Convention on Long-range Transboundary Air Pollution

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

ICP-WATERS REPORT 46/1998

Summary of The Nine Year Report from the ICP-Waters Programme

NIVA Norwegian Institute for Water Research

46/1998

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Norwegian Institute for Water Research

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Abstract

The International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP-Waters) is designed to assess the degree and geographical extent of acidification of surface waters. During the last ten years international emission reduction measures in Europe and North America have resulted in a decrease in atmospheric sulphur deposition of up to 50%. Nitrogen deposition has stayed almost constant.

Results from The Nine Year Report (Lükewille *et al.* 1997) show that trends in water chemistry indicate that sulphate concentrations are decreasing at almost all ICP-Waters sites, and in almost all cases the decreases in the 1990s are larger than in the 1980s. This is partly also reflected in a recovery of the invertebrate fauna at many sites. Decreasing sulphate concentrations emphasise the importance of nitrate as the second important acidifying anion.

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CONVENTION ON LONG-RANGE
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INTERNATIONAL COOPERATIVE PROGRAMME ON
ASSESSMENT AND MONITORING OF ACIDIFICATION
OF RIVERS AND LAKES

Summary of The Nine Year Report from the ICP-Waters Programme

Editors: Skjelkvåle, B.L., and Ulstein, M. J.
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ICP-Waters Programme Centre
Norwegian Institute for Water Research
Oslo, June 1998

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 1995. 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. The ICP-Waters programme has been lead by Berit Kvæven, Norwegian Pollution Control Authority.

The work plan of the Programme includes in-depth evaluations every third year. This Nine Year Report summarises the results achieved so far, along the lines of the programme objectives. Focus has been on trends and regional trends in surface water chemistry, assessment of nitrogen leaching and effects of acidification on biota. Project leader for The Nine Year Report has been Anke Lükewille, NIVA. Dean Jeffries, Canada, and John Stoddard, USA, are responsible for the trends work, Tor Traaen, NIVA, for the nitrogen evaluations and Gunnar Raddum, University of Bergen, for the biological section.

The programme was evaluated by external experts in 1992. As reported to Working Group on Effects "the Programme had been successful in establishing the methodologies and monitoring network". However, it is also concluded "only time can create the necessary data base". This Nine Year Report brings the ICP-Waters Programme a long step forward in that respect.

This report is a summary of "*The Nine Year Report: Acidification of Surface Waters in Europe and North America – Long-term Developments (1980s and 1990s)*" by Lükewille *et al.* 1997.

Oslo, June 1998

Merete Johannessen Ulstein	Brit Lisa Skjelkvåle
Programme leader ICP-Waters	Project leader ICP-Waters

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Summary

The International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP-Waters) is designed to assess the degree and geographical extent of acidification of surface waters. During the last ten years international emission reduction measures in Europe and North America have resulted in a decrease in atmospheric sulphur deposition of up to 50%. Nitrogen deposition has stayed almost constant.

Trends in surface water chemistry at the ICP-Waters sites were calculated by applying the Nonparametric Seasonal Kendall Test and, on a regional scale, by Trend Meta-Analyses. Empirical relationships between nitrogen deposition and stages of nitrogen saturation were used to assess the importance of nitrogen leaching at the sites. To show effects of acidification on aquatic fauna (geographic extent and long-term trends) presence/absence studies, acidification indexes and correlation analyses were used.

Trends in water chemistry indicate that sulphate concentrations are decreasing at almost all ICP-Waters sites, and in almost all cases the decreases in the 1990s are larger than in the 1980s. This is partly also reflected in a recovery of the invertebrate fauna at many sites. Decreasing sulphate concentrations emphasise the importance of nitrate as the second important acidifying anion. Besides nitrogen deposition, the overall nitrogen status of ecosystems, changes in climate or climate extremes and hydrology can have strong influences on leaching of excess nitrate (and ammonium) from a watershed.

1. Introduction

Over the past 25 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 and are affecting surface waters, groundwater and forest soils in other countries. Rethinking of air pollution control strategies was necessary, including long-term monitoring of effected receptors such as rivers and lakes.

The International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP-Waters) was established under the Executive Body of the Convention on Long-Range Transboundary Air Pollution (LRTAP) at its third session in Helsinki in July 1985 (EB AIR/7, Annex/V). It is one of five ICPs (Waters, Forests, Materials, Crops, Integrated Monitoring). The LRTAP convention went into effect in 1983 and was the first step to enforce emission reduction measures in the international sphere.

