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REPORT

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Abstract

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CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

INTERNATIONAL COOPERATIVE PROGRAMME ON ASSESSMENT AND MONITORING EFFECTS OF AIR POLLUTION ON RIVERS AND LAKES

Proceedings of the 25th meeting of the ICP Waters Programme Task Force in Burlington, Canada, October 19 - 21, 2009

Prepared at the ICP Waters Programme Centre
Norwegian Institute for Water Research
Oslo, August 2010

Preface

The international cooperative programme on assessment and monitoring of air pollution on rivers and lakes (ICP Waters) was established under the Executive Body of the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP) in July 1985. Since then ICP Waters has been an important contributor to document the effects of implementing the Protocols under the Convention. Numerous assessments, workshops, reports and publications covering the effects of long-range transported air pollution has been published over the years.

The ICP Waters Programme Centre is hosted by the Norwegian Institute for Water Research (NIVA), while the Norwegian Climate and Pollution Agency (Klif) leads the programme. The Programme Centre's work is supported financially by Klif.

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. More than 20 countries in Europe and North America participate in the programme on a regular basis.

ICP Waters is based on existing surface water monitoring programmes in the participating countries, implemented by voluntary contributions. The ICP site network is geographically extensive and includes long-term data series (more than 20 years) for many sites. The programme yearly conducts chemical and biological intercalibrations.

At the annual Programme Task Force, national ongoing activities in many countries are presented. This report presents national contributions from the 25th Task Force meeting of the ICP Waters programme, held in Burlington, Canada, October 19 - 21, 2009.

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Oslo, August 2010

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1. Introduction

The International Cooperative Programme on Assessment and Monitoring of Rivers and Lakes (ICP Waters) is a programme under the Executive Body of the Convention on Long-Range Transboundary Air Pollution. The main aims of the programme are:

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

The national contributions on ongoing activities that were presented during the ICP-Waters Task Force meeting in Burlington, Canada in October 2009 are grouped thematically;

- **Water chemistry – trends and status of S and N**

  - Results of 20 Year Interpretive Report for the UK Acid Waters Monitoring Network and the Review of the Gothenburg Protocol, *Chris Curtis, UK*
  - Old water chemistry data; possibilities and restrictions, *Anders Wilander, Sweden*
  - ICP Waters in Latvia, some results from monitoring, *Iveta Dubakova, Latvia*

- **Biological response**

  - Recovery Saudlandsvatn, Southern Norway, *Bjørn Olav Rosseland, Programme centre*

- **Heavy metals and POPs**

  - Risk of mixture toxicity in Dutch surface waters, *Ton C.M. de Nijs, Dick de Zwart, Willie Peijnenburg, the Netherlands*
  - The distribution of trace elements in small lakes in European Russia - from the tundra to arid zones, *Tatyana I. Moiseenko and Natalia A. Gashkina, Russia*

- **ICP Waters and EU-directives (WFD Water framework Directive, NEC National Ceiling Emission Directive)**

  - Critical loads and the Water Framework Directive – experiences from the UK, *Chris Curtis, UK*

2. Recently Surveyed Lakes in Western Canada:
Characteristics and Critical Loads of Acidity

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Introduction

Since the 1979s, acid rain concerns in Canada have focused on the southeastern part of the country because to this point, there has been little coincidence between local S and N emissions and acid sensitive terrain. As a result, lake chemistry data used in the most recent national acid rain assessment (the “2004 Assessment”; Jeffries et al., 2005 and Jeffries and Ouimet, 2005) for the four western provinces (Manitoba, MB; Saskatchewan, SK; Alberta, AB; and British Columbia, BC) were compiled from existing sources and therefore, had a number of limitations. For example, the data were: (1) spatially sparse and few in number in MB and SK, (2) sometimes more than two decades old, (3) sometimes of poor or unquantifiable quality due to incomplete analysis of major ions, (4) sometimes not collected in sensitive terrain (MB, BC), (5) rarely collected to assess acidification status, and (6) never collected to statistically represent the lake population being typically skewed to larger lakes. Only lake chemistry data collected in AB were considered sufficiently comprehensive and up-to-date to provide an adequate assessment of acidification sensitivity and status. Given that S and N deposition is expected to increase in western Canada, particularly from emissions related to oil sands processing in northeastern Alberta and ship emissions along the British Columbia coastline, new lake chemistry data were needed from MB, SK and BC for assessment purposes and critical load analyses.

This report briefly assesses acidification sensitivity, status and critical loads for lakes in western Canada using data from several recent surveys conducted in MB, SK and BC that were not available for the 2004 Assessment. It covers the same material orally presented during the ICP-Waters Taskforce Meeting in Burlington, Ontario in October, 2009. More comprehensive descriptions are given by Jeffries et al. (2010) for the MB and SK component of the work and by Strang et al. (2010) for the BC component.

Data Sets

The locations of lakes in western Canada having data used here are presented in Figure 1. As additions to the data available from the 2004 Assessment (Jeffries et al, 2005 and Jeffries and Ouimet, 2005), new information included:

- data from the central and southeastern parts of MB compiled and supplied by Manitoba Conservation from some of its monitoring programs and from Jacobs (2006);
- data collected for Vale-Inco Ltd (INCO) within a 300 km radius of its smelter at Thompson, central MB (UMA, 2007a, 2008);
- data collected for Hudson Bay Mining and Smelting (HBMS) within a 300 km radius of its smelter at Flin Flon on the SK-MB border (UMA, 2007b);
- data collected by Environment Canada (EC) in northwestern MB and central SK (Jeffries et al., 2010);
- data collected by Saskatchewan Environment (SK ENV) in west-central SK (Scott et al., 2010);
- data collected by Environment Canada in southwestern BC (Strang et al., 2010); and
- data collected from central and northern BC (J. Krzyzonowski, pers. comm.).

The lake selection procedures employed in these surveys or compilations varied greatly, ranging from a systematic stratified-random design to obtain a statistically representative sample population

(Jeffries et al., 2010), to radial distributions around specific point sources (UMA, 2007a, b, 2008; Scott et al., 2010), to selections governed by logistical or funding constraints. Taken as a whole, the recently obtained data do much to alleviate the assessment limitations, particularly the lack of representativeness, identified by Jeffries et al. (2005).

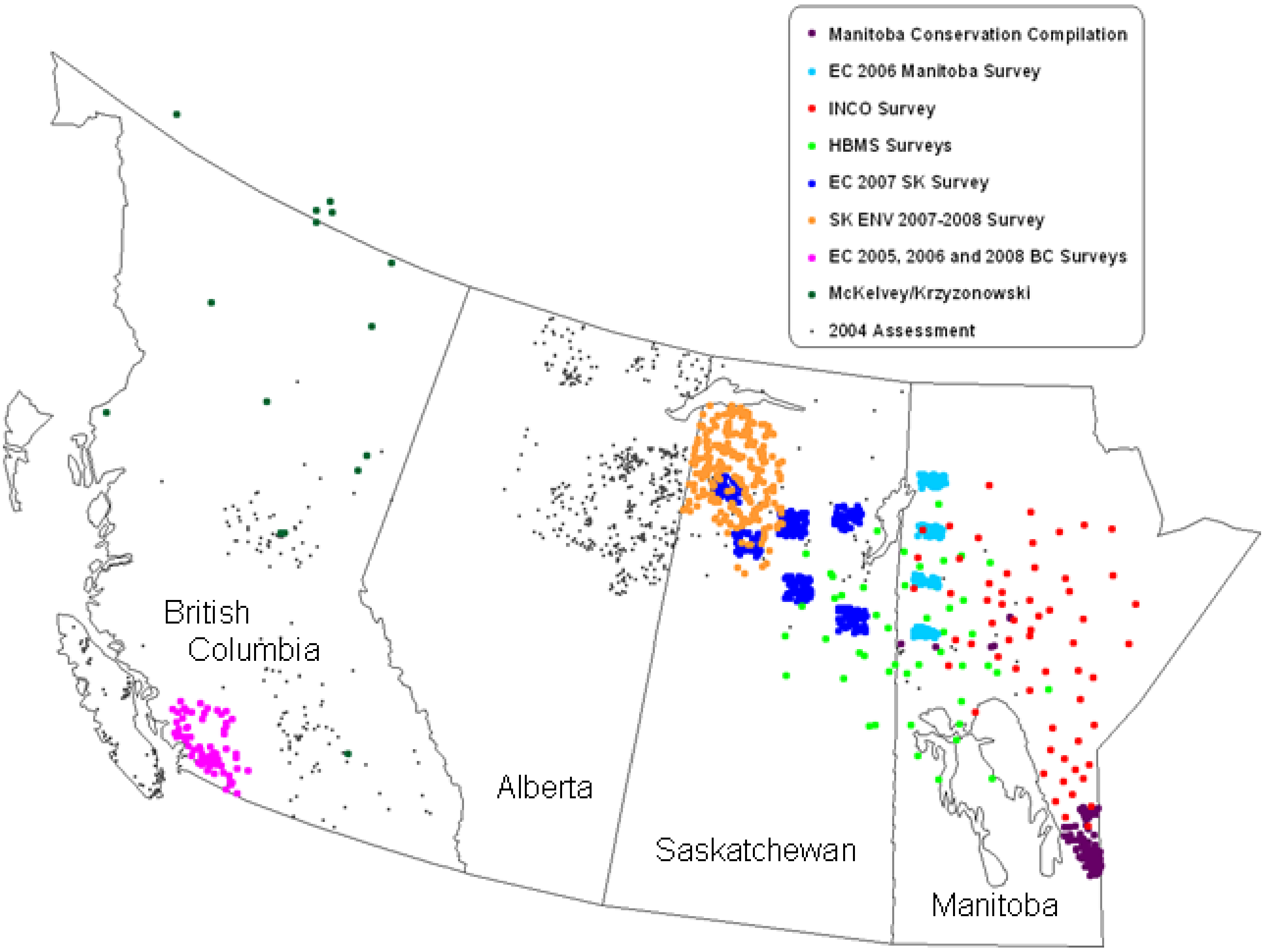

Figure 1*. Location of sample lakes in western Canada according to the data sources. Note that no lakes were sampled in the southern, agricultural regions of MB, SK and AB because of insensitive terrain.*

Western Canadian Lake Acidification Sensitivity and Status

After, the western lakes were grouped into four provincial subsets, cumulative frequency plots were used to assess the acidification sensitivity and status. Cumulative frequencies for both the 2004 Assessment data sets and the "new" data sets (i.e., now including data from the recent surveys) have been plotted to demonstrate the differences between the old and new information.

Table 1: Ca + Mg (µeq/L)

		Percentile		
	n	**5th**	**50th**	**95th**
MB	346	95.4	299	1670
SK	565	47.0	173	819
AB	450	191	1030	3020
BC	287	18.9	601	4330

Base cation concentrations (expressed here as the sum of Ca^{2+} and Mg^{2+}) have been used to assess lake sensitivity (Table 1 and Figure 2). All four western provinces exhibit a broad range in base cation concentrations (and hence acid sensitivity) which is expected from the geology of these regions. Saskatchewan's sample population has the highest proportion of sensitive lakes while Alberta has the lowest. 62 % of the MB sample population and 87

% of the SK sample population can be considered sensitive ($Ca^{2+}+Mg^{2+} < 400$ µeq L^{-1}). British Columbia has a small proportion of extremely sensitive lakes. Inclusion of new survey data in BC, SK and particularly MB resulted in much more sensitive sample populations than was evident in the 2004 Assessment, i.e., cumulative frequency distributions shifted to lower concentrations in Figure 2. Note that the new sample populations for MB and SK (356 and 565 lakes respectively) almost completely replaced the 2004 datasets (19 and 52 lakes respectively).

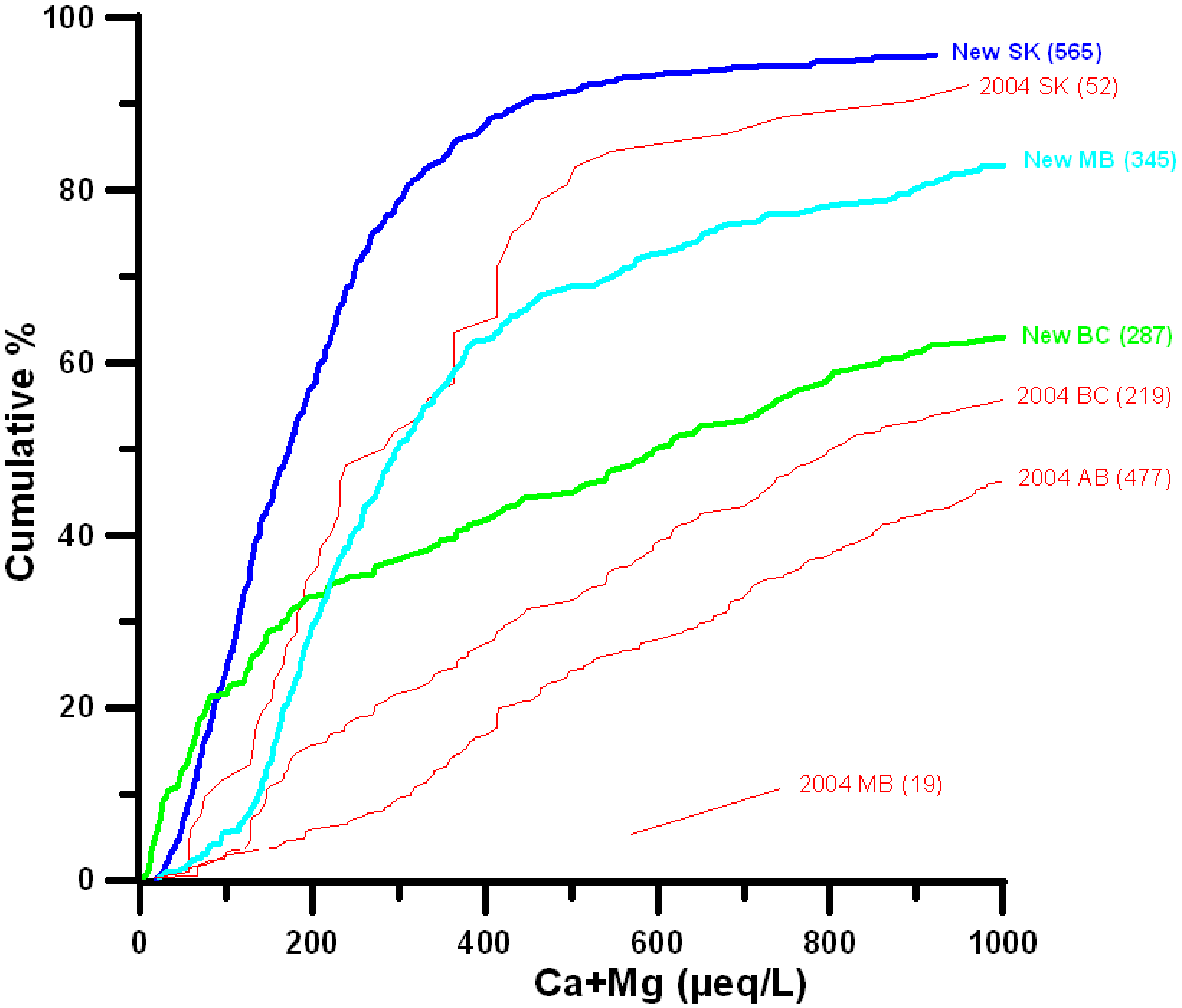

Figure 2. *Cumulative frequency distributions for base cations for provincial data sets in western Canada. Both "new" and "old or 2004" distributions are shown (see text for an explanation). Base cation concentrations < 400 µeq* L^{-1} *have been traditionally used to define acid sensitivity.*

Table 2:	Alk (µeq/L)			
		Percentile		
	n	5th	50th	95th
MB	346	54.6	214	1650
SK	565	26.0	146	875
AB	447	142	1000	2960
BC	287	34.9	587	4650

Data for Gran Alkalinity (Table 2 and Figure 3) also provide information on lake sensitivity. Based on the commonly used sensitivity threshold of 200 µeq L^{-1} for alkalinity, the proportion of sensitive lakes in the western provinces is a little lower than suggested by the base cation concentrations. Only SK has a median concentration (146 µeq L^{-1}) below this threshold, although the cumulative frequency plots (Figure 3) and fifth percentile values (Table 2) demonstrate that there are some extremely sensitive lakes (Alk < 50 µeq L^{-1}) within the sample population. There are four acidic lakes in the SK sample population (Alk < 0 µeq L^{-1}) due to extremely low base cation concentrations in combination with natural organic acids as reflected in high dissolved organic carbon (DOC) levels. Once again, the differences in the "new" and "2004" frequency distributions for alkalinity (particularly those for MB) demonstrate the unrepresentative nature of the data available for the 2004 Acid Rain Assessment. Though not shown here, pH data for the sample populations showed shifted distributions to lower values when the new survey data were included. Nevertheless, fifth percentile values were 6.0 or higher for all sample populations. There were a few low values, i.e. pH <5.5 (two lakes in MB, 11 lakes in SK, 13 lakes in AB, and two lakes in BC), once again frequently caused by natural organic acidity.

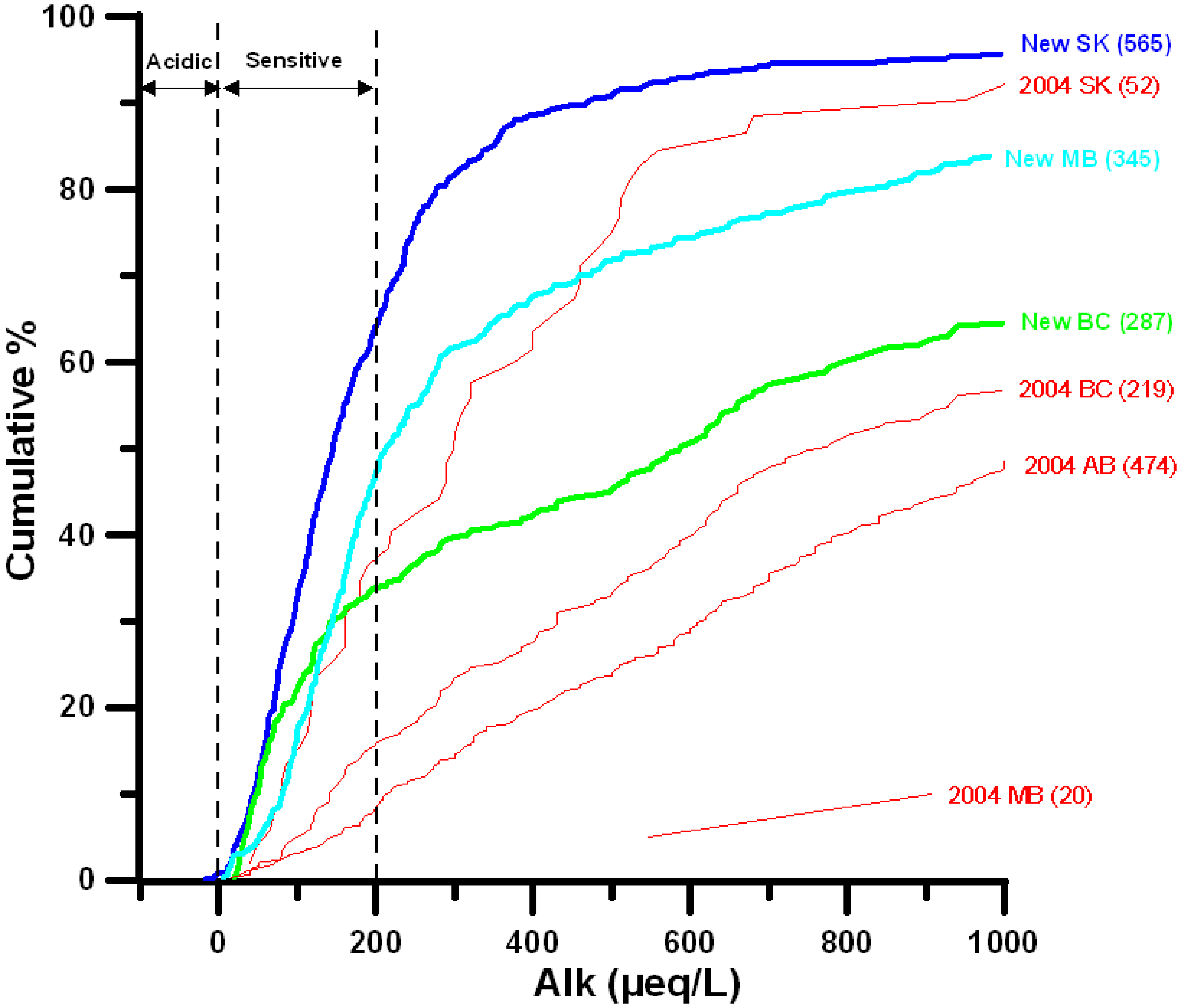

Figure 3. *Cumulative frequency distributions for Gran alkalinity for provincial data sets in western Canada. Both "new" and "old or 2004" distributions are shown (see text for an explanation). Alkalinity concentrations <200 µeq L^{-1} have been traditionally used to define acid sensitivity and values <0 µeq L^{-1} indicate acidic lakes.*

Table 3: DOC (mg/L)

		Percentile		
	n	**5th**	**50th**	**95th**
MB	336	6.0	15.4	30.2
SK	565	2.4	7.9	21.1
AB	398	7.9	19.4	37.0
BC	200	0.3	2.5	19.7

Natural organic acidity as reflected in DOC concentrations is an important component of MB, SK and AB lakes (median concentrations ranged from 7.9 to 19.4 mg L^{-1}), but much less so for alpine lakes in BC (median = 2.5 mg L^{-1}). Addition of new survey lakes shifted the MB and SK distributions (not shown) towards higher DOC concentrations, and markedly shifted the BC distribution to lower DOC concentrations.

