Convention on Long-Range Transboundary Air Pollution

International Cooperative Programme on Assessement and
Monitoring of Acidification of Rivers and Lakes

ICP Waters Report 87/2007

Trends in surface water chemistry and biota; The importance of confounding factors

NIVA Norwegian Institute for Water Research

Norwegian Institute for Water Research
– an institute in the Environmental Research Alliance of Norway

REPORT

Main Office	**Regional Office, Sørlandet**	**Regional Office, Østlandet**	**Regional Office, Vestlandet**	**Akvaplan-NIVA A/S**
Gaustadalléen 21	Televeien 3	Sandvikaveien 41	P.O.Box 2026	
N-0349 Oslo, Norway	N-4879 Grimstad, Norway	N-2312 Ottestad, Norway	N-5817 Bergen, Norway	N-9005 Tromsø, Norway
Phone (47) 22 18 51 00	Phone (47) 37 29 50 55	Phone (47) 62 57 64 00	Phone (47) 55 30 22 50	Phone (47) 77 68 52 80
Telefax (47) 22 18 52 00	Telefax (47) 37 04 45 13	Telefax (47) 62 57 66 53	Telefax (47) 55 30 22 51	Telefax (47) 77 68 05 09
Internet: www.niva.no				

Title Trends in surface water chemistry and biota; The importance of confounding factors	Serial No. 5385-2007	Date March 2007
	Report No. Sub-No. ICP Waters report 87/2007	Pages Price 89
Editors: Heleen de Wit and Brit Lisa Skjelkvåle	Topic group Acid rain	Distribution
	Geographical area Europe and North America	Printed NIVA

Client(s) United Nations Economic Commission for Europe The Norwegian Pollution Control Authority	Client ref.

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 surface water chemistry trend analyses for ICP Waters sites for the period 1994-2004, including nitrate and dissolved organic carbon, and an assessment of biological recovery. Additionally, effects of environmental factors other than acid deposition – so-called “confounding factors” - on chemical and biological recovery of surface waters are evaluated. Most regions in Europa and North America show significant decreases in sulphate whereas nitrate trends are more scattered. Indicators of chemical recovery – alkalinity, pH and ANC – show improvements, most clearly in Europe. Increases in organic acidity and seasalt deposition delay recovery in some regions. Climate change both delays and enhances chemical recovery depending on region and variable. International cooperative work to abate acidification has so far been very successful, but water chemistry and biology of many acidified systems is still far from any pre-industrial reference condition. Monitoring of future development of water chemistry and aquatic biota in acidified water bodies must continue in order to assess effects of further emission reductions of S and N and confounding 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. Trender i vannkjemi	3. Trends in water chemistry
4. Trender I biologi	4. Trends in biology

Brit Lisa Skjelkvåle	*Merete J. Ulstein*	*Jarle Nygard*
Project manager	Research manager	Strategy Director

ISBN 978-82-577-5120-3

CONVENTION ON LONG-RANGE
TRANSBOUNDARY AIR POLLUTION

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

Trends in surface water chemistry and biota; The importance of confounding factors

Prepared by the ICP Waters Programme Centre
Norwegian Institute for Water Research
Oslo, March 2007

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 UNIFOB at University of Bergen. The ICP Water programme is lead by Berit Kvæven, Norwegian Pollution Control Authority (SFT).

The objective of the Programme is to establish an international network of surface water monitoring sites and to promote international harmonization of monitoring practices. One of the aims is to detect long-term trends in effects of acidic deposition on surface water chemistry and aquatic biota, and to investigate dose/response relationships between water chemistry and aquatic biota.

The data collected within ICP Waters are well-suited for trend analysis. This report focuses on trends in surface water recovery from acidification, both in chemistry and in biology. Special focus is given to trends in nitrate and dissolved organic carbon. Confounding factors that may delay or enhance recovery are discussed.

The Programme Center acknowledges all countries that provide data to the ICP Waters database for use in the assessment work. We are also grateful for the contribution in the discussions of an earlier version of the report that was presented at the 22th Task Force meeting in Bergen 11-12 October 2006 and for all the written comments to the second draft of the report. In particular we want to thank Michela Rogora, Italy, Thomas Clair, Canada and Lars Eriksson, Sweden who were appointed by the 22th Task Force meeting to review the final draft.

Brit Lisa Skjelkvåle

ICP Waters Programme Centre,
Oslo, March 2007

Contents

Executive summary

The recovery of surface waters from acidification is continuing. This conclusion is based on trend analysis of water chemistry data from 179 ICP Waters sites in Europe (73) and North America (106) between 1994 and 2004. Sulphate concentrations are decreasing while trends in nitrate show no consistent regional pattern. Alkalinity concentrations, acid neutralizing capacity and pH show positive tendencies in most regions. Increases in organic acidity and seasalt deposition delay chemical recovery in some regions. Rates of sulphate decline appear to be lower than in the previous trend analysis for the period 1990-2001. Sulphate is still the most important acid anion in most ICP Waters sites.

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 Canada, Norway and the Czech Republic. At the most acidified central European sites, however, there is little evidence of biological recovery.

Trends in nitrogen are scattered and show no consistent regional pattern. Opposing trends in N deposition and N run-off indicate that other factors than N deposition regulate nitrate leaching to surface waters.

The widespread increases in dissolved organic carbon (DOC) throughout Europe and North America are correlated with declines in sulphate. This suggests that the current DOC rise is a response to reduced sulphate deposition.

Environmental factors other than acid deposition – so-called ‘confounding factors’ – are expected to affect chemical and biological recovery of freshwaters in response to reduced acid deposition. Climate contributes considerably to variability in surface water chemistry, for instance through seasalt episodes (increases water acidity and sets back biological recovery), droughts (enhances acidic episodes) and soil freezing and thawing (increases nitrate leakage). Climate change may both enhance and delay recovery depending on region and variable considered.

International cooperative work on emission reductions to abate surface water acidification has so far been very successful, but water chemistry and biology of many acidified systems is still far from any pre-industrial reference condition. 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.

Monitoring of future development of water chemistry and aquatic biota in acidified water bodies must continue in order to assess effects of further emission reductions of S and N and confounding effects of climate.

Summary

ICP Waters programme

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

Materials and methods

The water chemistry database we studied consists of chemical records from 179 sites (73 from Europe, 106 from North America) which were grouped in twelve fairly homogeneous regions with regard to deposition level and acid-sensitivity. In our analysis, only data from the 1994 to 2004 period were tested using the Mann-Kendall trend detection method. The biological data used for trend analysis were from the UK, Scandinavia, Central Europe and Canada.

Widespread chemical recovery

The most important finding is the widespread chemical recovery in streams and lakes in most regions in Europe and North America, despite the slightly reduced rate of decline in sulphate relative to the previously reported period 1990-2001. All regions except two showed a significant increase in pH and/or alkalinity, and/or acid neutralizing capacity (ANC). This was largely due to a slower decline in non-marine base cations relative to the decline in sulphate. In the UK, no improvements in alkalinity or ANC were found despite the large reduction in sulphate combined with a lower reduction in base cations. This was thought to be related to the increase in organic acidity through the increase in dissolved organic carbon. The pH increased significantly, however.

The regions without signs of chemical recovery were Ontario and the Virginia Blue Ridge mountains in North America. Soil characteristics in the Blue Ridge Mountains make a sulphate decrease unlikely in the short term. The lack of coherent trends in Ontario is probably due to the large variability in the trends in individual sites in the region.

No uniform trends in nitrate

Data on nitrate trends between 1990 and 2005 at ICP Waters sites are presented in a separate chapter. No consistent rise or decline in nitrate was detected, as nitrate trends varied considerably within each region. However, a significant decline was found in the Adirondacks, Appalachians and Virginia Blue Ridge, while the Alps were the only region with an increase in nitrate. At most sites, sulphate was the most important strong acid anion and the relative importance of nitrate in the anion load does not show any significant change despite the reductions in sulphate. N deposition has declined slightly since 1990 at many ICP Waters sites, and in very few sites similar trends in N deposition and N runoff were found. However, the commonly accepted concept of increasing stream or lake nitrate concentrations in catchments that receive N deposition above certain thresholds is supported. Opposing trends in N deposition and nitrate runoff illustrate that other factors (confounding factors) than N deposition alone regulate catchment nitrate leaching.

Increase in DOC is a response to reduced acid deposition

Dissolved organic carbon (DOC) is of great interest in analysis of surface water recovery because it is an indicator of organic (natural) acidity which may counteract the positive effect of declining sulphate. For the period 1990-2004, a widespread increase in DOC was found in formerly glaciated parts of North America and Europe. Statistical relations were found between declines of sulphate and chloride and the % increase in DOC, suggesting that the current rise in DOC is a response to reduced deposition of sulphate. Additionally, seasalt deposition also contributes to the variability in DOC.

Biology

The widespread improvements in chemical water quality have lead to biological recovery of acid-sensitive species, which has been first observed in regions with low buffer capacity. Examples are Canada, Norway and the Czech Republic. Regions with higher buffer capacity still show little evidence of biological recovery (Germany). Biological recovery occurs usually with a 1 up to possibly 20 years delay compared with chemical recovery, depending on the investigated communities and dispersal and colonisation ability of the acid-sensitive species.

Confounding factors in chemical and biological recovery

Environmental factors other than acid deposition – so-called ‘confounding factors’ – are expected to affect chemical and biological recovery of freshwaters in response to reduced acid deposition. A non-exhaustive overview on confounding factors is given. Climate contributes considerably to variability in surface water chemistry, for instance through seasalt episodes (increases water acidity and sets back biological recovery), droughts (enhances acidic episodes) and soil freezing and thawing (increases nitrate leakage). Climate change may both enhance and delay recovery depending on region and variable considered. Other confounding factors, not directly related to climate like insect outbreaks, can also delay recovery.

1. Introduction

Brit Lisa Skjelkvåle and Heleen de Wit

ICP Waters Programme Centre, Norwegian Institute for Water Research, Oslo, Norway

The ICP Waters Programme

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 across national boundaries. Acidifying compounds thus affect surface waters, groundwaters and forest soils far beyond their country of origin. 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 the World Health Organisation (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 LRTAP at its third session in Helsinki in July 1985. Canada was appointed as lead country for the first phase of the ICP Waters.

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. The ICP Waters Programme is based on existing programmes in participating countries, implemented by voluntary contributions.

The programme aims and objectives (reviewed at the ICP Waters 15th Task Force meeting in Pallanza, Italy October, 1999) 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 or 4 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 (Skjelkvåle et al. 2003) and this report.

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 Waters site network is geographically extensive and includes long-term data series (> 15 years) for more than a 100 sites. The network is thus well poised to document changes that result from implementation of the protocols.

The current trend report

The aim this 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 (2002-2004). Special attention is given to 'confounding factors', factors other than deposition that are expected to have an impact on chemical and biological recovery. Especially climate 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.

- **Water chemistry** -Trends in surface water chemistry 1994-2004 (Chapter 2)
- **Trends in nitrogen –** Analysis of N trends in relation to deposition and confounding factors (Chapter 3)
- **Trends in DOC –** the regional trends and possible causes of the increase in dissolved organic matter concentrations (Chapter 4)
- **Biology –** Updated trend analysis on biological recovery (Chapter 5)
- **Confounding factors –** an overview of factors other than deposition with a potential impact on chemical and biological recovery (Chapter 6)

References

Lükewille, A., Jeffries, D.S., Johannessen, M., Raddum, G.G., Stoddard, J.L., and Traaen, T.S. 1997. The Nine Year Report: Acidification of surface water in Europe and North America - Long-term Developments (1980s and 1990s). ICP-Waters Report 41/97 NIVA-report SNO 3637-97,

Skjelkvåle, B.L. (ed). 2003. The 15-year report: Assessment and monitoring of surface waters in Europe and North America; acidification and recovery, dynamic modelling and heavy metals. NIVA-report SNO 4716-2003, ICP Waters report 73/2003

Skjelkvåle, B.L.(ed.). 2000. The 12-year report; Acidification of surface water in Europe and North America; trends, biological recovery and heavy metals. SNO 4208/2000, ICP Waters report 52/2000

Skjelkvåle, B.L., Newell, A.D., Raddum, G.G., Johannessen, M., Hovind, H., Tjomsland, T., and Wathne, B.M. 1994. The six year report: Acidification of surface water in Europe and North America. Dose/response relationships and long-term trends. NIVA-report SNO 3041-94

Wathne, B.M. 1991. The Three Year Report: Summary and Results 1987-1989. Norwegian Institute for Water Research. ICP Waters report 14/1991

2. Trends in surface water chemistry 1994-2004

Heleen de Wit[1], Brit Lisa Skjelkvåle[1], Tore Høgåsen[1], Thomas Clair[2] , Luca Colombo[3], Jens Fölster[4], Dean Jeffries[5], Balázs László[6], Vladimir Majer[7], Don Monteith[8], Rosario Mosello[9], Michela Rogora[9], Dorota Rzychon[10], Sandra Steingruber[11], Sanita Stivrina[12], John L. Stoddard[12], Anatoly Srybny[13], Reet Talkop[14], Josef Vesely[7], Jussi Vuorenmaa[15], Joachim Wieting[16], Adam Worsztynowicz[10]

[1] ICP Waters Programme Centre, Norwegian Institute for Water Research, Oslo, Norway
[2] ICP Waters Focal Centre, Environment Canada, Sackville, Canada
[3] ICP Waters Focal Centre, Ufficio protezione aria, Bellinzona, Switserland
[4] ICP Waters Focal Centre, Swedish University of Agricultural Sciences, Uppsala, Sweden
[5] ICP Waters Focal Centre, National Water Research Institute, Ontario, Canada
[6] ICP Waters Focal Centre, Budapest University of Technology and Economics, Budapest, Hungary
[7] ICP Waters Focal Centre, Czech Geological Survey, Czech Republic
[8] ICP Waters Focal Centre, Environmental Change Research Centre, United Kingdom
[9] ICP Waters Focal Centre, Institute of Ecosystem Study, Verbania Pallanza, Italy
[10] ICP Waters Focal Centre, Institute for Ecology of Industrial Areas, Katowice, Poland
[11] ICP Waters Focal Centre, Latvian Environment, Geology and Meteorology Agency, Riga, Latvia.
[12] ICP Waters Focal Centre, US Environmental Protection Agency, Corvallis, USA
[13] ICP Waters Focal Centre, Ministry of Natural Res. and Environ. Protection, Vitebsk Region, Belarus
[14] ICP Waters Focal Centre, Estonian Environment Information Centre, Tallinn, Estonia
[15] ICP Waters Focal Centre, Finnish Environment Institute, Helsinki, Finland
[16] ICP Waters Focal Centre, Umweltbundesamt, Berlin, Germany

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, Skjelkvåle et al., 2003, Skjelkvåle et al., 2005). Here, we report trends from 179 ICP Waters monitoring sites for the period 1994-2004. We also compare these trends with trends for the period 1990-2001 to see if the rate of recovery is changing. The period of 1990-2001 was chosen because it was reported in the 15-year report (Skjelkvåle et al., 2003).

The 15-year report (Skjelkvåle et al., 2003) showed an almost universal decline in sulphate concentrations in combination with chemical recovery that varied in strength depending on region. Clearest evidence of recovery was found in southern Scandinavia, eastern central Europe and North America except Maine and Atlantic Canada. Thus, early signs of recovery were found in many regions during the 1980s while the 1990s showed compelling and more widespread improvements in water chemistry indicating an acceleration of recovery.

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.

Trends in concentrations of **nitrate** and **dissolved organic carbon** (DOC) or alternatively **total organic carbon (TOC)** are considered in **Chapters 3** and **4** respectively. DOC can be considered as a surrogate for organic acids, mostly derived through natural degradation of organic matter in catchment soils

Both SO_4^{2-} and base cation concentrations were sea-salt corrected, and pH was transformed to H^+ concentrations prior to statistical analysis.

Similar to the 15-year report, we present the trends for each individual site, as well as aggregated trends 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 have 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. Additionally, we plot trends for the period 1990 to 2001 against trends for 1994 to 2004 to see if rates of recovery have changed since the since the last trend analysis of ICP Waters.

2.2 ICP Waters 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 collection started no later than 1997 and where data collection continued at least until 2002
- sites where data were available for at least 7 out of 11 years (1994-2004).
- 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)
- sites sensitive to acidification (ANC < 300 µeq/L and alkalinity < 300 µeq/L)
- sites with undisturbed catchments

An overview of mean chemical data for each site for the time period 2002-2004 is presented in Appendix A. The results of this selection process are summarised in Appendix B. 179 sites had sufficient data for trend analysis.

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 (Anonymous, 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
- evaluation of continuity in time series
- calculation of ionic balance

Table 1. *Number of sites in each country, and number of sites per country included in trend analysis.*

Europe			North America		
Country	nr of sites in analysis	nr of ICP Waters sites	Country	nr of sites in analysis	nr of ICP Waters sites
Belarus	0	1	Canada	17	18
Czech Republic	6	6	USA	89	94
Estonia	0	1			
Finland	8	8			
Germany	26	31			
Hungary	0	1			
Italy	6	6			
Latvia	0	3			
Norway	5	5			
Poland	2	2			
Sweden	9	9			
Switzerland	5	5			
United Kingdom	6	6			
	73	84		106	112

2.4 Statistical methods used for trend analysis

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 Mann Kendall test (MKT) (Hirsch and Slack, 1984; Hirsch et al., 1982). This method is robust against outliers, missing data and does not demand a normal distribution of the data. The method only determines monotonic trends. The regional analyses we present in this report depend on the ability to calculate a robust estimator of slope for each site. The Sen slope estimator was used to calculate the trends (Sen, 1968). The estimator has similar strengths as the MKT, and does not demand a normal distribution of the data.

Only annual means were used in the statistical analyses. The frequency of observations per station varied from a single annual observation to weekly sampling, and the frequency of observations for some stations differed between years. For each site, a representative annual value was calculated for each variable by taking the arithmic mean. Thus, seasonality in the data only influenced the value of the annual value and did not affect the power of the statistical tests.

The slopes of individual trends aggregated within a region represent a distribution of results, which can in turn be examined and analysed for patterns. Within each region, we tested for a significant trend using an adapted version of the Mann-Kendall test designed to include multiple monitoring sites (Lettenmaier, 1988).

The non-parametric Wilcoxon test was used to test for differences in slope (calculated with the Sen slope estimator) between two time periods, i.e. 1990-2001 and 1994-2004. The sites were grouped into combinations of the regions used for the regional trend analysis to secure sufficient observations. The period of 1990-2001 was chosen because it was used in the previous trend analysis of ICP Waters data (15-year report).

2.5 Results of trend analysis

2.5.1 General trends 1994-2004

We analyzed 179 sites; 73 in Europe and 106 in North America which is a reduction of ten sites since the last 15-year report. The results of the trend analysis for the single sites and the calculated slopes are presented in Appendix C. and are summarised in ***Table 2***. 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 (65%) showed a significant decreasing trend in non-marine sulphate, whereas there were no sites where non-marine sulphate was increasing.

The majority of the sites (68%) showed no trend in nitrate whereas a notable minority (25%) showed a decreasing trend. A few sites (7%) showed an increasing trend. The mixed tendencies in nitrate trends have been shown previously in reports of ICP Waters. The lack of a uniform trend in nitrate concentrations illustrates that nitrate leakage from catchment is affected by a variety of processes, in contrast to sulphate leakage from catchment which is largely controlled by sulphate deposition.

Only 30% of the sites showed a significant decrease in non-marine base cation concentration, while the majority (65%) showed no trend. A few sites (5%) showed significant increasing trends. In contrast to the trends reported for the period of 1990-2001 in the 15-year report, decreasing trends in base cations have become far less prevalent. The proportional response of base cations concentrations to the reduction of strong acid anions determines if chemical recovery can be expected.

Table 2. *Results of trend analysis for 179 ICP Waters sites for the period 1994-2004. Number of sites with significantly increasing or decreasing trends for given variables. No trend at significance level p>0.05.*

	SO_4	**NO_3**	**Ca+Mg**	**Alkalinity**	**ANC**	**H^+**	**DOC/TOC**
Europe							
Increasing	**0**	**10**	**7**	**18**	**25**	**5**	**14**
No trend	21	48	40	43	40	42	38
Decreasing	**52**	**15**	**26**	**2**	**0**	**26**	**0**
North America							
Increasing	**0**	**3**	**1**	**32**	**31**	**3**	**14**
No trend	41	72	59	71	44	86	92
Decreasing	**61**	**29**	**19**	**1**	**1**	**17**	**0**
Total no of sites	**175**	**177**	**152**	**167**	**141**	**179**	**158**
Total no increasing	**0**	**13**	**8**	**50**	**56**	**8**	**28**
Total no of no trend	62	120	99	114	84	128	130
Total no decreasing	**113**	**44**	**45**	**3**	**1**	**43**	**0**
% increasing trends	**0**	**7**	**5**	**30**	**40**	**4**	**18**
% no trends	35	68	65	68	59	72	82
% decreasing trends	**65**	**25**	**30**	**2**	**1**	**24**	**0**

Alkalinity showed increasing trends at 30% of the sites while a significant decrease was found in only 2% of the sites. The trends in acid neutralizing capacity (ANC) were similar to those of alkalinity: an increase in 41% of the sites and a decrease in only 1% of the sites. This indicates that virtually no sites are currently being acidified further compared to 14% of the sites showing a decrease in alkalinity in our previous report (1990-2001).

A substantial minority of sites (24%) showed a decrease in H^+ concentrations (implying an increase in pH) but the majority of the sites had no significant trend. It is difficult to measure pH in low ionic strength waters typical for the most of the ICP Waters sites (Hovind 2002) and makes trend detection for pH more difficult.

Dissolved organic carbon (DOC) measurements were not available at all sites. In some sites, total organic carbon (TOC) concentrations are reported only. Here, we have used DOC preferably, but TOC if DOC data did not exist. A majority of sites (82%) showed no trend in

DOC, while the remaining 18% showed a significant increase. The proportion of sites with increasing trends in DOC has halved since the 15-year report (1990-2001).

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, ANC and alkalinity) across a large number of sites. For this reason, we are again reporting trends for clusters of ICP sites **(Table 3, *Figure 1*).** The sites are grouped into geographic regions based on similar acid-sensitivity (e.g., similar geology, soil characteristics) and rates of deposition. The regions, and sites they include, are as similar as possible to those used in previous ICP Waters assessments. The main differences with regard to regions defined in the 15-year report are i) the region UK/Ireland consists now only of UK sites and is renamed as “UK”; ii) the “Upper Midwest” region now only includes sites from central and western Ontario and has been renamed to ‘Ontario’ and iii) the ‘Alps’ region now contain data from Switzerland in addition to Italy. The list of regions on which we report is based on both scientific and pragmatic decisions resulting from availability of data.

Regional trend results are shown in **Table 4** and a comparison of trends between the time period 1990-2001 and 1994-2004 are shown in **Table 5**. This analysis was only performed for three regions, aggregated from the regions in ***Table 3***, to secure sufficient observations.

Table 3. *Regions in Europe and North America (including abbreviations) and number of sites in each region*

Regions in Europe	abbreviation	n	Regions in North America	abbreviation	N
Northern Nordic	NoN	7	Maine and Atlantic Canada	Atl	20
Southern Nordic	SoN	15	Vermont and Quebec	Vt/Que	17
U.K	UK	6	Adirondacks	Ads	50
West Central Europe	WCE	11	Appalachian Plateau	App	9
East Central Europe	ECE	23	Virginia Blue Ridge	BRi	3
Alps	Alps	11	Ontario	Ont	7
sum		73	sum		106

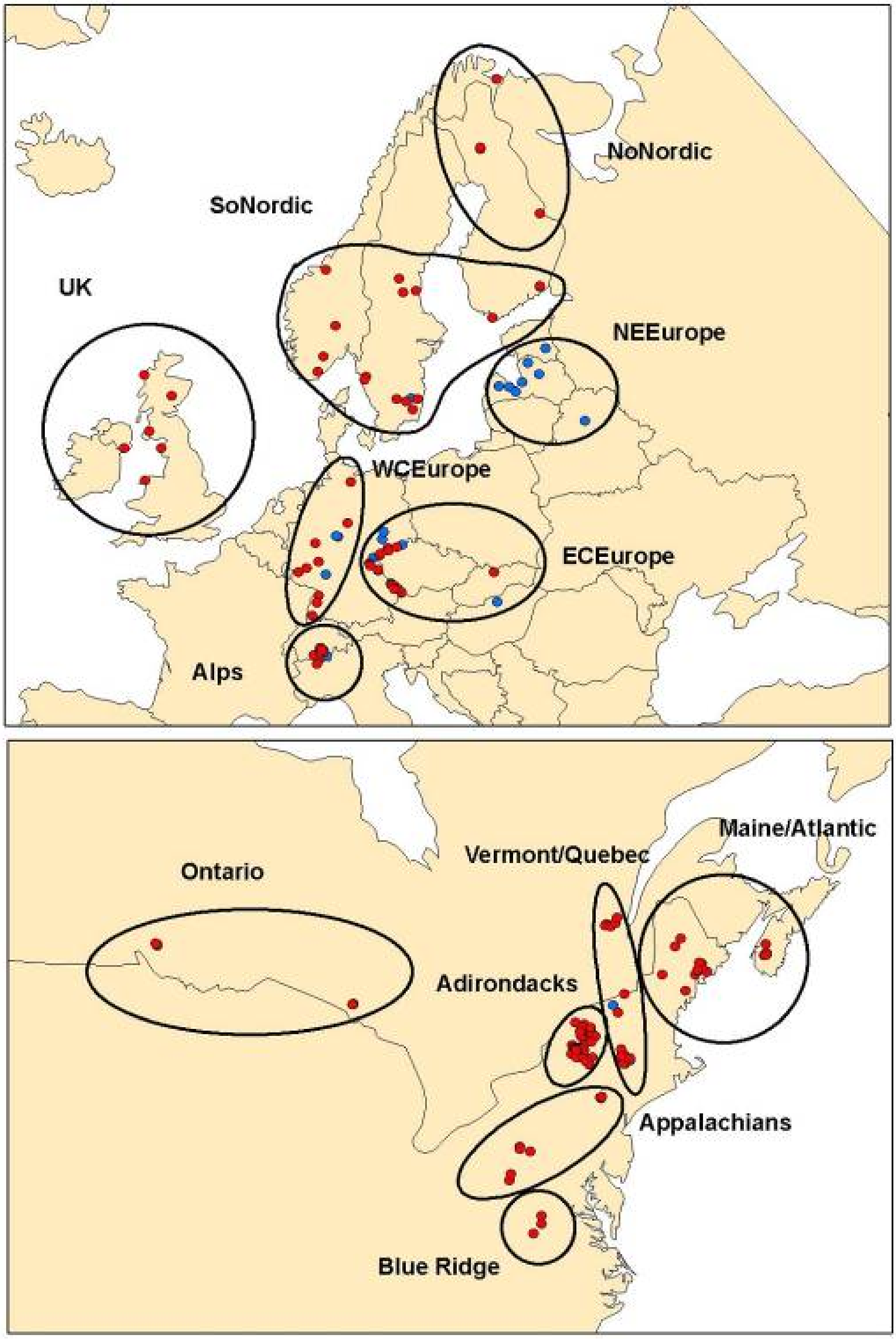

Figure 1. *Map showing location of ICP Waters sites used for trend analysis in this report and outline of geographical regions. Red dots are sites included in the trend analysis, while the blue dots are sites with trend analysis only for sulphate.*

Table 4. *Regional trend results for ICP Waters sites for the period 1994-2004. Values are median slopes, the value of the test statistic (Mann-Kendall test) and significance. n.s. is 'not significant' ($p > 0.05$); * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$. Units for non-marine sulphate, nitrate, non-marine base cations [Ca^{2+} + Mg^{2+}], alkalinity, ANC and hydrogen are µeq/L/year. Units for DOC are mg/L/year. Abbrevations are explained in* **Table 3**.

		SO_4			NO_3			H^+		
region	n	median	test stat	p	median	test stat	p	median	test stat	P
NoN	7	-1.4	-3.1	**	-0.05	-1.9	n.s.	-0.02	-2.0	*
SoN	15	-4.8	-3.6	***	-0.04	-1.3	n.s.	-0.05	-3.1	**
UK	5	-1.6	-2.1	*	-0.19	-1.7	n.s.	-0.54	-2.6	**
WCE	11	-5.6	-3.6	***	0.08	0.2	n.s.	-0.12	-2.8	**
ECE	23	-3.6	-3.4	***	-1.14	-1.7	n.s.	-0.15	-2.4	*
Alps	11	-1.3	-3.4	***	0.79	2.4	*	0.003	2.4	*
Vt/Que	17	-1.5	-2.7	**	0.05	0.6	n.s.	-0.05	-1.2	n.s.
Atl	20	-0.5	-1.5	n.s.	0.00	0.2	n.s.	-0.03	-2.4	*
Adk	50	-1.9	-3.5	***	-0.34	-2.4	*	-0.11	-1.8	n.s.
Apps	9	-1.4	-3.1	**	-0.53	-2.8	**	0.04	0.4	n.s.
Ont	7	-2.4	-3.3	**	-0.40	0.9	n.s.	0.005	1.3	n.s.
BRi	3	0.6	1.7	n.s.	-1.29	-3.2	**	0.002	-0.1	n.s.

		Alkalinity			ANC			Base Cations		
	n	median	test stat	p	median	test stat	p	median	test stat	P
NoN	7	0.9	1.3	n.s.	1.1	2.9	**	-0.8	-2.6	**
SoN	15	2.3	2.9	**	3.9	3.3	***	-2.2	-2.7	**
UK	5	0.1	0.6	n.s.	0.1	0.8	n.s.	-1.6	-1.7	n.s.
WCE	11	3.5	1.9	n.s.	7.5	3.3	***	-2.5	-1.6	n.s.
ECE	23	0.1	0.7	n.s.	4.2	2.3	*	-1.9	-1.6	n.s.
Alps	11	0.8	3.1	**	0.6	1.7	n.s.	1.0	0.7	n.s.
Vt/Que	17	0.2	0.7	n.s.	0.8	2.6	*	-0.1	-2.2	*
Atl	20	0.7	2.0	n.s.	0.2	0.0	n.s.	0.7	0.2	n.s.
Adk	50	0.9	2.4	*	1.9	2.4	*	-1.0	-1.4	n.s.
Apps	9	0.0	0.6	n.s.	1.3	2.3	*	-0.9	-2.1	*
Ont	7	0.2	1.3	n.s.	-0.7	-0.8	n.s.	-0.9	-2.0	n.s.
BRi	3	0.6	1.0	n.s.		no data			no data	

		DOC		
	n	median	test stat	p
NoN	7	0.05	1.6	n.s.
SoN	15	0.09	2.6	**
UK	5	0.12	2.3	*
WCE	11	0.09	2.2	*
ECE	23	0.08	1.3	n.s.
Alps	6		no data	
Vt/Que	17	0.03	0.7	n.s.
Atl	20	-0.01	-0.1	n.s.
Adk	50	0.04	1.7	n.s.
Apps	9	-0.01	-0.2	n.s.
Ont	7	0.03	2.1	*
BRi	3	-0.01	-0.8	n.s.

***Table 5.** Trends in surface water chemistry calculated for 1990-2001 and 1994-2004 for Central Europe (Alps, East Central Europe and West Central Europe), North West Europe (Nordic countries and UK) and North America (Canada and US). Median trends for each regions and period are given. The difference between the two periods is tested statistically with the non-parametric Wilcoxon test. n.s. is 'not significant' ($p > 0.10$); * $p < 0.10$; ** $p < 0.05$; *** $p < 0.01$. Units for non-marine sulphate, nitrate, non-marine base cations [$Ca^{2+} + Mg^{2+}$], alkalinity, ANC and hydrogen are μeq/L/year. Units for DOC are mg/L/year.*

	SO_4			NO_3			H^+					
Region	'90-'01	'94-'04	p	'90-'01	'94-'04	p	'90-'01	'94-'04	p			
Central Europe	-3.8	-3.5	n.s.	-0.4	0.0	n.s.	-0.02	-0.07	n.s.			
NW Europe	-3.4	-3.1	n.s.	0.0	-0.1	*	-0.05	-0.05	n.s.			
North America	-2.0	-1.5	***	-0.2	-0.1	n.s.	-0.05	-0.05	n.s.			
All	-2.4	-1.9	**	-0.1	-0.1	n.s.	-0.05	-0.05	n.s.			
	Alkalinity			ANC			Base Cations			DOC		
	'90-'01	'94-'04	p	'90-'01	'94-'04	p	'90-'01	'94-'04	p	'90-'01	'94-'04	p
Central Europe	0.7	0.6	n.s.	2.0	4.3	n.s.	-2.0	-1.5	n.s.	0.03	0.09	n.s.
NW Europe	0.3	0.6	n.s.	1.8	2.0	n.s.	-1.7	-1.2	n.s.	0.11	0.08	n.s.
North America	1.0	0.7	n.s.	1.1	1.3	**	-1.6	-0.9	***	0.02	0.03	***
all	0.8	0.7	n.s.	1.1	1.8	***	-1.7	-1.0	***	0.04	0.04	***

Trends in sulphate by region

A strong decrease in sulphate concentrations in lakes and streams was measured in almost all regions in Europe and North America was found, similar to previous trend analyses **(*Table 4*, Figure 2**). Two regions in North America did not show a significant SO_4^{2-} decrease, i.e. Maine and Atlantic Canada and Virginia Blue Ridge. In Virginia Blue Ridge, soil characteristics make a SO_4^{2-} decrease unlikely (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 have driven small but significant increases in surface water SO_4^{2-}, even during a time of decreasing rates of acidic deposition. In Maine and Atlantic Canada, the reduction in sulphate was among the lowest of all regions for the period 1990-2001 and is now no longer significant. A trend analysis of 63 lakes in Atlantic Canada showed significant decline in SO_4^{2-} for the period 1989-1997 (Clair et al., 2002).

The regional rates of SO_4 decline in Europe were between -1.3 μeq/L/yr in the Alps and -5.6 μeq/L/yr in West-Central Europe while rates of SO_4 decline in North America were between -0.5 and -2.5 μeq/L/yr. The rates of decline for the investigated period 1994-2004 were on the whole significantly lower than for the previously reported period 1990-2001 (***Table 5***). However, if tested by aggregated region, only North America showed a significantly lower decline of sulphate in the last period. These results are consistent with a slower decline of SO_4 in surface waters than in the period of 1990-2001. This suggest that the trends from 2001-2004 have fltattend out.

Deposition of S in Europe declined on average with 65% between 1990 and 2004 (EMEP, 2006) whereas reductions in S deposition in the eastern US were about 27% in the same period (CASTNET, 2006). Both in Europe and the US, the largest decreases in S deposition were obtained between 1990 and 2000. The steeper declines in surface water SO_4 in Europe as compared to North America are consistent with the larger reductions in SO_4 deposition in Europe.

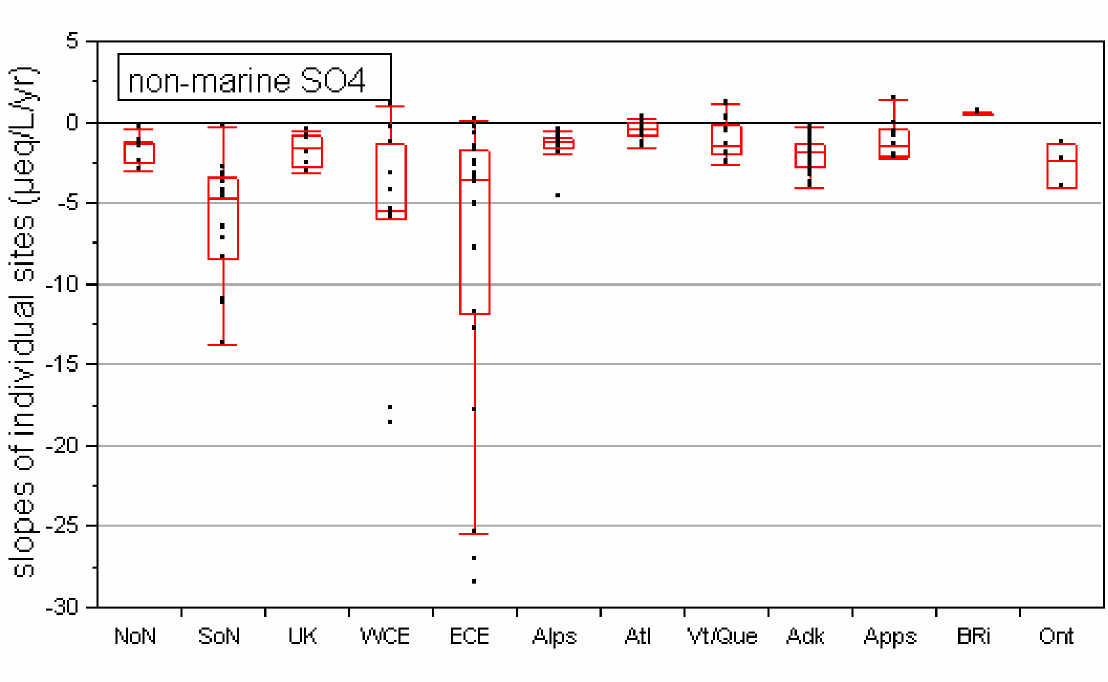

Figure 2. *Distributions of slopes for non-marine* SO_4^{2-} *trends in regions in Europe and North America. Each box shows the range (25th to 75th percentiles, with line at median) of slopes, while lines (whiskers) show the range of the data that lay within the upper (lower) quartile pluss 1.5 x the interquartile range (minus 1.5 x the interquartile range). Explanations of abbreviations are found in* ***Table 3****.*

Trends in sulphate in sites not sensitive to acidification

Some of the ICP Waters sites are regarded as insensitive to acidification (ANC > 300 µeq/L). However, we wanted to see if the general decrease in sulphate that is observed in acid sensitive sites is also found in the non-sensitive sites (***Table 6***). Only two of the eight sites show significant decreasing trends, and these trend is circa 5 to 10 times larger than for the acid-sensitive sites. Probably, the trends are influence by local sources of sulphate in the catchment, either from natural conditions (geology) or anthropogenic input (agriculture).

Table 6. *Trend slopes of nonmarine* SO_4 *in sites not sensitive to acidification for the period 1994-2004. Values are median slope and significance level (Mann-Kendall test). n = nr of years Significant slopes indicated in bold.*

		Trend slope SO_4^{2-} µeq/L/yr	p	n
Belarus	BY01	21.5	0.06	9
Estonia	EE01	1.1	0.59	11
Hungary	HU01	-54.5	0.06	9
Latvia	LV01	0.6	0.88	7
	LV02	**-23.1**	**0.02**	7
	LV03	-1.9	0.82	11
	LV04	**-23.8**	**0.01**	11
	LV05	-0.1	0.94	11

Trends in nitrate by region

Nitrate concentrations declined in three regions of North America (Adirondacks, Appalachians and Virginia Blue Ridge) (***Table 4***, ***Figure 3***). Only the Alps in Europe showed a significant increase. These findings are similar to the trends in nitrate found for 1990-2001 in the 15-year report. The comparison of trend strengths between 1990-2001 and 1994-2004 (***Table 5***) suggested a larger negative change in nitrate in North West Europe ($p<0.10$) in the latter period. In general, variation within each region was large. Positive and negative individual trends were present in all regions except the Alps and the Blue Ridge mountains, but here the number of sites per region was limited. In each region except the Alps and the Blue Ridge mountains, changes in SO_4 on an equivalent basis dominated changes in NO_3.