The ICP-Waters Programme has been designed to establish the degree and geographic extent of surface water acidification in UN/ECE countries. By means of long-term monitoring, trends and variations in aquatic chemistry and biota are analysed. The results are related to changes in (acidic) atmospheric deposition. Another aim is to evaluate dose/response relationships between water chemistry and biota.

The Programme objective is to establish an international network of surface water monitoring sites and promote international harmonisation of monitoring practices by:

- Compiling a Programme Manual on methods and operations. Sample collection at the ICP-Waters sites and analytical methodologies used by the participating countries need to be standardised. The manual is also an overall guide to activities of, and priorities set, by the Programme Centre.

- Conducting inter-laboratory quality assurance tests. The bias between analyses carried out by the individual participants of the Programme has to be clearly identified and controlled. Bias may arise through the use of different analytical methods, errors in the laboratory calibration solutions, or through inadequate within-laboratory control.

- Compiling a centralised database with data quality control and assessment capabilities. The purpose of the ICP-Waters’ database management is to assure accuracy of data, to accumulate and archive data, and to retrieve and summarise the data in response to user requirements. The management may include facilities for extensive data manipulation for interpretative purposes.

Another objective of the Programme is to develop and/or recommend chemical and biological methods for monitoring purposes. The ICP-Waters also conducts workshops on topics of central interest to the Programme Task Force and the aquatic effects research community.

Reporting of the ICP's findings cover the following aspects:

- Geographic extent of acidification using terrain sensitivity and current information sources.
- Long-term trends in water chemistry by using sites with data of more than 5 years.
- Dose/response relationships by:

⇒ determining changes in systems with similar buffering capacity and hydrology but different acid inputs;

⇒ Comparing chemical and biological responses of systems with different buffering capacities but similar deposition levels.

These topics are addressed by 3-year summary reports: 1987-89 (Wathne *et al.* 1991), 1989-1992 (Skjelkvåle *et al.* 1994), 1993-1995 (Lükewille *et. al* 1997).

2. Quality Control and Intercalibration

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

Three levels of quality control of water chemistry data can be distinguished:

- in-laboratory controls in the single countries,
- between-laboratory controls (intercalibration) 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.

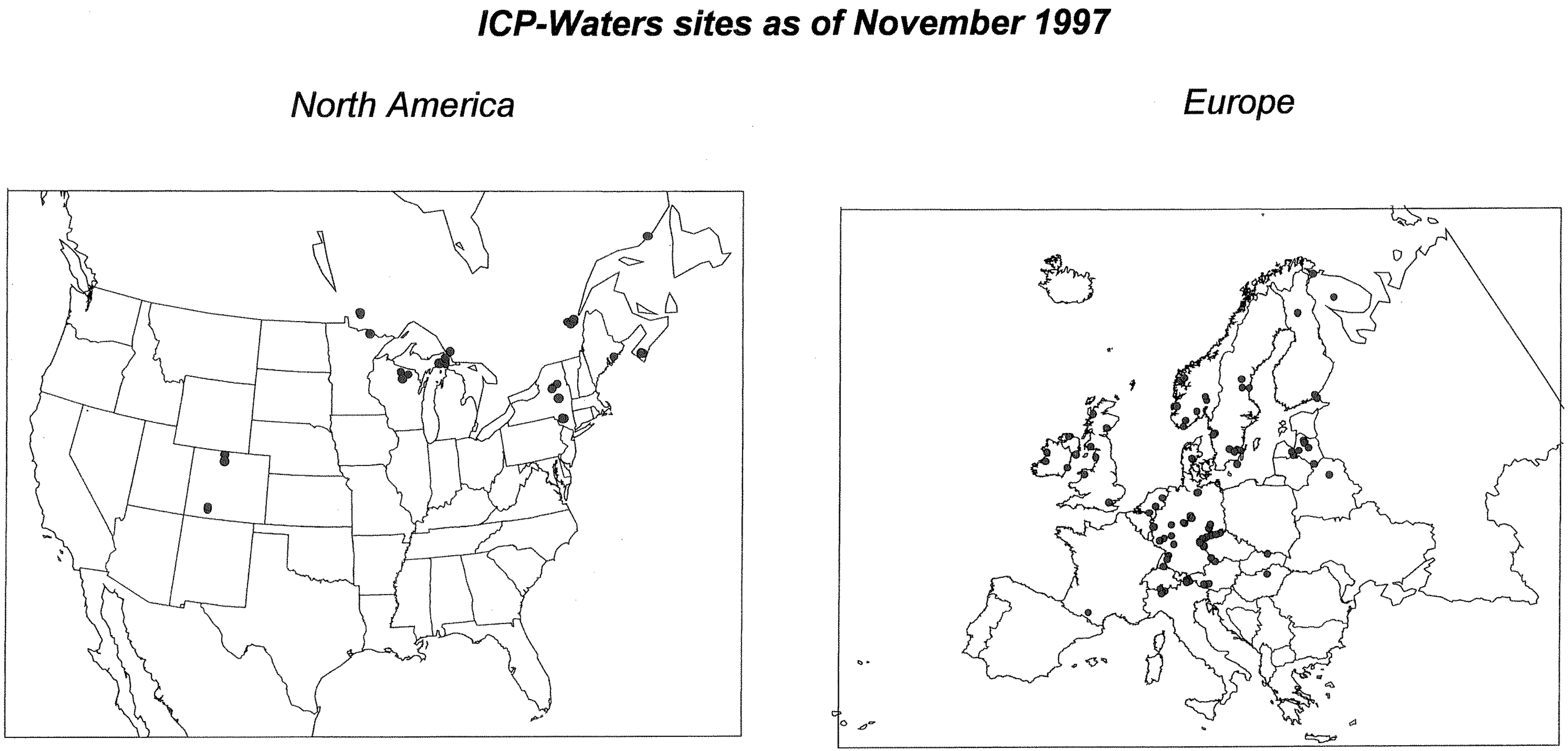
The latest between-laboratory quality control of chemical data was carried out in 1996 by NIVA (Hovind, 1996). 36 laboratories from 20 different countries participated. Two sample sets, one for the major ions and one for organic matter and aluminium fractions, were used. According to the general target accuracy of ± 20%, 70% of the results were acceptable. The best results were obtained for conductivity, nitrate, calcium, sodium and dissolved organic carbon. Rather poor comparability was observed for pH, alkalinity, chloride and aluminium species. To improve intercalibration results for these parameters, further harmonisation of the analytical methodologies is necessary, as they are among the most important parameters on which changes in acidification status are relying.