Aquatic Critical Loads (CLs) and Exceedances

Aquatic CLs were determined using the Steady-State Water Chemistry Model (SSWC; Henriksen et al., 2002; UNECE, 2004) using an ANC_{limit} that considers natural acidity whenever DOC concentration was available. The relationship between DOC and ANC_{limit} was from Lydersen et al. (2004) as recommended by UNECE (2004), i.e.,

$$ANC_{limit} = 10 + (10.2/3)*DOC \qquad (1)$$

where ANC_{limit} is in $\mu eq\ L^{-1}$ and DOC is in $mg\ L^{-1}$. The Lydersen et al. ANC_{limit} values ranged from 14.4 $\mu eq\ L^{-1}$ for a very clear, sensitive lake in SK (DOC = 1.3 $mg\ L^{-1}$; sum of base cations (Cb) = 162 $\mu eq\ L^{-1}$) to 145 $\mu eq\ L^{-1}$ for an extremely brown, insensitive lake, also in SK (DOC = 39.7 $mg\ L^{-1}$; Cb = 2660 $\mu eq\ L^{-1}$). The mean ANC_{limit} was 41 $\mu eq\ L^{-1}$ in SK (very close to the value of 40 used by Henriksen et al. 2002; Dupont et al. 2005; and Jeffries & Ouimet 2005); and 65 $\mu eq\ L^{-1}$ in MB, which was slightly less than the value of 75 used by WRS (2004) for high DOC lakes in AB. When no DOC value was available for a given lake, ANC_{limit} was set to 40 $\mu eq\ L^{-1}$ (cf. Henriksen et al., 2002). Finally, lake-specific values for runoff were available for use in the SSWC calculation for many of the new MB lakes and almost all the new SK and BC lakes (Gibson et al., 2010). When no lake-specific runoff was available, a value was interpolated from regional runoff maps.

Fifth percentile values for all lakes within a square on a 42 km grid are shown in Figure 4. This grid was to facilitate later presentation of exceedances since it is the same one used by AURAMS (A Unified Regional Air-quality Modelling System; (Moran et al. 2008) to estimate S and N deposition.

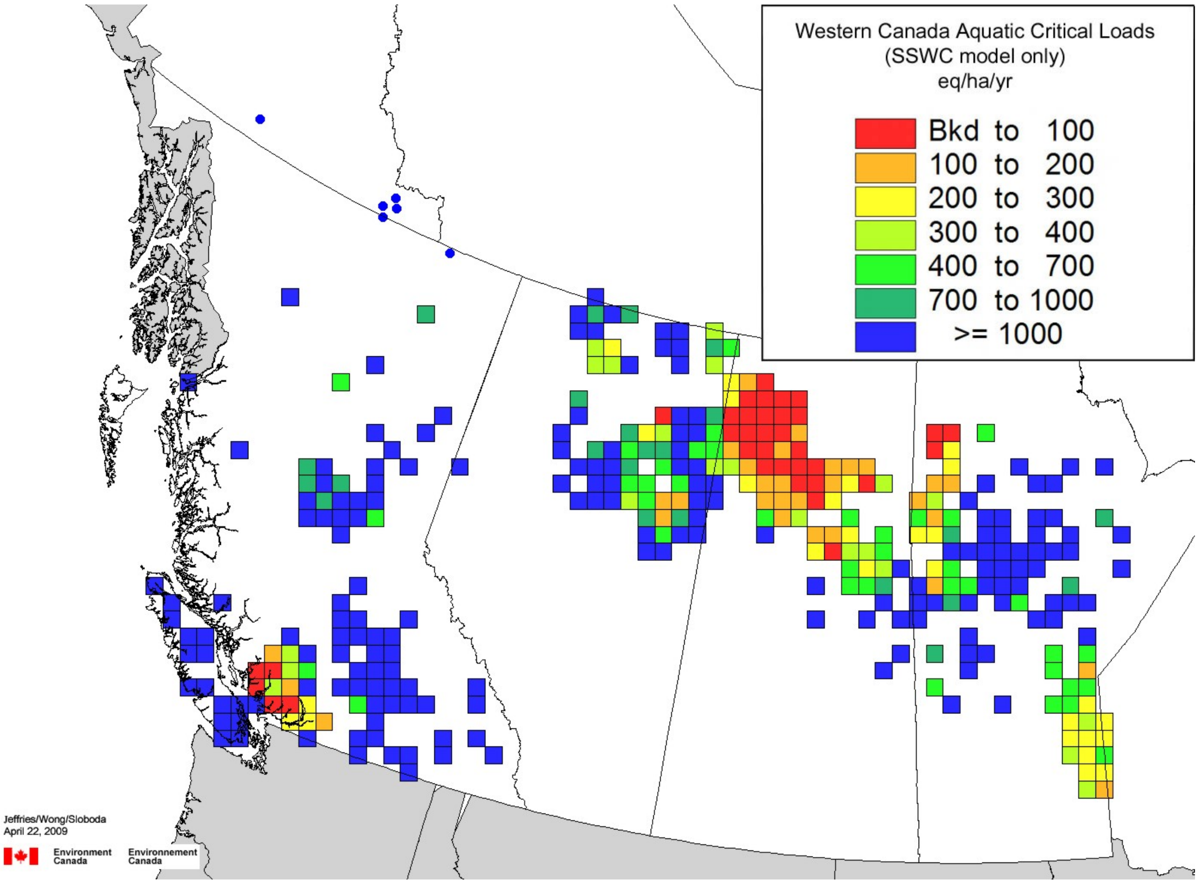

__Figure 4__. Map of aquatic critical loads for western Canada.

Many lakes with extremely low CLs occur throughout western Canada. The expanse of red grid squares in northwestern SK is the largest in the country.

Using the rationale described by Jeffries and Ouimet (2005), we used S and N deposition estimated by an AURAMS run for 2002 SO_2 and NO_x emissions to calculate two exceedance values that cover the possible range:

$$\text{“N-leaching Exceedance”} = \text{Total S Dep} + NO_3 \text{ leached} - CL \qquad (2)$$

$$\text{“Steady-state Exceedance”} = \text{Total S Dep} + \text{Total N Dep} - CL \qquad (3)$$

Our exceedance calculations assume that all S deposition is acidifying, i.e., there is no ecosystem storage of SO_4 inputs. The N-leaching exceedance (Figure 5) is as suggested by Henriksen et al. (2002) which estimates the “current” exceedance level by assuming that the acidifying component of N deposition and the exceedance is quantified by the NO_3 flux, i.e., lake NO_3 concentration x annual landscape runoff. The Steady-state exceedance (Figure 6) assumes that all N deposition is acidifying, i.e. the lake ecosystems are nitrogen saturated. It is the maximum possible exceedance for the deposition level estimated by AURAMS.

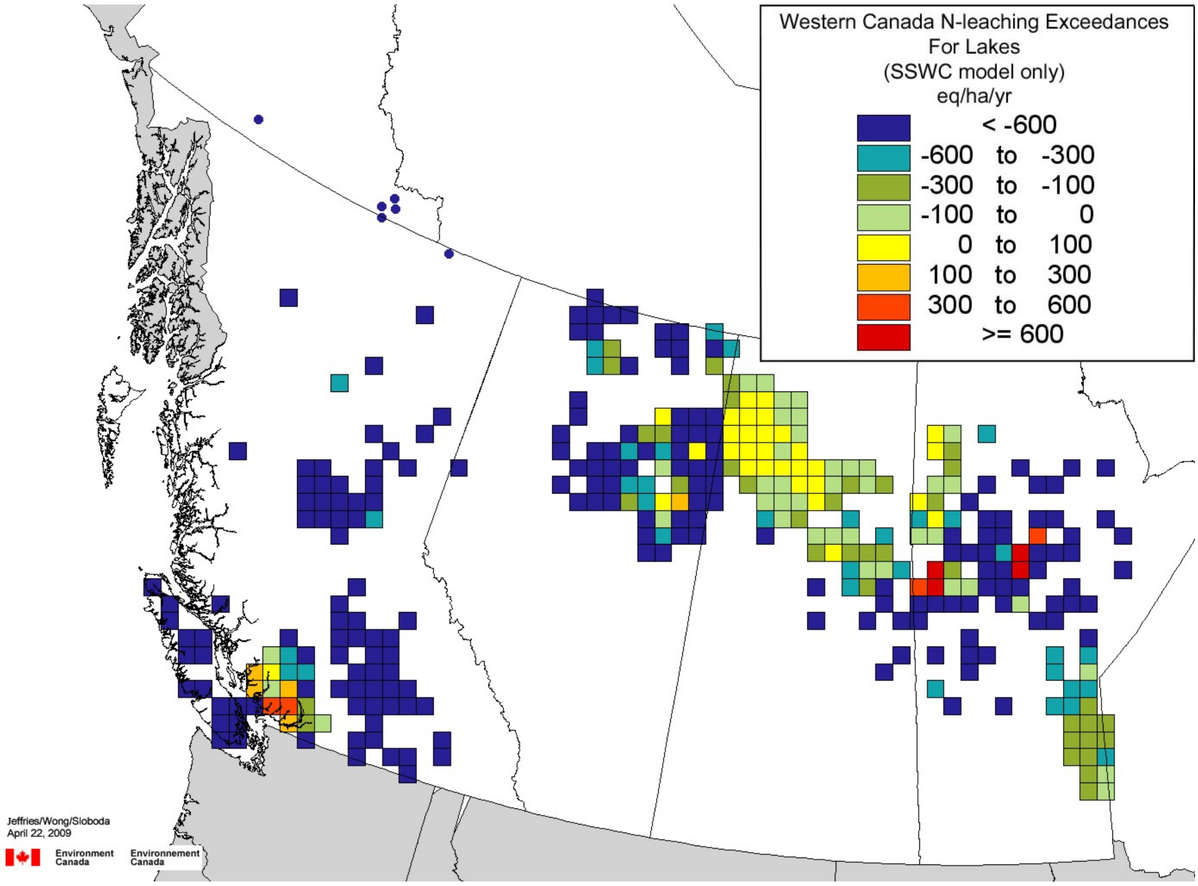

***Figure 5**. N-leaching critical load exceedances for lakes in western Canada calculated using annual S and N deposition estimated for 2002. This exceedance is our best estimate of the current situation. Hot colours (yellow to red) denote positive exceedances.*

The national exceedance map presented by Jeffries and Ouimet (2005) map showed no positive N-leaching exceedances in western Canada. However, inclusion of the survey data collected since then now shows that there are several occurrences. Positive exceedance can be related to very low CL, high

S and N deposition, or both. Maximum exceedances (300 to >600 eq h^{-1} yr^{-1}) result from the localised, high S deposition that occurs near smelters in Thompson and Flin Flon, MB, and near the metropolitan Vancouver area in southwest BC. The low but still positive N-leaching exceedances (yellow grid squares found mostly in northwestern SK) result from the extremely low CL values that occur throughout this area. Nitrate concentrations in almost all of our recently surveyed lakes were at or below analytical detections levels (generally < 3 μeq L^{-1}), so that the positive exceedances shown in Figure 5 are almost entirely due to S deposition.

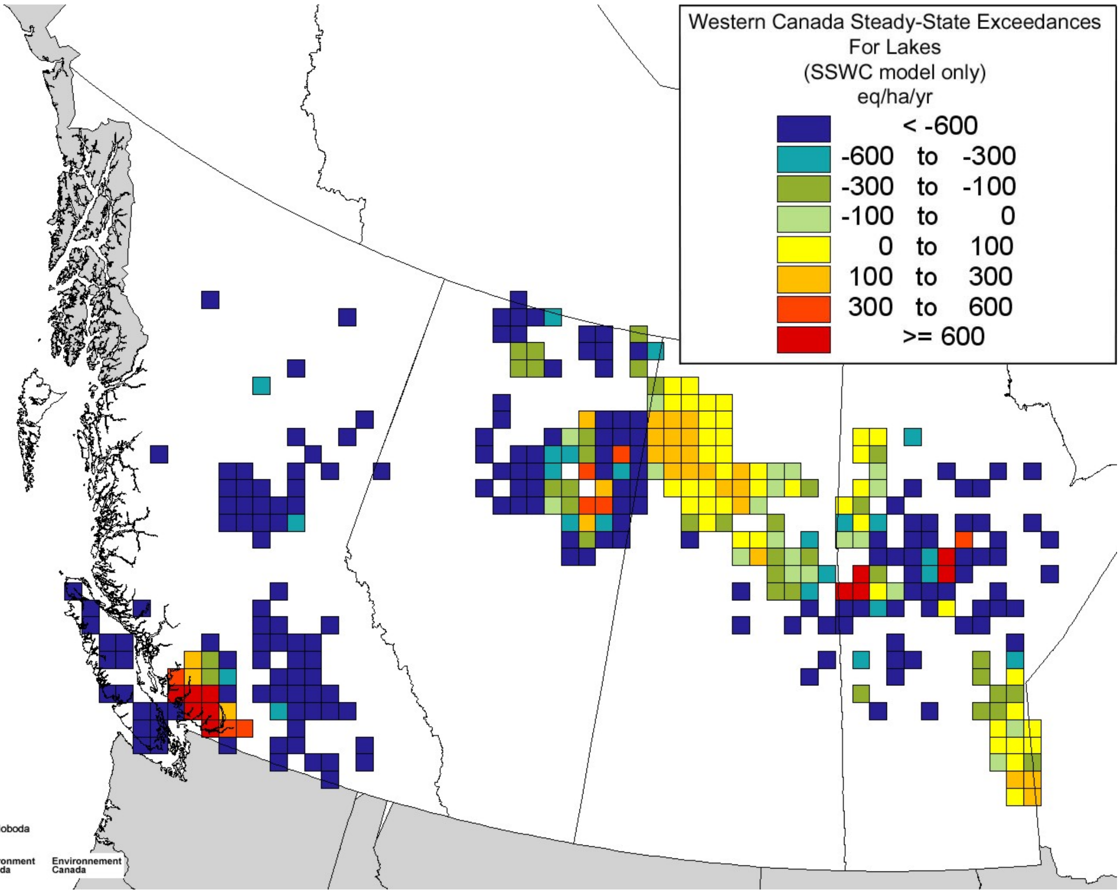

Figure 6. *Steady-state critical load exceedances for lakes in western Canada calculated using annual S and N deposition estimated for 2002. This exceedance is the maximum possible value assuming that all N deposition is acidifying. Hot colours (yellow to red) denote positive exceedances.*

The spatial distribution of high exceedance squares in the Steady-state Exceedance map is similar to that in the N-leaching Exceedance map, although the magnitude of the exceedances is obviously greater. Should aquatic ecosystems in western Canada become N saturated, exceedance levels will be much greater than is presently the case.

Conclusions

- New surveys have greatly improved the information available to assess lake acidification and status in western Canada, although spatial gaps in geologically sensitive areas still remain.
- Large populations of very acid sensitive lakes have been identified.
- Some of these lakes are likely to be affected by acidic deposition originating from Canadian (point or diffuse) emission sources.
- Lake populations typically exhibit broad ranges in chemical composition implying variable sources of dissolved constituents.
- DOC is a particularly important constituent of MB, SK and AB lakes.
- The aquatic CL map for western Canada is now much more detailed and complete; some very low CL grid squares are apparent.
- Positive, current (N-leaching) exceedances occur throughout the west due to low CLs or high, localised deposition.
- If ecosystem N-saturation progresses as a result of the cumulative effect of N deposition, then the degree of current exceedance will increase.

References

Dupont, J., Clair, T.A., Gagnon, C., Jeffries, D.S., Kahl, J.S., Nelson, S.J. and Peckenham, J.M. 2005. Estimation of critical loads of acidity for lakes in northeastern United States and eastern Canada. Environ. Monit. Assess. 109: 275–291.

Gibson, J.J., Birks, S.J., Jeffries, D.S., Kumar, S., Scott, K.A., Aherne, J. and Shaw, D.P. 2010. Site-specific estimates of water yield applied in regional acid sensitivity surveys across western Canada. J. Limnol. 69(Suppl. 1):67-76.

Henriksen, A., Dillon, P.J. and Aherne, J. 2002. Critical loads of acidity for surface waters in south-central Ontario, Canada: regional application of the Steady-State Water Chemistry (SSWC) model. Can. J. Fish. Aquat. Sci. 59: 1287-1295.

Jacobs, K. 2006. The effects of watershed characteristics and disturbance history on lake water quality of the boreal region of south eastern Manitoba. M.Sc. Thesis, University of Manitoba, Department of Botany, Winnipeg, Manitoba, 266 pp.

Jeffries, D.S. & R. Ouimet (Eds.). 2005. Chapter 8: Critical Loads – Are they being exceeded? In: 2004 Canadian Acid Deposition Science Assessment, Environment Canada, Ottawa, Ontario: 341-368.

Jeffries, D.S., D.K. McNicol & R.C. Weeber, R.C. (Eds.). 2005. Chapter 6: Effects on Aquatic Chemistry and Biology, in 2004 Canadian Acid Deposition Science Assessment, Environment Canada, Ottawa, Ontario: 203-278.

Jeffries, D.S., Semkin, R.G., Gibson, J.J. and Wong, I. 2010. Recently surveyed lakes in northern Manitoba and Saskatchewan, Canada: characteristics and critical loads of acidity. J. Limnol. 69(Suppl.1): 45-55.

Lydersen, E., Larssen, T. and Fjeld, E. 2004. The influence of total organic carbon (TOC) on the relationship between acid neutralizing capacity (ANC) and fish status in Norwegian lakes. Sci. Tot. Environ. 326: 63–69.

Moran, M.D., Zheng, Q., Pavlovic, R., Cousineau, S., Bouchet, V.S., Sassi, M., Makar, P.A., Gong, W. and Stroud, C. 2008. Predicted acid deposition critical-load exceedances across Canada from a one-year simulation with a regional particulate-matter model. Proc. 15th Joint AMS/A&WMA Conference on Applications of Air Pollution Meteorology, Jan. 21–24, New Orleans, American Meteorological Society, Boston: 20 pp.

Scott, K.A., Wissel, B., Gibson, J.J. and Birks, S.J. 2010. Chemical characteristics and acid sensitivity of boreal headwater lakes in northwest Saskatchewan. J. Limnol. 69(Suppl. 1):33-44.

Strang, D., Aherne, J. and Shaw, D.P. 2010. The hydrochemistry of high elevation lakes in the Georgia Basin, British Columbia. J.Limnol. 69(Suppl. 1):56-66.

UMA, 2007a. INCO Limited, environmental effects monitoring – sensitivity of Manitoba lakes to acidifying compounds, 2006 data report. UMA Engineering Ltd., Victoria, BC, 86 pp. (+ 3 appendices).

UMA, 2008. Vale INCO Limited and Manitoba Conservation, environmental effects monitoring – sensitivity of Manitoba lakes to acidifying compounds, 2007 data report. UMA Engineering Ltd., Winnipeg, MB, 40 pp. (+5 appendices).

UMA, 2007b. Hudson Bay Mining and Smelting Co., Limited, natural lake chemistry and sensitivity to acidification: lakes within 400 km of Flin Flon, MB. UMA Engineering Ltd., Victoria, BC, 33 pp. (+ 3 appendices).

UNECE, 2004. Section 5.4, Critical loads for aquatic ecosystems. In: Manual on methodologies and criteria for modeling and mapping critical loads and levels and air pollution effects, risks and trends. United Nations Economic Commission for Europe, Convention on Long-Range Transboundary Air Pollution, Geneva, Switzerland, pp. V29-V38. (also available at http://icpmapping.org/cms/zeigeBereich/11/manual_english.html)

WRS. 2004. Calculation of Critical Loads of Acidity to Lakes in the Athabasca Oil Sands Region. Report to the NOx-SOx Committee, Western Resource Solutions, Calgary, Alberta, 60 pp. (plus 9 Appendices).

3. Some thoughts about "old" data

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The present state of waters is often compared with that of "pre-industrial" times, often with the intention to lessen the anthropogenic pressure on the lake. This is a central intention in the EU's Water Framework Directive. Three different ways are available for the estimation of "pre-industrial" conditions in a lake:

1. "Old" data
2. Paleolimnological (sediment) studies
3. Models (e.g. MAGIC in the case of acidification)

Tomáš Pačes (1982, 1985), to our knowledge, was the first scientist to use 19th century data in a comparison with present day water chemistry. Quality control is a common difficulty with old data. Pačes' 1892 data seen to be in extremely good ion balance (Table 1), but most likely HCO_3 was calculated as the difference between cations and anions (thus ANC).

Table 1. *Concentrations of major ions at Elbe, Lovosice November 1892 (Paces 1982).*

Cations	*meq L^{-1}*	*Anions*	*meq L^{-1}*
Na	0.422	Cl	0.256
K	0.112	*HCO_3*	*1.967*
Mg	0.411	SO_4	0.394
Ca	1.696	NO_3	0.031
Sum cations	2.642	Sum anions	2.648

However the data quality seems fully acceptable and Pačes made a valuable evaluation of effects of acid rain and its effects on weathering.Löfvendahl (1990), following the ideas of Pačes, compared transport values for 1913–25 from JV Eriksson (1929) and data from the Swedish river monitoring for 1984–85. He found an increase in transport of alkalinity, but mostly in southern rivers. In southern rivers was the transport of sulphate doubled, while calcium increased by 50%. In northern rivers these changes were small. However, he ignored possible discharge variations between the years.

What is available of data in Sweden?

The earliest Swedish water chemistry data, still incomplete with regards to major constituents, found are from 1867-68 for 13 river samples. In 1902 a more complete analysis was preformed on five river samples. During later decades more lakes were sampled and analysed (Table 2).

Table 2*. Number of water samples collected in Swedish lakes during the first decades of 1900, and the parameters determined. Lohammar data are excluded.*

Period	*Secchi depth*	*pH*	*Conductivity*	*Colour*	*Ca*	*SO_4*	*Cl*	*COD_{Mn}*
1890–99	18	0	0	0	2	1	3	1
1900–09	0	0	0	0	25	12	39	36
1910–19	6	0	0	0	3	7	8	14
1920–29	44	38	37	1	1	0	0	1
1930–39	112	142	56	54	17	12	17	55
1940–49	56	370	351	292	274	238	266	303

Lake data are less complete than those for rivers. Not until 1930s become data more complete. The most complete lake study, covering 1929–37, was published by Lohammar (1938), also in this case no determination of alkalinity was performed (Table 2). River monitoring 1909–25 covering 147 stations contain several parameters, but is never complete (Table 3). In some publications ions are sometimes presented as oxides, thus weights of all compounds can be summed up and compared with dissolved inorganic compounds (residue on ignition).

