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RECENT RESULTS AND UPDATING OF SCIENTIFIC AND TECHNICAL KNOWLEDGE

**TRENDS IN SURFACE WATER CHEMISTRY AND BIOTA:
THE IMPORTANCE OF CONFOUNDING FACTORS**

Report by the Programme Centre of the International Cooperative Programme on Assessment
and Monitoring of Acidification of Rivers and Lakes (ICP Waters)

INTRODUCTION

1. The strongest evidence that emissions control programs have achieved their intended effect comes from a consistent pattern of recovery across a large number of sites. It is expected that decreasing sulphate (SO₄) in waters will result in increasing pH and alkalinity and a recovery of biota. This report aims to provide an overall synthesis and assessment of information on trends in water chemistry and biology in the period 1994–2004. The results are based on the ICP Waters report (deWit and Skjelkvåle 2007) and the report on a workshop on “confounding

factors”, given in the annex, and are presented here in accordance with the 2007 workplan (item 3.3).

2. Special attention is given to “confounding factors”, i.e. factors other than deposition and expected to have an impact on chemical and biological recovery. Especially climate change may significantly influence the behaviour of both terrestrial and aquatic ecosystems. Therefore, the extent of nitrogen (N) retention in the future, and consequently the future influence of N on surface water acidification, represents a key uncertainty in future recovery from acidification.

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

- (a) The acid anions of acidic deposition are sulphate and nitrate (NO_3). Trends in the concentrations of these anions reflect recent trends in deposition (especially SO_4) and in ecosystem response to long-term deposition (e.g. NO_3);
- (b) Base cations (calcium and magnesium) are mobilized by weathering and cation exchange that neutralize acids in watersheds. Base cations will respond indirectly to changes in SO_4 and NO_3 ;
- (c) Acidity, including pH, measured (Gran) alkalinity and calculated acid neutralizing capacity (ANC), reflects the outcome of interactions between changing concentrations of acid anions and base cations.

4. Methods for sample collection and analysis are described in the *ICP Waters Programme Manual*. Quality control of water chemistry data was done by annual between-laboratory controls (chemical intercomparisons). Biological intercalibration was carried out each year to check identifications of species.

5. Minimum requirements to include reported data in the trend analysis were the length of data series, site sensitivity to acidification, and availability of key variables. Chemical records from 179 sites (73 in Europe and 106 in North America) were used in the trend analysis. The sites were grouped in 12 fairly homogeneous regions (figure 1) with regard to deposition level and acid-sensitivity.

6. The Mann-Kendall test and the Sen slope estimator were used to determine the significance level and the slope of the trend. These methods are robust against outliers and missing data and do not require normal distribution of data. The analysis was based on annual means. Within each region, we tested for a significant trend using an adapted version of the Mann-Kendall test designed to include multiple monitoring sites. Differences in trend strength between two time periods (1990–2001 and 1994–2004) were also calculated.

