Acid Rain Research

REPORT 39/1995

NIVA contributions to ACID REIGN '95?

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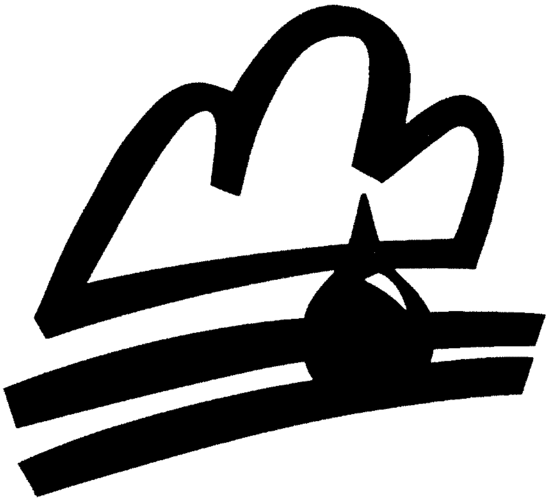
Gothenburg, Sweden,
26-30 June 1995.

ACID REIGN '95?



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Abstract:

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For the Administration

Richard F. Wright

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ACIDIFICATION OF HEAD WATER STREAMS IN THE CZECH REPUBLIC. PRELIMINARY RESULTS FROM MONITORING PHYSIC-CHEMICAL AND BIOLOGICAL PARAMETERS. A WORK TOWARDS A SYSTEM FOR WATER QUALITY CLASSIFICATION USING THE BENTHIC FAUNA.

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LAK40

Abstract: As a result of the bilateral environmental protection agreement between the Governments of Czech Republic and Norway one of the projects coming up and given priority is dealing with the Acid Rain problem. Scientists from the two countries established a team with the intention to develop a tool for the assessment of environmental quality of running headwater ecosystems in the Czech Republic affected by Acid Rain. This is done by integrating physico-chemical and biological data from brooks and streams to develop a response model : "The Czech Score Method for Biomonitoring Effects of Acid Rain". This is a system for water quality classification and biomonitoring effects generated by acid deposition using communities of benthic macro invertebrates. Samples are taken all over the country in mountains, all together 23 sites are visited and sampled up to 4 tunes a year. At the moment while writhing up the abstract we are at the phase working with the biological material. The regional description of the physico-chemical material are nearly finished and the multivariate approaches to build up the model start early spring next year.

Key words: water quality classification, benthic macro invertebrates, acidification.

MAGIC APPLIED TO ROOF EXPERIMENTS (RISDALSHEIA, N; GÅRDSJÖN, S; KLOSTERHEDE, DK) TO EVALUATE RATE OF REVERSIBILITY OF ACIDIFICATION FOLLOWING EXPERIMENTALLY REDUCED ACID DEPOSITION

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Abstract Soil and stream water responses to 'clean rain' treatments at 3 roof covered forest ecosystems in Norway, Sweden and Denmark were modelled by the MAGIC model. The model outputs were compared with measured responses. Over the wide span in site conditions among the three sites MAGIC successfully reproduced the observed effects in the 'clean rain' treatments. In particular the significant decreases in SO_4 output were well reproduced. The decrease in sulphur leaching caused a simultaneous change in base cation leaching, which in the long run will be the basis for the recovery of these acidified systems. The rate of recovery at the 3 studied sites was very slow. Single year discrepancies are observed because of seasalt influence. However, the long term trends are well reproduced.

1. Introduction

Emission and deposition of acidifying substances cause acidification of soils, waters and ecosystems. The effects of this acidification have been studied worldwide, and models have been developed to evaluate the observations and to predict the effects of future deposition levels. In recent years several whole ecosystem manipulation projects have been carried out in which the inputs of pollutants and nutrients to the ecosystem are manipulated by means of a roof cover, and the various effects are studied. Several of these projects include 'clean rain' experiments, where the acidifying input of S and N compounds are removed. Results from such studies offer a unique possibility for testing and evaluating the ability of matemathical models to predict the consequences of future protocols on emission of acidifying substances. The MAGIC model (Modelling of Acidification in Catchments; Cosby et al., 1985 a,b,c) was recently tested on the Norwegian site at Risdalsheia and proved to predict the observations nicely (Cosby et al., 1995). In the present study MAGIC was applied to three manipulated forest sites and the measured effects of experimentally reduced inputs of S and N was compared to predictions from the model. The aim has been to test MAGIC on a number of sites spanning a broader scale of site conditions.

2. Methods

The study was based on results from three Scandinavian whole ecosystem manipulation projects at Risdalsheia, Norway (Wright et al., 1993), Gårdsjön, Sweden (Hultberg et al.,

1993) and Klosterhede, Denmark (Beier et al.; 1993) (Table 1 and 2). These three sites comprise studies of the effects of removal of the ambient acidified input by means of 400-5000 m^2 roof covers and replacement by 'clean rain'.

Atmospheric deposition of non marine sulphur to the roof experiments at Klosterhede and Gårdsjön were almost identical and slightly lower at Risdalsheia whereas the marine deposition differed being 3 times higher at Klosterhede compared to Gårdsjön and Risdalsheia.

The sulphur input to the 'clean rain' plots were reduced by 80% at Gårdsjön, 75% at Risdalsheia and 95% at Klosterhede compared to the pre-treatment total sulphur deposition.

Table 1

Table 2 At each site the MAGIC model (Cosby et al., 1985a,b,c) was calibrated to the control plots or to the pre-treatment period. The calibration procedure involves estimation of historical base saturation and weathering rates based on present day cation exchange capacity, base saturation, deposition, hydrology, stream/soil water concentrations and estimated historical deposition and uptake/immobilization sequences (140 yrs). After calibration MAGIC was applied to the 'clean rain' plots by including all calibrated parameters from the control plot except for the inputs at the 'clean rain' plots. Details on the calibration procedure at Risdalsheia are given in Cosby et al. (1995), at Gårdsjön in Moldan et al. (1995 in prep.) and at Klosterhede in Beier (1995b in prep).

MAGIC is a lumped catchment scale model and predicts the present stream water chemistry which can then be compared to measured values. Klosterhede is not a catchment and here ecosystem output were from hydrological modelling and measured soil solution chemistry by two different procedures for the control and clean rain plots respectively. In the control plot the well known spatial pattern in input was taken into account in the calculations. In the clean rain plot sprinkling causes a complete change in this water pattern which has not been taken into account. Instead, average water flows and average soil solution chemistry were used to calculate outputs. The calculated outputs were increased by 40% in order to obtain a 5-year balance for chloride (Beier, 1995b in prep).

3. Results and discussion

The results of the calibrations and the predictions for the 'clean rain' experiments are shown in figure 1 and compared with measured stream water concentrations for SO_4, Al, sum of base cations (SBC), pH, acid neutralising capacity (ANC) and Cl.

Figure 1 Generally MAGIC is well calibrated to the control at each of the three sites. Even major fluctuations from year-to-year caused by hydrological changes are reproduced. However, MAGIC contains no 'damping' of salt concentrations. Therefore large inputs of sea salts in single years cause immediate response in the simulated output which is not

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the case in reality where a damping effect causes input and output of chloride to be out of phase (Beier, 1995a in prep; Hultberg and Grennfelt, 1992). Consequently modelled stream water concentrations exhibit more dynamic fluctuations than observed in the field. This is especially evident at Gårdsjön and Klosterhede. The biggest discrepancies between modelled and measured values in the 'clean rain' plots are seen at Klosterhede. Despite this problem MAGIC generally simulates the trends correctly.

Sulphur was subject to large input reductions at all three sites. The concentration of sulphur in output from the three sites started to decrease immediately from the start of the roof experiments. The concentration of sulphate in output at Klosterhede decreased by about 30% during the first year. At Gårdsjön sulphur decreased by 25% after two years and at Risdalsheia the decrease was slower amounting to about 40% during the first 3-4 years (Hultberg et al, 1992; Bishop and Hultberg, 1995; Wright et al, 1993). In terms of sulphur fluxes a 40 % reduction was measured already after 2 years in Gårdsjön and 50% after 3 years. Due to technical problems at Risdalsheia, less water than intended was sprinkled during the first years. This reduced the output of sulphur by about 70-80% after the second experimental year. Changed timing for water application in the clean rain plot also resulted in sharp decrease in sulphur output from Klosterhede during the first four years when the yearly fluxes decreased by 40-84% compared to pretreatment fluxes. MAGIC reproduced these responses well at all three sites.

Based on measurements and model predictions the accumulated net output was estimated and plotted against the accumulated input of sulphur (figure 2). All three sites were in steady state (input=output) prior to the treatment. At Risdalsheia the catchment reached a new steady state after 7 years, and no net release of sulphur occurred during the following four years. At Klosterhede MAGIC predicts the new steady state to occur after 10-12 years and at Gårdsjön after more than 15 years. The accumulated net output was estimated to about 100 meq/m^2 at Risdalsheia, 240 meq/m^2 at Klosterhede and 360 meq/m^2 at Gårdsjön (Figure 2). These net outputs of sulphur estimated from MAGIC predictions are almost identical to measured soil pools of water soluble sulphur at Risdalsheia and Gårdsjön (Wright et al, 1993; Hultberg et al, 1993; Mörth and Torssander, 1995).

The differences in the rate of sulphur response between the three sites mainly result from differences in soils, pool of water soluble sulphur and hydrology. The thin organic soils on bedrock at Risdalsheia with small amount of sulphur in the soil and high runoff of water result in a fast depletion of the soil pool and steady state. The soil is mainly sand at Klosterhede with a sulphate pool about twice as large as at Risdalsheia which together with low water fluxes result in a slower release of sulphate. At Gårdsjön the iron podzol with a well-developed B-horizon and a sulphate pool more than three times higher than at Risdalsheia will also have the longest time for leaching the sulphate pool and reaching the new steady state. The total transport of water seems less important and the net loss of sulphur in relation to the water transport is fastest from Klosterhede, slower at Gårdsjön and very slow at Risdalsheia. This indicates that a time-dependent process for the release of the water-soluble sulphate is more important than the water amounts for the output of soil-bound sulphate during the recovery process. The experiments also show that the sulphur response during the first 4-11 years is mainly determined by the pool of adsorbed sulphate and to a lesser extent of the large organic sulphur pool.

Figure 2 At all three sites the 'clean rain' treatment resulted in a gradual decrease in aluminum concentrations and to some extent a simultaneous increase in pH in the output. The decrease in Al concentrations reached 50% after 5-8 years. At Klosterhede and Risdalsheia the modelled and measured Al concentrations differ by up to a factor of 2. Since the Al concentrations are high at Klosterhede this difference is substantial in terms of equivalents. The reason for the differences may be that the calibrated Al chemistry in the control plot cannot be directly transferred to the clean rain plot. This might be caused by changes in the Al chemistry caused by treatment induced changes in organic or S chemistry.

MAGIC calculates the acid neutralising capacity (ANC=SBC-SAA (Wright et al., 1993)) which in many respects provides the "bottom line" for evaluation of the ability of MAGIC to simulate the observed changes at the roofed sites. ANC incorporates all the uncertainties in the values for the 4 base cations and 3 strong acid anions. Of these MAGIC estimates independently the concentrations of each of the 3 strong acid anions, while the concentrations of the base cations and the mix among the 4 base cations is the result of the calibration of the initial base saturation and weathering rates.

At all 3 sites the ANC in output water increased as a result of the decreased input of strong acids due to the roof treatment (Figure 1). The increase is most evident and smoothest at Risdalsheia, where the ANC increased from about -100 μeq/l before treatment to about -25 μeq/l after 9 years of reduced acid deposition. At both Gårdsjön and Klosterhede there is also an increase in ANC following the roof treatment, but at these sites the great year-to-year variations in seasalt inputs causes major year-to-year variations in output of seasalts and ANC. This is the well-known seasalt effect in which episodic inputs of seasalts causes short-term decreases in ANC due to the cation exchange of Na and Mg for acid cations Al and H (Norton et al., 1987; Wright et al., 1988).

As the sulphate flux in and out of the system is reduced, the accompanying cation flux is reduced as well. Restoring the base cations in the system determines an important step in the long-term deacidification and recovery of the ecosystem. The rates of the BC recovery at the three sites are indicated by the F-factors (ratio of change in non-marine (Ca+Mg) to change in non-marine SO_4) (Henriksen, 1980). The F-factors are very low at Klosterhede and Risdalsheia (0.2 and 0.1 respectively) indicating a slow build up of the base cations. At Gårdsjön the F-factor is about 0.6.

In general MAGIC successfully described the changes in the 'clean rain' plots. The 3 study sites span wide ranges in inputs, soils and stand characteristics, which strongly emphasize the capability of MAGIC to model the recovery of acidified forest soils especially with respect to sulphate and base cation concentrations in the soil and the consequent improvement of ANC following reduced input of acidity. At sites strongly influenced by sea salts the lack of 'damping' the sea-salt response in the model means that application of MAGIC to sea-salt influenced sites will need longer time series of measurements. Obviously the model calibrations are highly dependent on the quality of the calculated budgets/outputs, which may limit the use in non-catchment sites like Klosterhede. A crucial point in the calibrations is the uptake sequence estimated for the site. Uptake of base cations determines one of the most important sinks in the systems and consequently over or under estimations of the uptake will influence the long-term predictions of the historical base saturation, the weathering rate and the future soil solution concentrations.

4. Acknowledgements

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TABLE I
Site characteristc parameters measured/estimated or obtained by calibration of MAGIC (*) for Gårdsjön, Risdalsheia, and Klosterhede.