3. Programme status

21 countries are participating in the ICP-Waters Programme (Table 1). Altogether 220 sites are registered in the database with chemical data, and about half of the sites have both chemical and biological data. The geographical distribution of the sites is shown in Figure 1.

Table 1. Status of the ICP-Waters programme as of November 1997

		Participating in Task Force meetings	Chemical data	Participating in Chemical Intercalibration	Biological data	Participating in Biological Intercalibration
1	Austria	◆	◆	◆	◆	
2	Belgium	◆	◆		◆	◆
3	Bulgaria	◆				
4	Belarus		◆			
5	Canada	◆	◆	◆	◆	◆
6	Czech Republic	◆	◆	◆	◆	◆
7	Croatia	◆				
8	Denmark	◆	◆		◆	◆
9	Estonia	◆	◆	◆		
10	Finland	◆	◆	◆	◆	
11	France	◆	◆	◆	◆	
12	Germany	◆	◆	◆	◆	◆
13	Hungary	◆	◆			
14	Italy	◆	◆	◆		
15	Ireland	◆	◆	◆	◆	◆
16	Latvia	◆	◆	◆	◆	◆
17	Lithuania	◆		◆		
18	The Netherlands	◆	◆	◆	◆	
19	Norway	◆	◆	◆	◆	◆
20	Poland	◆	◆	◆		
21	Romania	◆		◆		
22	Russia	◆	◆	◆	◆	◆
23	Spain	◆				
24	Sweden	◆	◆	◆	◆	◆
25	Switzerland	◆		◆		
26	United Kingdom	◆	◆	◆	◆	◆
27	USA	◆	◆	◆		
		26	**21**	**20**	**15**	**11**



ICP-Waters sites as of November 1997

North America

Europe

Figure 1. Geographical distribution of the ICP-Waters sites

4. Long-term trends in surface water chemistry

During the last ten years international emission reduction measures in Europe and North America have resulted in a decrease in atmospheric sulphur deposition of up to 50%. Nitrogen deposition has stayed almost constant. To relate these developments to changes in surface water chemistry and biology, the ICP-Waters data base was used to calculate trends in surface water chemistry separately on data from the 1980s and 1990s for the single ICP-Waters sites and for geographic regions (clustering based on similarities in water chemistry). The results presented here is a short summary of the *"The Nine Year Report: Acidification of Surface Water in Europe and North America - Long-term Developments (1980s and 1990s)" by* Lükewille *et al.* 1997.