7. The biological data used for trend analysis were from Canada, Central Europe, Scandinavia, and the United Kingdom.

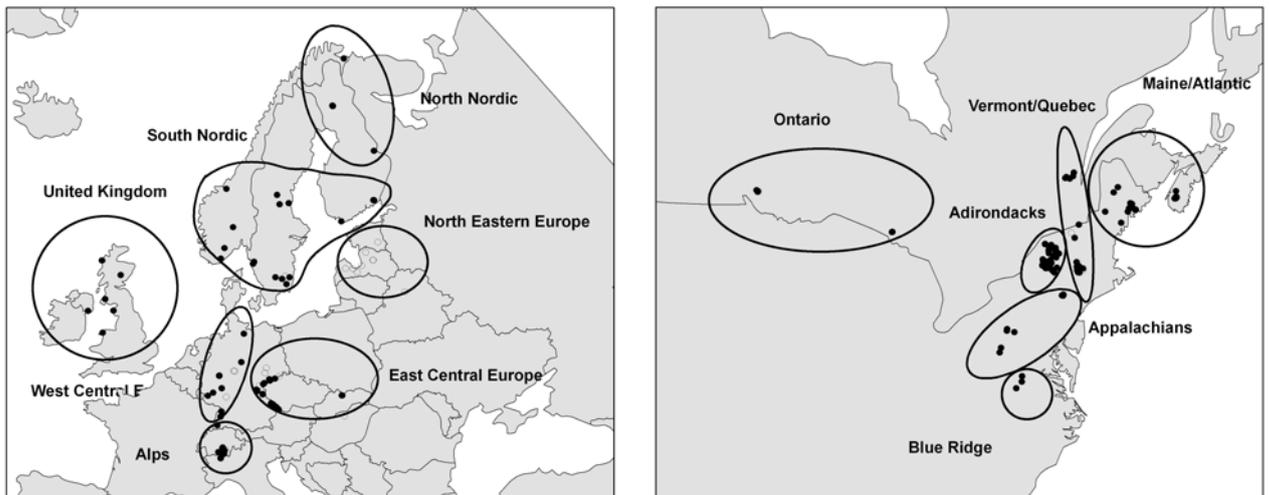


Figure 1. ICP Waters sites grouped in European and North American regions. Dark dots denote sites included in trend analysis and open circles are those not included.

I. WIDESPREAD CHEMICAL RECOVERY

8. The most important finding was the widespread chemical recovery in streams and lakes in most regions in Europe and North America (table 1), despite the slightly reduced rate of decline in SO_4 as compared to the previously reported period of 1990–2001. All regions except two showed a significant increase in pH, and/or alkalinity, and/or acid-neutralizing capacity (ANC). The regions without signs of chemical recovery were Ontario and the Blue Ridge mountains in North America. Soil characteristics in the Blue Ridge Mountains would make a SO_4 decrease unlikely in the short term. The lack of coherent trends in Ontario was probably due to the large variability in the trends in individual sites in the region.

9. Most sites showed a significant decreasing trend in non-marine SO_4 , whereas no site showed significant increase (figure 2). In contrast to the trends reported for the period 1990–2001 in “The 15-year report” (Skjelkvåle 2004), 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 could be expected.

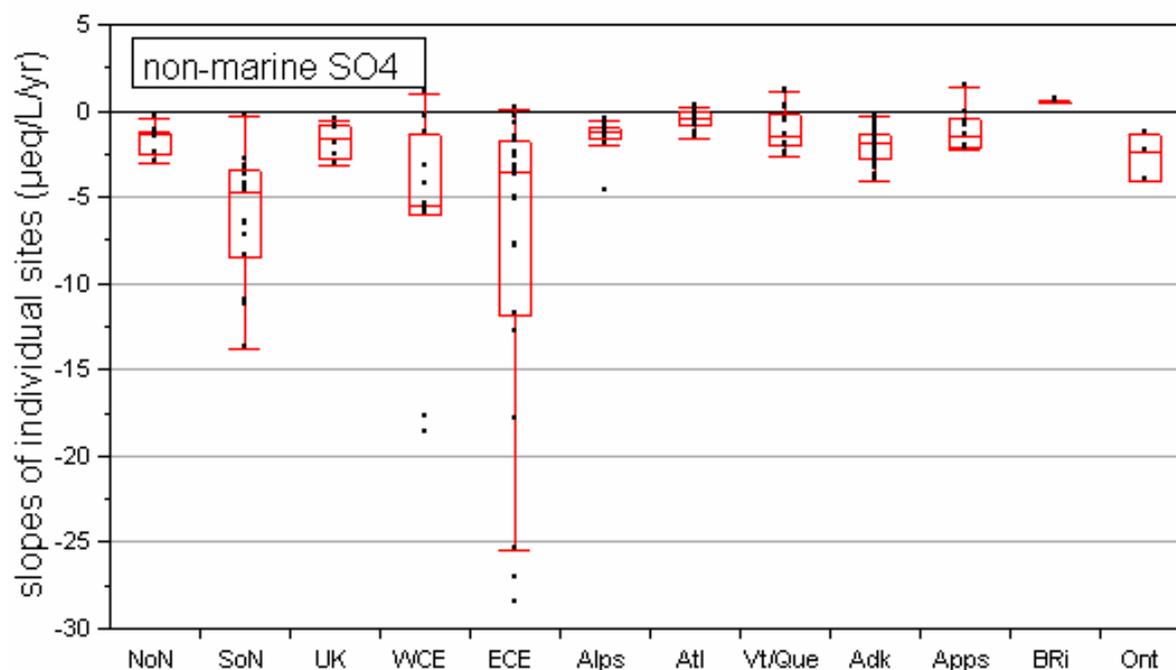


Figure 2. Distributions of slopes for non-marine sulphate (SO_4) trends in European and North American regions. Each box shows the range (from 25th to 75th percentile, with a horizontal line at median) of slopes, while vertical lines (whiskers) show the range of the data that lay within the upper (or lower) quartile plus 1.5 times the interquartile range (or minus 1.5 times the interquartile range). Abbreviations for regions, shown in figure 1, are noted in table 1.