***Table 3**. Summary of two important Swedish water chemistry data sets. Percentage of samples determined for the parameter.*

	Rivers	*Lakes*
	JV Eriksson	G. Lohammar
Sampling years	1909–25	1929–37
Number of stations	71	147
Number of samples	3614	739
Percent of all samples %		
Dissolved inorganic subst.	100 %	59 %
Dissolved organic subst.	100 %	60 %
Conductivity 20°		91 %
CaO	41 %	75 %
MgO	5 %	58 %
Na		75 %
K		52 %
Cl	42 %	64 %
SO_3	34 %	40 %
Alkalinity		25 %
COD_{Mn}		27 %
Colour (caramel scale)	24 %	
Colour (Pt scale)	4 %	
pH	5 %	87 %

Time series

Time series for a lake

Time series, in general starting around 1930s are available for 12 lakes. For some of these there is a lack of data until 1970s, for most of them data are available for 1985-2005 from national lake surveys. The example (Figure 1) clearly shows an increase in sulphate, but the expected drop in alkalinity, in this case is not evident. A recent drop in sulphate is also clear, however, alkalinity does not increase.

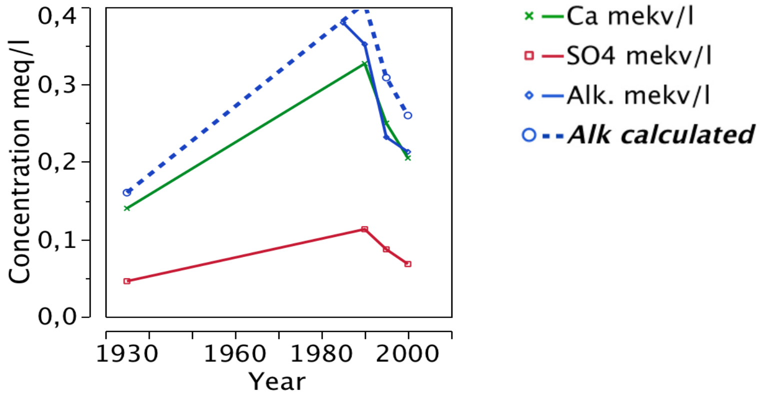

***Figure 1**. Time series for one Swedish lake. Data from Lohammar (1934) and lake surveys.*

Comparison of lake data from 1947–51 with present situation

Swedish lakes around Stockholm were studied by Silfersparre in 1947–51 and some were included in the Lake survey 2005 (Figure 2). Silfersparre's data, in general, are quite similar to those for 2005. Two lakes deviate; one (red dot) has been limed raising the pH value and the other (green dot) is eutrophic and during summer photosynthesis may raise the pH-value compared to late autumn in 2005.

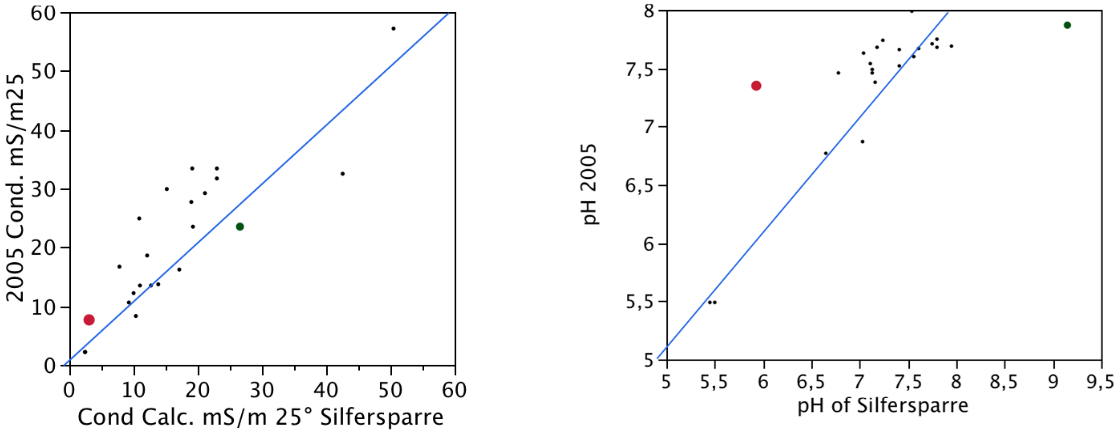

***Figure 2**. Lakes around Stockholm. Comparison of data for 1947–51 (Silfersparre) and the national Lake Survey in 2005.*

Time series for River Klarälven

River Klarälven; a tributary to Lake Vänern has been studied since long and is an example of a time series for some parameters (Figure 3). It is evident that interpretations are difficult. For sulphate early 20th century data seem to be somewhat lower than values at the end of the century. However, the large variation casts doubt about the quality of the data. Early alkalinity values are systematically higher than later data; probably caused by the method titrating to a lower pH endpoint. Chloride concentrations are likely to be unaffected by man. The two earliest reports give values of present day levels, but JV. Eriksson's data are systematically higher. The two methods for organic matter indicate lower concentrations than present day conditions.

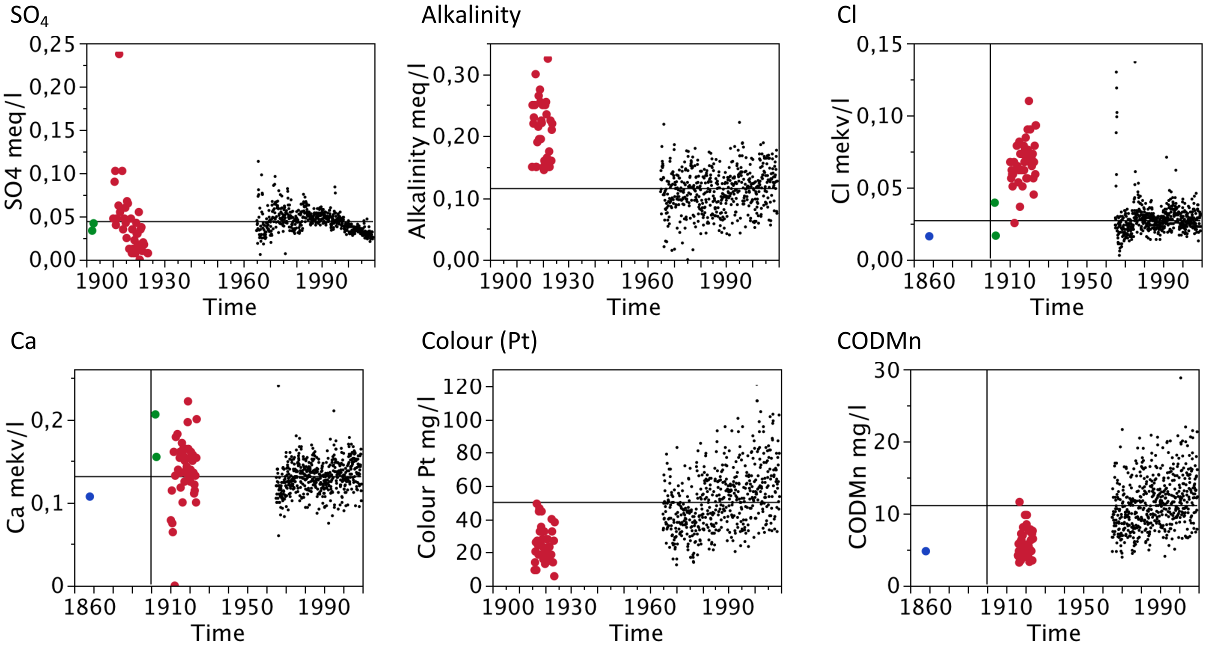

***Figure 3**. Time series for River Klarälven. Data from Almén (blue), Hofman-Bang (green), JV Eriksson (red) and national river monitoring.*

Challenges

There are some challenges for interpretations of old data; frequently the sampling season has changed, analytical methods have improved and for rivers sometimes the sampling station has been moved.

Seasonal variation

Several parameters exhibit a distinct seasonal variation, certainly for river water. The majority of old lake studies are for summer months, while many recent national lake surveys collected samples in late autumn. This may obscure interpretations since in the autumn often the concentrations of organic matter is higher and pH-values lower than during summer, but sulphate concentrations seem to vary little.

Method change

Even though changes of methods have lead to improved recent results, the skills of the individual analyst may be of more importance. An example, which is noted by Eriksson (1929), is the improvement in results, when Nanny Sahlbom took over the determinations of river water in 1913. Of course improvements in analytical methods both lower the detection limits and usually reduce interferences. A list of early methods is given in Table 4.

***Table 4**. Some changes in analytical methods.*

Parameter	*Methods*
pH	Colorimetric to electrode (Electrode performance)
Cations	Gravimetric Titrimetric (Ca and Mg)
Anions	Gravimetric (SO_4) Titrimetric (Cl)
Alkalinity	Sometimes calculated (ANC) Varying end-points
Organic matter	Loss on ignition (LOI) Permanganate oxidation (COD_{Mn})

pH-values are “infamous” for being doubtful; even today. pH-values were not recognised until Sörensen in 1909. Determinations were at first often made with various indicators. The precision of such determinations are disputed, some publications state that it is a low as 0.05 units, while others mention a value as high as two units. Probably the truth lies in between and depends on the quality of the sampled water as buffer capacity and water colour. Also the earliest glass electrodes had poor performance.

Results from gravimetric methods for determination of cations rely on both the volume used and the skills of the analyst. With the EDTA titration in late 1940s there was a great improvement for Ca and Mg.

For both sulphate and chloride, the “old” methods were less sensitive than present. However, for these methods the skills of the analyst were also central.

Alkalinity has been determined using various indicators for end point detection leading to some systematic differences.

Change of sampling point and/or local influence

Some river stations have been moved closer to the outlet, possibly receiving more pollution. In Sweden many waters (directly at least 7000) are affected by liming since 1970s. Thus knowledge about the local conditions may be essential.

Quality control

There are some ways to control the quality of the water chemistry data, but a ”complete” or ”near complete” set of parameters is needed. Some examples are presented below.

Sum of components versus residue on ignition

Residue on ignition was the first method for determination of total inorganic matter. An example of a quality control for data from 1902 is presented in Figure 4. The constituents are reported as oxides (with the natural exception of Cl); the sum should thus correspond to the determined residue on ignition when the residue is treated with ammonium carbonate and dried in order to restore carbonate content. The graph indicates a small systematic difference between the two estimates of total salt concentrations.

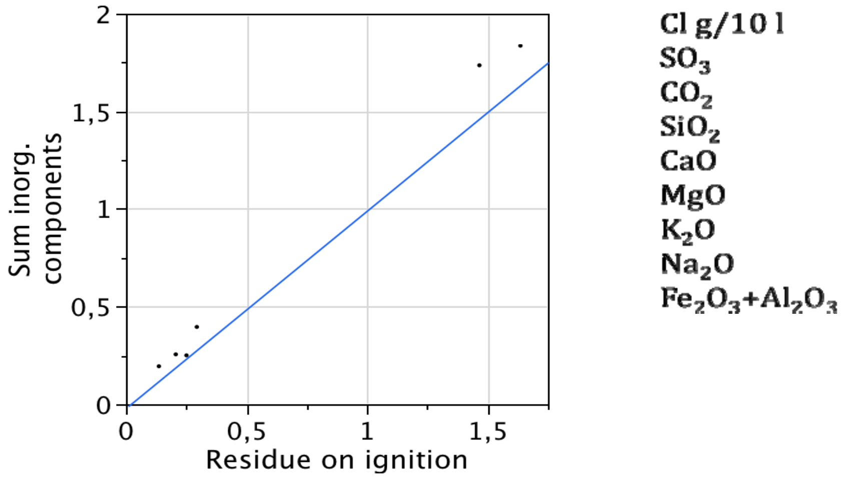

Figure 4. *Sum of components versus residue on ignition. The right the list of parameters determined. Data from Hofman-Bang 1903.*

Sum of cations versus sum of anions

An example of quality control based on determined major ions is shown in Figure 5. J.V. Eriksson’s data seem to have a quite good ion balance over the entire scale. Since Na concentrations in the monitored rivers usually are low the calculated Na should not hide any ion deficiency.

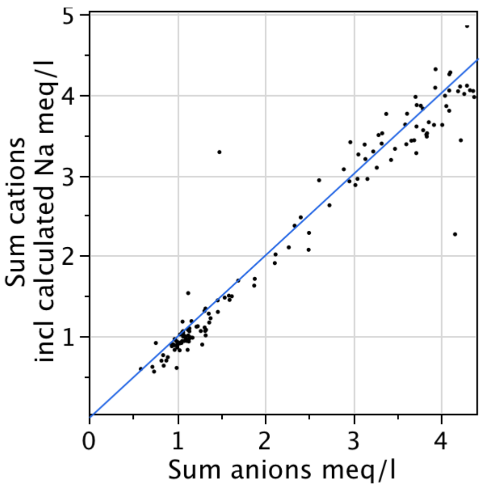

Figure 5. *The sum cations versus the sum of anions. JV Eriksson 1909–25. Na calculated from Cl using the Na/Cl ratio for seawater.*

Organic matter: Colour versus COD_{Mn}?

The methods for determination of organic matter as COD_{Mn} (permanganate consumption) have varied somewhat over time, but not likely to cause serious systematic differences. Comparisons between COD_{Mn} and colour measurements indicate quite a good correlation (Figure 6). In the graphs three samples (marked in red) deviate and certainly the COD_{Mn} values are too low.

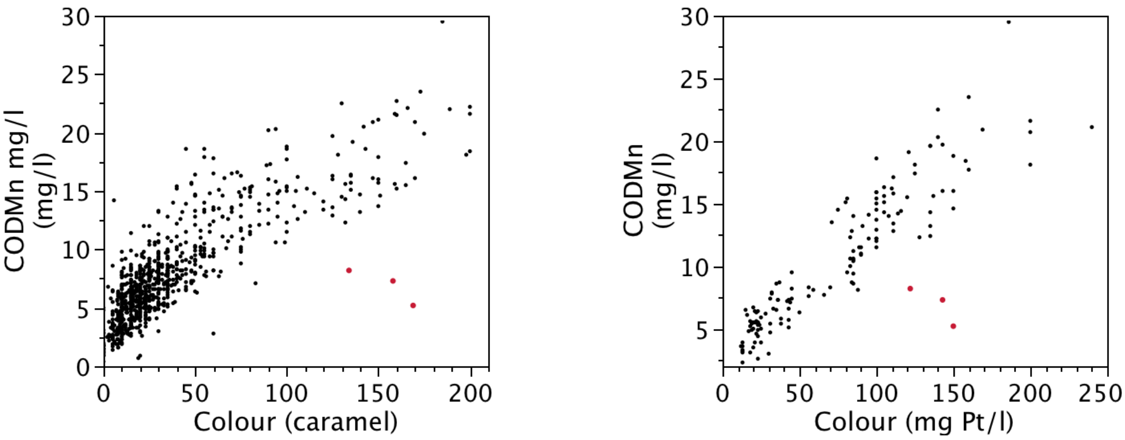

***Figure 6**. Organic matter. Comparison between COD_{Mn} and two methods for water colour determination. JV Eriksson 1909–25. Colour was determined by both methods for some samples. The three samples marked red deviate.*

Conclusions

Quality control is vital in order to avoid misinterpretations. ”Old” data can:

- Estimate ”pre-industrial” water chemistry
  For the 19th century, as far as known, there are only individual data from less than 20 rivers in Europe (Livingstone, 1963). Estimates of “pre-industrial” conditions thus have to rely on data from the beginning of the 20th century, when river monitoring starts. Even though sulphur deposition already had increased it is still low compared to the maximum levels
- Be a reference to modelled conditions
  Model results benefit from comparisons with measured data in order to “validate” them. This is of course also valid for early 20th century data.
- Be a reference to paleolimnological estimates
  Paleolimnological methods estimate among others pH-values, but also estimation has been attempted for organic matter and nutrients. Again comparisons between “old data” and data using these methods could be of value
- Pre-industrial dissolved organic matter can not be modelled and thus “old data” can give some information.

Additional data has been collected, mainly from 1950–1960, but not yet quality controlled. This is a period just before maximum deposition of acidity and the data may thus be of some value for the understanding of the development of acidification.

References

Almén, A, 1879. Huru bör ett dricksvattens godhet bedömmas från sanitär synpunkt? Svar grundadt på jemförande undersökning av 80 i Skandinavien förekommande naturliga vatten. Sv. Läkare-Sällskapets Nya Handlingar Serie II Del III

Eriksson, J.V. 1929. Den kemiska denudationen i Sverige. Meddel. fr. Statens Meteorologisk-Hydrografiska Anstalt. (Resumé en francaise) Band 5. No 3

Hofman-Bang, O. 1903. Studien über schwedische Flüsse- und Quellgewässer. Bull. Geol. Inst. Uppsala Vol VI

Livingstone, D.A. 1963. Data of Geochemistry. Chapter G. Chemical Composition of Rivers and Lakes. Sixth Ed. Geol Survey Prof. Paper 440-G

Lohammar, G. 1938. Wasserchemie und höhere Vegetation Schwedischer Seen. Symb. Bot. Upsalienses. III:1

Löfvendahl. R. 1990. Changes in the flux of some major dissolved components in Swedish rivers during present century. AMBIO 19 210–219

Pačes, T. 1982. Natural and Anthropogenic Flux of Major Elements from Central Europe. AMBIO Vol 11

Pačes, T. 1985. Sources of acidification in Central Europe estimated from elemental budgets in small basins. Nature 1985 315

4. Report of national ICP Waters activities in Latvia, 2008/2009

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Sites and observations

In 2008/2009, five sites, L. Jugla-Zaki, Amula-mouth, Tulija-Zoseni, Zvirbuli Stream and Tervete – upstream of Tervete were under the ICP Waters monitoring programme (Figure 1).

The ICP Waters sites have been involved as reference sites in the Latvia's State Monitoring Network, 2009-2012.

The main activities focused on the QA/QC of sampling, analyses, performance of new measurements under the ICP Waters programme and data handling and data assessment.

***Figure 1**. ICP Waters sites in Latvia.*

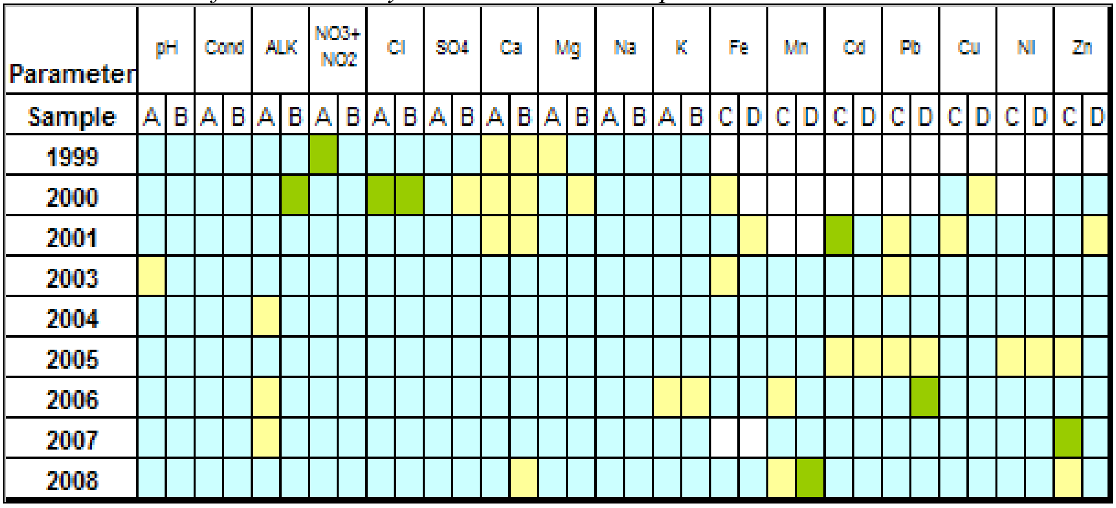
Quality assurance and quality control

The agency's laboratory has participated in yearly hydrochemical and hydrobiological intercomparison exercises held by NIVA. During 1999-2008, a total of 91% of the results were within the general target accuracy (Table 1).

The tendency towards improving the results of analysis was evident, yet the problems remained as to getting acceptable results for samples of very low reference concentrations which are lower then the sensitivity of the method.

On the whole, the results of the 2002-2008 invertebrate intercalibrations were good (Table 2). A low identification percent and a bit higher misidentifications both in species and genus in 1998 showed a lack of relevant key literature for proper identification of some of the groups. The 2002, 2004 and 2008 results for stoneflies were unacceptable.

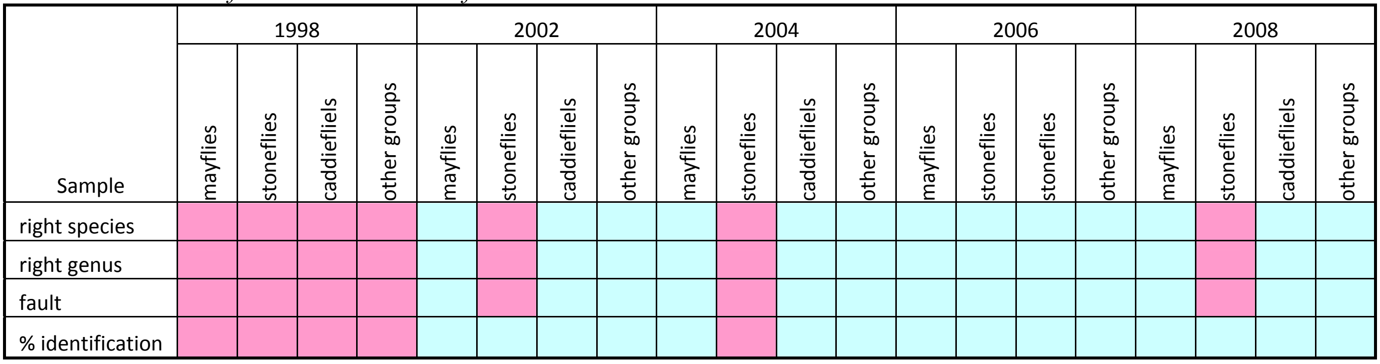
Table 1. *Results of ICP Waters hydrochemical intercomparison exercises.*



Parameter	pH		Cond		ALK		NO3+ NO2		Cl		SO4		Ca		Mg		Na		K		Fe		Mn		Cd		Pb		Cu		Ni		Zn	
Sample	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	C	D	C	D	C	D	C	D	C	D	C	D	C	D
1999	🟦	🟦	🟦	🟦	🟦	🟦	🟩	🟦	🟦	🟦	🟦	🟦	🟨	🟨	🟨	🟦	🟦	🟦	🟦	🟦														
2000	🟦	🟦	🟦	🟦	🟦	🟩	🟦	🟦	🟩	🟩	🟦	🟨	🟨	🟨	🟦	🟨	🟦	🟦	🟦	🟦	🟨								🟦	🟨			🟦	🟦
2001	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟨	🟨	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟨			🟩	🟦	🟨	🟦	🟨	🟦	🟦	🟦	🟦	🟨
2003	🟨	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟨	🟦	🟦	🟦	🟦	🟦	🟨	🟦	🟦	🟦	🟦	🟦	🟦	🟦
2004	🟦	🟦	🟦	🟦	🟨	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
2005	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟨	🟨	🟨	🟨	🟦	🟦	🟨	🟨	🟨	🟦
2006	🟦	🟦	🟦	🟦	🟨	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟨	🟨	🟦	🟦	🟨	🟦	🟦	🟦	🟦	🟩	🟦	🟦	🟦	🟦	🟦	🟦
2007	🟦	🟦	🟦	🟦	🟨	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦			🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟩	🟦
2008	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟨	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟨	🟩	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟨	🟦

blue - acceptable; yellow – unacceptable, above the reference value;
green – unacceptable, below the reference value

Table 2. *Results of intercalibrations of invertebrates.*



	1998				2002				2004				2006				2008			
Sample	mayflies	stoneflies	caddieflies	other groups	mayflies	stoneflies	caddieflies	other groups	mayflies	stoneflies	caddieflies	other groups	mayflies	stoneflies	stoneflies	other groups	mayflies	stoneflies	caddieflies	other groups
right species	🟥	🟥	🟥	🟥	🟦	🟥	🟦	🟦	🟦	🟥	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟥	🟦	🟦
right genus	🟥	🟥	🟥	🟥	🟦	🟥	🟦	🟦	🟦	🟥	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟥	🟦	🟦
fault	🟥	🟥	🟥	🟥	🟦	🟥	🟦	🟦	🟦	🟥	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟥	🟦	🟦
% identification	🟥	🟥	🟥	🟥	🟦	🟦	🟦	🟦	🟦	🟥	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦

blue - acceptable; red – unacceptable (misidentification, limit of faults >10%)

Summary of data assessment results

Nitrogen and sulphur total (wet and dry) deposition was calculated using the measured concentrations in the air and precipitation at Latvia's regional level GAW/EMEP stations Rucava and Zoseni that had operated since 1985 and 1995.