In the regional trend-analysis sites, whose trends were similar, were grouped together. This was done by clustering the sites geographically. This grouping has the advantage of allowing to test a number of important regional questions:

- are the regional decreases in deposition concentrations of sulphate observable in many parts of Europe and North America, reflected in surface water sulphate trends?
- do regional decreases in sulphate lead to recover values (improvement of water quality with regard to acidification) of surface water alkalinity?
- are nitrate concentrations, known to be increasing at many intensive research sites in Europe and North America, increasing on a regional level? and
- are base cation concentrations changing in response to declining sulphate concentrations in surface waters, and are the changes consistent with potential recovery from acidification?

The following regions were grouped together in the regional analysis:

(1) the Nordic Countries (Finland, Sweden and Norway);
(2) Europe (Italy, Germany, the Netherlands and Denmark);
(3) the U.K.;
(4) Midwestern North America (Wisconsin, Minnesota, Michigan and Ontario);
(5) the Adirondack Mountains (New York) and Quebec;
(6) the north Atlantic coast of North America (Vermont, Maine and Nova Scotia).

With a few exceptions, the assignment of sites to one of these regions was straight-forward; the Danish sites were grouped with Europe rather than the Nordic Countries largely on the basis of the chemistry of the two Danish sites (more typical of Europe than of Scandinavia).

It is important to recognise that this analysis determines only whether sites in each region are behaving similarly with respect to acidification. It indicates the central tendency of trends in each region, but it does not test whether the sites chosen are truly representative of the regions in which they reside. If the sites in ICP-Waters are regionally representative, then the regional trends presented below should represent valid regional phenomena. But there is no way, using only the trend information analysed here, to determine whether the sites included in ICP-Waters are representative of the population of sites in their regions. Homogeneity among the trends at individual sites in the ICP regions (as is generally observed) gives some confidence that the sites illustrate trends that are possible to generalise to the region level, but do not explicitly test this assumption in the results presented in Lükewille *et al.* 1997. This is also illustrated from U.K. where the 4 sites included in the ICP-Waters database, do not give exactly the same results as statistical analysis of all the sites in the U.K. monitoring network.

Results of more than 40 ICP-Waters sites show that curvilinear trends are common, particularly for sulphate, acid alkalinity and strong base cations (Σ Ca, Mg, K, Na). 1990 can be seen as the inflection point. The overall statistical results from the trend analysis and the yearly changes in surface water sulphate and alkalinity in 1980's and 1990's in the different regions are shown in Table 2 and Figure 2.

Important results of the regional trend analyses from The Nine Year Rleport are:

- Sulphate concentrations are decreasing at almost all sites, and in almost all cases the decreases in the 1990s are larger than in the 1980s.
- In the Nordic Countries (Finland, Sweden, Norway) alkalinity decreased in the 1980s (acidification), but increased in the 1990s (recovery). At many European sites (Italy, Germany, the Netherlands, Denmark) alkalinity also increased in the 1980s, but the rate accelerated in the 1990s. The remaining regions (Adirondacks and Quebec, midwestern North America, U.K.) show either no recovery or further acidification.
- Regions with declining sulphate that fail to show recovery in alkalinity in the 1990s (Adirondacks/Quebec, Midwestern North America) are characterised by strongly declining SBC concentrations. SBC concentrations are no longer declining in the Nordic Countries (regional recovery in alkalinity in the 1990s).
- All of the hydrogen ion (H^+) trends detectable at a regional level are consistent with the alkalinity trends observed within each region.
- The 1980s were characterised by increases in nitrate (NO_3^-) in almost all regions. These nitrate increases have levelled out in the 1990s. Compared with sulphur, nitrogen (N) is much more involved in biological processes within ecosystems. Hence changes in N deposition may not always directly correlate with changes in inorganic N leaching in runoff. It seems likely that regional-scale phenomena other than nitrogen deposition are responsible for the development in the 1990s (e.g., changes in climate or climate extremes).

The 4 U.K sites included in the statistical analysis in The Nine Year Report show no significant decrease in sulphate and no improvement in water quality with regard to increase in alkalinity and increase in pH (decrease in H^+). However, ongoing statistical work on the 22 sites in the U.K. monitoring network indicates that these results are not representative for U.K.

Table 2. Results of regional trend meta-analysis for sulphate, nitrate, alkalinity, sum of base cations, and H^+. Slope values are $\mu eq\, l^{-1}\, yr^{-1}$. Regional trends that are significant at $p<0.05$ are shown in bold.