10. Alkalinity and ANC showed increasing trends at roughly one third of the sites while hardly any site showed decreases. Virtually no sites were currently acidifying further, compared to 14 per cent of the sites with decreasing alkalinity in the period 1990–2001.

11. Two thirds of all sites showed no trend in NO_3 , whereas a quarter of all sites showed a decreasing trend. NO_3 increased in less than 10 per cent of the sites. The lack of a uniform trend in NO_3 concentrations illustrates that NO_3 leaching from catchment was affected by a variety of processes. This was in contrast to SO_4 leaching from catchment, which is largely controlled by SO_4 deposition.

12. Dissolved organic carbon (DOC) measurements were not available for all sites. About 80 per cent of the sites lacked a DOC trend, while the remaining ones showed a significant increase. The number of sites with increasing trends in DOC has halved compared to the period 1990–2001.

Table 1. Regional trends at ICP Waters sites in the period 1994–2004 for sulphate (SO₄), alkalinity and acid-neutralizing capacity (ANC). Values are median slopes at different significance levels denoted with p. Abbreviations: n = number of sites, - = no data, n.s. = not significant (p>0.05), significance in increasing order: * (p<0.05), ** (p<0.01) and *** (p<0.001). Units: µeq/L/year.

Region acronym	Region	n	SO ₄		Alkalinity		ANC	
			Median trend	p	Median trend	p	Median trend	p
NoN	Northern Nordic	7	-1.4	**	0.9	n.s.	1.1	**
SoN	Southern Nordic	15	-4.8	***	2.3	**	3.9	***
UK	United Kingdom	5	-1.6	*	0.1	n.s.	0.1	n.s.
WCE	West Central Europe	11	-5.6	***	3.5	n.s.	7.5	***
ECE	East Central Europe	23	-3.6	***	0.1	n.s.	4.2	*
Alps	Alps	11	-1.3	***	0.8	**	0.6	n.s.
Vt/Que	Vermont/Quebec	17	-1.5	**	0.2	n.s.	0.8	*
Atl	Maine/Atlantic Canada	20	-0.5	n.s.	0.7	n.s.	0.2	n.s.
Adk	Adirondacks	50	-1.9	***	0.9	*	1.9	*
Apps	Appalachians	9	-1.4	**	0.0	n.s.	1.3	*
Ont	Ontario	7	-2.4	**	0.2	n.s.	-0.7	n.s.
BRi	Blue Ridge Mountains	3	0.6	n.s.	0.6	n.s.	-	-

II. NO UNIFORM TRENDS IN NITRATE

13. NO₃ trends varied considerably within each region and between regions (figure 2). NO₃ concentrations declined in three regions of North America, while only the Alps in Europe showed a significant increase. These findings are similar to the trends in NO₃ found for the period 1990–2001 (Skjelkvåle, 2004). At most sites, SO₄ was the most important strong acid anion, and the relative importance of NO₃ in the anion load seemed to be constant despite reductions in SO₄.