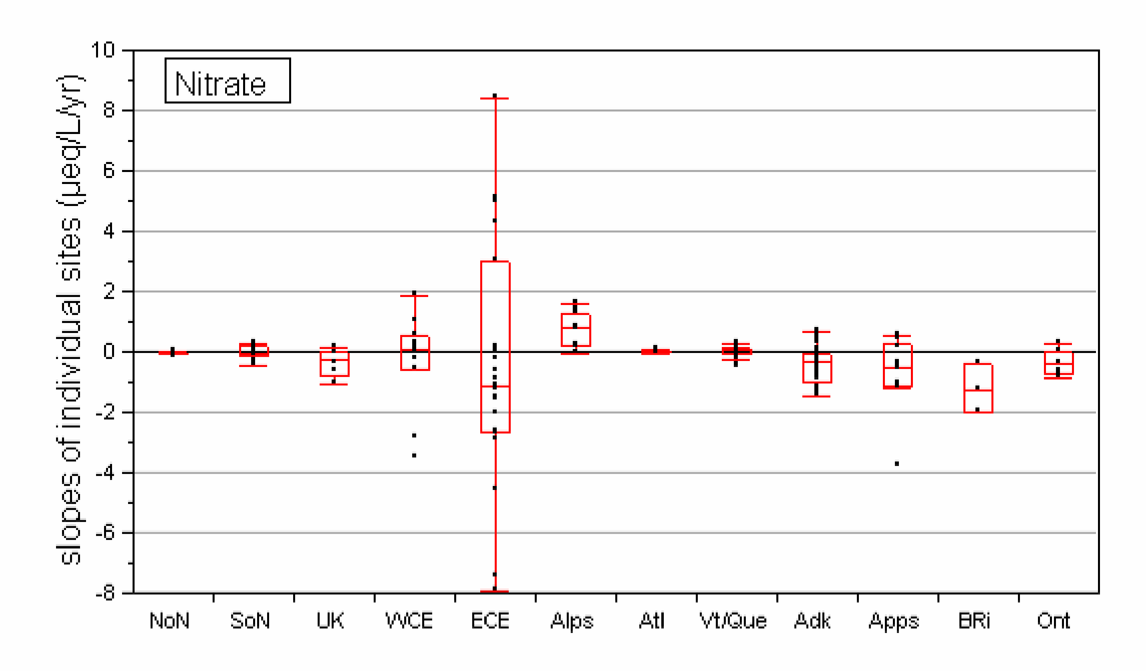

Figure 3. *Distributions of slopes for NO_3^- trends in ICP regions in Europe and North America. Interpretation of boxes and whiskers, as well as region names, are as in* ***Figure 2.***

Declines in nitrate have been observed in streamwater and lakes in New York state in USA during the period 1980-2000 (Burns et al., 2006), in reservoirs and streamwaters the Erzgebirge in southeast Germany in 1993-2003 (Ulrich et al., 2006), in alpine lakes in the Tatra mountains in Central Europe in the 1990s (Kopacek et al., 2005) and in streamwaters in forest catchments in the Czech Republic (Vesely et al., 2002). However, the lack of any consistent trends in nitrate is also commonly reported, for instance in the UK (Davies et al., 2005), in the USA (Binkley et al, 2004), for ICP Waters for the period 1980-1995 (Stoddard et al. 1999), 30 acid-sensitive catchments in Europe until the late 1990s (Wright et al., 2001) and for headwater catchments in Norway (De Wit et al., in press). The upward trend in nitrate in ICP Waters sites in the Alpine region appears thus to be an exception in reports of streamwater chemistry of acid-sensitive ecosystems. It should be noted that the upward trend in NO_3 is not a general tendency in the alpine region, but is only observed in subalpine old-growth forest catchments that have received 15-20 kg N ha^{-1} deposition over many years (Rogora et al., 2001) while high elevation lakes did not show significant trends.

Thus, while nitrate decline seems to be far more common than nitrate increases in surface waters, the majority of catchments shows no trend. The interpretation of various downward trends includes regrowth of young forest in the Central Europe (Vesely et al., 2002; Ulrich et al., 2002), increased retention of atmospherically deposited N because of increased frequency of snow melt events (De Wit et al., in press) and changes in hydrology (Burns et al., 2006). The upward nitrate trend in the Alps is interpreted as a sign of limited N retention capacity of old growth forests, and possibly climate warming (Rogora et al., in press).

As shown above, the distribution of nitrate trends and the mechanisms proposed to explain these tendencies differ greatly. It should be underlined, in agreement with the former trend report of ICP Waters, that reduced streamwater nitrate is not a certain indication of recovery.

Unlike SO_4, nitrate concentrations in many ICP Waters sites show substantial internannual variability (much of which may be linked to climatic variation, e.g. Monteith et al. (2000)) and the 10 year period assessed in this and previous reports is likely to be insufficiently long to reveal longer term trends.

Links between trends in deposition and runoff of nitrate are clearly more difficult to substantiate than for sulphate. Indeed, 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. However, large scale data analyses indicate that a combination of N deposition and ecosystem enrichment, expressed in the soil organic layer C to N ratio, can predict nitrate leaching in European forests (MacDonald et al., 2002). A similar assessment done for North American catchments (Aber et al., 2003) indicated a link between N deposition and N status of forest ecosystems.

Trends in nitrate and confounding factors are further discussed in **Chapter 3** and **Chapter 6**.

Trends in base cations by region

One of the expected responses of catchments to falling non-marine SO_4^{2-} inputs is the reduced leaching of non-marine base cations (Galloway et al., 1983). In this report, we use the sum of the concentrations of calcium and magnesium (Ca+Mg) as a surrogate for total base cation concentrations, because these cations are quantitatively most important at the majority of acid sensitive monitoring sites. Most of the ICP regions show no significant trends in base cations, although most tend to show decreases (***Table 4***; ***Figure 4***). Significant decreases in base cation concentrations are limited to the Northern and Southern Nordic regions in Europe and the Vermont/Quebec and Appalachians regions in North America.

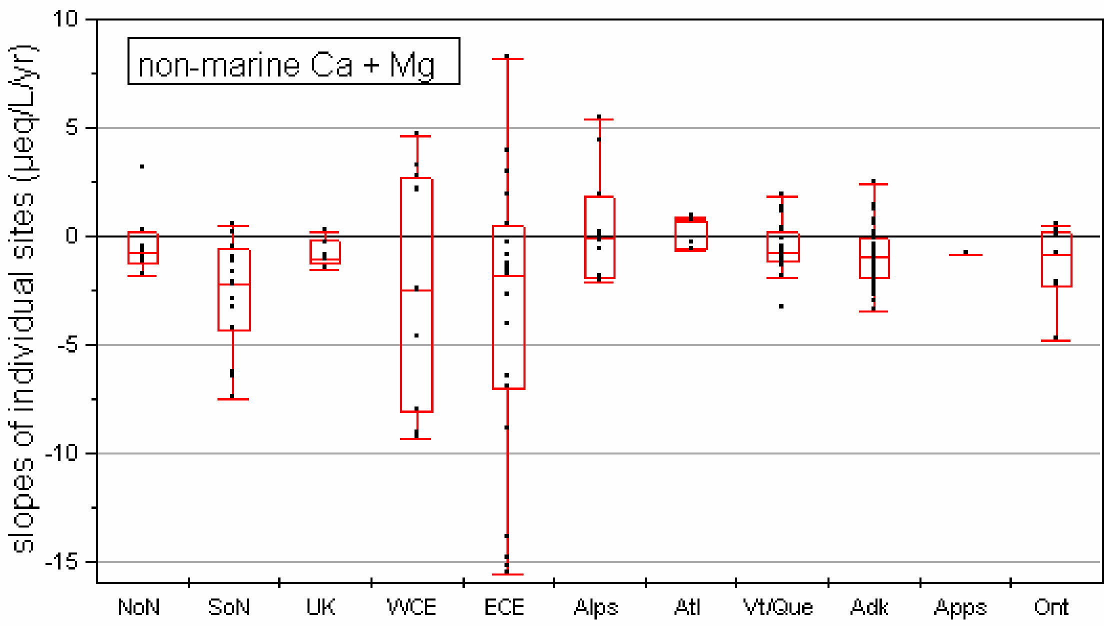

Figure 4. *Distributions of slopes for non-marine base cation (Ca+Mg) trends in ICP regions in Europe and North America. Interpretation of boxes and whiskers, as well as region names, are as in* ***Figure 2.***

For most regions the median decrease in base cations is less than the equivalent decline in SO_4. If the decrease in SO_4 was entirely balanced by a decrease in cations, no improvement of water chemistry (increase in pH, alkalinity and ANC) would be expected. The recent decline of base cations relative to SO_4 is less than observed in earlier regional assessments (Stoddard et al.

1999, Skjelkvåle et al. 2001a) and for the 1990-2001 period (***Table 5***). This is indicative of a stronger recovery of water quality than previously.

Trends in alkalinity and ANC by region

The dominating regional negative trend in SO_4, combined with the regional signal of either no change or decreasing NO_3, and the slower decline in base cations leads us to expect fairly universal increases in alkalinity, ANC and pH. Alkalinity is a measured variable that indicates the water's ability to buffer acidic inputs. ANC (acid neutralising capacity), calculated from sum of base cations minus acid anions, can be considered as a surrogate for alkalinity. However, in DOC-rich waters organic acidity can become significant compared with inorganic acidity. ANC will effectively overestimate the buffer capacity of the water under such circumstances.

Positive trends in alkalinity or ANC dominate in all but four regions (***Table 4***; **Figure 5**; ***Figure 6***). In the UK, Maine and Atlantic Canada, and Ontario neither alkalinity nor ANC show a positive trend. The strongest improvements in ANC are found in the southern Nordic region and West Central Europe, which is similar to the previous trend analysis. Evans et al. (2001a) reported that the strongest signs of recovery in the period from 1980 onwards were found in freshwaters in Central Europe. In North America, the Adirondacks and the Appalachians show the most prominent increases in ANC. There is no indication of continuing acidification, apart from a few sites in Central East Europe. On the contrary, most regions show significant recovery.

In the southern Nordic region the reduction in acid anions (-4.8 µeq/L/yr) was considerably larger than the reduction in base cations (-2.2 µeq/L/yr). The increase in alkalinity almost balanced the difference (+2.3 µeq/L/yr) whereas the trend in ANC suggests an even stronger recovery (+3.9 µeq/L/yr). In the calculation of ANC, increased organic acidity (***Table 4***) has not been included. The increase in organic acidity counteracts ongoing chemical recovery.

In the UK, the decrease in acid anions (-4.0 µeq/L/yr) was considerably larger than the reduction in base cations (-1.6 µeq/L/yr) and protons (-0.5 µeq/L/yr) but surprisingly, no increase in alkalinity or ANC was found. This may be connected to the large increase in DOC (+0.09 mg/L/yr), the influence of seasalt deposition and possibly other expressions of climatic variability (Evans et al., 2001b). Hruska et al. (2003) found a carboxyl group content of ca 8-10 µeq/mg DOC indicating a maximum charge density of 8-10 µeq/mg DOC. Thus, the annual increase in DOC in the UK has buffered the decrease in strong acid ions with possibly upto -0.8 µeq/L/yr. The UK experienced several large seasalt deposition events during the early 1990s (Evans et al., 2001) and its effects may have obscured trends in chemical recovery from acid deposition. However, the decrease in concentrations of H^+ gives a very strong indication of improved water quality in the UK. Furthermore, inorganic aluminium concentrations have declined sharply in several of the UK sites assessed here (Davies et al., 2005) and this is particularly beneficial to biological recovery.

In North America, alkalinity only improved in the Adirondacks (+0.9 µeq/L/yr) but ANC increased twice as much (+1.9 µeq/L/yr). In the previous trend analysis, four regions in North America showed a significant improvement in alkalinity, which was not found in older trend analyses (e.g. Stoddard et al. 1999, Skjelkvåle et al. 2001a). The comparison of trend strength in ANC in the periods 1990-2001 and 1994-2004 (***Table 5***) indicates a stronger increase in ANC in the most recent period in North America. This could be interpreted as an increased rate of chemical recovery in some regions in North America, in contrast to the results from the alkalinity trend analysis. Burns et al. (2006) report a slower increase in pH for the last decade in streamwater and lakes in New York state in USA for the period of 1984-2001 in contrast to the trends for the whole period.

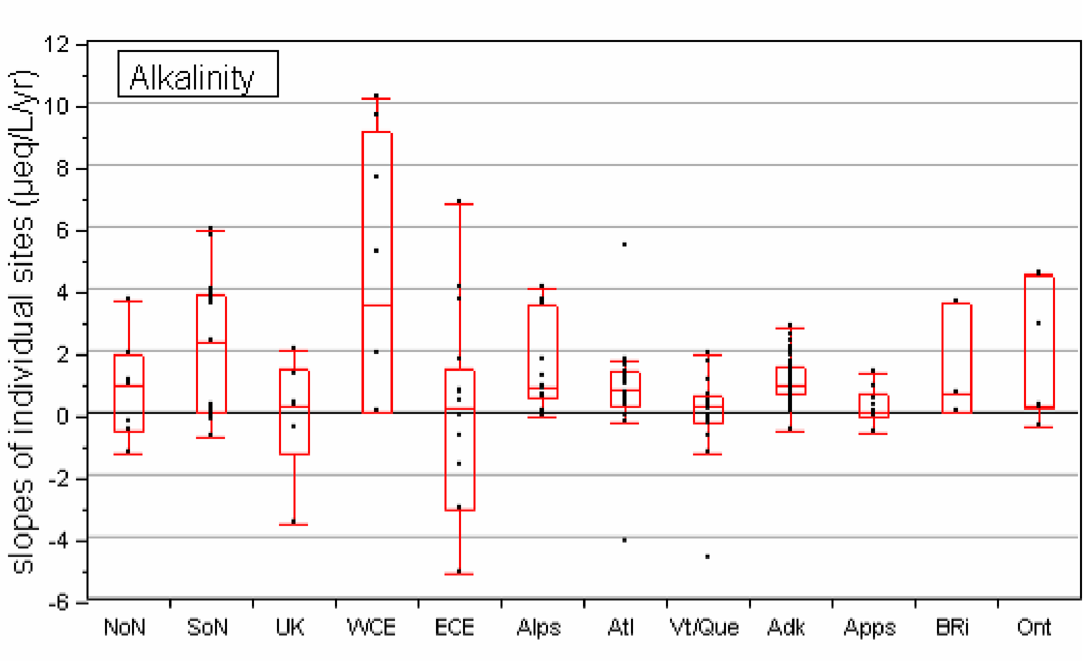

Figure 5. *Distributions of slopes for alkalinity trends in ICP regions in Europe and North America. Interpretation of boxes and whiskers, as well as region names, are as in **Figure 2.***

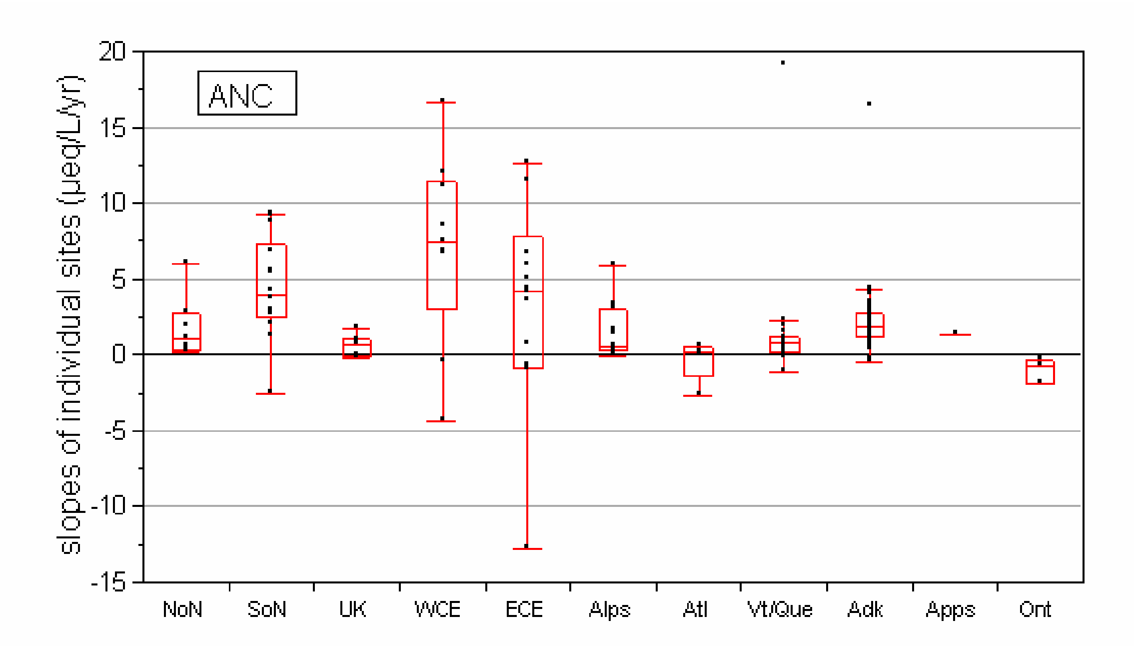

Figure 6. *Distributions of slopes for calculated ANC trends in ICP regions in Europe and North America. Interpretation of boxes and whiskers, as well as region names, are as in **Figure 2**.*

In East Central Europe, the overall decrease in acid anions was -4.7 µeq/L/yr and base cations and protons decreased ca -2.0 µeq/L/yr. Alkalinity did not increase significantly, but this variable showed a large variability (***Table 4***; **Figure 5**), probably caused by site characteristics and by variations in the analytical method to measure alkalinity employed by various laboratories (Hovind, 2005).

Trends in pH by region

Chemical recovery of surface waters involves a combination of changes towards a more natural historical, chemical composition. Increases in pH are biologically very relevant because high hydrogen concentrations can have toxic effects and also because inorganic aluminium is mobilized at low pH. Here we analyse trends in hydrogen concentrations, calculated from pH measurements. An increase in pH implies a decrease in hydrogen ion concentration.

All regions in Europe – with the possible exception of the Alps – and only one region in North America show a decrease in hydrogen ions, equivalent to an increase in pH (***Figure*** *7*; ***Table*** *4*). In the previous trend report for the period of 1990-2001, only two regions showed an increase in pH. However, there is no significant difference in trend strength in hydrogen between 1994-2004 and 1990-2001 (***Table*** *5*). The most significant changes in pH are found in West Central Europe, the south part of the Nordic countries and the UK. The first two regions experience also the most significant increases in ANC, whereas the UK lacks a trend in ANC.

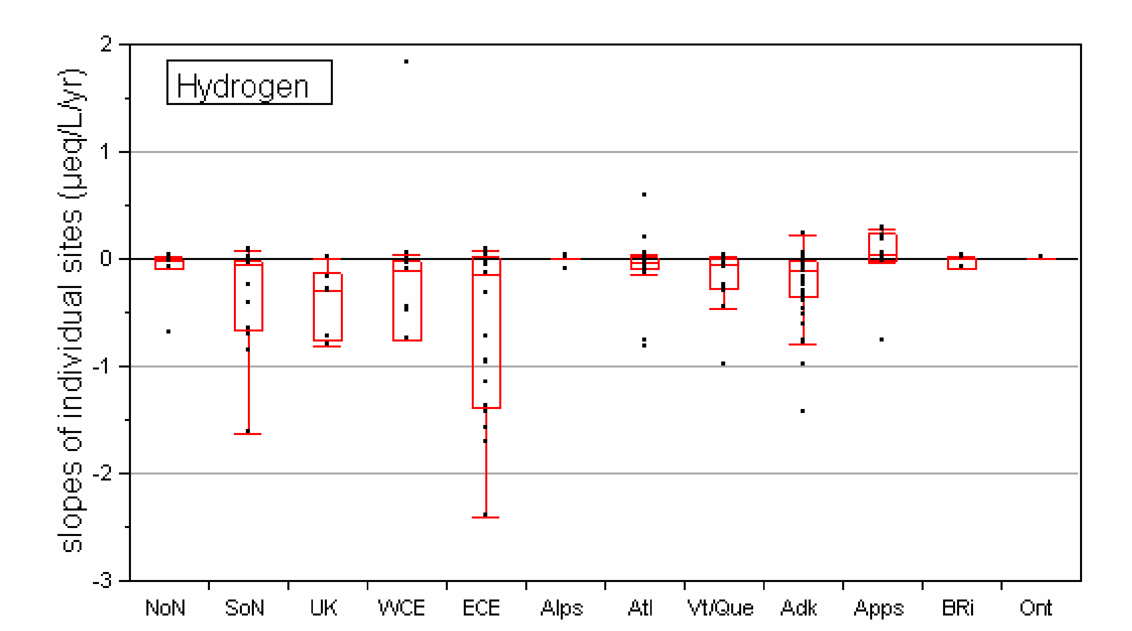

Figure 7. *Distributions of slopes for hydrogen ion trends in ICP regions in Europe and North America. Interpretation of boxes and whiskers, as well as region names, is as in* ***Figure 2****. Increasing pH (an indicator of recovery) is the same as decreasing* H^+.

Trends in DOC by region

Dissolved organic carbon (DOC) is of great interest in analyses of surface water recovery, because it is an indicator of natural organic acidity. Understanding the cause of recent increases is paramount to determining the likely ecological importance of these changes. If the rise in DOC is independent of the recovery process, an increase of organic acidity could counteract the positive effect of reduced inputs of acid anions on chemical recovery. However, if the rise in DOC is a response to reduced acid deposition, it should merely slow the rate of recovery but not overrule it. Organic molecules are also strong complexing agents for aluminium, thus potentially controlling the level of toxic aluminium in freshwaters. The previous ICP trends report (Skjelkvåle et al., 2003) was one of the first to note the widespread increases in DOC now being observed throughout Europe and North America (**Chapter 4**).

Positive trends dominate in all regions of Europe, while in North America only the Adirondacks and Ontario show an increase (**Figure 8**). Significant positive trends were found in all European regions except the furthest north and east, and in Ontario (***Table*** ***4***). The main difference with the previous trend analysis for the period 1990-2001 is the lower number of regions with significant DOC increases (4 regions in this report and 6 previously), especially due to the lack of significant trends in North America. No difference was found in the strength of the trends in different periods (***Table 5***).

Descriptions of regional patterns in DOC increases are disscussed in **Chapter 4** where it is argued that the increase in DOC in acid-sensitive ecosystems is a response to the reduction in acid deposition.

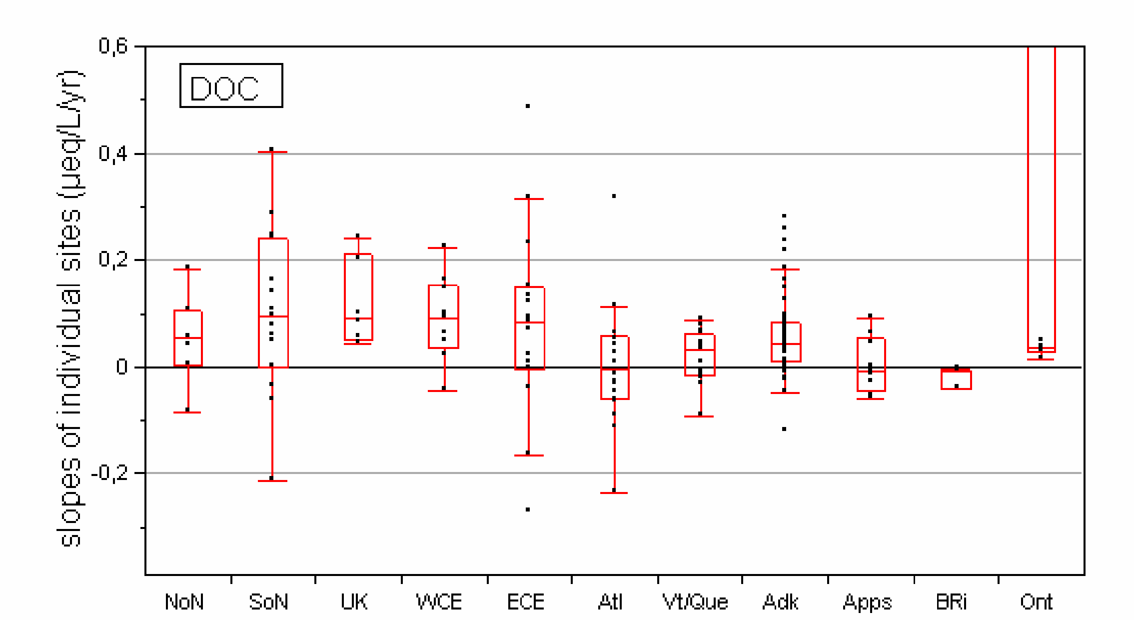

Figure 8. *Distributions of slopes for trends in dissolved organic carbon in ICP regions in Europe and North America. Interpretation of boxes and whiskers, as well as region names, are as in* ***Figure 2***.

2.6 Conclusions

The trend analysis of water chemistry between 1994 and 2004 in 179 sites (73 in Europe, 106 in North America) showed a widespread chemical recovery in streams and lakes in most regions in Europe and North America. The rate of decline in sulphate was slightly reduced relative to the previously reported period 1990-2001. All regions except two showed a significant increase in pH and/or alkalinity, and/or acid neutralizing capacity, largely due to a slower decline in non-marine base cations relative to the decline in sulphate. In the UK, no improvements in alkalinity or ANC were found despite the large reduction in sulphate combined with a lower reduction in base cations. This was thought to be related to the increase in organic acidity through the increase in dissolved organic carbon. In the Adirondacks, Appalachians and Virginia Blue Ridge a significant decline in nitrate was found while the Alps were only region with an increase in nitrate. At most sites, sulphate was the most important strong acid anion and the relative importance of nitrate in the anion load seems to be constant despite the reductions in sulphate.

The regions without signs of chemical recovery were Ontario and the Virginia Blue Ridge mountains in North America. Soil characteristics in the Blue Ridge Mountains make a sulphate decrease unlikely in the short term. The lack of coherent trends in Ontario might be due to the large variability in the trends in individual sites in the region.

References

Aber, J.D. and Driscoll, C.T. 1997. Effects of landuse, climate variation and N deposition on N cycling and C storage in the northern hardwood forests. *Global Biogeochemical Cycles* **11**: 639-648.

Aber, J.D., Goodale, C.L., Ollinger, S.V., Smith, M.L., Magill, A.H., Martin, M.E., Hallett, R.A. and Stoddard, J.L. 2003. s nitrogen deposition altering the nitrogen status of northeastern forests? *Bioscience* **53:** 375-389

Anonymous, 1996. International Cooperative Programme for Assessments and Monitoring of Acidification of Rivers and Lakes. Programme Manual. NIVA-report 3547-1996. 37 p.

Binkley, D., Ice, G.G, Kaye, J., and Williams, C.A. 2004. Nitrogen and phosphorus concentrations in forest streams of the United States. *J. of the American Water Res. Assoc.* **40**:1277-1291.

Burns, D.A., M.R. McHale, C.T. Driscoll, and K.M. Roy. 2006. Response of surface water chemistry to reduced levels of acid precipitation: comparison of trends in two regions of New York, USA. Hydrological Processes 20:1611-1627.

CASTNET. 2006. Clear Air Status and Trends Network (CASTNET). 2005 Annual Report. http://www.epa.gov/castnet/library/annual05/annual_report_2005.pdf

Clair, T.A., Ehrman, J.R, Ouellet, A.J., Brun, G., Lockerbie, D., and Ro, C. 2002. Changes in freshwater acidification trends in Canada's Atlantic Provinces: 1983-1997. *Water, Air and Soil Pollution* **135**: 335-354

Church, M.R., Shaffer, P.W, Eshelman, K.N, and Rochelle, B.P. 1990. Potential effects of sulphur deposition on stream chemistry in the Southern Blue Ridge Province. *Water Air Soil Pollut.* **50**: 39-48.

Davies, J.J.L., A. Jenkins, D.T. Monteith, C.D. Evans, and D.M. Cooper. 2005. Trends in surface water chemistry of acidified UK Freshwaters, 1988-2002. *Environmental Pollution* **137**:27-39.

De Wit, H.A., A. Hindar and L. Hole. In press. Winter climate affects long-term trends in stream water nitrate in acid-sensitive catchments in southern Norway. *Hydrol.Earth System Sci.* . 2007

Evans, C. D., Cullen, J. M., Alewell, C., Kopacek, J., Marchetto, A., Moldan, F.,Prechtel, A.,Rogora, M., Vesely, J. and Wright, R. 2001a. Recovery from acidification in European surface waters *Hydrol. Earth System Sci.* **5**: 283-297.

Evans, C.D., Monteith, D. T., and Harriman, R. 2001. Long-term variability in the deposition of marine ions at west coast sites in the UK Acid Waters Monitoring Network: impacts on surface water chemistry and significance for trend determination. *Sci.Tot.Environ.* **265**: 115-129.

EMEP. 2006. Transboundary acidification, eutrophication, and ground level ozone in Europe since 1990 to 2004. EMEP status report 1/2006. http://emep.int/publ/reports/2006/status_report_1_2006_ch.pdf

Galloway, J.N., Norton, S.A., and Church, M.R. 1983. Freshwater acidification from atmospheric deposition of sulfuric acid: A conceptual model. *Environ.Sci.Technol.* **17**: 541-545.

Hirsch, R.M. and Slack, J.R. 1984. A nonparametric trend test for seasonal data with serial dependence. *Water Resourc.Res.* **20**: 727-732.

Hirsch, R.M., Slack, J.R., and Smith, R.A. 1982. Techniques of trend analysis for monthly water quality analysis. *Water Resourc.Res.* **18**: 107-121.

Hovind, H. 2005. Intercomparison 0519. pH, Cond, HCO_3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni and Zn. ICP Waters Report 82/2005 NIVA-Report SNO 5068-2005, 70 pp.

Hruska, J., Kohler, S., Laudon, H. and Bishop, K. 2003. Is a universal model of organic acidity possible: Comparison of the acid/base properties of dissolved organic carbon in the boreal and temperate zones. *Environ. Sci. Technol.* **37:** 1726-1730

Kopacek, J., E. Stuchlik, and R.F. Wright. 2005. Long-term trends and spatial variability in nitrate leaching from alpine catchment - lake ecosystems in the Tatra Mountains (Slovakia-Poland). *Environmental Pollution* **136**:89-101.

Lettenmaier D.P. 1998. Multivariate nonparametric-tests for trend in water-quality. *Water Resources Bulletin* 24 (3): 505-512

Lükewille, A., Jeffries, D.S., Johannessen, M., Raddum, G.G., Stoddard, J.L., and Traaen, T.S. 1997. The Nine Year Report: Acidification of surface water in Europe and North America - Long-term Developments (1980s and 1990s). ICP-Waters Report 41/97 NIVA-report SNO 3637-97, Norwegian Institute for Water Research, Oslo. 168 pp.

MacDonald, J.A., N.B. Dise, E. Matzner, M. Armbruster, P. Gundersen, and M. Forsius. 2002. Nitrogen input together with ecosystem nitrogen enrichment predict nitrate leaching from European forests. Global Change Biology 8:1028-1033.

Monteith, D.T., Evans, C.D. and Reynolds, B. 2000. Are temporal variations in the nitrate content of UK upland freshwaters linked to the North Atlantic Oscillation? *Hydrological Processes* **14**: 1745-1749.

Newell, A.D. and Skjelkvåle, B.L. 1997. Acidification trends in surface waters in the International Programme on Acidification of Rivers and Lakes. *Water Air Soil Pollut.* **93**: 27-57.

Rogora, M., A. Morchetto and R. Mosello. 2001. Trends in the trends of atmospheric deposition and surface waters in the Lago Maggiore watershed. *Hydrol. Earth System Sci.* **5**: 379-390

Rogora, M., and R. Mosello. Climate as a confounding factor in the response of surface water to nitrogen deposition in an area South of the Alps. *Applied Geochemistry*, in press

Sen, P.K. 1968. Estimates of regression coefficients based on Kendall's tau. *J. of the American Statistical Assoc.***63**:1379-1389.

Skjelkvale, B.L., J.L. Stoddard, D.S. Jeffries, K. Torseth, T. Hogasen, J. Bowman, J. Mannio, D.T. Monteith, R. Mosello, M. Rogora, D. Rzychon, J. Vesely, J. Wieting, A. Wilander, and A. Worsztynowicz. 2005. Regional scale evidence for improvements in surface water chemistry 1990-2001. *Environmental Pollution* **137**:165-176.

Skjelkvåle, B.L. (ed). 2003. The 15-year report: Assessment and monitoring of surface waters in Europe and North America; acidification and recovery, dynamic modelling and heavy metals. NIVA-report SNO 4716-2003, ICP Waters report 73/2003

Skjelkvåle, B.L., Andersen, T., Fjeld, E., Mannio, J. and Wilander, A. 2001a. Recovery from acidification of lakes in Finland, Norway and Sweden 1990-1999. *Hydrol.Earth System Sci.* **5**: 327-338.

Skjelkvåle, B.L., Stoddard, J.L., and Andersen, T. 2001b. Trends in surface waters acidification in Europe and North America (1989-1998). *Water Air Soil Pollut.* **130**: 787-792.

Skjelkvåle, B.L.(ed.). 2000. The 12-year report; Acidification of surface water in Europe and North America; trends, biological recovery and heavy metals. SNO 4208/2000, ICP Waters report 52/2000, Norwegian Institute for Water Research, 108 pp.

Skjelkvåle, B.L., Newell, A.D., Raddum, G.G., Johannessen, M., Hovind, H., Tjomsland, T., and Wathne, B.M. 1994. The six year report: Acidification of surface water in Europe and North America. Dose/response relationships and long-term trends. NIVA-report SNO 3041-94, Norwegian Institute for Water Research, Oslo, Norway. 135 pp.

Stoddard, J.L., Kahl, J.S., Deviny, F.A, DeWalle, D.R, Driscoll, C.T., Herlihy, A.T., Kellogg, J.H., Murdoch, P.S., and Webster, K.E. 2003. Responses of Surface Water Chemistry to the Clean Air Act Amendments of 1990. EPA 620/R-03/001, EPA United States Environmental Protection Agency, 78 pp.

Stoddard, J.L., Jeffries, D.S., Lükewille, A., Clair, T.A., Dillon, P.J., Driscoll, C.T., Forsius, M., Johannessen, M., Kahl, J.S., Kellogg, J.H., Kemp, A., Mannio, J., Monteith, D., Murdoch, P. S., Patrick, S., Rebsdorf, A., Skjelkvåle, B.L., Stainton, M.P., Traaen, T.S., van Dam, H., Webster, K.E., Wieting, J. and Wilander, A. 1999. Regional trends in aquatic recovery from acidification in North America and Europe 1980-95. *Nature* **401**: 575-578.

Stoddard, J.L. 1994. Long-Term Changes in Watershed Retention of Nitrogen: its causes and aquatic consequences, p.223-284, In: Baker, L. A., *Environmental Chemistry of Lakes and Reservoirs*, ACS Advances in Chemistry Series no. 237. American Chemical Society, Washington DC.

Ulrich, K.U., L. Paul, and A. Meybohm. 2006. Response of drinking-water reservoir ecosystems to decreased acidic atmospheric deposition in SE Germany: Trends of chemical reversal. *Environmental Pollution* **141**:42-53.

Vesely, J., V. Majer, and S.A. Norton. 2002. Heterogeneous response of central European streams to decreased acidic atmospheric deposition. Environmental Pollution 120:275-281.

Wathne, B.M. 1991. The Three Year Report: Summary and Results 1987-1989. Norwegian Institute for Water Research. ICP Waters report 14/1991

Wright, R., Alewell, C., Cullen, J., Evans, C. ., Marchetto, A., Moldan, F., Prechtel, A., and Rogora, M. 2001. Trends in nitrogen deposition and leaching in acid-sensitive streams in Europe. *Hydrol.Earth System Sci.* **5**: 299-310.

3. Nitrogen runoff at ICP Waters sites 1990-2005: Increasing importance of confounding factors?

Øyvind Kaste, Heleen de Wit, Brit Lisa Skjelkvåle, Tore Høgåsen

ICP Waters Programme Centre, Norwegian Institute for Water Research, Oslo, Norway

3.1 Introduction

Emissions of oxidised N species from combustion of fossil fuels and emissions of reduced N compounds from agriculture increased dramatically in Europe during the 1900's and reached peak levels about 1980 (Schöpp et al. 2003). After this, the emissions levelled off during the 1980s, and a slight decrease has been reported since 1990. The European averaged decrease in N deposition from air during the 1990s is somewhat smaller than the reported emission decrease, although there are significant differences from country to country (Tarrasón et al. 2006).

Excess N deposition is viewed as a threat to the nutrient balance and health of forest and semi-natural terrestrial ecosystems (Aber et al, 1989, Stoddard 1994) by promoting increased leaching of inorganic N (generally NO_3^-) below the root zone and causing increased concentrations of inorganic N in runoff. In turn, this enhances the risk of acidification of soils and surface waters.

Even though N deposition is generally regarded as the main driver behind N leaching from soils to surface water, ecosystems are also affected by a number of other pressures that may cause disturbance and subsequent N losses. On a regional scale, climate variability or extreme events probably represent the major influence, whereas forest cutting, ditching and insect attacks can be important confounding factors on the local catchment level (Vitousek at al. 1979).

Since 1988, the ICP Waters programme has provided a valuable basis for evaluation of NO_3^- trends in surface waters in a large number of sites in Europe and North America. The aim of this chapter is to:

- give an updated report on status of NO_3^- in surface waters at ICP Waters sites
- identify sites where trends in N runoff may be a result of other factors than N deposition.

3.2 Sites and data sources

This chapter includes data from 177 ICP Waters sites with data covering the period from 1990 to 2004-05 (Canada: 17, Czech Republic: 6, Germany: 31, Estonia: 1, Finland: 8, Italy: 6, Norway: 5, Sweden: 9, UK: 6, and USA: 88). Not all sites have sufficient data for all types of analysis – therefore all tables and figures in this chapter contain information about the number of sites included. Nitrate concentrations reported in the ICP Waters programme are measured using a variety of analytical methods. However, annual cross-comparisons of methods using audit samples of known concentration, conducted by ICP Waters (Hovind, 2000), showed excellent agreement among the national laboraties.

All deposition data used here are provided by the European Monitoring and Assessment Programme (EMEP), both from Meteorological Synthesising Centre - West (MSC-W) and the Coordination centre for Chemistry (CCC). The data comprise measured concentrations in air and precipitation at EMEP sites across Europe and modelled total (wet + dry) deposition by country (Tarrasón et al. 2006; Fagerli and Aas, submitted). The EMEP model uses estimated annual emissions and actual meteorology for each year to calculate wet and dry deposition of S, oxidised N and reduced N compounds.

In this report, we have used measured concentrations in precipitation at EMEP sites located in the same region as the streamwater sites.

3.3 Results

3.3.1 Spatial variation

There is a large spatial variation in NO_3^- concentrations in the different regions included in the ICP Waters Programme (***Figure 9***; ***Figure 10***). The highest concentrations are in eastern and western central Europe (ECE and WCE) and in the Alps (represented by the northwestern parts of Italy). In North America, sites in the Adirondacks, Appalachian Plateau, and in the Upper Midwest show the highest concentrations, although much lower than in Central Europe. Lowest NO_3^- concentrations appear in the northern Nordic (NoN) and southern Nordic (SoN) regions and in the Atlantic part of USA and Canada.