Region	Decade	Sulphate	Nitrate	Alkalinity	Base cations	H^+
Adirondacks and Quebec	1980s	***-0.63***	***+0.46***	***-1.39***	***+0.39***	+0.00
	1990s	***-1.62***	***-1.57***	+0.53	***-3.41***	***-0.01***
Europe	1980s	***-1.26***	***+1.37***	***+2.50***	+0.00	-0.05
	1990s	***-4.50***	***-2.38***	***+7.94***	-6.25	-0.00
Midwestern North America	1980s	***-1.46***	+0.04	***+0.71***	+0.94	***-0.02***
	1990s	***-4.25***	-0.00	***-1.60***	***-4.79***	-0.00
Nordic Countries	1980s	***-0.83***	***+0.13***	***-1.41***	***-2.42***	***+0.01***
	1990s	***-2.95***	+0.01	***+2.50***	-0.05	***-0.15***
Atlantic North America	1980s	-0.00	+0.00	***+1.37***	-0.13	***-0.02***
	1990s	***-2.42***	-0.00	+1.14	-0.89	+0.01
U.K	1990s	-0.01	***+0.17***	+0.15	-1.46	-0.14

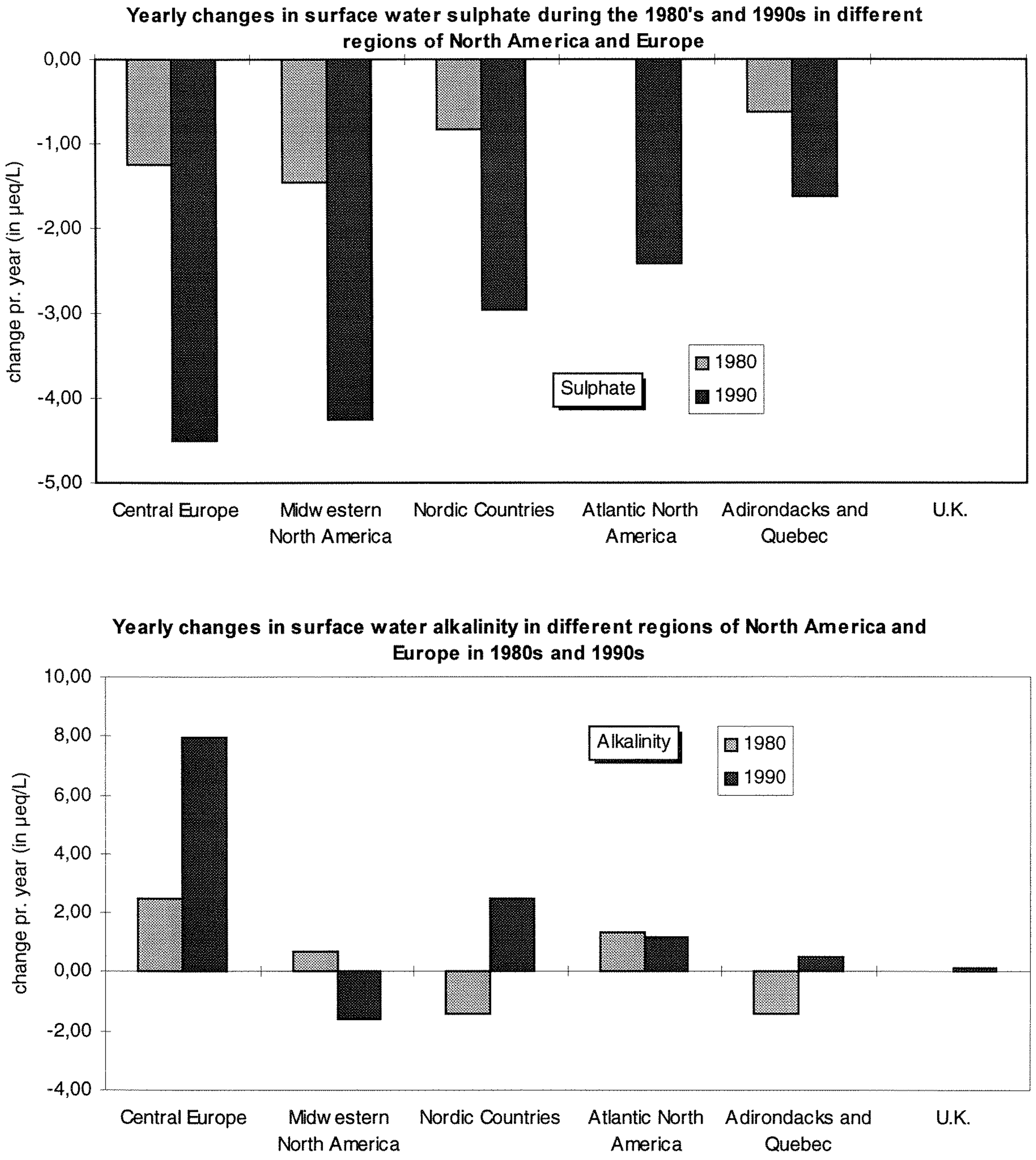


Figure 2. Yearly changes in surface water sulphate (top panel) and alkalinity (bottom panel) in the 1980s and 1990s in different regions of North America and Europe.