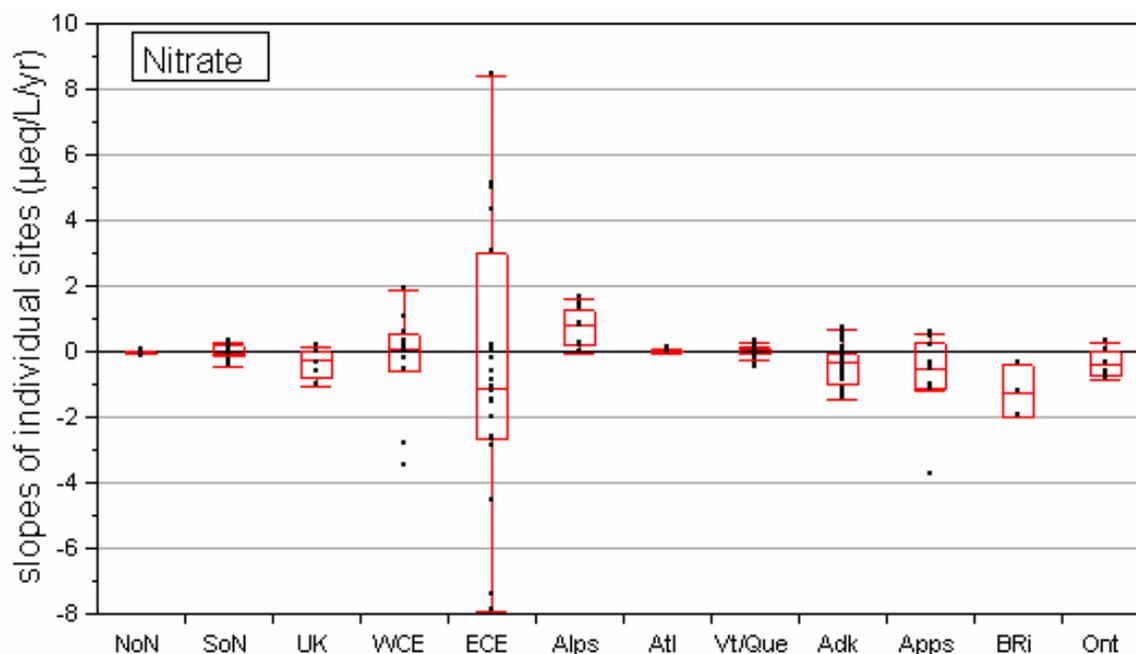


Figure 2. Distributions of slopes for nitrate (NO_3) trends European and North American regions. Each box shows the range (from 25th to 75th percentile, with a horizontal line at median) of slopes, while vertical lines (whiskers) show the range of the data that lay within the upper (or lower) quartile plus 1.5 times the interquartile range (or minus 1.5 times the interquartile range). Abbreviations for regions, shown in figure 1, are noted in table 1.

14. While NO_3 decline seemed to be far more common than NO_3 increase in surface waters, the majority of catchments showed no significant trend. The reasons for various decreasing NO_3 trends included regrowth of young forest in Central Europe, increased retention of atmospherically deposited N because of increased frequency of snow-melt events in Norway and changes in hydrology in the United States. The upward NO_3 trend in the Alps was interpreted as a sign of limited N retention capacity of old growth forests and possibly of climate warming.

15. The distribution of NO_3 trends and the mechanisms proposed to explain them differed greatly. It should be underlined, in agreement with Skjelkvåle (2004), that reduced stream-water NO_3 is not a certain indication of recovery. Unlike SO_4 , NO_3 concentrations at many ICP Waters sites showed substantial interannual variability. The 10-year period assessed in this and previous reports was likely to be insufficiently long to reveal responses to deposition.

16. Deposition of N has declined slightly since 1990 at many ICP Waters sites. At very few sites, similar trends in N deposition and N runoff were found (figure 3). However, the commonly accepted concept of increasing stream or lake NO_3 concentrations in catchments that receive N deposition above certain thresholds was supported. Opposing trends in N deposition and NO_3 run-off illustrated that other factors (confounding factors) than N deposition alone regulate catchment NO_3 leaching.

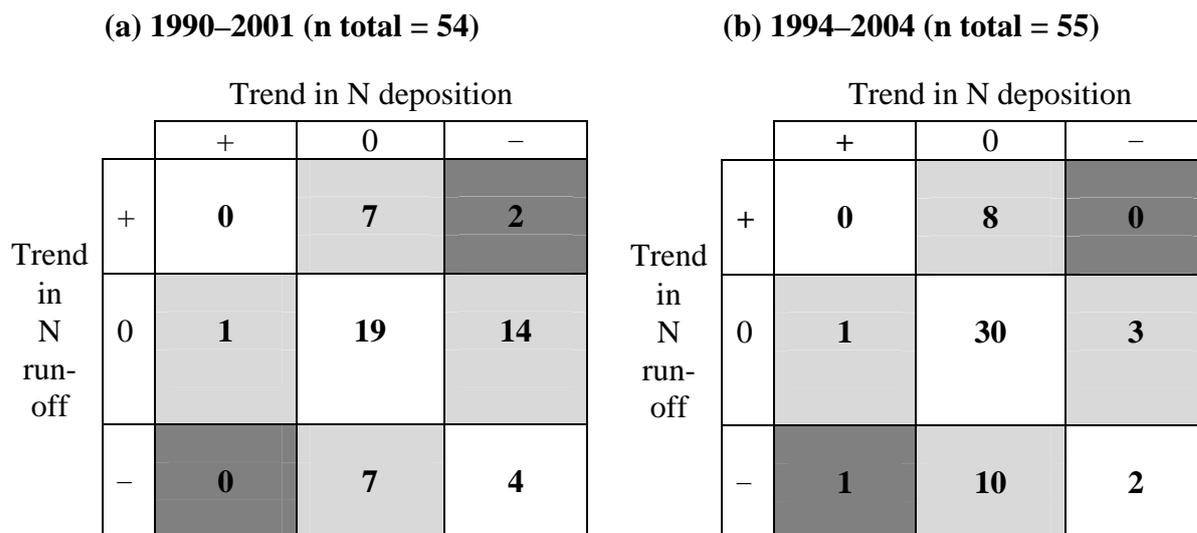


Figure 3. Number of ICP Waters sites (n) with trends in NO₃ concentrations in run-off of lakes and rivers compared to trends in total inorganic N concentrations in deposition. Results are shown for two time periods (a and b) analysed by the Mann-Kendall test. Notation: + = significant increase (p<0.05), 0 = no significant trend, – = significant decrease (p<0.05).