		Gårdsjön G1	Risdalsheia Rolf	Klosterhede K1+K5
	Stream parameters			
	Discharge - mm/yr	1300	350	275
*	Al(OH)$_3$ solubility - log10	6.6	8.4	8.8
	Temperature - °C	7	8	8
	CO$_2$ partial press. - atm.	0.0008	0.001	0.0056
	Total Organic acid - mmol/m^3	23	40	240
	Stand parameters			
	Tree specie I	Pine/birch	N. spruce	Pine
	Period	1850-1994	1850-1994	1850-1919
	Tree specie II			Norway spruce
	Period			1919-1994
	Net uptake+immobilization			
	Ca - mmol$_c$/m^2/yr	0	13	47
	Mg - mmol$_c$/m^2/yr	0	4.6	20
	Na - mmol$_c$/m^2/yr	0	0.5	5
	K - mmol$_c$/m^2/yr	0	3.5	11
	SO$_4$ - mmol$_c$/m^2/yr	0	0	25
	Soil parameters			
	Soil type	Podzol	Podzol	Typic haplorthod
	Soil depth - m	0.1	0.4	0.55
	Porosity - %	50	50	54
	Bulk density - kg/m^3	620	872	1110
	CEC - mmol$_c$/kg	62	49	31
	BS-modern - %	22.3	19.3	8.7
	Total organic acids - mmol/kg	120	150	240
	Temperature	7	8	8
	CO$_2$ partial pressure - atm.	0.002	0.005	0.035
*	Solubility Al(OH)$_3$ - log10	7.6	8.4	8.8
*	SO$_4$ halfsaturation - mmol$_c$/m^3	60	300	500
*	SO$_4$ ads. max capacity - mmol$_c$/kg	6	3	1
*	BS historical - %	60.1	38.8	19.3
	Weathering			
*	Ca - mmol$_c$/m^2/yr	3.6	4.4	17.3
*	Mg - mmol$_c$/m^2/yr	0	17.1	0
*	Na - mmol$_c$/m^2/yr	0	3.1	2.9
*	K - mmol$_c$/m^2/yr	0	4.9	9.2

TABLE II
Average annual input of elements and water to control or pre-treatment plots and clean rain plots at Risdalsheia, Gårdsjön and Klosterhede. Unit for elements is meq/m²/yr and water is mm/yr.

	Risdalsheia		Gårdsjön		Klosterhede	
	ROLF	KIM	G1-pre	G1	K1+K5	IR
	Cont.	Clean	Cont.	Clean	Cont.	Clean
H	94	27	8		26	3
Al	0	0	0	0	1	0
Ca	14	4	8	17	39	34
Mg	35	16	51	51	143	119
Na	145	67	217	230	627	473
K	6	2	5	36	13	1
NH_4	57	6	34	0	82	5
SO_4	112	26	133	26	208	9
Cl	169	84	266	288	742	710
NO_3	70	12	64	0	71	13
Volume	1460	990	650	1030	668	607

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Captions to figures

Figure 1

Mesaured concentrations (μeq/liter) of SO_4, Al, sum of base cations, ANC, pH and Cl in output water at Risdalsheia (a), Gårdsjön (b) and Klosterhede (c). Figures include measured concentrations in 'control' plots (open squares - Risdalsheia and Klosterhede) and 'clean rain' plots (filled squares) compared with MAGIC outputs for the 'clean rain' plots (bold solid line).

Figure 2

Accumulated input vs. accumulated output of sulphur at Risdalsheia, Gårdsjön and Klosterhede before and after reduced input of sulfur to the ecosystems. Input-output balances indicated by dotted 1:1 lines and the total losses of sulfur during the transition to the new steady states are indicated by arrows.

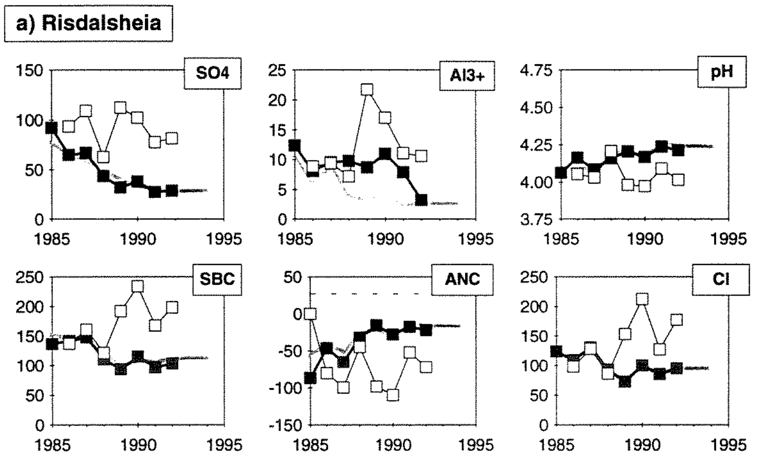

Figure 1a
Measured concentrations of SO4, Al, sum of base cations, Cl, ANC and pH in the stream water in the 'Control' catchment - ROLF' (open squares) and the 'clean rain' catchment - KIM (filled squares) at Risdalsheia, N, compared with modelled values for the 'clean rain' catchment (bold grey line). All units are µeq/l (except pH).

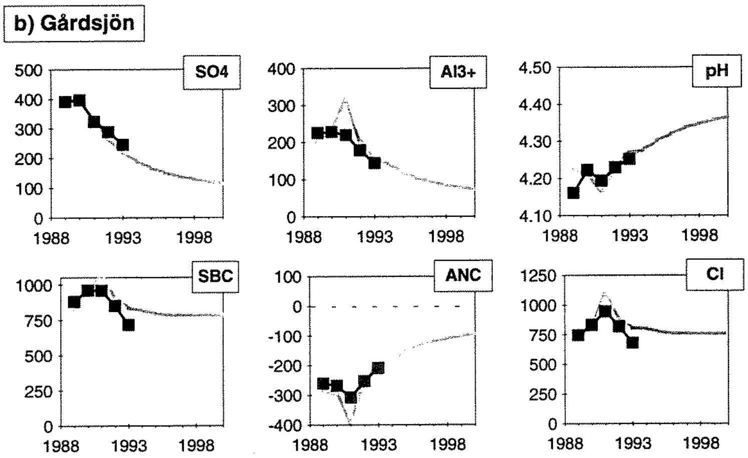

Figure 1b
Measured concentrations of SO4, Al, Sum of Base Cations, Cl, ANC and pH in the stream water of the 'clean rain' catchment, G1, (filled squares) at Gårdsjön, S, compared with values modelled by MAGIC (bold grey line). All units are µeq/liter (except pH).

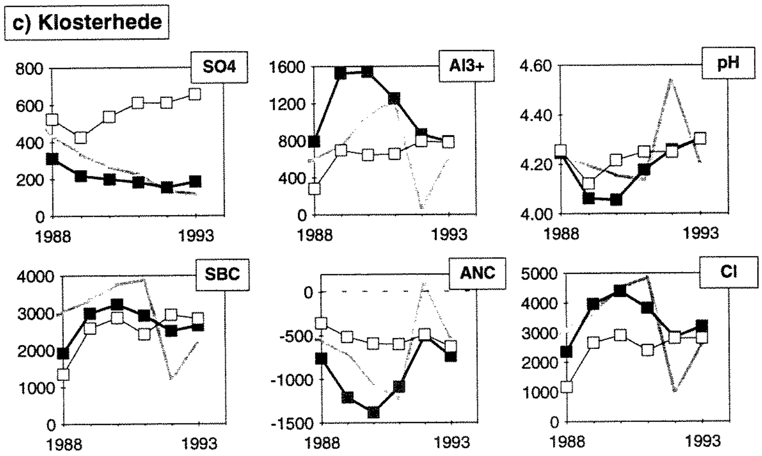

Figure 1c
Measured concentrations of SO4, Al, Sum of Base Cations, Cl, ANC and pH in the water leaving the root zone in the 'Control plot' (open squares) and the 'clean rain' plot (filled squares) at Klosterhede, DK, compared with modelled values for the 'clean rain' plot (bold grey line). All units are µeq/liter (except pH).

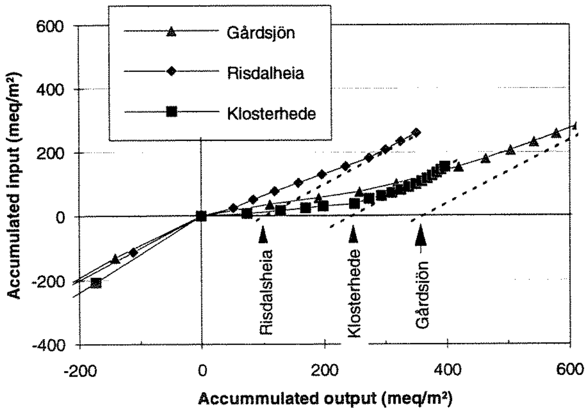

Figure 2
Accumulated input vs. accumulated output of sulfur at Risdalsheia, Gårdsjön and Klosterhede before and after reduced input of sulfur to the ecosystems. Input-output balances indicated by 1:1 lines for each site is indicated by dotted lines and the total losses of sulfur during the transition to the new steady states are indicated by arrows.

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ENHANCHED GROWTH OF THE MACROPHYTE Juncus bulbosus IN S NORWEGIAN LIMED LAKES. A REGIONAL SURVEY.

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LIM08

The effects of liming on the aquatic macrophyte vegetation have been investigated in S and SW Norway. In the western areas, a dominance of *Juncus bulbosus* was found in lakes that had been limed for 4-5 years or more, whilst only small populations of *Juncus* were found in the untreated lakes. A luxuriant and massiv nuisance growth of *Juncus* in the depth zone 0-3(-4) m was often developed, with shoots reaching surface and producing extensive, dense and vital surface mats, overgrowing the original isoetid vegetation. The plants had morphological characteristics indicating young populations, likely to have developed after liming. The massiv *Juncus* expansion was seen mainly in directly limed lakes with a sometimes visible layer of calcium carbonate on the sediment surface, but enhanched growth has been observed also in lakes downstream liming. The results from a sediment pore water study indicate that the *Juncus bulbosus* populations are stimulated by high levels of CO_2 and ammonium in the limed sediment. A (re-)establishment of some acid-intolerant species such as *Myriophyllum alterniflorum* and *Potamogeton* spp. has also been recorded after liming, and the species diversity appears to have increased slightly, at least in clearwater lakes.

Key words: liming, lakes, S Norway, aquatic macrophytes, *Juncus bulbosus*, nuisance growth, species diversity, sediment pore water.

Changes in the volume and composition of phytoplankton after experimental acidification of a humic lake

by

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In connection with the HUMEX-project carried out in Lake Skjervatjern, near Førde, in the western part of Norway, the effects of the experimental acidification on the phytoplankton volume and composition has been investigated.

The lake was divided in two basins by a thick plastic curtain, and one of the basins, Basin A and its entire catchment was acidified by a mixture of ammonium nitrate and sulphuric acid, while Basin B acted as a reference. The results of the phytoplankton analyses from both basins two years before and the period after the acidification started are presented. In Basin B, the control basin, the succession of the main groups of phytoplankton throughout the growth season remain almost identical the two first years after the onset of the acidification. The results from the acidified Basin A in 1991 and 1992 show marked changes in the phytoplankton composition and percentage of the main algae groups, compared to the reference basin. The percentage of the green algae decreased, especially the species *Oocystis submarina v. variabilis*, while the dinoflagellates, mainly the species *Peridinium umbonatum* (*P.* inconspicuum) and the cryptomonads increased in number and percentage of the total volume in the acidified basin. In 1993, however, and even more in 1994, there was a marked change in the composition also in the control Basin B compared to the previous years, with less green algae and more of chrysomonads. The total volume was much higher in the Basin A in 1994 than in Basin B, especially in the autumn, while the total volume throughout the growth season was more or less the same in both basins in 1993. In the acidified Basin A the dominance of the dinoflagellates was even more pronounced in 1993 and 1994 than previous years with acidification.

The reason for the different composition of phytoplankton registered in the control, Basin B, in 1993 and 1994 compared to previous years, is hard to explain.

As the changes in the composition of Basin A came immediately after the treatment of the Basin started, it is obvious that the addition of nitrogen, and especially the nitrate, through the treatment, was of importance in regulating the composition in this acid and humic lake. Increase in the phosphorus seems to contribute more to the level of the total biomass of phytoplankton than to the observed changes in the composition.

INTRODUCTION

A preliminary report on the changes in the phytoplankton volume and composition in Lake Skjervatjern as a result of artificial acidification of one of the basins and its catchment after division of the lake, was given by Brettum (1994). In this paper all the analyses on variations in phytoplankton volume and composition in the investigation period of the HUMEX-project are given, as the HUMEX step I and step II have come to an end.

Changes occur in the phytoplankton of lakes that are acidified. As the pH decreases, the species richness decreases and the species composition and dominance changes. This phenomenon has been reported by a number of workers, for instance Almer et al. (1974), Kwiatkowski and Roff (1978), Raddum et al. (1980), Lydén and Grahn (1985), Stokes and Yung (1986), Havens and DeCosta (1987), Findlay and Kasian (1986, 1991) , Arvola et al. (1990), Schindler (1990) and Stenson et al. (1993).

On the other hand acidification, when not brought to an extreme low pH-level, is reported to have none or very little influence on the total volume or biomass of the phytoplankton. This is primarely determined by nutrient availability as reported by Kwiatkowski and Roff (1976), Raddum et al. (1980), Stokes (1986), Havens and DeCosta (1984, 1986), Arvola et al. (1990), Findlay and Kasian (1991), Kippo-Edlund and Heitto (1990), Schindler (1990), Blomqvist et al. (1993) and Hörnström et al. (1993).

The tolerance of the single phytoplankton species to changes in the acidity has been studied by Hörnström (1979), Hörnström et al. (1984), Hörnström and Ekström (1986), Raddum (1980), Ilmavirta and Huttunen (1989), Willén et al. (1990), Brettum (1989, 1992), Pinel-Alloul et al. (1990) and Hörnström et al. (1993).

The phytoplankton volume and the composition of the community in a lake is the result of the total environmental conditions at any time. Changes in the environment in any direction will influence on the growth of some of the phytoplankton species and therefore change the composition and the dominance of these species in the phytoplankton community (Reynolds 1984, Sommer et al. 1986, and Sommer 1987). Registration of the phytoplankton community and volume and variations in these parameters throughout the growth season is an excellent way to follow changes in one basin of water compared to another with different ecological conditions, as was the case in Lake Skjervatjern.
Gjessing (1992) has given a comprehensive and thoroughly description of the HUMEX project.