During the period 1998-2008, at Rucava, nitrogen total deposition ranged between 5.4 and 8.7 kg N ha^{-1} and sulphur total deposition between 4.6 and 5.1 kg S ha^{-1}. At Zoseni, the values varied from 5.7-8.1 kg N ha^{-1} and 3.2 –6.7 kg S ha^{-1} (Figures 2 and 3). Compared to the 1986-1997 period, nitrogen total deposition has decreased 1.5 times and sulphur total deposition 2 times on average. The results of trend analysis for 1998-2008 showed no trend in nitrogen and sulphur total deposition at Rucava station and a significant decrease in nitrogen and sulphur total deposition at Zoseni station.

Table 3. *Nitrogen and sulphur total deposition trend results.*

Station	Period	Mann-Kendall trend (n.s.= not significant, *p<0.05, ***p<0.001)		Sen's slope estimate	
		N dep.	S dep.	N dep.	S dep.
Rucava	1998-2008	Ns	ns	0.13	0.00
Zoseni	1998-2008	**	***	-0.23	-0.29

In the 1998-2008 period, annual mean pH values (Figure 1) varied from 7.22 (Tulija River) to 8.11 (Amula River) except for Zvirbuli Stream (3.38-4.84) that flows through the Kemeri bog. Compared to the 1986-1997 period, mean pH values in the Tulija and Liela Jugla Rivers have decreased by 0.32 and 0.11 respectively, and Zvirbuli Stream has shown an increase of 0.16 on average.The Tulija, Liela Jugla, Amula Rivers and Zvirbuli Stream have shown the downward tendency in annual mean pH, yet the trends are insignificant (Table 4).

Sulphate (non-marine SO_4^{-2}*) concentrations were three times higher on average in the Liela Jugla and Tervete than at other ICP Waters sites, and ten times as high as in Zvirbuli Stream (Figure 2). The higher sulphate concentrations in the former two water bodies are likely to be due to weathering of gypsum present in the bedrock.

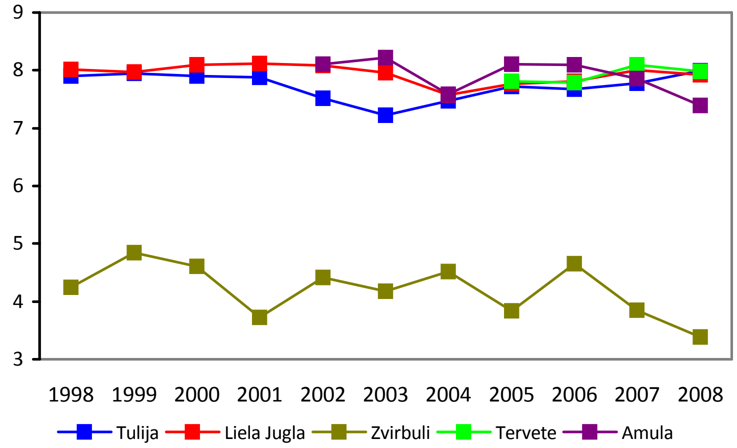


Figure 1. *Annual mean pH at ICP Waters stations.*

Table 4*. pH trend results.*

ICP site	Period	Mann-Kendall trend (n.s. – not significant)	Sen's slope estimate
Tulija	1998-2008	n.s	-0.02
Liela Jugla	1998-2008	n.s	-0.02
Zvirbuli	1998-2008	n.s	-0.09
Amula	2002-2008	n.s	-0.05
Tervete	2005-2008	n.s	0.08

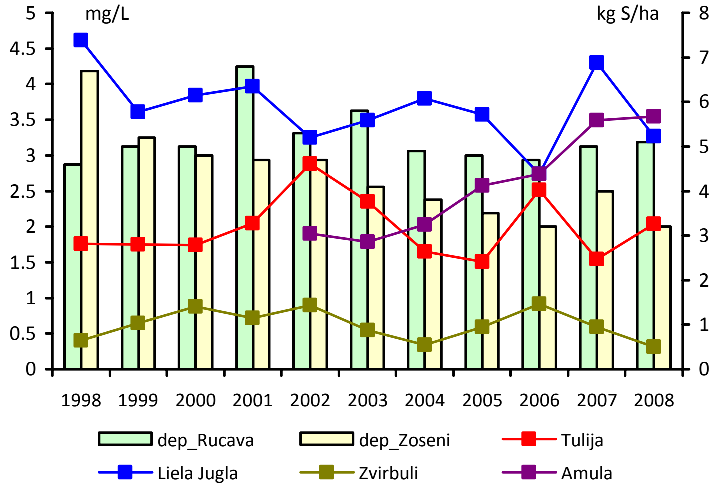


Figure 2*. Total N deposition at regional GAW/EMEP stations Rucava and Zoseni and mean annual non-marine sulphur concentrations at ICP Waters sites.*

Table 5*. SO_4^{-2}* (non-marine) trend results.*

ICP site	Period	Mann-Kendall trend (significance: +p<0.1, **p<0.01, ***p<0.001)	Sen's slope estimate
Tulija	1998-2008	***	-2,12
Liela Jugla	1998-2008	+	-1,42
Zvirbuli	1998-2008	**	-0,71
Amula	2002-2008	n.s	-0,22
Tervete	2005-2008	n.s	1.29

Compared to the 1986-1997 period, mean non-marine sulphate concentrations in the Tulija River and Zvirbuli Stream have decreased 2 times. The Liela Jugla has reported a less pronounced (1.2 times) decrease.

Surface waters in the Tulija, Liela Jugla Rivers and in Zvirbuli Stream showed a significant decreasing trend in non-marine sulphate (Table 5).

High correlation was observed between total sulphur deposition at the regional GAW/EMEP station Zoseni (situated near the ICP Waters site of Tulija) and non-marine SO_4^{-2}* concentrations in the Tulija River (r= 0.8), as well as with SO_4^{-2}* concentrations in Zvirbuli Stream (r=0.9) (Figure 2). Weekly correlation SO_4^{-2}* concentration in Liela Jugla River with sulphur deposition at both stations showed that sulphate runoff is regulated by other driving forces than deposition.

Dissolved inorganic nitrogen compounds, especially NO_3^- and NH_4^+, contribute much to N_{total} concentration in surface waters. At background stations, the main N sources are nitrogen deposition from the atmosphere, the soil, sediments of water bodies and inflow with groundwater.

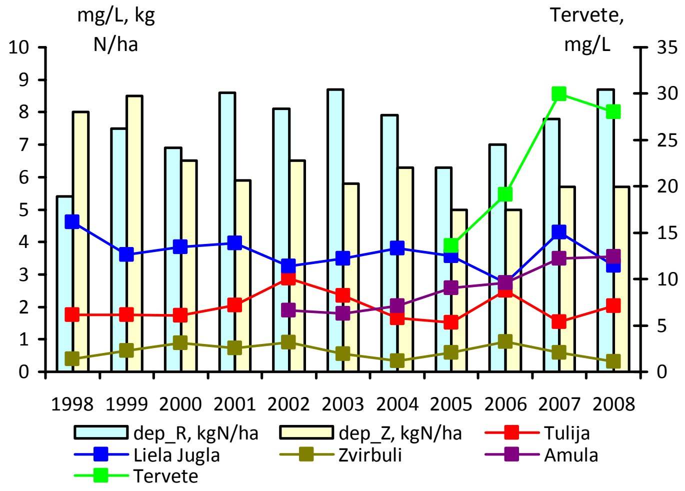


***Figure 3**. Total N deposition at regional GAW/EMEP stations Rucava and Zoseni and mean annual NO_3 concentrations at ICP Waters sites.*

***Table 6**. NO_3^- trend results*

ICP site	Period	Mann-Kendall trend (n.s. – not significant, **p<0.01)	Sen's slope estimate
Tulija	1998-2008	n.s	0.01
Liela Jugla	1998-2008	n.s.	-0.06
Zvirbuli	1998-2008	n.s.	-0.01
Amula	2002-2008	**	0.32
Tervete	2005-2008	n.s	5.14

In 1998-2008, lowest values were obtained for nitrate concentrations in Zvirbuli Stream, 0.10 mg L^{-1} on average. Mean nitrate values reported from the rivers Tulija, Liela Jugla and Amula ranged from 1.87 to 3.56 mg L^{-1}. In Tervete, high annual mean concentrations of 13.57 mg L^{-1} to 29.97 mg L^{-1} may be ascribed to the anthropogenic impact on the catchment, mostly due to agricultural activities (Figure 3). Compared to the 1986-1997 period, mean NO_3^- concentrations in the Tulija and Liela Jugla Rivers have decreased 2 times and showed no changes in Zvirbuli Stream.

In surface waters of the Tulija, Amula and Tervete Rivers, the observed annual mean NO_3 concentrations showed the upward tendency, statistically significant in the Amula River ($p<0.01$). Zvirbuli Stream and Liela Jugla showed no significant downward tendency in the NO_3 concentration (Table 6).

The elevated level of ammonium (NH_4^+) (0.10-0.60 mg L^{-1}) in the surface waters of Zvirbuli Stream is likely to be due to the influence exposed by bogs. Other ICP stations reported NH_4^+ annual mean values of 0.05-0.21 mg L^{-1}. Compared to the 1986-1997 period, practically no changes in mean NH_4^+ concentrations Zvirbuli stream and Tulija, Liela Jugla River showed a decrease of less than 1.5 times. Annual mean concentrations of NH_4^+ showed no changes at all ICP sites, with the statistically supported decrease only the Tulija River.

During 1998-2008, the ratio of HN_4^+ to NO_3^- was 1.08 (Zvirbuli Stream), 0.03-0.06 (Tulija, Liela Jugla, Amula Rivers) and 0.003 (Tervete River).

The empirical data for forested ecosystems in Europe show a distinct relationship between the N deposition and N loss. These data reflect the fact that very little NO_3 leaching to surface waters occur at N deposition below 9-10 kg N ha^{-1} $year^{-1}$, leaching can occur at intermediate deposition between 9 and 25 kg N ha^{-1} $year^{-1}$, and significant leaching occurs in N deposition of more than 25 kg ha^{-1} $year^{-1}$.

In terms of the significance of NO_3^- in acidification relative to non-marine SO_4^{-2*} in surface waters, ICP site were evaluated by division of the concentration of NO_3^- by the sum of SO_4^{-2*} and NO_3^-. NO_3^- is of minor significance when the N acidification ratio < 0.1, of moderate effect – 0.1< ratio <0.25, and of heavy effect - >0.25.

Over the whole observation period 1998-2008, NO_3^- has played a minor role in the acidification of the water in the Liela Jugla and Tulija Rivers and Zvirbuli Stream. Moderately affected has been the Amula River and heavily affected - the Tervete River (Figure 4).

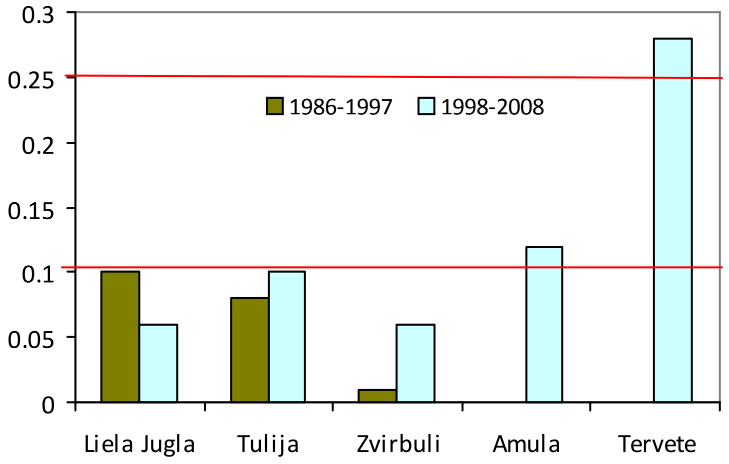


***Figure 4**. Importance of NO_3^- in acidification relative to non-marine SO_4^{*2-} (N acidification ratio)*.

The relationship between NO_3^- in surface waters of the ICP Waters sites and total nitrogen deposition at the regional GAW/EMEP stations Rucava and Zoseni (Figure 3) was weak with the correlation coefficient not exceeding r< 0.5.

During 1998-2008, N total deposition at Rucava and Zoseni would not exceed 9-10 kg N ha^{-1} $year^{-1}$ and, in the Tervete, Amula and Liela Jugla Rivers, the measured NO_3^- annual mean concentrations were above 50 µeq L^{-1} (3.05 mg L^{-1}). This suggests that these sites have been exposed also to other kinds of disturbance besides N deposition.

The marked increasing tendency in inorganic N concentrations at ICP Waters sites enhances the risk of acidification of soil and surface waters.

Future activities

- Participation in hydrochemical and hydrobiological intercomparison exercises
- Elaboration of methods for the preparation of surface water samples for the determination of labile aluminium, data processing
- Participation in the revision of the ICP Waters Manual under the ICP Programme Centre
- 2008 data reporting to the ICP Waters data base
- Assessment of data on macrozoobenthos at ICP Waters sites, 1989-2008
- Assessment of data from Zvirbuli Stream for the whole observation period
- Analyses of driving forces of sulphur, inorganic nitrogen, base cations and heavy metal concentrations in surface waters in ICP Waters sites.

References

Report “EMEP Assessment in Latvia (1985-2000)”, Latvian Environment, Geology and Meteorology Agency, Riga, 2002.

Report “Effect of Transboundary air pollution on ecosystems of Latvia”, Latvian Environment, Geology and Meteorology Agency, Riga, 2008.

ICP Waters Report 87/2007 “Trends in surface water chemistry and biota; the importance of confounding factors, Norwegian Institute for Water Research.

5. The UK Acid Waters Monitoring Network: 20 Year Interpretive Report – a brief summary

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Introduction

The UK Acid Waters Monitoring Network (AWMN) was set up in 1988 to monitor the status and response of upland surface waters to acid deposition. Chemical and biological monitoring has been carried out at 11 lakes (quarterly) and 11 streams (monthly) continuously since then. The AWMN contributes data for all ICP Waters sites in the UK and two Integrated Monitoring sites (Figure 1). In 2009, a major sponsor of the AWMN, the UK Government Department for Environment, Food and Rural Affairs, commissioned an interpretive report to carry out trend analysis of the first 20 years of data and interpret the results in terms of ecosystem responses to declining acid deposition inputs (sulphur + nitrogen) over this period (Kernan *et al.*, 2010). Previous interpretive reports used linear methods for analysis of trends but this is the first report to employ non-linear methods in response to recognised non-linearities in both acid deposition and surface water response trends.

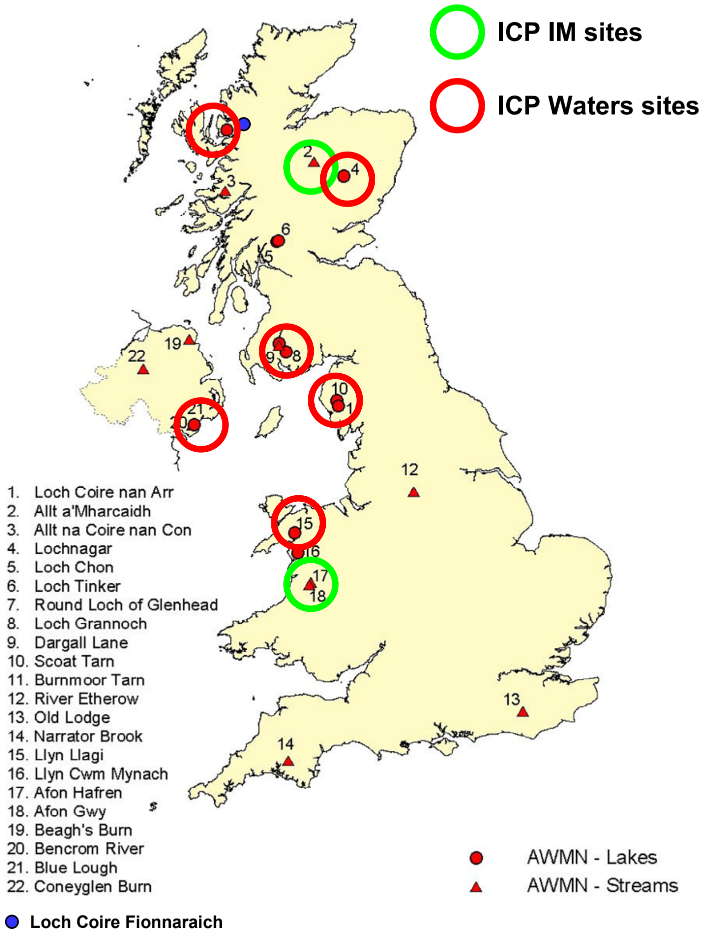


Figure 1. *AWMN sites contributing to ICP programmes*

Acid deposition trends in the UK

Bulk deposition of sulphur and nitrogen species has been measured for over 20 years at sites in the UK Acid Deposition Monitoring Network (ADMN). While a few of these bulk deposition collectors are co-located with AWMN sites, most are not, so for this study we selected the closest ADMN site for each of the AWMN sites following the approach of Cooper (2005) (Table 1). Results of a previous linear trend analysis at these sites over the period of AWMN monitoring showed strong declining trends in non-seasalt (nss) SO_4^{2-} but no significant trends in NO_3^- deposition, although in most cases NO_3^- deposition did appear to be declining (Lawrence *et al.*, 2009).

Table 1. *Linear trends in precipitation weighted concentrations at ADMN bulk deposition sites.*

Code	**Site Name**	**OS Grid Ref.**	**Alt. (m)**	**Matched AWMN sites**	**nss SO_4^{2-} µeq L^{-1} yr^{-1}**	**NO_3^- µeq L^{-1} yr^{-1}**
5103	Allt a'Mharcaidh	NH 876052	274	MHAR	-0.68^{++++}	-0.05 ns
5152	Balquhidder 2	NN 545207	130	CHON, TINK	-0.89^{+++}	-0.12 ns
5111	Bannisdale	NY 515043	265	SCOATT, BURNMT	-1.33^{++++}	-0.14 ns
5007	Barcombe Mills	TQ 437149	10	LODG	-0.96^{++}	-0.31 ns
5011	Glen Dye	NO 642864	185	NAGA	-1.66^{+++}	-0.25 ns
5107	Loch Dee	NX 468779	230	BENC, BLU, DARG, LGR, RLGH	-0.95^{+++}	-0.16 ns
5006	Lough Navar	IH 065545	130	BEAG, CONY	-0.53^{++++}	-0.07 ns
5150	Pumlumon	SN 823854	390	GWY, HAFR, LAG, MYN	-0.82^{++++}	-0.18 ns
5010	Strathvaich Dam	NH 347750	270	ARR, ANCC, VNG9402	-0.44^{+++}	-0.09 ns
5120	Wardlow Hay Cop	SK 177739	350	ETHR	-2.79^{+++++}	-0.28 ns
5008	Yarner Wood	SX 786789	119	NART	-0.67^{++}	0.14 ns

Here, additive models were used to analyse trends in the data while accounting for within-year seasonal variations to determine the underlying, non-linear trends in the data. Additive models take their form from the data and allow an assessment of whether trends fitted to the time-series data are significantly increasing or decreasing, by estimating significance using the first derivatives of the fitted spline for the trend, computed using finite differences (Kernan *et al.*, 2010). Additive models confirm the strong declining trends in excess SO_4^{2-} deposition found using linear methods, but show also that in many sites these trends only became significant since the mid-1990s (Figure 2). Trends in deposition of N species are mixed and often non-linear, but where significant generally show an overall decline for NO_3^- and/or NH_4^+ (Figure 3).

