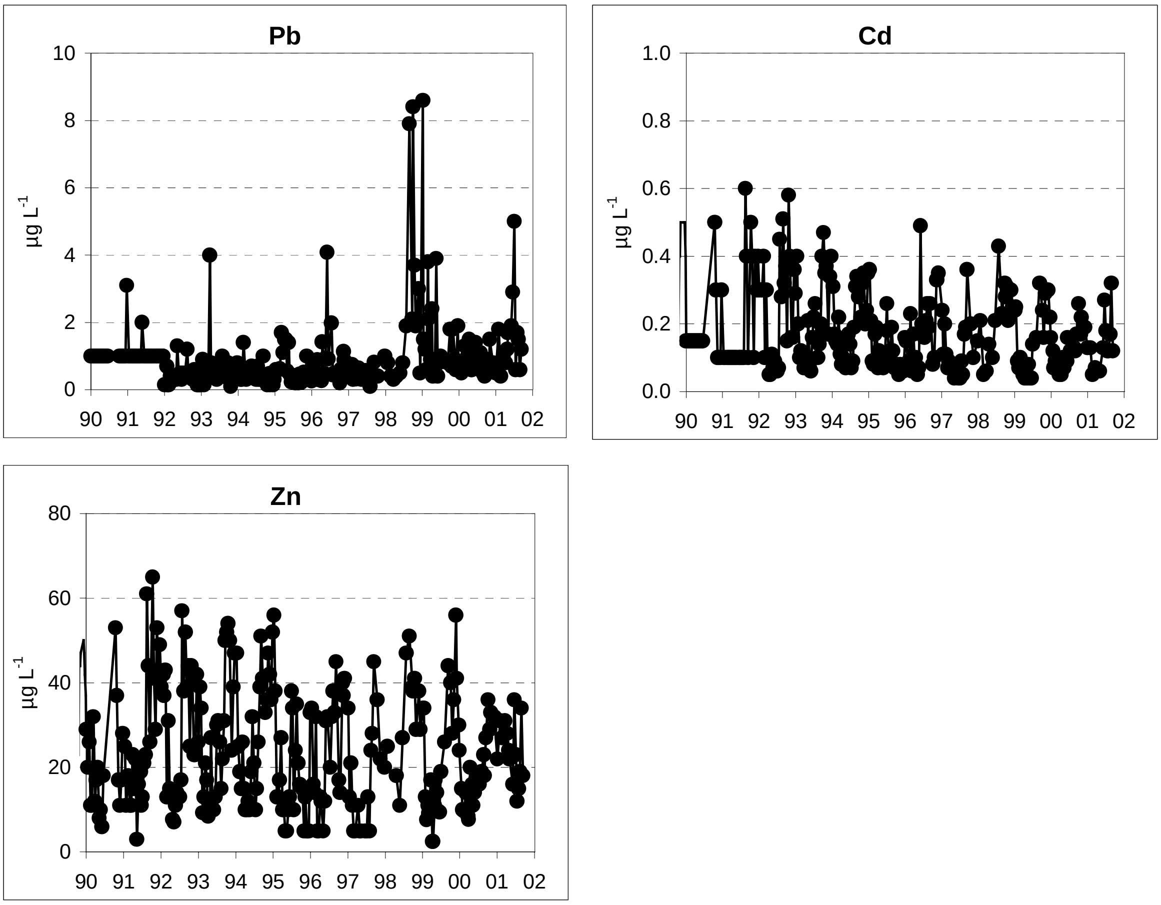

Figure 45. Trends in Pb, Cd and Zn for Elbendorfer Bach (DE03) in Germany.

Delångersån (SE01) Iggersund, Sweden

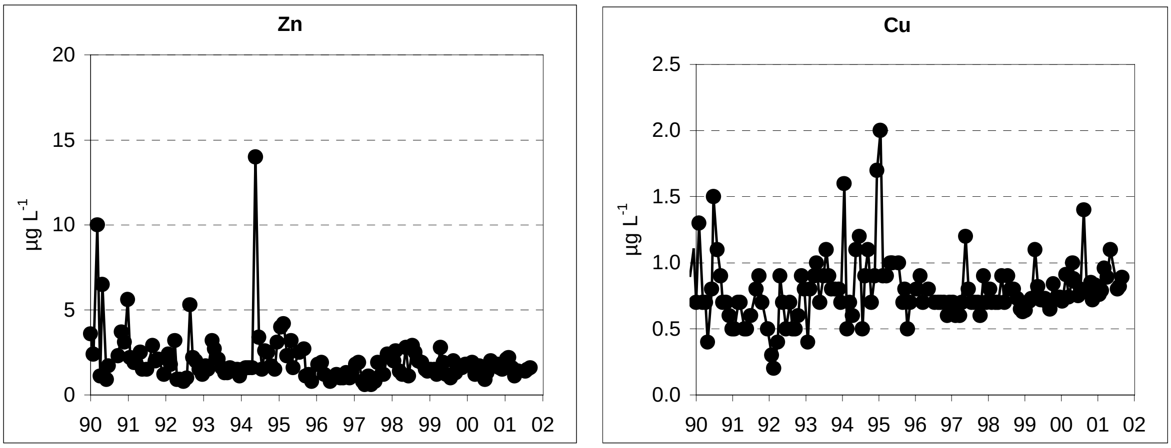

Figure 46. Trends in Zn and Cu for Delångersån (SE01) in Sweden.

Barta, Dukupji (LV02) Latvia

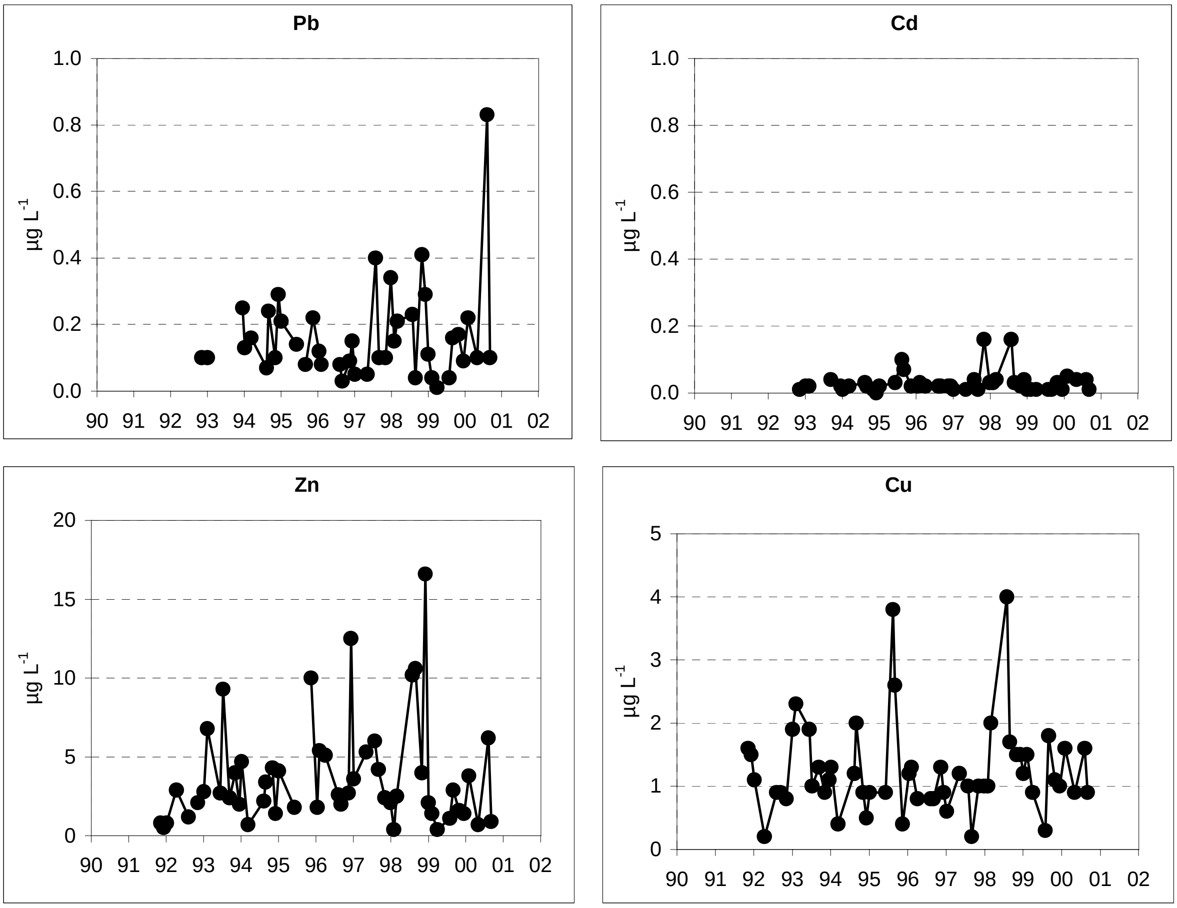

Figure 47. Trends in Pb, Cd, Zn and Cu for Barta, Dukupij (LV02) in Latvia.

Canada

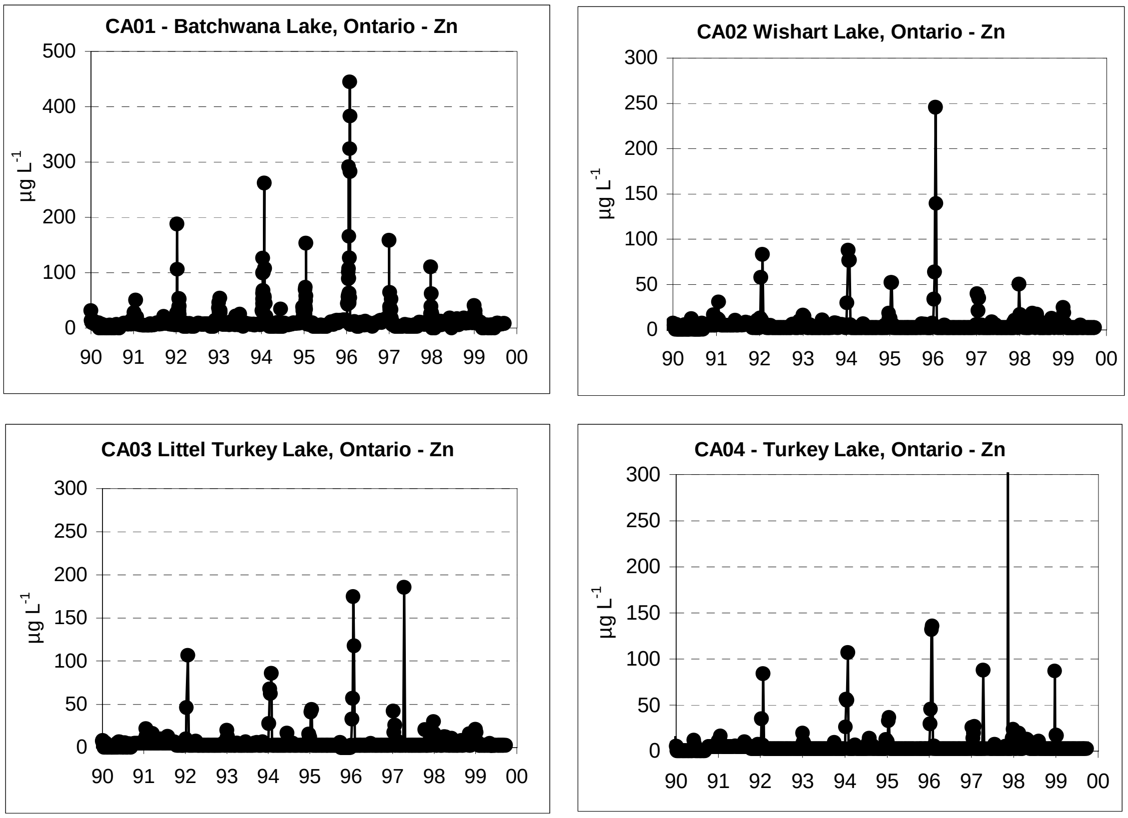

Figure 48. Trends in Zn for 4 Canadian sites (CA01 -CA04).

5.4 References

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Appendix A. Chemistry data

Table 8. Sites in the ICP Waters pr. 2001 with water chemistry. Mean water chemistry are for for samples collected 1999-2001. n indicates the number of observations in the 3-year period.