Lake Skjervatjern, a humic lake near Førde in the western part of Norway, was selected for studies on the effects of acid rain. The lake was divided in two separate basins by a thick plastic curtain in the summer 1988. One of the basins, Basin A, and its entire catchment was acidified by a mixture of sulfurous acid and ammonium nitrate, by means of sprinklers mounted at the top of trees. The treatment was initiated in October 1990, and has been synchronized with rainfall. The other basin, Basin B, and its catchment, remained untreated, and acts as a reference.

The acidified catchment is 2.7 ha and the corresponding part of the lake (Basin A) 0.9 ha. The area of the reference catchment is 6.2 ha and the part of the lake (Basin B) 1.5 ha.
The maximum depth, volume, and theoretical retention time of the two basins are 5.2 m, 9000 m^3, and 1.6 months and 10.4 m, 58000 m^3, and 4.5 months respectively for basin A and basin B (Gjessing 1992). Physiochemical as well as biological parameters have been monitored in the lake in the investigation period.

The results given by Gjessing (1992) and Lydersen (1995 in this volume) from analyses of the chemical composition in water samples taken before and after the acidification treatment of Basin A and its catchment started, show that sulfate, ammonium, and nitrate are the parameters that have increased markedly. This was expected, of course, since sulfurous and nitrogen compounds were used in the acidification procedure of Basin A and its catchment. In 1994 there was also a marked increase in the phosphorus in Basin A.

Experimental acidification has been carried out, using sulfurous and nitric acid by earlier workers, and the effects on the phytoplankton are reported by Findlay and Kasian (1990). They pointed out that once the pH decreased below 6.0, the diatoms (Bacillariophyceae) and the bluegreen algae (Cyanophyceae) were eliminated from the phytoplankton.

In Lake Skjervatjern, the pH was approximately 4.6 even before the acidification treatment started. Therefore, planktonic species of these two groups were not in the phytoplankton at any time. Findlay and Kasian (1990) also noted that the percentage of Chrysophyceae (golden algae) decreased, and the Chlorophyceae (green algae) and the Dinophyceae (dinoflagellates) increased with increasing amounts of nitrogen. They also noted that an increase in sulfur resulted in changes from the Chysophyceae dominance to a Dinophyceae dominance. Blomqvist et al. (1989) pointed out that with nitrate as nitrogen source, the dinoflagellate *Peridium umbonatum* (*P. inconspicuum*) was favoured.

MATERIAL AND METHODS

Phytoplankton samples were sampled from the two basins in lake Skjervatjern in the years 1989 - 1994. That means two years after the division of the lake, but before the onset of the treatment of basin A, and four years with the acidification of basin A going on.

Unfortunately only 3 sets of samples were collected and analysed the first year, 1989, but for the last 5 years a reasonable number of samples were collected throughout the growth seasons.

The samples of phytoplankton were quantitative mixed samples from the upper three meters of the water column, and they were fixed and preserved with Lugol's solution added acetic acid.

The samples were examined according to Utermöhl (1958) and the phytoplankton volume were determined using the recommendation given by Rott (1981). 10 and 50 ml chambers were used for the sedimentation procedure, and 2 to 4 transects were examined and the different species of phytoplankton counted, by means of an inverted microscope Leitz Fluovert FS with phase contrast. Large species were counted from the whole sedimentation area. A number of cells of each species were measured and the mean cell volume calculated comparing the form of the species with simple geometric figures (Rott 1981). Phytoplankton volume as volume of each species, the main groups (green algae. dinoflagellats e.t.c.) and the total volume, were then calculated from each sample.

The confidence interval = $\pm\, 2\text{x}100 / \sqrt{n}$ % where n = number of individuals counted. To get a statistical acceptable estimate of the number of individuals of each species in the sample, a bottom area of the sedimentation chamber giving at least 100 individuals of the important species were examined. At least a total of 500 individuals for the hole community of phytoplankton were counted in each sample according to Lund et al. (1958) and Venrick (1978).

RESULTS AND DISCUSSION

Figure 1 gives the results of the variations in total volume and percentage composition of the main groups of phytoplankton. The total volume are given as mm^3/m^3 which is approximately the same as mg/m^3 of fresh weight phytoplankton.The figure comprehends the results from all the samples taken from the two basins in the years 1989-1994. The variations of the main groups of phytoplankton, as well as the total volume, followed the same patterns in both basins during the two first years, 1989 and 1990.

As mentioned earlier, Lake Skjervatjern was rather acid even before the experimental period, with values of pH around 4.6-4.7. As usual in acid lakes, the number of species found in the phytoplankton are low. Only 20-30 taxons are common in the samples from Lake Skjervatjern. The effect of the experimental acidification in Basin A was therefore not a reduced number of species or taxons found, but changes in the percentage composition of the phytoplankton community.

Planktonic species among the diatoms (Bacillariophyceae) and the bluegreen algae (Cyanophyceae) were not registered.

In 1991 and 1992 when the acidification treatment of Basin A and its catchment was going on, marked changes were registered especially in the percentage composition of the main groups in Basin A, compared to the control, Basin B. Before the onset of the acidification procedure, Dinophyceae (dinoflagellates) and Chrysophyceae (golden algae) were the dominant groups in the early spring, but the Chlorophyceae (green algae) dominated during the rest of the growth season in both basins.

While the phytoplankton in the control (Basin B) followed a stable pattern these years, the green algae (Chlorophyceae) became of lesser importance in the Basin A after the acidification had started.

The dinoflagellates (Dinophyceae) and another group of flagellates, the cryptomonads (Cryptophyceae), increased in number of individuals and percentage of the total volume of phytoplankton. The cryptomonads increased marked in Basin A in the years of acidification.

The total volume, like the composition of the phytoplankton community, was very similar throughout the growth season before acidification.

As can be seen from Fig. 1, there was an increase in the total volume of phytoplankton in Basin A in the first year (1991) of acidification compared to the control, Basin B. The next year, however, the total volume was generally higher in the control basin than in the acidified basin.

In 1993 the variations in total volume was more or less identical in the two basins, while the total volume was marked higher in Basin A most of the growth season 1994, compared to Basin B.

The most striking feature was that the dinoflagellates (Dinophyceae) became more dominating in the phytoplankton of Basin A, through an increase of individuals of the species *Peridinium umbonatum* (*P. inconspiccum*). Also the cryptomonads (Cryptophyceae) increased marked in the phytoplankton in Basin A as soon as the treatment started as mentioned earlier, especially in the midsummer and the autumn.

Unfortunately the composition of the phytoplankton in Basin B (the control), that in the years 1990, 1991 and 1992 followed a more or less identical development throughout the growth seasons, and even started the same way in 1993, changes in the last part of 1993 and in 1994.

The quite different development of the phytoplankton composition in the control, especially in 1994 compared to previous years, is hard to explain, as there were no factors, as far as we could see, that had changed in the control basin and its catchment.

The Fig. 1 shows very well that the treatment has given pronounced changes in the percentage composition of the main groups of phytoplankton.

In Fig. 2 and Fig. 3 a more detailed picture of the development of the main groups and some dominant species in the phytoplankton community of lake Skjervatjern are given for the investigation period.

Fig. 2 gives the variations in volume of the green algae (Chlorophcyeae) as a group, and two of the species within this group, *Oocystis submarina* v. *variabilis* and *Botryococcus braunii.* The group increased immediately in Basin A when the treatment started, probably caused by the extra supply of nutrient through the treatment. The rest of the investigation period this group decreased marked in Basin A, and changed from the most important group in the phytoplankton, to a group of minor importance.

As seen from the figure, the reason for this is mainly the retarding effect the treatment seems to have on the amount or biomasses of the species of green algae, *Oocystis submarina* v. *variabilis* and *Botrococcus braunii.* The decrease of *Oocystis submarina* v. *variabilis* when nitrogen was added to Basin A through the treatment, is in contrast to the findings of Findlay and Kasian (1990). According to Hessen (1995 in this volume) the grazing from the zooplankton had but little influence on the phytoplankton changes. One exception is registered. It seems to be some connections between the variations of the zooplankton species *Holopedium gibberum* and the green alga *Oocystis submarina* v. *variabilis.*

As the biomasses of *Botryococcus braunii* increased very much in 1991-93 in the control Basin B, the reduction of this species in the treated basin was very perceptible.

In Figure 3 are given the variations throughout the period of investigation for three other main groups of phytoplankton. Generally, all three increased in biomass in Basin A as soon as the treatment started.

The golden algae (Chrysophyceae), that usually are the most dominant group of algae in nutrient-poor, humic, but less acid small lakes, were not so important in the acid waters of Lake Skjervatjern, before the treatment started. The increase in the treatment period consist mainly of small flagellates. The greatest differences between the two basins were in the beginning of each growth season.

The dinoflagellates (Dinophyceae) increased from year to year in the treatment period, and became more and more important in the phytoplankton of basin A throughout the growth season, and not only in the very beginning of each season as before the treatment started. The increase was mainly due to an increase in the number of individuals of the species *Peridinium umbonatum* (*P. inconspicuum*), but also the number of individuals of *Gymnodinium* cf. *lacustris* increased.

The cryptomonads (Cryptophyceae) increased, as the Fig. 3 shows, very much in the last part of the growth season 1994, at the same time as the Secchi disk depth decreased marked in Basin A from approximately 2-2.1 m to around 1 m, indicating a sudden reduction of the light penetration through the water in that basin (Figure 4). The cryptomonads are observed in several lakes to increase, while the green algae decrease in importance in the phytoplankton community when the light conditions in acid, humic lakes became worse.

Some observed changes in the environmental conditions due to the treatment of Basin A and its catchment are obviously contributing to the changes in the phytoplankton. As Figure 5 shows, there were marked changes throughout the investigation period with increase of nitrate and ammonium as could be expected from the treatment procedure. This certainly influenced on the composition of the phytoplankton community (Blomqvist et al. 1993).

The phosphorus content also increased throughout the investigation period and especially the last year, 1994, there was a marked increase in the total phosphorus in Basin A (Fig. 4). This reflects also an increase in the phosphate to the waters even through this was not registered, probably because all accessible phosphorus are used by the phytoplankton at once (Levine and Schindler 1980, Schindler 1990).

From the immediate changes we observed in the phytoplankton composition in Basin A (the growth season 1991) as soon as the treatment had started, it seems as if the nitrogen, and especially the nitrate addition, was the most important factor regulating the composition of the phytoplankton community of the acid and humic Lake Skjervatjern. Increase in the phosphorus seems to contribute more to the level of the total biomass of phytoplankton than to the observed changes in the composition.

ACKNOWLEDGEMENT

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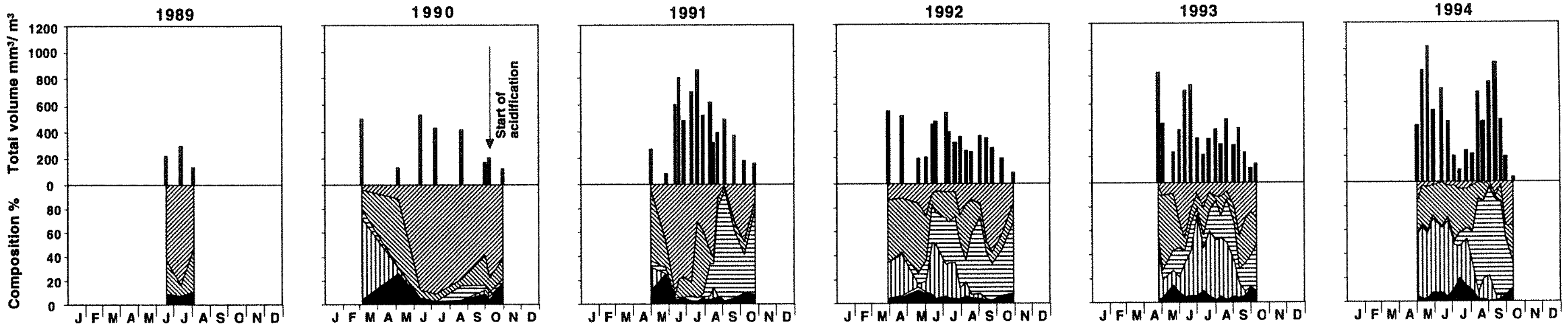
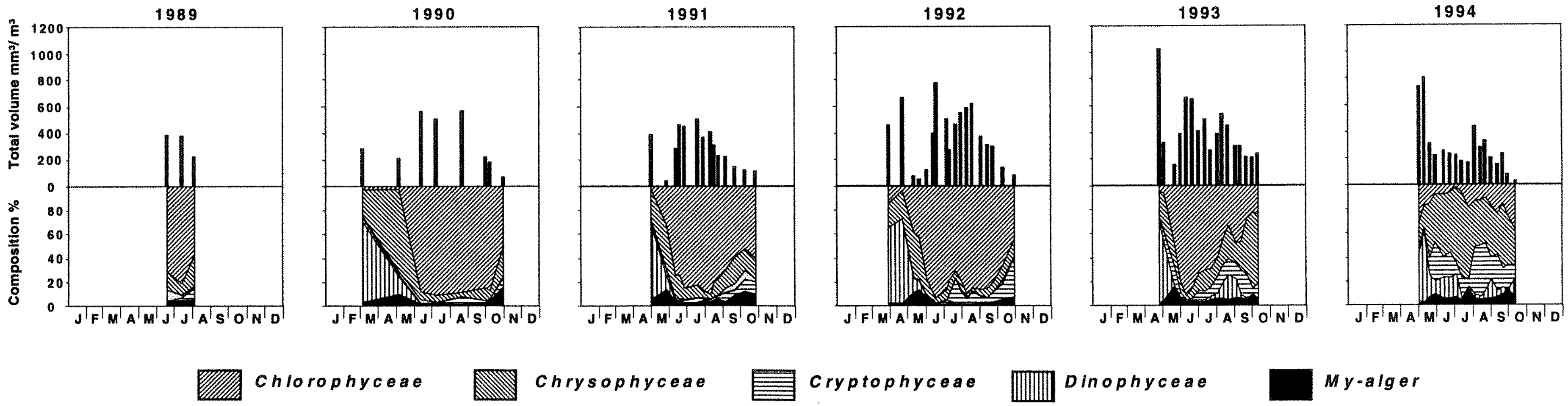
Fig. 1 Variations i total volume and composition of phytoplankton in Basin A and Basin B (control) in Lake Skjervatjern 1989 - 1994. The acidification of Basin A started in October 1990.