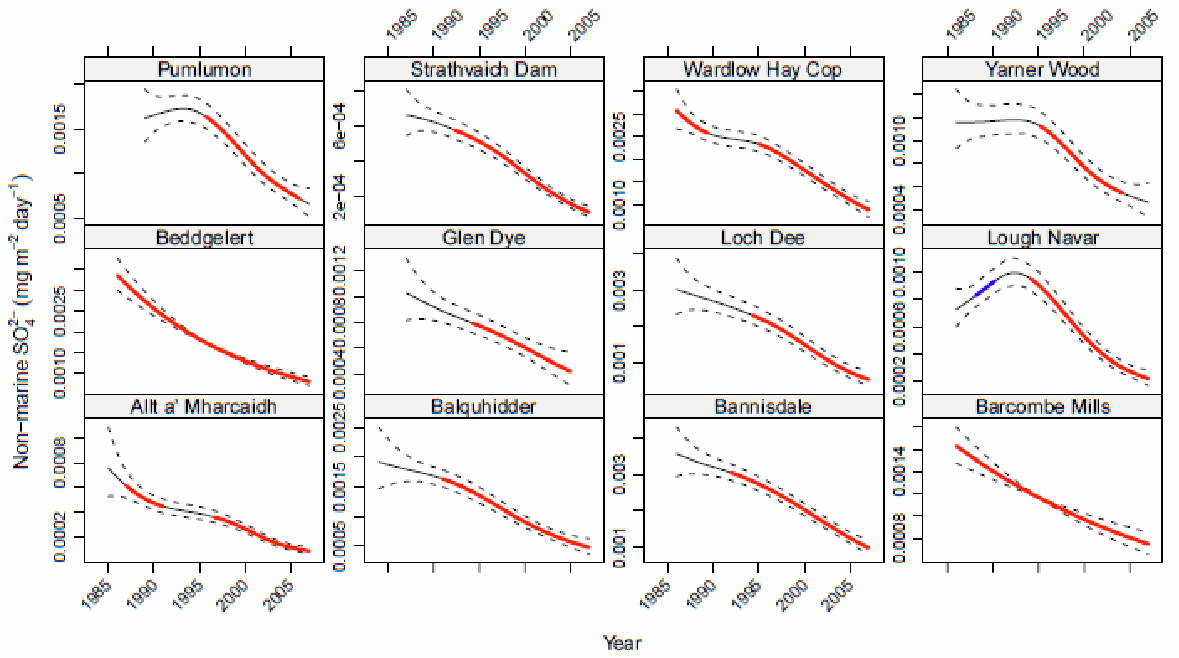


Figure 2*. Trends in precipitation weighted non-marine SO_4^{2-} in bulk deposition (blue highlighting = sig. increase; red = sig. decrease).*

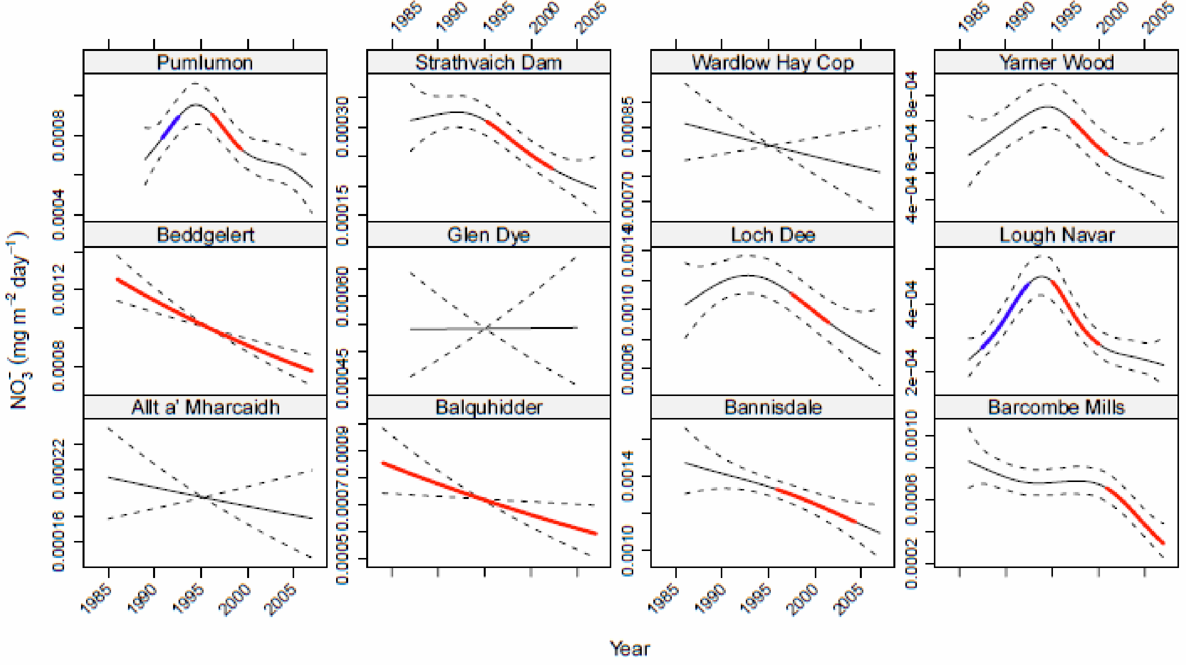


Figure 3*. Trends in precipitation weighted NO_3^- in bulk deposition.*

Trends in surface water chemistry

Overall there have been significant improvements in water quality, and this is indicated most clearly by the increases in acid neutralising capacity (ANC) that have occurred at all acidified sites (Figure 4). Concentrations of non-marine SO_4^{2-} have fallen substantially across the network over the last 20 years, although most sites show little further decrease since 2000, and in the majority, concentrations remain 3-6 times higher than those observed in the reference sites in north-west Scotland (e.g. Coire nan Arr). Trends in the concentration of NO_3^-, the secondary acidifying pollutant, are much less clear showing substantial inter-annual variability and seasonality (Figure 5).

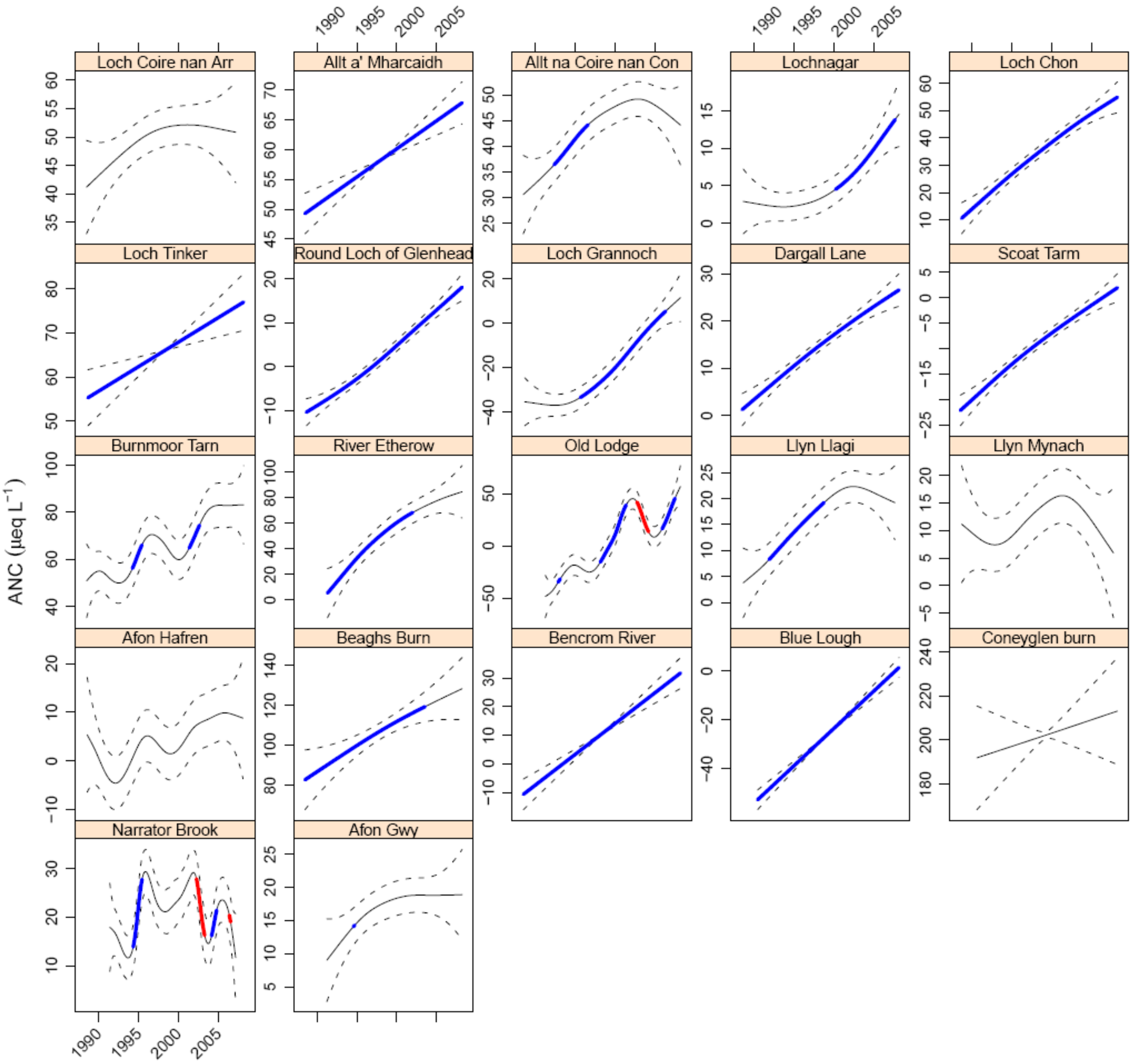
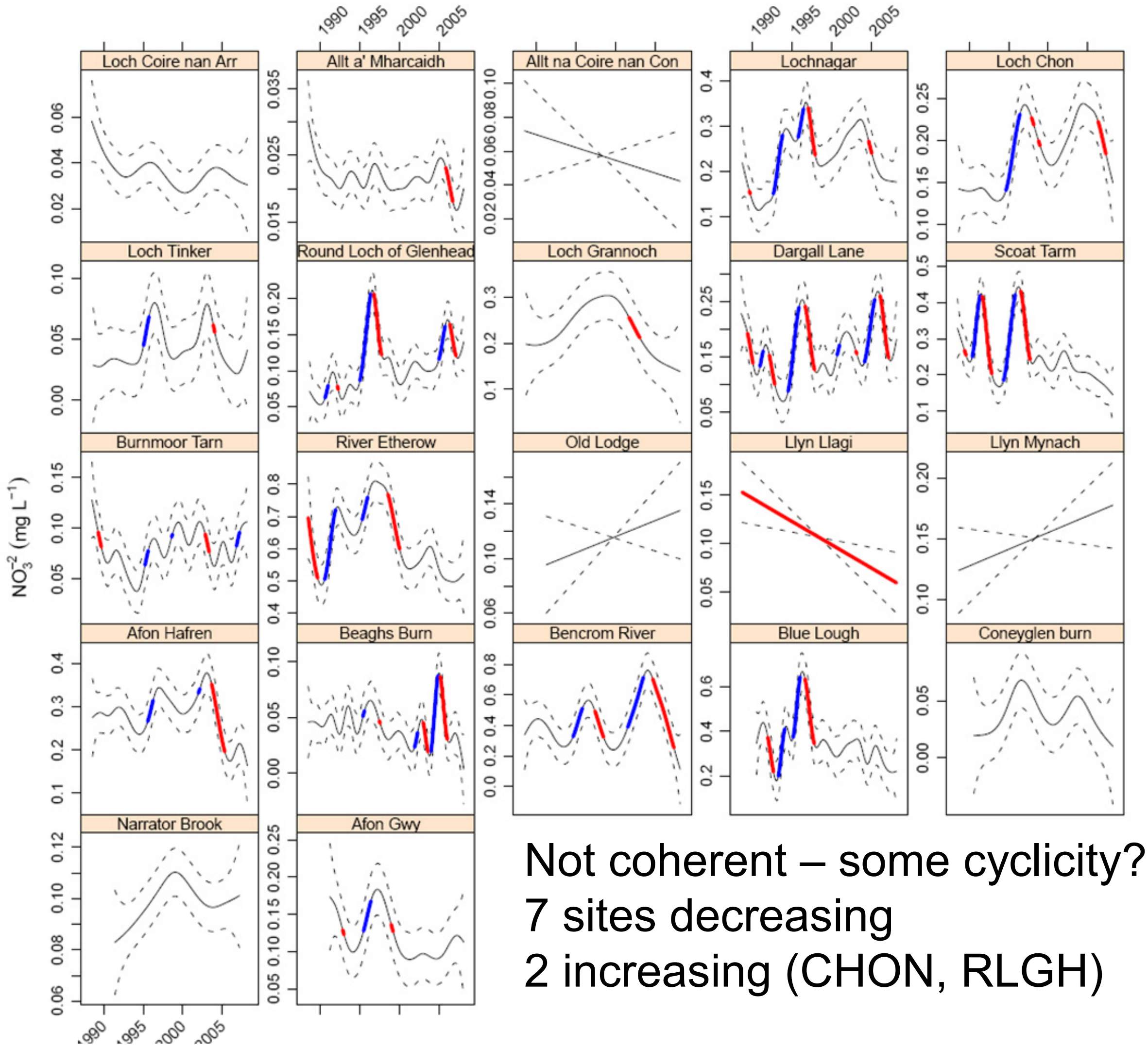


Figure 4. *Trends in ANC at AWMN sites.*



Not coherent – some cyclicity?
7 sites decreasing
2 increasing (CHON, RLGH)

Figure 5. *Trends in NO_3^- at AWMN sites.*

Chloride concentration, dominated by sea-salt inputs, has declined significantly in many sites following very high levels in the first few years of monitoring. These changes primarily reflect a reduction in the intensity of Atlantic storms over the last 20 years. Some sites may also have experienced significant reductions in chloride from decreased industrial emissions of hydrochloric acid. Both sources of chloride exert acidifying effects and their reductions will have contributed to the observed improvement in surface water chemistry. Overall there has been a significant decrease in acidity (increase in pH) at most acidified sites, a decrease in the strength of acid episodes in streams and decreases in toxic labile aluminium concentrations at the most severely acidified sites. However, concentrations of labile aluminium remain significantly above the safe “background” levels of 10 µg L^{-1} at many sites.

Dissolved organic carbon (DOC) concentrations have increased at all sites across the network. These increases are attributed principally to falling SO_4^{2-} concentrations and indicate a return to higher DOC concentrations that are assumed to have occurred naturally in the past. The DOC trend is also linked to the general reduction in sea-salt inputs over the monitoring period.

Biological trends

Epilithic diatoms (occurring on the surface of stones) have been monitored throughout. There has been a clear change in epilithic diatom species composition over the last 20 years at all acidified sites, consistent with the increase in pH described above. However, while some sites are showing a return to pre-acidification assemblages (e.g. Llyn Llagi), other sites are showing new assemblages not previously observed even in the pre-acidification period in lake sediment cores (e.g. Round Loch of Glenhead; Figure 6). It is likely that new assemblages are linked to other drivers of change, for example climate change or nutrient N deposition effects.

New aquatic plant species have appeared in seven of the lake sites and four of the stream sites. In most cases these are acid-sensitive species e.g. *Myriophyllum alterniflorum* (alternate water milfoil) and *Subularia aquatica* (water awlwort), which may simply be returning due to chemical recovery from acidification. However, the appearance of *S. aquatica* in Lochnagar could also be linked to recent warming as winter ice-cover at this alpine site has decreased significantly in recent years, while an expansion of *Juncus bulbosus* at this site may also in part be a response to an increase in the availability of deposited NO_3^- acting as a fertiliser.

Benthic invertebrates are starting to show modest responses to the long-term chemical changes, with significant temporal trends now apparent at about half of the sites in the Network. The shifts in assemblage composition that have taken place are those expected as a result of reduced acidity. Acid deposition caused severe reductions and, in some cases, the elimination of salmonid fish (i.e. brown trout and Atlantic salmon) from many of the most sensitive lakes and streams in the UK. There are now new populations of brown trout at three of the most acidified sites in the network (Old Lodge, Scoat Tarn and Blue Lough), reflecting improvements in water quality. However, there are many sites where fish densities remain low compared to less acidified sites.

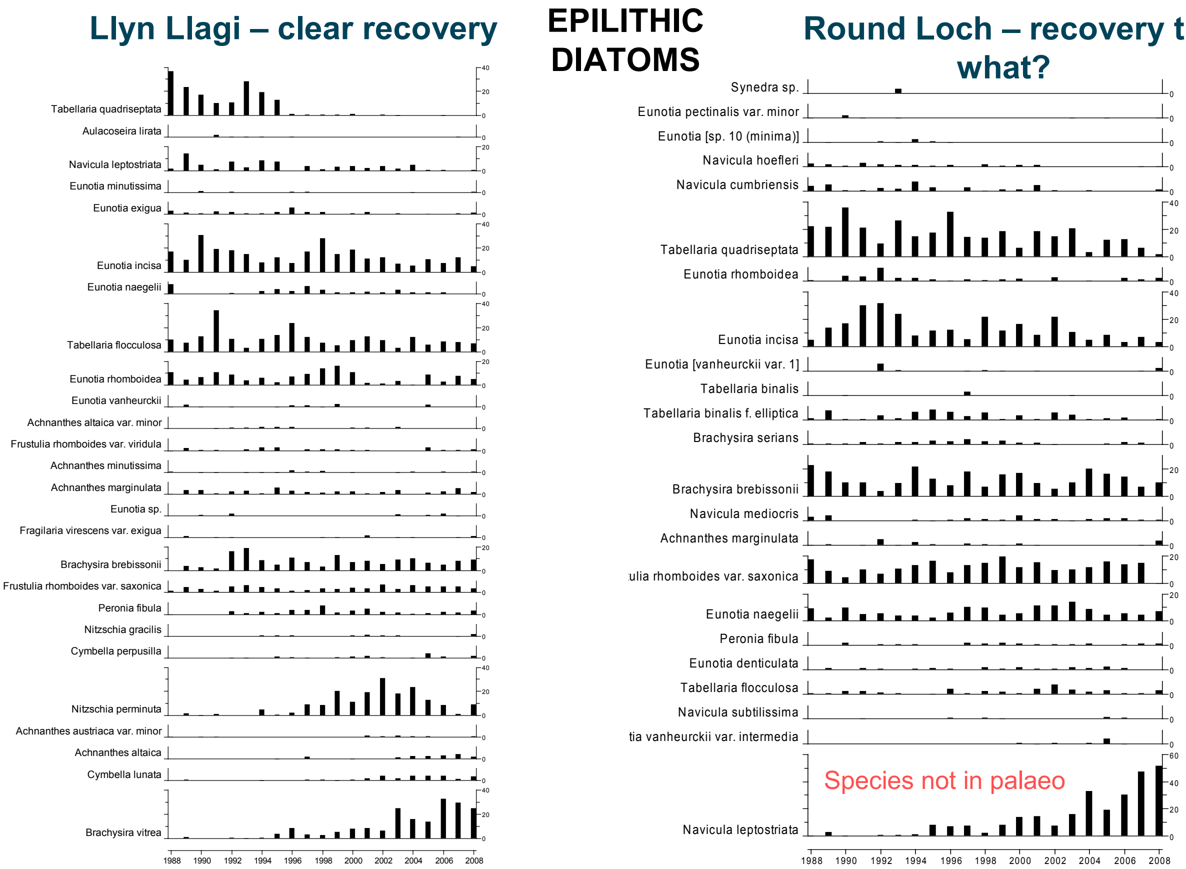


Figure 6. *Changes in dominant epilithic diatom species over the monitoring period at two contrasting sites.*

References

Cooper, D.M. (2005) Evidence of sulphur and nitrogen signals at the United Kingdom Acid Waters Monitoring Network Sites. Environmental Pollution 137: 41-54.

Kernan, M., Battarbee, R.W, Curtis, C.J., Monteith, D.T. and Shilland, E.M. (Eds.) (in press) UK Acid Waters Monitoring Network 20 Year Interpretive Report. ECRC Research Report #141, University College London, London, UK, 477pp.

Lawrence, H., Vincent, K., Donovan, B., Davies, M., Smith, M., Colbeck, C., Tang, Y.S., van Dijk, N., Anderson, M., Simmons, I., Smith, R.I., Cape, J.N., Fowler, D., Sutton, M.A. (2008) UK Acid Deposition Monitoring Network: Data Summary 2007. Report Number AEAT/ENV/R/2706 Issue 1, AEA Harwell, Didcot, UK, 48pp plus Appendices.

6. Lake Saudlandsvatn, Southern Norway, a lake still under the process of recovery from acidification

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During the 1900s large areas of southern Norway were affected by acid deposition, with widespread acidification of lakes and damage to fish populations (Overrein *et al*., 1980; Hesthagen *et al*., 1999). Acid deposition reached its peak in the late 1970s and declined by about 70% (sulphur) and 20% (nitrogen) since the mid-1980s (Aas *et al*., 2009). Acidified lakes have shown substantial recovery, with increasing pH, acid neutralising capacity (ANC) and lower concentrations of labile aluminium (Skjelkvåle *et al*., 2001, 2003, 2007).

Here we report data on acidification and recovery of water chemistry and of brown trout (*Salmo trutta*) and *Baetis rhodani* in Lake Saudlandsvatn, southernmost Norway, during the 33-year period 1977-2009. The lake has over the years been followed through different projects, like the SNSF-project (1977-79) (Overrein et al. 1980), the Norwegian Climate and Pollution Agency (the former Norwegian State Pollution Control Authority (SFT)) (1980 to present), and the ANC-Recovery Project, financed by the Norwegian Research Council (2001-2003). The situation up to 2005 has been reported by Rosseland et al. 2006, but the "full history" of Lake Saudlandsvatn (chemistry, biology and MAGIC-modelling) is found in Hesthagen et al. (2010).

We have investigated the relationship between water chemistry and the abundance of brown trout (*Salmo trutta*) in Lake Saudlandvatn and its inlet and outlet stream as well as the . The lake population was sampled with benthic gill-nets every second year from 1977 to 2009. From 1977 to 1995, the sampling was carried out by a SNSF-gillnet series (Rosseland *et al.,* 1980), while from 1997 to 2003 with Nordic multi-mesh gill nets (Appelberg *et al*., 1995). Both gill nets series catches fish with about equal efficiency (Jensen and Hesthagen, 1996). During the 1970s and early 1980s the lake was highly acid, with pH less than 5.0, sulphate concentration around 140 µeq L^{-1} and an ANC between -30 and -20 µeq L^{-1} (Hesthagen et al. (2010). In spite of this, the lake supported a relatively dense population of brown trout, with CPUE-values (Catch Per Unit Effort; numbers per 100 m^2 gill net area per night) ranging between 16-18 specimens (1977-83), Figure 2. Later, their abundance declined gradually to nearly extinction in the early 1990s (CPUE = 2 in 1993). Chemical recovery following reduced deposition of sulphur became evident in the 1990s, when pH rose to about 5.5 (Figure 1). In the late 1990's, the brown trout population also started to recover, and from 2003 to 2009 it had achieved a higher density than in the late 1970s (Figure 2).