Country	ICP Site Number	Site Name	n	K25	pH	Ca	Mg	Na	K	Cl	SO_4	Alkalinity	ANC	NH_4N	NO_3N	TOTN	TOTP	TOC	DOC
				mSm^{-1}		$mg\ L^{-1}$	$mg\ L^{-1}$	$mg\ L^{-1}$	$mg\ L^{-1}$	$mg\ L^{-1}$	$mg\ L^{-1}$	$\mu eq\ L^{-1}$	$\mu eq\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$mgC\ L^{-1}$	$mgC\ L^{-1}$
Belarus	BY01	Berezinsky Biosphere Reserve	21	34.55	7.56	48.90	13.89	3.42	1.27	6.60	26.44	3009	2961	579	848	1437	47		
Canada	CA01	Ontario, Algoma Region, Batchawana Lake	63	2.19	6.04	2.12	0.35	0.43	0.17	0.31	4.66	39	36		216	527	5		5.37
Canada	CA02	Ontario, Algoma Region, Wishart Lake	66	2.79	6.61	3.15	0.39	0.51	0.19	0.29	4.89	82	79		379	540	4		4.51
Canada	CA03	Ontario, Algoma Region, Little Turkey Lake	73	3.40	6.92	4.13	0.43	0.55	0.21	0.30	5.20	141	132		307	566	5		4.27
Canada	CA04	Ontario, Algoma Region, Turkey Lake	65	3.81	6.93	4.90	0.45	0.56	0.22	0.31	5.07	189	176		290	463	4		4.12
Canada	CA05	Quebec, Lac Veilleux	2	1.77	6.16	1.07	0.19	0.40	0.17	0.20	1.65	0	49	24	15				3.05
Canada	CA06	Quebec, Lac Josselin	2	1.19	5.80	1.11	0.20	0.43	0.13	0.15	2.10	0	44	23	25				3.05
Canada	CA07	Quebec, Lac Bonneville	2	1.21	5.17	0.78	0.19	0.26	0.07	0.25	2.50	0	7		15				5.65
Canada	CA08	Quebec, Lac Laflamme	45	1.84	6.38	1.78	0.40	0.89	0.16	0.24	2.88	0	95	21	52				4.54
Canada	CA09	Quebec, Lac Macleod	2	1.09	5.56	0.82	0.20	0.42	0.07	0.30	2.20	0	21	32	15				5.50
Canada	CA10	Nova Scotia, Mount Tom Lake	4	2.67	4.63	0.26	0.32	2.36	0.23	3.43	1.73	-20	15		10	83			8.93
Canada	CA11	Nova Scotia, Mountain Lake	4	2.15	5.22	0.32	0.32	2.47	0.19	3.50	1.98	-1	13		15	65			3.13
Canada	CA12	Nova Scotia, Little Red Lake	4	3.86	4.32	0.28	0.38	2.90	0.25	4.03	1.98	-45	23		10	113			15.85
Canada	CA13	Nova Scotia, Kejimkujik Lake	4	2.91	4.99	0.61	0.41	3.19	0.23	4.80	2.23	-5	26		13	70			6.58
Canada	CA14	Nova Scotia, Beaverskin Lake	4	2.14	5.42	0.31	0.33	2.56	0.22	3.63	2.08	0	13		10	60			2.45
Canada	CA16	Ontario,Lake224	12	1.77	6.92	1.66	0.46	0.69	0.34	0.26	2.65	76	98	8	1	175	2		3.38
Canada	CA17	Ontario,Lake239	16	3.21	6.77	2.84	0.94	1.17	0.58	0.40	3.43	174	201	11	19	256	2		7.08
Canada	CA20	Ontario,Lake373	17	2.89	7.05	2.79	0.69	0.80	0.42	0.30	2.35	175	184	15	2	199	2		4.26
Czech Republic	CZ01	Bohemian Forest, Cerné	6	3.02	4.77	0.79	0.44	0.76	0.46	0.74	3.99	0	-45		868				1.38
Czech Republic	CZ02	Bohemian Forest, Certovo	6	3.41	4.45	0.44	0.32	0.62	0.29	0.61	4.47	0	-67		536				2.71
Czech Republic	CZ03	Bohemian Forest, Plešné	6	2.04	5.05	0.84	0.19	0.88	0.37	0.48	4.12	0	-3		116				3.33
Czech Republic	CZ04	Bohemian Forest, Prášilské	6	1.92	4.87	0.58	0.31	0.63	0.29	0.58	2.31	0	4		300				4.35
Czech Republic	CZ05	Bohemian Forest, Laka	6	1.88	5.74	0.92	0.43	1.13	0.40	0.71	1.81	1	46		510				3.41
Czech Republic	CZ06	Bohemian Forest, Zd´árské	6	3.45	6.28	2.26	0.56	2.60	0.50	0.85	6.42	39	125		34				6.89

Country	ICP Site Number	Site Name	n	K25	pH	Ca	Mg	Na	K	Cl	SO_4	Alka-linity	ANC	NH_4N	NO_3N	TOTN	TOTP	TOC	DOC
				mSm^{-1}		$mg L^{-1}$	$mg L^{-1}$	$mg L^{-1}$	$mg L^{-1}$	$mg L^{-1}$	$mg L^{-1}$	$\mu eq L^{-1}$	$\mu eq L^{-1}$	$\mu g L^{-1}$	$\mu g L^{-1}$	$\mu g L^{-1}$	$\mu g L^{-1}$	$mgC L^{-1}$	$mgC L^{-1}$
Estonia	EE01	River Ahja, Kiidjärve	18	41.21	8.04	63.00	12.78	4.43	1.60	6.87	13.52	4004	3889	53	904	1216	51		
Finland	FI01	Southeast Finland, Hirvilampi	18	3.17	5.59	1.53	0.42	1.44	0.94	1.57	6.20	13	19	50	76	394	6	3.87	
Finland	FI02	Southeast Finland, Vuorilampi	18	3.08	5.84	1.89	0.52	1.62	1.02	1.27	5.66	48	72	111	117	628	10	6.20	
Finland	FI03	Southeast Finland, Mäkilampi	18	2.33	5.56	1.75	0.32	0.97	0.42	1.08	5.13	13	28	27	28	321	7	4.83	
Finland	FI05	Lapland, Suopalampi	14	1.59	6.25	0.78	0.26	0.97	0.17	0.40	0.98	43	74	11	16	304	13	7.03	
Finland	FI06	Lapland, Vasikkajärvi	17	3.44	6.02	0.37	0.13	0.52	0.18	0.45	1.53	7	10	12	20	143	4	1.66	
Finland	FI07	Uusimaa, Vitsjön	18	3.76	6.45	2.16	0.89	2.74	0.63	3.30	6.16	57	92	32	46	345	6	5.13	
Finland	FI08	North Karelia, Kakkisenlampi	17	0.71	5.33	0.31	0.10	0.34	0.22	0.29	1.71	-5	-2	12	23	165	5	2.45	
Finland	FI09	Häme, Sonnanen	19	3.14	6.66	2.86	0.47	1.51	0.56	2.22	4.19	77	110	27	16	229	4	2.19	
Germany	DE01	Schwarzwald, Dürreychbach	38	3.50	5.96	2.47	0.50	0.82	2.31	2.67	3.58	69	25	18	1187		6		3.55
Germany	DE02	Fichtelgebirge, Eger	36	5.62	5.79	2.68	1.26	5.05	1.13	9.83	4.59	57	55		815			2.57	
Germany	DE03	Rothaargebirge, Elberndorfer Bach	66	5.99	6.31	3.44	2.89			2.56	12.04			39	974				2.07
Germany	DE04	Sächsische Tieflandsbucht, Ettelsbach	20	42.03	4.91	42.72	10.48	6.64	2.52	11.49	156.20	30	-372	78	1989			11.82	10.98
Germany	DE05	Schwarzwald, Goldersbach	37	2.58	6.56	2.13	0.50	1.07	1.47	1.91	2.98	58	93	20	321		5		4.59
Germany	DE06	Hunsrück, Gräfenbach	33	7.84	4.75	3.94	2.37	3.07	0.65	4.31	20.35	22	-26	19	313		9		8.02
Germany	DE07	Erzgebirge, Grosse Pyra	28	6.54	4.67	4.55	1.04	2.15	0.92	1.29	17.96	18	-47	22	921			4.59	3.81
Germany	DE08	Bayerischer Wald, Grosse Ohe	78	2.89	6.03	1.96	0.64	1.78	0.65	0.99	2.81		74	36	1179		15	3.98	
Germany	DE09	Sächsische Tieflandsbucht, Heidelbach	21	43.85	5.04	46.10	7.81	9.72	2.53	20.10	153.35	88	-364	256	478			8.58	7.36
Germany	DE10	Bayerischer Wald, Hinterer Schachtenbach	33	2.76	5.90	2.07	0.56	1.59	0.58	0.78	2.65		36		1688				
Germany	DE11	Schwarzwald, Kleine Kinzig	38	4.06	6.45	3.23	0.74	1.47	1.48	3.09	4.01	178	113	27	570		8		1.44
Germany	DE12	Harz, Lange Bramke	153	20.62	6.14	3.29	1.70	1.82	0.68	2.91	10.84	41	58	91	491	626	50	0.80	1.04
Germany	DE13	Erzgebirge, Talsperre Neunzehnhain	16	16.89	7.06	13.62	6.96			11.36	38.88			35	1947		20	0.19	
Germany	DE14	Kaufunger Wald, Nieste 3	11	12.07	6.19	10.48	4.10	3.55	1.81	4.67	30.64	221	220	35	994			3.55	1.30
Germany	DE16	Lauenburgische Seenplatte, Pinnsee	9	3.96	5.44	1.21	0.58	3.24	0.89	5.60	4.19	40	26	22	50	809	37	8.31	7.29
Germany	DE17	Bayerischer Wald, Rachelsee	9	2.89	4.63	0.75	0.44	0.75	0.52	1.12	3.03		-79	62	1449		6	2.87	
Germany	DE18	Fichtelgebirge, Röslau	36	4.10	5.20	2.24	0.57	2.96	0.54	1.80	9.64	45	24		366			5.55	
Germany	DE19	Taunus, Rombach 2	35	11.48	4.69	4.16	2.59	5.53	0.56	9.48	17.89	15	-118	38	2231		10	1.95	1.60
Germany	DE20	Taunus, Rombach 3	24	8.45	6.73	6.44	2.62	3.35	0.78	6.34	7.73	191	222	39	1954		10	2.51	1.37
Germany	DE21	Erzgebirge, Rote Pockau	30	11.70	5.84	9.64	3.30	5.36	1.23	6.41	31.48	70	88	52	1303			9.25	
Germany	DE23	Bayerischer Wald, Seebach	34	2.27	6.04	1.51	0.62	1.44	0.58	0.86	2.56		53		1018				
Germany	DE24	Erzgebirge, Talsperre Sosa	41	7.81	5.25	5.93	2.67			3.58	20.35			56	589		27	0.20	8.70

Country	ICP Site Number	Site Name	n	K25	pH	Ca	Mg	Na	K	Cl	SO_4	Alka-linity	ANC	NH_4N	NO_3N	TOTN	TOTP	TOC	DOC
				mSm^{-1}		$mg\ L^{-1}$	$mg\ L^{-1}$	$mg\ L^{-1}$	$mg\ L^{-1}$	$mg\ L^{-1}$	$mg\ L^{-1}$	$\mu eq\ L^{-1}$	$\mu eq\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$mgC\ L^{-1}$	$mgC\ L^{-1}$
Germany	DE25	Elbsandsteingebirge, Taubenbach	21	19.59	7.24	27.91	1.80	1.97	1.82	3.50	53.60	424	343	15	1521			4.36	3.96
Germany	DE26	Hunsrück, Traunbach 1	37	6.42	4.74	2.20	1.45	4.75	0.52	8.96	7.83	28	5	12	407		9		7.56
Germany	DE27	Bayerischer Wald, Vorderer Schachtenbach	33	2.92	6.21	2.30	0.65	2.07	0.68	0.84	3.15		103		1165				
Germany	DE28	Oberpfälzer Wald. Waldnaab 2	7	4.30	6.64	3.17	1.42	3.04	1.01	1.90	6.02	281	166	16	1229		29	3.27	2.50
Germany	DE29	Oberpfälzer Wald, Waldnaab 8	7	5.79	5.82	4.18	0.98	4.49	1.22	2.22	15.47	141	84	17	663		35	5.44	4.60
Germany	DE30	Erzgebirge, Wilde Weisseritz	26	9.03	6.98	8.36	1.86	2.80	1.47	2.98	21.96	211	116	46	1038		23	5.03	4.62
Germany	DE31	Erzgebirge, Wolfsbach	28	19.38	7.15	16.13	5.60	10.10	2.28	18.79	33.07	387	358	32	2721		40	5.42	3.70
Germany	DE32	Rothaargebirge, Zinse	66	5.24	5.98	3.22	2.33			2.50	10.75			36	648				2.15
Germany	DE33	Fichtelgebirge, Zinnbach	34	8.01	4.09	3.40	0.83	2.65	1.02	1.90	18.43	39	-125		925			6.16	
Germany	DE34	Odenwald, Schmerbach 1	35	9.83	4.42	3.85	2.14	1.99	1.78	4.44	20.71	21	-119	43	859		64	3.68	3.27
Germany	DE35	Taunus, Rombach 4	9	12.09	6.14	5.04	3.10	10.37	0.60	16.33	13.00	85	130	35	1556			2.78	2.31
Hungary	HU01	Matra Mountains, Csórrét Reservoir	4	19.53	7.45	20.95	5.90	10.00	1.03	18.50	32.03	583	761	76	598				
Ireland	IE01	Wicklow, Glendalough, Lake Upper, Mid Lake	2	0.04	6.19	1.38	0.70	4.31	0.29	5.85	3.00	5	82	13	155				
Ireland	IE02	Wicklow, Glendalough, Lake Upper, Inflow 1	2	0.05	6.64	2.26	0.73	4.22	0.26	4.60	3.60	16	149	5	115				
Ireland	IE03	Wicklow, Glendalough, Lake Upper, Inflow 2	2	0.06	7.05	3.89	1.38	4.94	0.25	6.55	6.25	47	179	5	490				
Ireland	IE04	Wicklow, Glendalough, Lake Upper, Inflow 3	2	0.04	5.46	0.72	0.74	5.65	0.16	8.25	3.25	0	29	5	225				
Ireland	IE05	Galway, Lough Maumwee, Mid Lake	2	0.06	6.33	1.78	1.21	10.26	0.56	17.15	2.60	0	108	12	35				
Ireland	IE06	Galway, Lough Maumwee, Inflow 1	2	0.08	6.29	1.63	1.39	11.97	0.41	20.00	3.20	0	93	5	40				
Ireland	IE07	Galway, Lough Maumwee, Inflow 2	2	0.08	6.23	2.80	1.33	11.47	0.44	19.65	2.90	2	142	5	25				
Ireland	IE08	Donegal, Lough Veagh, Mid Lake	2	0.07	6.27	1.30	1.34	10.63	0.44	17.10	2.60	0	109	36	43				
Ireland	IE09	Donegal, Lough Veagh, Inflow 1	2	0.07	5.89	1.32	1.35	11.78	0.35	19.05	2.50	8	108	19	10				
Ireland	IE10	Donegal, Lough Veagh, Inflow 2	2	0.07	5.19	0.91	1.23	10.82	0.37	18.05	2.50	0	65	22	8				
Italy	IT01	Piemonte, Lake Paione Inferiore	7	1.42	6.38	1.33	0.13	0.35	0.36	0.32	1.99	7	21	9	420	450	3		
Italy	IT02	Piemonte, Lake di Mergozzo	3	5.65	6.93	5.40	1.41	2.10	0.85	1.40	8.30	213	239	5	660	808	5		
Italy	IT03	Piemonte, Lake Paione Superiore	11	1.06	5.87	0.76	0.09	0.22	0.31	0.17	1.55	0	-2	59	397	433	4		
Italy	IT04	Piemonte, River Cannobino	36	4.58	7.30	3.87	1.37	1.72	0.69	0.96	5.16	190	211	7	741	868	7		
Italy	IT05	Piemonte, River Pellino	36	5.65	7.16	4.43	1.14	3.43	0.54	2.18	4.29	179	199	6	1783	1951	18		
Italy	IT06	Piemonte, River Pellesino	36	4.99	7.17	3.52	0.80	3.77	0.58	2.51	3.15	142	166	27	1656	1931	33		
Latvia	LV01	Burtnieku Lake, hydrosite	10	31.64	8.02	47.26	10.82	3.05	2.29	6.27	24.68	2675	2725	43	341	1149	35		
Latvia	LV02	Barta, Dukupji	20	42.43	8.22	65.72	13.10	5.74	2.37	8.62	28.45	3767	3780	94	728	1690	53		
Latvia	LV03	Liela Jugla, Zaki	28	42.74	8.08	64.90	14.64	3.51	2.22	6.41	45.53	3456	3464	80	843	1793	53		