Basin A



Basin B



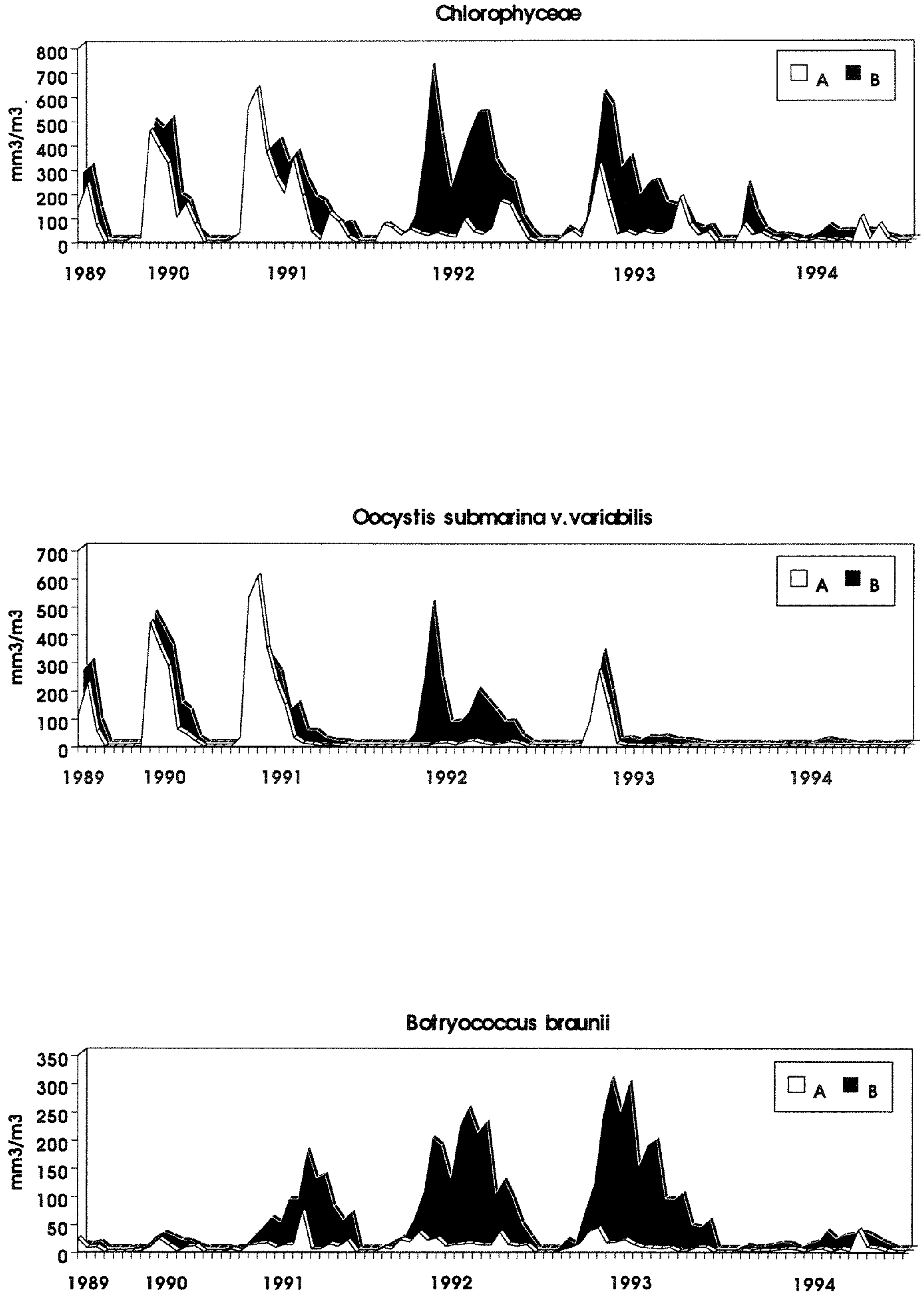


Fig.2 **Variations in volumes of Chlorophyceae, *Oocystis submarina v.variabilis* and *Botryococcus braunii* in Basin A and Basin B in lake Skjervatjern, 1989-94.**

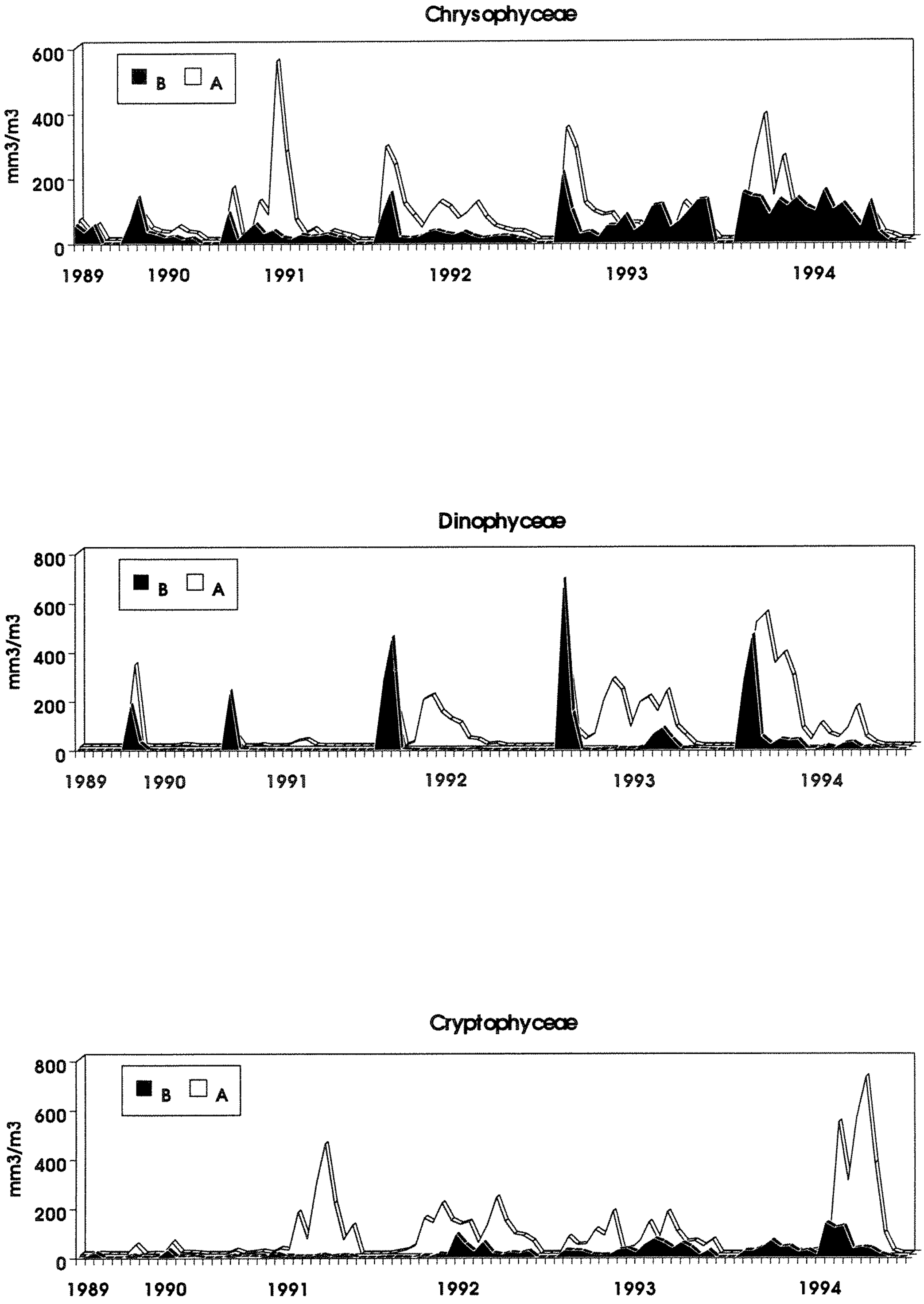


Fig.3 **Variations in the groups Chrysophyceae, Dinophyceae and Cryptophyceae in Basin A and Basin B in lake Skjervatjern, 1989-94.**

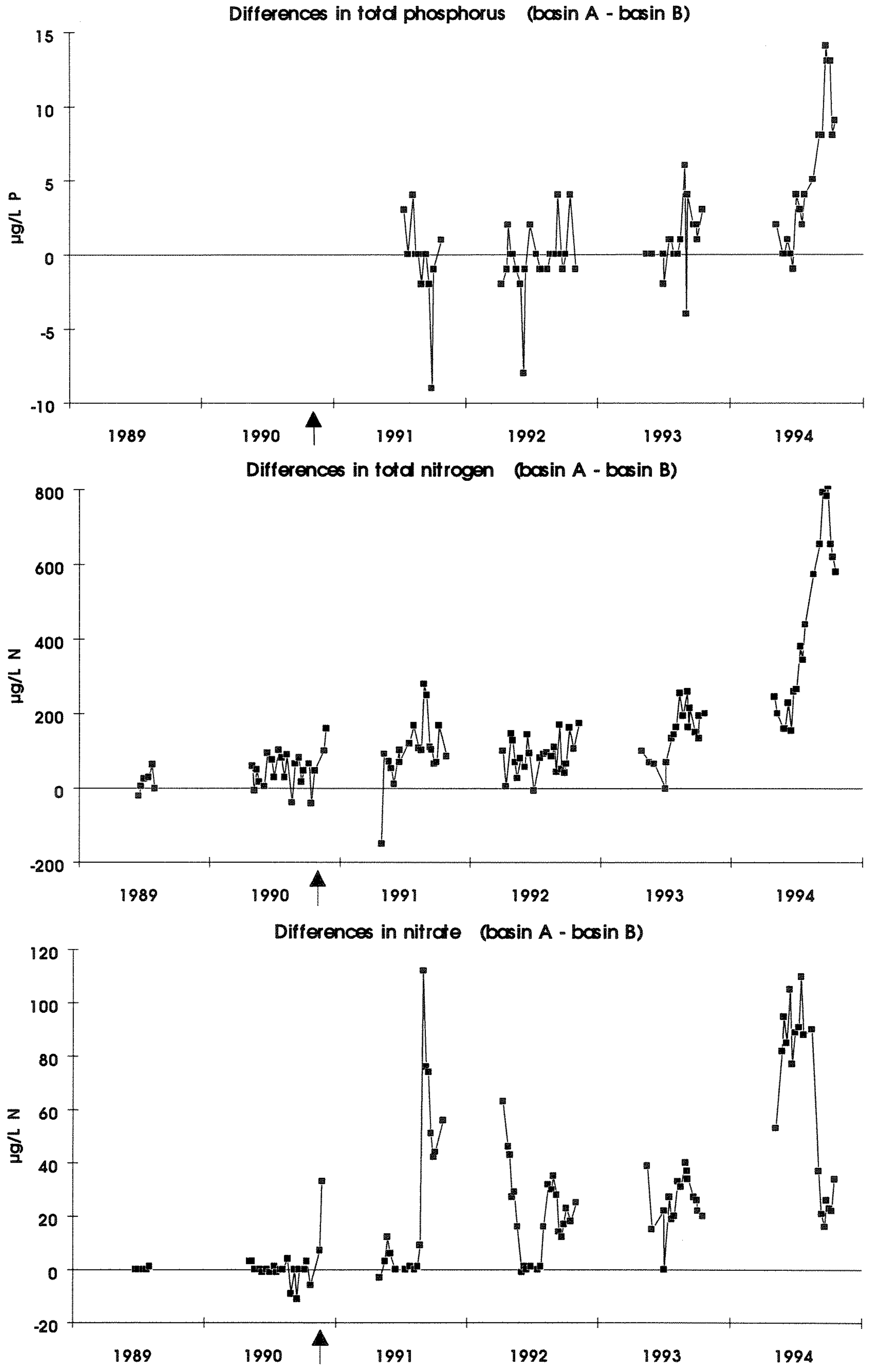


Fig.4 Differences in total phosphorus, total nitrogen and nitrate between the two basins in lake Skjervatjern, 1989-94. ↑ Start of acidification of Basin A.