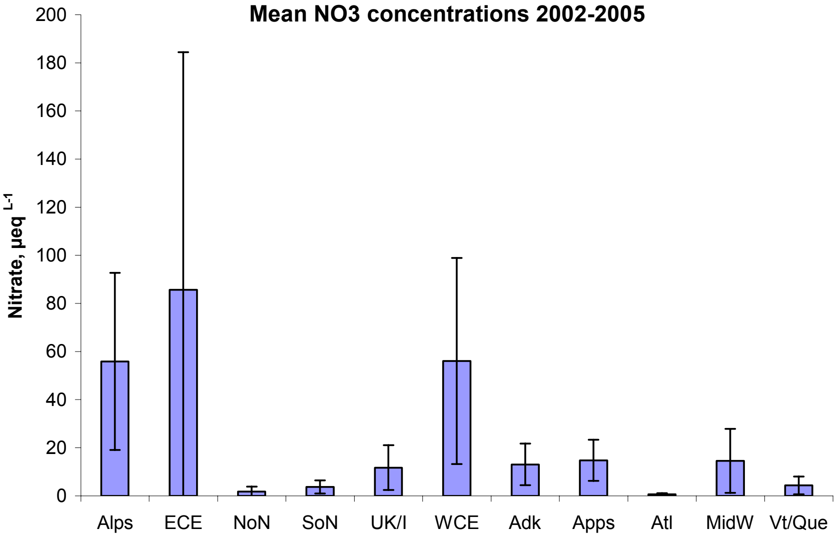

Figure 9. *Mean nitrate concentrations surface waters in different regions of Europe and North America during the period 2002-2005. Y-error bars indicate the standard deviation.*

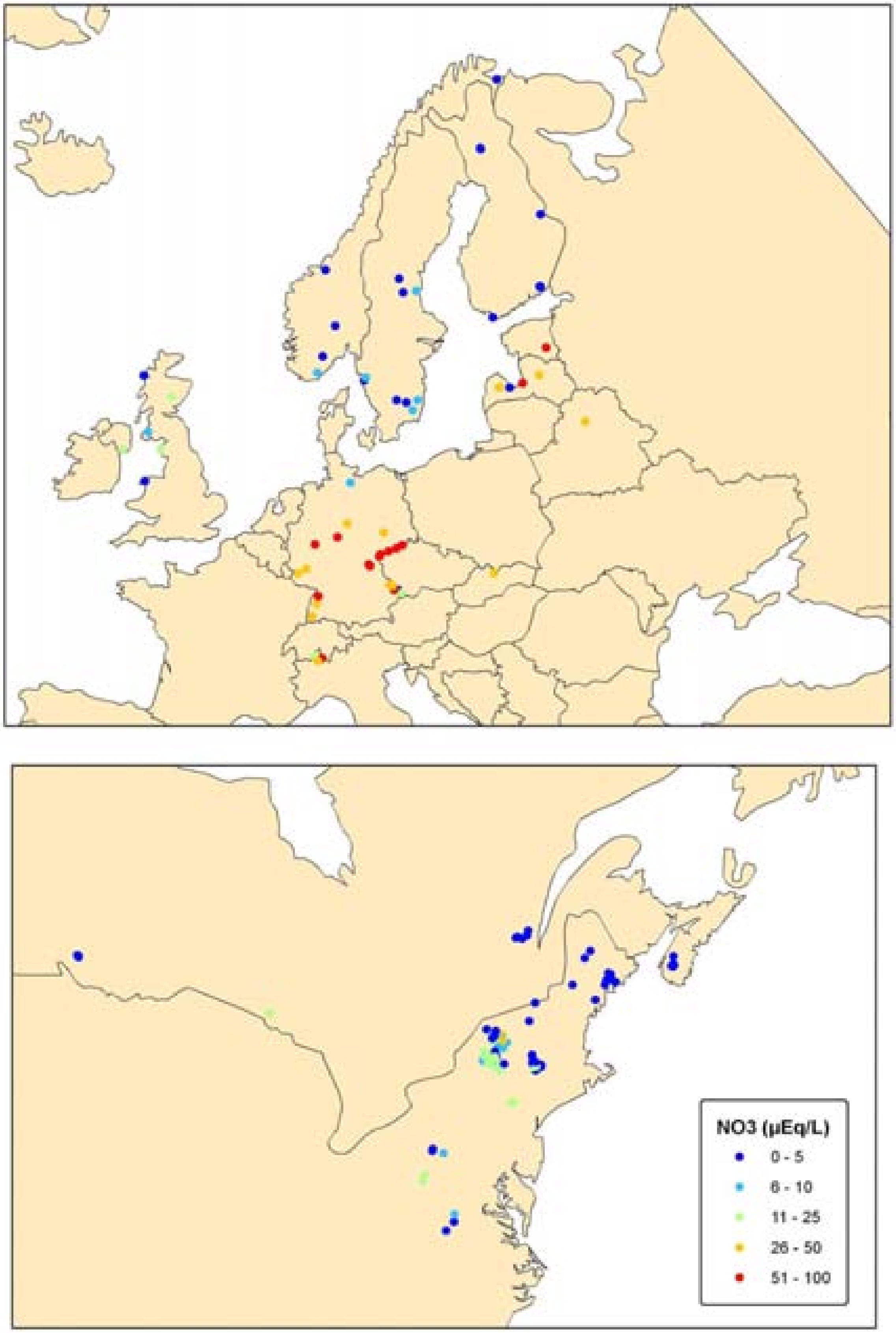

Figure 10. *Maps showing mean annual* NO_3^- *concentrations at European and North American ICP Waters sites in 2004 (unit µeq* L^{-1}*). The maps also include sites not included in the main analysis.*

3.3.2 Nitrogen runoff concentrations 1990-2005

Nitrate

There has been a slight increase in the number of sites with mean concentrations of NO_3^- below 5 µeq L^{-1}, from 34% in 1990-93 to 41% in 2002-05 (***Figure 11***). About half of the sites have NO_3^- concentrations above 10 µeq L^{-1}. Due to the seasonal and episodic patterns of NO_3^-, however, the significance of NO_3^- in acidification is usually greater in certain parts of the year (e.g., spring) than illustrated by the mean concentrations in this Figure. The largest decrease has occurred in the concentration interval 25-50 µeq L^{-1}. In 2002-05, 9% of the lakes belonged to this category, compared to 18% during 1990-93.

The frequency of sites with NO_3^- concentrations greater than 50 µeq L^{-1} has remained surprisingly stable during the study period (16%). This might indicate that sites within this group are exposed also to other kinds of disturbance than N deposition alone. Most of the sites with mean NO_3^- concentrations higher than 50 µeq L^{-1} are located in Germany, Latvia, Estonia, Italy, Czech Republic, Belarus and Hungary. Unweighted mean values, as used here, may underestimate actual annual means, particularly in catchments with heavy snowmelt in spring.

A division of data between Europe and North America reveals relatively large differences in frequency distribution (***Figure 12***). 50% the North American sites are presently found within the <5µeq L^{-1} group, while only 28% of the European sites are found here. On the other hand, 40% of the European sites had NO_3^- concentrations greater than 50 µeq L^{-1}, while no sites in North America were found within this category. Additionally, the regions of North America included in ICP Waters have experienced a strong reduction in the number of sites with NO_3^- concentrations in the range 25-50 µeq L^{-1} (from 18% in 1990-93 to 6% in the latest period).

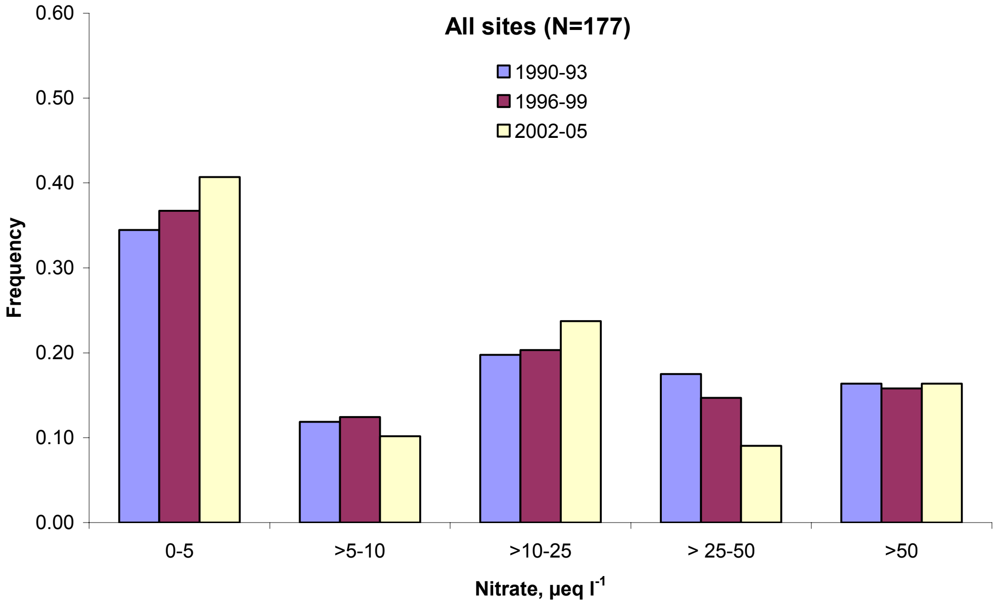

Figure 11. *Frequency distribution of mean annual NO_3^- concentrations at 177 ICP Waters sites with data from the periods 1990-93, 1996-99 and 2002-05.*

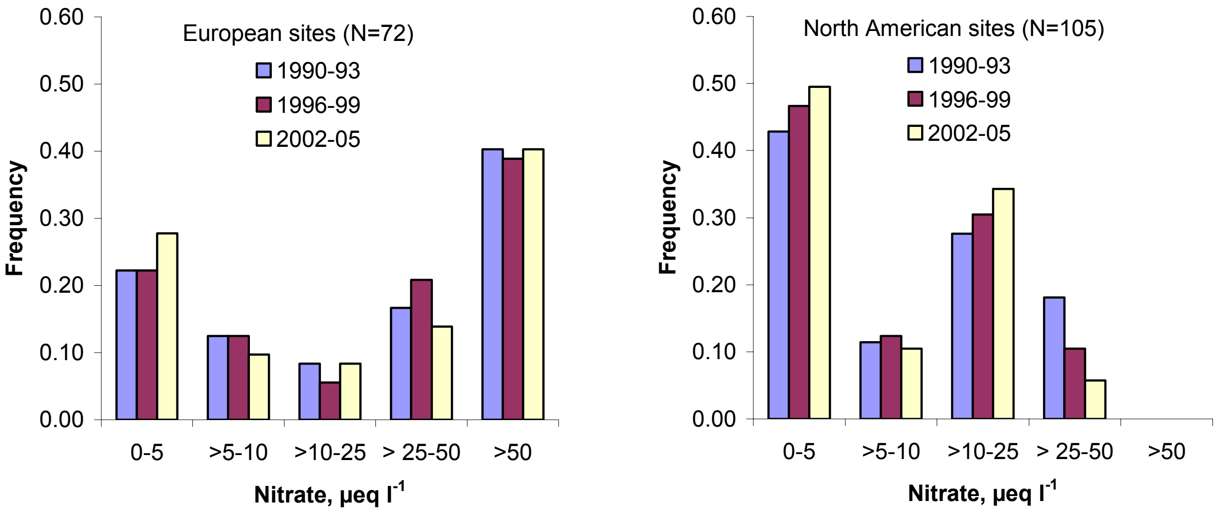

Figure 12. *The same data as shown in* ***Figure 11****, but divided between Europe and North America.*

Ammonium

Concentrations of NH_4^+ are generally low at the ICP Waters sites. About 65% of the sites have NH_4^+ concentrations below 2 µeq L^{-1}, and about 90% show concentrations below 5 µeq L^{-1}. There are only small differences between the time periods 1990-93, 1996-99 and 2002-05 with respect to NH_4^+ concentrations. Within the latest period no sites showed NH_4^+ concentrations higher than 15 µg L^{-1}. During 2002-05, the ratio of NH_4^+ to NO_3^- averaged 0.09 at the 119 sites with both species analysed, with a range from 0.01 to 3.85.

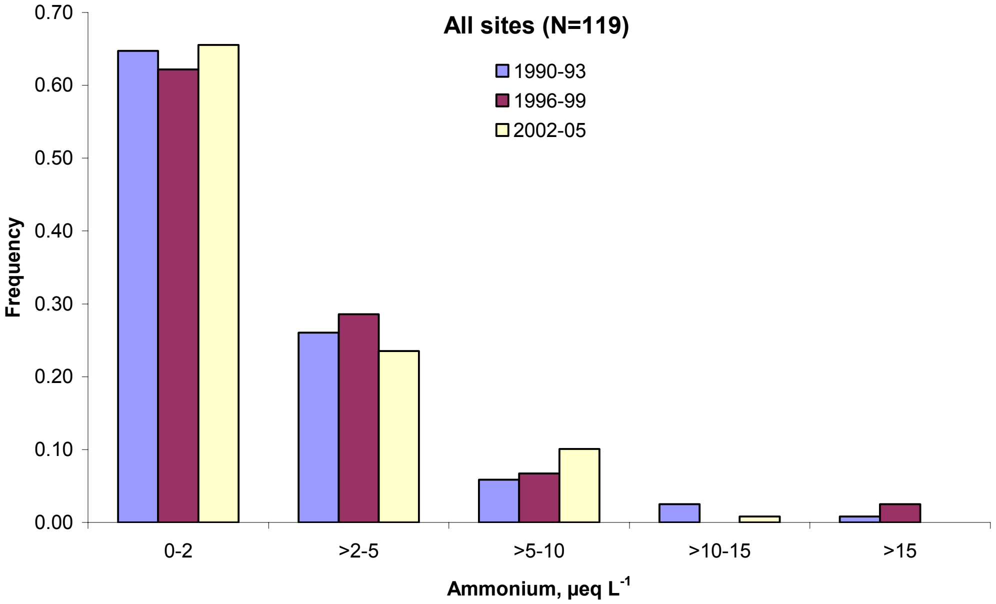

Figure 13. *Frequency distribution of mean annual* NH_4^+ *concentrations at 119 ICP Waters sites with data from the periods 1990-93, 1996-99 and 2002-05.*

3.3.3 Relative importance of nitrate vs. sulphate

The importance of NO_3^- in acidification relative to SO_4^{2-} in surface waters can be estimated by the concentration of NO_3^- divided by the sum of non-marine SO_4^{2-} (denoted by asterisk) and NO_3^-

$$\text{N acidification ratio (NAR)} = \frac{NO_3^-}{\left(SO_4 * + NO_3^-\right)} \quad \text{(all concentrations in µeq L}^{-1}\text{)}$$

Given the large reduction in SO_4^{2-} deposition since 1990, there has been a surprisingly little change in NAR-values at the ICP Waters sites up to now (***Figure 14***). The main reason for this is that many sites have experienced decreasing NO_3^- concentrations during the same period. At about 50% of the sites, NO_3^- played a minor role in the acidification of surface water during 2002-05 (NAR-values < 0.1). During the same period, 1/3 of the sites were moderately affected (0.1 < NAR < 0.25) and 17% heavily affected (NAR > 0.25). At 6% of the sites, most of them located in Germany and Italy, NO_3^- was a more important factor than SO_4^{2-} in the acidification of surface waters (NAR > 0.5). This fraction has increased from 2% in 1990-93 to 6% in 2002-2005.

It is important to note that the analysis above is based on mean values. NO_3^- usually have a stronger seasonal pattern than SO_4^{2-}, with the highest concentrations appearing during the dormant season, while the concentrations may decrease below the detection limits during summer. The contribution of NO_3^- to acidification of rivers and lakes therefore can be much higher during certain parts of the year than indicated in ***Figure 14***.

A division of data between Europe and North America (***Figure 15***) shows that the American sites are more moderately affected by N-acidification than many European sites. During the latest period, 98% of the North American sites had NAR-values below 0.25, while the corresponding fraction for the European sites was 63%. At 14% of the European sites NO_3^- was a more important factor than SO_4^{2-} in the acidification of surface waters during 2002-05.

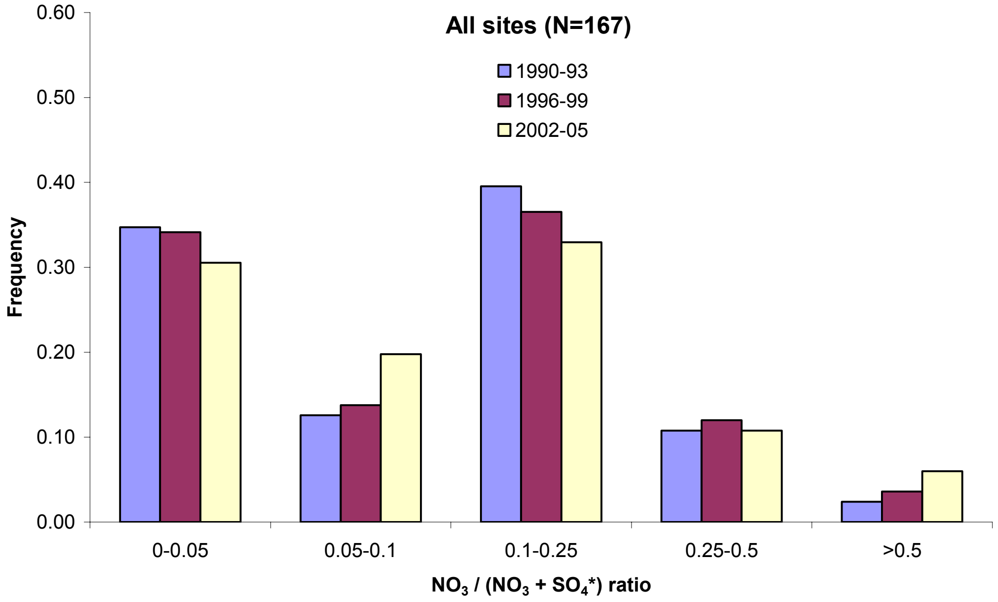

Figure 14. *Relative importance of NO_3^- in acidification at 167 ICP Waters sites in 1990-93 compared to the period 2002-05 for the same sites.*

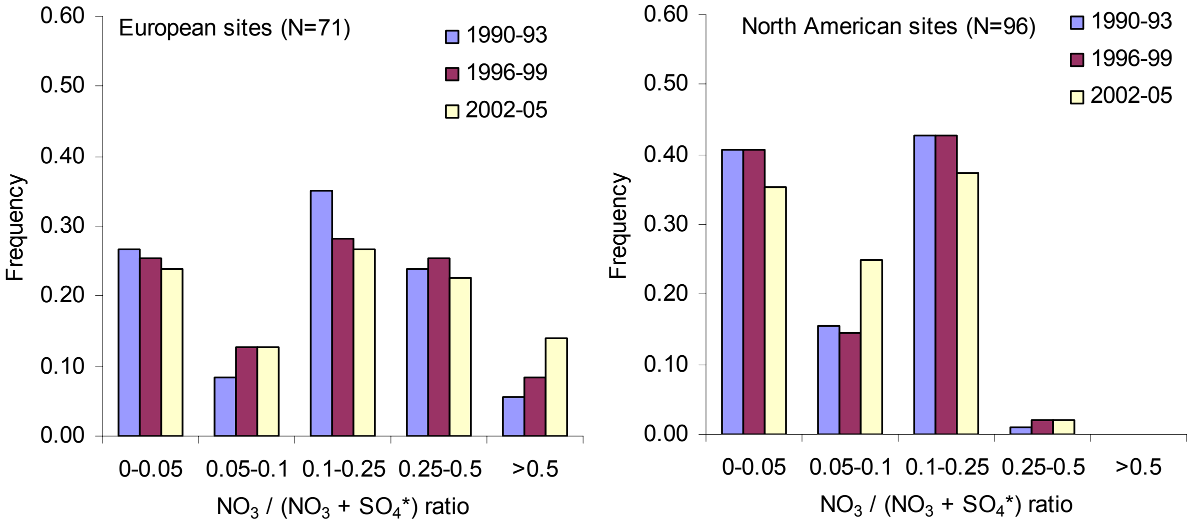

Figure 15. *The same data as shown in* ***Figure 14*** *but divided between North America and Europe.*

3.3.4 Relationships between deposition and runoff of nitrogen

Empirical data from forested ecosystems in Europe show a clear relationship between N deposition and N loss (Dise and Wright 1995, Gundersen et al. 1998). These data indicate that very little NO_3^- leaching occurs at N deposition below 9-10 kg N ha^{-1} yr^{-1}, leaching can occur at intermediate deposition between 9 and 25 kg N ha^{-1} yr^{-1}, and significant leaching occurs at all sites receiving deposition greater than 25 kg N ha^{-1} yr^{-1}. These thresholds are based on data from monitoring plots across a gradient of current N deposition in Europe and from several experimental sites.

Input/output data for NO_3^- are not available for most of the ICP Waters sites. However, a general view of N leakage is obtained by comparing the concentrations of total inorganic N (TIN = NO_3^- + NH_4^+) in runoff with TIN concentrations in precipitation interpolated from adjacent EMEP stations (***Figure 16***). Altogether 54 sites with long-term data for both TIN runoff and TIN deposition are included in this analysis. The North American sites are not included due to lack of deposition data.

The results support the general picture that increased TIN concentrations occur in catchments receiving N deposition above certain thresholds. At sites with precipitation concentrations below 0.25 mg N L^{-1}, runoff TIN concentrations did not exceed 5 µeq L^{-1}. This was typically remote sites in Scandinavia and Scotland. In areas with precipitation concentrations in the range 0.25 – 0.7 mg N L^{-1}, TIN runoff reached 30 µeq L^{-1}. This included the more polluted locations in Scandinavia together with sites in the Czech Republic, UK, and Italy. Above this deposition level, runoff concentrations spanned a wide range from below 2 µeq L^{-1} to more than 300 µeq L^{-1}. The latter illustrates that catchment N retention capacity is highly variable among sites, depending on landscape characteristics, site history and different types of disturbance. Sites included in this group were located in Germany, the Czech Republic and in Italy. Absolute threshold values for ICP Waters sites are uncertain for several reasons; the deposition data are not site specific, the sampling frequency is low at many sites, and the amount of N leaked is influenced by both deposition level and site history.

From earlier assessments, it appears that North American catchments show substantial N leaching at much lower deposition levels than in Europe (Stoddard 1994). The possible difference in threshold values between the European and North American continents is an interesting phenomenon, but not yet possible to study within the ICP Waters programme.

When comparing the periods 1990-93, 1996-99 and 2002-05, there was a successive reduction in TIN concentrations in precipitation, with maximum concentrations reaching 1.55, 1.28 and 1.11 mg N L^{-1}, respectively (***Figure 16***). In most cases this was followed by a corresponding decrease in maximum concentrations of TIN in runoff. This suggests a relatively fast response of the ecosystems to the reduced loading of atmospheric N, which is in good accordance with results from various ‘roof experiments’ (where acid deposition was removed from an area by shielding it with a roof) (Tietema et al. 1998, Wright et al. 2001).

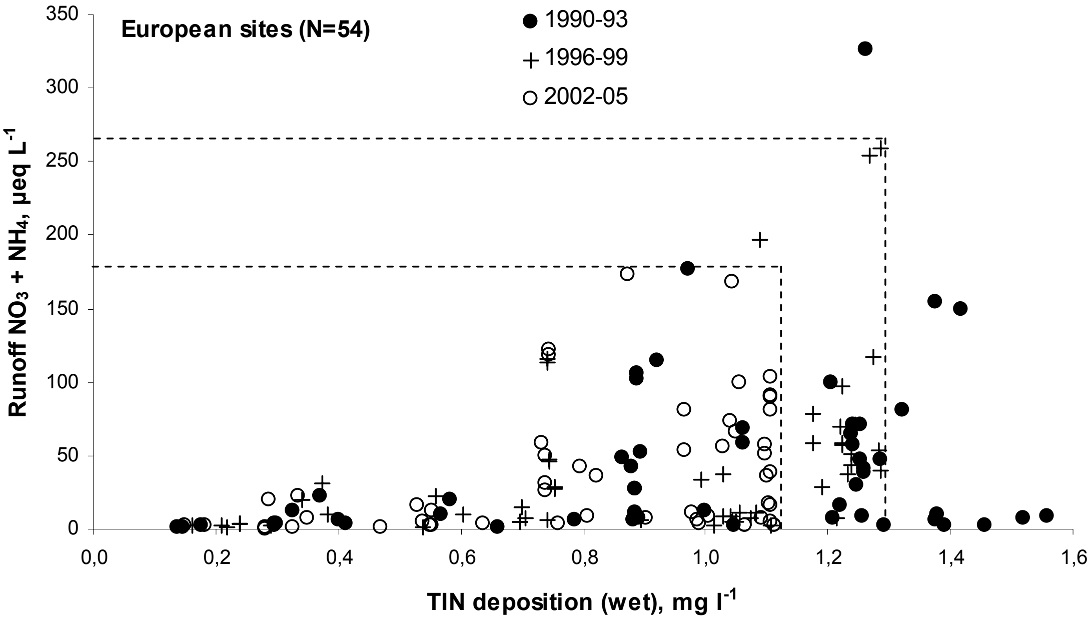

Figure 16. *Nitrogen (NO_3^- + NH_4^+) concentration in runoff and total inorganic N concentrations in deposition for 54 European ICP Waters sites in 1990-93, 1996-99, and 2002-05 (deposition data for 2002-03 only). The dotted lines indicate the successive change in maximum TIN deposition and TIN runoff with time.*

3.4 Possible roles of confounding factors in trends of N runoff

Trend analyses of surface water chemistry are presented in **Chapter 2**. Altogether there were 55 sites with sufficient data for trend analysis of both N deposition and NO_3^- runoff during the period 1994-2004 (54 sites covering the period 1990-2001). ***Figure 17*** combines the two types of analysis, in an attempt to categorise sites with converging trends in precipitation and runoff versus sites with diverging trends. Within the latter group, there is a possibility that NO_3^- runoff is regulated by other driving forces (confounding factors) than deposition.

At most sites, there are no clear trends in precipitation or runoff concentrations of N. During the earliest period (1990-2001) there were more sites with significantly decreasing trends in N deposition than in the period 1994-2004 (***Figure 17***). In both periods there are only two sites with significantly increasing N deposition. These are located in northern Norway and Finland, both close to the Russian border.

Only four sites in 1990-2001 and two sites in 1994-2004 show decreasing trends in both N deposition and NO_3^- runoff. These were located in Norway (2), Czech Republic (1) and

Germany (2). Diverging (opposite) trends were recorded at two Swedish sites (increasing NO_3^- runoff despite reduced deposition) and one site in northern Norway (decreasing N runoff despite increased deposition).

A) 1990-2001 (N=54)

		Trend in N deposition		
		+	0	-
Trend in N runoff	+	**0**	**7**	**2**
	0	**1**	**19**	**14**
	-	**0**	**7**	**4**

B) 1994-2004 (N=55)

		Trend in N deposition		
		+	0	-
Trend in N runoff	+	**0**	**8**	**0**
	0	**1**	**30**	**3**
	-	**1**	**10**	**2**

Figure 17. *Trends in* NO_3^- *runoff vs. trends in N deposition (concentration of total inorganic N in precipitation) at 54 ICP Waters sites during two different time periods analysed by the Mann-Kendall test (se chapter 2). Notation: + significant increase (p<0.05), 0 No significant trend, - significant decrease (p<0.05).*

3.5 Summary and conclusions

Many of the ICP Waters sites have been experiencing a slight decrease in precipitation N concentrations since the early 1990s. The results from the ICP Water Programme during 1990-2005 support the general picture that high TIN concentrations occur in catchments that receive N deposition above certain thresholds. Catchment N retention capacity is highly variable among sites, depending on landscape characteristics, site history and different types of disturbance. Comparison of the periods 1990-93, 1996-99 and 2002-05 at 55 ICP Waters sites shows a successive reduction in maximum concentrations of TIN in precipitation. In most cases this has been followed by a corresponding decrease in maximum concentrations of TIN in runoff.

When looking at individual sites, however, relatively few show significant downward trends in NO_3^- runoff concentrations (also **see Chapter 2**). There might be several reasons for this, for instance large inter-annual variation, large internal N stores or different types of disturbance. At some sites, there are in fact diverging (opposite) trends in deposition and runoff, which indicate that NO_3^- runoff is regulated by other driving forces (confounding factors) than deposition alone. Many of these can be directly or indirectly related to climate (floods, droughts, storms, heat waves, insect outbreaks, etc.) or catchment management (e.g., water regulations, ditching, forest cutting and re-growth). Many of these possible confounding factors are discussed further in **Chapter 6** of this report.

References

Aber, J. D., Nadelhoffer, K. J., Steudler, P., and Melillo, J. 1989. Nitrogen saturation in northern forest ecosystems. *Bioscience* **39**: 378-386.

Dise, N. B. and Wright, R. F. 1995. Nitrogen leaching from European forests in relation to nitrogen deposition. *For.Ecol.Manage.* **71**: 153-162.

Gundersen, P., Callesen, I., and de Vries, W. 1998. Nitrate leaching in forest ecosystems is controlled by forest floor C/N ratio. *Environ.Pollut.* **102**: 403-407.

Hovind, H. 2000. Trends in intercomparisons 8701-9812: pH, K25, NO3 + NO2, Cl, SO4, Ca, Mg, Na, K and aluminium - reactive and nonlabile, TOC, COD-Mn. NIVA-Report SNO 4281-2000, ICP Waters Report 56/2000. ISBN 82-577-3910-3.

Schöpp, W., Posch, M., Mylona, S., and Johansson, M. 2003. Long-tern development of acid deposition (1880-2030) in sensitive freshwater regions in Europe. *Hydrol. Earth Syst. Sci.* **7**: 436-446.

Stoddard, J. L. 1994. Long-Term Changes in Watershed Retention of Nitrogen: its causes and aquatic consequences, p.223-284, In: Baker, L. A., *Environmental Chemistry of Lakes and Reservoirs*, ACS Advances in Chemistry Series no. 237., American Chemical Society, Washington,DC.

Tarrasón, L., Fagerli, H., Klein, H., Simpson, D., Benedictow, A.C., Vestreng, V., Rigler, E., Emberson, L., Posch, M., and Spranger, T. 2006. Transboundary acidification, eutrophication and ground level ozone in Europe from 1990 to 2004 in support for the review of the Gothenburg Protocol. EMEP Status report 1/2006, ISSN 1504-6192 (online), 93 pp.

Tietema, A., Boxman, A.W., Bredemeier, M., Emmett, B.A., Moldan, F., Gundersen, P., Schleppi, P., and Wright, R.F. 1998. Nitrogen saturation experiments (NITREX) in coniferous forest ecosystems in Europe: A summary of results. *Environ. Pollut.* **102**: 433-437.

Vitousek, P.M., Gosz, J.R., Grier, C.C., Melillo, J.M., Reiners, W.A. & Todd, R.L. 1979. Nitrate losses from disturbed ecosystems. *Science* **204**: 469-474.

Wright, R.F., Alewell, C., Cullen, J., Evans, C., Marchetto, A., Moldan, F., Prechtel, A., and Rogora, M. 2001b. Trends in nitrogen deposition and leaching in acid-sensitive streams in Europe. *Hydrol. Earth System Sci.* **5**: 299-310.

4. Increases in DOC in remote lakes and rivers

A signal of climate change or return to pre-acidification conditions?

D.T. Monteith (Environmental Change Research Centre, UCL, London, UK)
J.L. Stoddard (U.S. EPA, Corvallis, Oregon, USA)
C.D. Evans (Centre for Ecology and Hydrology, Bangor, UK)
H.A. de Wit (Norwegian Institute of Water Research, Oslo, Norway)
M. Forsius (Finnish Environment Institute, Helsinki, Finland)
T. Høgåsen (Norwegian Institute of Water Research, Oslo, Norway)
D.S. Jeffries (Environment Canada, Burlington, Ontario, Canada)
J. Kopácek (Hydrobiological Institute, Ceske Budejovicé, Czech Republic)
B.L. Skjelkvåle (Norwegian Institute of Water Research, Oslo, Norway)
J. Vesely (Czech Geological Survey, Prague, Czech Republic)
J. Vuorenmaa (Finnish Environment Institute, Helsinki, Finland)
A. Wilander (University of Agricultural Sciences, Uppsala, Sweden)

Abstract

Lake and stream water in glaciated landscapes across substantial areas of North America and northern and central Europe has become enriched in dissolved organic carbon (DOC) over the past two decades. The reduction in water quality and transparency has increased costs of water treatment, and the potential increase in the export of carbon from the land to the sea has raised concerns that terrestrial carbon stores may be becoming unstable, with unpredictable consequences for the global carbon cycle. To date there is little agreement as to underlying causes, but hypotheses range from rising ambient CO2 concentration, climate-change driven changes in temperature and precipitation, changing land-use, and changes in nitrogen deposition. Recently, changing soil chemistry, resulting from a decline in anthropogenic sulphur deposition, has been proposed as the dominant driver, and this contrasts with other hypotheses as it implies that surface water quality is returning to a pre-industrial “reference state”, rather than deteriorating. It is clearly important for water management and our understanding of the acidification/recovery process and the wider carbon cycle that this issue is resolved. Here we show, through the assessment of time series from over 500 acidification-sensitive sites in North America and northern Europe, that the tendency for DOC increases in most regions between 1990-2004 can be explained by changes in the acid anion concentration of atmospheric deposition. DOC concentrations have increased proportionally with the decline both in anthropogenic sulphur, and, in some regions, seasalt deposition. While mechanisms require further elucidation, results suggest that DOC concentrations should stabilise as anthropogenic sulphur emissions decline toward negligible levels, while revealing a potential weakness in the ability of current geochemically-based models to predict the impact of sulphur declines on the acidity of sensitive waters.

Introduction

Natural waters contain varying amounts of dissolved organic matter derived from plant and animal remains and exudates, represented analytically by the measurement of dissolved organic matter (DOC). DOC compounds are multifarious in origin and character, and show a broad range of molecular weights, solubility, hydrophobicity and charge density. The dominant type in relatively unproductive headwater regions is high molecular weight humic matter, comprising humic and fulvic acids and humin, largely products of plant and soil organic matter degradation (Lenheer and Croué, 2003)**.** These compounds are efficient at absorbing visible light, thus strongly influencing transparency and imparting a characteristic brown staining to surface waters. Hydrophobic fractions have relatively high charge density which can be nullified by the addition of aluminium and iron salts, thereby leading to coagulation and the loss of DOC from solution.

Observations of DOC increases in remote surface waters are drawn predominantly from national networks concerned with assessing the effects of emission reductions on acid-sensitive lakes and streams. These programmes have reported that surface water acidity has declined in response to declining sulphur deposition. However, expected increases in alkalinity and pH often appear muted, possibly as a result of the observed increases in organic acidity (i.e., DOC) over the same period (Driscoll et al., 2003; Stoddard et al., 2003). The apparent geographical coherence of DOC increases hints at a dominant driver and several reports have suggested links to aspects of global climate change (Freeman et al., 2001; Freeman et al., 2004). Here, however, we amalgamated lake and stream water chemistry monitoring data from a large number of monitoring programmes to test the hypothesis that trends in surface water DOC concentration were being driven by trends in atmospheric deposition. Analysis was restricted to sites with at least annual measurements for 10 of the 15 years between 1990 and 2004. Data for sites with more frequent sampling were reduced to one representative observation per year, by estimating annual mean values. For reasons explained below, we excluded sites with median values for the sum of divalent cations (Ca^{2+} + Mg^{2+}) greater than 150 µeq/L. Data were analyzed for trends by the Mann-Kendall test (Sokal and Rohlf, 1969), with slopes estimated by the Sen estimator (Sen, 1968).

Our trend results reinforce previously published reports of widespread increases in DOC across large areas of glaciated, acid-sensitive terrain in Europe and North America (***Figure 18*** and ***Figure 19*** and). Upward slopes (n = 334) greatly outnumbered downward slopes (n = 147; 24 sites had slopes equal to zero), and 85% of the significant trends (i.e., those with $p < 0.05$) were upward. Upward slopes were particularly dominant in the southernmost regions (lower than 62 degrees latitude) of the Nordic Countries, in the United Kingdom, and in the northeastern U.S.; these are all areas where sulphur and/or chloride deposition has declined strongly during the 1990-2004 time period. There were strong tendencies for DOC to increase in the northern Nordic region, as well as in Ontario and Quebec, although many of these slopes were not significant. Atlantic Canada was the only region with little evidence of increasing DOC.

The magnitude of DOC change was dependent on absolute DOC concentrations (***Figure 20***), with the largest trends generally occurring in sites dominated by peatlands and/or wetlands; to control for this, subsequent analyses centred on relative DOC change (i.e., DOC change per year as a percentage of the site median, or %ΔDOC).