5. Assessment of Nitrogen Leaching

Reports of increased nitrate concentrations in runoff first appeared in the 1980s. The Norwegian 1000-lake survey in 1986 revealed that NO_3 concentrations in some areas in southern Norway had almost doubled since investigations in 1974-75 (Henriksen *et al.* 1988). Increasing trends in NO_3 concentrations were also revealed in the US EPA's Long-term Monitoring Project. Nine of 15 drainage lakes monitored in the Adirondack area showed increases in nitrate concentrations, ranging from 0.5 to 2.0 $\mu eq\ l^{-1}\ yr^{-1}$ in the period 1982 - 1991 (Driscoll and van Dreason, 1993). Further, 5 of 8 streams in the Catskill area exhibited significant upward trends in nitrate, ranging from 1.3 to almost 3 $\mu eq\ l^{-1}\ yr^{-1}$ in the period 1983 - 1989 (Murdoch and Stoddard, 1992). These trends have partly disappeared in the 1990s (Stoddard *et al.*, in press), a phenomenon that can also be observed at many ICP-Waters sites. Nevertheless, any excess nitrate leaving a catchment will contribute to acidification of the watershed by removing base cations from soil and by mobilising aluminium and H^+ ions. NO_3, when accompanied by H^+ instead of base cations, will reduce the acid neutralising capacity (ANC). An assessment of nitrogen leaching in the ICP-Waters sites are reported in Traaen and Stoddard, (1995) and Lükewille *et al.* (1997). The results summarised here are taken from these two reports.

Concerning the leaching of nitrogen important observations for the ICP-Waters sites are:

- More than 50% of all sites have yearly average NO_3^- concentrations > 10 $\mu eq\ l^{-1}$. NO_3^- values > 50 $\mu eq\ l^{-1}$ are found at 27% of the sites. All Dutch sites have ammonium values > 100 $\mu eq\ l^{-1}$ (Figure 3).
- Sulphate is the most important acidifying anion, but nitrate constitutes more than 10% of the non-marine acid anions at 63% of the ICP-Waters sites. All Canadian, Finnish, Swedish and Russian sites are exceptions.
- There is a clear coherence between high N saturation stages and high N deposition loads and more than 50% of the analysed ICP-Waters sites show a high degree of nitrogen saturation (stages 2 or 3 according to Stoddard's classification system) (Figure 4).
- There is evidence that inorganic N leaching below the empirically found deposition limit of 10 kg N $ha^{-1}\ yr^{-1}$ occurs especially at sites with very high annual precipitation (Norway, Ireland, Italy, U.K.) (Figure 5).

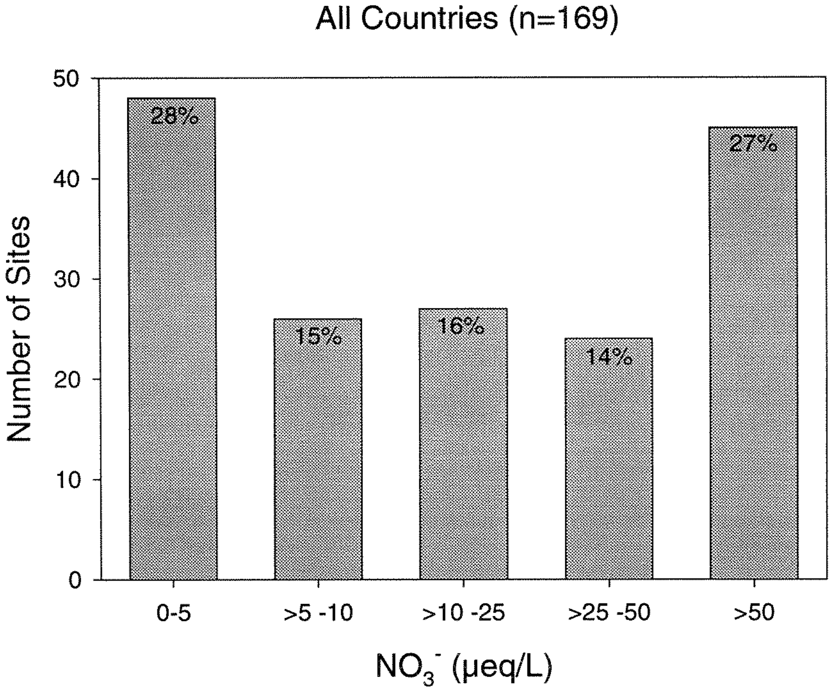


Figure 3. Frequency distribution of means annual NO_3^- concentrations at 169 ICP-Waters sites.