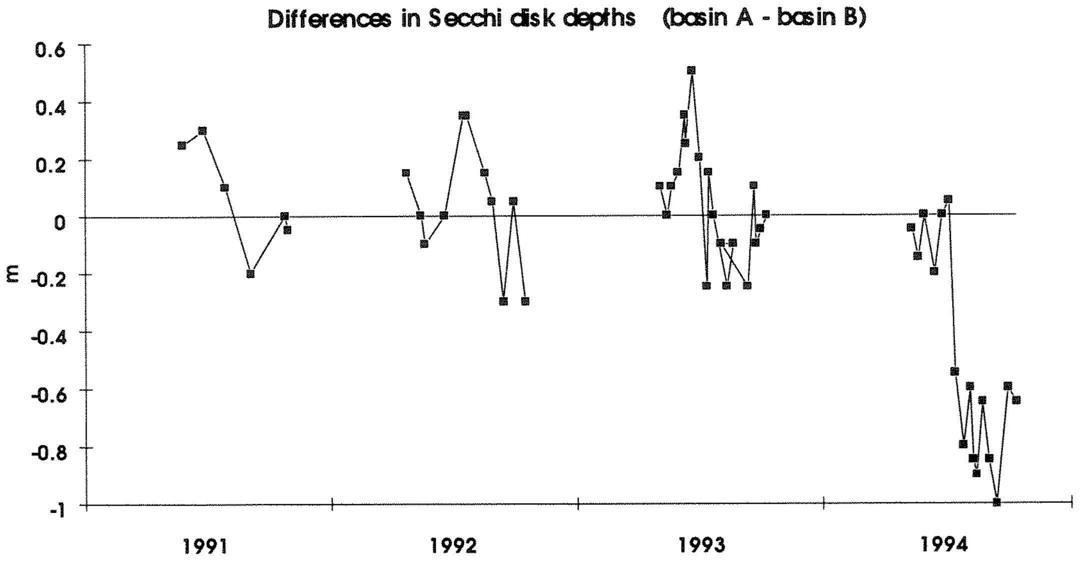


Fig.5 **Differences in Secchi disk depths between Basin A and Basin B in the treatment period of Basin A, 1989-94.**

THE REFISH (RESTORING ENDANGERED FISH IN STRESSED HABITATS) PROJECT, 1988-1994

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Abstract. The REFISH (Restoring Endangered Fish In Stressed Habitats) Project was established in 1988 to assess acid-tolerance among indigenous Norwegian strains of brown trout. The work, comprising both laboratory and field studies, has involved the restocking and subsequent test-fishing of thirteen lakes with five brown trout strains. There was considerable variation in the ability of individual lakes to support adult trout. This did not appear related to ANC (acid neutralising capacity) or any single chemical factor. One strain, Bygland, was found to be relatively acid-tolerant, accounting for more than 60% of all fish recaptured by test-fishing over 1990-1994. This is consistent with better survival of young life-stages of the Bygland strain, compared with that of the other strains, in laboratory experiments employing acidic conditions. Strain-specific differences in calcium metabolism may be the physiological basis for acid tolerance.

1. Introduction

Many lakes in southern Norway are acidic and are unable to support brown trout, *Salmo trutta* L., the dominant fish species. Many other lakes have water qualities which are marginal for trout survival (i.e. they have low pH, low calcium (Ca) concentrations and elevated concentrations of inorganic aluminium (Al_i)).

Biological recovery, or improvement in water quality, of acidified lakes and other surface waters is possible (Wright & Haus, 1991) but is predicted to be a long process (Christophersen *et al.*, 1990, Wright *et al.*, 1991, Warfvinge *et al.*, 1992, Skeffington & Brown, 1992).

In the meantime, liming to reduce acidity is currently the most commonly used method for restoring (or protecting) fish populations in acidified surface waters (Hindar & Rosseland, 1991). This is costly and has to be repeated in order to remain effective. An additional method of fishery restoration might be to restock acidified lakes with relatively acid-tolerant strains of brown trout.

Differences in salmonid acid tolerance are well documented (Jensen & Snekvik, 1972; Grande *et al.*, 1978; Rosseland & Skogheim, 1984). Laboratory work has shown strain-specific acid tolerance in brook trout, *Salvelinus fontinalis* (Robinson *et al.*, 1976) and brown trout (Gjedrem, 1976, 1980; McWilliams, 1980, 1982; Rosseland & Skogheim, 1987; Swarts *et al.*, 1978; Turnpenny *et al.*, 1988). Studies employing both laboratory experiments and long-term field trials have, however, been lacking. The REFISH (Restoring Endangered Fish In Stressed Habitats) Project started in 1988 with the intention of assessing, through laboratory experiments and field work, acid tolerance in indigenous Norwegian strains of brown trout.

Results from the laboratory experiments and field work have been reported in internal reports of the sponsoring agencies. For example, Sadler & Lynam (1989a, b), Dalziel & Lynam (1991, 1992, 1993) - laboratory work, and Rosseland *et al.* (1990), Kroglund *et al.* (1992) and Rosseland (1994) - field work. This paper provides an overview of data collected for the Project over 1988-1994.

2. Materials and methods

The five strains of trout chosen for the study were selected from populations inhabiting waters covering the range of chemical conditions encountered in southern Norway. The strains are known as *Tunhovd* (from the high mountain Lake Tunhovd), *Fossbekk* (from Fossbekken Brook), *Bygland* (Lake Byglandsfjorden), *Bustul* (Lake Bustul/Oyevatn) and *Gjedrem*, a product of a selective breeding programme to select acid tolerant trout involving 250 strains from southern Norway (Gjedrem, 1980).

Laboratory experiments using ranges of pH, Ca concentration and Al_i concentration, were conducted in the UK over 1988-1992 using imported eyed eggs and fry of the five strains. The experiments were conducted in a temperature-controlled room and involved the use of flow-through systems with artificial soft water media to simulate as closely as possible field water qualities. In addition to obtaining survival data, sublethal effects on whole body mineral concentrations and extent of skeletal calcification were also assessed (Sadler & Lynam, 1989a, b; Dalziel & Lynam, 1991, 1992, 1993).

For field trials, thirteen lakes in three regions in southern Norway were selected for restocking and subsequent test-fishing. All lakes had lost their native fish populations of perch (*Perca fluviatilis*) and brown trout since the 1970s. The three regions are known as *Birkeland*, *Lyngdal* and *Valle/Njardarheim*.

Restocking of the lakes commenced in September 1988 and was subsequently repeated at the same time each year to 1992. First year (0+) fish (4-5 cm) of the five strains were stocked on each occasion, based on lake size. Fish of each strain were fin-clipped in a specific way to allow strain identification of those caught subsequently by test-fishing.

Test-fishing, using gill nets, commenced in 1989 and continued at the same time in each subsequent year, following the procedure employed in the SNSF Project (Rosseland *et al.*, 1979, 1980) and the Norwegian Monitoring Programme (SFT, 1983). Data were collected on numbers of fish of each strain caught (from fin-clipping), length, weight, sex, stage of sexual maturity, flesh colour and degree of stomach fullness. Samples of scales and otoliths were taken to assess fish ages, and samples of stomach contents for eventual dietary composition analysis.

Water samples from the lakes were collected periodically (biweekly or monthly for most lakes, except in the Valle/Njardarheim region: three or four times per year), and sent immediately to NIVA at Oslo for analysis.

3. Results

The laboratory experiments (Sadler & Lynam, 1989a, b; Dalziel & Lynam, 1991, 1992, 1993) showed the Bygland strain to be consistently more acid-tolerant than the other strains. The extent of skeletal calcification of the developing Bygland strain fry was, however, always less than that of the other strains, irrespective of pH. Conversely, Tunhovd strain fry consistently showed the most advanced calcification of any strain but, under acidic conditions, very poor survival.

A total of 479 fin-clipped brown trout were caught in the thirteen lakes over 1990-1994, comprising 62% Bygland, 20% Gjedrem, 8% Bustul, 5% Fossbekk, and 4% Tunhovd. Table I shows the numbers of fish of each strain caught in each lake. The most successful lake, in terms of recaptures was Mjåvatn (Lyngdal region), which yielded 25% of all fish caught.

TABLE I

Numbers of fish of each strain caught, 1990-1994

(Region) Lake	Bygland	Gjedrem	Fossbek	Bustul	Tunhovd	Σ
(Birkeland)						
Repstadvatn	17	4	0	3	0	**24**
Barkevatn	25	9	4	8	3	**49**
Mørkelivatn	0	0	0	0	0	**0**
(Lyngdal)						
Homsvatn	12	3	0	1	0	**16**
Mjåvatn	85	19	5	8	3	**120**
Skjekelivatn	22	12	2	7	3	**46**
Sandvatn	48	15	4	4	6	**77**
Trollselvvatn	2	2	0	0	0	**4**
(Valle/Njardarheim)						
Rennevatn	0	0	0	0	0	**0**
Hyttetjørni	0	0	0	0	0	**0**
Skammevatn	2	1	0	0	0	**3**
Kringlevatn	33	9	0	3	0	**45**
Smalevatn	52	22	10	6	5	**95**
Totals	**298**	**96**	**25**	**40**	**20**	**479**

All fish caught had been feeding well and were in good condition, in terms of length, weight and flesh consistency and colour. Older fish were sexually mature and some had evidently spawned in the previous autumn.

Mean lake water chemistry data are shown in Table II.

TABLE II

Mean lake water chemistry, September 1988 - December 1994

(Region) Lake	pH	$[Ca^{2+}]$ mg/l	$[Al_i]$ μg/l	[TOC]* mg/l	[ANC]+ μeq/l	n
(Birkeland)						
Repstadvatn	4.8	1.02	170.9	2.49	-34.8	113
Barkevatn	4.7	1.03	159.0	3.69	-29.8	115
Mørkelivatn	4.6	0.68	166.9	4.29	-38.7	117
(Lyngdal)						
Homsvatn	4.8	0.56	97.4	1.93	-28.7	57
Mjåvatn	4.7	0.60	52.7	4.97	-9.5	58
Skjekelivatn	4.7	0.48	63.6	3.69	-22.0	58
Sandvatn	4.7	0.50	63.7	3.99	-19.5	58
Trollselvvatn	4.5	0.35	55.9	4.89	-22.0	61
(Valle/Njardarheim)						
Rennevatn	5.2	0.44	135.8	0.46	-17.5	18
Hyttetjørni	5.1	0.29	80.6	0.50	-18.9	24
Skammevatn	5.3	0.37	67.4	0.38	-10.1	21
Kringlevatn	5.2	0.33	51.1	0.42	-12.6	27
Smalevatn	5.2	0.29	53.2	0.75	-12.3	29

*Total organic carbon concentration
+Acid neutralising capacity

4. Discussion

ANC is used to classify lakes according to their ability to support fish. An ANC of 20 μeq/l is proposed as an acceptable limit for fish in Norwegian freshwaters (Lien *et al.*, 1992). However, the fact that fish survive in most of the thirteen lakes used in the REFISH Project, particularly in Repstadvatn, Barkevatn and Homsvatn (Tables I and II), suggests that ANC may not be a sufficient measure of whether fish can be supported. The REFISH Project data suggest that no single chemical factor is adequate to explain the occurrence or absence of fish. Instead, this seems to be lake-specific and is determined by several factors including pH and concentrations of Ca and/or Al_i.

Differences in strain-specific acid tolerance in brown trout have been reported by Brown & Lynam (1981), Turnpenny *et al.* (1988), Gjedrem (1976, 1980), McWilliams (1980, 1982), Rosseland & Skogheim (1987) and Swarts *et al.* (1978). The REFISH Project results over 1990-1994 demonstrate marked differences in acid tolerance between strains of Norwegian brown trout, with one strain, Bygland, being markedly superior compared with the others.

Sayer *et al.* (1993) discuss possible reasons for strain-specific acid tolerance, suggesting that fertilization and hardening of eggs in hard hatchery water prior to introduction into soft, acid water may lead to greater chance of survival than if fertilization occurred within treatment. The water quality of origin of a particular strain, rather than hatchery water, may also be important. So, too, may be the maternal contribution to the mineral and nutrient stores of each individual. In most years, all the strains used to stock the different lakes were raised from the eyed egg stage to summer-old fry in the same hatchery (OFA Fish Farm). Since most of the pre-stocking history is identical, the significant differences in lake survival most probably are due to genetic differences in tolerance.

The laboratory experiments showed fry development, in terms of skeletal calcification, to be most advanced in the Tunhovd strain. However, Tunhovd also consistently demonstrated poor acid tolerance and provided only 4% of fish caught by test-fishing. Conversely, Bygland fry showed less advanced development with age than fry of the other strains, but greater acid tolerance; Bygland fish accounted for 62% of all fish caught. It might be that acid tolerance in the Bygland strain arises through more body calcium being utilized in gill membrane integrity (rather than in skeletal calcification), thus helping to protect against the effect of acidity increasing the rate of passive ion loss to the external medium. McWilliams (1982) demonstrated that trout from a population inhabiting low pH, low Ca, water (similar to the water of origin of the Bygland strain) had much lower gill permeability to H^+ and Na^+ ions (i.e. increased gill membrane integrity), than that of another population from higher pH, higher Ca concentration water.

In addition to continuing to collect data on adult fish survival, the Project is currently focusing efforts on assessing the reproductive success of the strains. Over the last two winters, freshly fertilised eggs have been planted out in mesh egg boxes in tributary streams. Data from this work should be reported shortly.

5. Conclusions

Lake ANC may not be the most important chemical factor determining adult trout survival. Rather, this appears to be lake-specific and determined by several factors including pH and concentrations of Ca and/or Al_i.

The Bygland strain is significantly more acid-tolerant than the other strains assessed in the REFISH Project. Laboratory survival experiments corroborate this. Strain-specific differences in Ca metabolism may be the physiological basis for acid tolerance.

Restocking with relatively acid-tolerant strains of trout may offer a useful fishery management tool in areas with acidic waters in which fisheries have been lost. Further data are required, however, on survival throughout the complete life-cycle.

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LAND USE & DEPOSITION INTERACTIONS: AN EVALUATION OF THE EFFECTS OF FUTURE N DEPOSITION SCENARIOS ON THE GALLOWAY REGION OF SW SCOTLAND USING A COUPLED SULPHUR & NITROGEN MODEL (*MAGIC-WAND*).

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Abstract: The Galloway region of Southwest Scotland has been subject to decades of acidic deposition which has resulted in damage to soils, surface waters and aquatic biota. A survey of lochs was conducted in 1979, 1988, and 1993, over which time there have been dramatic changes in total sulphur and nitrogen deposition. The MAGIC model successfully reproduced the major chemical changes in water chemistry from 1979 to 1988 during which time there was a rapid decline in sulphur deposition. A new coupled sulphur and nitrogen model (MAGIC-WAND) has been used to evaluate the regional hydrochemical response to changing patterns of N & S deposition from the period 1988 to 1993. Details of the model structure and parameterisation are discussed. The model under-predicts the response of non-marine sulphate in the region suggesting that there has been a slight increase in deposition over this period. Future hydrochemical responses to different nitrogen deposition scenarios are presented, indicating that the potential increase of nitrogen in surface waters is closely linked to the age and extent of different mosaics of commercial afforestation within the individual catchments.