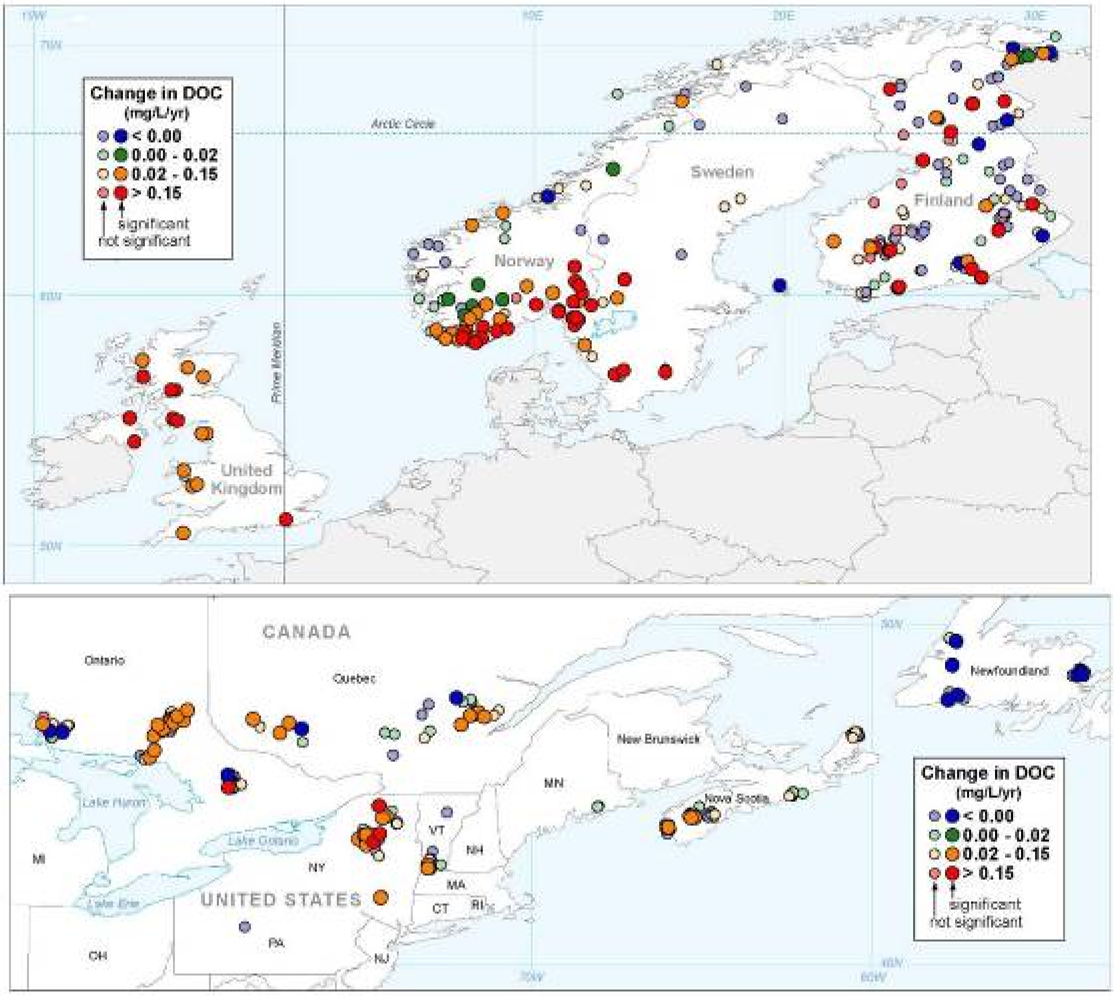

Figure 18. *Trends in dissolved organic carbon (mg/L/yr) at monitoring sites on acid-sensitive terrain in (upper panel) Europe and (lower panel) North America for the time period 1990-2004.*

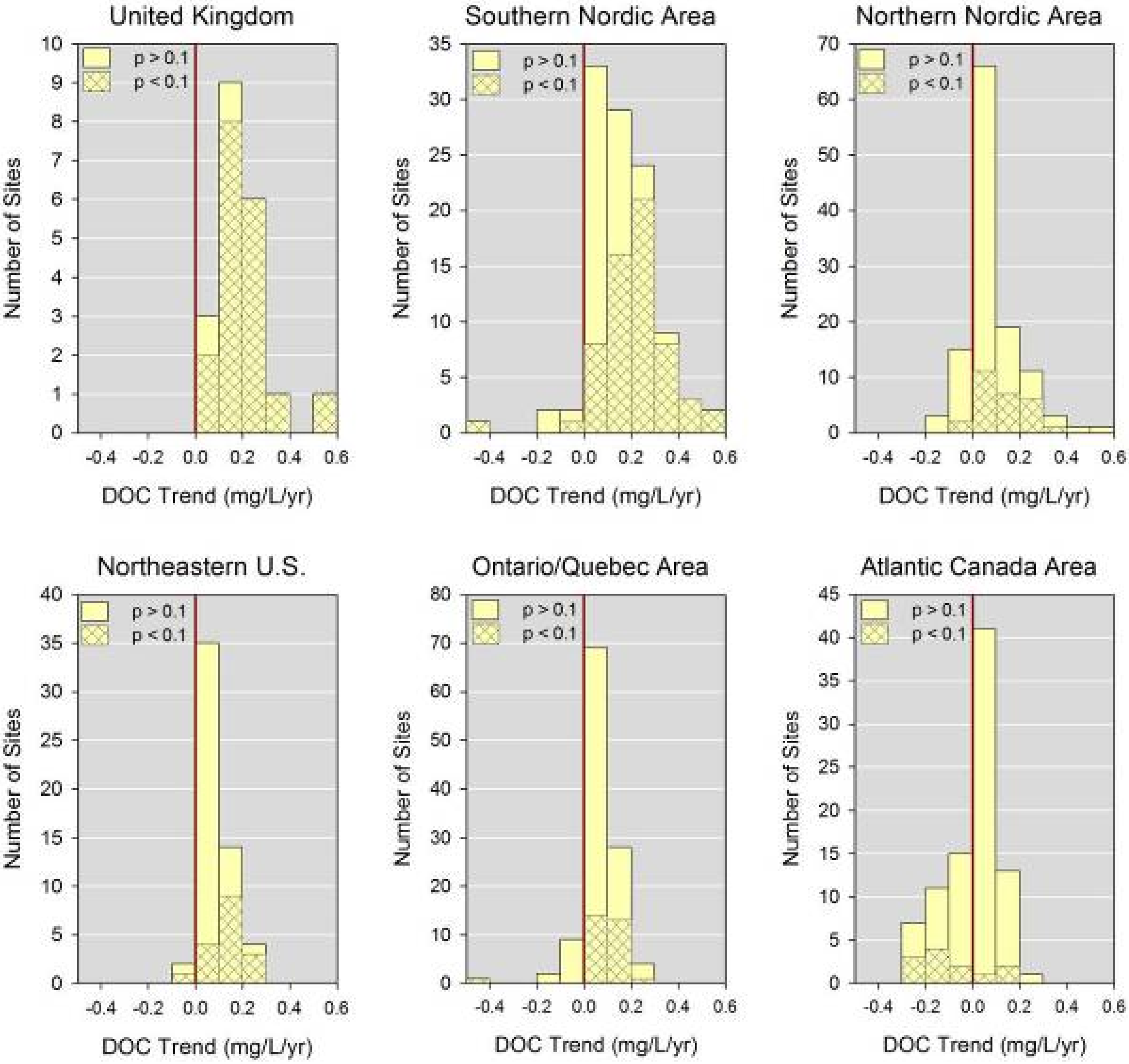

__Figure 19.__Histograms of trend magnitudes (and significance) for regions of Europe (upper panels) and North America (lower panels). Bars show total number of sites in each trend class; cross-hatched portions of bars represent trend slopes significant at $p < 0.10$. Trends in all regions except Atlantic Canada are dominated by positive slopes; in the U.K., the southern Nordic area and Northeastern U.S., these trends are mostly significant.

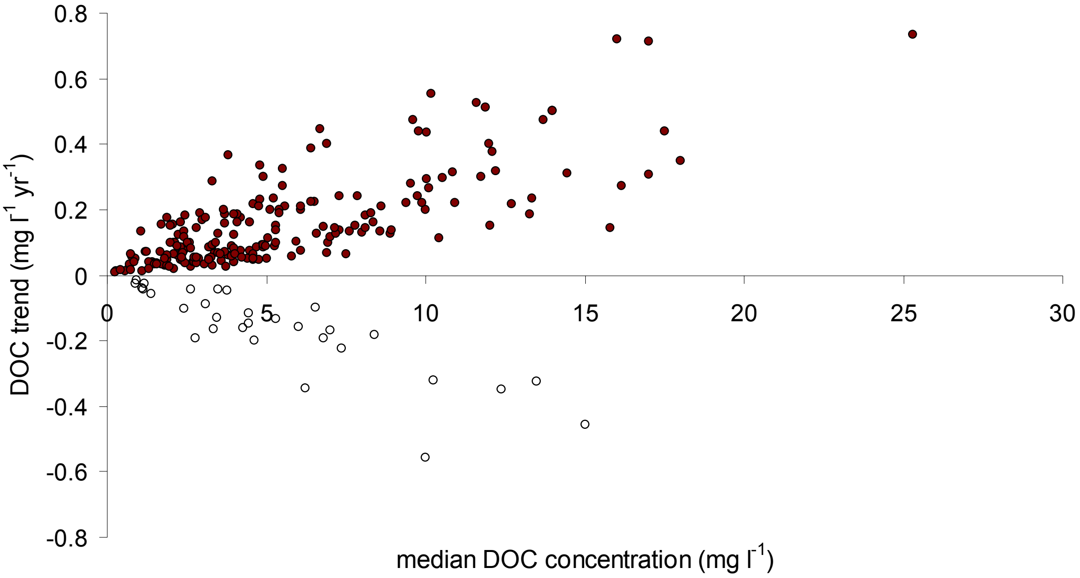

Figure 20. Relationship between DOC trend (mg/L/yr) and absolute DOC concentration (presented as the median at each site for the period 1990-2004). Positive and negative trends ($p < 0.1$) indicated by filled and empty circles respectively. Because DOC change is strongly related to absolute DOC concentration, we use % change in DOC (DOC trend/median concentration) in many of our analyses.

As site-specific deposition estimates were not available for most of the surface water monitoring sites, we focused on changes in measured surface water concentrations of SO_4^{2-} ($\Delta SO_4{}^{2-}$) and Cl^- (ΔCl^-), as potential drivers, on the assumption that change in these conservative acid anions were representative of changes in the chemistry of deposition. For the majority of these relatively remote systems SO_4^{2-} is derived predominantly from fossil fuel pollutant deposition, whereas significant Cl^- concentrations mainly reflect seasalt inputs deposited sporadically in coastal areas during storms. We could not explore the influence of changing nitrogen deposition on DOC trends on this basis, because atmospheric nitrogen is retained strongly in the vast majority of the catchments represented here, and is thus non-conservative. Similarly we excluded sites where SO_4^{2-} is not conservative, such as those in the Southern Appalachian region of the U.S.(Rochelle and Church, 1987), and parts of Germany(Prechtel et al., 2001), where soils often adsorb SO_4^{2-} strongly.

%ΔDOC was strongly related to both $\Delta SO_4{}^{2-}$ and ΔCl^- (***Figure 21***). In several cases where %ΔDOC was large relative to ΔSO_4, ΔCl^- was found to dominate the net change in the two acid anions. For example, the site with the largest %ΔDOC (Scoat Tarn in the U.K.) exhibited only a moderate decrease in SO_4^{2-} (-1.6 μeq/L/yr) over the period 1990-2004, but a very large decrease in Cl^- (-8.2 μeq/L/yr), due to less frequent seasalt episodes. For Newfoundland sites, where DOC concentrations declined, change in SO_4^{2-} was mostly small and statistically insignificant whereas Cl^- concentrations had increased significantly.

Trends in SO_4^{2-} and Cl^- were the strongest predictors of %ΔDOC in a multiple regression (forward selection) exercise, involving the trend slopes and median concentrations of a range of chemical determinants and a range of climatic variables (see methods for details). $\Delta SO_4{}^{2-}$ and ΔCl^- alone accounted for 30% of the variance; the inclusion of median non-marine Ca^{2+} + Mg^{2+} concentration (CaMg*), a variable included to represent catchment sensitivity to acidification, explained an additional 4% of the variance (**Table 7**). The negative coefficient for CaMg* suggested that the response of DOC to changing anion concentrations was greatest in the most acid sensitive systems.

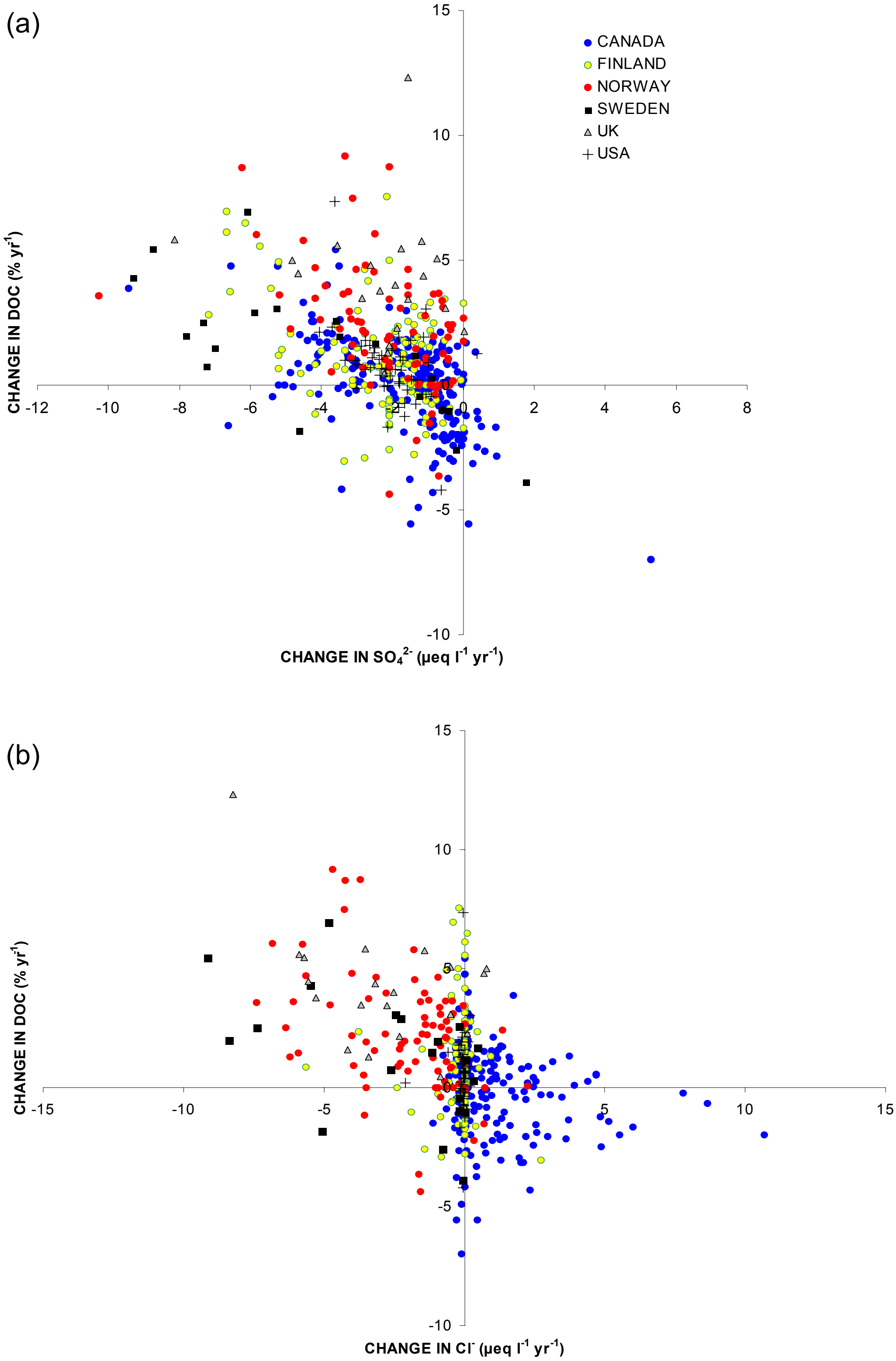

Figure 21. *Relationships between relative annual change in DOC (% DOC/yr) and trends in (a) surface water sulphate and (b) surface water chloride, both used as surrogates for changes in atmospheric deposition.*

Figure 22 provides a comparison of distributions of %ΔDOC with those for the residuals from the multiple regression with ΔSO_4^{2-}, ΔCl^- and CaMg*. Here sites were mostly classified on a national basis as this provided a convenient geographical division of the data and large acid anion trend gradients in each of these regions. **Figure 22** illustrates that this simple model was sufficient to explain the upward tendency in DOC trends in most regions. Sites in the U.K. exhibited DOC trends not fully explained by changes in acid anions; this is one region where both deposition and climate (increased temperature) have been implicated as drivers of DOC change(Evans, In Press).

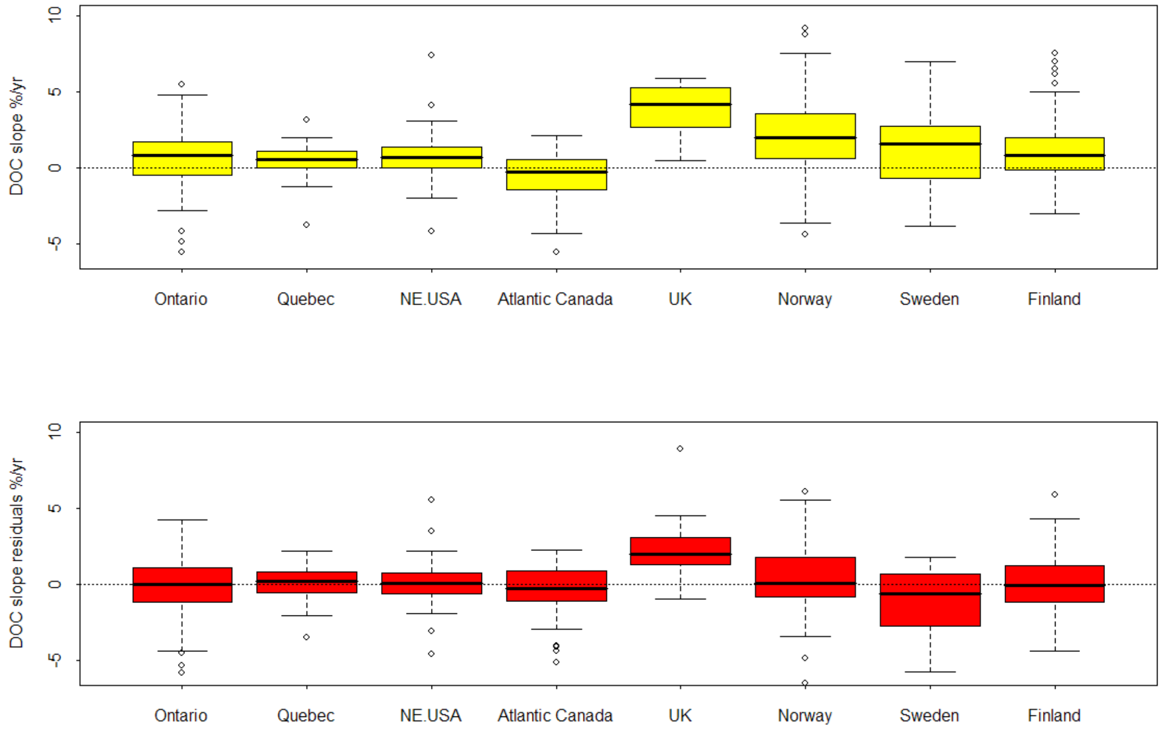

Figure 22. *Regional distributions of (a) % DOC change per year and (b) residuals calculated from a multiple regression predicting % DOC change from* ΔSO_4^{2-}, ΔCl^- *and median CaMg* concentrations.. Residual values center around zero for all regions, with the possible exception of the U.K., indicating that the regression model built on all data reliably explains the tendency for DOC concentrations to deviate from "no trend" in each separate region. Due to large sample size and geographic coverage, data from Canada were broken into three regions (Ontario, Quebec and Atlantic Canada.*

The alternative hypotheses, many can be dismissed as universal explanations of DOC behaviour, because they do not operate at the scale at which we observe changing DOC (***Figure 18***). Landuse change, such as altered forestry practices, the draining of peatlands(Worrall et al., 2003), or changes in grazing or burning practices in grassland and moorlands(Garnett et al., 2000), can influence the export of organic carbon from catchments, but there have been no consistent land-use changes over the large areas where we currently observe increasing DOC trends (***Figure 18***). Changes in hydrology can also influence the export of DOC. Increased flows may lead to runoff more dominated by products accumulated from shallow soil layers (where much of the production of DOC occurs) (Tranvik and Jansson, 2002), while changes in stream discharge in the absence of changing DOC flux can lead either to decreased concentrations (through dilution) or increased concentrations (through concentration)(Evans et al., 2005). While it is clear that hydrologic changes have the potential to influence DOC flux, recent analyses of data from riverine catchments in the U.K.(Evans et al., 2005), the eastern U.S.(McCabe and Wolock, 2002; Zhu and Day, 2005), Canada(Whitfield and Cannon, 2000) and Finland (Hyvärinen, 2003) suggest no consistent hydrologic trends over the last 2 or 3 decades.

Findlay (Findlay, 2005) has proposed that increasing DOC in the Hudson River results from higher rates of soil microbial processing (e.g., decomposition) due to the accumulation of atmospherically deposited nitrogen. While there is evidence that N is accumulating in many ecosystems, both the amount of N deposition, and recent temporal trends, are highly variable across our sites. Surface water nitrate concentrations do not exhibit the increases that would be expected if widespread ecosystem 'N saturation' were occurring (indeed in the northeast US, nitrate leaching has decreased (Goodale et al., 2003)), and we are unable to identify any similarity in geographical patterns of N accumulation rates and DOC increases. Further, this hypothesis cannot account for the tendency for DOC declines in parts of eastern Canada.

Two alternative proposed drivers of DOC change may operate at the appropriate geographic scale. Freeman et al.(Freeman et al., 2004) have demonstrated in the laboratory that increased primary production due to increased atmospheric CO_2 can produce elevated concentrations of DOC in soil solutions. However, the magnitude of the ambient CO_2 increase measured at global monitoring stations since 1990 is ca. 8% of that used in the experiments and even these fail to reproduce the scale of DOC increases reported here. Increasing temperature and its effects on organic matter decomposition rates have also been widely proposed as an explanation for increasing DOC(Freeman et al., 2001; Hejzlar et al., 2003) but we did not find any correlation between regional patterns of temperature and DOC trends (***Figure 23***).

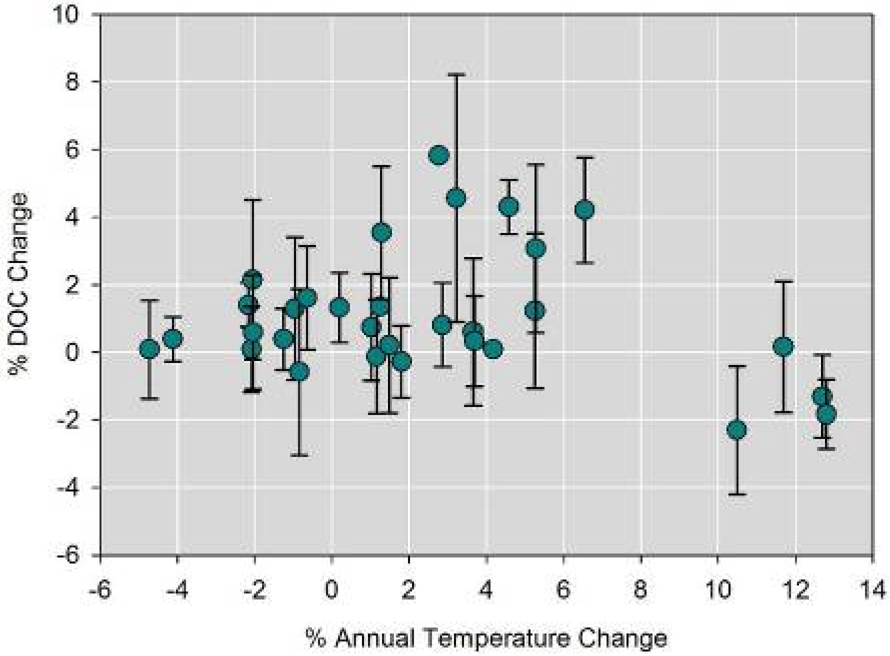

Figure 23. *Relationship between relative DOC change at surface water monitoring sites and trends in annual air temperature (both for the period 1990-2004), compiled in a 5x5 degree grid. Multiple surface water monitoring sites are located in each temperature grid cell, resulting in a range of DOC trends for each estimated (grid-based) change in air temperature.*

Changes in the chemistry of atmospheric deposition, therefore, provide the only regionally consistent explanation for widespread upward trends in surface water DOC concentrations. At least two potential mechanisms have been identified. DOC solubility has been linked to soil pH in numerous laboratory (Clarke et al., 2006; de Wit et al., 2001) and field(Vogt et al., 1994) studies. Our observation of the apparent importance of acid sensitivity is consistent with a soil pH/DOC solubility mechanism. In fact, at CaMg* concentrations above 150 μeq/L, the relationship between %ΔDOC and ΔSO_4^{2-} and ΔCl^- disappears (not shown). This is the primary reason for excluding less acid-sensitive monitoring sites from the database used in this analysis.

A second, potentially more important mechanism is the effect of coagulation of DOC by aluminium. The addition of aluminum (e.g., alum) is the primary process by which DOC is removed from drinking water during treatment, and aluminium solubility declines with increasing soil pH. Coagulation results from the powerful effect aluminium has on ionic strength of the water; independent studies have shown that increasing the ionic strength of soil solutions reduces the rate of DOC flux (Evans Jr. et al., 1988; Tipping and Hurley, 1988; Vance and David, 1989). Since reducing atmospheric deposition also reduces ionic strength, it is very difficult to separate the soil pH/DOC solubility and ionic strength effects. When the multiple regression shown in **Table 7** is repeated using standardized values of ΔSO_4^{2-} and ΔCl^-, (by subtracting the mean and multiplying by the standard deviation) in order to gauge relative weights of effect, the back-transformed regression coefficient for SO_4^{2-} is approximately twice that for Cl^- . This is consistent with the expected difference in the effects of the two anions on ionic strength. However SO_4^{2-} (deposited mainly as sulphuric acid) would also be expected to have a greater impact on acidity than Cl (deposited as neutral seasalt). Further experimental work is required to elucidate the relative roles of these factors.

Table 7. Results of stepwise multiple regression for % change in DOC. Estimates for intercept and slope of individual relationships are for the final three variable model.

Variable	Estimate	p	Cumulative R^2
Intercept	0.83	0.0004	.
Change in SO_4^{2-} (μeq/L/yr)	-0.57	<0.0001	0.225
Change in Cl^- (μeq/L/yr)	-0.26	<0.0001	0.300
Median CaMg* (μeq/L)	-0.01	<0.0001	0.344

* seasalt-corrected divalent cation concentration

Other investigators have shown that variation in hydrology, temperature and land-use all exert influences on DOC concentrations and fluxes. However, this international study indicates that decreasing rates of atmospheric deposition, and their effects on increased DOC solubility, have dominated the inter-regional pattern of DOC trends on both continents since 1990. Trends in Cl^- appear to have been important over this period, but the tendency for decadal cycles in seasalt deposition in some coastal regions(Evans and Monteith, 2001) suggests that, in the longer term, reductions in anthropogenic sulphate will become the dominant driver. Our findings have two important and related implications for our understanding of processes. First, they demonstrate convincingly, and for the first time, that DOC concentrations are sensitive to changes in acid deposition, and, therefore, that the decline in surface water acidity in response to falling levels of acid deposition is being partially offset by increasing organic acidity. Second, they suggest a current propensity to over-attribute changes in carbon fluxes to effects of changing climate, thereby implying that the threat of widespread destabilization of terrestrial carbon reserves may have been over-stated. Clearly, therefore, the development of models which seek to predict the response of surface water acidity to future emission scenarios, and those concerned with developing a better understanding of the linkages between climate and the carbon cycle stand to benefit from a better integration of understanding of both pollutant and climatic impacts on terrestrial carbon dynamics.

References Cited

1. Evans, C. D., Monteith, D. T. & Cooper, D. M. Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental Pollution* **137**, 55-71 (2005).
2. Skjelkvåle, B. L. et al. Regional scale evidence for improvements in surface water chemistry 1990-2001. *Environmental Pollution* **137**, 165-176 (2005).
3. Stoddard, J. L. et al. (U.S. Environmental Protection Agency, Corvallis, Oregon, 2003).
4. Vuorenmaa, J., Forsius, M. & Mannio, J. Increasing trends of total organic carbon concentrations in small forest lakes in Finland from 1987 to 2003. *Science of the Total Environment* **365**, 47-65 (2006).
5. Lenheer, J. A. & Crou⌈, ϑ.–Π. Characterising aquatic dissolved organic matter. *Environmental Science and Technology* **37**, 18A-26A (2003).
6. Driscoll, C. T., Driscoll, K. M., Roy, K. M. & Mitchell, M. J. Chemical response of lakes in the Adirondack region of New York to declines in acidic deposition. *Environmental Science and Technology* **37**, 2036-2042 (2003).
7. Freeman, C., Evans, C. D., Monteith, D. T., Reynolds, B. & Fenner, N. Export of organic carbon from peat soils. *Nature* **412**, 785 (2001).
8. Freeman, C. et al. Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels. *Nature* **409** (2004).
9. Sokal, R. R. & Rohlf, F. J. *Biometry* (W.H. Freeman, San Francisco, 1969).
10. Sen, P. K. On a class of aligned rank order tests in two-way layouts. *Annals of Mathematics and Statistics* **39**, 1115-1124 (1968).
11. Rochelle, B. P. & Church, M. R. Regional patterns of sulfur retention in watersheds of the eastern U.S. *Water Air and Soil Pollution* **36**, 61-73 (1987).
12. Prechtel, A. et al. Response of sulphur dynamics in European catchments to decreasing sulphate deposition. *Hydrology and Earth System Sciences* **5**, 311-326 (2001).
13. Evans, C. D. This is a dummy citation, to represent Chris' latest DOC paper. (In Press).
14. Worrall, F., Burt, T. & Shedden, R. Long term records of riveine dissolved organic matter. *Biogeochemistry* **64**, 165-178 (2003).
15. Garnett, M. H., Ineson, P. & Stevenson, A. C. Effects of burning and grazing on carbon sequestration in a Pennine blanket bog. *Holocene* **10**, 729-736 (2000).
16. Tranvik, I. J. & Jansson, M. Terrestrial export of organic carbon. *Nature* **415**, 861-862 (2002).
17. McCabe, G. J. & Wolock, D. M. A step increase in streamflow in the conterminous United States. *Geophysical Research Letters* **29**, 2185-2185 (2002).
18. Zhu, Y. & Day, R. L. Analysis of streamflow trends and the effects of climate in Pennsylvania, 1971 to 2001. *Journal of the American Water Resources Association* **41**, 1393-1405 (2005).
19. Whitfield, P. H. & Cannon, A. J. Recent variations in climate and hydrology in Canada. *Canadian Water Resources Journal* **25**, 19-65 (2000).
20. Hyvärinen, V. Trends and characteristics of hydrological time series in Finland. *Nordic Hydrology* **34**, 71-90 (2003).
21. Findlay, S. E. G. Increased carbon transport in the Hudson River: unexpected consequence of nitrogen deposition? *Frontiers in Ecology and the Environment* **3**, 133-137 (2005).
22. Goodale, C. L., Aber, J. D. & Vitousek, P. M. An unexpected nitrate decline in New Hampshire streams. *Ecosystems* **6**, 75-86 (2003).
23. Hejzlar, J., Dubrovsky, M., Buchtele, J. & Ruzicka, M. The apparent and potential effects of climate change on the inferred concentation of dissolved organic matter in a temperate stream (the Malse River, South Bohemia). *Science of the Total Environment* **310**, 142-152 (2003).
24. de Wit, H. A., Groseth, T. & Mulder, J. Predicting aluminum and soil organic matter solubility using the mechanistic equilibrium model WHAM. *Soil Science Society of America Journal* **65**, 1089-1100 (2001).
25. Clarke, J. M., Chapman, P. J., Heathwaite, A. L. & Adamson, J. K. Suppression of dissolved organic carbon by sulphate induced acidification during simulated droughts. *Environmental Science and Technology* **40**, 1776-1783 (2006).
26. Vogt, R. D., Ranneklev, S. B. & Mykkelbost, T. C. The impact of acid treatment on soilwater chemistry at the HUMEX site. *Environmental International* **3**, 277-286 (1994).
27. Evans Jr., A., Zelazny, L. W. & Zipper, C. E. Solution parameters influencing dissolved organic carbon levels in three forest soils. *Soil Science Society of America Journal* **52**, 1789-1792 (1988).
28. Tipping, E. & Hurley, M. A. A model of solid-solution interactions in acid organic soils, based on the complexation properties of humic substances. *Journal of Soil Science* **39**, 505-519 (1988).

29. Vance, G. F. & David, M. B. Effect of acid treatment on the leachate chemistry of a New England spodosol: importance of the B horizon on dissolved organic carbon retention. *Soil Science Society of America Journal* **53**, 1242-1247 (1989).
30. Evans, C. D. & Monteith, D. T. Chemical trends at lakes and streams in the UK Acid Waters Monitoring Network, 1988-2000: Evidence for recent recovery at a national scale. *Hydrology and Earth Systems Sciences* **5**, 351-366 (2001).

5. Biological recovery

Gunnar G. Raddum[1], Arne Fjellheim[1], Lars Erikson[2], Jan Fott[3], Godtfred A. Halvorsen[1], Einar Heegaard[4], Leos Kohout[3], Bruno Kifinger[5], Jochen Schaumberg[6], Annette Maetze[6], Helga Zahn[6]

[1]ICP Waters Programme Subcentre, LFI, University of Bergen, Norway
[2]SLU, Sweden
[3]Charles University, Czech Republic
[4]Department of Biology, University of Bergen, Norway
[5]Geo-Oekologie Consulting, Germany
[6]Bayerische LW, Germany

5.1 Introduction

Over the past 35 years acidification of freshwater habitats has received considerable attention as an international ecological problem. In connection with this the ICP Water monitoring programme was established in 1987, with the aim to assess the degree and geographical extent of acidification of streams and lakes. Changes in acid deposition are monitored with respect to effects on water chemistry, dose/response relationships, and biological responses. This chapter focuses on trends in biological recovery, evaluated against the background of trends in water chemistry. This topic was treated in a separate report from ICP Water in 2004 (Raddum et al. 2004). Here, a brief summary of this report is given with the addition of new data. Special attention is given to confounding factors that may enhance or obscure the observed trends. Until now, several regions have shown chemical recovery and the trends in biological recovery generally agree well with the chemical improvements. However, there are also examples on lack of responses or setbacks in the biological recovery process which may be related to known and unknown confounding factors, some of them related to climate change.

There are important differences between processes leading to biological damage under acidification, and processes leading to biological recovery when water quality has improved. The main driver for biological change during acidification is the increasing toxic effect of the water quality. Sensitive organisms die out and the community structure is in general predictable at different levels of acidity. Biotic interactions occur in relation to the disappearance of key sensitive organisms. An example is the effect of fish absence and the immediate increase of species sensitive to fish predation. Among these, the groups Odonata, Coleoptera and Corixidae are very important. Several species among these groups become the new top predators in absence of fish and will structure the community. A general good understanding exists about the acid communities and the processes leading to acid assemblages. The damaging development is of a “linear” nature in relation to tolerance limits of sensitive species. This makes the development of biological communities under acidified conditions more or less predictable. The basis for this understanding of biotic and abiotic interactions is a large number of community structure studies at different acidification levels.

The recovery process is different since the main driver during acidification, the toxicity, is of minor importance and will disappear. The main structuring drivers of the community during recovery are therefore connected to the physical environment in the region, i.e. dispersal and colonisation ability of different species and their biological interactions. The recovery of invertebrates may therefore not follow the opposite direction of the changes in community structure during acidification. Due to the possible lack of “linearity” during recovery it will be difficult to predict the process and the biological target. In fact, the definition of the ‘end-point’ of biological recovery is problematic. It is unlikely that the recovery will result in the community recorded before acidification due to the dynamic nature in general of biological processes.

The trend analysis of biological data was carried out for time series of 10 years or more. Such series are available from the UK, Scandinavia and Central Europe. Biological investigations are also available from long term monitoring programs in Canada.

5.2 Invertebrate recovery in different regions

This overview is based on results reported in Raddum et al. (2004). New data and analyses are added where they were available. The recovery of sensitive invertebrates was studied through different methods. These methods were:

- Trends in acidification index, useful in the pH range of 4.7-6.0, where most sensitive species have their critical limits.
- Trends in number of sensitive taxa over time.
- Multivariate statistical analyses. These analyses take into account the whole invertebrate community and in contrast to the acidification indexes they are also useful at pH < 4.7 and > 6.0.
- Inferred pH development by use of core analyses of lake sediments, a long term analysis.

A workshop on Models for Biological Recovery from Acidification in a Changing Climate (Wright and Lie, 2002) was held in collaboration with other research programmes. Here, evidence for biological recovery was presented and analysed. Different stages in biological recovery time were identified, such as arrival time for the species, internal dispersal time and time for obtaining natural fluctuations of organisms. Recovery time is dependent on type of organism. As an example, some algae species need 0-1 year, some sensitive invertebrate species 1-3 years, some zooplankton species 3-7 years and some fish species 2-20 years.

Biological recovery in Canada

Biological recovery has been studied in lakes with various rates of chemical recovery and with various degrees of acid damage. The rate of biological recovery was less pronounced in low pH lakes (pH < 6) than in high pH lakes (pH > 6). Zooplankton showed recovery in lakes that chemically have recovered from pH < 6 to pH > 6. Zooplankton recovery has also occurred in lakes that have not reached pH > 6.

Lakes in the Killarney Park, Canada, have been seriously acidified especially from the smelters in Sudbury. The sulphur emission at Sudbury has been strongly reduced during the last decades starting in the 1970s. In the 1990s a total sulphur reduction of > 90% was achieved compared with the top emissions in the 1960s (Keller et al. 1999).

The recovery of water chemistry in the monitored lakes has varied after the strong reduction in sulphur deposition. The lowest increase in pH was measured in the most acidified lakes, while the highest increases were found in the less acidified lakes. Biological recovery is studied in lakes with different rate of chemical recovery and with different degree of acid damage.

Recovery of an amphipod and of mayflies was observed in Killarney lakes (Snucins 2003). A synoptic investigation of 119 lakes for the amphipod *Hyalella azteca* and 77 lakes for the mayflies *Stenacron interpunktatum* and *Stenonema femoratum* made it possible to estimate pH thresholds for these organisms. The most tolerant species, *S. interpunctatum*, had a pH threshold of 5.3, while the two other species had a threshold of 5.6. Intensive study of two acidified lakes and two reference lakes showed that the species occurred 4-8 years after reaching the pH threshold. After observation of the first recolonization in a small lake it took about three years before all suitable habitats were colonized within the lake. In large lakes it was suggested that the internal lake dispersal would take much more time. Snucins (2003) estimated that the time lag from pH-threshold recovery to reestablishment and occupation of all suitable habitats would be 11 to 22 years or more.

Biological recovery in the Czech Republic

Eight small glacial lakes are situated on forested slopes of the Bohemian Forest (local names: Böhmerwald and Bayerischer Wald, or Šumava) along the border between Bohemia (Czech Republic), Bavaria (Germany) and Austria at altitudes of about 1000 m.a.s.l. The expected biological recovery in response to recovering water chemistry in these lakes has been slow (Vrba *et al.* 2003).

The first signs of zooplankton recovery have, however, taken place recently in some of the Bohemian Forest lakes (***Table 8*** and ***Figure 24***). Zooplankton was more affected by acidification in the Černé lake than in the Prášilské lake. Data on changes in hydrochemistry of these lakes are in Kopáček *et al.* (2002). Recent trends in their recovery have been dealt by Kohout and Fott (2006) and Nedbalová et al. (2006).

Table 8 *Presence of key crustacean species in the open water of the lakes Černé and Prášilské, 1871 – present. The grey column indicates presence of remains in the sediment (note that Holopedium and Cyclops disappear completely). Explanation of symbols: X: present;, ◊: found in 1-2 specimens; 0: not found; ?: species status unclear.*

	Referenced study									
	(7a), (10)	(1)	(2)	(3)	(4)	(5)	(6)	(7b)	(8)	(9)
		Sampling period								
	Sediment record	1871	1892 -1892	1935 - 1937	1947	1960- 1961	1969	1979	1980- 1997	1999- 2003
ČERNÉ lake										
Ceriodaphnia quadrangula	X	0	X	X	X	X	X	◊	0	X
Daphnia longispina s. lat.	X	X	X	◊	0	0	0	0	0	0
Holopedium gibberum		X	X	0	X	0	0	0	0	0
Cyclops abyssorum		X	X	X	X	?	0	0	0	0
PRÁŠILSKÉ lake										
Ceriodaphnia quadrangula	X	X				0		0	0	X
Daphnia longispina s. lat.	X	X				X		X	X	X
Cyclops abyssorum		X				?		X	X	X

(1) Frič 1872, (2) Frič & Vávra 1896, (3) Šrámek-Hušek 1942, (4) Weiser 1947, (5) Procházková & Blažka 1999 and their unpublished protocols, (6) Ošmera 1971, (7a) Pražáková & Fott 1994, (7b) Fott & al. 1994, (8) Vrba & al. 2003, (9) Nedbalová & al. 2006, (10) Pražáková unpublished.