Both the inlet and outlet brook are used as spawning brooks, and studies of egg survival has been performed in periods from 1977 while electrofishing for fry density has been performed regularly at time of testfishing since 1986. In Lake Saudlandsvatn, the success of not becoming a barren lake has clearly been due to a 4 m^2 spawning area in the outlet brook, acting as a refuge for survival in periods with marginal water quality when the inlet (major) spawning brook could not produce any recruits to the lake. The development in the abundance of 1+ fish obtained in Lake Saudlandsvatn was well explained by fry densities (0+) in the inlet and outlet stream one year earlier (year of hatching). An increase in ANC from about 0 to 20 µeq L^{-1} gave a pronounced increase in CPUE-1+. There was also a positive correlation between fry densities (age 0+) in the inlet and outlet stream each autumn and ANC (Hesthagen et al. 2010). The density of brown trout fry in these sites increased significantly when ANC rose from about 10 to 20-30 µeq L^{-1}. Thus, the recruitment strength in the tributary streams reflects the abundance of fish in the lake itself. The reason for the decline in the abundance of brown trout in our study lake is therefore to a large extent due to recruitment failure.

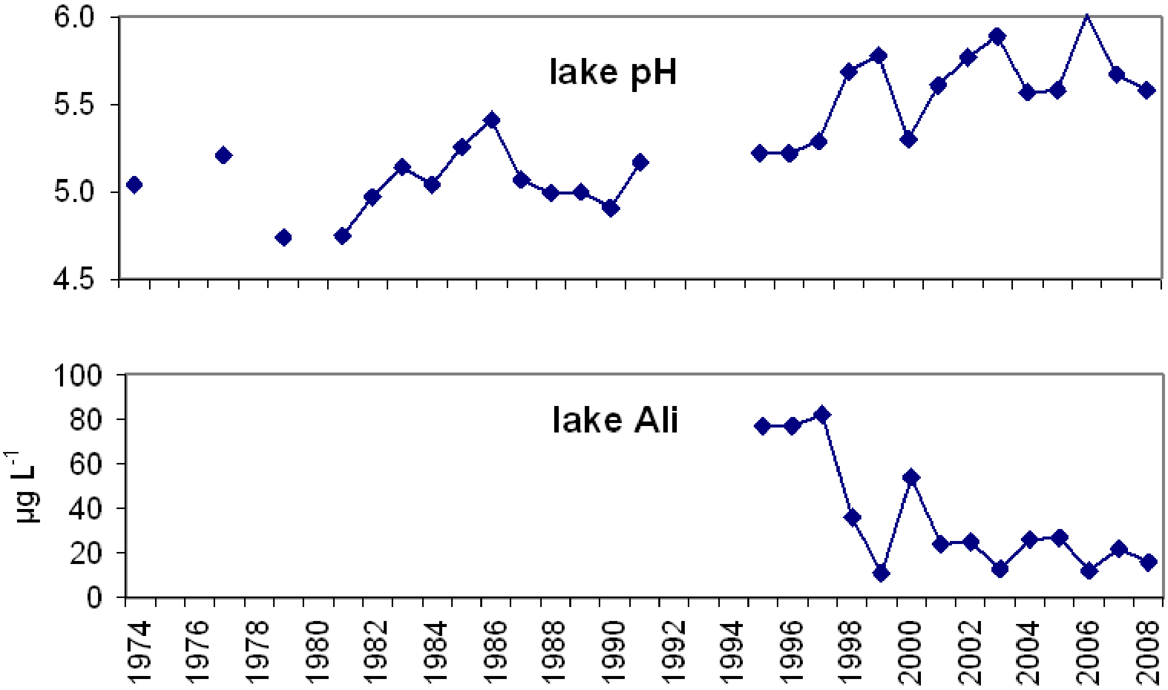

***Figure 1**. pH and Ali in the outlet stream of Lake Saudlandsvatn. From: Hesthagen et al. (2010).*

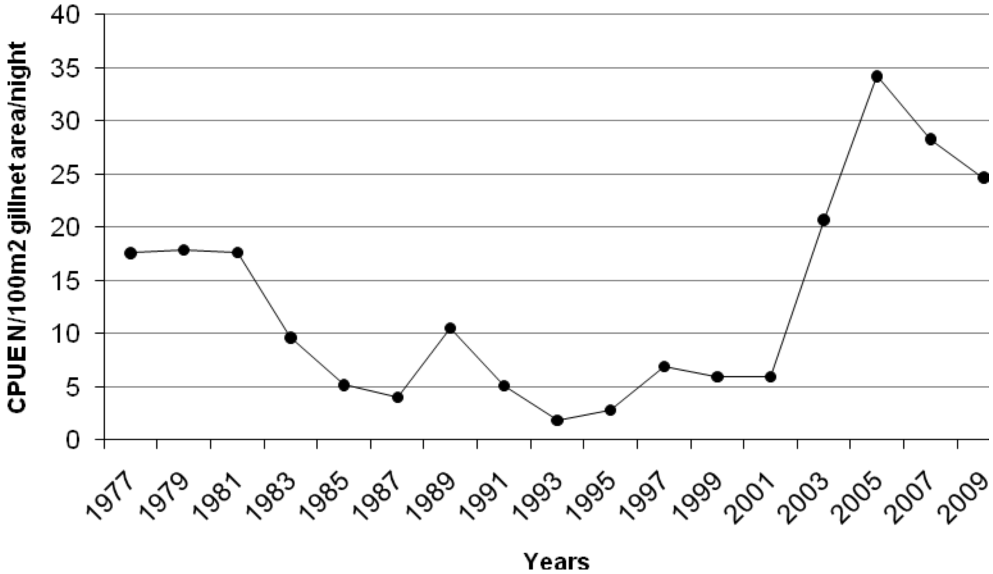

***Figure 2**. Catch of brown trout (as CPUE) in Lake Saudlandsvatn in the period 1977-2009.*

The fish population size (measured as CPUE) showed significant lag times to changes in water chemistry (measured as ANC) both during the acidification phase and the recovery phase (Hesthagen et al. 2010). When modelling the ANC for Lake Saudlandsvatn, the data thus indicate that the lag time in population response to changes in water chemistry in Lake Saudlandsvatn is more than 10 years (Hesthagen et al. 2010).

Based on the CPUE in 2003 and 2005-2009, one might be led to think that the brown trout population in Lake Saudlandsvatn has fully recovered relative to the results from late 1970s. The rapid increase in catch since 2001 is also in agreement with the increased invertebrate recovery in Lake Saudlandsvatn, see Fjellheim and Raddum (2006) and Figure 3. However, by looking at the year-class distribution, it is evident that it is one single year class (hatched in 2002) that make up the high CPUE in 2003, and still dominates in 2005, Table 1. Also the lack of older fish in 2007 (catches from 2009 are not yet aged) indicates a biased population structure.

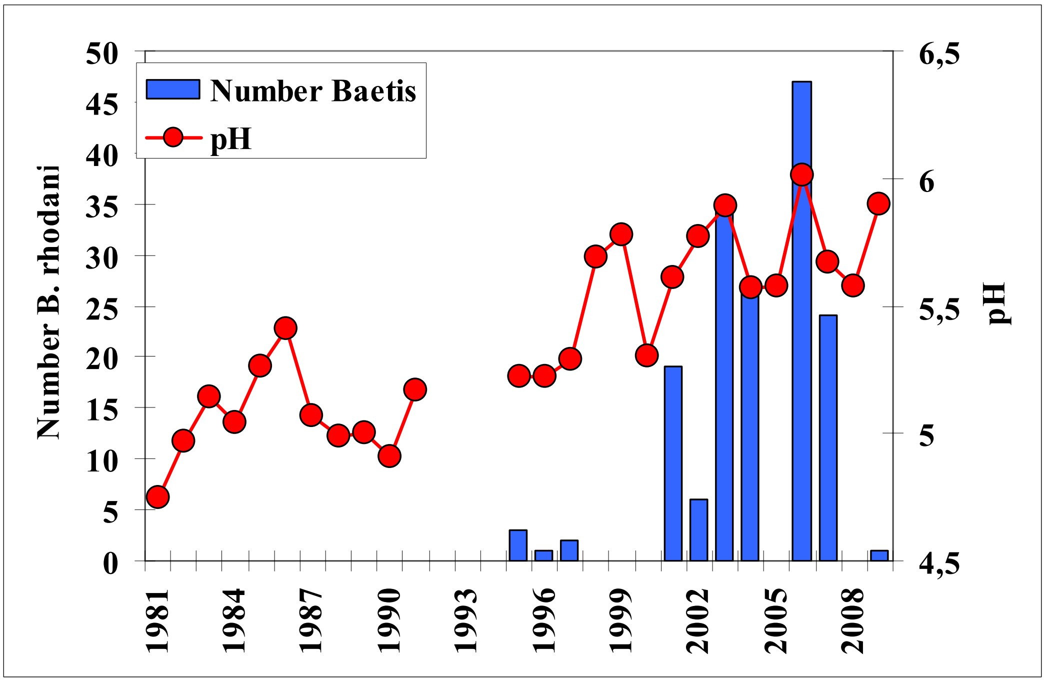

Figure 3. *Number of Baetis rhodani in samples from the Lake Saudlandsvatn area during 1981 –2009.*

Another sign of existing water quality problems in Lake Saudlandsvatn is indicated by the representation of the vulnerable life history stage “postspawners” (older fish that have spawned before), Table 2. Rosseland *et al.* 1980, reported lack of postspawners in Lake Tveitvatn as a first sign of a declining population of brown trout going from stunted (over populated) to barren during the process of acidification. This phenomenon was probably due to an increased sensitivity of postspawners to acidic waters, demonstrated by Rosseland and Skogheim (1987). By looking at the age composition in Lake Saudlandsvatn and their maturation status, it is evident that with one specimen exception (a female in 1991), the first postspawners since 1987 was found in 2007, but none were found in 2009 (Table 2). No male postspawner has been found since 1987. This confirms the results from Lake Tveitvatn that the brown trout population in Lake Saudlandsvatn was going towards extinction. However, as the water chemistry improved during the process of recovery, the population structure of brown trout in Lake Saudlandsvatn seems to follow the same pattern on the way back to a healthy population, namely young recruits but with a lack of old postspawners.

Table 1. *Age composition of the brown trout catches in Lake Saudlandsvatn in the period 1977 - 2007. The 2009 material is still not aged.*

		Age (years)							
		0	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Year	**1977**	0	3	24	19	11	0	0	0
	1979	0	9	8	8	22	10	1	0
	1981	0	9	29	12	11	7	2	5
	1983	0	4	23	8	3	1	2	0
	1987	0	1	11	1	0	0	0	0
	1989	0	2	5	21	4	2	0	0
	1991	0	14	14	4	0	1	0	1
	1993	0	0	3	0	2	0	1	0
	1995	0	5	0	2	1	0	1	0
	1997	0	8	8	3	0	1	1	0
	1999	1	6	7	1	2	1	0	0
	2001	1	5	7	2	2	1	0	0
	2003	0	42	8	3	8	2	0	0
	2005	0	31	26	33	14	0	0	0
	2007	9	26	28	18	10	6	0	0

Table 2. *Numbers of brown trout being first time spawners (Recruit spawners) and trout that had spawned before (Post spawners), separated into male and females in the catches from Lake Saudlandsvatn in the period 1977 – 2009.*

	MALE		**FEMALE**	
Year	**Recruit spawners**	**Post spawners**	**Recruit spawners**	**Post spawners**
1977	12	7	15	3
1979	2	13	15	14
1981	12	3	17	14
1983	7	5	5	2
1987	3	4	2	3
1989	13	0	16	0
1991	10	0	5	1
1993	3	0	3	0
1995	3	0	3	0
1997	5	0	3	0
1999	5	0	7	0
2001	3	0	5	0
2003	13	0	10	0
2005	27	0	27	0
2007	8	0	19	4
2009	19	0	13	0

Based on the criteria for the FIB model (Rosseland *et al.* 2005, Raddum and Rosseland 2005) and Hesthagen et al. (2010), the brown trout population in Lake Saudlandsvatn can not be characterized as healthy. A continuous monitoring of the lake water quality and fish population is therefore highly recommended.

References

Aas, W., Solberg, S., Manø, S., and Yttri, K. E.: 2009, Overvåking av langtransportert forurenset luft og nedbør. Atmosfærisk tilførsel 2008. Statlig program for forurensningsovervåking. Rapport, **1051**. Statens forurensningstilsyn, Oslo. [In Norwegian].

Appelberg, M., Berger, H. M., Hesthagen, T., Kleiven, E., Kurkilahti, M., Raitaniemi, J., and Rask, M.: 1995. Development and intercalibration of methods in Nordic freshwater fish monitoring. Water, Air and Soil Pollut 85, 401-406.

Fjellheim, A. & Raddum, G. G. 2005. Natural recovery of benthic invertebrates in the Saudland area, southernmost Norway. In: deWit, H and Skjelkvåle, B. L. (eds.) Proceedings of the 21th meeting of the ICP waters Programme Task Force in Tallinn, Estonia, October 17-19, 2005. ICP Waters report. 84/2006 NIVA, pp.38-43.

Hesthagen, T., Sevaldrud, I. H., and Berger, H. M.: 1999. Assessment of damage to fish populations in Norwegian lakes due to acidification. Ambio 28, 112-117.

Hesthagen, T., Fjellheim, A., Schartau, A. K., Wright, R. F., Saksgård, R. and Rosseland, B.O. 2010. Chemical and biological recovery of Lake Saudlandsvatn, a highly acidified lake in southernmost Norway, in response to decreased acid deposition. Submitted. Can. J. Fish and Aquat. Sci.

Jensen, J.W. and Hesthagen, T. 1996. Direct estimates of the selectivity of a multimesh and a series of gillnets for brown trout, *Salmo trutta*. J. Fish Biol. **49**: 33-40.

Overrein, L., Seip, H. M., and Tollan, A.: 1980, Acid precipitation. Final report of the SNSF-project 1972-1980, FR 19/1980. Oslo-Ås, Norway.

Raddum, G.G and Rosseland, B.O. 2005. Dynamic biological response models - an overview. In: deWit, H. and Skjelkvåle, B.L. (Eds.), Page 45 – 54, 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. ISBN 82-577-4717-3.

Rosseland, B.O., Sevaldrud, I., Svalastog, D. & Muniz, I.P. 1980. Studies on freshwater fish populations - effects of acidification on reproduction, population structure, growth and food selection. Pp 336-337 in: Tollan, A. & Drabløs, D. (eds.) Ecological impact of acid precipitation. - SNSF-project FA 105/80.

Rosseland, B.O., Kristensen, T. and Bulger, A. 2005. The FIB-model. A dynamic model for prediction of recovery of a fish population after influence from acidic water or other environmental stressors. Air Pollution, it's effects and future. Acid Rain 2005. 7th International Conference on Acid Deposition, Prague, Czech Republic, June 12-17, 2005. Conference Abstract Book; 434.

Rosseland, B.O., Hesthagen, T., Wright, R.F. Kroglund, F., Kristensen, T. 2006. Lake Saudlandsvatn, Southern Norway, a lake under the process of recovery from acidification. Page 33-37, In: de Witt, H. and Skjelkvåle, B.L. (eds.), Proceedings of the 21st meeting of the ICP Waters Programme Task Force in Tallinn, Estonia, October 17-19, 2005. ICP-WATERS Report 84/2006, 69 pp., ISBN 82-577-4923-0.

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

Skjelkvåle, B. L., Evans, C., Larssen , T., Hindar, A., and Raddum, G. G. 2003. Recovery from Acidification in European Surface Waters: A view to the future. Ambio **32**: 170-175.

Skjelkvåle, B. L., Borg, H., Hindar, A., and Wilander, A. 2007. Large scale patterns of chemical recovery in lakes in Norway and Sweden: Importance of seasalt episodes and changes in dissolved organic carbon. Appl. Geochem. 22: 1174-1180.

7. Risk of mixture toxicity in Dutch surface waters

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The Water Framework Directive (WFD) requires the development of river basin management plans. The effect of these plans has been evaluated by the Netherlands Environmental Assessment Agency [1]. Within that study the potential effects of toxic substances and toxic mixtures on aquatic ecosystems have been assessed [2]. This paper presents the results on mixture toxicity and discusses the relevance to address mixture toxicity in regulatory risk assessment.

Materials and methods

Mixture toxicity can not be measured directly in the surface water. In a pT test the toxicity of non volatile compounds in the surface water can be quantified but not the toxicity caused by metals. In order to assess the potential negative influence of toxic substance on the aquatic ecosystem the Potentially Affected Fraction (PAF) and multi-substance Potentially Affected Fraction (msPAF) [3, 4] have been estimated. The PAF is derived from the measured concentration and the species sensitivity distribution (SSD) of a compound. To derive the msPAF, of a mixture of substances, the effect of compounds with the same toxic mode of action is summed. Next, the various toxic modes of action are aggregated on a response-additive manner. If the SSD is based on no-observed effect concentrations (NOEC) a msPAF-Chronic can be estimated, reflecting the potential effect of chronic exposure. Accordingly, msPAF-Acute can be estimated if the SSD is based on median lethal concentrations (LC50).

Organisms in the aquatic ecosystem are not exposed to the total concentration in the surface water. Only a fraction of the compound is bioavailable, the rest is bounded to suspended matter (SM), dissolved organic carbon (DOC) or other consituents of the surface water. In this study the bioavailability of organic compounds has been corrected for complexation with 5 mg L^{-1} DOC in Dutch surface waters. The bioavailability of metals has been corrected for sorption to 30 mg L^{-1} SM and for the influence of pH, DOC, alkalinity and other consituents using one generic correction factor. This generic correction is based on the bioavailability of copper and zinc in various watertypes as reported in the European risk assessment reports [5, 6]. According to these studies the fraction which is bioavailable ranges from 0.25 to 1 with a median of 0.4. This value has been applied for all metals.

In this study 330 000 measurements from 2005 and 2006 have been used covering nearly 2500 monitoring stations and 125 toxic substances. In most cases various water samples have been taken over time to analyse metals, organic pollutants or pesticides. To estimate the mixture toxicity, the data of various samples are combined to create one mixture. In practice, the average monthly concentrations of the substances analysed at each station are assumed to be one mixture. In this way the toxicity of nearly 22 000 mixtures have been estimated.

Results and discussion

The estimated msPAF-Chronic is higher than 0.05 at 978 locations during half of the time. The general Dutch policy objective, to protect 95% of the species potentially present, is not met at these locations. The estimated msPAF-Acute is higher than 0.01 at 182 locations and higher than 0.05 at 33 locations also during half of the time. At these locations there may be a potential loss in aquatic species. Additional ecological research on the functioning of the aquatic ecosystem is advisable at these sites. A wide range of substances contribute to the mixture toxicity of the Dutch surface waters: pesticides, metals and other organic pollutants. The spatial distribution of the msPAF shows highest values in the south-eastern part of the Netherlands, where the soils are historically heavily contaminated by zinc-smelters.

The number of substances per mixture varies. Most mixtures (90%) contain five substances or less. Figure 2 shows that the msPAF-Chronic increases with the number of substance per mixture. The msPAF-Chronic is on average higher than 0.05 for mixtures with eight substances. Mixtures containing 50 substances, pesticides, hebicides, metals, PAH's and other organic pollutants have an average msPAF-Chronic of 0.25.

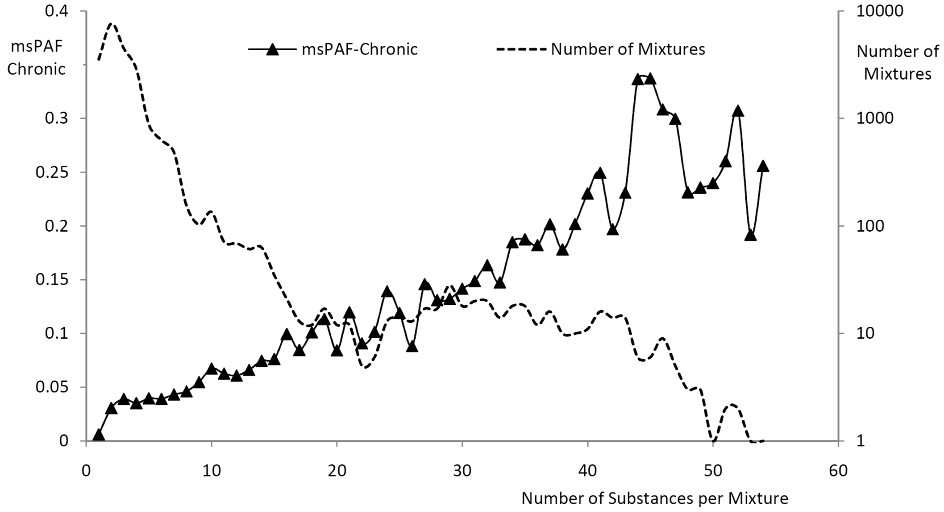

***Figure 1**. Relation between the msPAF-Chronic and the number of substances per mixture.*

Conclusions

- The estimated chronic mixture toxicity is so high at 40% of the locations that the general objective of Dutch governmental policy has not been reached
- At 182 locations, the estimated acute toxicity is so high that there may be a potential loss in aquatic species. Additional ecological research on the functioning of the aquatic ecosystem is advisable at these sites
- A large number of substances contribute to the mixture toxicity. As only a limited number of substances have been measured in most samples, the actual toxicity of the surface waters will be higher in most cases
- Given the exposure of our aquatic ecosystems to mixtures of toxic substances far beyond levels accepted for single compounds the need to develop a regulatory procedure within the WFD to limit the effect of toxic mixtures is high.

References

1. Ligtvoet, W., G.P. Beugelink, and R. Franken, *Evaluation of the Water Framework Directive in the Netherlands; costs and benefits*. 2008, NEAA: Bilthoven, The Netherlands. p. 40.
2. de Nijs, A.C.M., et al., *Risks of toxic substances in Dutch surface waters*. 2008, RIVM: Bilthoven. p. 83.
3. de Zwart, D., *Observed regularities in SSDs for aquatic species*, in *Species Sensitivity Distributions in Ecotoxicology*, L. Posthuma, Suter, G. W., II, and Traas, T. P, Editor. 2002, Lewis Publishers: Boca Raton, FL, USA. p. 133-154.
4. Posthuma, L., G.W.I. Suter, and T.P. Traas, *Species Sensitivity Distributions in Ecotoxicology.* . 2002, Boca Raton, FL, USA: Lewis Publishers.
5. EU, *European Union Risk assessment Reports on Zinc and Zinc compounds, Final draft of August 2006, Part 1 Environment: European Chemicals Bureau*. 2006.
6. Van Sprang, P., et al., *European Union Risk Assessment Report, Voluntary Risk Assessment: Copper, Copper(II)sulphate pentahydrate, Copper(I)oxide, Copper(II)oxide, Dicopper chloride trihydroxide. Environmental effects- Chapter 3.2 (Part 1). (draft)*. 2007, European Copper Institute: Brussel.