Country	ICP Site Number	Site Name	n	K25	pH	Ca	Mg	Na	K	Cl	SO$_4$	Alka-linity	ANC	NH$_4$N	NO$_3$N	TOTN	TOTP	TOC	DOC
				mSm^{-1}		mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	µeq L^{-1}	µeq L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	mgC L^{-1}	mgC L^{-1}
Latvia	LV04	Tulija, Zoseni	34	34.55	7.91	50.33	11.03	2.64	1.74	4.75	21.73	2896	2884	78	392	1364	27		
Latvia	LV05	Zvirbuli stream, hydrosite	18	11.20	4.22	10.39	3.26	1.51	0.87	4.99	17.47	428	362	194	113		27		
Norway	NO01	Aust-Agder, Birkenes	156	3.32	4.80	0.80	0.27	2.76	0.11	4.59	3.30	0	-21		110	300		5.27	
Norway	NO03	Buskerud, Langtjern	155	1.38	5.03	0.94	0.13	0.53	0.10	0.47	1.42	2	40		15	258		10.02	
Norway	NO04	Finnmark, Dalelv	156	3.59	6.24	1.45	0.81	3.46	0.28	5.35	4.48	35	51	3	19	134	5	3.34	
Norway	NO05	Oppland, Aurdøla	46	1.29	6.31	1.22	0.18	0.72	0.22	0.61	1.79	37	56		37	212	3	3.36	
Norway	NO06	Rogaland, Vikedalselva	46	1.94	5.82	0.66	0.31	1.93	0.18	3.33	1.66	7	8		141	221	2	1.06	
Norway	NO07	Sogn og Fjordane, Gaula	38	1.22	5.78	0.45	0.18	1.09	0.20	1.95	0.92	7	9		85	154	3	1.14	
Norway	NO08	Sogn og Fjordane, Nausta	48	1.60	6.03	0.60	0.26	1.56	0.27	2.76	0.99	16	23		65	150	5	1.45	
Norway	NO09	Sogn og Fjordane, Trodøla	156	1.54	5.72	0.39	0.25	1.61	0.22	2.79	0.98	6	12		66	132	3	1.41	
Norway	NO10	Telemark, Storgama	154	1.50	4.87	0.49	0.09	0.73	0.07	1.02	1.43	0	1		80	308		5.03	
Poland	PL01	Tatra Mountains, Dlugi Staw Gasienicowy	23	1.87	6.11	1.78	0.11	0.36	0.12	0.38	2.40	6	21	18	496		5		
Poland	PL02	Tatra Mountains, Zielony Staw Gasienicowy	23	2.16	6.38	2.51	0.19	0.33	0.14	0.42	2.22	15	84	32	238		16		
Sweden	SE01	Delångersån Iggersund	37	4.49	6.89	3.65	1.21	2.73	0.71	2.60	4.40	172	245	10	122	394	11	6.35	
Sweden	SE02	Alsterån Getebro	36	7.56	6.71	6.22	1.58	5.56	0.80	7.53	9.49	148	286	21	99	654	13	12.94	
Sweden	SE03	Alsterån Strömsborg	12	8.06	6.66	7.03	1.33	6.19	0.83	7.58	8.77	208	345	25	141	737	14		
Sweden	SE05	Tväringen	12	2.40	6.49	2.45	0.62	1.20	0.47	0.64	1.97	107	171	12	17	265	8	8.04	
Sweden	SE06	Stensjön	24	1.75	6.24	1.29	0.38	1.19	0.27	0.75	2.05	34	89	17	27	315	7	6.95	
Sweden	SE08	Brunnsjön	24	5.96	5.53	3.75	1.45	4.51	0.71	5.81	10.21	0	137	22	101	653	11	18.21	
Sweden	SE09	Fiolen	24	5.34	6.52	3.07	1.12	4.00	1.31	6.60	7.24	56	111	21	76	520	12	6.96	
Sweden	SE10	Storasjö	12	3.41	5.38	1.47	0.62	3.03	0.40	4.10	4.04	-6	64	37	37	468	18	10.74	
Sweden	SE11	Fräcksjön	24	5.97	6.40	3.28	1.11	5.87	0.72	9.08	5.69	65	146	17	108	470	10	9.88	
Sweden	SE12	Härsvatten	24	5.48	4.65	0.62	0.74	5.60	0.42	9.43	5.36	-41	-39	26	103	329	4	3.50	
Switzerland	CH03	Tomè	3	1.04	5.75	0.87	0.08	0.30	0.14	0.10	1.63	0	-1	27	427	640	7		0.23
Switzerland	CH04	Lago Di Mognola	3	1.75	6.83	1.62	0.24	0.56	0.46	0.10	3.05	25	53	23	247	443	7		0.33
Switzerland	CH05	Laghetti (Lago Inferiore)	12	1.20	6.44	1.08	0.12	0.33	0.36	0.13	1.73	3092	26	42	295	456	3		0.46
Switzerland	CH06	Laghetti (Lago Superiore)	10	1.17	6.29	1.02	0.10	0.31	0.33	0.15	1.73	1	18	45	322	447	3		0.46
Switzerland	CH08	Lago Della Froda	3	1.35	6.68	1.51	0.10	0.27	0.24	0.10	2.03	13	39	23	240	507	4		0.37
Switzerland	CH09	Lago Nero	3	1.54	6.92	1.66	0.15	0.33	0.40	0.10	2.44	28	54	13	167	487	6		0.33
Switzerland	CH10	Laghetti Di Antabia (Lago 1)	3	1.42	6.89	1.50	0.07	0.41	0.24	0.17	1.35	33	48	130	333	457	5		0.33
Switzerland	CH11	Laghi Della Crosa (Lago Superiore)	3	0.85	6.30	0.85	0.07	0.25	0.14	0.10	1.17	0	16	17	270	390	3		0.33

Country	ICP Site Number	Site Name	n	K25	pH	Ca	Mg	Na	K	Cl	SO_4	Alka-linity	ANC	NH_4N	NO_3N	TOTN	TOTP	TOC	DOC
				mSm^{-1}		$mg\ L^{-1}$	$mg\ L^{-1}$	$mg\ L^{-1}$	$mg\ L^{-1}$	$mg\ L^{-1}$	$mg\ L^{-1}$	$\mu eq\ L^{-1}$	$\mu eq\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	$mgC\ L^{-1}$	$mgC\ L^{-1}$
Switzerland	CH12	Lago D'orsalia	3	1.04	6.23	0.92	0.09	0.30	0.16	0.13	1.31	0	11	37	387	530	5		0.33
Switzerland	CH13	Schwarzsee	3	1.20	6.35	1.12	0.10	0.29	0.23	0.17	1.48	10	25	33	303	463	4		0.30
Switzerland	CH14	Lago Di Pozzoi	3	0.96	6.42	0.82	0.11	0.33	0.18	0.17	1.49	1	23	17	147	333	5		0.73
Switzerland	CH16	LAGO Di Sfille	3	1.07	6.39	1.00	0.12	0.37	0.12	0.17	1.71	0	23	23	213	373	3		0.50
Switzerland	CH18	Lago Di Sascola	3	1.08	5.98	0.88	0.14	0.30	0.32	0.13	1.65	0	11	20	377	537	4		0.57
Switzerland	CH19	Lago D'alzasca	3	1.67	6.88	1.78	0.20	0.48	0.44	0.20	2.22	39	66	30	273	410	3		0.53
Switzerland	CH20	Lago Di Starlaresc Da Sgiof	3	1.14	5.25	0.62	0.11	0.33	0.19	0.20	1.73	0	-9	33	360	557	4		0.83
Switzerland	CH21	Lago Barone	3	0.97	6.10	0.88	0.07	0.24	0.18	0.10	1.69	0	6	30	283	570	5		0.40
Switzerland	CH22	L.To Gardiscio	3	0.91	5.40	0.48	0.09	0.21	0.23	0.13	1.73	0	-8	40	210	487	5		0.23
Switzerland	CH23	Lago Di Morghirolo	3	1.25	6.50	1.07	0.15	0.30	0.39	0.10	2.15	1	26	17	213	393	6		0.33
Switzerland	CH24	Leit (Lago 1)	3	1.49	6.35	1.24	0.23	0.33	0.39	0.13	3.37	0	16	27	210	440	8		0.33
United Kingdom	CH25		3	1.91	6.68	2.07	0.13	0.41	0.41	0.13	3.24	27	49	40	313	463	6		0.27
United Kingdom	CH26		24	5.96	7.32	7.25	0.64	1.52	1.41	0.91	8.92	246	269	33	503	662	8		0.45
United Kingdom	CH27		24	4.33	7.04	4.25	0.88	1.59	0.53	0.82	5.91	114	148	44	1025	1180	9		0.52
United Kingdom	CH28		24	2.35	6.77	2.47	0.22	0.68	0.51	0.44	3.59	29	50	32	663	795	6		0.36
United Kingdom	CH29		7	2.06	6.50	1.83	0.21	0.73	0.41	0.21	3.50	7	24	56	680	894	8		0.49
United Kingdom	UK01	Scotland, Loch Coire nan Arr	5	5.24	6.12	0.91	0.96	6.68	0.34	12.52	2.06	0	26		27	157			2.68
United States	UK04	Scotland, Lochnagar	5	2.24	5.36	0.52	0.40	2.10	0.19	3.18	2.30	0	0		235	303			1.38
United States	UK07	Scotland, Round Loch of Glenhead	5	3.98	4.94	0.60	0.52	4.12	0.25	7.70	2.26	0	-13		96	245			3.56
United States	UK10	England, Scoat Tarn	5	3.48	5.04	0.52	0.50	3.50	0.23	6.26	2.48	0	-21		258	319			1.12
United States	UK15	Wales, Llyn Llagi	5	3.04	5.58	0.93	0.54	3.96	0.17	7.16	2.30	0	10		107	54			2.94
United States	UK21	N.Ireland, Blue Lough	5	5.63	4.77	0.67	0.70	6.00	0.48	10.42	3.40	0	-25		347	511			4.24
United States	US05	Maine, Little Long Pond	2	2.15	5.70	0.65	0.31	2.20	0.31	3.11	3.20	11	7	23	4				1.65
United States	US06	Maine, Tilden Pond	2	2.30	6.34	1.00	0.37	2.23	0.31	2.80	2.59	50	52	23	4				2.95
United States	US11	New York, Adirondack Mnt., Arbutus	24	20.49	6.56	2.79	0.51	0.72	0.27	0.35	5.71	73	84	5	86				4.68
United States	US12	New York, Adirondack Mnt., Constable	24	17.95	5.02	1.45	0.27	0.50	0.32	0.31	5.23	0	-10	8	232				6.08
United States	US13	New York, Adirondack Mnt., Dart Lake	29	13.25	5.63	1.67	0.30	0.58	0.31	0.36	4.72	14	15	11	252				4.44
United States	US14	New York, Adirondack Mnt., Heart Lake	30	11.52	6.38	2.02	0.30	0.56	0.14	0.27	3.98	50	52	7	151				2.93
United States	US15	New York, Adirondack Mnt., Lake Rondaxe	24	17.44	6.24	2.02	0.40	0.72	0.34	0.37	4.70	46	51	11	201				4.01
United States	US16	New York, Adirondack Mnt., Moss Lake	18	26.98	6.60	2.65	0.52	0.88	0.38	0.43	5.05	81	94	7	165				3.99
United States	US17	New York, Adirondack Mnt., Otter Lake	24	15.06	5.32	1.27	0.33	0.59	0.17	0.32	5.23	4	-8	4	148				2.50