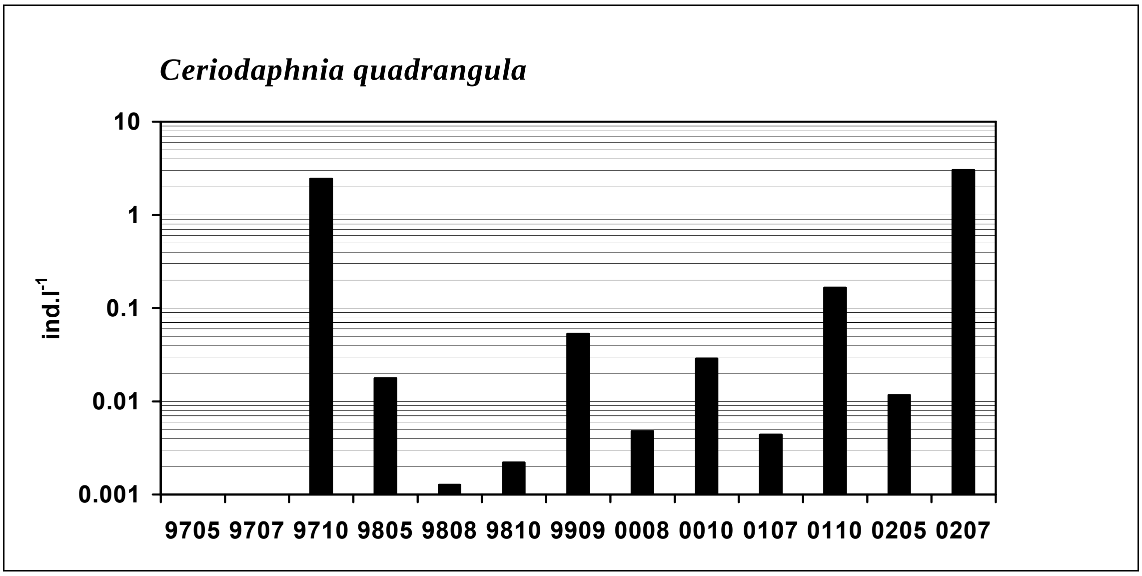

***Figure 24** Abundance of Ceriodaphnia quadrangula in the open water (average column densities) of the lake Černé. In the years 1980–1996 no Ceriodaphnia were found, while the species occurred again in the fall of 1997. Date of sampling in the form YYMM.*

Biological recovery in Germany

Four different categories of acidification status are used for Germany according to the description given by the Bayerischen Landesamtes für Wasserwirkschaft (1999). The method is named “Säuerezustandsklasse” SZKL. The categories are:

1. Not acidic. This means that pH is mostly > 6.5 and minimum pH is seldom measured below 6. The most sensitive species are present.
2. Slightly acidic. pH drops can occur, but seldom below 5.5. The most acid sensitive species are absent.
3. Clearly acidic in periods. pH is normally < 6.5, but seldom below 4,3. During low-water periods, for example in summer, pH can increase to neutral levels. Fish populations are damaged. pH is fatal for successful salmonid reproduction, and only acid tolerant species are present.
4. Chronically acidic. pH is usually below 5.5 during the year. Minimum pH during snowmelt or heavy rain is < 4.3 and often drops lower. Only a few of the most acid tolerant indicator species are present. pH is fatal for sensitive fish.

***Table* 9** gives an overview of German sites, indicating the acid status at the start of the monitoring and at the last year with biological data. The period with observations vary from a few years to 12 years.

There are some signs of recovery of sensitive species in several of the German sites, but a clear stabile significant recovery is difficult to point out. However, the small positive changes that have been detected can after some time turn out to be significant. The highest potential for significant improvements seems to be in the eastern parts of the country. The general lack of clear trends so far in the German biological data corresponds mostly with the results from the chemical analysis, see Skjelkvåle *et al.* (2003) and chapter 2 in this report, where a small positive development in pH is shown, but not significant. The site in Central and Western Germany shows no direction in mean pH. Due to thick soils and probably high accumulation of acidic components a quite long delay in chemical recovery is expected which in turn explains the low biological recovery in the German sites.

Table 9. *Sites in Germany with time series of biological data and corresponding water chemistry. Changes in pH development for the spring /fall period are indicated. + = slightly increase in pH, - = no clear trend in pH and -- = slightly negative trend in pH. Acid category explained in text above*

	SiteName	Nationa Designation	acid category at start of the monitoring		acid category last sampling year		pH development
DE08	Bayerischer Wald, Grosse Ohe	Gro33	1983	2/3	2002	2	-
DE10	Bayerischer Wald, Hinterer Schachtenbach	Hin31	1983	3/4	2002	3	-
DE23	Bayerischer Wald, Seebach	See30	1983	2/3	2002	3	-
DE27	Bayerischer Wald, Vorderer Schachtenbach	Vor32	1983	2	2002	2	-
DE25	Elbsandsteingebirge, Taubenbach	Tau5	1992	3	2002	1/2	+
DE07	Erzgebirge, Grosse Pyra	Gro2	1992	4	2002	4	+
DE21	Erzgebirge, Rote Pockau	Rot3	1992	3	2002	2/4	+
DE30	Erzgebirge, Wilde Weisseritz	Wil4	1992	3/4	2002	2/3	+
DE31	Erzgebirge, Wolfsbach	Wol1	1992	1	2002	1	-
DE02	Fichtelgebirge, Eger	Ege1	1989	3	2002	1	-
DE18	Fichtelgebirge, Röslau	Roe2	1989	4	2002	4	-
DE33	Fichtelgebirge, Zinnbach	Zin3	1989	4	2002	4	-
DE06	Hunsrück, Gräfenbach	Gra5	1982	4	1999	4	+
DE26	Hunsrück, Traunbach 1	Tra1	1983	4	2001	4	+
DE14	Kaufunger Wald, Nieste 3	Nie3	1987	2	2002	2	--
DE15	Kaufunger Wald, Nieste 5	Nie5	1987	4	2002	4	-
DE29	Oberpfälzer Wald, Waldnaab 8	Wal8	1986	4	2002	4	+
DE28	Oberpfälzer Wald. Waldnaab 2	Wal2	1986	2	2002	2	-
DE22	Odenwald, Schmerbach 3	Sch3	1987	4	2002	4	-
DE03	Rothaargebirge, Elberndorfer Bach	Elb1	1988	2/3	2002	2	-
DE32	Rothaargebirge, Zinse	Zin2	1988	3	2002	3	-
DE01	Schwarzwald, Dürreychbach	Due6	1987	3/4	2002	3/4	+
DE05	Schwarzwald, Goldersbach	Gol7	1986	1	2002	1	-
DE11	Schwarzwald, Kleine Kinzig	Kle1	1985	2	2002	2	-
DE04	Sächsische Tieflandsbucht, Ettelsbach	Ett6	1992	3/4	2002	4	+
DE09	Sächsische Tieflandsbucht, Heidelbach	Hei7	1992	4	2002	4	+
DE19	Taunus, Rombach 2	Rom2	1987	4	2002	3	-

Biological recovery in Norway

The Norwegian monitoring programme includes 100 lakes in pristine areas sampled every fourth year for biology, and five rivers with sampling every spring and fall. The river monitoring reports to the ICP Waters and has lasted for more than 20 years. Chemical and biological recovery in several of these sites was significant in the last decade. In this report recovery of sensitive invertebrates is shown, where data was collected with different methods. The trend analyses are carried out as follows:

- With the mean acidification index, which is especially useful in the pH range, 4.7 – 6.0, where most sensitive species have their critical limits, see Raddum (1999).
- By testing trends in the numerical development of selected sensitive species.
- By testing correlations between water chemistry and biological responses (species abundances) using multivariate statistical analysis. These analyses are also useful at pH< 4.7 and pH > 6.0, sections of the scale where the acidification index loose power.

Biological recovery in Norwegian watersheds is described in detail in Raddum et al. (2004). In the section on Confounding Factors (below), some additional data are shown.

The statistical method used is described in Skjelkvåle *et al.* (2000), and Halvorsen *et al.* (2002, 2003). A partial redundancy analysis (RDA) is used to find the amount of variation in the biological data that can be explained by linear trends in water chemistry, and a Spearman rank correlation test is used to test the linear relations between the different water chemistry variables and time.

All of the localities in the tributaries and most of the localities in the main River Nausta showed a significant biological recovery in the benthic community. The trend in recovery was related to the trends in water chemistry in the main river (***Figure 25***) and the Trodøla tributary (***Figure 26***) for a 13-years period. The uppermost locality in the main river showed a significant relation between biological recovery and chemistry of the main river only when the period from 1989 to 1998 was analysed.

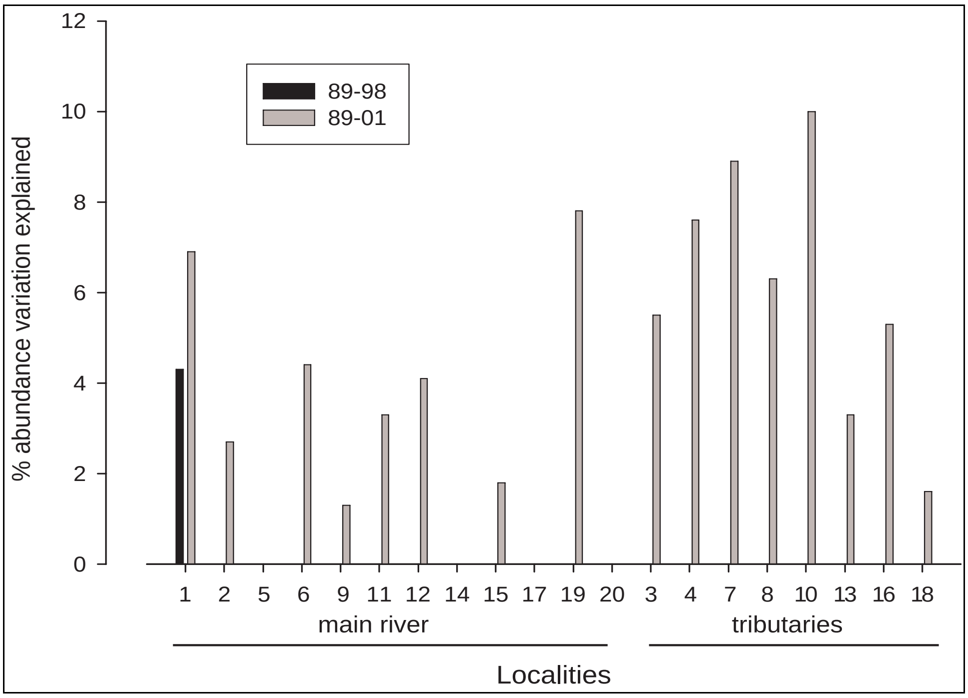

***Figure 25** Amount of variation (%) in the abundance data of the total benthic community from different localities in the Nausta watershed between 1989 and 2001 explained by time trends in water chemistry variables from the main river (found in **Table 10**). On X.axis localities with significant linear trends ($p \leq 0.05$)*

The correlation tests (***Table 10***) show a strong and significant positive linear relation between time and pH and ANC, and a significant negative relation with labile aluminum.

***Table 10** Spearman Rank Correlation matrix of time and water chemisty in the main river in the Nausta watershed from 1989 - 2001 used in the RDA's. (Two tailed tests. ** significant at the 0.01 level. * significant at the 0.05 level).*

	pH	Ca	ANC	TOC	LAl	Time
pH	1	0.427*	0.793**	0.465*	-0.723**	0.778**
Ca		1	0.450*	0.085	-0.248	0.320
ANC			1	0.569**	-0.700**	0.614**
TOC				1	-0.290	0.059
LAl					1	-0.703**

When benthic communities of several localities of river Nausta were related to the water chemistry from the tributary Trodøla, the number of localities with significant relations between variations in the benthic community and water chemistry increased. The number of significant relations increased especially for the first period (1989-1998). Locality 2 was the only one that showed a significant trend in the first period, but not when the three more years were included. The correlation tests between linear time and the water chemistry from Trodøla (***Table 11***) indicate that the linear trends in the benthic community can be interpreted as a response to chemical recovery in the watershed.

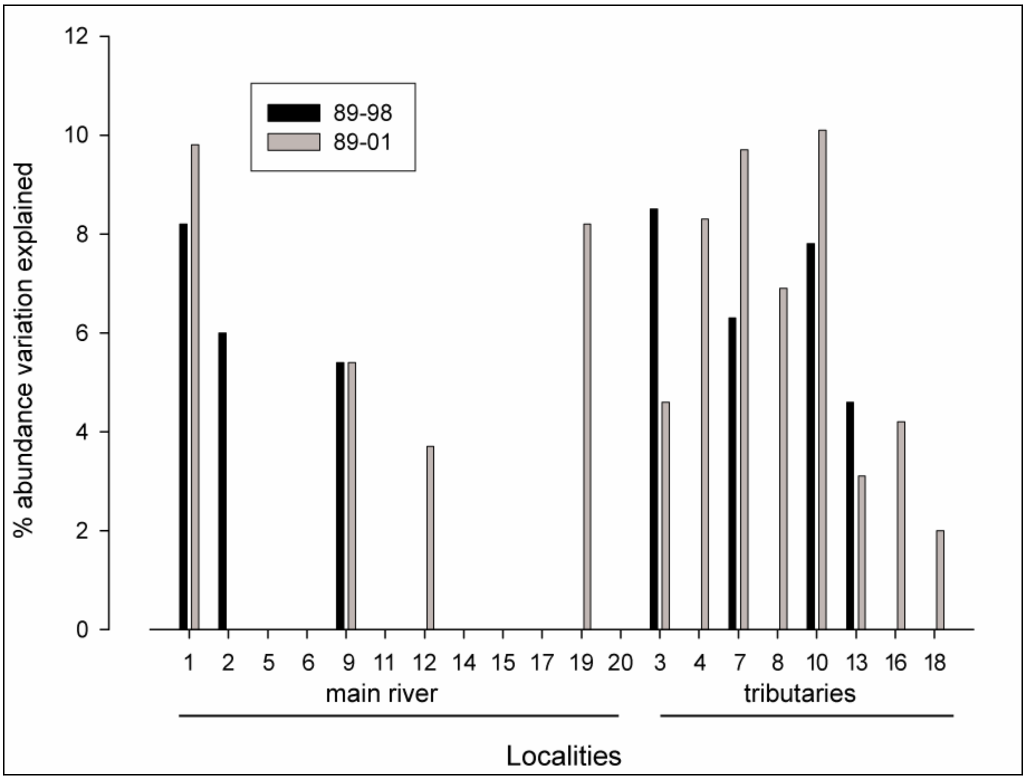

Figure 26. *Amount of variation (%) in the abundance data of the total benthic community from different localities in the Nausta watershed between 1989 and 2001 explained by time trends in water chemistry variables from the Trodøla tributary (found in **Table 11**). On X-axis localities in Nausta watershed with significant linear trends (p<0.05)*

Table 11. *Spearman Rank Correlation matrix of time and water chemisty in Trodøla tributatry in the Nausta watershed from 1989 - 2001 used in the RDA's. (Two tailed tests. ** significant at the 0.01 level. * significant at the 0.05 level).*

	pH	Ca	ANC	TOC	LAl	Time
pH	1	0.631**	0.947**	0.415*	-0.925**	0.843**
Ca		1	0.697**	-0.001	-0.522**	0.643**
ANC			1	0.473*	-0.848**	0.784**
TOC				1	-0.337	0.258
LAl					1	-0.841**

The difference between the two water chemistry datasets (***Table 10*** and ***Table 11***) is that calcium also shows a significant correlation with linear time in the Trodøla tributary, but not in the main river. The correlation tests (***Table 12***) for River Vikedal show that pH, ANC and the calcium concentration are positively correlated with linear time, while labile aluminum is negatively correlated.

The Norwegian watersheds Nausta, Gaula and Vikedal show increasing numbers of localities where we can see significant linear trends of positive change in the total benthic community, trends which can be explained as a response to a recovery in chemistry. This is consistent with the results based on the acidity indices, which have also been increasing in all three watersheds. It should be noted that the amount of variation explained by these linear changes in water chemistry becomes larger in almost all localities when more years of monitoring are added.

***Table 12**. Spearman Rank Correlation matrix of time and water chemisty in the Vikedal watershed from 1989 - 2002 used in the RDA's. (Two tailed tests. ** significant at the 0.01 level. * significant at the 0.05 level).*

	pH	Ca	ANC	TOC	LAl	Time
pH	1	0.472*	0.786**	0.405*	-0.937**	0.871**
Ca		1	0.488**	-0.209	-0.337	0.407*
ANC			1	0.260	-0.789**	0.836**
TOC				1	-0.421*	0.268
LAl					1	-0.860**

Biological recovery in Sweden

Based on annual samples in general during fall, the mean acidification index for the Swedish sites has been estimated for the period 1985-1989, 1990-1995, 1997, 1998, 1999 and 2000. The index for Lake Härsvatn has been 0 through the whole period. In Lake Brunnsjøn and Fiolen the index has been 0.5 and 1 since 1997, respectively, while in Lake Fräcksjøn and Stensjøn a stable index 1 has occurred since 1995. The situation in Lake Storasjø has varied with an index between 0 and 0.5, while in Lake Tväringen the index has been stable 1 during the whole period.

The Swedish material consists of quantitative benthic samples (individuals/m^2) from the sublittoral and the profundal zone of 7 lakes, taken annually in October. The time series started between 1989 and 1991, and data including 2002 have been analyzed with the same multivariate methods as described for the Norwegian material (see above).

The results from the first 8 - 10 years period and 10-12 years period are presented in **Table 13** (Halvorsen *et al.* 2002 and Raddum et al 2004). All of the lakes with sublittoral samples except Lake Fiolen showed significant linear trends in the abundance data from the sublittoral samples when the longest data series were analysed. In the profundal zone only Lake Storasjö had a significant linear trend that can be explained as a response to linear trends in acidity chemistry. However, this lake is shallow, and the sampling depth is between 4 and 6 meter, about the same depths as the sublittoral samples in the deeper lakes.

Table 13. *Results from the multivariate analyses of the benthic communities from the Swedish ICP Waters lakes.The amount of variation in the abundance data explained by significant linear changes in the water chemistry variables ($p \leq 0.05$) are given as percentages. n.s means no significant trend.*

	Sublittoral zone				**Profundal zone**			
	1st period	Trend	2nd period	trend	1st period	trend	2nd period	trend
Brunnsjön	1991-1998	n.s.	1991-2002	19.0 %	1990-1998	n.s.	1990-2002	n.s.
Fiolen	1989-1998	n.s.	1989-2002	n.s.	1989-1998	n.s.	1989-2002	n.s.
Fräcksjön	1990-1998	n.s.	1990-2002	17.8 %	1990-1998	n.s.	1990-2002	n.s.
Härsvatten	1990-1998	17.2%	1990-2002	10.2 %	1989-1998	n.s.	1989-2002	n.s.
Stensjön	1990-1998	n.s.	1990-2002	7.4 %	1990-1998	n.s.	1990-2002	n.s.
Storasjö					1990-1998	n.s.	1990-2002	33.9 %
Tväringen					1990-1998	n.s.	1990-2002	n.s.

The lack of signals of recovery in the lakes with a "real" profundal zone may be a caused by several factors. One important is the confounding effect the oxygen content may have on the profundal community. Oxygen data show that all of the lakes, except Storasjö, experience oxygen depletion during the summer season in the deep waters, at least in some of the years analysed here. Oxygen depletion during one summer season may strongly alter the profundal community, and thus confound any trend of biological recovery.

Lake Storasjö is the only lake which shows a linear trend in the profundal community of invertebrates. This lake is shallow with a maximum depth of about 6 meter. This is so shallow that oxygen saturation in the bottom water may not drop below critical level for longer periods. The oxygen data for this lake shows oxygen depletion for a few years during the examined time period, in addition to winter depletion in some years.

Biological recovery in the UK

Biological data from UK have been analyzed in earlier reports and in publications by participants from the country. Low or no recovery in biology is reported earlier. However, signs of recovery are seen in data from the latest years. These data is not yet analyzed for the ICP, but this will be done in cooperation with scientists from UK and presented in a later report.

5.3 Confounding factors in biological recovery

Seasalt episodes

Input of seasalts leads to changes in water chemistry with decreased pH, increased Al and decreased ANC. Streamwater chemistry crosses toxicity limits for a certain period and could affect sensitive invertebrates depending on time in the life cycle and tolerance limit. If few sensitive organisms are present like in heavily acidified sites, the effect of seasalts is limited as most of the fauna consists of tolerant taxa. An example of this is the the seasalt episode in Farsund in 1993 (***Figure 27***). However, the Farsund watershed has experienced a significant recovery after 1993 with increasing number of sensitive taxa until the period 2002 – 2004. A seasalt episode in 2005 resulted in relatively strong damage, stronger than during the episode in 1993. In 2005 a higher number of sensitive taxa inhabited the watershed and all these were subjected to damage during the episode.

In River Nausta, which is less acidified than the Farsund watershed, moderate seasalt episodes in 1988 and 1989 had a significant influence on the sensitive community (***Figure 28***). Also the 1993 episode was recorded in this river, but the episode was relatively weaker in this region in the southern part of Norway.

Examples of damaging effect of seasalt on species level are shown for the stonefly taxa *Isoperla* sp. and the mayfly *Baetis rhodani* in Farsund area (***Figure 29*** and ***Figure 30***). *Isoperla* sp. was recorded at the start of the monitoring in 1981, but the taxa became extinct until 1990. After 1990 the taxa has been recovering, but the number of individuals has been unstable over time. The increasing trend in number of individuals was completely cut off in 2000 probably due to high seasalt input and high flow (***Figure 31***). After this event the density has increased and the episode in 2005 had only a minor effect on this moderately sensitive taxa.

The highly sensitive mayfly *B. rhodani* was absent from the area until 1995 (***Figure 30***). A few individuals were recorded in the period 1995-1997. The taxa was then absent until 2001. The population increased in density during 2002 – 2004 and indicated good health. However, the 2005 seasalt event wiped out the whole population again, while several of the moderate sensitve species survived this episode.

In spite of setbacks on separate species, the general trend of EPT taxa (Lenat and Penrose 1996) is significant increasing in numbers over time in Farsund (***Figure 31***). The lowest number was recorded in 1984 -1985, a period with the highest damage. The highest number of taxa was found in 2003. At that time the EPT numbers had increased > 2 times the numbers recorded in 1984.

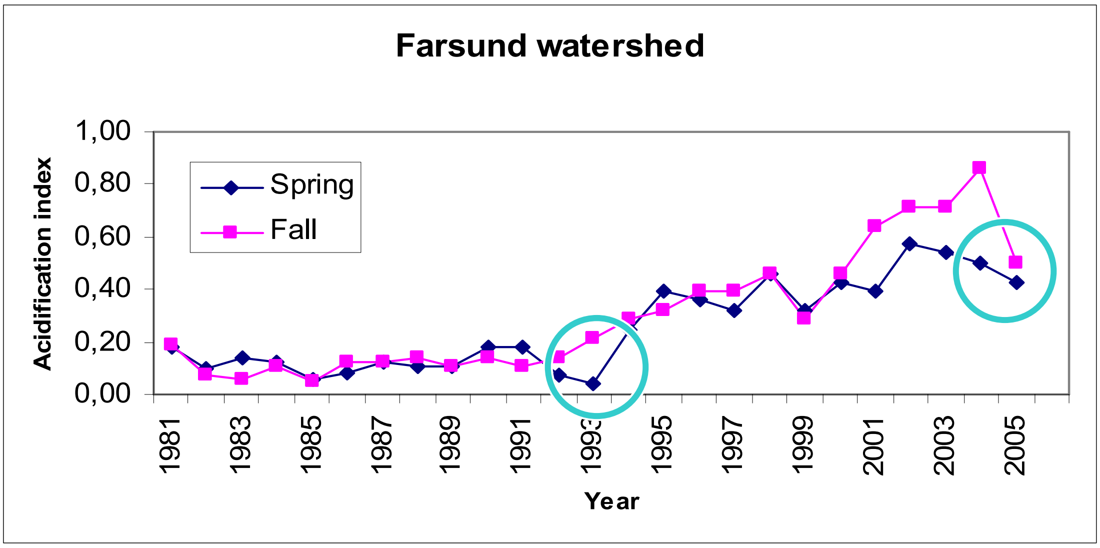

Figure 27 *Effects of a seasalt episode in 1993 and 2005 on the acidification index in heavily acidified Farsund watershed.* ○ *= seasalt episode.*

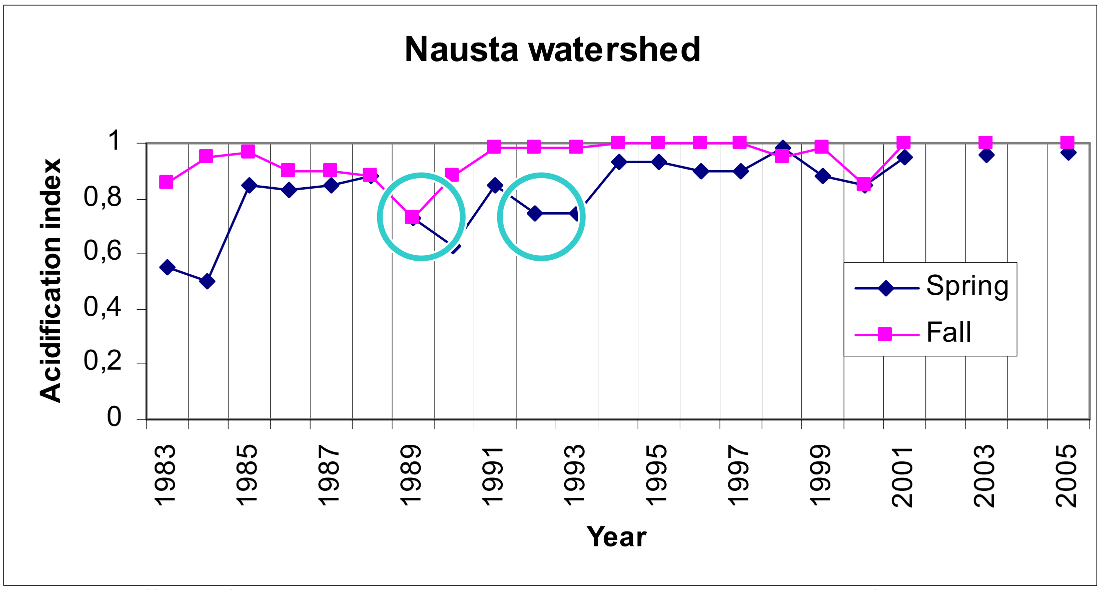

Figure 28 *Effects of a seasalt episode in 1988-1989 and 1993 on the acidification index in the less acidified River Nausta.* ○ *= seasalt episode.*

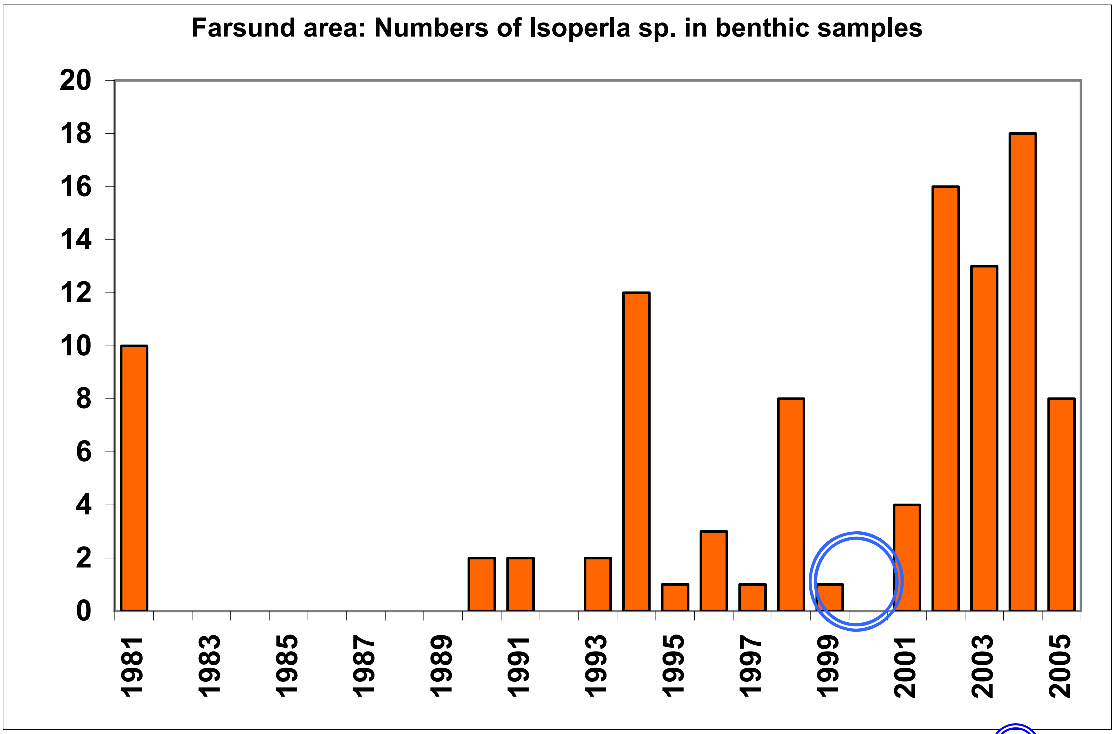

Figure 29 *Recovery of the stonefly taxa Isoperla sp. and setbacks due to seasalt inputs =* ○

The Norwegian monitoring program has mostly focused on invertebrates in streamwaters. The reason for this is that these communities seem to respond much quicker on changes in water quality than lake communities. Improvements in lakes have so far been more difficult to detect. However, after 2000 improvements are also seen in lakes. Examples on this are from two lakes, Lake Røyravatn and Lake Flotwatn, both Vikedal watershed (***Figure 32*** and ***Figure 33***). The already mentioned seasalt episodes on 1993, 2000 and 2005 seem to have influenced on the recovery in these lakes since sensitive taxa either are lacking or strongly reduced after these events.

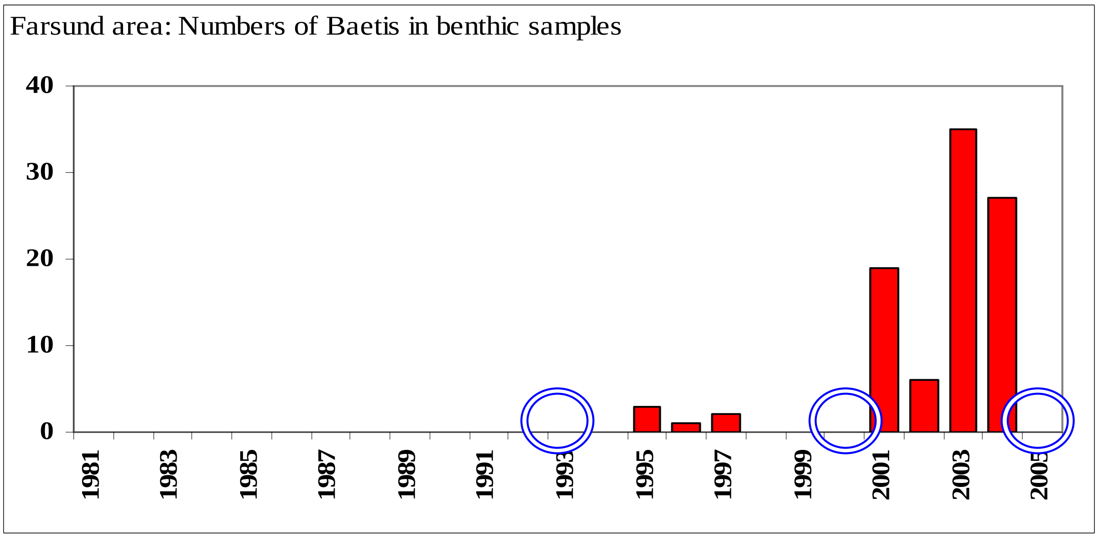

Figure 30*. Recovery of the mayfly B. rhodani and responds to known seasalt episodes =* ○

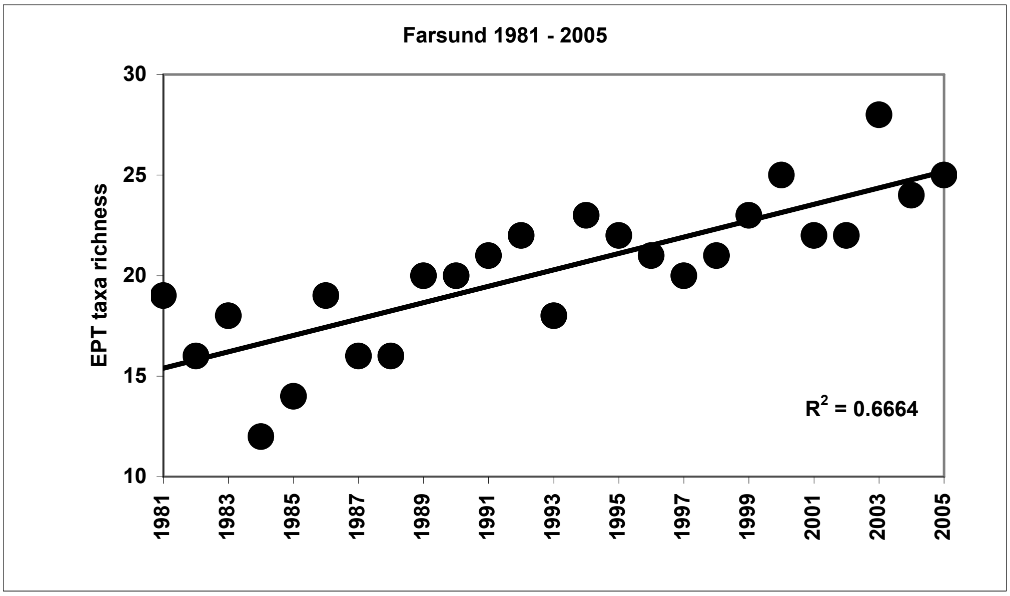

Figure 31. *Number of EPT taxa recorded in Farsund during the monitored period.*

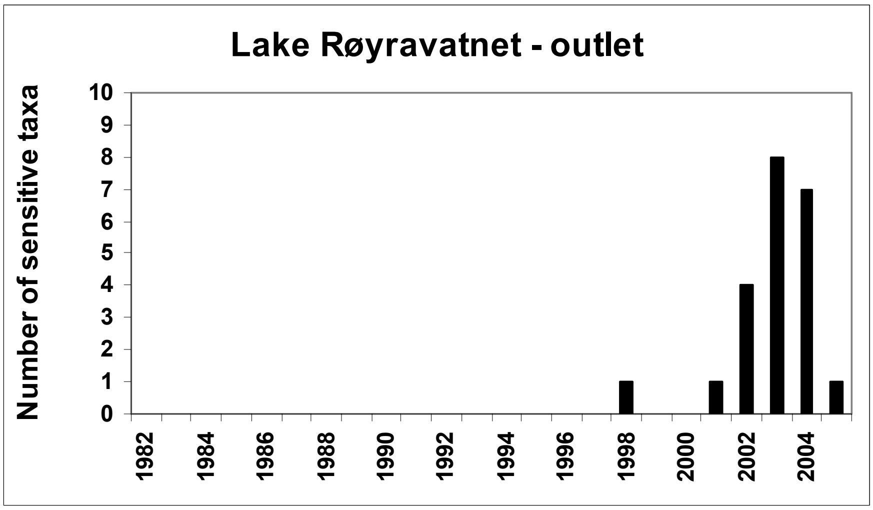

***Figure 32**. Number of sensitive tax at the outlet of Lake Røyravatn*

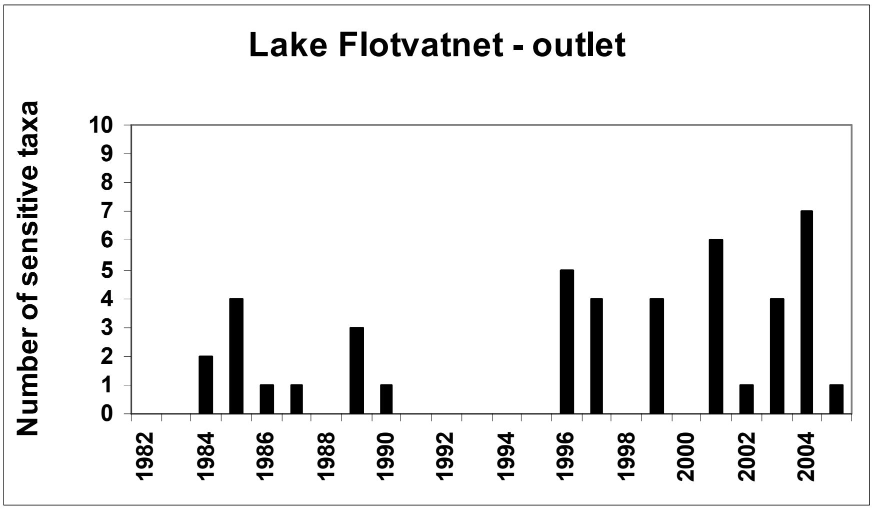

***Figure 33**. Number of sensitive tax at the outlet of Lake Flotvatn*

Floods/droughts

Catastrophic water flow has been observed in several watersheds on the west coast during the period of monitoring. Catastrophic flow, turning around the bottom substrate in most of the river bed, is so far not recorded in monitored watersheds. Such a flow will have a very damaging effect on the whole fauna composition. The reason is that benthic invertebrates normally can hide in safe refuges in the bottom during high flow events. Such refuges are destroyed during catastrophic flow.

The flow and water current is the structuring factor for the river bed, the habitat for invertebrates. The communities respond quickly on habitat changes, effects that can mask recovery processes. High flow makes a coarser substrate, while decreased flow allows sedimentation of finer particles. So far such effects have not been taken into account during studies of recovery. Knowledge about this can be found in the literature dealing with regulated rivers.

Temperature

Increased temperature has so far not been a topic in the recovery studies. However, there are several studies on effects of increased temperature on invertebrates, showing faster growth rate, changed life cycles, changed distribution area etcetera from the regulated river literature. In the monitored watersheds temperature differences from year to year can be detected, but the general increase in temperature is for the moment seldom a task in the recovery discussion. However, the predicted raise in temperature will have a significant effect on the invertebrate assemblage in general and be of high importance for the recovery after acidification.

DOC

Changes in carbon, DOC and TOC, has been attributed raises in temperature and reduced acid deposition. Increases in DOC may complex aluminium and reducity toxicity for sensitive invertebrates. The opposite could happen during acidification when DOC in lakes is reduced. Increased DOC can have many indirect effects that can influence on the recovery of invertebrates. Examples are changes in light penetration, productivity, warming, stratification, oxygen distribution and consumption. Oxygen depletion may have masked recovery in the profundal of Swedish lakes, see above.

References

Fott J., Pražáková M., Stuchlík E., Stuchlíková M., 1994: Acidification of lakes in Šumava (Bohemia) and in the High Tatra Mountains (Slovakia). *Hydrobiologia* **274:** 37-47.

Frič A., 1872: Über die Fauna der Böhmerwald-Seen. – Sitzungberichte der königl. böhmischen Gesselschaft der Wiss., Jahrgang 1871, Prag, 1-13.

Frič A., Vávra V., 1896: Untersuchungen über Fauna der Gewässer Böhmens III. Untersuchung zweier Böhmerwaldseen, des Schwarzen und Teufelssees. – Archiv für naturwissenschaftl. Landesdurchforschung von Böhmen, Prag, 10(3): 1-73.

Halvorsen, G.A., E. Heegaard and G.G. Raddum 2002. Tracing recovery from acidification-a multivariate approach. NIVA-report SNO 4208/2000.

Halvorsen, G.A., E. Heegaard, A. Fjellheim and G.G. Raddum 2002. Tracing recovery from acidification in the Western Norwegian Nausta Watershed. *AMBIO* **32**:235-239.

Keller, W., W. Heneberry and J.M.Gunn 1999. Effect of emission reductions from theSudbury smelters on the recovery of acid and metal-damaged lakes. *J. Aquat. Ecosyst. Stress Recover.* **6**: 189-198

Kopáček J., Stuchlík E.,Veselý J., Schaumburg J., Anderson I., Fott J., Hejzlar J., Vrba J., 2002. Hysteresis in reversal of Central European mountain lakes from atmospheric acidification. *Water, Air and Soil Pollut.:Focus* **2**: 91-114.