III. INCREASE IN DISSOLVED ORGANIC CARBON IS A RESPONSE TO REDUCED ACID DEPOSITION

17. DOC, an indicator of organic (natural) acidity, is of great interest in the analysis of surface water recovery, since it may counteract the positive effect of declining SO₄. A widespread increase in DOC was found in formerly glaciated parts of North America and Europe in the period 1990–2004.

18. To date, there is little agreement as to underlying causes for the rise in DOC, but hypotheses include rising ambient carbon dioxide concentration, climate change driven changes in temperature and precipitation, changes in land use and N deposition. Recently, changing soil chemistry, resulting from a decline in anthropogenic sulphur deposition, has been proposed as the dominant driver. Contrary to other hypotheses, this proposal implies that surface water quality would be returning to a pre-industrial “reference state” rather than deteriorating. We show, through the assessment of time series from over 500 acidification-sensitive sites in North America and northern Europe, that increasing DOC trends in most regions in the period 1990–2004 could 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, sea salt deposition. Further elucidation of mechanisms is required; however, the results suggest that DOC concentrations should stabilize 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.

IV. SIGNS OF BIOLOGICAL RECOVERY VARY BETWEEN REGIONS

19. Biological recovery from acidification is not the opposite of the processes leading to biological damage under acidification. The main driver for biological change during acidification is the increasing toxicity of chemical elements in water. Sensitive organisms die out and the community structure is generally predictable at different levels of acidity. The recovery process is different since the main driver during acidification, the toxicity, is of minor importance. The main structuring drivers of the community during recovery are connected to the physical environment in the region, i.e. dispersal and colonisation ability of different species and their biological interactions. It is unlikely that recovery would result in the community recorded prior to acidification (“reference condition”) due to the dynamic nature of biological processes.

20. The widespread improvements in chemical water quality have led to biological recovery of acid-sensitive species, which was first observed in regions with low buffering capacity. As compared with chemical recovery, biological recovery occurs usually with a delay from one to possibly 20 years,. It depends on the investigated communities as well as dispersal and colonization ability of acid-sensitive species.

21. In Canada, rates of biological recovery were less pronounced in lakes with low pH (<6) than with high pH (>6). Recovery of invertebrates (mayflies and amphipods) was observed, but their presence in lakes over the pH threshold occurred four to eight years after reaching this threshold. The estimated lag time from pH-threshold recovery to reestablishment and occupation of all suitable habitats could take from 11 to 22 years or more.

22. In the Czech Republic, little biological recovery was observed in glaciated lakes showing chemical recovery. Some signs of recovery of zooplankton were found in Bohemian forest lakes.

23. In Germany, there were some signs of recovery of sensitive species at several sites. In general, positive trends were lacking. This was in agreement with slow signs of chemical recovery, especially for pH. The highest potential for significant improvements seemed to be in eastern Germany. Sites in central and western Germany showed no improvement in pH, probably due to leaching of long-term accumulated acidic components.

24. In Norway, chemical and biological recovery was significant during the last decade at several sites. Recovery of invertebrates was documented through increased numerical development of sensitive species. Linear trends of change in the total benthic community were statistically related to trends in water chemistry.

25. In Sweden, positive trends in acidification index in acid-sensitive lakes have been documented, although not for all monitored lakes.