8. The distribution of trace elements in water: Case study lakes of east European plain of Russia

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The understanding of the regularities in the occurrence of elements in surface continental waters and the factors that cause their concentrations to increase at the regional or global level is among the major problems of the current ecology and geochemistry. The chemical composition of surface waters, including trace element composition, forms as a result of complex multistage processes taking place both in the catchment area and in the water body proper. One of the main factors that govern water chemistry is the lithology, namely, the geological structure of watershed, the chemical composition of rocks and the proportions of their types, and the weathering resistance. The climatic factors in the zonal aspect (temperature, precipitation, evaporation, etc.) have an indirect effect on the concentrations of elements via the rate of chemical weathering, bioproduction and destruction processes, and the rates of chemical and biological processes within water bodies. In the past decades, the effect of anthropogenic factors on the continental waters has become comparable with natural processes.

The chemical composition of water in small lakes (in the absence of any direct pollution sources) more clearly reflects the zonal, regional, and local features of trace element distributions in water and the effect of global anthropogenic processes that took place in the environment in the recent years (Henriksen et al., 1997).

The objective of this study is to form a notion of the zonal features and variations in the elemental composition of small-lake waters (not subject to direct anthropogenic impact), identify the key natural and anthropogenic processes that determine the concentrations of trace elements, and evaluate the coefficients of water migration of the element in different climatic ecoregions.

The subject and methods of studies

The work is based on the generalisation of the data collected during the study of the chemical composition of 280 small lakes in the East European Plain along the transect from Kola Peninsula (tundra zone) to Caspian Lowland (arid zone), which was carried out in 2003 -2006 by a single methodological procedure (Henriksen et al., 1997). The study involved the lakes that are less than 20 km^2 in area and are not subject to any direct pollution. In order to minimise the effect of long-term and seasonal variations in water chemistry, water samples were taken within a short time interval during autumn cooling, when vegetation processes are at their minimum, homothermy has formed in the lake, and there is no stratification.
Trace element concentrations in the prepared water samples were determined in parallel by two methods: Sr, Al, Fe, Mn, Cr, Cu, Ni, Zn, Cd, Co, Pb, and As were analysed by atomic absorption technique with nonflame atomiser; more than 60 elements were determined by the method of inductively coupled plasma by using a plasma mass spectrometer. Strict intralaboratory control of measurement quality was performed.

Results and discussion

An important aspect of the analysis of the elemental composition of water is the assessment of its enrichment with some elements as compared with rocks or dispersion of such elements. For this purpose, the mean relative contents (in percents) of elements that occur in the ionic or suspended mineral or organic forms ("mineral residue") in lake water were calculated. Table 1 gives their values for the lakes of the East European Plain as a whole and groups of lakes in different regions, depending on the types of rocks that compose their catchment areas. The regions of predominant occurrence of rock types in the catchments of the lakes under study were determined from the petro–density and structure–formation maps. Analysis of the process of enrichment and dispersion in the surface continental waters was based on the comparison of the relative concentrations of elements in the dry residue of lake waters with their concentrations in different types of rocks, which are determined for the earth crust and magmatic rocks (Vinogradov, 1962) and sedimentary rocks (Turekian Wedepohl, 1961).

As distinct from rocks, more active migrants into water systems are the major water salinity components (macrocomponents) Ca, Mg, Na, Cl, and S. Water saturation with C_{org} takes place because of biogenic migration, C_{inorg} migrates because of weathering of carbonates and dissolution of CO_2 in water from the air and the gas released by phytoplankton in the process of respiration. As compared with the earth crust, the water is enriched with N because of its biogenic migration.

The most active accumulation of biogenic elements in water takes place in forest regions, where they actively participate in biogeochemical cycles. Relatively low concentrations of biogenic elements are recorded in the tundra region because of the low level of energy and mass exchange in high latitudes and in subarid and arid regions as a result of their rapid utilization in bioproduction processes.

The main rocks contain maximum amounts of not only Ca and Mg, but also of many other elements, such as Fe, Mn, Al, Co, Zn, Cu, V, Ti, and Cr. The waters of lakes that have formed on these rocks are neutral (pH~6.8), which hampers their enrichment. Under these conditions, alkaline and alkaline-earth elements, as well as the majority of anionogenic elements, actively migrate.

Acid rocks contain higher concentrations of alkaline elements, Ba, Y, lantanoids, and actinoids. However, the waters of lakes in the occurrence areas of acid rocks are not enriched in these elements (except for Rb and Cs). The conditions for their leaching from acid rocks can be different. Subacid medium (pH~6.3) is typical of most lakes; the catchments of many lakes have bogs. In such lakes, subacid water medium facilitates water enrichment with Zn, Cu, Ni, Ag, and Cd. The humic acids carried out from the catchment involve Sb, Sn, and Sc into transport fluxes (the correlation coefficients of these elements with CI $r \sim 0.70$, $n = 8$), which results in the enrichment of waters of "blooming" lakes with these elements. Eutrophication of water accelerates the biogeochemical turnover of Mn, which is confirmed by the correlation coefficients between the concentrations of this element and Ptot ($r = 0.70$, $n = 38$), Rb ($r = 0.95$, $n = 8$), and Cs ($r = 0.70$, $n = 8$).

Clay deposits in sedimentary rocks concentrate most elements. However, it should be taken into account that clay rocks are not only sources of elements, but also a sorption barrier on the way of their migration in water. Therefore, waters of lakes, the catchments of which are composed predominantly of these rocks, do not feature enrichment in most these elements. The only exceptions are I, Br, B, As, Mo, Se, Re, as well as Ag and Cd (in the forest region).

Among sedimentary rocks, the most intense leaching (other conditions being equal) takes place from carbonate rocks, which are enriched mostly by Ca, Sr, Br, Mn, and V. The waters of lakes on these rocks, in addition to these elements, are also enriched in Li, Ba, Zn, Cu, Co, and Sn.

Sandy rocks are less saturated with elements. In the region of forests, sandy rocks determine anthropogenic acidification of waters (pH < 6.0), which results in their enrichment with Zn, Co, Cr, Sc, and Cd, which is confirmed by their reliable correlation with pH ($r > 0.75$, $n= 6$). In the arid region, not withstanding the high absolute concentrations of many elements, the relative concentrations of most elements are low. The occurrence of different types of rocks determines the migration conditions of elements on catchments and in the lake proper. Therefore, the enrichment of lake waters in the process of rock leaching is not proportional to the concentrations of elements in these rocks, as can be seen from the comparison of the percentages of these elements in the rocks and lake waters. The leaching of elements depends on a combination of conditions under which the process proceeds—these conditions may be favorable for some elements and unfavorable for others.

An important role in the enrichment or dispersion of trace elements in continental waters is the anthropogenic activity, which can affect not only their direct input (via water or air), but also the migration conditions, both via the influence on the pH and ionic balance, and through the transformation of landscapes of catchments (ploughing, deforestation, etc.).

Throughout the territory of East European Plain (irrespective of the type of underlying rocks, the conditions of leaching or migration, and the zonal specificity), waters of these lakes are notably enriched with elements, such as Re, I Br, B, Se, As, Mo, Sb, Cd, Ag, Sc, and Ni. Many of these elements are involved in the geochemical cycle by anthropogenic activity, as can be seen from their concentrating in the continental surface waters on the global scale.

A.I. Perel'man (1982) proposed an estimate of migration of chemical elements in water by a coefficient equal to the ratio of the concentration of the element in the mineral residue of water to its concentration in rocks or soils (or to the lithosphere clarke). This coefficient reflects the rate of the element's migration in water (which is determined by the properties of the element) and the degree of its concentration or dispersion in the surface waters. For the sake of comparison, Table 2 gives the values of migration coefficients of chemical elements both for the lakes in the identified regions and for the entire European Russia. The water migration coefficients for waters of the East European Plain were evaluated with respect to lithospheric clarkes, whereas these coefficients for waters in the regions were evaluated with respect to the rocks to which the lakes are confined, thereby allowing more accurate regional characteristics to be obtained.

The values of the water migration coefficient depend on the extent of occurrence of the element in the lithosphere (rocks), its involvement in the biogeochemical processes on the catchment and in the water body, and the anthropogenic input. It is also worth mentioning that considerable differentiation both between individual zones and within the zones is found to exist for the natural conditions of water formation and the level of anthropogenic load, which determines the difference between the migration coefficients of the elements for the identified regions and the waters of European Russia as a whole.

The elements most widespread in the earth crust are Fe, Al, Mn, and Ti; however, they do not accumulate in the terminal water for runoff and are more passive in terms of migration. However, the mobility of Fe somewhat increases in the tundra–taiga and forest regions because of its higher biogenic migration (Table 2). Lesser occurrence in rocks is typical of Ba, Sr, Rb, and Zr, the first three of which are active water migrants. The migration coefficients of rare elements also feature wide variations. The migration characteristics of Br and I increase owing to their migration in the atmosphere. Similarly to Fe, migration of Sn increases in the tundra–taiga region, and similarly to Mn, the biogenic migration of B, Zn, and Cu increases in the forest and subarid regions. The migration coefficient of Zn and Cu in surface waters increases, in particular, because of their considerable involvement in technogenic flows, especially in southern regions. The concentration of Ni in water also features the anthropogenic effect. The high technophilicity of Pb and Cr has a lesser effect on their migration and concentration in surface waters, with the exception of southern regions.

In terms of migration, Li and Sc are relatively active, notwithstanding their low involvement in technogenic activity. Be, Ga, Nb, Y and rare-earth elements disperse in the surface waters. It is worth mentioning that the migration coefficients of Zr, Y, and the group of rare-earth elements in the tundra–taiga region are relatively high because of their higher concentration in magmatic rocks than in sedimentary rocks. The rare elements Mo, As, U, Bi, Sb, Cd, Ag, Se, and Re, the high concentration coefficient of which is mostly due to the anthropogenic load on the global scale, are marked (bolded) in Table 2.

Conclusions

In modern conditions, the formation of concentrations of elements in surface continental waters is determined by the complex effect of natural and anthropogenic factors. Small lakes (in the absence of any direct pollution sources) most adequately reflect both the natural features of the formation of water chemistry and the anthropogenic dispersion of elements on the regional and global scale.

The specific features of the microelement composition of waters in the tundra region are the elevated concentrations of I and Br, which enter the catchments with marine aerosols, an increase in Ti migration in acidified waters, and an increase in the concentrations of Ni, Cu, Co, Cd, and Se because of the aerotechnogenic dispersion of elements by copper–nickel plants. Specific features of water chemistry in the taiga region is an increase in the concentrations of alkali metals, Sc, Y, lantanoids, and Zr and the high variability of Fe and Al concentrations owing to the development of bogs in this region. A characteristic feature of the chemical composition of water in the forest regions is the elevated concentration of Mn because of humification of catchment areas. In arid and subarid zones, the evaporative concentrating and precipitation of poorly soluble salts of Ca results in an increase in the concentrations of a large group of elements. An alkaline barrier limits the migration of Fe and Al, while the high concentrations of Cd, Cr, Sc, and Re are due to the higher anthropogenic load on lake systems.

The estimated migration coefficients of elements (based on the ratios of the concentrations of elements in the dry residue to their clarkes in the lithosphere) demonstrated differences in the migration of elements in water in different natural climatic zones, which are due to both natural and anthropogenic factors. Overall, the fresh waters of the East European Plain feature high coefficients of concentration of Mo, As, U, Bi, Sb, Cd, Ag, Se, and Re, which are mostly due to the anthropogenic load onto the catchments.

Acknowledgments

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References

Henriksen, A., Skjelkvale, B.L., Mannio, J., et al., *Results of National Lake Surveys 1995 in Finland, Norway, Sweden, Denmark, Russian Kola, Russian Karelia, Scotland, and Wales*, Oslo: NIVA, 1997. Rep. 47/97.

Perel'man, A.I., Geochemistry of Landscapes of Ore Provinces, Moscow: Nauka, 1982.

Turekian, K.K. and Wedepohl, K.H., Distribution of Elements in Some Major Units of the Earth's Crust, *Bull. Geol. Soc. Am.,* 1961, vol. 72.

Vinogradov, A.P., Mean Concentrations of Chemical Elements in the Main Types of Igneous Rocks in the Earth Crust, *Geokhimiya*, 1962, no. 7, pp. 565–571.

***Table 1.** Elemental composition, %, in waters of lakes in the occurrence areas of different types of rocks (bolded are the values exceeding those in the lithosphere or in the respective types of rocks, dash means no data available).*

Element	Lakes of European plains	Lakes of undra and taiga regions				Lakes of forest region			Lakes of subarid region			Lakes of arid region
		Rock of catchments										
		Base rocks (basalt gabbro, etc)	Neutral rocks (diorites, syenites)	Acid rocks	Gneiss - shale rocks	Clayey	Carbonate	Sandy	Clayey	Carbonate	Sandy	Sandy
$C_{\text{орг}}$ $*10^{0}$	10.8	28.2	37.7	47.9	36.5	18.4	15.8	33	6.2	3.6	14.6	0.3
$C_{\text{неорг}}$ $*10^{0}$	**9.3**	**9.8**	**10.4**	**5.4**	**9.3**	**25.2**	**24.5**	**9.5**	**24.8**	**12.4**	**17.5**	**2.1**
S $*10^{0}$	**10**	**4.5**	**3.5**	**2.9**	**5.6**	**3.2**	**3.7**	**10.6**	**2.6**	**12.7**	**5.3**	**14**
Cl $*10^{0}$	**24.4**	**14.9**	**7.6**	**11.2**	**8.1**	**5**	**6.5**	**6**	**11.9**	**19**	**11.2**	**39.5**
Ca $*10^{0}$	**15.5**	**10.7**	**10.6**	**7.3**	**11.7**	**35.6**	**34.4**	**22.3**	**6.8**	22.5	**19.4**	**10.7**
Mg $*10^{0}$	**5.9**	**4.8**	**4.7**	**3.2**	**4.8**	**6.4**	**7.1**	**5.9**	**12.2**	**7.3**	**6.5**	**5.3**
Na $*10^{0}$	**19.7**	**14.1**	**10.5**	**10**	**9.8**	**3.3**	**4.7**	**6.1**	**27.4**	**19.7**	**10.1**	**27.3**
K $*10^{0}$	1.6	**2.6**	**2.9**	2.2	3.2	2	**1.7**	**2.2**	2.3	**2.1**	**14.1**	0.7
Si $*10^{0}$	2.03	8.96	9.78	7.39	9.26	2.08	0.63	2.75	2.46	0.37	0.71	0.04
N $*10^{0}$	**0.13**	**0.21**	**0.26**	**0.37**	**0.3**	**0.28**	**0.56**	**0.94**	**0.15**	**0.12**	**0.41**	0.01
P $*10^{0}$	**0.009**	**0.009**	**0.02**	**0.028**	0.024	0.026	0.011	**0.05**	0.007	0.008	0.012	0.0003
Li $*10^{-3}$	**5.47**	**2.1**	**4.04**	1.71		1.61	**0.83**	**2.05**	3.09	**0.73**	**6.04**	**2.33**
Rb $*10^{-2}$	**1.92**	**6**	**7.53**	**7.04**		**3.47**	**1.82**	**6**	0.43	**0.77**	**5.54**	0.05
Cs $*10^{-4}$	**34.81**	**396.154**	**51.579**	**522.633**		0.081	0.13	**0.568**	0.019	0.048	0	0.004
Cu $*10^{-3}$	1.15	3.5	3.01	**3.42**	3.44	1.37	**3.43**	**1.72**	0.69	**0.72**	0.35	0.25
Ag $*10^{-6}$	**36.6**	**200.1**	0	**484.4**		**26.2**	**17.3**	**78.3**	0	3.2	0	2.2
Be $*10^{-4}$	0.19	0.28	0.45	0.42		0.08	0.44	**1.39**	0.03	0.05	0.09	0.01
Sr $*10^{-2}$	**7.7**	**12.4**	**18.8**	**7.1**	**12.5**	**12.9**	3.7	**8.8**	**4.9**	4.3	**9.1**	**7.9**
Ba $*10^{-2}$	1.8	**4.2**	2.7	3		2	**2**	**3.9**	0.5	**1.4**	**2.3**	0.2
Zn $*10^{-3}$	2.64	4.33	5.51	**11.95**	4.21	3.21	**10.11**	**29.16**	0.93	**3.15**	**5.89**	0.56
Cd $*10^{-6}$	**75.3**	**232.2**	**196.5**	**343.8**	**196.8**	**146.2**	**89.5**	**62.1**	0	**129.6**	**76.4**	1.7
Sc $*10^{-3}$	0.89	**3.66**	**6.89**	**2.13**		**0.94**	**0.69**	**3.9**	**1.18**	**0.25**	**0.5**	0.03
Y $*10^{-3}$	0.054	0.357	0.521	0.309		0.023	0.051	0.021	0	0.008	0.013	0.005
La $*10^{-3}$	0.36	**2.77**	9.79	2.22		0.03	0.12	0.51	0	0.03	0.02	0.02
Ce $*10^{-3}$	0.3	**1.85**	1.94	2.91		0.03	0.2	0.69	0	0.04	0.03	0.03
Pr $*10^{-4}$	0.36	2.21	2.95	2.91		0.03	0.19	1.12	0	0.05	0	0.04
Nd $*10^{-3}$	0.098	0.636	0.907	0.824		0.022	0.066	0.05	0	0.005	0	0.011
Gd $*10^{-4}$	0.18	1.6	3.17	1.28		0	0	0.15	0	0.02	0	0.01
Th $*10^{-3}$	0.013	0.066	0.039	0.058		0.001	0.025	0.038	0.003	0.003	0	0.006
U $*10^{-4}$	**3.72**	**3.03**	**1.36**	1.11		1.28	0.64	0	0.11	0.44	**0.46**	**1.76**
B $*10^{-3}$	**48.53**	**1.58**	**1.56**	0.42		**7.63**	**6.89**	**13.17**	**34.34**	**6.38**	**5.7**	**22.46**
Al $*10^{0}$	0.082	0.238	0.546	0.354	0.334	0.081	0.109	0.153	0	0.018	0.008	0.005
Ga $*10^{-3}$	0.012	0.05	0.068	0.054		0.01	0.008	0.005	0	0.003	0	0.002
Ti $*10^{0}$	0.0052	0.0098	0.0049	0.012		0.0022	0.0015	0.004	0.0004	0.0007	0.0007	0.0019
Zr $*10^{-2}$	0.0119	0.1061	0.2403	0.1048		0.002	0.0027	0.001	0	0.0006	0	0.0005
Sn $*10^{-4}$	0.97	**6.07**	**3.63**	**6.9**		0.82	**0.36**	0	0	**0.54**	0	0.07
Pb $*10^{-4}$	0.19	0.24	0	0.36	0.03	0.49	0.44	**3.29**	0	0.49	0	0.06
V $*10^{-4}$	0.88	1.88	0.5	2.27		0.47	0.77	1.62	0.79	0.39	0.57	0.16
Nb $*10^{-3}$	0.011	0.097	0.126	0.046		0.012	0.004	0.004	0	0.001	0	0.001
As $*10^{-4}$	**7.68**	**11.5**	**25.69**	**16.14**	**22**	**10.91**	**5.92**	**10.53**	**5.76**	**4.6**	**8.54**	**2.12**
Sb $*10^{-5}$	**9.65**	**32.5**	**36.27**	**25.43**		10.21	**8.15**	**19.49**	1.09	**4.37**	**10.35**	**1.28**
Bi $*10^{-6}$	**8.3**	**47.1**	0	**146.3**		3.8	0	0	0	1.2	0	0.6

Element	Lakes of European plains	Lakes of undra and taiga regions				Lakes of forest region			Lakes of subarid region			Lakes of arid region
		Rock of catchments										
		Base rocks (basalt gabbro, etc)	Neutral rocks (diorites, syenites)	Acid rocks	Gneiss - shale rocks	Clayey	Carbonate	Sandy	Clayey	Carbonate	Sandy	Sandy
Cr $*10^{-3}$	0.53	0.85	1.41	0.95	0.92	0.49	**2.15**	**8.05**	1.96	0.69	1.1	0.06
Mo $*10^{-4}$	**5.45**	**9.46**	**15.41**	**7.75**		**3.07**	**1.61**	**54.64**	0	**90.11**	**4.51**	**2.04**
W $*10^{-4}$	0.17	1.18	0	1.27		0.06	0.04	0	0	0.06	0	0.03
Se $*10^{-6}$	**393**	**1397**	**861**	**1284**		**422**	**102**	**621**	**156**	**130**	**342**	**77**
Mn $*10^{0}$	0.017	0.028	0.06	**0.076**	0.058	0.046	0.021	0.03	0.001	0.002	0.002	0.001
Re $*10^{-8}$	**14177**	**1536**	**226**	**1332**		**7862**	**40763**	**3660**	**30690**	**4064**	**1880**	**328**
Br $*10^{-4}$	**313**	**336**	**231**	**131**		**25**	**12**	0	**150**	**103**	**80**	**132**
I $*10^{-5}$	**2902**	**3489**	**1473**	**1438**		**1397**	**1605**	**4512**	**1957**	**9801**	**7224**	**338**
Fe $*10^{0}$	0.25	0.54	1.22	1.38	1.02	0.33	0.15	0.43	0	0.02	0	0.01
Co $*10^{-3}$	0.07	0.25	0.06	0.18	0.03	0.09	**0.23**	**0.49**	0.02	**0.06**	0.04	0.03
Ni $*10^{-3}$	1.29	**4.96**	**2.89**	**2.72**	**3.66**	**13.33**	**2.92**	0	2.72	1.2	**6.23**	**5.4**

Table 2. *The rate of migration in water (concentration and dispersion) of elements in the surface waters (lakes) of different ecoregions. Bolded are figures for the rare elements for which the high coefficient of concentration in surface continental waters is due mostly to anthropogenic loads on the global scale, dash means there are no elements with the given migration coefficient.*

Rate of migration in water	Coefficient of water migration	Surface waters - lakes in ecoregions			
		Tundra–taiga	Forest	Subarid and arid	European Russia
Very strong	> 100	C, Cl, **U**, I, **Se**, *Cs*?, **Re**	**Re**, Cl, C, I	Cl, **Re**, I, Na, S, **Mo**,	**Re**, Cl, C, I, S, Br
Strong	1 - 100	Br, **Bi**, N, S, **Ag**, **Cd**, Ni, Na, Rb, **Mo**, **Sb**, **As**, Sc, Ca, Mg, Sn, Sr, V, Ce, B, K, Li	S, **Mo**, **Se**, Na, Rb, **Ag**, Sc, Ca, Ba, **Cd**, **Sb**, **As**, Sr, Co, N, Mn, B, Mg, Br, Zn, Cu, K, Ni, **Bi**, Li	Br, C, **Se**, **Cd**, Sr, Rb, Ni, B, Ba, K, Mg, **As**, **Sb**, Co, Sc, Ca, N, Li, **U**, Zn, Cu, Mn	**Se**, N, **Cd**, B, *Cs*?, **Bi**, Na, **Ag**, **Mo**, **As**, Ca, Mg, Sr, **Sb**, Li, **U**, Rb
Median	0.05 - 1	W, Ba, La, Zn, Cu, Mn, Be, Pr, Si, Fe, Gd, Nd, P, Cr, Y, Th, Pb, Co, Zr,	Be, Pb, Cr, P, V, Sn, Cs, Si, **U**, Fe, La, Th, Pr, Ce, Nb, Nd	**Bi**, Sn, **Ag**, Cr, Pb, V, P, Si, Be, W	Sc, K, Sn, Zn, Ba, Cu, Ni, Mn, W, La, P, Si, Cr, Fe
Weak	0.001 – 0.05	Nb, Al, Ga, Ti	W, Ti, Gd, Al, Y, Ga, Zr	Cs, La, Fe, Pr, Nb, Th, Ce, Ti, Nd, Ga, Gd, Al, Y, Zr	Be, Ce, Pr, Co, Y, Nd, Gd, Pb, Ti, Al, Th, V, Zr, Ga, Nb

9. Critical loads and the Water Framework Directive – experiences from the UK

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The major international legislation covering the effects of atmospheric pollution, in particular sulphur and nitrogen deposition, on freshwater ecosystems, occurs mainly under two protocols of the Convention on Long-Range Transboundary Air Pollution of the UNECE and two EU Directives:

1. UNECE Oslo Protocol on Further Reduction of Sulphur Emissions (second sulphur protocol) 1994;
2. UNECE Gothenburg Protocol to Abate Acidification, Eutrophication and Ground-level Ozone, 1999;
3. EU Proposal for a National Emission Ceilings Directive (NECD) (1999);
4. EU Water Framework Directive (WFD) (2000).