Kohout, L. & Fott, J. 2006: Restoration of zooplankton in a small acidified mountain lake (Plešné Lake, Bohemian Forest) by reintroduction of key species. Biologia, Bratislava 61, Suppl. 20: S477–S483.

Lenat, D. R. and Penrose, D. L. 1996. History of the EPT taxa richness metric. *Bulletin of the North American Benthological Society* **13**: 305-307

Nedbalová, L., Vrba, J., Fott, J., Kohout, L., Kopáček, J., Macek, M. & Soldán, T. 2006: Biological recovery of the Bohemian Forest lakes from acidification. Biologia, Bratislava 61, Suppl. 20: S453–S465.

Ošmera S., 1971: [A contribution to the ~~better~~ knowledge of zooplankton in Bohemian Forest lakes]. In Czech. – Ochranářský průzkum 2: 5-8.

Pražáková M., Fott J., 1994: Zooplankton decline in the Černé Lake (ŠumavaMountains, Bohemia) as reflected in the stratification of cladoceran remains in the sediment. *Hydrobiologia* **274**: 121-126.

Procházková L, Blažka P., 1999: [Chemistry and biology of the Bohemian Forest lakes in the early 1960s]. In Czech, with English summary. *Silva Gabreta* **3**: 65-72.

Raddum, G. G. 1999. Large scale monitoring of invertebrates: Aims, possibilities and acidification indexes. In Raddum, G. G., Rosseland, B. O. & Bowman, J. (eds.). Workshop on biological assessment and monitoring; evaluation of models. ICP-Waters Report 50/99, pp.7-16, NIVA, Oslo

Raddum, G. G., Erikson , L., Fott, J., Halvorsen, G. A., Heegaard, E., Kohout, L., Schaumberg, J., Maetze, A. and Zahn, H. 2004. Recovery from acidification of invertebrate fauna in ICP Water sites in Europe and North America. ICP Waters report 75/2004, 54 pp., NIVA, Oslo.

Skjelkvåle B. L., C. Evans, T. L., A. Hinda, G. G. Raddum 2003. Recovery from acidification in European surface waters: a view to the future. *AMBIO* **32**: 170-175

Skjelkvåle, B. L., Andersen, T., Halvorsen, G. A., Heegaard, E., Stoddard, J. L., and Wright, R. F. 2000. The 12-year report; Acidification of surface water in Europe and North America; trends, biological recovery and heavy metals. SNO 4208/2000, ICP Waters report 52/2000, Norwegian Institute for Water Research, 108 pp.

Snucins, E. 2003. Recolonization of acid-damaged lakes by the benthic invertebrates *Stenacron interpunctatum*, *Stenonema femoratum* and *Hyalella azteca*. *AMBIO* **32**: 225-229.

Šrámek-Hušek R., 1942: Revision der Cladoceren- und Eucopepodenfauna des Schwarzen Sees in Böhmerwald nach 66 Jahren. In Czech, with German summary.- Věstník královské české společnosti nauk, tř. mat.-přír., Praha, 1-22.

Vrba J., Kopáček J., Fott J., Kohout L., Nedbalová L., Pražáková M., Schaumburg J., 2003: Long-term studies on acidification and recovery of lakes in the Bohemian Forest (central Europe). *Sci.Tot.Environ*. **310**: 73-85.

Weiser J., 1947: [On limnological research of Černé Lake]. In Czech. – Příroda 40: 30-31.

Wright, R.F. and Lie M.C. 2002: Workshop on Models for Biological Recovery from Acidification in a Changing Climate 9-11 September 2002 in Grimstad, Norway Workshop report. NIVA-report 4589-2002.

6. Confounding factors in future recovery of water chemistry and biology

Heleen de Wit, Brit Lisa Skjelkvåle and Richard F. Wright
ICP Waters Programme centre
University of Bergen, Department of Zoology, LFI, Bergen, Norway

6.1 Introduction

Environmental factors other than acid deposition – so-called ‘confounding factors’ – are expected to affect chemical and biological recovery of freshwaters in response to reduced acid deposition. Confounding factors with a regional rather than local occurrence are worthwhile to study in order to grasp their potential effect on the future behaviour of acid-sensitive ecosystems.

Better understanding of confounding factors is relevant for the Gothenburgh Protocol. The protocol 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 limited evidence of large losses of N from catchments in Europe or North America (Campbell et al, 2004; MacDonald et al., 2002; this report). Counteracting of declining sulphate export by increasing nitrate export will delay recovery from acidification. 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.

Climate change is expected to have large impacts on water chemistry and freshwater biology. Changes in large-scale weather patterns and increased temperature can in concert affect regional patterns and timing of precipitation intensity, wind speed and direction, snow and ice cover and other weather variables. However, non-climate related factors like insect outbreaks or presence of exotic fish species may also change chemical and biological recovery. The aim of this chapter is to give an overview of confounding factors that are expected to have a regional impact on both biological and chemical recovery, interspected with illustrative examples. The overview is non-exhaustive.

6.2 Climate-related confounding factors

Patterns of dominating wind direction affect deposition

The North Atlantic Oscillation (NAO) Index describes the large-scale weather systems in the North Atlantic Ocean which influence weather patterns in Europe, particularly in winter. These weather patterns include information on air mass trajectories. Hole et al. (in press) show that various types of climate indices (NAO, EU-blocking pattern) correlate with winter deposition of nitrate in western Norway, suggesting that warm, humid winters with strong westerlies (positive NAO index) bring high N deposition. The link between the NAO index and sea-salt deposition in near-coastal surface waters in the UK and Norway is fairly well established (Evans et al. 2001, Hindar et al. 2004). Episodic acidification of surface waters from seasalt deposition may obscure long-term trends in recovery related to decreasing acid deposition.

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 and possibly higher loads of acidifying compounds may therefore be expected in coastal surface waters.

Episodic deposition of Saharan dust can also 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 (Psenner, 1999).

Deposition of sea-salts delays recovery

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. Above it is argued that seasalt episodes in coastal areas in North Western Europe may increase in severity and frequency in a warmer climate. However, independent of climate change, sea-salt episodes can delay biological recovery. Monitoring data of the River Lygna in southern Norway demonstrate a clear relation between a seasalt even in 1993, increased Al and a reduction in an acid-sensitive mayfly species (***Figure 34***). Relations between seasalt episodes and delays in biological recovery are discussed in more detail in **Chapter 5.3.**

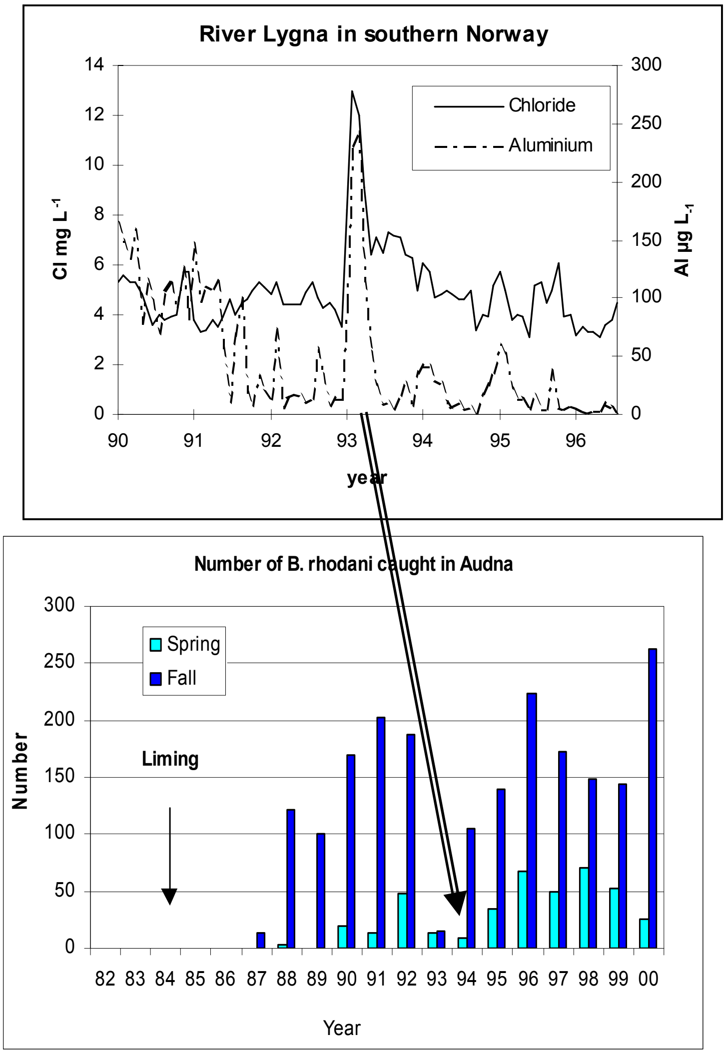

Figure 34. *Effects on water chemistry and biology of a winter storm with high transport of sea-salt 1993 in southern Norway. Upper panel shows chloride and inorganic aluminium in River Lygna from 1990 to 1996. The decrease in Al from 1990 to 1993 is due to chemical recovery in this river, while the 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 (from Raddum in Skjelkvåle et al. 2003).*

Droughts increase sulphate export and generate acidic episods

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). In the UK, large flushes of sulphate were widely observed in streams following a drought in 1995 (Harriman et al. 2001, Clarke et al. 2006) and in Norway following a summer drought in 1976 (Cristophersen and Wright 1980).

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.

Climate warming of soils has ambiguous effects on acidification

Climate change is expected to lead to warmer winters. Warmer winters in areas where snow accumulation is common may be associated with colder soils, surprisingly. An unstable snowpack caused by frequent thaw periods has less insulative power than a thick, continuous snowpack. Thus, soils during winter may become colder in an overall warmer climate with a large effect on temperature-sensitive processes that drive N leaching. Internal ecosystem cycling of N greatly exceeds inputs by deposition and outputs by runoff. Any disturbance of the N cycle has the potential to completely obscure the relationship between N deposition and runoff.

Groffman et al. (2001) suggest that a higher frequency of freeze-thaw cycles increase nitrate release from soils. 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).

Statistical analysis of a long-term nitrate series in an acid-sensitive catchment in Norway indicates a relation between snowdepth and winter nitrate (***Figure 35***) (De Wit et al. in press). Here the long-term downward trend in nitrate appears to be largely controlled by the snow pack, suggesting that climate warming and less snow lead to lower nitrate losses, in contrast to the mechanism suggested by Groffman et al. (2001).

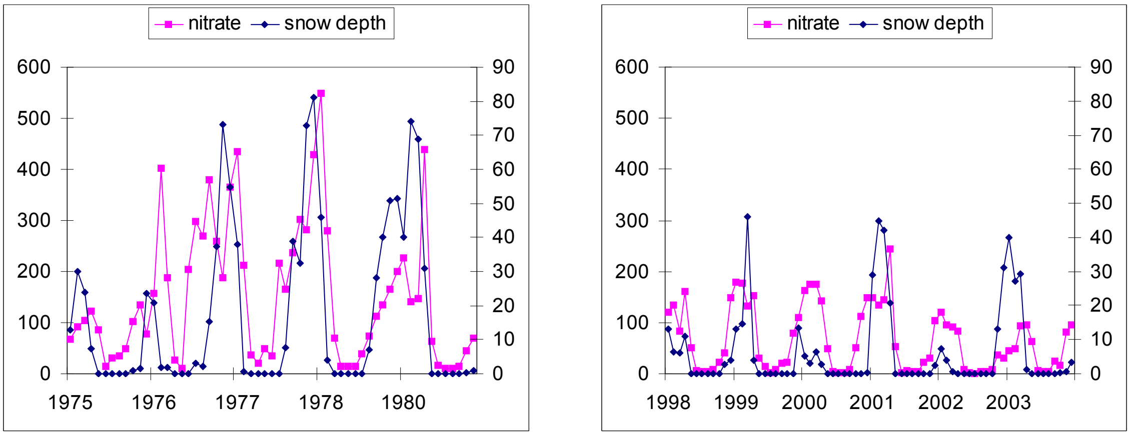

Figure 35. *Nitrate concentrations (µg N/L) and snow depth (cm) at Storgama in southeast Norway. Left panel shows years 1975-1982, right panel shows 1998-2003.*

Climate warming has increased the length of the growing season, and could lead to higher summer temperatures and warmer soils. The effect of warmer soils on surface water acidity is complicated. 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. On the other hand, Vesely et al. (2003) explained 10% of the decrease in Al in Czech lakes from 1984-1999 by an increase in average annual temperature, which was interpreted as the effect of lower Al solubility at higher temperatures. This suggests an enhanced rate of recovery due to climate warming.

Catastrophic flow destroys habitat for benthic organisms

Climate change is expected to lead to more intense precipitation events in some regions of the world. Flow and water current affect the structure of the river bed which is the habitat of for example invertebrates. High flow makes a coarser substrate, while decreased flow allows sedimentation of finer particles. Catastrophic flow can lead to large disturbance of the bottom substrate in riverbeds with potentially very damaging effects on the fauna composition. The reason is that benthic organisms normally can hide in safe refuges in the bottom during high flow events, while such refuges are destroyed during catastrophic flow.

Studies of high flow versus low flow periods in rivers show changes in benthic taxa in relation to flow intensity (Suren and Jowett, 2006).

6.3 Other confounding factors

Increased DOC – ambiguous effects on recovery

The regional trends of increasing organic carbon have been documented sufficiently in **Chapter 4.** Whether the rise in DOC is a response to reduced acid deposition or an effect of climate change is not relevant for the present ecological effects of higher DOC, but will determine the future importance of DOC in delaying or enhancing recovery.

The delaying effect of a rise in DOC is illustrated by the trend in surface water chemistry in the UK (see **2.5.2**). The decreasing trend in acid anions was considerably larger than the decreasing trend in base cations and protons. Contrary to the expected response to net less acidity, no significant chemical recovery in terms of an increase in alkalinity or ANC was found. The increase in DOC was most prominent in the UK of all ICP Water regions (see ***Table 4*** **in Chapter 2)**. Assuming that the rise in DOC fully compensated the ‘missing’ acidity, the charge density of the DOC should be ca -20 μeq/mg DOC. This is roughly twice as large as reported carboxyl contents of DOC (Hruska et al. 2003), suggesting that other factors in addition to the increase in DOC delay the expected chemical recovery of surface waters in the UK.

An example of a beneficary effect of DOC on salmon is given by Wright et al. (2002). In an experiment conducted in two rivers with different DOC, twice as much inorganic Al was needed in the DOC-rich river to produce a given accumulation of Al onto the gill surface of salmon. Accumulated Al on the gill surface is related to negative physiological responses, possibly ending up in reduced survival of the fish. Similar results are shown in limed rivers where gill reactivity of inorganic Al was shown to depend on TOC and Si concentrations (Teien et al., 2006).

Increased DOC concentrations may have indirect effects on water quality that can influence the recovery of invertebrates. For example, changes in light penetration, productivity, warming, stratification and oxygen distribution may be affected. Oxygen depletion may have masked recovery in the profundal of Swedish lakes (this report **Chapter 5.3)**.

Insect outbreaks in forests may generate acidity

Nitrogen uptake by vegetation is a significant flux in the nitrogen cycle. A sudden reduction in this flux, as caused by for example an insect outbreak leading to massive defoliation, is likely to lead to streamwater acidification. Forested watershes in the Appalachians were defoliated by massive outbreaks of the gypsy moth caterpillar which induced large nitrate peak concentrations, reduced pH and ANC (Eshleman et al., 1998). Other studies show similar effects of canopy loss by ice-storms on nitrate export (Houlton et al., 2003), while nitrate leakage after forest harvest is very well documented (i.e. Gundersen et al. 2006). Insect outbreaks of known and of exotic species could be promoted by increased climate variability (Stireman et al., 2005). Outbreaks of bark beetle in spruce forests in Europe have been related to occurrence of summer drought (Rolland and Lemperiere, 2004) and excess of dead wood after storms (Bouget and Duelli, 2004).

6.4 Conclusions

Confounding factors in future recovery of water chemistry and biology were defined as the effects of environmental factors other than acid deposition which affect recovery from acidification of surface waters. In this overview, we focused on confounding factors related to climate, and ‘other’ confounding factors. These factors either reduce our ability to detect recovery, or could alter recovery rates in the long term.

Climate related extreme events like droughts, storms and floods can affect surface water acidity and the habitat of aquatic organisms. Long term gradual changes in climate can affect run off processes and population dynamics. Examples of factors that enhance and that delay recovery were given. Key processes in acidification and recovery are still not properly understood, such as climate effects on N leaching and the lag time between chemical and biological recovery.

References

Bouget, C., and P. Duelli. 2004. The effects of windthrow on forest insect communities: a literature review. *Biological Conservation* 118:281-299.

Campbell, J.L., J.W. Hornbeck, M.J. Mitchell, M.B. Adams, M.S. Castro, C.T. Driscoll, J.S. Kahl, J.N. Kochenderfer, G.E. Likens, J.A. Lynch, P.S. Murdoch, S.J. Nelson, and J.B. Shanley. 2004. Input-output budgets of inorganic nitrogen for 24 forest watersheds in the northeastern United States: A review. *Water Air and Soil Pollution* 151:373-396.

Christophersen, N., and R.F. Wright. 1980. Sulfate flux and a model for sulfate concntrations in streamwater at Birkenes, a small forested catchment in southernmost Norway 70/80. SNSF-prosjekt, Ås.

Clark, J.M., P.J. Chapman, A.L. Heathwaite, and J.K. Adamson. 2006. Suppression of dissolved organic carbon by sulfate induced acidification during simulated droughts. *Environmental Science & Technology* 40:1776-1783.

De Wit, H.A., A. Hindar and L. Hole. In press. Winter climate affects long-term trends in stream water nitrate in acid-sensitive catchments in southern Norway. *Hydrol.Earth System Sci* 2007

Dillon, P.J., and B.D. Lazerte. 1992. Response Of The Plastic Lake Catchment, Ontario, To Reduced Sulfur Deposition. *Environmental Pollution* 77:211-217.

Dillon, P.J., L.A. Molot, and M. Futter. 1997. The effect of El Nino-related drought on the recovery of acidified lakes. *Environmental Monitoring and Assessment* 46:105-111.

Eshleman, K.N., R.P. Morgan, J.R. Webb, F.A. Deviney, and J.N. Galloway. 1998. Temporal patterns of nitrogen leakage from mid-Appalachian forested watersheds: Role of insect defoliation. *Water Resources Research* 34:2005-2016.

Evans, C.D., Monteith, D.T. and Harriman, R. 2001. Long-term variability in the deposisiton of marine ions at west coast sites in the UK Acid Waters Monitoring Network: impacts on surface water chemistry and significance for trend determination. *Sci.Tot.Environ.* **265**: 115-129.

Groffman, P.M., C.T. Driscoll, T.J. Fahey, J.P. Hardy, R.D. Fitzhugh, and G.L. Tierney. 2001. Colder soils in a warmer world: A snow manipulation study in a northern hardwood forest ecosystem. *Biogeochemistry* 56:135-150.

Gundersen, P., I.K. Schmidt, and K. Raulund-Rasmussen. 2006. Leaching of nitrate from temperate forests - effects of air pollution and forest management. *Environmental Reviews* 14:1-57.

Harriman, R., A.W. Watt, A.E.G. Christie, P. Collen, D.W. Moore, A.G. McCartney, E.M. Taylor, and J. Watson. 2001. Interpretation of trends in acidic deposition and surface water chemistry in Scotland during the past three decades. *Hydrology and Earth System Sciences* 5:407-420.

Heath, R. H., Kahl, J. S., Norton, S. A., and Fernandez, I. J. 1992. Episodic acidification caused by the seasalt effect in coastal Maine streams. *Water Resourc.Res.* 28: 1081-1088.

Henriksen, A., and M. Posch. 2001. Steady-state models for calculating critical loads of acidity for surface waters. *Water Air and Soil Pollution: Focus* 1:375-398.

Hindar, A., A. Henriksen, K. Tørseth, and A. Semb. 1994. Acid water and fish death. Nature 372:327-328.

Hindar, A., K. Torseth, A. Henriksen, and Y. Orsolini. 2004. The significance of the North Atlantic Oscillation (NAO) for sea-salt episodes and acidification-related effects in Norwegian rivers. *Environmental Science & Technology* 38:26-33.

Houlton, B.Z., C.T. Driscoll, T.J. Fahey, G.E. Likens, P.M. Groffman, E.S. Bernhardt, and D.C. Buso. 2003. Nitrogen dynamics in ice storm-damaged forest ecosystems: Implications for nitrogen limitation theory. *Ecosystems* 6:431-443.

Hruska, J., S. Kohler, H. Laudon, and K. Bishop. 2003. Is a universal model of organic acidity possible: Comparison of the acid/base properties of dissolved organic carbon in the boreal and temperate zones. *Environmental Science & Technology* 37:1726-1730.

Hulme, M., G.J. Jenkins, X. Lu, J.R. Turnpenny, T.D. Mitchell, R.G. Jones, J. Lowe, J.M. Murphy, D. Hassell, P. Boorman, R. McDonald and S. Hill. 2002. Climate Change Scenarios for the United Kingdom: The UKCIP02 Scientific Report. Tyndall Centre, UEA, Norwich, April 2002.

Hole, L., de Wit, H. and Aas, W. In press. Influence of climate variability on nitrogen wet deposition in Norway. *Hydrol.Earth System Sci* 2007

Langan, S.J. 1989. Sea-salt induced streamwater acidification. *Hydrological Processes* **3**: 25-41.

Löye-Pilot, M.D., J.M. Martin, and J. Morelli. 1986. Influence of Saharan Dust on the Rain Acidity and Atmospheric Input to the Mediterranean. *Nature* 321:427-428.

MacDonald, J.A., N.B. Dise, E. Matzner, M. Armbruster, P. Gundersen, and M. Forsius. 2002. Nitrogen input together with ecosystem nitrogen enrichment predict nitrate leaching from European forests. *Global Change Biology* 8:1028-1033.

Mitchell, M.J., C.T. Driscoll, J.S. Kahl, G.E. Likens, P.S. Murdoch, and L.H. Pardo. 1996. Climatic control of nitrate loss from forested watersheds in the northeast United States. *Environmental Science & Technology* 30:2609-2612.

Monteith, D.T., C.D. Evans, and B. Reynolds. 2000. Are temporal variations in the nitrate content of UK upland freshwaters linked to the North Atlantic Oscillation? *Hydrological Processes* 14:1745-1749.

Psenner, R. 1999. Living in a dusty world: Airborne dust as a key factor for alpine lakes. Water Air And Soil Pollution 112:217-227.

Rolland, C., and G. Lemperiere. 2004. Effects of climate on radial growth of Norway spruce and interactions with attacks by the bark beetle Dendroctonus micans (Kug., Coleoptera: Scolytidae): a dendroecological study in the French Massif Central. Forest Ecology and Management 201:89-104.

Skjelkvåle B. L., C. Evans, T. L., A. Hindar, G. G. Raddum 2003. Recovery from acidification in European surface waters: a view to the future. *AMBIO* 32: 170-175

Stireman, J.O., L.A. Dyer, D.H. Janzen, M.S. Singer, J.T. Li, R.J. Marquis, R.E. Ricklefs, G.L. Gentry, W. Hallwachs, P.D. Coley, J.A. Barone, H.F. Greeney, H. Connahs, P. Barbosa, H.C. Morais, and I.R. Diniz. 2005. Climatic unpredictability and parasitism of caterpillars: Implications of global warming. Proceedings Of The National Academy of Sciences of the United States of America 102:17384-17387.

Suren, A.M., and I.G. Jowett. 2006. Effects of floods versus low flows on invertebrates in a New Zealand gravel-bed river. Freshwater Biology 51:2207-2227.

Teien, H.C., F. Kroglund, B. Salbu, and B.O. Rosseland. 2006. Gill reactivity of aluminium-species following liming. *Science of the Total Environment* 358:206-220.

Vesely, J., V. Majer, J. Kopacek, and S.A. Norton. 2003. Increasing temperature decreases aluminum concentrations in Central European lakes recovering from acidification. *Limnology and Oceanography* 48:2346-2354.

Wiklander, L. 1975. The role of natural salts in the ion exchange between acid precipitation and soil. *Geoderma* 14:93-105.

Wright, R.F., and A. Jenkins. 2001. Climate change as a confounding factor in reversibility of acidification: RAIN and CLIMEX projects. *Hydrology and Earth System Sciences* 5:477-486.

Wright, R.F and Lie, M.C. 2002. Workshop on models for Biological Recovery from Acidification in a Changing Climate. 9-11 September 2002 in Grimstad, Norway. Workshop report. NIVA-report 4589-2002.

Yan, N.D. Leung, B. Keller, B. Arnott, S.E, Gunn, J. and Raddum, G.G. 2003. Developing a conceptual framework for the recovery of aquatic biota from acidification. *AMBIO* 32: 165-169.

Appendix A. Chemistry data

Sites in the ICP Waters pr. 2004 with water chemistry. Mean water chemistry are for for samples collected 2002-2004. n indicates the number of observations in the 3-year period.

Country	Station Code	Station name	n	K25	pH	Ca	Mg	Na	K	Cl	SO4	ANC	Alkalinity	NH4N	NO3N	TOTN	TOTP	TOC/ DOC	AVG H+
				mS m^{-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 N L^{-1}	µg L^{-1}	mg C L^{-1}	µEq L^{-1}
Belarus	BY01	Berezinsky Biosphere Reserve	21	37.30	6.23	51.85	14.80	3.76	1.53	6.89	27.79	3201	3251	551	409	972	33		0.59
Canada	CA01	Ontario, Algoma Region, Batchawana Lake	137	2.09	5.72	2.09	0.33	0.61	0.18	0.31	4.55	42	45	63	235	498	4	4.94	1.91
Canada	CA02	Ontario, Algoma Region, Wishart Lake	138	2.75	5.82	3.28	0.38	0.64	0.17	0.29	4.80	89	90	38	415	498	3	3.85	1.52
Canada	CA03	Ontario, Algoma Region, Little Turkey Lake	138	3.25	6.77	4.15	0.42	0.68	0.19	0.31	5.05	134	134	48	390	496	3	3.93	0.17
Canada	CA04	Ontario, Algoma Region, Turkey Lake	138	3.77	6.35	5.10	0.45	0.74	0.20	0.32	5.14	188	190	35	346	445	3	3.80	0.45
Canada	CA05	Quebec, Lac Veilleux	4	1.38	4.77	1.33	0.26	0.52	0.30	0.33	2.53	52	23	17	68			2.87	16.93
Canada	CA06	Quebec, Lac Josselin	4	1.18	6.64	1.10	0.19	0.45	0.14	0.18	2.43	35	12	20	48			3.05	0.23
Canada	CA07	Quebec, Lac Bonneville	4	1.25	6.44	0.92	0.25	0.48	0.12	0.28	2.98	17	7	72	55			4.85	0.37
Canada	CA08	Quebec, Lac Laflamme	24		5.63	1.88	0.44	0.97	0.22	0.22	2.86	110	44	16	34			4.44	2.33
Canada	CA09	Quebec, Lac Macleod	4	1.17	5.45	0.92	0.24	0.48	0.09	0.23	2.78	21	8	21	50			4.68	3.57
Canada	CA10	Nova Scotia, Mount Tom Lake	4	2.57	4.44	0.26	0.28	2.32	0.30	3.33	1.30	22			20	95		9.55	36.66
Canada	CA11	Nova Scotia, Mountain Lake	4	2.19	6.40	0.37	0.31	2.53	0.20	3.78	1.80	14			20	65		4.08	0.40
Canada	CA12	Nova Scotia, Little Red Lake	4	3.58	4.82	0.23	0.29	2.62	0.24	3.35	1.60	26			20	120		15.83	15.25
Canada	CA13	Nova Scotia, Kejimkujik Lake	4	3.07	5.81	0.62	0.38	3.26	0.28	4.85	1.97	32			20	90		9.25	1.55
Canada	CA14	Nova Scotia, Beaverskin Lake	4	2.21	6.39	0.42	0.37	2.62	0.22	4.03	1.93	15			23	70		2.70	0.41
Canada	CA16	Ontario,Lake224	23	1.84	5.28	1.68	0.43	0.67	0.33	0.19	2.24	105	93	21	5	240	2	3.42	5.26
Canada	CA17	Ontario,Lake239	32	2.95	5.21	2.75	0.85	1.10	0.50	0.31	2.69	200	168	16	30	303	2	111.01	6.22
Canada	CA20	Ontario,Lake373	27	2.68	5.06	2.85	0.68	0.76	0.40	0.22	2.19	189	178	21	6	236	2	65.83	8.81
Czech Republic	CZ01	Bohemian Forest, Cerné	6	2.44	5.99	0.76	0.44	0.73	0.47	0.60	3.45	-28	-15		803			1.51	1.02
Czech Republic	CZ02	Bohemian Forest, Certovo	6	2.71	4.95	0.38	0.30	0.59	0.30	0.54	3.77	-53	-29		513			2.79	11.20
Czech Republic	CZ03	Bohemian Forest, Ple¿né	6	2.56	4.65	0.77	0.17	0.88	0.36	0.45	3.42	-2	-3		249			3.84	22.65
Czech Republic	CZ04	Bohemian Forest, Prá¿ilské	6	1.53	5.75	0.52	0.30	0.63	0.31	0.55	2.09	11	-1		231			4.33	1.79
Czech Republic	CZ05	Bohemian Forest, Laka	6	1.86	6.18	0.86	0.44	1.07	0.44	0.75	1.98	35	24		547			4.01	0.65
Czech Republic	CZ06	Bohemian Forest, Zd´árské	6	3.25	5.89	2.09	0.54	2.42	0.52	0.80	6.76	99	57		67			7.71	1.28

Country	Station Code	Station name	n	K25	pH	Ca	Mg	Na	K	Cl	SO4	ANC	Alka-linity	NH4N	NO3N	TOTN	TOTP	TOC/ DOC	AVG H+
				mS m^{-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 N L^{-1}	µg L^{-1}	mg C L^{-1}	µEq L^{-1}
Estland	EE01	River Ahja, Kiidjärve	29	37.78	4.41	62.89	11.75	4.32	1.74	6.90	14.31	3766	3709	64	1101	1502	64		39.15
Finland	FI01	Hirvilampi	12	2.63	6.99	1.53	0.41	1.35	0.77	1.13	5.84	33	19	27	17	298	6	4.49	0.10
Finland	FI02	Vuorilampi	12	3.10	6.64	2.16	0.51	1.77	0.88	1.19	4.93	110	69	131	38	584	10	8.19	0.23
Finland	FI03	Mäkilampi	12	2.34	6.39	1.77	0.33	1.04	0.44	0.98	4.74	44	18	25	15	303	7	4.93	0.41
Finland	FI05	Lapland, Suopalampi	12	1.23	6.28	0.75	0.30	1.03	0.22	0.43	1.03	78	51	5	16	297	13	5.55	0.53
Finland	FI06	Lapland, Vasikkajärvi	12	0.76	4.96	0.36	0.10	0.54	0.17	0.45	1.43	11	11	5	3	127	4	1.53	10.98
Finland	FI07	Vusimaa, Vitsjön	12	3.92	4.93	2.15	0.89	2.93	0.59	3.45	5.78	103	71	19	28	319	5	5.58	11.79
Finland	FI08	N-Karelia,Kakkisenlampi	12	0.60	5.09	0.30	0.06	0.32	0.16	0.29	1.58	-4	-6	20	20	180	7	2.85	8.15
Finland	FI09	Unknown	14	3.37	7.25	3.10	0.48	1.65	0.58	2.37	4.08	128	88	14	12	230	4	2.81	0.06
Germany	DE01	Schwarzwald, Dürreychbach	37	19.75	6.75	2.46	0.90	2.00	2.17	2.52	3.56	111	98	18	1164		10	2.58	0.18
Germany	DE02	Fichtelgebirge, Eger	35	5.70	6.27	2.74	1.28	5.32	1.01	10.32	4.90	41	100		768			3.80	0.54
Germany	DE03	Rothaargebirge, Elberndorfer Bach	42	7.16	5.59	3.35	2.89	2.30	0.43	2.51	11.32	126		50	1087			2.04	2.59
Germany	DE04	Sächsische Tieflandsbucht, Ettelsbach	36	39.84	5.13	43.25	11.19	7.36	2.73	10.75	152.64	-150	65	75	1917			11.34	7.44
Germany	DE05	Schwarzwald, Goldersbach	35	15.20	6.16	2.48	0.82	2.00	1.13	1.74	3.34	154	148	16	481		5	4.72	0.70
Germany	DE06	Hunsrück, Gräfenbach	25	8.43	6.02	4.45	2.40	2.78	0.88	5.64	19.74	-16	50	43	464		11	6.03	0.95
Germany	DE07	Erzgebirge, Grosse Pyra	33	6.17	5.03	4.06	0.92	2.25	1.04	1.51	17.12	-57	44	21	850			3.68	9.37
Germany	DE08	Bayerischer Wald, Grosse Ohe	77	2.70	5.04	2.16	0.66	1.65	0.67	1.57	2.77	63	97	33	1219		15		9.18
Germany	DE09	Sächsische Tieflandsbucht, Heidelbach	31	47.63	6.10	51.55	8.80	10.65	2.67	20.61	179.10	-521	320	194	536			7.71	0.80
Germany	DE10	Bayerischer Wald, Hinterer Schachtenbach	36	2.44	4.94	2.24	0.57	1.58	0.59	0.72	2.60	65	76		1442				11.60
Germany	DE11	Schwarzwald, Kleine Kinzig	39	22.31	5.60	3.51	1.07	1.96	1.42	2.42	3.99	201	214	33	448		6	2.14	2.48
Germany	DE12	Harz, Lange Bramke	156	5.15	5.35	3.37	1.77	1.77	0.69	2.71	10.87	23	34	123	589	270	25	0.93	4.49
Germany	DE13	Erzgebirge, Talsperre Neunzehnhain	36	16.75	4.60	13.54	6.51			12.09	38.36			44	6762		10		25.03
Germany	DE14	Kaufunger Wald, Nieste 3	17	15.21	5.05	11.25	4.59	3.78	1.53	4.85	27.65	369		78	858	1		1.62	8.84
Germany	DE16	Lauenburgische Seenplatte, Pinnsee	20	3.54	5.47	1.03	0.47	3.00	0.74	5.59	3.94	-8	90	66	103	160	35	7.27	3.41
Germany	DE17	Bayerischer Wald, Rachelsee	8	2.90	4.58	1.68	0.85	1.38	0.85	0.80	2.38	58	50	70	1463	8	6	3.90	26.35
Germany	DE18	Fichtelgebirge, Röslau	35	3.75	4.80	2.22	0.57	3.03	0.56	1.76	9.06	8	73		463			7.04	15.67
Germany	DE19	Taunus, Rombach 2	18	12.70	4.58	4.40	2.61	8.61	0.85	14.15	12.17	10		72	2356	2		1.22	26.57
Germany	DE21	Erzgebirge, Rote Pockau	33	11.18	6.32	8.68	3.03	4.70	1.15	4.63	32.97	34	76	22	911			5.83	0.48
Germany	DE23	Bayerischer Wald, Seebach	38	2.28	6.89	1.89	0.68	1.48	0.58	0.79	2.41	62	84		1130				0.13
Germany	DE24	Erzgebirge, Talsperre Sosa	46	6.72	5.12	4.90	2.38			2.72	18.18			50	1341		14		7.58
Germany	DE25	Elbsandsteingebirge, Taubenbach	29	19.40	6.63	29.27	1.83	2.17	2.05	3.95	52.17	465	572	26	1326	2	48	4.26	0.24

Country	Station Code	Station name	n	K25	pH	Ca	Mg	Na	K	Cl	SO4	ANC	Alka-linity	NH4N	NO3N	TOTN	TOTP	TOC/ DOC	AVG H+
				mS m^{-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 N L^{-1}	µg L^{-1}	mg C L^{-1}	µEq L^{-1}
Germany	DE26	Hunsrück, Traunbach 1	37	6.52	6.53	2.26	1.71	3.92	0.92	8.00	6.68	67	81	86	513		11	8.65	0.30
Germany	DE27	Bayerischer Wald, Vorderer Schachtenbach	36	2.67	5.70	2.58	0.68	1.99	0.68	0.84	3.01	111	107		1270				1.99
Germany	DE28	Oberpfälzer Wald. Waldnaab 2	7	4.05	4.27	7.70	1.80	2.77	1.36	1.76	6.90	145	235	32	3180		22	3.73	53.54
Germany	DE29	Oberpfälzer Wald, Waldnaab 8	7	6.15	5.61	7.80	1.43	3.78	1.67	1.82	15.61	95	386	32	1813		33	5.67	2.44
Germany	DE30	Erzgebirge, Wilde Weisseritz	36	9.03	6.69	8.45	1.89	2.96	1.52	3.53	22.39	107	187	35	1003	1	40	4.53	0.20
Germany	DE31	Erzgebirge, Wolfsbach	33	19.96	4.85	16.36	5.52	10.25	2.04	17.82	36.97	330	368	22	2324	3	43	4.79	14.01
Germany	DE32	Rothaargebirge, Zinse	42	6.13	6.28	3.03	2.28	2.10	0.32	2.33	10.03	112		50	703			2.03	0.52
Germany	DE33	Fichtelgebirge, Zinnbach	29	6.99	5.39	3.15	0.73	2.55	0.91	1.75	16.46	-124	50		790			7.46	4.03
Germany	DE34	Odenwald, Schmerbach 1	19	8.62	4.82	3.93	2.12	2.06	1.87	4.58	16.95	-25		75	720	1		4.08	15.00
Germany	DE35	Taunus, Rombach 4	15	11.83	5.22	5.71	3.71	27.59	0.58	47.13	9.87	147		70	1720	1		2.08	6.01
Italy	IT01	Piemonte, Lake Paione Inferiore	4	1.40	5.40	1.39	0.13	0.34	0.39	0.15	1.83	33	41	7	424	501	3		3.99
Italy	IT02	Piemonte, Lake di Mergozzo	3	5.68	6.44	5.73	1.37	2.12	0.96	1.40	7.63	267	252	5	701	835	5		0.37
Italy	IT03	Piemonte, Lake Paione Superiore	4	1.00	5.14	0.82	0.09	0.26	0.34	0.20	1.48	8	12	21	340	434	4		7.28
Italy	IT04	Piemonte, River Cannobino	36	4.85	5.25	4.38	1.49	1.83	0.79	1.16	5.74	231	226	9	808	937	8		5.68
Italy	IT05	Piemonte, River Pellino	36	5.62	5.92	4.88	1.18	3.57	0.64	2.73	4.48	225	214	11	1639	1806	14		1.20
Italy	IT06	Piemonte, River Pellesino	36	5.55	6.08	4.24	0.91	4.22	0.73	3.84	3.35	191	179	30	1681	1918	40		0.83
Latvia	LV03	Liela Jugla, Zaki	36	314.24	6.72	67.03	15.19	3.86	2.30	5.24	61.41	3341	3743	108	761	1454	58	16.07	0.19
Latvia	LV04	Tulija, Zoseni	35	258.83	5.42	54.07	12.54	2.82	1.78	2.89	17.09	3425	3530	74	497	1244	46	17.50	3.77
Latvia	LV05	Zvirbuli stream, hydrosite	30	58.35	5.72	3.69	1.03	1.64	0.66	2.21	4.23	203	97	293	47	1535	33	64.76	1.91
Latvia	LV06	Sesava mouth	36	521.56	6.80	102.19	32.67	10.99	5.19	23.89	86.44	5590	6205	122	4302	5371	121	11.98	0.16
Latvia	LV07	Amula mouth	36	333.06	5.73	64.72	21.59	4.96	3.19	5.78	24.18	4607	4729	55	415	1011	57	12.11	1.86
Norway	NO01	Aust-Agder, Birkenes	156	2.98	4.81	0.80	0.25	2.78	0.10	3.93	3.21	-3	2	19	120	327		5.91	15.56
Norway	NO04	Finnmark, Dalelv	157	3.59	6.91	1.57	0.85	3.77	0.27	5.91	4.00	69	37	6	11	127		3.40	0.12
Norway	NO11	Møre og Tomsdal, Kårvatn	156	1.28	6.85	0.75	0.21	1.38	0.15	2.09	0.72	42	29		30	72		0.92	0.14
Norway	NO03	Buskerud, Langtjern, outlet	155	1.26	4.17	0.98	0.14	0.57	0.10	0.41	1.18	51	5	9	13	267	5	10.82	68.34
Norway	NO10	Telemark, Storgama	152	1.27	5.34	0.51	0.08	0.65	0.05	0.72	1.31	11	0	14	43	280		5.76	4.55
Poland	PL01	Tatra Mountains, Dlugi Staw Gasienicowy	32	1.88	5.59	1.96	0.12	0.36	0.11	0.26	2.34	33	42		530	860	7		2.56
Poland	PL02	Tatra Mountains, Zielony Staw Gasienicowy	32	2.16	6.11	2.63	0.21	0.42	0.15	0.23	2.26	99	63		255	424	4		0.77
Poland	PL03	Karkonosze, Maly Stav	12	1.79	5.55	1.11	0.24	1.32	0.21	0.46	3.52	43	42	31	121				2.83
Sweden	SE01	Delångersån Iggersund	34	4.31	7.19	3.66	1.16	2.91	0.79	2.72	3.82	262	185	11	91	352	9	6.05	0.06
Sweden	SE02	Alsterån Alster	36	6.78	5.96	5.64	1.48	5.29	1.07	6.63	7.62	305	169	31	133	679	20	13.53	1.09