Country	ICP Site Number	Site Name	n	K25	pH	Ca	Mg	Na	K	Cl	SO_4	Alka-linity	ANC	NH_4N	NO_3N	TOTN	TOTP	TOC	DOC
				mSm^{-1}		$mg L^{-1}$	$mg L^{-1}$	$mg L^{-1}$	$mg L^{-1}$	$mg L^{-1}$	$mg L^{-1}$	$\mu eq L^{-1}$	$\mu eq L^{-1}$	$\mu g L^{-1}$	$\mu g L^{-1}$	$\mu g L^{-1}$	$\mu g L^{-1}$	$mgC L^{-1}$	$mgC L^{-1}$
United States	US19	Wisconsion, Luna	2	16.35		1.41	0.45	0.35	0.24	0.34	4.56	10	19		78				3.45
United States	US20	Wisconsion, Nichols	2	12.05		1.14	0.34	0.28	0.41	0.19	2.27	24	45		137				7.35
United States	US21	Wisconsion, Sand	2	17.30		1.14	0.40	0.66	0.57	1.05	4.05	9	15		69				3.30
United States	US23	New York, Catskill Mnt., E. Branch Neversink, Head	91	19.82	5.40	1.38	0.50	0.36	0.26	0.50	4.68	2	-3	38	318				2.04
United States	US24	New York, Catskill Mnt., Rondout Creek	109	20.59	4.89	0.99	0.47	0.29	0.21	0.44	4.40	-12	-14	33	240				3.00
United States	US25	W Br Neversink R At Winnisook, Catskills	104	21.84	4.74	0.83	0.39	0.25	0.18	0.39	4.64	-20	-34	52	215				2.56
United States	US26	Biscuit Brook, Catskills	210	19.76	6.20	2.10	0.48	0.32	0.18	0.49	4.67	28	36	23	225				1.86
United States	US27	Little Hope Pond, Adirondacks	29	14.82	5.77	1.99	0.54	0.66	0.50	0.37	3.84	45	86	25	119				11.95
United States	US28	Big Hope Pond, Adirondacks	24	16.45	6.20	1.89	0.53	0.77	0.40	0.67	3.80	46	80	14	49				8.46
United States	US29	East Copperas Pond, Adirondacks	24	16.09	4.57	0.76	0.15	0.14	0.25	0.24	2.57	-20	-1	59	49				10.14
United States	US30	Sunday Pond, Adirondacks	29	7.46	5.18	0.60	0.22	0.06	0.26	0.19	2.40	0	0	5	21				2.80
United States	US31	Sochia Pond, Adirondacks	24	11.11	4.68	0.35	0.11	0.08	0.13	0.19	2.00	-15	-17	41	46				4.28
United States	US32	Marcy Dam Pond, Adirondacks	25	13.26	5.86	1.57	0.26	0.59	0.06	0.25	3.98	24	19	4	250				3.24
United States	US33	Grass Pond, Adirondacks	24	12.97	4.58	0.46	0.15	0.09	0.33	0.22	1.56	-18	6	34	39				9.15
United States	US35	Loon Hollow Pond, Adirondacks	22	16.00	4.70	0.58	0.13	0.33	0.21	0.27	4.00	-13	-46	37	210				4.31
United States	US36	Willys Lake, Adirondacks	22	16.36	4.87	1.08	0.18	0.39	0.26	0.26	4.93	-7	-37	6	271				2.93
United States	US37	Woods Lake, Adirondacks	22	15.31	5.95	2.19	0.25	0.40	0.23	0.26	4.63	25	30	7	274				4.06
United States	US38	Middle Settlement Lake, Adirondacks	23	12.05	5.52	0.99	0.21	0.61	0.21	0.24	4.05	10	1	24	86				2.97
United States	US39	Grass Pond, Adirondacks	24	16.81	5.89	1.57	0.35	0.87	0.31	0.29	4.71	32	28	8	265				4.44
United States	US40	Middle Branch Lake, Adirondacks	22	16.07	6.41	1.84	0.42	0.88	0.33	0.30	4.28	60	70	9	84				4.38
United States	US41	Limekiln Lake, Adirondacks	29	14.09	6.06	1.91	0.35	0.74	0.26	0.73	4.57	28	31	5	219				3.12
United States	US42	Squaw Lake, Adirondacks	22	12.92	6.03	1.53	0.38	0.38	0.19	0.27	4.25	21	27	4	82				3.54
United States	US43	Indian Lake, Adirondacks	22	14.40	5.00	1.16	0.27	0.41	0.15	0.28	4.33	-1	-7	6	161				5.53
United States	US44	Brook Trout Lake, Adirondacks	22	11.83	5.58	1.08	0.26	0.42	0.19	0.26	4.05	10	1	9	83				3.06
United States	US45	Lost Pond, Adirondacks	22	14.63	5.08	1.13	0.28	0.56	0.14	0.28	4.17	2	0	9	180				6.31
United States	US46	South Lake, Adirondacks	24	14.04	5.57	1.32	0.30	0.52	0.23	0.29	4.09	9	3	7	318				2.80
United States	US47	North Lake, Adirondacks	24	16.04	5.24	1.39	0.33	0.54	0.23	0.30	4.58	6	1	7	293				5.10
United States	US48	Willis Lake, Adirondacks	23	18.69	6.09	2.59	0.48	0.92	0.13	0.79	4.07	75	103	8	31				9.21
United States	US49	Long Pond, Adirondacks	24	19.13	4.59	1.02	0.38	0.45	0.29	0.32	3.82	-16	18	10	40				14.02
United States	US50	Carry Pond, Adirondacks	22	10.73	4.97	0.72	0.18	0.17	0.19	0.19	3.26	-5	-12	18	28				2.21

Country	ICP Site Number	Site Name	n	K25	pH	Ca	Mg	Na	K	Cl	SO_4	Alka-linity	ANC	NH_4N	NO_3N	TOTN	TOTP	TOC	DOC
				mSm^{-1}		mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	µeq L^{-1}	µeq L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	mgC L^{-1}	mgC L^{-1}
United States	US51	Lake Colden, Adirondacks	24	15.52	5.12	1.40	0.22	0.46	0.08	0.23	4.15	4	-14	7	435				4.20
United States	US52	Avalanche Lake, Adirondacks	24	18.06	4.98	1.38	0.21	0.43	0.14	0.27	3.86	1	-19	23	556				5.99
United States	US53	Little Simon Pond, Adirondacks	24	20.46	6.41	2.97	0.33	0.59	0.23	0.33	5.31	64	61	5	361				3.61
United States	US54	Raquette Lake Reservoir, Adirondacks	29	17.44	5.50	2.03	0.49	0.79	0.31	0.37	5.87	28	33	5	245				7.25
United States	US55	G Lake, Adirondacks	24	13.70	5.71	1.25	0.33	0.54	0.15	0.27	4.21	16	9	5	170				3.26
United States	US56	Middle Pond, Adirondacks	24	22.43	6.62	2.92	0.60	0.95	0.36	0.46	4.89	117	126	31	68				5.57
United States	US57	Sagamore Lake, Adirondacks	29	16.36	5.88	2.17	0.55	0.79	0.28	0.33	5.52	36	52	3	237				7.69
United States	US58	Black Pond Outlet, Adirondacks	24	29.06	7.14	3.76	1.16	1.05	0.37	0.33	5.05	220	219	12	57				3.73
United States	US59	Windfall Pond Outle, Adirondacks	24	24.08	6.62	3.68	0.46	0.37	0.24	0.31	5.04	101	103	14	337				3.90
United States	US60	Queer Lake, Adirondacks	22	14.68	5.74	1.69	0.31	0.41	0.30	0.29	4.78	15	11	13	229				3.00
United States	US61	Big Moose Lake, Adirondacks	29	13.31	5.55	1.61	0.30	0.58	0.31	0.34	4.76	13	11	9	255				4.58
United States	US62	Cascade Lake Outlet, Adirondacks	24	18.87	6.45	2.33	0.47	0.78	0.35	0.31	5.22	59	63	4	236				3.45
United States	US63	Little Echo Pond, Adirondacks	29	16.92	4.36	0.57	0.33	0.19	0.23	0.37	1.92	-36	18	50	22				16.97
United States	US64	Squash Pond Outlet, Adirondacks	24	19.22	4.50	0.72	0.15	0.38	0.23	0.28	3.84	-27	-32	13	207				8.71
United States	US65	West Pond Outlet, Adirondacks	24	14.54	5.19	1.31	0.27	0.54	0.22	0.25	4.13	7	16	14	105				7.32
United States	US66	Bubb Lake Outlet, Adirondacks	24	15.63	6.36	1.83	0.41	0.71	0.33	0.29	4.19	48	59	6	132				3.97
United States	US67	Owen Pond, Adirondacks	29	22.71	6.66	3.84	0.72	0.84	0.23	0.43	5.89	116	121	10	530				4.96
United States	US68	Jockeybush Lake, Adirondacks	24	14.37	5.42	1.33	0.33	0.45	0.17	0.31	4.64	5	-5	14	236				2.42
United States	US69	Clear Pond, Adirondacks	24	19.87	6.89	2.92	0.36	0.88	0.09	0.28	4.72	104	106	4	59				3.47
United States	US70	Nate Pond, Adirondacks	22	19.24	6.50	2.46	0.62	0.77	0.30	0.30	5.55	71	82	5	123				5.30
United States	US71	Bean Pond, Maine	4	1.78	6.06	1.50	0.46	0.93	0.21	0.58	2.94	50	79	18	34				8.20
United States	US72	Bracey Pond, Maine	3	2.60	6.61	2.29	0.44	1.52	0.29	2.22	2.13	98	117	23	9				4.80
United States	US73	Anderson Pond, Maine	1	1.80	5.65	0.50	0.26	2.18	0.27	2.73	2.40	12	20	0	7				2.30
United States	US74	Mud Pond, Maine	4	2.85	4.65	0.58	0.31	2.36	0.41	3.79	4.16	-17	-26	21	6				3.95
United States	US75	Salmon Pond, Maine	4	2.26	6.32	1.29	0.39	2.13	0.35	2.67	2.38	58	73	19	12				3.50
United States	US76	Wiley Pond, Maine	4	2.33	6.39	2.94	0.54	0.72	0.12	0.39	2.50	124	162	12	13				9.58
United States	US77	Second Pond, Maine	4	2.20	6.20	1.67	0.41	1.82	0.32	1.69	2.98	61	94	8	16				5.40
United States	US78	Abol Pond, Maine	4	2.83	6.74	2.76	0.37	1.56	0.78	0.59	2.81	171	180	10	12				2.45
United States	US79	Duck Pond, Maine	3	2.27	4.43	0.13	0.16	0.93	0.20	1.54	1.94	-39	-19	21	10				5.70
United States	US80	Jellison Hl Pd, Maine	4	2.25	6.02	1.30	0.39	2.02	0.27	2.31	3.50	30	53	15	12				4.13
United States	US81	Crystal Pond, Maine	3	1.07	5.48	0.27	0.15	0.80	0.19	1.00	1.65	-2	3	14	7				2.77

Country	ICP Site Number	Site Name	n	K25	pH	Ca	Mg	Na	K	Cl	SO$_4$	Alka-linity	ANC	NH$_4$N	NO$_3$N	TOTN	TOTP	TOC	DOC
				mSm^{-1}		mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	µeq L^{-1}	µeq L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	mgC L^{-1}	mgC L^{-1}
United States	US82	Newbert Pond, Maine	4	3.43	4.58	1.60	0.53	1.80	0.36	2.45	3.40	-24	70	33	15				18.38
United States	US83	Partridge Pond, Maine	4	1.70	5.83	0.88	0.26	1.53	0.24	1.56	2.68	19	37	16	12				3.13
United States	US84	Benner Run, Mid-Apps	24	24.56	5.98	1.32	0.83	1.31	0.70	3.37	5.26	19	-20	14	130				1.55
United States	US85	Linn Run, Mid-Apps	25	32.44	6.15	1.95	0.83	0.68	0.42	1.24	10.08	36	-74	17	313				1.49
United States	US86	Roberts Run, Mid-Apps	24	26.42	5.56	0.98	0.91	0.50	0.56	1.06	7.93	18	-63	15	60				2.27
United States	US87	Stone Run, Mid-Apps	24	25.79	5.39	0.91	0.82	0.54	0.43	1.08	8.64	-2	-93	12	26				1.44
United States	US88	Baldwin Creek, Mid-Apps	25	32.93	6.35	2.53	0.98	0.51	0.61	1.54	9.16	54	-36	20	458				1.50
United States	US89	Bourn, Vermont	6	11.78	5.43	0.71	0.30	0.51	0.32	0.27	2.54	8	28		28				5.65
United States	US90	Grout, Vermont	10	16.43	5.69	1.31	0.33	0.55	0.45	0.43	3.11	23	39		182				
United States	US91	Hardwood, Vermont	48	19.93	5.77	1.85	0.50	0.59	0.24	0.41	3.93	38	59		169				
United States	US92	Little – Woodford, Vermont	10	22.96	4.86	1.02	0.24	0.63	0.50	0.42	4.13	-7	-28		578				
United States	US93	Stamford, Vermont	6	15.82	5.78	1.22	0.27	0.79	0.31	0.40	3.82	17	25		128				3.24
United States	US95	Sunset, Vermont	8	16.21	5.77	1.23	0.31	0.78	0.21	0.74	3.74	21	23		64				
United States	US96	Big Mud, Vermont	6	14.77	5.30	1.26	0.29	0.41	0.25	0.27	3.08	9	37		35				8.58
United States	US97	Branch, Vermont	6	15.60	4.82	0.62	0.22	0.50	0.30	0.26	3.01	-11	5		52				6.22
United States	US98	Beaver Pond, Vermont	9	24.82	5.91	2.74	0.33	0.68	0.23	0.49	4.06	53	76		347				
United States	US99	Big Muddy, Vermont	8	14.46	4.77	0.52	0.14	0.30	0.11	0.37	2.30	-15	-20		210				1.60
United States	US100	Howe, Vermont	10	18.69	5.73	1.55	0.35	0.67	0.36	0.55	3.74	28	37		189				
United States	US102	Forester, Vermont	6	95.07	4.88	1.50	0.27	14.40	0.47	23.83	3.83	-9	-17		10				3.03
United States	US103	Paine Run, Virginia	142	14.51	5.81	0.61	0.62	0.52	1.80	0.79	5.40	7	13	5	33				1.18
United States	US104	Piney River, Virginia	150	23.87	6.94	2.84	1.41	1.75	0.26	0.94	3.30	218	236	25	131				1.51
United States	US105	Staunton River, Virginia	163	13.23	6.56	1.30	0.34	1.37	0.43	0.76	2.23	81	94	17	12				1.42
United States	US112	Upper Midwest, McGrath	2	9.75		0.76	0.29	0.30	0.28	0.33	1.93	17	32		9				5.15
United States	US114	Upper Midwest, Vandercook	2	12.80		1.07	0.30	0.28	0.34	0.32	2.72	17	21		167				4.00
United States	US115	Upper Midwest, Greater Bass	2	20.30		1.23	0.52	0.93	0.58	1.46	3.65	13	37		69				5.80
United States	Us116	Upper Midwest, Long(WI)	2	13.45		1.06	0.35	0.30	0.55	0.40	3.05	28	31		40				3.15
United States	US117	Upper Midwest, Clear	2	16.45		0.92	0.43	0.59	0.49	0.83	2.84	5	33		60				7.60
United States	US118	Upper Midwest, Camp Twelve	2	9.25		0.72	0.23	0.15	0.31	0.21	2.02	5	15		90				4.20
United States	US119	Upper Midwest, Lake Clara	1	44.10		1.99	0.59	4.57	0.70	7.86	2.88	70	83		1				4.10
United States	US120	Upper Midwest, Sugarcamp	2	20.75		1.44	0.36	0.80	0.49	1.28	5.37	3	2		1				1.65
United States	US121	Upper Midwest, Morgan	2	17.00		1.09	0.41	0.23	0.40	0.31	4.57	-2	3		22				3.55

Appendix B. Heavy metals in ICP Waters sites

Concentrations of heavy metals measured at ICP Waters sites in the period 1999-2001. Figures are mean values for all samples analyzed for heavy metals in the 3 year period. *n* gives the total number the number of samples of which one ore more heavy metal species have been analyzed. Values under detectionlimit are treated as 2/5 of the detection limit.