While the UNECE protocols and the NECD employ the critical loads approach, there is an intrinsic difference in the approach of the WFD; the first three are based on selected chemical targets to prevent “harmful effects” while the WFD requires the achievement of “good ecological status” relative to “reference conditions”. Here we consider the challenges in reconciling the critical loads approach and assessments of recovery from acidification with the requirements of the WFD.

Critical loads for freshwaters in the UK

The definition of a critical load for any pollutant requires the specification of both a harmful effect and a sensitive indicator organism with the most widely used definition being: *“a quantitative estimate of the loading of one or more pollutants below which significant harmful effects on specified sensitive elements of the environment are not likely to occur according to present knowledge”* (Nilsson and Grennfelt 1988).

Critical loads of acidity for freshwaters in the UK are calculated with the First-order Acidity Balance model of Posch *et al.* (1997) for the purposes of national data submissions under the Gothenburg Protocol.

In a recent analysis of 20 years of data from the UK Acid Waters Monitoring Network (Kernan *et al.*, 2010), “worst-case” FAB critical load exceedances have been compared with “best case” critical load exceedances calculated using the Steady-State Water Chemistry (SSWC) Model described in Henriksen & Posch (2001). Both model applications employ a well established relationship between acid neutralizing capacity (ANC) of lakes and the health of brown trout populations to identify a critical chemical value for ANC associated with an “acceptable” level of risk or damage to brown trout populations (Lien *et al.*, 1996). In the UK and elsewhere in Europe a critical ANC value of 20 μeq L^{-1} is used representing a 10% probability of reduced brown trout populations.

Chemical recovery towards the target ANC value was calculated for the period of monitoring as the percentage change from the initial gap (20 - ANC value at start of monitoring) to the most recent measured data, where for most sites there has been an increasing trend in ANC which has resulted in “gap closure” towards the target (Table 1). Seven sites have been above the critical ANC value throughout the period of monitoring, while five have experienced a recovery above the critical ANC during this period. The other 10 sites show varying degrees of recovery including a further deterioration in ANC at Llyn Cwm Mynach.

The WFD approach – investigating recovery towards reference conditions

The dynamic acidification model MAGIC has been applied to all AWMN sites (Kernan *et al.*, 2010) and hindcasts the pre-industrial ANC, thereby providing a chemical reference value, against which gap closure can be estimated in the same way to provide a comparison of approaches using modelled and measured ANC. Although the WFD uses ecological definitions rather than chemical, we assume that chemical recovery is a necessary if not sufficient condition for biological restoration and achievement of "good ecological status".

***Table 1**. Assessment of chemical recovery and 'gap closure' based on ANC trends (yellow highlighting = recovery, red = still acidified, with ANC 'gap closure' given as % relative to ANC difference between baseline and start of monitoring).*

Site Code	Sitename	ANC Trend		Baseline	Initial monitoring		2005-07	Critical	Recovery relative to:	
		Sig.	Monotonic	ANC	Period	ANC	ANC	ANC	ANCcrit	Baseline
North-west Scotland										
ARR	Loch Coire nan Arr	ns	Mostly	51.0	1989-91	44.2	43.0	20	n/a	-18%
ANCC	Allt na Coire nan Con	***	Mostly	57.2	1989-91	33.5	44.4	20	n/a	46%
North-east Scotland										
MHAR	Allt a'Mharcaidh	***	Yes	85.8	1989-91	51.7	68.0	20	n/a	48%
NAGA	Lochnagar	***	Since 2000	41.0	1989-91	3.7	14.3	20	65%	29%
Trossachs										
CHN	Loch Chon	***	Yes	81.4	1989-91	11.1	49.5	20	yes	55%
TINK	Loch Tinker	**	Yes	79.9	1989-91	55.7	72.1	20	n/a	68%
Galloway										
DARG	Dargall Lane	***	Yes	80.4	1989-91	4.3	23.0	20	yes	25%
RLGH	Round Loch of Glenhead	***	Yes	31.3	1989-91	-9.4	14.1	20	80%	58%
LGR	Loch Grannoch	***	Yes	25.3	1989-91	-33.8	5.4	20	73%	66%
Northern Ireland										
BEAH	Beaghs Burn	**	Yes	128.9	1989-91	97.5	132.0	20	n/a	yes
CONY	Coneyglen Burn	ns	~Yes	209.1	1991-93	198.4	227.4	20	n/a	yes
BENC	Bencrom River	***	Yes	93.0	1989-91	-4.1	32.4	20	yes	38%
BLU	Blue Lough	***	Yes	17.6	1991-93	-43.6	-4.0	0	91%	65%
Lake District										
BURNMT	Burnmoor Tarn	***	~Almost	131.2	1989-91	55.5	81.6	20	n/a	34%
SCOATT	Scoat Tarn	***	Yes	34.7	1989-91	-20.3	-0.7	20	49%	36%
Pennines										
ETHR	River Etherow	***	Yes	253.9	1992-94	14.7	91.4	20	yes	32%
North Wales										
LAG	Llyn Llagi	***	Mostly	40.8	1989-91	3.6	17.5	20	85%	37%
MYN	Llyn cwm Mynach	ns	No	86.2	1989-91	10.7	7.1	20	-40%	-5%
Mid-Wales										
GWY	Afon Gwy	ns	~Yes	54.8	1992-94	9.1	19.8	20	98%	23%
HAFR	Afon Hafren	*	No	55.7	1989-91	1.7	10.4	20	48%	16%
South-east England										
LODG	Old Lodge Stream	***	No	99.6	1992-94	-28.5	31.6	20	yes	47%
South-west England										
NART	Narrator Brook	***	No	69.6	1992-94	13.5	20.0	20	99%	12%

The historical simulation of water chemistry is driven by sequences defined for acid deposition. MAGIC simulated ANC for 1860 illustrates that, prior to industrialisation, ANC values of all surface waters in the AWMN were above the critical limit of 20 μeq L^{-1}, with the exception of Blue Lough, which has a baseline ANC value of <20 μeq L^{-1}. The majority of sites (18 in total) have a simulated pre-industrial ANC below 100 μeq L^{-1}, indicating sensitivity to acidification but for the remaining four sites the reference ANC is predicted to range from 129 to 254 μeq L^{-1}. These surface waters can therefore be considered relatively well buffered, and would probably have supported relatively diverse acid-sensitive plant and animal communities at this time. Table 1 shows that only two of the least acid-sensitive sites in the AWMN have recovered to their reference ANC values (Beagh's Burn and Coneyglen Burn). The degree of recovery towards reference in the other sites varies from <0 (ANC lower at end than at start of monitoring) to 68%.

The difference in approach between the fixed ANC target and the reference ANC target is illustrated in Figure1. Ten sites still have ANC values below both the critical limit of 20 μeq L^{-1} and the reference value (Figure 1a) while eight sites which currently have ANC >20 μeq L^{-1} still have ANC values below reference values (Figure 1b). For this latter group of sites, critical loads under the Gothenburg Protocol would be achieved but a decline in ANC from reference conditions has still been allowed. In the case of more circumneutral sites, this ANC decline may represent a large departure from reference conditions with associated biological impacts. Hence the Gothenburg Protocol may be much less demanding that the WFD.

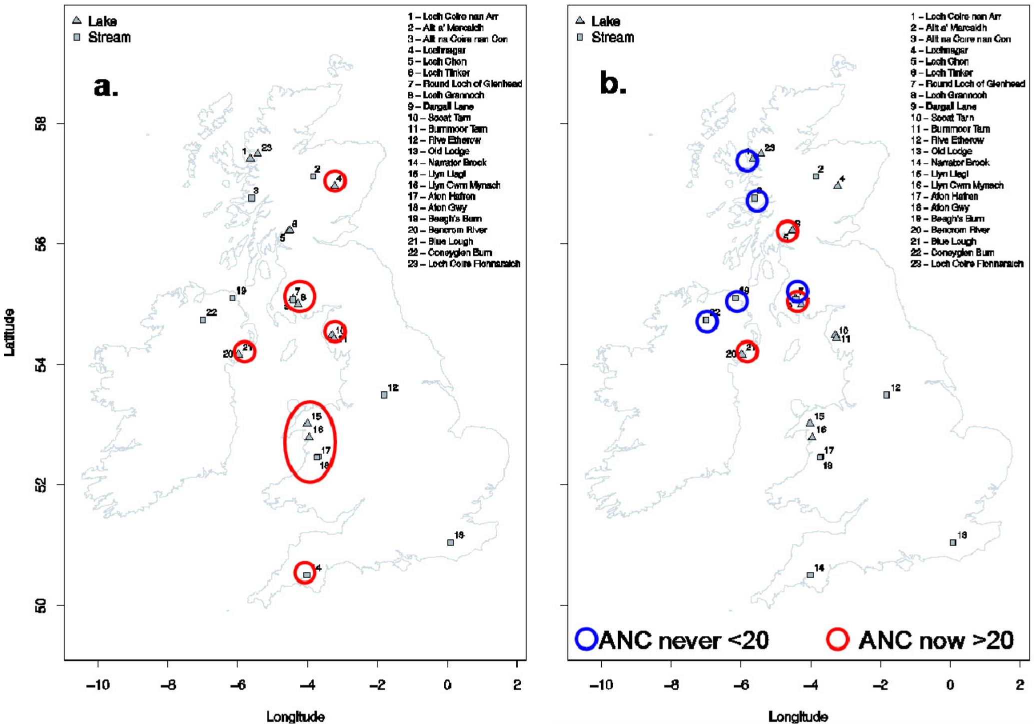


***Figure 1**. a) Ten AWMN sites with current ANC below both 20 μeq L^{-1} and pre-industrial reference value (4, 7, 8, 10, 14-18, 21); b) sites with ANC>20 μeq L^{-1} but < reference (5, 9, 20 have recovered to 20; 1, 3, 6, 19, 22 were never <20).*

Biological recovery and the WFD

There are other processes in addition to chemical changes in acidity status that may affect biological status. A direct method of assessing the degree of biological recovery at the AWMN lake sites is a comparison between the diatom assemblages of sediment core reference samples and the monitoring record of diatom change from samples taken from the sediment traps installed in each AWMN lake in 1991 and emptied annually since then.

To follow the changes in the diatom assemblages at each site we entered core and trap data passively into a Principal Components Analysis (PCA) of diatom assemblage data from a large data-set of 121 low alkalinity lakes from across the UK. The sites represent the full range of low alkalinity lake types found in the UK (Battarbee *et al.* in press). Each of the 121 sites is represented by two samples, one from the ca 1800 AD level in a core from that site and one from the surface sediment sample (= present day at the time of sampling). The diatom data from each AWMN site are thereby constrained by the range of variability in the overall data-set, and the time trajectory for each site shows the post-1800 changes in diatom assemblages caused by acidification and the post-1985-1990 (sediment core top) changes that represent the response to emission reduction and the degree of recovery.
Of special interest is the evidence provided by the analysis of the direction of the recovery arrow. In some cases (Figure 2), the data show that the diatoms are tracking back broadly in the direction of the reference assemblage. However, in some sites (Figure 3) the back-trajectory is deflected away from the reference direction, indicating that the current diatom assemblage in those lakes contains a different mixture of species, or a different relative abundance of species, compared with the compositional change that occurred in the lakes during the equivalent acidifying stages. The significance of these specific responses is not yet fully understood but may be related either to the influence of other external factors, such as climate change and nutrient enrichment from N deposition, or changes in within-lake processes.

Summary

- Methods are available for defining chemical reference conditions (e.g. MAGIC model)
- Definition of biological targets may be more difficult – what are the "reference" communities?
- Palaeolimnological approaches useful for some organisms in lakes (e.g. diatoms) but not all groups are well preserved, and what about streams?
- Evidence from AWMN is that diatoms in some sites are recovering towards communities that differ from reference conditions; could be due to influence of N deposition, DOC, climate, seasalts, landuse?
- Factors other than acid deposition may prevent achievement of biological targets
- Conceptual differences between Gothenburg Protocol and WFD are still to be resolved but long-term monitoring datasets and palaeolimnology provide powerful tools.

References

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

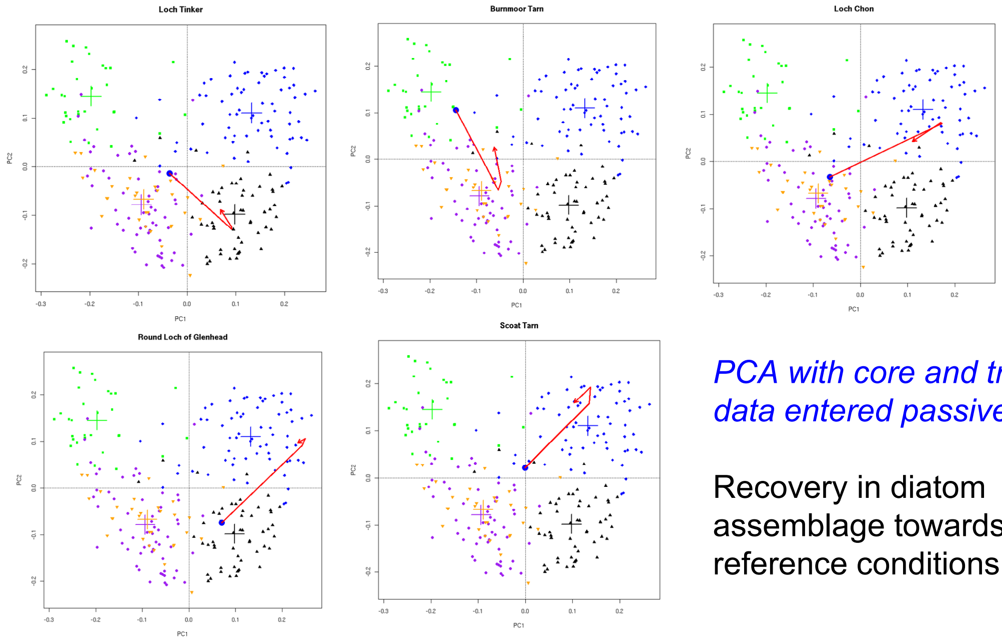
Battarbee, R.W., Simpson, G.L., Bennion, H. & Curtis, C. (in press) A reference typology of upland lakes in the UK based on pre-acidification diatom assemblages from lake sediment cores. *Journal of Paleolimnology*

Kernan, M., Battarbee, R.W, Curtis, C.J., Monteith, D.T. and Shilland, E.M. (Eds.) (in press) *UK Acid Waters Monitoring Network 20 Year Interpretive Report.* ECRC Research Report #141, University College London, London, UK, 477pp.

Lien, L., Raddum, G.G. , Fjellheim, A. and Henriksen, A. (1996) A critical limit for acid neutralizing capacity in Norwegian surface waters, based on new analyses of fish and invertebrate responses. *Sci. Tot. Env.* **177**, 173-193.

Nilsson, J. and Grennfelt, P. (Eds.) (1988) *Critical loads for sulphur and nitrogen.* UNECE/Nordic Council workshop report, Skokloster, Sweden, 19-24 March, 1988. Miljørapport 1988:15. Nordic Council of Ministers, Copenhagen, 418pp.

Posch, M., Kämäri, J., Forsius, M., Henriksen, A. and Wilander, A. (1997) Environmental auditing. Exceedance of critical loads for lakes in Finland, Norway and Sweden: reduction requirements for acidifying sulphur and nitrogen deposition. *Environ. Manag.* **21**, 291-304.



PCA with core and trap data entered passively

Recovery in diatom assemblage towards reference conditions

Figure 2. *AWMN sites showing biological recovery towards reference conditions.*

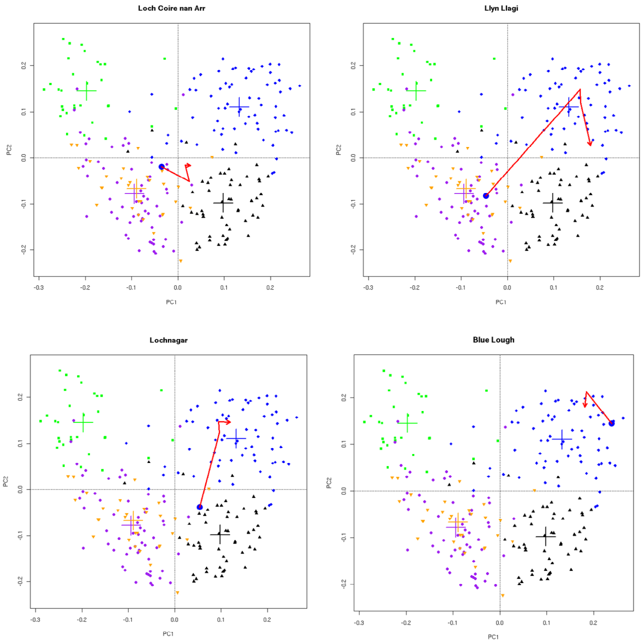


***Figure 3**. AWMN sites showing biological change towards new assemblages*

10. Reports and publications from the ICP-Waters Programme

All reports from the ICP Waters programme from 1987 up to present are listed below. All reports are available from the Programme Centre. Reports and recent publications are also accessible through the ICP-Waters website; http://www.icp-waters.no/

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.**

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**.

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. 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 18th 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.**

ICP Waters report 76/2004. 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, 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.**

De Wit, H., and Skjelkvåle, B.L. (eds.) 2007. Trends in surface water chemistry and biota; The importance of confounding factors. NIVA-report SNO 5385-2007. **ICP Waters report 87/2007.**

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.**

Wright, R.F., Posch, M., Cosby, B. J., Forsius, M., and Skjelkvåle, B. L. 2007. Review of the Gothenburg Protocol: Chemical and biological responses in surface waters and soils. NIVA-report SNO 5475-2007. **ICP Waters report 89/2007.**

Hovind, H. 2007. Intercomparison 0721: pH, Cond, HCO3, NO3-N, Cl, SO4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA-report SNO 5486-2007. **ICP Waters report 90/2007**

Fjellheim, A and Raddum, G.G. 2008. Biological intercalibration: Invertebrates 1107. NIVA-report SNO 5551 – 2008, **ICP Waters report 91/2008**

De Wit, H. Jenssen, M. T. S. and Skjelkvåle, B.L. (eds.) 2008. Proceedings of the 23rd meeting of the ICP Waters Programme Task Force in Nancy, France, October 8 – 10 , 2007. NIVA-report SNO 5567-2008. **ICP Waters report 92/2008.**

Hovind, H. 2008. Intercomparison 0822: pH, Cond, HCO_3, NO_3-N, Cl, SO_4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA-report SNO 5660-2008. **ICP Waters report 93/2008.**

Skjelkvåle, B.L., and De Wit, H. (eds.) 2008. ICP Waters 20 year with monitoring effects of long-range transboundary air pollution on surface waters in Europe and North-America. NIVA-report SNO 5684-2008. **ICP Waters report 94/2008.**

Fjellheim, A and Raddum, G.G. 2008. Biological intercalibration: Invertebrates 1208. NIVA-report SNO 5706-2008 **ICP Waters report 95/2008**

Skjelkvåle, B. L., Jenssen M. T. S. and de Wit, H. (eds.) 2009. Proceedings of the 24th meeting of the ICP Waters Programme Task Force in Budapest, Hungary, October 6 – 8, 2008. NIVA-report SNO 5770-2009. **ICP Waters report 96/2009**

Ranneklev, S. B., de Wit, Heleen A., Jenssen, Marthe T.S., Skjelkvåle, Brit Lisa, 2009. An assessment of Hg in the freshwater aquatic environment related to long-range transported air pollution in Europe and North America. **ICP-Waters report 97/2009.**

Hovind, H. 2009. Intercomparison 0923: pH, Cond, HCO_3, NO_3-N, Cl, SO_4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA-report SNO 5845-2009. **ICP Waters report 98/2009.**

Fjellheim, A. 2009. Biological intercalibration: Invertebrates 1309. NIVA-report SNO 5883-2009. **ICP Waters report 99/2009.**

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