Country	Station Code	Station name	n	K25	pH	Ca	Mg	Na	K	Cl	SO4	ANC	Alka-linity	NH4N	NO3N	TOTN	TOTP	TOC/ DOC	AVG H+
				mS m^{-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 N L^{-1}	µg L^{-1}	mg C L^{-1}	µEq L^{-1}
Sweden	SE05	Tväringen	16	2.47	6.69	2.59	0.63	1.36	0.59	0.64	1.90	197	128	14	13	307	6	6.79	0.21
Sweden	SE06	Stensjön	34	1.61	5.16	1.27	0.36	1.23	0.26	0.69	1.82	94	40	21	17	290	6	6.05	6.94
Sweden	SE08	Brunnsjön	36	6.06	5.76	4.05	1.48	4.69	0.80	6.00	10.63	151	-3	34	89	610	11	18.72	1.72
Sweden	SE09	Fiolen	35	4.93	5.15	2.93	1.05	3.97	1.51	5.95	6.14	143	71	21	61	501	14	6.64	7.09
Sweden	SE10	Storasjö	15	3.01	5.67	1.39	0.58	3.10	0.45	3.66	3.53	84	-2	28	30	385	15	10.73	2.15
Sweden	SE11	Fräcksjön	33	6.02	6.54	3.35	1.15	6.15	0.82	9.68	5.06	166	74	15	82	466	9	9.19	0.29
Sweden	SE12	Härsvatten	35	4.73	6.06	0.62	0.68	5.40	0.43	8.96	4.03	-9	-26	35	70	302	4	3.60	0.87
Switzerland	CH03	Lago di Tomè	10	1.13	5.73	0.99	0.08	0.34	0.16	0.16	1.58	2	3	24	504	609	5	0.64	1.88
Switzerland	CH05	Laghetto Inferiore	12	1.14	5.04	1.12	0.10	0.33	0.35	0.11	1.62	30	31	21	279	370	4	0.29	9.13
Switzerland	CH06	Laghetto Superiore	12	1.08	4.93	1.05	0.09	0.27	0.28	0.10	1.41	27	28	23	274	354	4	0.26	11.72
Switzerland	CH09	Lago Nero	6	1.68	5.90	1.98	0.15	0.35	0.38	0.10	2.66	67	64	13	161	265	8	0.34	1.25
Switzerland	CH19	Lago d'Alzasca	6	1.79	6.41	1.92	0.21	0.50	0.43	0.16	2.14	78	74	21	273	396	5	0.49	0.39
Switzerland	CH20	Lago del Starlaresc da Sgiof	12	1.19	7.61	0.71	0.12	0.35	0.20	0.20	1.64	-6	0	37	436	590	4	0.64	0.02
Switzerland	CH26	Maggia	39	6.35	4.64	7.75	0.64	1.66	1.49	1.08	9.13	287	286	59	576	641	4	0.59	23.16
Switzerland	CH27	Vedeggio	40	4.71	6.70	4.53	0.91	1.67	0.60	0.94	6.41	154	147	53	1058	1142	5	0.57	0.20
Switzerland	CH28	Verzasca	39	2.51	6.51	2.65	0.22	0.71	0.54	0.21	3.61	61	60	50	733	828	4	0.41	0.31
United Kingdom	UK01	Scotland, Loch Coire nan Arr	11	4.04	4.83	0.85	0.73	4.96	0.31	8.87	1.68	39	15		37	132		3.27	14.86
United Kingdom	UK04	Scotland, Lochnagar	12	1.95	4.65	0.50	0.36	1.76	0.18	2.65	2.16	-5	0		291	306		1.54	22.45
United Kingdom	UK07	Scotland, Round Loch of Glenhead	11	2.78	5.06	0.57	0.46	3.12	0.29	5.71	2.02	-2	-2		106	260		6.55	8.62
United Kingdom	UK10	England, Scoat Tarn	12	2.73	6.22	0.49	0.46	2.77	0.22	4.97	2.42	-18	-4		217	261		4.58	0.60
United Kingdom	UK15	Wales, Llyn Llagi	12	2.59	6.24	0.86	0.50	3.48	0.13	6.28	1.92	17	2		68	335		3.28	0.58
United Kingdom	UK21	N.Ireland, Blue Lough	12	4.54	6.69	0.57	0.56	5.09	0.41	8.51	3.04	-19	-5		317	449		5.93	0.20
United States	US24	New York, Catskill Mnt., Rondout Creek	110	1.95	7.57	1.33		0.35	0.26	0.46	4.46		1	32	285			2.46	0.03
United States	US25	W Br Neversink R At Winnisook, Catskills	133	2.24	6.96	0.80		0.26	0.18	0.40	4.37		-17	21	282			2.92	0.11
United States	US26	Biscuit Brook, Catskills	210	1.97	4.32	2.09		0.33	0.18	0.49	4.41		22	21	288			2.20	47.42
United States	US23	New York, Catskill Mnt., E. Branch Neversink, Head	139	2.07	5.64	1.00		0.30	0.21	0.44	4.21		-9	52	288			3.25	2.27
United States	US27	Little Hope Pond, Adirondacks	35	2.12	5.73	2.04	0.54	0.60	0.35	0.29	3.49	97	41	21	48			12.23	1.87
United States	US28	Big Hope Pond, Adirondacks	35	2.17	5.52	2.02	0.58	0.75	0.37	0.57	3.72	94	52	16	46			8.17	2.99
United States	US29	East Copperas Pond, Adirondacks	35	1.94	5.13	0.70	0.14	0.14	0.28	0.21	2.12	7	-16	77	35			10.31	7.36
United States	US30	Sunday Pond, Adirondacks	35	1.09	4.59	0.56	0.20	0.06	0.26	0.17	2.40	-2	-2	9	13			1.94	25.55
United States	US31	Sochia Pond, Adirondacks	35	1.31	4.21	0.35	0.10	0.09	0.14	0.21	1.85	-15	-8	94	43			4.74	61.77

Country	Station Code	Station name	n	K25	pH	Ca	Mg	Na	K	Cl	SO4	ANC	Alka-linity	NH4N	NO3N	TOTN	TOTP	TOC/ DOC	AVG H+
				mS m^{-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 N L^{-1}	µg L^{-1}	mg C L^{-1}	µEq L^{-1}
United States	US32	Marcy Dam Pond, Adirondacks	35	1.88	6.98	1.64	0.28	0.68	0.06	0.27	3.80	29	28	7	284			3.01	0.10
United States	US33	Grass Pond, Adirondacks	34	1.67	4.81	0.49	0.16	0.10	0.32	0.22	1.52	10	-18	39	34			8.99	15.54
United States	US34	Little Clear Pond, Adirondacks	35	2.22	5.01	2.61	0.74	0.09	0.43	0.19	1.55	167	143	73	21			7.07	9.80
United States	US35	Loon Hollow Pond, Adirondacks	35	2.10	5.72	0.55	0.13	0.36	0.23	0.27	3.78	-41	-16	28	190			4.43	1.90
United States	US36	Willys Lake, Adirondacks	35	2.11	6.84	0.98	0.17	0.41	0.28	0.27	4.42	-31	-8	13	282			2.55	0.14
United States	US37	Woods Lake, Adirondacks	35	1.97	6.18	2.11	0.24	0.43	0.25	0.28	4.22	37	25	10	245			4.15	0.66
United States	US38	Middle Settlement Lake, Adirondacks	34	1.54	6.42	0.91	0.19	0.61	0.22	0.26	3.57	6	10	31	80			3.14	0.38
United States	US39	Grass Pond, Adirondacks	35	2.20	5.45	1.56	0.34	0.92	0.32	0.31	4.48	28	30	16	349			3.97	3.54
United States	US40	Middle Branch Lake, Adirondacks	35	1.99	6.35	1.69	0.40	0.89	0.35	0.28	3.82	72	53	9	74			4.40	0.45
United States	US41	Limekiln Lake, Adirondacks	35	2.07	6.32	1.91	0.35	0.73	0.26	0.59	4.09	43	32	7	189			3.37	0.48
United States	US42	Squaw Lake, Adirondacks	35	1.70	5.61	1.44	0.36	0.41	0.22	0.29	3.75	29	19	13	141			3.51	2.48
United States	US43	Indian Lake, Adirondacks	35	1.94	4.53	1.12	0.28	0.45	0.15	0.27	3.90	0	0	11	185			5.47	29.54
United States	US44	Brook Trout Lake, Adirondacks	35	1.61	5.43	1.07	0.27	0.47	0.19	0.28	3.84	5	8	21	108			3.33	3.75
United States	US45	Lost Pond, Adirondacks	33	2.13	6.03	1.22	0.31	0.66	0.18	0.29	4.10	11	10	38	225			6.15	0.94
United States	US46	South Lake, Adirondacks	35	1.89	6.92	1.37	0.30	0.58	0.22	0.32	3.75	13	14	10	338			2.94	0.12
United States	US47	North Lake, Adirondacks	35	2.07	5.35	1.32	0.32	0.58	0.22	0.29	4.15	6	6	7	315			5.04	4.42
United States	US48	Willis Lake, Adirondacks	34	2.34	4.64	2.55	0.46	0.92	0.10	0.69	3.89	106	65	9	27			8.06	22.75
United States	US49	Long Pond, Adirondacks	35	2.55	5.73	1.16	0.43	0.53	0.29	0.35	3.95	28	-12	17	33			14.54	1.86
United States	US50	Carry Pond, Adirondacks	35	1.39	6.50	0.78	0.18	0.21	0.22	0.21	3.10	-6	-1	33	59			2.23	0.31
United States	US51	Lake Colden, Adirondacks	35	2.00	7.10	1.41	0.23	0.52	0.09	0.24	3.91	-6	6	12	448			4.18	0.08
United States	US52	Avalanche Lake, Adirondacks	35	2.16	5.55	1.44	0.22	0.48	0.12	0.26	3.69	-8	4	15	535			5.46	2.81
United States	US53	Little Simon Pond, Adirondacks	35	2.87	4.93	3.46	0.34	0.67	0.23	0.35	5.10	97	91	7	311			3.44	11.65
United States	US54	Raquette Lake Reservoir, Adirondacks	35	2.49	6.71	1.91	0.47	0.85	0.36	0.41	4.95	51	30	13	204			8.91	0.19
United States	US55	G Lake, Adirondacks	35	1.79	5.65	1.20	0.31	0.57	0.15	0.29	3.90	7	12	7	235			2.59	2.26
United States	US12	New York, Adirondack Mnt., Constable	35	2.15	5.55	1.55	0.28	0.61	0.32	0.30	4.57	15	9	11	227			5.68	2.81
United States	US11	New York, Adirondack Mnt., Arbutus	35	2.66	4.96	2.90	0.52	0.81	0.27	0.41	5.45	98	73	7	98			4.77	10.97
United States	US57	Sagamore Lake, Adirondacks	35	2.52	6.31	2.19	0.57	0.88	0.30	0.35	5.26	67	44	5	226			7.60	0.49
United States	US58	Black Pond Outlet, Adirondacks	35	3.67	5.61	3.62	1.16	1.11	0.38	0.32	4.67	220	210	10	103			3.62	2.46
United States	US59	Windfall Pond Outle, Adirondacks	35	2.38	4.76	2.50	0.47	0.54	0.29	0.32	4.56	71	56	8	261			4.95	17.46
United States	US60	Queer Lake, Adirondacks	35	1.92	7.01	1.66	0.30	0.46	0.30	0.30	4.34	20	15	13	233			3.09	0.10
United States	US14	New York, Adirondack Mnt., Heart Lake	34	1.77	7.04	1.94	0.27	0.54	0.09	0.27	3.54	56	47	10	102			2.39	0.09

Country	Station Code	Station name	n	K25	pH	Ca	Mg	Na	K	Cl	SO4	ANC	Alka-linity	NH4N	NO3N	TOTN	TOTP	TOC/ DOC	AVG H+
				mS m^{-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 N L^{-1}	µg L^{-1}	mg C L^{-1}	µEq L^{-1}
United States	US61	Big Moose Lake, Adirondacks	35	1.96	5.08	1.54	0.28	0.62	0.30	0.37	4.25	19	12	11	226			4.42	8.36
United States	US62	Cascade Lake Outlet, Adirondacks	35	2.69	4.92	2.59	0.52	1.00	0.38	0.33	4.83	97	78	7	256			4.37	12.08
United States	US13	New York, Adirondack Mnt., Dart Lake	35	1.96	6.20	1.62	0.29	0.64	0.31	0.38	4.28	25	17	11	222			4.27	0.63
United States	US63	Little Echo Pond, Adirondacks	35	2.70	7.00	0.59	0.36	0.23	0.17	0.39	2.04	19	-44	29	16			16.45	0.10
United States	US16	New York, Adirondack Mnt., Moss Lake	35	2.58	7.28	2.48	0.49	0.91	0.39	0.39	4.73	88	72	9	233			3.89	0.05
United States	US15	New York, Adirondack Mnt., Lake Rondaxe	35	2.21	4.92	2.01	0.40	0.80	0.35	0.39	4.28	63	50	11	198			3.89	12.15
United States	US64	Squash Pond Outlet, Adirondacks	35	2.56	5.24	0.77	0.17	0.47	0.27	0.28	4.11	-32	-23	20	252			7.37	5.71
United States	US65	West Pond Outlet, Adirondacks	35	1.95	6.21	1.24	0.26	0.57	0.25	0.28	3.48	27	3	24	106			8.95	0.62
United States	US66	Bubb Lake Outlet, Adirondacks	35	2.09	6.68	1.88	0.40	0.77	0.38	0.31	3.96	64	49	15	204			3.30	0.21
United States	US67	Owen Pond, Adirondacks	35	3.42	5.00	3.83	0.72	0.93	0.19	0.44	5.76	135	123	10	390			4.85	10.05
United States	US68	Jockeybush Lake, Adirondacks	35	1.82	5.92	1.24	0.31	0.49	0.17	0.34	4.28	-2	5	12	234			2.28	1.20
United States	US69	Clear Pond, Adirondacks	35	2.55	6.03	2.94	0.37	0.97	0.09	0.28	4.44	116	105	7	78			3.22	0.93
United States	US17	New York, Adirondack Mnt., Otter Lake	35	1.88	6.55	1.26	0.34	0.67	0.19	0.34	4.71	5	10	5	162			2.36	0.28
United States	US70	Nate Pond, Adirondacks	35	2.60	5.38	2.54	0.66	0.87	0.33	0.31	5.08	105	81	11	105			5.35	4.14
United States	US71	Bean Pond, Maine	5	2.04	5.57	1.73		1.17	0.20	0.58	3.30		65	14	0			7.20	2.68
United States	US89	Bourn, Vermont	9	1.22	5.77	0.64	0.29	0.53	0.34	0.29	2.42	27	8		35			5.48	1.70
United States	US90	Grout, Vermont	9	1.39	7.40	1.15	0.32	0.55	0.42	0.47	2.62	49	32		33			3.41	0.04
United States	US91	Hardwood, Vermont	9	1.69	7.23	1.79	0.50	0.51	0.14	0.29	3.11	81	57		27			5.79	0.06
United States	US125	Lily, Vermont	1	1.85	7.91	1.19	0.43	0.98	0.51	1.51	3.06	44	39		0				0.01
United States	US92	Little ¿ Woodford, Vermont	9	1.55	6.10	0.86	0.21	0.64	0.37	0.32	3.76	-2	2		167			2.01	0.80
United States	US126	Little, Winhall, Vermont	1	1.34	6.29	0.97	0.24	0.48	0.30	0.28	2.51	25	10		160				0.51
United States	US93	Stamford, Vermont	9	1.58	5.44	1.18	0.26	0.78	0.30	0.39	3.49	27	17		164			3.61	3.60
United States	US94	Stratton, Vermont	1	1.31	4.54	0.98	0.27	0.53	0.34	0.31	2.90	30	16		60				28.98
United States	US95	Sunset, Vermont	9	1.41	6.77	1.12	0.30	0.80	0.20	0.70	3.14	34	26		20			1.78	0.17
United States	US96	Big Mud, Vermont	9	1.51	4.60	1.13	0.31	0.45	0.26	0.31	3.12	39	6		13			8.19	25.05
United States	US97	Branch, Vermont	9	1.46	6.54	0.62	0.23	0.52	0.30	0.29	2.88	8	-4		50			5.71	0.29
United States	US98	Beaver Pond, Vermont	9	1.98	5.35	2.53	0.31	0.66	0.18	0.45	3.40	98	65		59			5.96	4.52
United States	US123	Haystack, Vermont	9	1.27	6.69	0.63	0.18	0.36	0.11	0.41	2.51	-10	-6		159			1.01	0.21
United States	US100	Howe, Vermont	9	1.59	6.71	1.62	0.34	0.67	0.35	0.45	2.72	75	48		33			5.59	0.19
United States	US122	Cow Mountain, Vermont	1	2.23	6.41	2.82	0.70	0.87	0.49	0.20	3.26	175	107		0				0.39
United States	US101	South ¿ Marlboro, Vermont	1	1.74	6.09	1.53	0.38	0.67	0.30	0.62	3.72	48	44		20				0.80

Country	Station Code	Station name	n	K25	pH	Ca	Mg	Na	K	Cl	SO4	ANC	Alka-linity	NH4N	NO3N	TOTN	TOTP	TOC/ DOC	AVG H+
				mS m^{-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 N L^{-1}	µg L^{-1}	mg C L^{-1}	µEq L^{-1}
United States	US102	Forester, Vermont	9	10.47	6.42	1.65	0.28	16.56	0.47	26.18	3.68	17	-7		21			2.71	0.38
United States	US72	Bracey Pond, Maine	6	2.64	4.32	2.58		1.52	0.26	2.07	1.96		112	12	6			5.78	48.01
United States	US73	Anderson Pond, Maine	3	1.92	6.28	0.63		2.06	0.27	2.78	2.56		11	11	11			2.50	0.53
United States	US05	Maine, Little Long Pond	2	2.37	5.34	0.85		2.34	0.33	3.44	3.17		17	20	3			2.20	4.60
United States	US06	Maine, Tilden Pond	2	2.50	5.57	1.20		2.49	0.32	3.05	2.59		53	20	9			3.20	2.70
United States	US74	Mud Pond, Maine	6	2.84	4.84	0.50		2.64	0.30	3.23	3.94		-11	20	3			4.65	14.47
United States	US75	Salmon Pond, Maine	6	2.45	5.11	1.38		2.32	0.35	2.95	2.23		61	16	4			3.88	7.79
United States	US76	Wiley Pond, Maine	6	2.67	5.83	3.60		0.79	0.13	0.39	2.48		138	17	1			9.85	1.48
United States	US84	Benner Run, Mid-Apps	21	2.63	6.07	1.52		1.09	0.70	3.18	4.79		13	22	95			1.41	0.85
United States	US85	Linn Run, Mid-Apps	21	3.51	6.18	3.69		0.80	0.42	1.24	9.61		31	20	260			1.18	0.67
United States	US77	Second Pond, Maine	6	2.47	5.11	1.78		1.94	0.32	1.88	2.83		68	17	7			5.25	7.68
United States	US78	Abol Pond, Maine	6	3.28	5.67	3.28		1.76	0.87	0.67	2.62		205	14	2			2.35	2.16
United States	US79	Duck Pond, Maine	5	2.44	6.20	0.23		0.88	0.21	1.52	1.93		-37	10	10			6.00	0.63
United States	US80	Jellison Hl Pd, Maine	6	2.50	6.05	1.35		2.23	0.21	2.56	3.27		40	15	1			4.10	0.90
United States	US81	Crystal Pond, Maine	6	1.07	5.56	0.38		0.82	0.20	1.10	1.67		1	7	2			2.90	2.75
United States	US82	Newbert Pond, Maine	6	4.41	6.43	2.26		2.10	0.27	2.27	4.96		-32	22	7			22.35	0.37
United States	US83	Partridge Pond, Maine	6	1.75	6.70	0.90		1.59	0.25	1.43	2.27		35	14	4			3.75	0.20
United States	US103	Paine Run, Virginia	100	1.96	3.85	0.64		0.56	1.86	0.87	5.60		8	6	16			1.40	140.17
United States	US104	Piney River, Virginia	106	3.31	5.82	2.84		1.73	0.26	0.99	3.53		213	5	89			1.27	1.51
United States	US86	Roberts Run, Mid-Apps	21	2.79	4.67	1.86		0.68	0.55	0.93	8.08		0	12	62			2.03	21.53
United States	US105	Staunton River, Virginia	99	1.69	5.97	1.32		1.40	0.43	0.79	2.34		80	3	2			1.05	1.07
United States	US87	Stone Run, Mid-Apps	21	2.71	5.76	1.73		0.66	0.41	0.96	8.17		-5	18	17			1.31	1.73
United States	US88	Baldwin Creek, Mid-Apps	21	3.60	7.04	3.44		0.79	0.60	1.39	9.15		49	20	349			0.94	0.09

Appendix B. Sites without trend analysis

WDID	Trend	Insensitive to acidification	Record too short	Possible other sources of sulphate	Other disturbances in the catchment
BY01	Only sulphate	*			
EE01	Only sulphate	*			
HU01	Only sulphate	*			
LV01	Only sulphate	*			
LV02	Only sulphate	*			
LV03	Only sulphate	*			
LV04	Only sulphate	*			
LV05	Only sulphate	*			
CH26	no		*		
CH27	no		*		
CH28	no		*		
DE04	no			*	Sulphate source in the catchment
DE09	no			*	Sulphate source in the catchment
DE14	no				Local source of disturbance
DE25	no			*	Sulphate source in the catchment
DE31	no			*	Sulphate source in the catchment
US101	no		*		
US122	no		*		
US125	no		*		
US126	no		*		
US94	no		*		

Appendix C. Results of trend analysis for individual 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	CH03	**-1.33**	**0.004**	7	1.25	0.453	7	0.00	1.000	7	0.00	0.881	7	0.34	0.652	7	0.06	0.881	7			
Alps	CH05	**-1.02**	**0.003**	10	0.19	0.590	10	-0.15	0.788	10	0.01	0.325	10	0.61	0.788	10	**-1.95**	**0.025**	10			
Alps	CH06	**-1.58**	**0.026**	8	0.11	1.000	8	**1.12**	**0.006**	8	0.02	0.621	8	1.53	0.083	8	-0.30	0.621	8			
Alps	CH09	-0.90	0.176	7	-0.04	0.652	7	0.83	0.453	7	0.00	0.881	7	-0.13	0.881	7	-2.09	0.176	7			
Alps	CH19	**-1.95**	**0.011**	7	0.79	0.176	7	0.50	0.176	7	0.00	0.881	7	1.29	0.881	7	-2.12	0.453	7			
Alps	IT01	**-1.26**	**0.006**	11	**0.80**	**0.016**	11	**1.67**	**0.006**	10	0.00	0.938	11	0.16	0.815	11	-0.72	0.586	11			
Alps	IT02	**-4.72**	**0.000**	11	**0.75**	**0.001**	11	**4.00**	**0.004**	10	0.00	0.637	11	**5.93**	**0.003**	10	1.79	0.180	10			
Alps	IT03	**-0.61**	**0.004**	11	0.17	0.586	11	0.56	0.089	10	-0.11	0.102	11	0.31	0.815	11	-0.14	0.484	11			
Alps	IT04	-0.93	0.243	11	0.79	0.073	11	0.72	0.245	10	**0.00**	**0.000**	11	0.52	0.697	11	0.11	0.938	11			
Alps	IT05	-1.00	0.052	11	1.62	0.139	11	**3.57**	**0.025**	10	**0.00**	**0.002**	11	**3.25**	**0.024**	11	**5.40**	**0.004**	11			
Alps	IT06	**-1.26**	**0.004**	11	1.43	0.073	11	3.50	0.128	10	**0.00**	**0.010**	11	3.03	0.073	11	**4.30**	**0.001**	11			
ECEurope	CZ01	**-3.60**	**0.000**	11	**-1.14**	**0.016**	10	-0.12	0.753	9	**-0.97**	**0.010**	11	**3.55**	**0.006**	10	**-1.65**	**0.024**	11	-0.01	0.929	10
ECEurope	CZ02	**-5.13**	**0.001**	11	-0.64	0.243	11	0.65	0.128	10	**-1.44**	**0.004**	11	**4.05**	**0.001**	11	**-1.88**	**0.016**	11	0.00	0.857	10
ECEurope	CZ03	**-7.80**	**0.001**	11	-1.30	0.243	11	0.62	0.463	9	**-0.96**	**0.016**	11	**6.67**	**0.016**	11	**-2.83**	**0.010**	11	**0.13**	**0.048**	10
ECEurope	CZ04	**-2.77**	**0.000**	11	**-2.95**	**0.001**	11	1.67	0.089	10	**-1.59**	**0.000**	11	**4.29**	**0.002**	11	-1.41	0.102	11	0.07	0.325	10
ECEurope	CZ05	-0.89	0.186	11	-0.92	0.186	11	0.60	0.369	10	-0.04	0.815	11	0.71	0.312	11	-0.37	0.484	11	0.02	0.857	10
ECEurope	CZ06	-1.80	0.139	11	0.00	0.392	11	-3.13	0.209	10	0.03	0.484	11	-1.03	0.392	11	-0.96	0.102	11	-0.04	0.788	10
ECEurope	DE02	-0.50	0.404	9	0.14	0.369	10	**3.99**	**0.012**	9	0.04	0.938	11				0.42	0.484	11	0.12	0.532	9
ECEurope	DE07	**-17.94**	**0.002**	10	**-4.57**	**0.001**	11	**-1.76**	**0.022**	9	**-2.41**	**0.006**	11	**22.44**	**0.025**	10	**-8.97**	**0.016**	10	0.09	0.325	10
ECEurope	DE08	**-1.63**	**0.010**	11	**4.29**	**0.001**	11				0.07	0.484	11	-1.03	0.297	9	**2.90**	**0.036**	11			
ECEurope	DE10	**-1.88**	**0.001**	11	**5.04**	**0.024**	11				-0.03	0.697	11	5.83	0.083	8	**3.86**	**0.000**	11			
ECEurope	DE13	**-12.82**	**0.011**	7	19.05	0.881	7				-0.06	0.293	7				-15.34	0.051	7			
ECEurope	DE17	**-5.29**	**0.001**	11	**8.38**	**0.005**	11				**2.36**	**0.036**	11	11.41	0.243	11	**8.21**	**0.002**	11	0.15	0.211	9
ECEurope	DE18	**-7.97**	**0.001**	9	-0.30	0.281	10	3.60	0.167	9	-1.16	0.073	11				**-2.83**	**0.016**	11	**0.23**	**0.037**	9
ECEurope	DE21	-11.89	0.392	11	**-7.48**	**0.001**	11	-0.79	0.835	9	**-1.73**	**0.006**	11	12.60	0.484	11	-14.95	0.052	11	0.32	0.128	10
ECEurope	DE23	**-1.77**	**0.004**	11	**3.03**	**0.006**	11				0.02	0.938	11	-0.75	0.652	7	1.79	0.245	10			
ECEurope	DE24	**-25.45**	**0.000**	11	-1.53	0.484	11				**-1.38**	**0.000**	11				-6.54	0.186	11			
ECEurope	DE27	**-2.57**	**0.000**	11	**4.90**	**0.001**	11				0.03	0.586	11	4.27	0.458	8	**2.86**	**0.010**	11			
ECEurope	DE28	0.06	0.938	11	-2.64	0.325	10	-14.31	0.835	9	-0.07	0.243	11	-12.78	0.531	10	-15.59	0.484	11	-0.16	0.325	10
ECEurope	DE29	-1.58	0.586	11	-1.58	0.655	10	-16.94	0.677	9	-0.74	0.484	11	-15.33	0.245	10	-4.11	0.815	11	-0.27	0.245	10
ECEurope	DE30	**-28.52**	**0.009**	10	**-7.95**	**0.003**	10	6.74	0.138	8	**-0.15**	**0.040**	10	22.82	0.060	10	**-13.96**	**0.040**	10	0.08	0.532	9
ECEurope	DE33	**-27.19**	**0.001**	8	**-2.72**	**0.022**	9	-5.21	0.068	7	**-5.54**	**0.016**	10				**-7.00**	**0.001**	10	**0.48**	**0.026**	8
ECEurope	PL01	**-3.28**	**0.004**	9	**-1.28**	**0.022**	9	0.34	0.805	8	-0.33	0.293	7	4.12	0.061	9	-1.87	0.297	9			
ECEurope	PL02	**-3.79**	**0.004**	9	**-2.04**	**0.012**	9	-3.16	0.095	9	0.03	0.458	8	5.00	0.061	9	-1.54	0.404	9			
NoNordic	FI05	-0.47	0.325	10	-0.05	0.180	10	1.83	0.060	10	-0.03	0.245	10	0.25	0.788	10	0.17	0.929	10	0.18	0.180	10
NoNordic	FI06	-1.41	0.060	10	-0.04	0.472	10	**1.03**	**0.003**	10	-0.09	0.128	10	0.19	0.788	10	**-0.76**	**0.040**	10	0.04	0.128	10
NoNordic	FI08	**-1.60**	**0.000**	10	-0.06	0.128	10	**0.88**	**0.025**	10	**-0.70**	**0.003**	10	**1.12**	**0.040**	10	**-0.55**	**0.009**	10	0.11	0.089	10
NoNordic	NO04	**-3.01**	**0.000**	11	**-0.09**	**0.024**	11	-0.33	0.073	11	**-0.02**	**0.024**	11	1.89	0.186	11	**-1.81**	**0.024**	11	**0.05**	**0.036**	11

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
NoNordic	SE01	**-2.47**	**0.002**	11	-0.20	0.243	11	-0.60	0.815	11	0.00	0.586	11	**2.77**	**0.002**	11	**-1.11**	**0.016**	11	0.05	0.186	11
NoNordic	SE05	**-1.24**	**0.036**	11	-0.03	0.484	11	3.62	0.139	11	-0.01	0.052	11	**5.98**	**0.002**	11	**3.10**	**0.036**	11	-0.08	0.392	11
NoNordic	SE06	**-1.20**	**0.024**	11	-0.02	0.586	11	-1.31	0.243	11	0.02	0.139	11	0.51	0.243	11	**-1.23**	**0.010**	11	0.00	0.938	11
SoNordic	FI01	**-6.63**	**0.000**	10	0.01	0.788	10	**3.67**	**0.000**	10	**-0.72**	**0.002**	10	**5.47**	**0.002**	10	**-3.43**	**0.001**	10	**0.28**	**0.003**	10
SoNordic	FI02	**-7.31**	**0.001**	10	0.22	0.325	10	**5.89**	**0.003**	10	**-0.42**	**0.009**	10	**9.11**	**0.001**	10	0.12	0.788	10	**0.40**	**0.003**	10
SoNordic	FI03	**-4.58**	**0.000**	10	-0.16	0.089	10	-0.17	0.929	10	0.07	0.655	10	-2.58	0.089	10	**-7.49**	**0.001**	10	-0.04	0.369	10
SoNordic	FI07	**-6.56**	**0.000**	10	-0.14	0.245	10	**3.61**	**0.001**	10	**-0.05**	**0.002**	10	**4.17**	**0.001**	10	**-2.20**	**0.006**	10	0.08	0.072	10
SoNordic	FI09	-3.39	0.099	7	-0.14	0.099	7	**3.44**	**0.011**	7	-0.01	0.293	7				0.12	0.652	7	**0.16**	**0.024**	7
SoNordic	NO11	-0.35	0.052	11	0.05	0.102	11	-0.30	0.484	11	-0.01	0.484	11	**1.16**	**0.036**	11	0.42	0.186	11	0.00	0.938	11
SoNordic	NO01	**-3.85**	**0.004**	11	**0.26**	**0.024**	11	0.07	0.212	11	**-0.86**	**0.006**	11	2.65	0.073	11	**-1.29**	**0.036**	11	-0.06	0.484	11
SoNordic	NO03	**-2.91**	**0.001**	11	**-0.08**	**0.000**	11	0.18	0.484	11	-0.26	0.073	11	**2.01**	**0.010**	11	-1.05	0.052	11	0.05	0.484	11
SoNordic	NO10	**-3.28**	**0.004**	11	**-0.47**	**0.016**	11	0.00	0.639	11	**-0.66**	**0.004**	11	**2.65**	**0.001**	11	-0.63	0.073	11	**0.09**	**0.016**	11
SoNordic	SE02	**-13.78**	**0.004**	11	0.29	0.186	11	**5.65**	**0.024**	11	-0.01	0.243	11	**8.66**	**0.024**	11	-4.33	0.102	11	**0.24**	**0.024**	11
SoNordic	SE08	-4.32	0.186	11	**-0.32**	**0.016**	11	0.21	0.697	11	-0.05	0.697	11	2.93	0.073	11	-3.00	0.484	11	-0.21	0.586	11
SoNordic	SE09	**-11.31**	**0.000**	11	0.26	0.243	11	**3.78**	**0.001**	11	-0.01	0.312	11	**9.26**	**0.000**	11	**-6.52**	**0.000**	11	0.06	0.435	11
SoNordic	SE10	**-4.78**	**0.001**	11	-0.04	0.392	11	-0.81	0.312	11	0.06	0.815	11	**3.70**	**0.024**	11	**-2.35**	**0.004**	11	0.11	0.484	11
SoNordic	SE11	**-11.03**	**0.000**	11	0.19	0.186	11	**2.29**	**0.024**	11	**-0.02**	**0.024**	11	**5.40**	**0.002**	11	**-6.39**	**0.016**	11	0.14	0.102	11
SoNordic	SE12	**-8.42**	**0.000**	11	**-0.35**	**0.002**	11	**3.94**	**0.000**	11	**-1.62**	**0.000**	11	**6.81**	**0.000**	11	**-1.76**	**0.004**	11	0.25	0.073	11
UK	UK01	-0.57	0.139	11	-0.06	0.586	11	-3.62	0.052	11	0.00	0.815	11	-0.13	0.938	11	0.13	0.938	11	0.09	0.484	11
UK	UK04	**-1.11**	**0.036**	11	0.16	0.697	11	0.19	0.139	11	**-0.30**	**0.001**	11	0.74	0.312	11	-0.35	0.139	11	0.04	0.274	11
UK	UK07	**-2.70**	**0.006**	11	-0.07	0.938	11	1.21	0.086	11	**-0.74**	**0.010**	11	0.75	0.392	11	-1.18	0.186	11	**0.20**	**0.006**	11
UK	UK10	-0.99	0.139	11	-0.67	0.052	11	0.25	0.586	11	-0.18	0.312	11	-0.19	0.586	11	-0.97	0.052	11	0.05	0.309	11
UK	UK15	**-2.01**	**0.036**	11	-0.43	0.392	11	**-0.53**	**0.024**	11	**-0.31**	**0.010**	11	0.90	0.484	11	-1.14	0.243	11	**0.10**	**0.036**	11
UK	UK21	-3.19	0.102	11	**-1.09**	**0.004**	11	**1.98**	**0.016**	11	**-0.82**	**0.010**	11	1.75	0.312	11	**-1.54**	**0.010**	11	**0.24**	**0.008**	11
WCEurope	DE01	-0.40	0.073	11	-0.63	0.312	11	9.55	0.293	7	**-0.50**	**0.006**	11	**11.93**	**0.001**	11	4.65	0.102	11	0.10	0.586	11
WCEurope	DE03	**-5.69**	**0.000**	11	1.84	0.139	11				-0.05	0.325	10				**-9.18**	**0.016**	11	0.05	0.180	10
WCEurope	DE05	-1.40	0.102	11	-0.24	0.815	11	10.11	0.453	7	-0.01	0.484	11	7.49	0.073	11	2.08	0.243	11	0.06	0.212	11
WCEurope	DE06	**-18.75**	**0.001**	11	-3.53	0.061	9	0.00	0.661	9	**-6.14**	**0.002**	11	6.59	0.095	9	**-9.37**	**0.024**	11	0.14	0.312	11
WCEurope	DE11	0.94	0.392	11	**-2.85**	**0.004**	11	**7.50**	**0.024**	7	**0.04**	**0.006**	11	**8.40**	**0.006**	11	3.20	0.139	11	**0.16**	**0.006**	11
WCEurope	DE12	**-5.98**	**0.002**	9	**0.53**	**0.024**	11				-0.03	0.586	11	-0.52	1.000	9	-2.66	0.392	11	-0.05	0.083	8
WCEurope	DE16	**-5.56**	**0.006**	10	**0.00**	**0.026**	11	**5.12**	**0.024**	8	**-0.77**	**0.006**	11	-4.31	0.061	9	**-4.77**	**0.007**	9	0.09	0.160	11
WCEurope	DE19	-3.36	0.655	10	0.15	0.929	10	0.00	0.411	8	-0.46	0.531	10	11.05	0.128	10	2.00	0.180	10			
WCEurope	DE26	**-4.36**	**0.024**	11	0.98	0.144	9	1.87	0.677	9	**-8.73**	**0.004**	11	**6.73**	**0.022**	9	2.70	0.243	11	**0.22**	**0.036**	11
WCEurope	DE32	**-5.72**	**0.000**	11	0.08	0.938	11				-0.12	0.655	10				**-8.12**	**0.016**	11	0.02	0.421	10
WCEurope	DE34	**-17.82**	**0.003**	10	0.25	0.788	10	0.00	0.250	8	1.81	0.421	10	**16.60**	**0.009**	10	-2.50	0.060	10			
Adirondacks	US23	**-1.87**	**0.036**	11	0.58	0.312	11	**0.82**	**0.036**	11	-0.19	0.697	11							-0.02	0.815	11
Adirondacks	US27	**-2.96**	**0.010**	11	0.02	0.938	11	2.07	0.073	11	-0.33	0.312	11	**2.69**	**0.036**	11	-0.21	0.938	11	-0.12	0.243	11
Adirondacks	US28	**-1.30**	**0.024**	11	-0.09	0.484	11	**2.72**	**0.004**	11	**-0.10**	**0.024**	11	**4.32**	**0.004**	11	**2.38**	**0.006**	11	0.07	0.484	11
Adirondacks	US29	-0.35	0.697	11	-0.06	0.484	11	0.91	0.073	11	-0.22	0.186	11	1.30	0.052	11	0.63	0.139	11	**0.26**	**0.010**	11
Adirondacks	US30	-0.60	0.102	11	**-0.17**	**0.004**	11	0.06	0.586	11	0.22	0.052	11	-0.50	0.312	11	**-0.89**	**0.010**	11	-0.05	0.102	11
Adirondacks	US31	-0.60	0.139	11	-0.12	0.312	11	**1.78**	**0.024**	11	-1.01	0.052	11	**1.07**	**0.006**	11	0.13	0.484	11	**0.16**	**0.002**	11
Adirondacks	US32	**-1.39**	**0.000**	11	0.25	0.312	11	0.70	0.484	11	-0.07	0.102	11	0.66	0.392	11	-0.67	0.484	11	-0.01	0.938	11
Adirondacks	US33	**-0.94**	**0.001**	11	-0.16	0.243	11	**0.45**	**0.036**	11	-0.31	0.052	11	**1.30**	**0.016**	11	0.09	0.586	11	**0.18**	**0.010**	11
Adirondacks	US34	**-0.86**	**0.002**	11	-0.26	0.102	11	**15.39**	**0.024**	11	-0.14	0.052	11	**16.41**	**0.024**	11	15.85	0.073	11	0.04	0.312	11
Adirondacks	US36	**-2.96**	**0.000**	11	-1.37	0.052	11	**0.85**	**0.024**	11	-0.54	0.052	11	**3.20**	**0.002**	11	**-1.59**	**0.000**	11	0.06	0.186	11
Adirondacks	US37	**-2.80**	**0.002**	11	-0.30	0.073	11	0.43	0.186	11	-0.01	0.815	11	**1.72**	**0.010**	11	-2.02	0.073	11	0.09	0.102	11
Adirondacks	US38	**-1.92**	**0.001**	11	**-0.45**	**0.010**	11	0.35	0.484	11	0.03	0.586	11	**1.26**	**0.002**	11	**-0.98**	**0.006**	11	**0.04**	**0.006**	11
Adirondacks	US39	**-1.85**	**0.001**	11	-0.19	0.312	11	0.71	0.392	11	-0.11	0.697	11	1.71	0.186	11	-1.20	0.139	11	0.00	0.938	11