Country	ICP Site Number	Site Name	*n*	Pb	Cd	Cu	Zn	Ni
				µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
Belarus	BY01	Berezinsky Biosphere Reserve	21		2.4	5.3	16	4.8
Canada	CA01	Ontario, Algoma Region, Batchawana Lake	63				10	
Canada	CA02	Ontario, Algoma Region, Wishart Lake	66				3.8	
Canada	CA03	Ontario, Algoma Region, Little Turkey Lake	73				3.9	
Canada	CA04	Ontario, Algoma Region, Turkey Lake	65				4.2	
Canada	CA08	Quebec, Lac Laflamme	45			1.2	6.6	
Czech Republic	CZ01	Bohemian Forest, Cerné	6	0.37	0.19	1.4	14	
Czech Republic	CZ02	Bohemian Forest, Certovo	6	0.67	0.15	1.0	15	
Czech Republic	CZ03	Bohemian Forest, Plešné	6	0.65	0.15	0.36	13	
Czech Republic	CZ04	Bohemian Forest, Prášilské	6	0.36	0.08	1.1	8.2	
Czech Republic	CZ05	Bohemian Forest, Laka	6	0.36	0.04	1.0	5.0	
Czech Republic	CZ06	Bohemian Forest, Zd´árské	6	0.38	0.02	0.33	4.0	
Finland	FI01	Southeast Finland, Hirvilampi	18	0.22	0.04	0.24	4.4	0.30
Finland	FI07	Uusimaa, Vitsjön	18	0.16	0.02	0.37	2.5	0.30
Finland	FI08	North Karelia,Kakkisenlampi	17	0.29	0.02	0.27	4.4	0.16
Finland	FI09	Häme, Sonnanen	19	0.09	0.01	0.21	0.8	0.10
Germany	DE03	Rothaargebirge, Elberndorfer Bach	66	1.5	0.15		22	
Germany	DE04	Sächsische Tieflandsbucht, Ettelsbach	20	1.6	1.05	2.4	98	31
Germany	DE06	Hunsrück, Gräfenbach	33	1.3	0.46	1.1	25	5.2
Germany	DE07	Erzgebirge, Grosse Pyra	28	1.0	0.43	1.8	18	2.1
Germany	DE08	Bayerischer Wald, Grosse Ohe	78	0.47	0.06	0.85	7.6	0.44
Germany	DE09	Sächsische Tieflandsbucht, Heidelbach	21	0.66	0.34	1.4	61	8.0
Germany	DE14	Kaufunger Wald, Nieste 3	11	2.4	0.15	2.4	12	2.8
Germany	DE16	Lauenburgische Seenplatte, Pinnsee	9	0.24	0.02	0.66	3.0	1.8
Germany	DE19	Taunus, Rombach 2	35	2.4	0.85	2.4	60	7.0
Germany	DE20	Taunus, Rombach 3	24	2.4	0.12	2.4	10	2.4
Germany	DE21	Erzgebirge, Rote Pockau	30	1.4	0.59	2.0	21	2.6
Germany	DE25	Elbsandsteingebirge, Taubenbach	21	0.29	0.20	2.2	16	4.2
Germany	DE26	Hunsrück, Traunbach 1	37	1.2	0.19	1.0	15	2.3
Germany	DE28	Oberpfälzer Wald. Waldnaab 2	7	1.5	0.05	1.1	3.8	13
Germany	DE29	Oberpfälzer Wald, Waldnaab 8	7	2.3	0.14	0.83	7.5	14
Germany	DE30	Erzgebirge, Wilde Weisseritz	26	1.2	0.48	1.3	23	2.0
Germany	DE31	Erzgebirge, Wolfsbach	28	0.48	0.05	1.9	6.7	2.5
Germany	DE32	Rothaargebirge, Zinse	66	1.3	0.18		22	
Germany	DE34	Odenwald, Schmerbach 1	35	2.4	0.30	2.4	11	4.0
Germany	DE35	Taunus, Rombach 4	9	2.4	0.22	2.4	12	3.2
Hungary	HU01	Matra Mountains, Csórrét Reservoir	4	2.0	0.20	4.0	12	4.0
Ireland	IE01	Wicklow, Glendalough, Lake Upper, Mid Lake	2	9.6	0.44	1.4	71	0.69
Ireland	IE02	Wicklow, Glendalough, Lake Upper, Inflow 1	2	14	0.75	0.70	101	0.20
Ireland	IE03	Wicklow, Glendalough, Lake Upper, Inflow 2	2	0.76	0.02	0.60	3.7	3.6
Ireland	IE04	Wicklow, Glendalough, Lake Upper, Inflow 3	2	0.20	0.08	0.70	8.6	2.2
Ireland	IE05	Galway, Lough Maumwee, Mid Lake	2	0.02	0.02	0.02	5.3	0.02
Ireland	IE06	Galway, Lough Maumwee, Inflow 1	2	0.02	0.02	0.02	3.7	0.02

Country	ICP Site Number	Site Name	*n*	Pb	Cd	Cu	Zn	Ni
				µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
Ireland	IE07	Galway, Lough Maumwee, Inflow 2	2	0.02	0.02	0.02	3.1	0.02
Ireland	IE08	Donegal, Lough Veagh, Mid Lake	2	0.02	0.02	0.02	3.2	0.02
Ireland	IE09	Donegal, Lough Veagh, Inflow 1	2	0.02	0.02	0.02	3.3	0.02
Ireland	IE10	Donegal, Lough Veagh, Inflow 2	2	0.02	0.02	0.02	4.4	0.02
Latvia	LV01	Burtnieku Lake, hydrosite	10	0.18	0.06	1.0	2.5	
Latvia	LV02	Barta, Dukupji	20	0.20	0.02	1.2	3.3	
Latvia	LV03	Liela Jugla, Zaki	28	0.17	0.05	0.70	4.1	
Latvia	LV04	Tulija, Zoseni	34	0.15	0.02	0.85	2.9	
Poland	Pl01	Tatra Mountains, Dlugi Staw Gasienicowy	23	0.90	0.19	1.7	7.3	
Poland	Pl02	Tatra Mountains, Zielony Staw Gasienicowy	23	0.70	0.14	1.8	5.7	
Sweden	SE01	Delångersån Iggersund	37	0.11	0.01	0.82	1.6	0.65
Sweden	SE03	Alsterån Strömsborg	12	0.37	0.04	1.6	3.7	0.90
Sweden	SE05	Tväringen	12	0.10	0.01	0.38	1.1	0.41
Sweden	SE06	Stensjön	24	0.47	0.02	0.42	1.9	0.20
Sweden	SE08	Brunnsjön	24	0.82	0.04	1.0	7.0	0.70
Sweden	SE09	Fiolen	24	0.27	0.04	2.0	7.5	0.46
Switzerland	CH03	Tomè	3	7.0		10	6.5	
Switzerland	CH04	Lago Di Mognola	3			5.0	3.7	
Switzerland	CH05	Laghetti (Lago Inferiore)	12	8.0		14	11	
Switzerland	CH06	Laghetti (Lago Superiore)	10			16	12	
Switzerland	CH08	Lago Della Froda	3			3.3	3.7	
Switzerland	CH09	Lago Nero	3			3.4	2.6	
Switzerland	CH10	Laghetti Di Antabia (Lago 1)	3			3.6	3.8	
Switzerland	CH11	Laghi Della Crosa (Lago Superiore)	3			2.0	3.0	
Switzerland	CH12	Lago D'orsalia	3			4.4	7.6	
Switzerland	CH13	Schwarzsee	3			4.0	6.7	
Switzerland	CH14	Lago Di Pozzoi	3			4.0	6.3	
Switzerland	CH16	Lago Di Sfille	3	3.0		5.2	10	
Switzerland	CH18	Lago Di Sascola	3			2.3	5.2	
Switzerland	CH19	Lago D'alzasca	3			2.7	5.2	
Switzerland	CH20	Lago Di Starlaresc Da Sgiof	3	6.0		3.8	14	
Switzerland	CH21	Lago Barone	3			2.4	5.7	
Switzerland	CH22	L.To Gardiscio	3			2.0	6.1	
Switzerland	CH23	Lago Di Morghirolo	3			4.0	3.8	
Switzerland	CH24	Leit (Lago 1)	3			2.5	4.5	
Switzerland	CH25		3			3.6	4.8	
Switzerland	CH26		24			3.0	3.8	
Switzerland	CH27		24	3.0		2.1	4.1	
Switzerland	CH28		24			3.0	3.5	
Switzerland	CH29		7			2.0	2.5	
United Kingdom	UK01	Scotland, Loch Coire nan Arr	5			20	48	
United Kingdom	UK04	Scotland, Lochnagar	5			20	28	
United Kingdom	UK07	Scotland, Round Loch of Glenhead	5			20	20	
United Kingdom	UK10	England, Scoat Tarn	5			20	25	
United Kingdom	UK15	Wales, Llyn Llagi	5			20	20	
United Kingdom	UK21	N.Ireland, Blue Lough	5			20	20	

Appendix C. Sites without trend analysis

WDID	Trend	Multiple Locations	Insentiv to acidification	Record too short	Possible other sources of sulphate	Other disturbances in the catchment
AT03	no			*	*	Sulphate source in the catchment
BY01	only sulphate				*	
CA19	no					
CH01	no			*		
CH02	no			*		
CH03	no			*		
CH04	no			*		
CH05	no			*		
CH06	no			*		
CH07	no			*		
CH08	no			*		
CH09	no			*		
CH10	no			*		
CH11	no			*		
CH12	no			*		
CH13	no			*		
CH14	no			*		
CH15	no			*		
CH16	no			*		
CH17	no			*		
CH18	no			*		
CH19	no			*		
CH20	no			*		
CH21	no			*		
CH22	no			*		
CH23	no			*		
CH24	no			*		
DE04	no				*	
DE09	no				*	
DE13	no					
DE15	no			*		
DE16	no			*		
DE17	no			*		
DE21	no			*		
DE24	no			*		
DE25	no				*	
DE30	no					
DE35	no			*		
EE01	only sulphate				*	
FI03	no					Liming in 1991
HU01	only sulphate		*	*		
IE02	no	*				
IE03	no	*				
IE04	no	*				
IE06	no	*				
IE07	no	*				
IE09	no	*				
IE10	no	*				
LV01	only sulphate		*		*	
LV02	only sulphate		*		*	
LV03	only sulphate		*		*	
LV04	only sulphate		*		*	
LV05	only sulphate		*		*	
US07	no					

WDID	Trend	Multiple Locations	Insentiv to acidification	Record too short	Possible other sources of sulphate	Other disturbances in the catchment
US08	no					
US09	no					
US10	no					
US100	no					
US106	no					
US107	no					
US108	no					
US109	no					
US110	no					
US111	no					
US113	no					
US18	no					
US22	no					
US25	no					
US34	no					
US82	no					
US83	no					
US94	no					

Appendix D. Statistical output of trend analysis for single sites

The figures for the slopes represent annual change in the given units for each parameter. The p-values refer to the probabilities from the two sided t-tests with the null hypothesis that the slope equals zero. Probabilities below 0.05 and their associated slopes appear in bold.