V. CONFOUNDING FACTORS IN CHEMICAL AND BIOLOGICAL RECOVERY

26. Environmental factors other than acid deposition – confounding factors – are expected to affect chemical and biological recovery of freshwaters in response to reduced acid deposition.
27. Dominating wind directions affect the deposition patterns of sea salts and both acidifying components. Sea salts lead to periodic acidification of acid-sensitive catchments. Climate change may lead to large-scale changes in dominant wind directions. A greater frequency and intensity of sea-salt episodes and possibly higher loads of acidifying compounds in coastal surface waters may be a consequence.
28. Other extreme climate events are droughts, which can generate acidic episodes, and floods, which can destroy riverbeds that serve as habitats for acid-sensitive species. Non-extreme and more chronic climate effects may affect the export of acidifying components in surface waters. Reduced snow cover is likely to result in fewer high NO₃ exports during snowmelt in Norwegian watersheds. However, the opposite effect on NO₃ has also been observed, possibly due to interactions of winter temperatures, insulating snow pack and NO₃ deposition.
29. Factors that are not directly related to climate, like insect outbreaks, can also affect chemical recovery. This is due to increased NO₃ leaching when plant uptake stops.
30. While some of these confounding factors are understood fairly well, others require more study. Some of the key processes in acidification and recovery, such as climate effects on N leaching and lag times between chemical and biological recovery, are still not properly understood.

REFERENCES

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Skjelkvåle BL (editor) (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.

Note: The references have been reproduced as received by the secretariat.

Annex

Workshop on Confounding Factors in Recovery from Acid Deposition in Surface Waters

1. The Workshop on confounding factors in recovery from acid deposition in surface waters took place on 9 and 10 October 2006 in Bergen, Norway. The workshop was organized by ICP Waters, ICP Integrated Monitoring and the EU project, Eurolimpacs.
2. The workshop was attended by 52 experts from the following Parties to the Convention: Canada, the Czech Republic, France, Finland, Germany, Hungary, Italy, Latvia, the Netherlands, Norway, Poland, Russian Federation, Spain, Sweden, Switzerland, the United Kingdom and the United States. A Vice-Chair of the Working Group on Effects and a member of the UNECE secretariat also attended.
3. The workshop agreed on the definition of confounding factors as effects of environmental factors other than acid deposition that affect recovery from acidification of surface waters. These factors were expected to affect chemical and biological recovery of freshwaters in response to reduced acid deposition. Regional rather than local confounding factors were worthwhile to study to understand their potential effects on future behaviour of acid-sensitive ecosystems.
4. To understand fundamental processes that drive ecosystem responses to predict future acidification status of freshwaters, the workshop aimed to:
 - (a) Quantify relations between drivers and responses of different processes affecting recovery;
 - (b) Improve existing models;
 - (c) Enhance interpretation of monitoring data;
 - (d) Provide input to the review of the 1999 Gothenburg Protocol.
5. Confounding factors were classified into three types of processes:
 - (a) Those not fully understood, but considered inherent for recovery (e.g. competition between species);
 - (b) Those reducing recovery detection (e.g. natural climate fluctuations);
 - (c) Those slowing, accelerating or counteracting long-term recovery (e.g. climate change, nitrogen saturation, exotic species invasion).

6. Climate change was expected to have significant impacts on freshwater chemistry and biology. Changes in large-scale weather patterns and increased temperature could affect regional patterns and timing of e.g. precipitation intensity, wind speed and direction and snow cover. The changes comprise:

(a) Long-term gradual changes: increasing temperature, precipitation and light (ultraviolet B) penetration, changing wind speed and direction, and duration and thickness of snow and ice cover;

(b) Extreme events: droughts, floods and storms.

7. Organic carbon and nitrogen were considered important in chemical and biological recovery. Their long-term trends were not fully understood. Dose-response relationships were under development.

8. Factors such as insect outbreaks could cause massive tree defoliation and thereby increase nitrogen leaching, potentially leading to streamwater acidification. Invasion of new species competing for food and habitats could confound local recovery.

9. Biological recovery was deemed to require better understanding. The workshop recommended further consideration of biological confounding factors and evaluation of lag times between recovering water chemistry and biology.

10. The workshop agreed that:

(a) Modelling could be used in the possible revision of Gothenburg Protocol;

(b) Modelling should include assessment of biological lag times;

(c) Emissions should be reduced more and faster if biological lag times were considered in addition to chemical lag times;

(d) More nitrogen research and modelling was needed;

(e) More countries should submit target load data for surface waters;

(f) Confounding factors, in particular climate, could be included in target loads;

(g) Climate patterns, such as the North Atlantic Oscillation, Arctic Oscillation and European Blocking, were deemed useful surrogates and integrators of climate data.

11. The workshop agreed that:

(a) More research was necessary on the importance of climate change for recovery from acidification and biological lag times;

(b) Monitoring should continue and biological monitoring must be enhanced;

(c) ICP Waters and ICP Integrated Monitoring be encouraged to acquire meteorological data for their sites for test drivers such as temperature and precipitation.