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	US40	**-1.66**	**0.006**	11	-0.68	0.052	11	0.60	0.586	11	-0.05	0.484	11	1.32	0.312	11	-1.16	0.139	11	0.01	0.697	11
Adirondacks	US41	**-2.50**	**0.000**	11	**-0.76**	**0.036**	11	**1.82**	**0.002**	11	-0.10	0.102	11	**3.09**	**0.002**	11	-0.47	0.697	11	**0.07**	**0.036**	11
Adirondacks	US42	**-4.08**	**0.000**	11	-0.66	0.139	11	**1.12**	**0.024**	11	-0.05	0.312	11	**2.54**	**0.004**	11	**-2.81**	**0.010**	11	**0.10**	**0.016**	11
Adirondacks	US43	**-2.51**	**0.004**	11	**-1.27**	**0.010**	11	**0.85**	**0.006**	11	-0.41	0.139	11	**1.89**	**0.006**	11	**-2.18**	**0.024**	11	0.08	0.118	11
Adirondacks	US44	**-3.08**	**0.000**	11	**-1.39**	**0.024**	11	**1.82**	**0.010**	11	**-0.79**	**0.006**	11	**4.09**	**0.004**	11	-0.53	0.073	11	**0.23**	**0.001**	11
Adirondacks	US45	-1.13	0.186	11	**-1.35**	**0.016**	11	0.00	0.938	11	-0.08	0.697	11	1.06	0.243	11	-1.92	0.052	11	0.00	0.938	11
Adirondacks	US46	**-1.85**	**0.000**	11	**-1.36**	**0.006**	11	**2.49**	**0.000**	11	**-0.79**	**0.016**	11	**3.95**	**0.010**	11	0.11	0.938	11	**0.07**	**0.001**	11
Adirondacks	US47	**-1.90**	**0.010**	11	**-1.46**	**0.016**	11	**0.96**	**0.006**	11	-0.26	0.102	11	**1.84**	**0.006**	11	-1.64	0.102	11	0.05	0.274	11
Adirondacks	US48	-1.28	0.392	11	-0.02	0.697	11	1.52	0.243	11	0.01	0.586	11	3.14	0.052	11	0.53	0.586	11	-0.03	0.938	11
Adirondacks	US49	-1.39	0.073	11	-0.15	0.243	11	1.35	0.102	11	-0.63	0.139	11	**2.40**	**0.006**	11	1.32	0.243	11	0.21	0.073	11
Adirondacks	US50	**-1.20**	**0.010**	11	0.01	0.938	11	**1.31**	**0.010**	11	**-0.63**	**0.024**	11	**1.27**	**0.002**	11	-0.06	0.815	11	0.01	0.532	11
Adirondacks	US51	**-2.06**	**0.006**	11	0.65	0.186	11	**0.68**	**0.001**	11	**-0.22**	**0.010**	11	**1.12**	**0.036**	11	-0.78	0.484	11	0.05	0.139	11
Adirondacks	US52	**-1.59**	**0.010**	11	0.42	0.484	11	**0.63**	**0.010**	11	-0.18	0.102	11	1.69	0.073	11	-0.50	0.697	11	0.06	0.312	11
Adirondacks	US53	**-1.72**	**0.000**	11	0.05	0.815	11	0.83	0.697	11	-0.04	0.697	11	2.23	0.392	11	-0.21	0.938	11	0.02	0.392	11
Adirondacks	US54	**-4.02**	**0.000**	11	**-1.47**	**0.001**	11	0.81	0.392	11	-0.04	0.392	11	2.96	0.186	11	**-3.53**	**0.006**	11	**0.28**	**0.036**	11
Adirondacks	US55	**-1.42**	**0.001**	11	-0.53	0.243	11	**1.30**	**0.036**	11	-0.36	0.102	11	2.61	0.052	11	0.04	0.938	11	-0.02	0.586	11
Adirondacks	US12	**-2.85**	**0.000**	11	**-1.17**	**0.006**	11	1.26	0.073	11	-0.38	0.073	11	2.78	0.052	11	-1.79	0.102	11	**0.12**	**0.029**	11
Adirondacks	US11	-1.30	0.102	11	**-0.37**	**0.006**	11	0.88	0.312	11	-0.02	0.139	11	1.01	0.586	11	-0.82	0.586	11	0.01	0.815	11
Adirondacks	US57	**-3.40**	**0.010**	11	**-1.49**	**0.004**	11	0.50	0.102	11	-0.04	0.586	11	2.41	0.073	11	-2.28	0.102	11	0.15	0.052	11
Adirondacks	US58	**-1.78**	**0.000**	11	-0.03	0.815	11	0.73	0.697	11	0.00	0.392	11	-0.37	0.938	11	-2.33	0.073	11	0.01	0.815	11
Adirondacks	US59	**-3.82**	**0.000**	11	**-0.77**	**0.024**	11	0.21	0.586	11	-0.04	0.312	11	2.42	0.052	11	-3.10	0.073	11	**0.09**	**0.036**	11
Adirondacks	US60	**-2.53**	**0.000**	11	-0.35	0.073	11	**1.08**	**0.024**	11	-0.20	0.243	11	**2.35**	**0.002**	11	-0.86	0.139	11	0.05	0.073	11
Adirondacks	US14	**-2.03**	**0.000**	11	-0.14	0.312	11	0.87	0.052	11	-0.02	0.186	11	0.93	0.186	11	-1.35	0.243	11	-0.01	0.484	11
Adirondacks	US61	**-3.15**	**0.000**	11	**-1.45**	**0.004**	11	**1.06**	**0.010**	11	**-0.35**	**0.016**	11	**3.11**	**0.001**	11	-1.72	0.052	11	0.07	0.160	11
Adirondacks	US62	**-1.42**	**0.010**	11	-0.68	0.139	11	-0.61	0.392	11	0.01	0.392	11	0.48	0.697	11	**-2.60**	**0.036**	11	0.04	0.435	11
Adirondacks	US13	**-2.85**	**0.000**	11	**-1.20**	**0.006**	11	**1.47**	**0.002**	11	-0.23	0.073	11	**2.44**	**0.004**	11	-1.67	0.052	11	0.06	0.392	11
Adirondacks	US63	-1.02	0.102	11	**-0.19**	**0.036**	11	**1.84**	**0.036**	11	-1.45	0.052	11	**1.70**	**0.010**	11	0.46	0.243	11	0.02	0.586	11
Adirondacks	US16	**-1.74**	**0.001**	11	**-1.29**	**0.024**	11	1.36	0.102	11	-0.02	0.312	11	1.88	0.186	11	-2.12	0.139	11	0.03	0.139	11
Adirondacks	US15	**-2.41**	**0.000**	11	**-0.93**	**0.004**	11	**1.58**	**0.024**	11	-0.05	0.392	11	**2.83**	**0.036**	11	-1.13	0.243	11	0.04	0.274	11
Adirondacks	US64	**-1.93**	**0.024**	11	-0.84	0.073	11	**0.83**	**0.004**	11	**-0.49**	**0.016**	11	**2.13**	**0.006**	11	-0.56	0.392	11	0.08	0.102	11
Adirondacks	US65	**-2.86**	**0.004**	11	-0.36	0.052	11	0.36	0.312	11	-0.02	0.938	11	1.77	0.052	11	-2.00	0.073	11	0.09	0.484	11
Adirondacks	US66	**-2.60**	**0.001**	11	-0.19	0.484	11	0.64	0.312	11	-0.01	0.697	11	1.46	0.102	11	-1.60	0.052	11	-0.01	0.484	11
Adirondacks	US67	**-3.31**	**0.002**	11	0.55	0.312	11	2.26	0.073	11	**-0.01**	**0.006**	11	2.25	0.243	11	-2.39	0.186	11	0.04	0.312	11
Adirondacks	US68	**-1.88**	**0.000**	11	-0.81	0.139	11	**0.82**	**0.001**	11	-0.35	0.052	11	**2.03**	**0.016**	11	**-0.98**	**0.016**	11	0.03	0.102	11
Adirondacks	US69	**-1.90**	**0.001**	11	0.09	0.484	11	0.03	0.815	11	0.00	0.697	11	0.30	0.697	11	-2.31	0.102	11	0.04	0.243	11
Adirondacks	US17	**-2.25**	**0.000**	11	-0.34	0.073	11	0.46	0.312	11	-0.11	0.186	11	1.26	0.073	11	**-1.53**	**0.006**	11	0.03	0.212	11
Adirondacks	US70	**-2.30**	**0.004**	11	0.03	0.815	11	1.91	0.073	11	-0.01	0.484	11	3.44	0.073	11	1.18	0.586	11	0.05	0.586	11
Appalachians	US24	**-2.10**	**0.001**	11	0.50	0.186	11	-0.08	0.938	11	0.17	0.139	11							0.06	0.392	11
Appalachians	US25	**-2.31**	**0.002**	11	0.41	0.392	11	0.78	0.073	11	0.25	0.312	11							0.09	0.073	11
Appalachians	US26	**-2.17**	**0.002**	11	0.14	0.815	11	0.37	0.586	11	0.04	0.586	11							0.04	0.139	11
Appalachians	US23	**-0.90**	**0.016**	11	**-1.05**	**0.010**	11	**1.29**	**0.016**	11	-0.78	0.052	11	**1.31**	**0.024**	11	**-0.90**	**0.036**	11	-0.01	0.815	11
Appalachians	US84	-0.19	0.484	11	**-0.53**	**0.010**	11	-0.16	0.815	11	-0.01	0.938	11							-0.01	0.586	11
Appalachians	US85	**-2.11**	**0.006**	11	**-1.20**	**0.024**	11	-0.02	0.938	11	-0.03	0.586	11							-0.06	0.052	11
Appalachians	US86	-0.69	0.243	11	**-0.59**	**0.002**	11	-0.04	0.815	11	0.27	0.697	11							-0.03	0.484	11
Appalachians	US87	-1.43	0.186	11	**-0.41**	**0.001**	11	-0.69	0.392	11	0.21	0.312	11							0.00	0.938	11
Appalachians	US88	1.34	0.243	11	**-3.83**	**0.000**	11	0.19	0.697	11	0.02	0.586	11							-0.06	0.073	11
Blue Ridge Mountains	US103	0.60	0.128	10	**-1.29**	**0.001**	10	0.57	0.180	10	-0.09	0.128	10							-0.01	0.917	9

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
Blue Ridge Mountains	US104	0.45	0.421	10	**-2.01**	**0.016**	10	3.50	0.325	10	0.00	0.788	10							-0.04	0.297	9
Blue Ridge Mountains	US105	0.55	0.180	10	**-0.41**	**0.000**	10	0.01	0.929	10	0.01	0.325	10							-0.01	0.600	9
Maine/Atlantic	US71	-0.25	0.835	9	-0.04	0.249	9	0.60	0.677	9	-0.05	0.061	9							-0.07	0.753	9
Maine/Atlantic	US72	0.26	0.929	10	-0.09	0.146	10	1.50	0.060	10	**-0.01**	**0.016**	10							0.06	0.531	10
Maine/Atlantic	US73	0.21	0.655	10	0.04	0.192	10	0.20	0.528	10	-0.13	0.106	10							0.01	0.917	9
Maine/Atlantic	US05	**-0.40**	**0.025**	10	0.00	0.575	10	**1.27**	**0.009**	10	**-0.15**	**0.025**	10							0.04	0.199	9
Maine/Atlantic	US06	-0.22	0.655	10	0.00	1.000	10	**1.67**	**0.012**	10	**-0.04**	**0.009**	10							-0.05	0.206	9
Maine/Atlantic	US74	-0.93	0.060	10	0.01	0.417	10	**1.18**	**0.025**	10	**-0.83**	**0.025**	10							-0.03	0.719	10
Maine/Atlantic	US75	-0.19	0.421	10	0.01	0.531	10	0.53	0.421	10	**-0.02**	**0.006**	10							-0.06	0.089	10
Maine/Atlantic	US76	-0.57	0.655	10	-0.03	0.469	10	-0.11	0.929	10	**0.02**	**0.040**	10							-0.23	0.245	10
Maine/Atlantic	CA10	-0.83	0.458	8							0.19	0.677	9	0.19	1.000	8	-0.43	0.532	9	0.11	0.805	8
Maine/Atlantic	CA11	-0.26	0.677	9	0.00	0.602	10	0.23	0.881	7	-0.06	0.788	10	-0.02	1.000	9	0.72	0.245	10	0.05	0.138	8
Maine/Atlantic	CA12	-1.38	0.138	8	0.00	1.000	8				-0.78	0.138	8	-2.71	0.322	8	-0.74	0.805	8	-0.09	1.000	8
Maine/Atlantic	CA13	-0.56	0.677	9				0.97	0.293	7	**0.57**	**0.020**	10	0.55	0.677	9	0.70	0.655	10	0.31	0.249	9
Maine/Atlantic	CA14	-0.06	0.835	9	0.00	0.117	10	1.57	0.128	7	-0.09	0.180	10	0.58	0.677	9	0.88	0.128	10	-0.03	0.677	9
Maine/Atlantic	US77	-0.96	0.245	10	-0.03	0.787	10	1.08	0.089	10	**-0.03**	**0.006**	10							-0.11	0.128	10
Maine/Atlantic	US78	-0.06	0.929	10	0.00	0.927	10	**5.34**	**0.040**	10	**-0.01**	**0.006**	10							-0.02	0.472	10
Maine/Atlantic	US79	-0.62	0.144	9	0.03	0.532	9	0.36	0.211	9	0.02	1.000	9							0.06	0.092	9
Maine/Atlantic	US80	-0.74	0.325	10	0.00	0.927	10	0.38	0.245	10	**-0.06**	**0.006**	10							0.01	0.787	10
Maine/Atlantic	US81	**-0.60**	**0.025**	10	0.00	0.516	10	-0.34	0.180	10	0.04	0.655	10							-0.02	0.472	10
Maine/Atlantic	US82	7.82	0.051	7	-0.09	0.293	7	-4.19	0.068	7	**3.83**	**0.024**	7							0.66	0.176	7
Maine/Atlantic	US83	**-1.66**	**0.003**	10	0.00	0.856	10	0.85	0.128	10	-0.04	0.089	10							0.03	0.857	10
Ontario	CA01				**-0.40**	**0.040**	10	0.12	0.929	10	0.01	0.655	10				-0.85	0.245	10	0.05	0.245	10
Ontario	CA02				-0.88	0.128	10	**2.83**	**0.040**	10	0.00	0.655	10				-0.06	0.929	10	0.03	0.325	10
Ontario	CA03				-0.71	0.180	10	4.40	0.089	10	0.00	0.788	10				0.43	0.929	10	0.04	0.245	10
Ontario	CA04				-0.69	0.180	10	**4.47**	**0.040**	10	0.00	0.929	10				0.14	0.788	10	0.01	0.655	10
Ontario	CA16	**-2.45**	**0.000**	10	**0.03**	**0.040**	10	0.21	0.472	10	0.01	0.421	10	-0.30	0.655	10	**-2.24**	**0.002**	10	0.03	0.128	10
Ontario	CA17	**-4.03**	**0.000**	10	**0.24**	**0.001**	11	-0.48	0.212	11	0.01	0.052	11	**-1.88**	**0.025**	10	**-4.80**	**0.001**	10	**14.95**	**0.004**	11
Ontario	CA20	**-1.33**	**0.006**	11	**0.03**	**0.002**	11	0.13	0.938	11	0.00	0.180	10	-0.71	0.243	11	-2.30	0.073	11	**6.56**	**0.001**	11
Vermont/Quebec	US89	**-1.96**	**0.002**	11	0.04	0.349	11	-0.16	0.697	11	-0.07	0.392	11	**1.03**	**0.016**	11	**-0.83**	**0.016**	11	0.01	0.917	9
Vermont/Quebec	US90	**-1.48**	**0.006**	11	0.01	0.376	11	0.56	0.186	11	0.02	0.312	11	0.59	0.073	11	-0.57	0.392	11	-0.02	0.292	9
Vermont/Quebec	US91	-0.57	0.243	11	0.07	0.129	11	**1.85**	**0.036**	11	0.01	0.484	11	2.28	0.052	11	1.25	0.139	11	0.06	0.404	9
Vermont/Quebec	US92	**-2.53**	**0.001**	11	0.25	0.435	11	0.20	0.697	11	-0.05	0.586	11	0.30	0.586	11	**-0.96**	**0.010**	11	-0.03	0.463	9
Vermont/Quebec	US93	-0.56	0.392	11	-0.45	0.312	11	-0.38	0.815	11	-0.05	0.586	11	-0.26	0.312	11	**-1.25**	**0.006**	11	-0.09	0.211	9
Vermont/Quebec	US95	**-1.53**	**0.004**	11	0.00	0.937	11	0.26	0.815	11	0.01	0.586	11	0.63	0.312	11	**-1.42**	**0.024**	11	-0.01	0.399	9
Vermont/Quebec	US96	-1.48	0.243	11	-0.26	0.160	11	0.55	0.349	11	-0.25	0.139	11	**1.86**	**0.010**	11	-0.68	0.392	11	0.04	0.677	9
Vermont/Quebec	US97	**-2.13**	**0.004**	11	-0.11	0.392	11	0.99	0.052	11	-0.31	0.312	11	**1.45**	**0.001**	11	**-0.74**	**0.010**	11	0.09	0.404	9
Vermont/Quebec	US98	**-2.17**	**0.004**	11	-0.06	0.583	11	0.03	0.938	11	0.01	0.186	11	0.35	0.697	11	-1.98	0.052	11	0.06	0.345	9
Vermont/Quebec	US99	**-1.49**	**0.000**	11	0.05	0.938	11	0.21	0.392	11	-0.09	0.697	11	**0.94**	**0.000**	11	-0.25	0.312	11	0.03	0.532	9
Vermont/Quebec	US100	**-1.95**	**0.001**	11	0.11	0.133	11	-0.26	0.697	11	0.00	0.938	11	0.09	0.938	11	-1.11	0.139	11	-0.02	0.835	9
Vermont/Quebec	US101	-2.63	0.095	9	0.15	0.338	9	1.59	0.061	9	-1.01	0.144	9	**19.08**	**0.022**	9	1.81	0.144	9	-0.01	0.652	7
Vermont/Quebec	CA05	1.10	0.404	9	0.18	0.236	10	-0.82	0.180	10	**-0.09**	**0.040**	10	0.81	0.404	9	1.08	0.089	10	**0.09**	**0.019**	10
Vermont/Quebec	CA06	0.26	0.677	9	0.09	0.171	10	**-1.32**	**0.020**	10	-0.05	0.325	10	-1.08	0.297	9	**-0.89**	**0.003**	10	0.04	0.209	10
Vermont/Quebec	CA07	0.13	0.835	9	0.05	0.531	10	0.19	0.531	10	-0.47	0.128	10	0.95	0.211	9	0.26	0.531	10	0.06	0.281	10
Vermont/Quebec	CA08	-0.71	0.211	9	**-0.56**	**0.003**	10	-4.71	0.060	10	-0.03	0.089	10	-1.10	0.297	9	**-3.43**	**0.025**	10	0.01	0.805	8
Vermont/Quebec	CA09	0.97	0.532	9	0.12	0.136	10	0.35	0.245	10	-0.30	0.128	10	0.88	0.404	9	0.15	0.655	10	0.07	0.369	10

Appendix D. Reports and publications from the ICP-Waters Programme

Manual for Chemical and Biological Monitoring. Programme Manual. Prepared by the Programme Centre, Norwegian Institute for Water Research. NIVA, Oslo 1987.

Norwegian Institute for Water Research, 1987. Intercalibration 8701. pH, Ks, SO_4, Ca. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1988. Data Report 1987 and available Data from Previous Years. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1988. Intercalibration 8802. pH, K_{25}, HCO_3, NO_3, SO, Cl, Ca, Mg, Na, K. Programme Centre, NIVA, Oslo.

Proceedings of the Workshop on Assessment and Monitoring of Acidification in Rivers and Lakes, Espoo, Finland, 3rd to 5th October 1988. Prepared by the Finnish Acidification Research Project, HAPRO, Ministry of Environment, October 1988.

Norwegian Institute for Water Research, 1989. Intercalibration 8903: Dissolved organic carbon and aluminium fractions. Programme Centre, NIVA, Oslo. NIVA-Report SNO 2238-89.

Note: Some reflections about the determination of pH and alkalinity. Prepared by the Programme Centre, Norwegian Institute for Water Research. Håvard Hovind, NIVA, Oslo October 1989.

Hovind, H. 1990. Intercalibration 9004: pH and alkalinity. Programme Centre, NIVA, Oslo. NIVA-Report SNO 2465-90.

Skjelkvåle, B.L. and Wright, R.F. 1990. Overview of areas sensitive to acidification: Europe. Programme Centre, NIVA, Oslo. Acid Rain Research Report 20/1990. NIVA-Report 2405-90. ISBN 82-577-1706-1.

Johannessen, M. 1990. Intercalibration in the framework of an international monitoring programme. Proceedings of the third annual Ecological Quality Assurance Workshop, Canada Centre for Inland Waters, Burlington Ontario. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1990. Data Report 1988. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1990. Data Report 1989. Programme Centre, NIVA, Oslo.

Proceedings for the 5th Meeting of the Programme Task Force Freiburg, Germany, October 17 -19, 1989. Prepared by the Umweltbundesamt, Berlin July 1990.

Hovind, H. 1991. Intercalibration 9105: pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K and TOC. Programme Centre, NIVA, Oslo. NIVA-Report 2591-91.

Norwegian Institute for Water Research, 1991. The Three Year Report. Summary and results 1987 – 1989: Results from the International Co-operative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1991. Summary of The Three Year Report 1987 – 1989. Programme Centre, NIVA, Oslo.

Scientific papers presented at the Sixth Task Force meeting in Sweden 23 - 24 October 1990. Swedish Environmental Protection Agency, Sweden, September 1991.

Seventh Task Force meeting of international Co-operative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes. Galway, Ireland. September 30 - October 3 1991. Proceedings.

Johannessen, M., Skjelkvåle, B.L. and Jeffries, D. 1992. International cooperative Programme on Assessment and Monitoring of Rivers and Lakes. In: Conference Abstracts, Intern. Conference on Acidic Deposition, Glasgow 16-21, sept. 1992, p. 449. Kluwer Academic Press.

Hovind, H. 1992. Intercalibration 9206: pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, Al and DOC. Programme Centre, NIVA, Oslo. NIVA-Report 2784-92.

Norwegian Institute for Water Research, 1992. Data Report 1990. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1992. Evaluation of the International Co-operative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes. Programme Centre, NIVA, Oslo.

Hovind, H. 1993. Intercalibration 9307: pH, k_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, reactive and non-labile aluminium, TOC and COD-Mn. Programme Centre, NIVA,Oslo. NIVA-Report 2948-93.

Raddum, G.G. 1993. Intercalibration of Invertebrate Fauna 9301. Programme Centre, NIVA, Oslo. NIVA-Report SNO 2952-93.

Proceedings of the 9th Task Force Meeting in Oisterwijk, the Netherlands, November 1-3, 1993. Programme Centre, NIVA, Oslo.

Skjelkvåle, B.L., Newell, A.D, and Johannessen, M. 1993. International Cooperative Programme on Assessment and Monitoring of Rivers and lakes: Status and Results. In: BIOGEOMON - Symposium on Ecosystem Behaviour: Evaluation of Integrated Monitoring in small catchments. Prague, September 18-20, 1993. Czech Geological Survey, Prague 1993. s. 274-275.

Hovind, H. 1994. Intercomparison 9408. pH, k_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, TOC and COD-Mn. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3142-94.

Skjelkvåle, B.L., Newell, A.D., Raddum, G.G., Johannessen, M., Hovind, H., Tjomsland, T. and Wathne, B.M. 1994. The six year report: Acidification of surface water in Europe and North America. Dose/response relationships and long-term trends. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3041-94.

Norwegian Institute for Water Research, 1994. Data Report 1991. Programme Centre, NIVA, Oslo.

Stoddard, J.L. and Traaen, T.S. 1994. The stages of Nitrogen Saturation: Classification of catchments included in "ICP on Waters". In: M. Hornung, M.A. Stutton and R.B. Wilson (eds.) Mapping and Modelling of Critical Loads for Nitrogen: a Workshop Report. Proceedings of a workshop held in Grange-over-Sands (UK), 24-26 October 1994. pp.69-76.

Hovind, H. 1995. Intercomparison 9509. pH, k_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium-reactive and nonlabile, TOC and COD-Mn. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3331-95. ISBN 82-577-2849-7.

Traaen, T.S. and Stoddard, J.L. 1995. An Assessment of Nitrogen Leaching from Watersheds included in ICP on Waters. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3201-95.

Norwegian Institute for Water Research, 1995. Data Report 1992-93. Draft 1994. Part 1, Introduction and Chemistry. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1995. Data Report 1992-1993. Draft 1994. Part 2, Biology and Site-data. Programme Centre, NIVA, Oslo.

Raddum, G.G. 1995. Aquatic Fauna. Dose/response and long term trends. Programme Centre, NIVA, Oslo.

Raddum, G.G. 1995. Intercalibration of Invertebrate Fauna 9502. Programme Centre, NIVA, Oslo.

Raddum, G.G., and Skjelkvåle, B.L. 1995. Critical limits of acidification to invertebrates in different regions of Europe. *Water Air Soil Poll.* 85: 475-480.

Hovind, H. 1996. Intercomparison 9610. pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC and COD-Mn. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3550-96.

Newell, A.D, and Skjelkvåle, B.L. 1996. Acidification trends in surface waters in the International Program on Acidification of Rivers and Lakes. *Water Air Soil Poll.* 93:27-57.

Proceedings of the 10th Task Force Meeting in Budapest 1994. Prepared by the Programme Centre, NIVA, Oslo March 1996.

Norwegian Institute for Water Research, 1996. Programme Manual. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3547-96.

Raddum, G.G. 1996. Intercalibration of invertebrate fauna 9603. Programme Centre, NIVA, Oslo.

Lükewille, A., Jeffries, D., Johannessen, M., Raddum, G.G., Stoddard, J.L and Traaen, T.S. 1997. The Nine Year Report. Acidification of Surface Water in Europe and North America. Long-term Developments (1980s and 1990s). Programme Centre, NIVA, Oslo. NIVA-Report SNO 3637-97.

Hovind, H. 1997. Intercomparison 9711. pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC and COD-Mn. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3716-97.

Johannessen, M., and Skjelkvåle, B.L. 1997. International Co-operative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes - ICP-Waters; Programme objectives, organization and main results. In: Proceedings to "International Conference on management of Transboundary Waters in Europe" 22-25 September 1997 in Poland. Programme Centre, NIVA, Oslo. **ICP-Waters Report 43/1997**.

Henriksen, A. and Posch, M. 1998. Critical loads and their exceedances for ICP-Waters sites. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3821-98, **ICP-Waters Report 44/1998**.

Smith, D. and Davis, I. 1997. International Cooperative programme on Assessment and Monitoring of Acidification of Rivers and lakes: 8th Task Force Meeting, 1992. Can.Tech.Rep.Fish.Aquat.Sci. 2155: iv 68 p.

Summary of The Nine Year Report from the ICP Waters Programme. NIVA-Report SNO 3879-98, **ICP-Waters report 46/1998**.

Raddum, G.G. 1998. Intercalibration 9804: Invertebrate fauna. NIVA-Report SNO 3912-98, **ICP-Waters Report 47/1998**.

Larsen, S.E., Friberg, N. and Rebsdorf, Aa.. (eds.) 1999. Proceedings from the 12th Task Force Meeting in Silkeborg, Denmark, October 23-25, 1996. National Environmental Research Institute, Denmark 52 pp NERI Technical Report, No. 271

Hovind, H. 1998. Intercomparison 9812. pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC and COD-Mn. NIVA-Report SNO 3939-98, **ICP-Waters Report 49/1998**.

Rosseland, B.O., Raddum, G.G. and Bowman, J. 1999. Workshop on biological assessment and monitoring; evaluation and models. NIVA-Report SNO 4091-99, **ICP Waters Report 50/1999**.

Hovind, H. 1999. Intercomparison 9913. pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC and COD-Mn. NIVA-Report SNO 4093-99, **ICP Waters Report 51/1999**.

Skjelkvåle, B. L., Andersen, T., Halvorsen, G. A., Raddum, G.G., Heegaard, E., Stoddard, J. L., and Wright, R. F. 2000. The 12-year report; Acidification of Surface Water in Europe and North America; Trends, biological recovery and heavy metals. NIVA-Report SNO 4208/2000, **ICP Waters report 52/2000.**

Stoddard, J. L., Jeffries, D. S., Lükewille, A., Clair, T. A., Dillon, P. J., Driscoll, C. T., Forsius, M., Johannessen, M., Kahl, J. S., Kellogg, J. H., Kemp, A., Mannio, J., Monteith, D., Murdoch, P. S., Patrick, S., Rebsdorf, A., Skjelkvåle, B. L., Stainton, M. P., Traaen, T. S., van Dam, H., Webster, K. E., Wieting, J., and Wilander, A. 1999. Regional trends in aquatic recovery from acidification in North America and Europe 1980-95. Nature 401:575- 578.

Skjelkvåle, B.L., Olendrzynski, K., Stoddard, J., Traaen, T.S, Tarrason, L., Tørseth, K., Windjusveen, S. and Wright, R.F. 2001. Assessment of trends and leaching in Nitrogen at ICP Waters Sites (Europe And North America). NIVA-report SNO 4383-2001, **ICP Waters report 54/2001.**

Hovind, H. 2000. Intercomparison 0014. pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-Report SNO 4281-2000, **ICP Waters Report 55/2000**.

Hovind, H. 2000. Trends in intercomparisons 8701-9812: pH, K_{25}, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K and aluminium - reactive and nonlabile, TOC, COD-Mn. NIVA-Report SNO 4281-2000, **ICP Waters Report 56/2000**.

Wright, R.F. 2001. Note on: Effect of year-to-year variations in climate on trends in acidification. NIVA-report SNO 4328-2001, **ICP Waters report 57/2001**.

Kvaeven, B. Ulstein, M.J., Skjelkvåle, B.L., Raddum, G.G. and Hovind. H. 2001. ICP Waters – An international programme for surface water monitoring. *Water Air Soil Poll*.**130**:775-780.

Skjelkvåle, B.L. Stoddard J.L. and Andersen, T. 2001. Trends in surface waters acidification in Europe and North America (1989-1998). *Water Air Soil Poll.***130:**781-786.

Stoddard, J. Traaen, T and Skjelkvåle, B.L. 2001. Assessment of Nitrogen leaching at ICP-Waters sites (Europe and North America). *Water Air Soil Poll*. **130**:825-830.

Raddum, G.G. and Skjekvåle B.L. 2000. Critical Load of Acidifying Compounds to Invertebrates In Different Ecoregions of Europe. *Water Air Soil Poll.* **130**:825-830.

Raddum.G.G. 2000. Intercalibration 0005: Invertebrate fauna. NIVA-report SNO4384-2001, **ICP Waters report 62/2001**.

Lyulko, I. Berg, P. and Skjelkvåle, B.L. (eds.) 2001. National presentations from the 16th meeting of the ICP Waters Programme task Force in Riga, Latvia, October 18-20, 2000. NIVA-report SNO 4411-2001. **ICP Waters report 63/001**.

Hovind, H. 2001. pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-Report SNO 4416-2002, **ICP Waters report 64/2001**.

Bull, K.R. Achermann, B., Bashkin, V., Chrast, R. Fenech, G., Forsius, M., Gregor H.-D., Guardans, R., Haussmann, T., Hayes, F., Hettelingh, J.-P., Johannessen, T., Kryzanowski, M., Kucera, V., Kvaeven, B., Lorenz, M., Lundin, L., Mills, G., Posch, M., Skjelkvåle, B.L. and Ulstein, M.J. 2001. Coordinated Effects Monitoring and Modelling for Developing and Supporting International Air Pollution Control Agreements. *Water Air Soil Poll.* **130**:119-130.

Raddum.G.G. 2002. Intercalibration 0206: Invertebrate fauna. NIVA-report SNO-4494-2002, **ICP Waters report 66/2002**.

Skjelkvåle, B.L. and Ulstein, M. (eds). 2002. Proceedings from the Workshop on Heavy Metals (Pb, Cd and Hg) in Surface Waters; Monitoring and Biological Impact. March 18-20, 2002, Lillehammer, Norway. NIVA-report SNO-4563-2002, **ICP Waters report 67/2002**.

Hovind. H. 2002. Intercomparison 0216. pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-Report SNO 4558-2002, **ICP Waters Report 68/2002**.

Halvorsen, G.A, Heergaard, E. and Raddum, G.G. 2002. Tracing recovery from acidification - a multivariate approach. NIVA-report SNO 4564-2002, **ICP Waters report 69/2002**.

Jenkins, A. Larssen, Th., Moldan, F., Posch, M. and Wrigth R.F. 2002. Dynamic Modelling of Surface Waters: Impact of emission reduction - possibilities and limitations. NIVA-report SNO 4598-2002, **ICP Waters report 70/2002.**

Wright, R.F and Lie, M.C. 2002.Workshop on models for Biological Recovery from Acidification in a Changing Climate. 9-11 september 2002 in Grimstad, Norway. Workshop report. NIVA-report 4589-2002.

Skjelkvåle, B.L. (ed.). 2003. Proceedings of the 18^{th} meeting of the ICP Waters Programme Task Force in Moscow, October 7-9, 2002. NIVA-report SNO 4658-2003, **ICP Waters report 71/2002**.

Raddum.G.G. 2003. Intercalibration 0307: Invertebrate fauna. NIVA-report SNO-4659-2003, **ICP Waters report 72/2003**.

Skjelkvåle, B.L. (ed). 2003. The 15-year report: Assessment and monitoring of surface waters in Europe and North America; acidification and recovery, dynamic modelling and heavy metals. NIVA-report SNO 4716-2003, **ICP Waters report 73/2003.**

Hovind, 2003. Intercomparison 0317. pH, K25, HCO3, NO3 + NO2, Cl, SO4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-report SNO 4715-2003, **ICP Waters report 74/2003.**

Raddum, G.G, et al. 2004. Recovery from acidification of invertebrate fauna in ICP Water sites in Europe and North America. NIVA-report SNO 4864-2004, **ICP Waters report 75/2004.**

Skjelkvåle, B.L. (ed). Proceedings of the 19th meeting of the ICP Waters Programme Task Force in Lugano, Switzerland, October 18-20, 2003. NIVA-report SNO 4858-2004, **ICP Waters report 76/2004.**

Raddum, G.G. 2004. Intercalibration: Invertebrate fauna 09/04. NIVA-report SNO 4863-2004, **ICP Waters report 77/2004.**

Hovind, H. 2004. Intercomparison 0418. pH, K25, HCO3, NO3 + NO2, Cl, SO4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-report SNO 4875-2004, **ICP Waters report 78/2004.**

Skjelkvåle et al 2005. Regional scale evidence for improvements in surface water chemistry 1990-2001. *Environmental Pollution, 137: 165-176*

Fjeld, E., Le Gall, A.-C. and Skjelkvåle, B.L. 2005. An assessment of POPs related to long-range air pollution in the aquatic environment. NIVA-report SNO 5107-2005, **ICP Waters report 79/2005.**

De Wit, H. and Skjelkvåle, B.L (eds.). 2005. Proceedings of the 20th meeting of the ICP Waters Programme Task Force in Falun, Sweden, October 18-20, 2004. NIVA-report SNO 5018-2005, **ICP Waters report 80/2005.**

Raddum, G.G. 2005. Intercalibration 0307: Invertebrate fauna. NIVA-report SNO 5067-2005. **ICP Waters report 81/2005**

Hovind, H. 2005. Intercomparison 0317. pH, K25, HCO3, NO3 + NO2, Cl, SO4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-report SNO 5068-2005. **ICP Waters report 82/2005**

Wright, R.F., Cosby, B.J., Høgåsen, T., Larssen, T., Posch, M. 2005. Critical Loads, Target Load Functions and Dynamic Modelling for Surface Waters and ICP Waters Sites. NIVA-report SNO 5166-2005. **ICP Waters report 83/2006.**

De Wit, H. and Skjelkvåle, B.L. (eds.) 2006. Proceedings of the 21th meeting of the ICP Waters Programme Task Force in Tallinn, Estonia, October 17-19, 2005. NIVA-report SNO 5204-2006, **ICP Waters report 84/2006.**

Raddum, G.G. and Fjellheim, A. 2006. Biological intercalibration 1006: Invertebrate fauna. NIVA-report SNO 5314-2006, **ICP Waters report 85/2006.**

Hovind, H. 2006. Intercomparison 0620. pH, K25, HCO3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-report SNO 5285-2006. **ICP Waters report 86/2006.**

Skjelkvåle, B.L., Forsius, M., Wright, R.F., de Wit, H., Raddum, G.G., and Sjøeng, A.S.M. 2006. Joint Workshop on Confounding Factors in Recovery from Acid Deposition in Surface Waters, 9-10 October 2006, Bergen, Norway; Summary and Abstracts. NIVA-report SNO 5310-2006. **ICP Waters report 88/2006.**