REGION	WDID	SO4* (µekv L^{-1})			ENO3(µekv L^{-1})			Alkalinity (µekv L^{-1})			H^+(µekv L^{-1})			ANC(µekv L^{-1})			Ca+Mg (µekv L^{-1})			TOC/DOC (mgC L^{-1})		
		trend slope	p	n	trend slope	p	n	trend slope	p	n	trend slope	p	n	trend slope	p	n	trend slope	p	n	trend slope	p	n
Alps	IT01	**-1.55**	**0.00**	55	0.14	0.47	55	**-2.91**	**0.00**	55	0.01	0.45	55	-0.46	0.23	55	**-1.72**	**0.00**	55			
Alps	IT02	**-4.44**	**0.00**	12	**0.55**	**0.00**	12	**3.02**	**0.00**	12	0.00	0.90	12	1.62	0.08	11	**-1.69**	**0.03**	11			
Alps	IT03	**-1.30**	**0.00**	63	0.50	0.07	63	-0.36	0.06	56	**-0.12**	**0.00**	63	-0.24	0.23	63	**-1.02**	**0.01**	63			
Alps	IT04	**-2.65**	**0.00**	224	0.16	0.46	224	-1.75	0.07	224	0.00	0.13	224	0.19	0.84	224	**-2.56**	**0.02**	224			
Alps	IT05	**-1.41**	**0.00**	142	**2.65**	**0.00**	143	-0.84	0.26	143	**0.00**	**0.00**	143	0.76	0.36	142	**2.15**	**0.00**	142			
Alps	IT06	**-2.05**	**0.00**	143	**1.56**	**0.00**	143	**-2.51**	**0.00**	143	0.00	0.08	143	-0.67	0.41	143	-0.94	0.10	143			
ECEurope	CZ01	**-3.97**	**0.00**	24	-0.77	0.12	15	1.23	0.11	16	**-0.53**	**0.01**	24	1.83	0.09	15	**-2.09**	**0.00**	24	-0.04	0.53	13
ECEurope	CZ02	**-6.80**	**0.00**	24	**-0.96**	**0.04**	24	**3.99**	**0.00**	17	-0.44	0.13	24	**5.56**	**0.00**	24	**-2.43**	**0.00**	24	0.10	0.17	13
ECEurope	CZ03	**-9.68**	**0.00**	24	**-1.62**	**0.01**	24	0.66	0.37	17	**-1.24**	**0.00**	24	**7.42**	**0.00**	24	**-3.50**	**0.00**	24	**0.14**	**0.02**	13
ECEurope	CZ04	**-3.85**	**0.00**	24	**-1.62**	**0.00**	24	1.38	0.07	17	**-0.86**	**0.00**	24	**4.11**	**0.00**	24	**-1.41**	**0.00**	24	0.11	0.08	13
ECEurope	CZ05	**-1.27**	**0.02**	24	-0.03	0.96	24	**-3.03**	**0.00**	20	-0.02	0.91	24	0.93	0.22	24	**-0.61**	**0.05**	24	-0.14	0.36	12
ECEurope	CZ06	**-2.40**	**0.02**	24	-0.37	0.22	24	**-6.62**	**0.00**	20	0.01	0.84	24	-1.11	0.47	24	**-2.04**	**0.01**	24	-0.38	0.24	13
ECEurope	DE02	-1.13	0.08	164	0.09	0.74	164	**1.93**	**0.01**	161	-0.17	0.65	163	1.77	0.71	47	0.97	0.06	164	0.07	0.27	161
ECEurope	DE07	**-33.99**	**0.00**	77	**-8.61**	**0.00**	101	**-2.41**	**0.00**	91	**-2.50**	**0.00**	100	**41.53**	**0.00**	77	**-10.49**	**0.00**	77	**0.24**	**0.00**	64
ECEurope	DE08	**-1.96**	**0.00**	284	**1.98**	**0.00**	396	1.21	0.83	153	-0.05	0.55	396	**2.47**	**0.00**	240	**0.66**	**0.03**	280	**0.06**	**0.00**	360
ECEurope	DE10	**-1.80**	**0.00**	132	**5.55**	**0.00**	132				0.16	0.33	132	1.08	0.68	53	**1.92**	**0.00**	132			
ECEurope	DE17	**-6.30**	**0.00**	34	**6.26**	**0.00**	34				0.87	0.25	34	-1.39	0.30	34	-0.49	0.27	34	0.08	0.06	34
ECEurope	DE18	**-7.80**	**0.00**	159	**-1.43**	**0.00**	159	1.16	0.08	149	-0.70	0.28	159	8.52	0.15	46	**-3.21**	**0.00**	159	**0.24**	**0.00**	157
ECEurope	DE23	**-1.97**	**0.00**	133	0.51	0.18	133				0.00	1.00	133	-2.44	0.48	51	-0.42	0.31	133			
ECEurope	DE27	**-2.39**	**0.00**	131	**2.55**	**0.00**	131				0.11	0.12	131	2.57	0.63	52	0.81	0.09	131			
ECEurope	DE28	-4.40	0.49	22	-7.13	0.49	22	16.23	0.31	22	-0.27	0.30	23	2.53	0.88	22	-11.30	0.47	22	-0.11	0.41	21
ECEurope	DE29	**-16.34**	**0.01**	23	**-2.86**	**0.00**	23	24.82	0.63	20	-2.43	0.17	24	16.88	0.34	23	-4.81	0.73	23	-0.07	0.71	22
ECEurope	DE31	**-43.10**	**0.00**	96	**-20.76**	**0.00**	97	**10.07**	**0.04**	99	**-0.01**	**0.00**	98	**35.05**	**0.00**	90	**-44.16**	**0.00**	93	0.06	0.63	74
ECEurope	DE33	**-12.03**	**0.00**	125	**-4.65**	**0.00**	125	0.75	0.50	84	**-5.28**	**0.01**	125	**17.90**	**0.00**	44	**-6.00**	**0.00**	125	**0.26**	**0.00**	123
ECEurope	PL01	**-3.18**	**0.00**	129	**-4.12**	**0.00**	128	0.36	0.45	110	-0.08	0.56	103	**3.32**	**0.00**	128	**-3.37**	**0.00**	129	-0.01	0.57	90
ECEurope	PL02	**-3.44**	**0.00**	125	-0.18	0.54	125	**-6.86**	**0.00**	121	**0.18**	**0.00**	115	**-5.76**	**0.00**	125	**-8.24**	**0.00**	125	-0.01	0.57	86
NoNordic	FI05	-0.15	0.42	76	-0.08	0.40	71	0.72	0.31	77	-0.07	0.33	77	-1.24	0.07	70	**-1.23**	**0.02**	76	0.06	0.60	35
NoNordic	FI06	**-1.22**	**0.00**	83	0.04	0.76	77	**1.81**	**0.00**	84	-0.08	0.36	85	0.19	0.89	74	-0.76	0.53	81	**0.04**	**0.01**	40
NoNordic	FI08	**-2.55**	**0.00**	89	**-0.18**	**0.04**	67	**1.24**	**0.00**	89	**-0.67**	**0.00**	88	**2.27**	**0.00**	67	**-0.52**	**0.00**	89	**0.14**	**0.00**	81
NoNordic	NO04	**-2.79**	**0.00**	611	0.00	0.86	598	**0.87**	**0.00**	611	**-0.07**	**0.00**	611	**1.00**	**0.00**	598	**-2.28**	**0.00**	611	**0.04**	**0.01**	598
NoNordic	SE01	**-2.28**	**0.00**	139	-0.02	0.85	139	-0.20	0.44	139	0.00	0.08	139	**2.28**	**0.00**	139	0.00	0.99	139	**0.10**	**0.00**	139
NoNordic	SE05	**-1.68**	**0.00**	63	0.01	0.88	64	**-2.12**	**0.00**	64	**0.01**	**0.05**	64	-0.42	0.55	63	**-1.81**	**0.00**	63	0.05	0.17	64
NoNordic	SE06	**-1.18**	**0.00**	87	0.09	0.06	87	**-1.34**	**0.00**	87	0.02	0.21	87	0.26	0.49	87	-0.65	0.05	87	0.04	0.23	87
SoNordic	FI01	**-6.75**	**0.00**	61	0.23	0.11	58	**2.15**	**0.00**	60	**-0.40**	**0.00**	61	**5.13**	**0.00**	57	**-3.10**	**0.00**	60	**0.15**	**0.00**	55

REGION	WDID	SO4* (µekv L^{-1})			ENO3(µekv L^{-1})			Alkalinity (µekv L^{-1})			H$^+$(µekv L^{-1})			ANC(µekv L^{-1})			Ca+Mg (µekv L^{-1})			TOC/DOC (mgC L^{-1})		
		trend slope	p	n	trend slope	p	n	trend slope	p	n	trend slope	p	n	trend slope	p	n	trend slope	p	n	trend slope	p	n
SoNordic	FI02	**-7.06**	**0.00**	60	**0.58**	**0.03**	58	**3.50**	**0.00**	61	**-0.30**	**0.05**	61	**5.24**	**0.00**	55	**-2.97**	**0.00**	58	**0.16**	**0.00**	54
SoNordic	FI07	**-6.84**	**0.00**	54	0.04	0.78	52	**3.69**	**0.00**	54	**-0.07**	**0.01**	54	**4.54**	**0.00**	52	**-2.58**	**0.00**	54	**0.05**	**0.01**	50
SoNordic	FI09	**-2.82**	**0.00**	53	-0.12	0.13	44	**1.92**	**0.00**	64	0.00	0.91	63	**1.40**	**0.02**	40	**-1.42**	**0.00**	54	0.01	0.11	53
SoNordic	NO01	**-3.72**	**0.00**	607	**-0.21**	**0.02**	607	**-0.20**	**0.04**	365	**-0.93**	**0.00**	607	**2.95**	**0.00**	607	**-1.78**	**0.00**	607	0.00	0.99	607
SoNordic	NO03	**-3.53**	**0.00**	598	**-0.06**	**0.00**	598	**-0.45**	**0.00**	389	**-0.46**	**0.00**	598	**1.80**	**0.00**	598	**-1.60**	**0.00**	598	**0.13**	**0.00**	598
SoNordic	NO05	**-1.55**	**0.00**	140	0.05	0.22	140	**0.84**	**0.00**	140	**-0.03**	**0.00**	140	**1.45**	**0.00**	140	-0.45	0.13	140	**0.05**	**0.00**	140
SoNordic	NO06	**-0.68**	**0.00**	158	**-0.25**	**0.00**	158	**0.83**	**0.00**	138	**-0.34**	**0.00**	158	**2.28**	**0.00**	158	**0.53**	**0.00**	158	**0.02**	**0.00**	158
SoNordic	NO07	**-0.35**	**0.00**	146	-0.08	0.18	146	**0.67**	**0.00**	125	**-0.30**	**0.00**	146	**1.52**	**0.00**	146	0.46	0.06	146	0.00	0.69	146
SoNordic	NO08	**-0.46**	**0.00**	196	-0.05	0.41	196	**1.32**	**0.00**	191	**-0.16**	**0.00**	196	**1.79**	**0.00**	196	**0.86**	**0.00**	196	0.02	0.18	196
SoNordic	NO09	**-0.41**	**0.00**	549	0.02	0.39	549	**0.66**	**0.00**	527	**-0.23**	**0.00**	549	**1.30**	**0.00**	549	**0.44**	**0.00**	549	**0.03**	**0.00**	549
SoNordic	NO10	**-3.64**	**0.00**	605	**-0.23**	**0.00**	605	-0.02	0.62	371	**-1.25**	**0.00**	605	**3.13**	**0.00**	605	**-0.86**	**0.00**	605	**0.11**	**0.00**	605
SoNordic	SE02	**-15.65**	**0.00**	140	-0.04	0.77	140	**4.59**	**0.00**	140	-0.01	0.37	140	**10.60**	**0.00**	140	**-5.97**	**0.00**	140	**0.41**	**0.00**	140
SoNordic	SE03	**-17.89**	**0.00**	86	-0.52	0.06	93	**13.71**	**0.00**	93	**-0.05**	**0.00**	93	**19.90**	**0.00**	86	1.92	0.50	86			
SoNordic	SE08	**-20.25**	**0.00**	97	-0.03	0.77	98	**-2.17**	**0.00**	72	-0.04	0.70	98	**3.36**	**0.00**	97	**-16.57**	**0.00**	97	**0.55**	**0.00**	98
SoNordic	SE09	**-8.38**	**0.00**	95	-0.22	0.11	95	**1.73**	**0.00**	95	**-0.03**	**0.00**	95	**4.85**	**0.00**	95	**-4.87**	**0.00**	95	0.01	0.93	95
SoNordic	SE10	**-7.28**	**0.00**	70	0.16	0.06	70	**-2.34**	**0.00**	37	-0.01	0.95	70	**3.61**	**0.00**	70	**-3.38**	**0.00**	70	**0.37**	**0.00**	70
SoNordic	SE11	**-10.59**	**0.00**	95	0.14	0.35	95	**2.00**	**0.00**	94	**-0.03**	**0.00**	95	**4.24**	**0.00**	95	**-8.34**	**0.00**	95	**0.19**	**0.00**	95
SoNordic	SE12	**-6.99**	**0.00**	87	**-0.58**	**0.00**	87	**2.94**	**0.00**	44	**-1.86**	**0.00**	87	**3.30**	**0.00**	87	**-3.93**	**0.00**	87	**0.14**	**0.02**	87
UKIreland	IE01	**-2.15**	**0.00**	13	**-1.30**	**0.02**	15	0.64	0.15	13	-0.26	0.17	16	5.92	0.42	11	0.18	0.97	13			
UKIreland	IE05	-2.03	0.30	14	0.13	0.76	13	0.51	0.37	15	-0.45	0.06	15	22.25	0.29	11	3.01	0.61	13			
UKIreland	IE08	-1.32	0.28	14	0.02	0.91	13	0.34	0.34	16	**-0.29**	**0.00**	16	-3.24	0.61	10	4.19	0.32	14			
UKIreland	UK01	-0.61	0.14	37	-0.03	0.70	41	0.00	0.98	41	0.01	0.57	41	0.61	0.68	37	0.71	0.31	41	**0.14**	**0.03**	40
UKIreland	UK04	**-0.95**	**0.00**	36	**0.57**	**0.05**	38	0.00	0.29	39	0.06	0.58	40	-0.20	0.73	34	-0.15	0.61	40	**0.08**	**0.00**	40
UKIreland	UK07	**-2.36**	**0.00**	38	**0.46**	**0.03**	42	0.00	0.37	42	-0.23	0.16	42	0.78	0.23	38	-0.60	0.12	42	**0.14**	**0.00**	42
UKIreland	UK10	-0.50	0.21	36	-0.32	0.54	40	0.00	0.09	40	**-0.48**	**0.01**	40	-0.08	0.93	35	**-1.30**	**0.00**	39	**0.11**	**0.00**	40
UKIreland	UK15	**-1.45**	**0.02**	36	-0.29	0.53	40	0.00	0.74	41	**-0.57**	**0.00**	40	0.33	0.70	36	**-1.62**	**0.02**	40	**0.11**	**0.04**	39
UKIreland	UK21	**-3.37**	**0.00**	33	0.63	0.37	38	**0.00**	**0.00**	40	**-0.69**	**0.00**	38	-1.35	0.63	33	-4.30	0.11	37	**0.20**	**0.00**	38
WCEurope	DE01	**-0.83**	**0.02**	139	-0.30	0.22	143	**6.49**	**0.00**	107	**-0.83**	**0.00**	143	**4.99**	**0.00**	129	**3.41**	**0.00**	129	0.15	0.18	143
WCEurope	DE03	**-4.42**	**0.00**	248	0.60	0.18	249	**-28.04**	**0.00**	83	0.07	0.08	236	5.14	0.17	142	**-5.42**	**0.00**	244	**0.05**	**0.00**	226
WCEurope	DE05	**-3.48**	**0.00**	130	**-1.67**	**0.00**	132	**6.78**	**0.02**	100	-0.01	0.60	132	**2.93**	**0.03**	118	-1.52	0.13	123	0.03	0.54	133
WCEurope	DE06	**-18.90**	**0.00**	119	**-10.06**	**0.00**	118	0.32	0.38	117	**-2.53**	**0.01**	119	**14.88**	**0.00**	116	**-15.58**	**0.00**	117	**0.34**	**0.00**	117
WCEurope	DE11	**0.76**	**0.04**	142	**-2.18**	**0.00**	146	**5.38**	**0.02**	117	**0.05**	**0.00**	147	1.38	0.29	132	-0.73	0.51	135	0.00	0.95	146
WCEurope	DE12	**-2.41**	**0.00**	582	**-0.88**	**0.00**	594	**48.36**	**0.03**	44	**0.08**	**0.00**	590	**-3.95**	**0.00**	579	**-6.66**	**0.00**	586	**-0.06**	**0.00**	298
WCEurope	DE19	3.26	0.28	131	-0.07	0.96	130	**-6.08**	**0.00**	126	0.23	0.75	130	**13.75**	**0.01**	127	**14.22**	**0.00**	131	-0.03	0.27	64
WCEurope	DE20	-2.61	0.36	123	**0.85**	**0.02**	122	**-7.24**	**0.00**	119	-0.21	0.33	122	**11.14**	**0.01**	119	**5.98**	**0.00**	123	-0.03	0.28	52
WCEurope	DE22	**-19.93**	**0.00**	64	**-9.15**	**0.00**	64	**-9.04**	**0.00**	46	-11.28	0.08	63	**23.11**	**0.00**	64	**-7.16**	**0.00**	64	**2.85**	**0.00**	17
WCEurope	DE26	**-5.71**	**0.00**	133	**-2.49**	**0.00**	133	0.72	0.42	133	**-3.30**	**0.04**	134	**9.11**	**0.00**	130	-1.17	0.49	130	0.08	0.13	132
WCEurope	DE32	**-4.88**	**0.00**	244	**-1.11**	**0.00**	246	**-22.88**	**0.00**	81	**0.27**	**0.01**	232	4.74	0.23	135	**-5.53**	**0.00**	241	0.03	0.07	224
WCEurope	DE34	**-9.50**	**0.00**	133	0.70	0.18	132	-0.29	0.08	122	0.57	0.70	133	6.91	0.07	132	**-3.46**	**0.01**	133	**-0.11**	**0.02**	64
Adirondacks	020058O	**-2.32**	**0.01**	132	0.62	0.16	132	1.40	0.21	132	-0.12	0.66	132				-0.93	0.40	132	0.01	0.93	132
Adirondacks	020059O	**-1.67**	**0.01**	132	-0.02	0.95	132	**2.45**	**0.03**	132	-0.07	0.31	132				-0.05	0.95	132	0.15	0.07	132
Adirondacks	020138O	**1.06**	**0.00**	132	0.14	0.55	132	**-1.15**	**0.03**	132	0.43	0.41	132				0.49	0.25	132	0.03	0.76	132