1. Introduction

The Galloway region of south-western Scotland is characterised by highly siliceous granitic bedrock covered by thin, patchy, organic rich and generally acidic soils which offer only a limited ability to neutralise acid inputs from the atmosphere. Long-term deposition of acidic compounds in the region has caused changes in hydrochemistry and extensive damage to fish and aquatic organisms (Flower and Battarbee, 1983; Harriman et al. 1987). Extensive commercial forestry development in the area since 1940 has exacerbated the problem; the growing forests scavenge pollutants from the atmosphere, alter catchment hydrology, and draw base cations from the soil (Cosby et al., 1990; Jenkins et al., 1990).

The acidifying effects of sulphur and nitrogen from the atmosphere are a function of the mobility and retention of these anions in the ecosystem. Changes in sulphur deposition appear in the hydrochemical signal rather quickly, especially in highly impacted systems. Nitrogen on the other hand, shows a much more complex pattern of response. Nitrogen is generally retained in terrestrial systems, particularly young coniferous forests, largely because it is a growth-limiting nutrient. However chronic elevated levels of nitrogen deposition can produce quantities of inorganic nitrogen in soils in excess of that required by the biota for growth. The unassimilated nitrogen can be leached from soils and appears as nitrate in surface and groundwater runoff. The determination of the exact processes responsible for this net ecosystem loss of nitrogen are difficult to quantify, with the best available information on the magnitude and timing of nitrogen saturation and retention coming from empirical observations (Dise and

Wright 1995). Emmett et al., (1993) indicated that for forest stands of Sitka spruce in Wales, nitrogen in surface water was related to the age of the forest in the catchment, with a linear pattern of breakthrough of nitrogen observed in forest stands greater that 20 years of age. It is proposed that this was due to a reduction of ecosystem utilization of available nitrogen during forest maturation.

The importance of land-use interactions in the Galloway region has been evaluated using the Model of Acidification of Groundwaters In Catchments (MAGIC) (Wright et al. 1994). The regional simulation analysis illustrated the separate and combined effects of different land-use and deposition scenarios. A key element of this analysis was the incorporation of spatial and temporal data for historical and potential future strategies of afforestation. This previous analysis was based on the response to altered sulphur deposition which represented the largest decline in total acid loading to the region between 1979 and 1988. However given the importance of temporal behaviour of forest ecosystems, the current and future response to nitrogen deposition requires further investigation. The hydrochemistry of individual catchments and within the region as a whole, may be influenced by the age and extent of commercial forestry.

Afforestation in the Galloway region peaked between 1965 and 1970. In the Forestry Commission census of 1980, the average extent of land under trees in the Dumfries and Galloway region was 21%. Fully 29% of the area of the catchments of the loch studied are forested. A major feature of Scotland's and Galloway's commercial forests is the predominance of younger age classes. At the time of the 1980 census, 30% of the area of forest was less than 10 years old, 56% was less than 20 years old, and about 75% less than 30 years.

This paper describes (1) the regional parameterisation of the MAGIC-WAND model, (2) the observed changes in water chemistry between 1979, 1988, and 1993, and (3) the prediction of nitrogen 'breakthrough' given alternative scenarios of future sulphur and nitrogen deposition.

2. Materials and methods

2.1 The MAGIC-WAND MODEL

The Model of Acidification of Groundwaters In Catchments With Aggregated Nitrogen Dynamics (MAGIC-WAND) represents an extention to the MAGIC model to incorporate the major nitrogen fluxes and their changes through time. The key soil chemical processes lumped at the catchment scale to simulate soil and water chemistry consist of; (1) soil-soil solution equilibria equations in which the chemical composition of soil solution which is assumed to be governed by simultaneous reactions involving sulphate adsorption, cation exchange, dissolution and precipitation of aluminium, and dissolution of inorganic carbon, and (2) mass balance equations in which the fluxes of major ions to and from the soil and surface waters are assumed to be governed by atmospheric inputs, mineral weathering, net uptake in biomass, and loss in runoff (Cosby et al. 1985a, 1985b). In MAGIC-WAND the nitrogen dynamics are fully coupled to the existing sulphur driven model (Figure 1).

MAGIC-WAND considers two species of inorganic nitrogen, nitrate (NO_3) and ammonium (NH_4). Both species are assumed to be present only in soil water. The model explicitly incorporates the major terrestrial fluxes of nitrogen, such that;

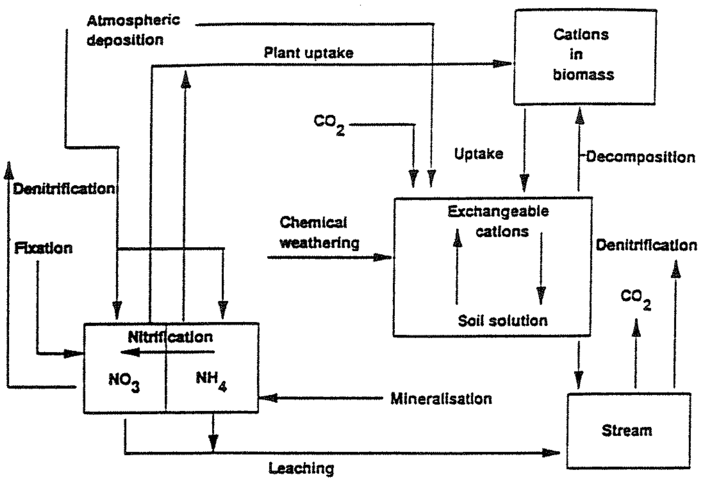

Fig. 1. Schematic representation of the major processes and stores in MAGIC-WAND

NO_3 leaching = deposition + nitrification + external addition - uptake - denitrification, &
NH_4 leaching = deposition + external addition + mineralisation - nitrification - uptake.

If the net result of these fluxes is positive (surplus NO_3 and/or NH_4), leaching to surface waters occurs. Nitrogen inputs to the system are in the form of inorganic nitrogen added to soil solution. Mineralisation in the model represents the release of inorganic N that was formerly bound in organic matter, and the mineralisation product is NH_4. Nitrogen losses from the model system are as inorganic nitrogen, and the primary output is hydrologic runoff from the soils. The runoff fluxes are calculated as the product of the simulated concentrations of NO_3 and/or NH_4 at any time step and the hydrologic discharge at that time. Provision is also made in the model for other losses of inorganic nitrogen, such as denitrification from soil or surgface water. The magnitude and timing of these additional outputs of N may be specified a priori or they may be keyed to external inorganic nitrogen concentrations using first order reactions. The microbial mediated transformation of NH_4 to NO_3 (nitrification) is represented in the model by a first order reaction such that the rate of loss of NH_4 (equal to the rate of production of NO_3) is given by the product of a rate constant and the concentration of NH_4 at each time step.0

Plant uptake is modelled as a non-linear process that depends upon the the concentration of available NH_4 and NO_3. The equation is hyperbolic (representation of a typical Michaelis-Menten uptake function) such that;

$$d(N)/dt = K_{max} * ((N) / (K_{1/2} + (N))), \text{ where,}$$

(N) is the concentration of either NH_4 or NO_3, K_{max} is the maximum uptake rate ($meqm^{-3}yr^{-1}$), and $K_{1/2}$ is the half-saturation constant of the reaction ($meqm^{-3}$). The values of K_{max} and $K_{1/2}$ can be varied through time *a priori*, to represent the dynamics of ecosystem response to available nitrogen.

2.2 REGIONAL PARAMETERISATION OF THE MAGIC-WAND MODEL

Calibration of the nitrogen dynamics requires selection of values for the rate constants and to describe the uptake function. In this curent application, rates of mineralisation, denitrification, and fixation were set to values derived from the literature (Emmett et al., 1995; Gosz 1981). The uptake function is the single most important process in MAGIC-WAND for producing breakthrough in response to increased deposition, or a reduction in ecosystem utilization. It is possible to set realistic values of K_{max} and $K_{1/2}$ when (i) the selection of half saturation is not too high as to cause historical breakthrough at a site where this is not presently occuring, (ii) the selection of maximum uptake rates is greater than the sum of the external sources when nitrogen concentrations in surface waters are low. For the purposes of this regional analysis, the half-saturation constant was set to a fixed value for all catchments relative to the current N concentration in deposition, while the determination of K_{max} was done on an individual catchment basis such that output matched observed behaviour, for both forested and moorland catchments.

The effect of forest maturation on the temporal response of K_{max} was represented assuming a linear decline in K_{max} to 70% of maximum value from year 20 to 50. Fifty years is the normal rotation length for commercial forests in the region. The determination of the temporal response of individual catchment K_{max} values represents the spatial integration of a mosaic of different age and extents of plantations.

For the determination of the response to altered nitrogen deposition, three future 50 yr scenarios affecting the region were selected, (i) no change, (ii) step change to half of current deposition values, and, (iii) a doubling of present day deposition. Sulphur deposition was set to that predicted by the HARM model for the Galloway region. Namely, 52% of 1990 values by 2005, with a further reduction to 44% of 1990 values by 2010, then constant to 2038. Land use change was selected as a 'steady state' , where foresest are harvested at year 50, and then replanted to the same extent. There was no regional increase in the total amount or distribution of forests.

3. Results and Discussion

There was a substantial reduction in observed non-marine sulphate in the lochs of the region from 1979 to 1988 (Figure 2). The decline in strong acid anions was comnpenated in part by decreases in concentrations of base cations from 155 to 90 μeql^{-1} and in part by increases in ANC (Wright et al., 1994). However between 1988 and 1993 there was no continuation of recovery in water quality throughout the region. Because of the rapid response in chemistry in relation to a deposition reduction in the precceding nine years, this would suggest that there was no regional reduction in deposition of strong anions from 1988 to 1993. This is confirmed when the modelled response of non-marine sulphate is compared to that measured in the lochs in 1993 (Figure 3). Deposition was held constant in the model for the period 1988 to 1993, however, the model consistently under-predicts the observed data. This confirms that there has not been a continued reduction of sulphur deposition in the region, over the five years from 1988 to 1993. Future responses to different nitrogen deposition scenarios have been calculated assuming that there will be a further reduction in sulphur

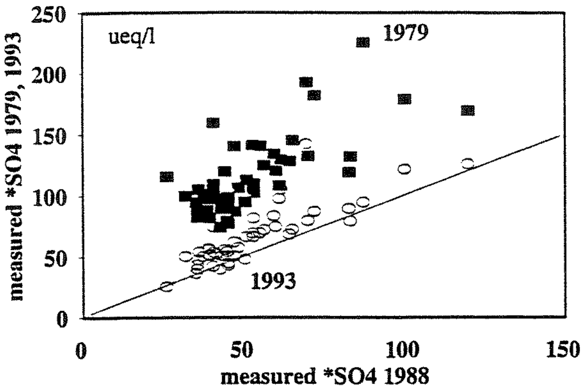

Fig. 2. Measured non-marine sulphate in lochs of the Galoway region. Surveys were carried out in 1979, 1988, and 1993.

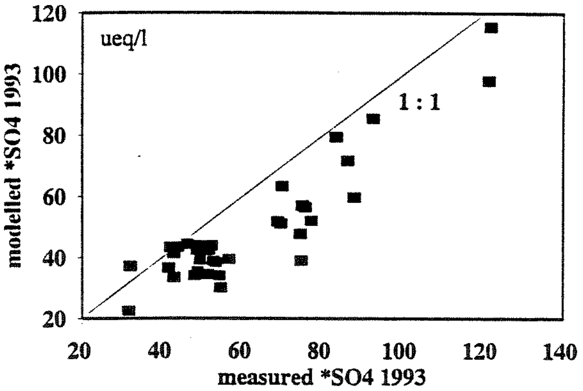

Fig. 3. Comparison of model predicted non-marine sulphate assuming no decrease in S deposition (1988-1993), and measured concentrations in loch waters in Galloway.

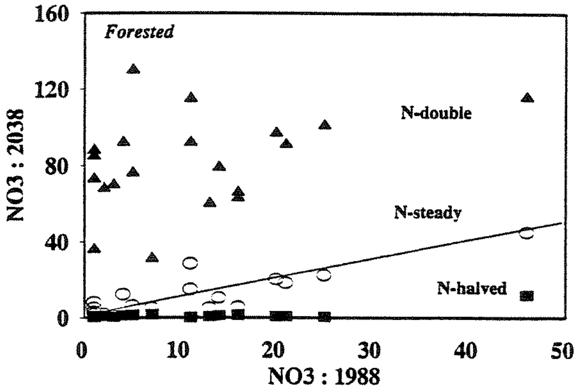

Fig. 4. Predicted loch concentration of nitrate in 2038 for the forested catchments in Galloway, under three different scenarios of nitrogen deposition.

deposition in the region . Results of this analysis, indicate the importance of temporal trends in the response of forests to nitrogen deposition (Figure 4), and the role of spatial integration. Should there be a reduction in deposition to half that of present day then the observed concentration in loch water will be substantially reduced to low background levels (<5 μeql-1). As forests mature then ecosystem retention of nitrogen declines and the magnitude of the response is a function of the age and extent of different plantations within individual catchments. Currently replanting maturing forests at 50 yrs of age increases the value of K_{max} and should increase the potential for N retention (Figure 4). However, there is clear evidence of breakthrough in some of the catchments under a steady state nitrogen deposition scenario; these catchments being characterised by large amounts of maturing afforestation (regional mean nitrate concentration increases by c.20%). The response is further amplified when deposition is increased, but under this higher deposition all catchments leach nitrate to surface waters (mean regional concentration represents a 4-fold increase in NO_3). The high degree of regional variability reflects the interaction of ecosystem demand, altered hydrology, and increased interception of N species as different areas of the catchments are replanted, and mature by 2038.

In summary, regional protection of water resources can only be achieved with a continued reduction in sulphur and nitrogen load, if the substantial regional recovery between 1979 and 1988 is to be maintained. The interaction of afforestation and deposition have successfully been modelled using both MAGIC and MAGIC-WAND, and the results suggest that the catchment based processes included in these models are robust enough such that long-term predictions can be made (Wright et al., 1994). This analysis has also highlighted that MAGIC-WAND provides an unique tool for the determination and selection of optimal land management strategies given changes in the deposition of sulphur and nitrogen. The integration of spatial data at the catchment scale is a fundamental element to the success of this approach.