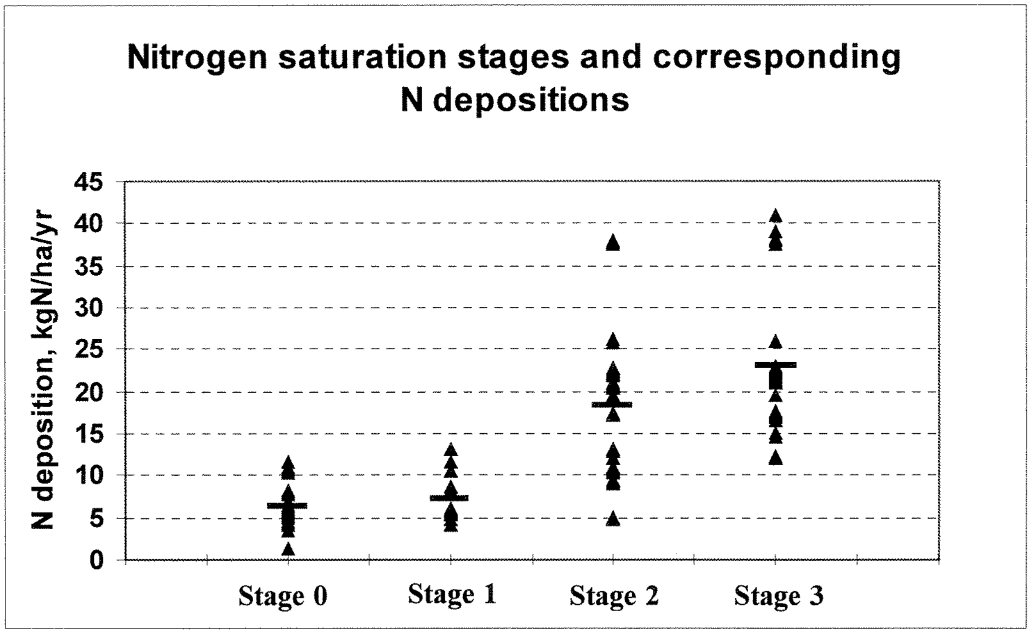


Figure 4. Nitrogen (NO_3^- + NH_4^+) concentration in runoff vs. total nitrogen deposition fluxes (wet + dry) for European ICP- Waters sites in 1990-1992. The deposition data are 1990 values for the EMEP grids in which the respective sites are situated (data from Norwegian Meteorological Institute). Most runoff data are yearly averages for 1990.