REGION	WDID	SO4* (μekv L^{-1}) trend slope	p	n	ENO3(μekv L^{-1}) trend slope	p	n	Alkalinity (μekv L^{-1}) trend slope	p	n	H^+(μekv L^{-1}) trend slope	p	n	ANC(μekv L^{-1}) trend slope	p	n	Ca+Mg (μekv L^{-1}) trend slope	p	n	TOC/DOC (mgC L^{-1}) trend slope	p	n
Adirondacks	020188E	**-1.27**	**0.00**	132	-0.10	0.58	132	-0.81	0.12	132	**0.33**	**0.03**	132				**-2.10**	**0.00**	132	-0.08	0.24	132
Adirondacks	020197E	**-1.57**	**0.00**	132	0.18	0.52	132	**1.16**	**0.00**	132	**-1.56**	**0.00**	132				-0.12	0.77	132	0.07	0.19	132
Adirondacks	020265O	**-2.52**	**0.00**	132	-0.06	0.95	132	0.20	0.82	132	-0.22	0.07	132				**-2.36**	**0.02**	132	-0.03	0.57	132
Adirondacks	030171E	**-1.72**	**0.00**	132	0.00	0.99	132	0.73	0.08	132	-0.13	0.69	132				**-0.87**	**0.01**	132	**0.19**	**0.01**	132
Adirondacks	040186O	**-3.53**	**0.00**	132	-0.39	0.68	132	**2.44**	**0.01**	132	**-1.49**	**0.02**	132				**-1.31**	**0.00**	132	-0.10	0.23	132
Adirondacks	040210O	**-3.55**	**0.00**	132	-1.60	0.13	132	**2.75**	**0.01**	132	-0.76	0.16	132				**-2.42**	**0.00**	132	0.10	0.25	132
Adirondacks	040704O	**-1.65**	**0.00**	132	-0.25	0.65	132	1.63	0.06	132	-0.56	0.06	132				-0.54	0.15	132	-0.04	0.39	132
Adirondacks	040706O	**-1.66**	**0.00**	132	-0.94	0.50	132	1.37	0.49	132	-0.34	0.18	132				-1.37	0.11	132	-0.03	0.66	132
Adirondacks	040707O	-0.69	0.06	132	-0.44	0.45	132	0.67	0.67	132	-0.14	0.35	132				-0.67	0.39	132	-0.08	0.22	132
Adirondacks	040826O	**-2.64**	**0.00**	132	-0.31	0.56	132	1.25	0.27	132	-0.09	0.27	132				**-1.84**	**0.02**	132	0.06	0.20	132
Adirondacks	040850O	**-4.74**	**0.00**	132	-1.35	0.06	132	**1.76**	**0.02**	132	-0.21	0.17	132				**-4.34**	**0.00**	132	0.06	0.24	132
Adirondacks	040852O	**-3.94**	**0.00**	132	-1.47	0.24	132	1.48	0.16	132	-0.65	0.15	132				**-3.74**	**0.00**	132	0.07	0.36	132
Adirondacks	040874O	**-4.33**	**0.00**	132	**-1.94**	**0.00**	132	**4.30**	**0.00**	132	-1.05	0.12	132				**-1.92**	**0.00**	132	**0.22**	**0.00**	132
Adirondacks	040887O	-1.45	0.10	132	-2.42	0.15	132	-0.09	0.94	132	-0.64	0.26	132				**-3.73**	**0.00**	132	-0.07	0.59	132
Adirondacks	041004O	**-1.96**	**0.00**	132	-0.91	0.38	132	1.72	0.20	132	-0.53	0.29	132				**-1.22**	**0.04**	132	0.02	0.72	132
Adirondacks	041007O	**-2.10**	**0.00**	132	-1.22	0.33	132	0.83	0.60	132	-0.42	0.37	132				**-2.37**	**0.00**	132	-0.04	0.65	132
Adirondacks	050215O	-1.02	0.26	132	0.08	0.63	132	1.00	0.63	132	-0.04	0.20	132				0.02	0.98	132	0.09	0.78	132
Adirondacks	050649O	**-3.92**	**0.00**	132	-0.08	0.66	132	1.28	0.18	132	-0.39	0.52	132				**-2.40**	**0.01**	132	0.24	0.15	132
Adirondacks	050669E	**-1.21**	**0.01**	132	-0.31	0.31	132	0.03	0.95	132	-0.71	0.09	132				**-1.35**	**0.00**	132	-0.09	0.12	132
Adirondacks	050706O	**-2.76**	**0.00**	132	0.06	0.97	132	0.44	0.63	132	**-0.38**	**0.02**	132				**-2.19**	**0.02**	132	0.00	0.99	132
Adirondacks	050707O	**-3.84**	**0.00**	132	0.19	0.90	132	0.57	0.67	132	-0.17	0.58	132				**-3.03**	**0.00**	132	**0.13**	**0.05**	132
Adirondacks	060315AO	**-3.84**	**0.00**	132	-0.51	0.68	132	0.37	0.91	132	-0.01	0.98	132				-4.05	0.06	132	0.02	0.87	132
Adirondacks	070859O	**-1.80**	**0.00**	132	-0.34	0.79	132	1.06	0.56	132	-0.38	0.41	132				-1.29	0.07	132	-0.04	0.41	132
Adirondacks	1A1-017S	**-3.14**	**0.00**	132	-1.78	0.11	132	1.79	0.22	132	-0.55	0.13	132				**-2.67**	**0.00**	132	**0.15**	**0.00**	132
Adirondacks	1A1-029O	-0.73	0.26	132	-0.24	0.58	132	-0.83	0.71	132	-0.01	0.57	132				-2.24	0.19	132	-0.02	0.80	132
Adirondacks	1A1-052O	**-2.38**	**0.00**	132	-0.72	0.10	132	**-2.05**	**0.00**	132	0.00	0.83	132				**-4.22**	**0.00**	132	0.03	0.21	132
Adirondacks	1A1-059O	**-4.23**	**0.00**	132	-1.87	0.07	132	1.11	0.58	132	-0.02	0.89	132				**-4.71**	**0.01**	132	**0.39**	**0.00**	132
Adirondacks	1A1-071S	**-1.26**	**0.00**	132	-0.34	0.41	132	-2.15	0.07	132	0.00	0.29	132				**-3.02**	**0.01**	132	-0.07	0.11	132
Adirondacks	1A1-087S	**-2.90**	**0.00**	132	-1.28	0.18	132	1.26	0.47	132	-0.06	0.28	132				**-2.50**	**0.02**	132	**0.12**	**0.04**	132
Adirondacks	1A1-089O	**-2.75**	**0.00**	132	-0.44	0.45	132	1.70	0.07	132	-0.47	0.08	132				**-1.59**	**0.01**	132	**0.10**	**0.01**	132
Adirondacks	1A1-102O	**-2.00**	**0.00**	132	-0.64	0.11	132	-0.53	0.34	132	-0.01	0.69	132				**-2.71**	**0.00**	132	-0.01	0.81	132
Adirondacks	1A1-103O	**-2.49**	**0.00**	132	**-2.08**	**0.00**	132	1.09	0.13	132	**-0.57**	**0.01**	132				**-2.77**	**0.00**	132	0.07	0.09	132
Adirondacks	1A1-105S	**-2.59**	**0.00**	132	**-2.20**	**0.00**	132	-0.94	0.73	132	-0.01	0.68	132				**-4.81**	**0.00**	132	**0.15**	**0.02**	132
Adirondacks	1A1-106O	**-2.42**	**0.00**	132	**-1.89**	**0.00**	132	**1.39**	**0.04**	132	**-0.50**	**0.01**	132				**-2.47**	**0.00**	132	**0.09**	**0.01**	132
Adirondacks	1A1-107E	**-1.43**	**0.00**	132	-0.01	0.94	132	**1.42**	**0.00**	132	**-1.10**	**0.00**	132				0.27	0.51	132	**0.19**	**0.04**	132
Adirondacks	1A1-109O	**-2.04**	**0.00**	132	**-2.04**	**0.01**	132	0.67	0.69	132	-0.05	0.22	132				**-2.67**	**0.00**	132	**0.06**	**0.03**	132
Adirondacks	1A1-110O	**-2.29**	**0.00**	132	**-1.82**	**0.01**	132	1.37	0.27	132	-0.16	0.08	132				**-2.33**	**0.00**	132	**0.08**	**0.01**	132
Adirondacks	1A1-111S	**-2.27**	**0.00**	132	-1.37	0.15	132	1.31	0.10	132	**-0.68**	**0.00**	132				**-1.80**	**0.00**	132	**0.11**	**0.03**	132
Adirondacks	1A1-112S	**-3.72**	**0.00**	132	-0.87	0.06	132	**-2.93**	**0.00**	132	**0.61**	**0.00**	132				**-6.08**	**0.00**	132	**0.24**	**0.02**	132
Adirondacks	1A1-113S	**-2.26**	**0.00**	132	-0.87	0.16	132	0.98	0.29	132	-0.02	0.18	132				**-1.57**	**0.01**	132	**0.07**	**0.05**	132
Adirondacks	1A2-028O	**-5.10**	**0.00**	132	1.37	0.30	132	-0.07	0.98	132	-0.01	0.51	132				-4.01	0.07	132	0.17	0.06	132
Adirondacks	1A2-066O	**-2.14**	**0.00**	132	-0.76	0.56	132	1.80	0.10	132	**-0.90**	**0.01**	132				-1.29	0.06	132	0.02	0.59	132