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PREDICTING FISH STATUS FROM WATER CHEMISTRY OF NORWEGIAN LAKES

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Abstract. This study is based on data from the "1000 lake survey", a combined fish-status/water-chemistry survey carried out by the Norwegian Institute for Water Research in 1986. A principal component analysis (PCA) showed 3 factors to describe most of the variation in the environmental variables studied: an acidification factor containing ANC, pH and labile aluminium (Al_i); a humic-complexation factor containing non-labile aluminium (Al_o) and total organic carbon (TOC); and a geological derived factor, containing the calcium concentration and the ionic strength of lake water. A logistic regression showed that the acidification factor and the geological factor together were well suited to predict changes in fish status. A logistic regression with fish status on ANC, had a slightly lower prediction power than the PCA-regression. Initial biological effects of acidification were found at ANC-values about 20 μeq/L, but perch (*Perca fluviatilis*) was far more resistant towards acidification than brown trout *(Salmo trutta)* and arctic char (*Salvelinus alpinus*). To better relate fish status to the most important chemical variables regarding fish physiology, a model containing Al_i, pH, Ca and ionic strength was tested. pH had the strongest effect, although Al_i represents the primary toxic factor. Ionic strength seemed to have a detoxifying effect, whereas Ca did not significantly improve the model. This model had a predictive power similar to the ANC model. Our main conclusions are that ANC is well related to fish status in Norwegian lakes, and that ionic strength affects fish status in acidified waters.

Key words: acidification, aluminium, calcium, fish, ionic strength, toxicity, water chemistry.

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RESPONSE OF ZOOPLANKTON, BENTHOS, AND FISHES TO ACIDIFICATION: AN OVERVIEW

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Abstract: This paper presents an overview of the response to acidification of aquatic fauna with special emphasis on zooplankton, benthos, and fishes. Changes in behavior, body chemistry, reproduction, and species diversity are presented based on laboratory experiments and field studies in both Europe and North America. Differences in species sensitivity are discussed as they relate, not only to acidification but also to low calcium concentrations in the water, elevated aluminum concentrations, and presence of naturally occurring organic acids. The mechanisms—behavioral, physiological and ecological—enabling aquatic fauna to survive in acidified waters are discussed.

Key Words: fish, invertebrates, osmoregulation, ionoregulation, aluminum, calcium, organic acids, low pH, acid lakes, refugia, mixing zones

1. Introduction

The environmental problem of aquatic acidification involves effects on organisms at all trophic levels. Early studies focused on the loss of fish populations, especially the salmonids. Later studies reported that zooplankton, insect larvae, benthic invertebrates, especially crayfish, snails and freshwater mussels, are sensitive and are often reduced or absent from acidified lakes and streams (see review by Havas 1986a). Water hardness, represented by the calcium concentration, significantly affects the distribution of species and their ability to survive in acidified environments. Early studies that failed to report water hardness or those that used hard water for bioassays often report considerably higher tolerance to acid than is observed in nature. Aluminum, leached by acid precipitation from the drainage basin, complicated the picture considerably since the various forms of aluminum differ in their toxicity. Aluminum and hydrogen ions interact both synergistically and antagonististically depending on conditions (Muniz and Leivestad 1980, Havas 1985, Herrmann 1993, Rosseland and Staurnes 1994) and, in the presence of naturally occurring organic acids, aluminum toxicity can be neutralized.

The importance of these water quality variables emerged as scientists across two continents tried to understand why some circumneutral lakes are almost devoid of life while other, more acidic lakes are teaming with life. In an attempt to explain apparent discrepancies the importance of water quality, especially pH, Ca, Al, and organic acids became better understood.

CRITICAL WATER QUALITY

SAFE PLACES (REFUGIA): CHRONIC TOXICITY

Other discrepancies in the presence and distribution of species began to emerge that could not be explained by surface water quality. Fishes, in particular, and possibly other species, can sense the pH of their environment in so far as they can avoid areas of low pH. Since water quality parameters in lakes are seldom uniform from top to bottom, organisms that are mobile and can sense the pH of their environment can move to more favorable areas. These refugia can be found just above or within the top few cm of sediments, in sheltered bays among macrophytes, or in areas that receive alkaline inputs from surface or groundwater drainage. Hence we learned that spatial distribution of pH and other water quality parameters was important for explaining the presence/absence of species within spatially heterogeneous environments. Often symptoms of stress in these environments resembled chronic toxicity.

TOXIC PLACES/EVENTS (EPISODES AND MIXING ZONES): ACUTE TOXICITY

Just as spatially heterogeneous environments or refugia enable some species to survive in otherwise unfavorable chemical conditions, temporal heterogeneity often has the opposite effect. During periods of high runoff, following spring snow melt, autumn or summer showers, waters of different chemical composition come together to produce chemically distinct episodes. When acid, Al-rich water mixes with alkaline water Al precipitates as $Al(OH_3)$. This precipitate can then accumulate on the gills and filtering apparatus of aquatic organisms causing acute toxicity. Since aluminum hydroxide is an insoluble precipitate it will eventually settle or otherwise be removed from the water column hence this acute toxicity is short-lived and limited in space. Even short-term exposure, in the matter of a few hours and, in some cases, a few minutes, can be lethal.

The consequences of acidic episodes, particularly spring snow melt, have been well documented. Mixing zones, however, have received less attention despite the fact that they can be acutely toxic to aquatic biota. This appears at first to be a contradiction to the concept of refugia. Whether an area of acidic water that comes in contact with alkaline water is a safe haven or a toxic zones depends on many parameters but one of the most important may very well be the amount and form of Al produced at the boundaries.

BIOCHEMICAL/PHYSIOLOGICAL STUDIES

SENSITIVE SPECIES

We learned from the early studies that some species are particularly sensitive to acid water, these include Atlantic salmon (*Salmo salar*), Brown trout (*Salmo trutta*), Arctic char (*Salvelinus alpinus*), and among the invertebrates gastropods, crustaceans, and some species of insect larvae (Havas 1986a). Much of this sensitivity could be explained by biochemical/physiological failures to regulate osmotically essential ions. Interestingly, the biochemical/physiological response of fishes and invertebrates is similar. The identification and understanding of these failures became of fundamental importance for predicting future changes related to reductions/increases in pollution loads and to the optimalization of mitigation techniques in relation to recolonization, liming, and restocking strategies. For the ecophysiologist, the key focus was to identify these biochemical/physiological failures, and thereby contribute to the explanation of the decline or disappearance of biota in acidic waters.

Attention has also been paid to mechanisms of acid-resistance or acid-tolerance. At the individual level the effects of chemical toxicants can be reduced in a number of ways (Calow 1991) including avoidance or escape reactions; exclusion (e.g. excretion of more mucous onto exposed surfaces of aquatic animals); removal (in-coming toxicants might be actively pumped out); neutralization (i.e. by complexation with protective proteins, e.g. metalothionins); excretion, and/or repair of damage caused by the toxicant.

SENSITIVE LIFE STAGES AND LIFE PROCESSES
A life history study of fish populations and other aquatic biota in a lake undergoing acidification, involves all the physiological mechanisms in the area of toxic effects and resistance. All temporary and chronic changes in water chemistry can have different impacts on organisms and populations depending on species and the life history stages represented. For fish, the previous acid-acclimation history, year class composition, the population size, spawning strategy and spawning facilities as well as competition between other fish species in the lake are also important. Controlled, short-term, laboratory studies, which have given us most of the detailed insight into the complex chemistry involved, can represent only a small fraction of what happens in nature. As we discover the complexities of nature we become aware of the limitations of these short-term laboratory studies. However, it is these very limitations that provide us with clues that enable us to see a larger portion of the whole picture.

The purpose of this paper is to provide an overview of the research on the response of fishes and aquatic invertebrates to airborne acid deposition and the subsequent acidification of freshwater systems. Special emphasis is placed on biochemical and physiological responses.

2. Critical Water Quality

Today, the three elements, hydrogen ions (pH), aluminum (Al), and calcium (Ca), are still considered to be of most importance for the toxicity of acid water to freshwater biota (reviewed by Havas 1986a, Wood and McDonald 1987, Rosseland et al. 1990, Rosseland and Staurnes 1994).

The effects of H^+ and Al are dependent not only on animal species, but also on the life history stage of the animals and previous acclimation history. In the field, the effects of Al alone are difficult to isolate from a variety of potentially interrelated adverse factors. During episodes of high water flow, and in lakes and streams where different water qualities mix, large variations in pH, Al-species, Ca and other ions and metals, and organic substances occur (Henriksen et al. 1984, Lydersen et al. 1994, Skogheim et al. 1984). When pH of an acidic water body increases, for example, or when acid Al-rich water mixes with limed or neutral water, low molecular inorganic forms of Al are transformed to high molecular weight forms and hence precipitate. In such mixing zones, rapid Al-precipitation onto fish gills and the filtering apparatus of invertebrates, combined with osmoregulation failure, inhibition of enzyme activities, and gill lesions have been observed. Hence, water in the mixing zone is often more toxic than the original acid water (Rosseland et al. 1992, Poléo et al. 1994), and in rivers fish seems to avoid or have disappeared from such areas (Åtland and Barlaup 1995).

The situation is made even more complex by the fact that the organisms themselves can influence their chemical micro environment near their body surface (see Exley et al. 1991). The basic chemistry of the external water may not necessarily represent the true toxic components relevant to the organism. Our knowledge about an exact chemical threshold level for a certain physiological response, might therefore be based on wrong assumptions.

Calcium has a fundamental biological importance for water breathing animals and plays a key role in membrane permeability. In many acidified areas, the Ca concentration is so low that it is close to the concentration limit for snails and mussels and even for the softwater-tolerant salmonid species. In such areas, one must be aware of any substance that can have an adverse effect on Ca metabolism.

ENVIRONMENTAL VARIABILITY

STREAMS

Streams are spatially heterogeneous and temporally dynamic environments and many of the organisms that inhabit streams have learned to tolerate or adapt to the constant chemical fluxes. When the chemical stress becomes extreme, many invertebrates can avoid the stress by drifting down stream to more favorable conditions. Fishes, that require first order streams to spawn in the spring or fall are not nearly as fortunate and often find themselves moving into more and more acidic and hence unfavorable environments. In the event that adverse chemical conditions of low pH and elevated Al concentrations persist downstream and avoidance is not possible, the consequence can be seen as massive fish kills and the loss of the invertebrate population.

LAKES

In lake systems there are more escape possibilities than in rivers for fishes. In accordance with this, massive fish kills have primarily been reported from rivers and brooks. Most brown trout populations spend their early low mobility stages in brooks and streams. Thus, the effects on these stages seem to be the most important for the fish decline. River-dwelling species/stocks have very restricted escape possibilities, and this fact renders them especially vulnerable to acidic waters. For anadromous fish the situation is even worse since they have the smolt stage that is extremely sensitive to acidic waters.

Invertebrates can minimize exposure to stressful water quality in lakes by living close to the water/sediment interface where the sediments offer some buffering. They can also drift to more favorable conditions among macrophytes and filamentous algae that can increase the pH of the surrounding medium as they photosynthesize.

ESTUARIES

For the anadromous fish populations, the situation is more complex, and effects on older life history stages are possibly of greater importance. The smolt stage is considered to be the most sensitive one, especially for Atlantic salmon, but spawning fish also have a low tolerance (see reviews by Rosseland 1986, Rosseland et al. 1990). During the short smoltification period when the bottom-dwelling and territorial freshwater parr change to become smolt prepared for a pelagic marine life, the gill epithelium gradually change toward that of a marine fish; characterized by great increase in membrane permeability, chloride cell number and structure complexity, and activity of the ion pump enzyme Na-K-ATPase (reviewed by e.g. Hoar 1988). These changes render the smolt epithelium extremely sensitive to the deleterious effects from H^+ and Al complexes. Returning fish from sea (e.g. spawners) also have a seawater-like gill epithelium, rendering them very vulnerable for acidic/Al stress. Atlantic salmon smolts demonstrate inhibition of gill Na-K-ATPase activity to parr level, ionoregulatory failure and complete loss of seawater tolerance exposed in acidic water with a low Al concentration. These results indicate impaired smoltification that might cause poorer seawater survival or cause the fish not to migrate (organism level: life performance). This will certainly cause effects on the salmon population and river community. Since the results are from a laboratory study, they are just indicative of what happens in nature. There is thus a need for future verification under natural conditions for interpretation of possible environmental implications (see Staurnes et al. 1995).

3. Physiological Response

A toxicant exerts its effects when it comes in contact with an organism. In fish and other water-breathing animals in acidic water, the primary target organs for toxicants are sensory organs and the gills. In early life history stages of some species the skin is also used for major regulatory processes between the animal and the environment. When the gills and the circulatory system develop, these functions are gradually taken over by the highly specialized gill organ, and the skin becomes nearly impermeable.

EFFECTS ON SENSE ORGANS

Superficial sense organs, like olfactory and taste organs, are not protected by "external barriers", and are therefore vulnerable to pollutants. The toxicants may disrupt normal chemosensory functions by masking or counteracting biologically relevant chemical signals, or they may cause direct morphological and physiological damage to the receptors. Such effects on olfactory and taste organs are likely to cause behavioral effects, e.g. interfere with avoidance and escape reactions related to chemical perception (which are primary resistance mechanisms), social interactions (e.g. reproduction), schooling behavior, predator avoidance, territoriality, as well as interfering with the ability to search for food items and maybe also contribute to a reduced appetite.

Another possible disturbance with great environmental implication, is the inhibition of the olfactory system in seaward migrating smolts of anadromous species. As olfaction is one of the main senses believed to be important for homing in Atlantic salmon, a reduced imprinting caused by acidic or "mixing zone" water quality on leaving their home river, may be hypothesized to increase straying on their return. Effects on chemoreception and chemical communication are sublethal per se, but may have important implications for long-term survival of fish populations.