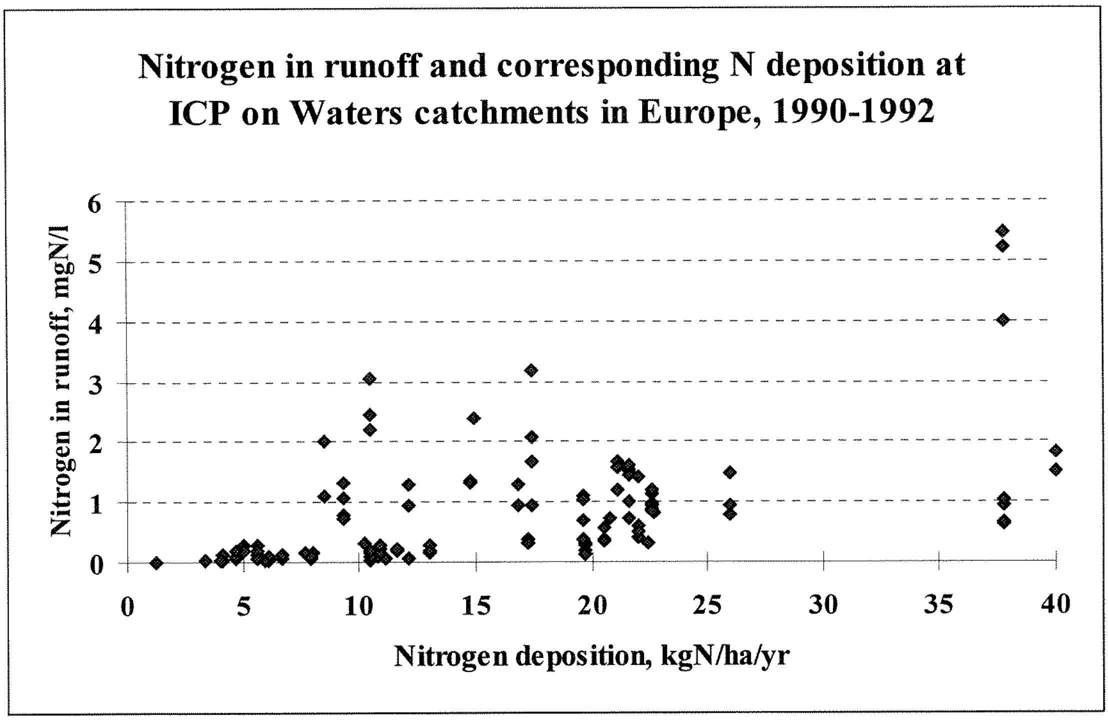


Figure 5. Nitrogen ($NO_3^- + NH_4^+$) concentration in runoff and total nitrogen deposition fluxes (wet + dry) for European ICP on Waters sites in 1990-1992. The deposition data are 1990 values for the EMEP grids in which the respective sites are situated (data from Norwegian Meteorological Institute). Most runoff data are yearly averages for 1990.

6. Effects of Acidification on Aquatic Fauna

The biological monitoring of the ICP-Waters Programme consists of national activities of the participating countries. Monitoring practice varies from country to country with regard to time-series and type of studies. In the ICP-Waters programme we concentrate on invertebrate studies. The longest biological monitoring series are from Norway, starting in 1981 and 1982. Other countries with several years of monitoring are Germany, Sweden, United Kingdom and Ireland, while newcomers such as Latvia and Poland have just started to report biological data to the Programme Centre. So far 397 data sets, consisting of invertebrates and water chemistry, have been evaluated for the geographical extent and dose/response relationships. Trends can only be assessed for sites with the long-term data series.

Invertebrates respond to different compounds in the water. One main task of the ICP-Waters Programme is to compare results from different regions in Europe and North America. It was therefore important to harmonise sampling and data handling when the programme started in 1985. Since the geographical distribution of many species is restricted, universal indicator species or communities are usually not available. The strategy for monitoring biological effects was therefore to develop methods based on the influence of acidified water on the various species/communities. Many invertebrates are sensitive to acid water and become extinct at different levels of acidity. Presence or absence of such species indicates both current and recent past acidity (age/lifetime of certain organisms/species). This knowledge has been utilised in a simple model, calculating an acidification index (ICP-Waters Programme Manual 1988 and 1996), which gives a number between 0 and 1, indicating strong to low/no acidification. The index is a universal number, comparable between regions and independent of the geographical distribution of invertebrates.

Results from studies on the presence/absence (acidification index) of sensitive species are the basis for evaluating the geographical extent of acidification. The presence/absence studies in combination with water chemistry data from the ICP-Waters Programme are also the basis for assessing dose/response relationships. In this evaluation the multivariate analyses are of high importance for verifying the validity of indicator species as well as for detecting new indicators. The trend analyses are based both on presence/absence and on multivariate techniques, where they can be applied.

Important findings within the ICP-Waters Programme (reported in Lükewille *et al.* 1997) are:

- From different invertebrate assemblages, pH can be predicted with an accuracy of 0.3 pH units.
- In areas with originally high pH (6.0 - 8.0) and high calcium concentrations (e.g., southern Sweden and Germany), a critical alkalinity limit of 50 $\mu eq\ l^{-1}$ is proposed. In areas where fauna is adapted to water with low conductivity, low pH (5.5 - 6.5) and low calcium concentrations (e.g., Finland, Norway), alkalinity values should be ≥ 20 $\mu eq\ l^{-1}$ to protect invertebrates and fish. These critical levels are the basis for setting critical loads of acidity for surface waters.
- By comparing invertebrate samples taken before and after 1990, improvements at many Norwegian and German sites can be observed. This is confirmed by correlation analyses between time and acidification index applied to Norwegian long-term data

series (periods chosen: 1981 - 1988 and 1989 - 1994).

- Detrended canonical correspondence analysis (Norwegian data sets) shows a high correlation of invertebrate assemblages with pH and total aluminium (Al), and also a significant correlation with calcium. Trend analyses indicate considerable improvements from 1991 to 1995 (increase in pH, decrease in total Al).
- As no data on fish has yet been added, no fish data are available for the ICP-Waters sites.

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

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