REGION	WDID	SO4* (µekv L^{-1})			ENO3(µekv L^{-1})			Alkalinity (µekv L^{-1})			H^+(µekv L^{-1})			ANC(µekv L^{-1})			Ca+Mg (µekv L^{-1})			TOC/DOC (mgC L^{-1})		
		trend slope	p	n	trend slope	p	n	trend slope	p	n	trend slope	p	n	trend slope	p	n	trend slope	p	n	trend slope	p	n
Adirondacks	1A2-077O	**-1.48**	**0.00**	132	-0.17	0.47	132	**-2.31**	**0.00**	132	0.00	0.97	132				**-3.39**	**0.00**	132	-0.01	0.60	132
Adirondacks	1A2-078S	**-1.64**	**0.00**	132	-1.47	0.09	132	0.89	0.40	132	-0.33	0.10	132				**-1.98**	**0.00**	132	0.00	0.80	132
Adirondacks	1A3-001O	**-1.27**	**0.04**	132	-0.18	0.81	132	-1.28	0.41	132	-0.04	0.43	132				-2.59	0.08	132	**0.12**	**0.05**	132
Appalachians	01364959	**-2.42**	**0.00**	99	**-1.64**	**0.00**	99	0.16	0.52	99	-0.09	0.24	99				**-2.66**	**0.00**	99	**0.09**	**0.00**	99
Appalachians	0143400680	**-2.56**	**0.00**	103	**-1.78**	**0.00**	103	-0.17	0.31	103	-0.02	0.86	103				**-2.90**	**0.00**	103	**0.15**	**0.00**	103
Appalachians	01434021	**-3.15**	**0.00**	98	**-1.37**	**0.00**	98	**0.69**	**0.01**	98	0.10	0.62	98				-1.38	0.20	98	**0.16**	**0.00**	98
Appalachians	01434025	**-3.31**	**0.00**	105	**-2.44**	**0.00**	105	**0.61**	**0.02**	105	**-0.05**	**0.00**	105				**-4.05**	**0.00**	105	**0.03**	**0.01**	105
Appalachians	BNR	1.37	0.15	84	-0.14	0.37	84	**1.25**	**0.00**	84	-0.08	0.39	84				-1.79	0.11	66	-0.04	0.27	84
Appalachians	LNN	**-1.35**	**0.01**	84	**-0.97**	**0.02**	84	1.60	0.20	84	-0.14	0.22	84				**-7.48**	**0.02**	66	0.00	0.98	84
Appalachians	RBS	**-2.27**	**0.01**	85	-0.28	0.16	85	**2.40**	**0.02**	85	-0.17	0.59	85				-2.97	0.12	65	0.04	0.22	85
Appalachians	STN	**-2.25**	**0.00**	80	-0.09	0.42	80	**0.79**	**0.05**	80	-0.27	0.16	80				**-5.89**	**0.00**	64	**-0.06**	**0.02**	80
Appalachians	WWW	**2.40**	**0.00**	79	**-3.37**	**0.00**	79	**2.53**	**0.01**	79	-0.01	0.58	79				**-7.07**	**0.01**	60	-0.01	0.66	79
Blue Ridge	PAIN	0.35	0.50	45	-1.36	0.50	45	0.06	0.50	45	-0.07	0.50	45				-0.58	0.50	45	-0.07	0.50	45
Blue Ridge	PINE	-0.03	0.50	35	-2.23	0.50	35	2.12	0.50	35	0.00	0.50	35				-0.04	0.50	35	-0.04	0.50	35
Blue Ridge	STAN	0.55	0.50	45	-0.65	0.50	45	-1.23	0.50	45	0.00	0.50	45				-1.60	0.50	45	-0.02	0.50	45
Maine/Atlantic	1C1-078E	**-2.82**	**0.00**	33	0.08	0.17	33	**-4.97**	**0.01**	33	**0.08**	**0.00**	33				**-6.28**	**0.00**	33	0.13	0.38	33
Maine/Atlantic	1E1-060E	-0.76	0.19	33	-0.07	0.43	33	-1.06	0.39	33	-0.01	0.60	33				**-3.51**	**0.00**	33	0.08	0.09	33
Maine/Atlantic	1E1-131E	**-0.47**	**0.04**	33	0.00	0.99	33	**0.72**	**0.05**	33	-0.05	0.20	33				0.11	0.72	33	0.00	0.93	33
Maine/Atlantic	1E1-132E	**-1.02**	**0.00**	33	-0.02	0.45	33	0.32	0.53	33	-0.06	0.10	33				**-0.62**	**0.02**	33	-0.03	0.12	33
Maine/Atlantic	1E1-133E	-0.50	0.09	33	0.01	0.75	33	-0.07	0.93	33	-0.01	0.39	33				-0.28	0.38	33	-0.03	0.22	33
Maine/Atlantic	1E1-134E	**-1.47**	**0.00**	33	0.01	0.66	33	0.29	0.53	33	-0.16	0.56	33				**-0.75**	**0.03**	33	0.05	0.46	33
Maine/Atlantic	1E1-135E	-0.17	0.12	33	**0.04**	**0.03**	33	-0.82	0.23	33	-0.01	0.13	33				-0.24	0.56	33	0.03	0.45	33
Maine/Atlantic	1E2-060E	**-3.61**	**0.00**	33	0.03	0.52	33	0.66	0.83	33	0.01	0.18	33				-2.16	0.44	33	-0.09	0.70	33
Maine/Atlantic	CA10	-0.55	0.19	18	-0.08	0.10	18	-1.16	0.24	18	1.29	0.16	18	0.88	0.43	18	0.27	0.55	18	0.71	0.12	17
Maine/Atlantic	CA11	**-1.12**	**0.01**	26	0.00	0.90	26	-0.21	0.59	26	0.08	0.61	26	0.03	0.97	26	-0.44	0.49	26	0.08	0.32	20
Maine/Atlantic	CA12	0.02	0.96	15	-0.07	0.17	15	-1.00	0.39	15	1.45	0.11	15	-0.63	0.67	15	-0.52	0.53	15	0.49	0.33	15
Maine/Atlantic	CA13	-0.59	0.15	28	**0.04**	**0.00**	28	-0.92	0.12	28	0.44	0.06	28	0.11	0.92	28	-0.09	0.83	28	0.25	0.11	25
Maine/Atlantic	CA14	**-1.13**	**0.00**	45	0.01	0.80	45	-0.57	0.22	45	-0.01	0.86	45	0.38	0.57	45	-0.51	0.11	45	**0.14**	**0.00**	42
Maine/Atlantic	ME-0441E	**-1.94**	**0.00**	21	0.09	0.26	21	-1.65	0.12	21	0.01	0.68	21				**-2.75**	**0.00**	21	0.00	0.98	21
Maine/Atlantic	ME-2068E	-0.55	0.14	20	0.05	0.09	20	-2.26	0.30	20	0.00	0.63	20				**-3.10**	**0.03**	20	-0.06	0.13	20
Maine/Atlantic	ME-4474E	**-1.08**	**0.01**	21	0.14	0.14	21	-0.58	0.21	21	-0.50	0.26	21				**-0.86**	**0.02**	21	**0.10**	**0.01**	21
Maine/Atlantic	ME-4575E	**-1.06**	**0.00**	22	0.07	0.12	22	**-2.28**	**0.02**	22	0.02	0.58	22				**-2.87**	**0.00**	22	0.04	0.30	22
Maine/Atlantic	ME-4778E	**-1.05**	**0.00**	24	0.04	0.25	24	**-1.62**	**0.00**	24	0.08	0.28	24				**-1.39**	**0.00**	24	-0.03	0.14	24
Upper Midwest	2B1-047E	**-5.73**	**0.00**	23	0.02	0.89	23	**3.39**	**0.00**	23	-0.73	0.08	23				**-2.40**	**0.00**	23	**0.13**	**0.03**	23
Upper Midwest	2B1-048E	**-4.41**	**0.00**	23	-0.03	0.88	23	**3.73**	**0.00**	23	-0.12	0.67	23				**-1.01**	**0.00**	23	**-0.03**	**0.02**	23
Upper Midwest	2B2-101E	**-1.67**	**0.02**	23	-0.16	0.52	23	0.54	0.40	23	0.05	0.35	23				**-1.34**	**0.00**	23	0.08	0.29	23
Upper Midwest	2B2-103E	**-3.12**	**0.00**	23	0.05	0.75	23	**1.58**	**0.00**	23	-0.13	0.58	23				**-1.62**	**0.00**	23	0.06	0.13	23
Upper Midwest	2B2-105E	**-3.44**	**0.00**	23	0.01	0.96	23	**2.52**	**0.00**	23	**-0.18**	**0.03**	23				**-1.04**	**0.00**	23	**0.17**	**0.00**	23
Upper Midwest	2B2-106E	**-3.29**	**0.00**	23	0.02	0.94	23	2.06	0.07	23	0.00	0.55	23				-0.64	0.51	23	0.06	0.17	23
Upper Midwest	2B3-082E	**-6.32**	**0.00**	23	0.24	0.11	23	**2.41**	**0.00**	23	**0.31**	**0.01**	23				**-3.56**	**0.00**	23	**0.60**	**0.00**	23
Upper Midwest	2B3-083E	**-1.48**	**0.00**	23	0.02	0.87	23	**0.90**	**0.00**	23	-0.05	0.69	23				-0.29	0.10	23	0.00	0.95	23

REGION	WDID	SO4* (µekv L^{-1})			ENO3(µekv L^{-1})			Alkalinity (µekv L^{-1})			H^+(µekv L^{-1})			ANC(µekv L^{-1})			Ca+Mg (µekv L^{-1})			TOC/DOC (mgC L^{-1})		
		trend slope	p	n	trend slope	p	n	trend slope	p	n	trend slope	p	n	trend slope	p	n	trend slope	p	n	trend slope	p	n
Upper Midwest	2C1-029E	**-7.58**	**0.00**	23	-0.18	0.28	23	**2.97**	**0.00**	23	**-0.25**	**0.00**	23				**-4.09**	**0.00**	23	0.11	0.10	23
Upper Midwest	2C1-063E	**-0.97**	**0.00**	23	0.06	0.72	23	0.37	0.41	23	0.02	0.07	23				-0.63	0.09	23	-0.01	0.68	23
Upper Midwest	2C1-064E	**-2.15**	**0.00**	23	0.50	0.12	23	-0.73	0.32	23	-0.01	0.69	23				**-1.70**	**0.00**	23	-0.02	0.75	23
Upper Midwest	2C1-069E	**-2.97**	**0.00**	23	0.48	0.13	23	**1.86**	**0.01**	23	-0.02	0.07	23				-0.24	0.49	23	0.11	0.06	23
Upper Midwest	2C1-073E	**-2.47**	**0.00**	23	0.07	0.51	23	**1.62**	**0.00**	23	**-0.02**	**0.01**	23				**-0.63**	**0.00**	23	**0.07**	**0.03**	23
Upper Midwest	2C1-075E	**-3.71**	**0.00**	23	0.24	0.19	23	**1.79**	**0.00**	23	**-0.20**	**0.01**	23				**-1.80**	**0.00**	23	**0.09**	**0.03**	23
Upper Midwest	2C2-062E	**0.92**	**0.01**	23	**0.33**	**0.03**	23	**-1.74**	**0.00**	23	0.04	0.18	23				**0.96**	**0.01**	23	-0.04	0.27	23
Upper Midwest	2D3-071E	**-11.56**	**0.00**	23	**-0.69**	**0.00**	23	**7.25**	**0.00**	23	**-1.40**	**0.00**	23				**-3.56**	**0.00**	23	**0.33**	**0.00**	23
Upper Midwest	CA01	**-1.46**	**0.00**	715	-0.21	0.33	715	**0.82**	**0.00**	715	-0.01	0.50	717	**-1.75**	**0.00**	711	**-3.10**	**0.00**	715	**0.06**	**0.00**	717
Upper Midwest	CA02	**-1.40**	**0.00**	718	-0.06	0.82	718	0.02	0.94	718	0.01	0.10	718	**-1.73**	**0.00**	717	**-3.04**	**0.00**	717	0.03	0.14	716
Upper Midwest	CA03	**-1.69**	**0.00**	727	-0.16	0.48	727	-0.01	0.97	727	0.00	0.36	727	**-1.61**	**0.00**	723	**-3.22**	**0.00**	723	**0.03**	**0.00**	726
Upper Midwest	CA04	**-1.92**	**0.00**	717	-0.07	0.75	718	**-1.21**	**0.02**	716	0.00	0.57	717	**-1.79**	**0.00**	714	**-3.62**	**0.00**	716	**0.03**	**0.02**	717
Upper Midwest	CA16	**-2.35**	**0.00**	114	0.00	0.92	113	0.32	0.42	114	0.00	0.74	53	0.22	0.32	113	**-1.96**	**0.00**	114	**0.06**	**0.00**	116
Upper Midwest	CA17	**-5.13**	**0.00**	149	0.06	0.10	149	-0.49	0.09	150	**0.01**	**0.03**	85	0.19	0.57	149	**-3.51**	**0.00**	149	**0.11**	**0.00**	152
Upper Midwest	CA20	**-1.82**	**0.00**	74	**0.02**	**0.05**	73	0.61	0.19	86	**0.01**	**0.00**	58	**-1.89**	**0.02**	73	**-3.09**	**0.00**	74	-0.01	0.33	97
Vermont/Quebec	1C1-089E	**-1.94**	**0.00**	44	-0.13	0.45	44	**0.84**	**0.05**	44	-0.02	0.87	44				**-1.03**	**0.00**	44	**0.18**	**0.02**	44
Vermont/Quebec	1C1-090E	**-1.93**	**0.00**	44	-0.11	0.59	44	0.56	0.20	44	0.04	0.16	44				**-1.29**	**0.00**	44	0.02	0.54	44
Vermont/Quebec	1C1-091E	-0.11	0.71	44	0.01	0.90	44	-0.68	0.14	44	0.02	0.16	44				**-1.00**	**0.01**	44	**0.19**	**0.05**	44
Vermont/Quebec	1C1-093E	**-2.46**	**0.00**	44	-1.05	0.08	44	0.89	0.17	44	-0.04	0.81	44				**-2.31**	**0.00**	44	0.00	0.98	44
Vermont/Quebec	1C1-095E	**-1.65**	**0.00**	44	**-1.81**	**0.02**	44	1.28	0.32	44	-0.10	0.36	44				**-1.80**	**0.00**	44	-0.19	0.24	44
Vermont/Quebec	1C1-097E	-1.77	-1.77	44	0.01	0.94	44	-0.23	0.53	44	0.03	0.35	44				**-2.00**	**0.00**	44	0.03	0.34	44
Vermont/Quebec	1C1-100E	**-1.97**	**0.01**	44	0.16	0.26	44	0.38	0.57	44	-0.21	0.40	44				-1.56	0.11	44	0.22	0.29	44
Vermont/Quebec	1C1-101E	**-2.88**	**0.00**	44	-0.27	0.35	44	**1.65**	**0.00**	44	-0.32	0.12	44				**-1.40**	**0.00**	44	**0.25**	**0.00**	44
Vermont/Quebec	1C1-107E	**-2.38**	**0.00**	44	0.07	0.86	44	0.96	0.41	44	0.02	0.14	44				-1.64	0.19	44	0.05	0.30	44
Vermont/Quebec	1C1-110E	**-2.02**	**0.00**	44	**-0.36**	**0.04**	44	**0.94**	**0.01**	44	-0.17	0.33	44				**-1.39**	**0.00**	44	0.06	0.25	44
Vermont/Quebec	1C1-112E	**-2.03**	**0.00**	44	-0.26	0.23	44	-0.43	0.80	44	0.05	0.21	44				**-2.52**	**0.01**	44	0.01	0.96	44
Vermont/Quebec	CA05	**-3.33**	**0.00**	21	**-0.31**	**0.01**	21	**0.00**	**0.01**	20	-0.05	0.18	21	**3.56**	**0.00**	20	-0.35	0.40	20	0.03	0.49	19
Vermont/Quebec	CA06	**-3.93**	**0.00**	20	**-0.47**	**0.05**	21	**0.00**	**0.02**	20	-0.20	0.10	21	**4.36**	**0.00**	19	**-0.62**	**0.01**	20	0.05	0.12	18
Vermont/Quebec	CA07	**-4.16**	**0.00**	54	-0.22	0.25	54	**0.00**	**0.03**	51	**-0.53**	**0.02**	54	**3.07**	**0.00**	54	**-1.24**	**0.02**	54	**0.16**	**0.01**	29
Vermont/Quebec	CA09	**-3.90**	**0.00**	21	-0.17	0.14	21	0.00	0.80	19	-0.20	0.40	21	**2.78**	**0.00**	20	-1.36	0.17	20	0.10	0.19	19