EFFECTS ON GILLS AND HOMEOSTASIS

In water-breathing animals, the gills are the primary organ for respiration, ionoregulation, osmoregulation, acid-base balance, and excretion of nitrogenous waste. Any environmental stressor that influences the function of this organ may therefore cause homeostatic disorder. Breakdown of some key physiological functions may result in rapid death or induce physiological compensatory responses to maintain homeostasis at least for some time, thus greatly interfering with the overall life performance of the animal. Toxicity thresholds are specific to species and life history stages, but the resultant physiological disturbances are generally similar across species. Prominent physiological disturbances for fish and many invertebrates exposed to acid waters are iono/osmoregulatory failure, acid-base regulatory failure, respiratory and circulatory failure. Most of these effects can directly be attributed to effects on gill functions or structure in the case of fish and the gill equivalent (chloride cells, anal papillae, etc.) in the case of invertebrates.

Environmental irritants, including toxicants, can affect gill functions by direct interference with biochemical/physiological processes and by causing structural changes (gill lesions). When in contact with such an irritant, one of the first responses is increased mucous secretion to protect the epithelial cells and prevent entrance of the toxicant. Prominent structural changes including epithelial necrosis, hypertrophy, hyperplasia, lamellar fusion, bulbing of lamella, as well as changes in chloride cells (number and size) have been observed (Mallat 1985). Most of these lesions can be documented in fish exposed to acid Al-rich waters both in laboratory and field (Rosseland et al. 1990), where the main target of Al/H^+ effects is the chloride cells. Since chloride cells seem to be the main targets in invertebrates, similar studies could provide useful insights regarding acid/Al sensitivity. However, except for mucous secretion and resulting respiratory effects, studies on direct effects of such gill lesions on biochemical/physiological processes are few and warrant further research.

TOXIC EFFECTS OF H^+

The acute toxicity of H^+ in acidic waters (reviewed by e.g. McDonald 1983, Havas 1986a, Exley and Phillip 1988) results in the loss of Ca from important binding sites in the gill epithelium, which reduces the ability of the gill to control membrane permeability causing ionregulatory disturbance and loss of ions (primarily Na^+ and Cl^-). An additional effect of the H^+ is blood acidosis. Very high acidity (found in acid mine drainage ponds, and in a few extremely acidic environments, see Havas and Hutchinson 1983a) causes interlamellar mucous clogging and resulting hypoxia and also severe gill lesions. While acidity alone has been held responsible for the decline of aquatic biota in some acidic waters, Al is now recognized as the principal toxicant.

SYMPTOMS AND MODE OF ALUMINUM TOXICITY

The toxic effects of Al on fish and invertebrate physiology are numerous (reviewed by Havas 1986b, Wood and McDonald 1987, Exley and Phillips 1988, Rosseland et al. 1990, Rosseland and Staurnes 1994). The main consequences, all contributing to mortality when exposure is acute, appear to be respiratory disturbances (due to interlamellar mucous clogging and Al precipitation and reduced membrane fluidity) and iono/osmoregulatory disturbances (due to decreased uptake and increased loss of Na^+, Cl^- and Ca^{2+} caused by Al binding to gill surface). Circulatory disturbances, characterized by very high hematocrit due to reduced blood plasma volume and erythrocyte swelling, increases the blood viscosity (Mazeaud and Mazeaud 1981).

At the present state of knowledge then, the main factor in H^+ toxicity is thought to be iono-regulatory failure, whereas in Al/H^+-toxicity, respiratory and circulatory distress are added.

Whereas the consequences of Al to some extent are characterized, the toxic mechanisms are yet poorly understood. Aluminum is found on the epithelial surface and inside the epithelium cells (see e.g. Rosseland et al. 1990). Several potential sites of Al interaction are suggested in the toxic mechanism model recently suggested by Exley et al. (1991).

Important biochemical properties of the gill epithelium for the explanation of Al precipitation and binding, are its net negative charge, the glycoproteins and sialic acid in mucous, the phosphate groups on membrane phospholipids, carboxylate groups on the membrane proteins, and the binding structure of membrane transport proteins (Exley and Phillips 1988, Exley et al. 1991). Of crucial importance is also the fact that the gill boundary layer closest to the epithelium, is both chemically and physically dissimilar to water outside this layer. The chemistry of boundary layer is very much influenced by the organism itself. The pH of the layer is determined by the hydration equilibrium of expiration products (mainly carbon dioxide and ammonia) and diffusion into and out of the boundary layer of acid or base equivalents from both the water and the organism. An important property is the facility to maintain a circumneutral boundary layer pH even at low environmental pH. This protects biota in acidic waters from deleterious effects of acidity per se. When organisms are exposed to non-acutely toxic pH, there is an initial increase in ion efflux that is followed by a relatively rapid recovery of the efflux (McDonald 1983, Havas 1986b). The mechanisms involved are unknown. Since the boundary layer is the first surface to come in contact with the environment, this boundary layer should receive more attention since it may help us to better understand acclimation effects and acid tolerance, including species, strain and life history stage differences.

The toxicity of Al is caused by inorganic monomeric Al-species, and presence of Al-complexing ligands other than OH^- such as fluoride, sialic acid, organic substances such as humic acids and citrate etc., generally reduces the toxicity of aluminum (see review by Havas 1986b, Rosseland et al. 1990 and Rosseland and Staurnes 1994). At pH about 5, the sialic acid in the mucous is primarily negatively charged, and positively charged Al-hydroxides may therefore bind to mucous. The polymerization of Al may cause irritation of the gill epithelium, stimulation of mucous secretion that along with the Al-precipitation, causes interlamellar clogging and several of the gill lesions. Since polymerization kinetics are temperature dependent, it is not surprising that Al toxicity is reduced at low temperatures (Poleo et al. 1991).

On gill membrane Al binds to small electronegative species such as common biological oxygen-based functional groups (phosphates, carboxylates, carboxyls and hydroxyls) (see Exley et al. 1991). The circumneutrality of the boundary layer at moderate pH (4.5 - 5.5) favors binding to such oxygen-based functional groups. Thus, Al may bind to and neutralize the charge of both the phosphate groups on membrane phospholipids and carboxylate groups on the membrane proteins, subsequently reducing the membrane fluidity. Exley et al. (1991) also suggested that Al may substitute for metal co-factors in the functional domains of transport proteins or also for the transport species per se. All these effects on apical cell surface may be summarized in the prediction of interference with both important transcellular diffusional and active processes, of which could be the uptake of ions (Na^+, Cl^-, Ca^{2+}), excretion of waste products (NH^{4+}, HCO^{3-}) and diffusion of respiratory gases (O_2, CO_2). Al has also been suggested to substitute for Ca^{2+} in the intercellular cement. Increased paracellular permeability caused by H^+ and Al-induced removal of Ca from the anionic sites in the cement, especially between chloride cells and adjacent pavement epithelial cells, probably contributes to the increased efflux of ions in acidic water. The ameliorating effect of Ca on Al and pH response is probably by tightening of the junctions, thereby preventing the passive loss of ions (Wood and McDonald 1987). Prolactin production increases after a chronic exposure to sublethal acidic waters, mainly as a response to a drop in plasma electrolytes (Wendelaar Bonga et al. 1987). Prolactin reduces the gill epithelium permeability, and this time-dependent increase is clearly a mechanism of resistance.

Chemical analysis of invertebrates suggests that there is a poor relationship between total Al content and Al toxicity (Havas and Hutchinson 1983b). Histochemical staining for Al shows that Al can bind to the carapace (physiologically inactive) and be shed with each molt. Aluminum can be associated with filtering appendages as a particulate and hence more Al can be accumulated by active than inactive individuals. Aluminum can also be found on chloride cells, but the surface area of chloride cells is considerably smaller than that of the carapace which may account for the lack of correlation between toxicity and Al content (Havas 1986c).

How Al comes into the cells is not known. Excley et al. (1991) suggested, based on in vitro experiments with phospholipid vesicles, that apical bound Al alters membrane permeability to allow the intracellular accumulation of Al. The possibility for entrance via carrier systems should be investigated. Inside the cell, citrate might be an excellent ligand to Al and act as an intermediate chelator, passing Al to groups with higher affinity. The gill activities of the enzymes carbonic acid anhydrase and Na-K-ATPase are inhibited in acid/Al-exposed salmonids (Staurnes et al. 1984, Rosseland et al. 1990, 1992). The interaction between Al and ATP (mainly the tendency for ATP to form stronger complexes with Al than with Mg) may imply that Al can affect many enzymes reactions where ATP is a substrate, and possibly disturb the energy metabolism of the cells (Ganrot 1986). Aluminum also binds to calmodulin, which is a multifunctional, Ca-dependent protein that regulates a variety of cellular reactions, including regulation of many enzymes (Ganrot 1986). The cytosolic plasma Ca^{2+} concentration is well regulated, and higher concentrations can breakdown cellular functions (Wiercinski 1989). The overall effects of the possible interference of Al with basic processes in the gill epithelial cells may thus be severe effects on the epithelial barrier properties (Exley et al. 1991).

In spite of the importance of the sensory system, however, studies on the effect of acidic waters on sense organs are relatively few and should be encouraged. However, low pH alone has been found to reduce the olfactory response to amino acids and increase the mucous layer in the olfactory organ (Klaprat et al. 1988). Adding Al to the water depresses olfactory response even more and causes histopathological changes such as swelling and dysformation of the olfactory epithelium (Klaprat et al. 1988). Even in cases where no changes in structure of the chemosensory tissue have been observed, complete elimination of feeding response have occurred at low pH (Lemly and Smith 1987). Behavioral effects can also be caused by homeostatic changes. In accordance with this, avoidance reactions to low pH waters have been observed when plasma cation concentrations have been moderately reduced by acidic water exposures (see Rosseland et al. 1990).

HORMONES RELATED TO OSMOREGULATION

Prolactin and cortisol are important hormones related to osmoregulation; prolactin reduces ion permeability and increases mucous production, while cortisol stimulates the onset of cellular proliferation and differentiation in the primary gill epithelium, and increases the specific activity of Na-K-ATPase. Both hormones are affected by acidic waters (Wendelaar Bonga et al. 1987, Witters et al. 1991). Plasma cortisol increases in fish exposed to low pH only when aluminum is present at high concentration, presumably as a response to compensate the H^{+}/Al-toxicity (Witters et al. 1991), as well as in fish exposed to low external NaCl-concentration (Perry and Laurent 1989) and chronic stress in general (Pottinger and Pickering 1992). Prolactin production increases after a chronic exposure to sublethal acidic waters, mainly as a response to a drop in plasma electrolytes (Wendelaar Bonga et al. 1987). As this is a time dependent increase, an increased prolactin production is clearly a mechanism of resistance.

Although hormones play an important role in various resistance mechanism towards acid waters (Exley and Phillips 1988), an important and yet undiscussed aspect, is the potential negative effects of an increased level of cortisol as a response to prolonged (chronic) exposure to acid aluminum-rich waters. As a permanent increased level of cortisol has a negative effect on the immune system (Mazeaud and Mazeaud 1981, Pickering and Pottinger 1985), such a response might thus have a negative effect on the health status of fish populations in acid lakes in general. Another important aspect is a possible post-episodic effect. A combination of a primary sublethal physiological stress (osmoregulatory and circulatory problems) and a secondary reduced immunity caused by a cortisol response, might lead to an increased mortality over a long period. The overall effect might thus be substantially greater than the direct observed mortality during and shortly after an episode or an exposure to a "mixing zone chemistry" (Rosseland and Staurnes 1994). If such a relation exists, it might explain the phenomena of post spawning mortality and "juvenilization", where brown trout post spawners disappears in some populations after their first spawning resulting in lack of older year-classes in the population (see Rosseland 1986).

METABOLISM AND GROWTH

Metabolic activity, measured as oxygen uptake, is not affected by moderate H^+ concentrations alone, but increases as a response to Al in the water. The increased respiratory and heart rate observed in acidic waters are not believed to cause the increased energy expenditure per se, as the increased metabolism rather reflects the increased activity of the intrinsic compensatory mechanism trying to restore homeostasis. Hyperventilation in acidic waters seems to be a specific response to the labile Al-concentration, as the addition of chelator such as citrate depresses hyperventilation (see reviews by Wood and McDonald 1987, Rosseland et al. 1990).

In long-term experiments, even low concentrations of Al have reduced growth (Sadler and Turnpenny 1986). Results from a study of stocking brown trout in the limed Lake Hovvatn to study the growth during the reacidification period, have documented the relation between reduced growth and increased mortality, and critical levels of pH, Al concentrations and Ca concentrations (Barlaup et al. 1994). A decreased appetite have been observed in brook trout exposed to acid water (see Rosseland et al. 1990). The growth reduction response seen in Lake Hovvatn might thus have been caused by a combination of both an increased metabolism as the lake water reacidified, combined with a general decrease in appetite and food conversion rate.

SENSITIVE LIFE STAGES AND PROCESSES

REPRODUCTION AND EARLY LIFE STAGE: OOGENESIS

Among fish and invertebrate oogenesis and fertilization period have been pointed to as sensitive to low pH. Reduced serum and plasma Ca in female fish from acidic lakes have been reported, indicating a probability for failure in producing viable eggs. A depletion of Ca from bone and increased numbers of females with unshed eggs have also been reported. However, several studies indicate that females from acidic lakes develop eggs and spawn normally, even though the plasma Ca during oogenesis has been low (see reviews by Rosseland 1986, Muniz 1991).

EGG STAGE

After fertilization, the embryo seems to be susceptible to acidic waters throughout the whole period of development, although the period shortly after fertilization and also prior to hatching seems to be most critical (Rosseland 1986). For a long period of time, H^+ alone was considered to be the major toxicant at the egg stage, although some effects of Al at intermediate pH-ranges was demonstrated. Low pH in the surrounding waters results in pH-depression inside the egg (in the perivitelline fluid), leading to either a prolongation of the hatching or to a reduced hatching success. The low pH of the perivitelline fluid also depresses the activity of the hatching enzyme, chorionic dehydrogenase, which then reduces an effective break down of the eggshell (chorion). Species and strain differences in sensitivity to acid waters at hatching may therefore reflect variation in levels of inactivation of the hatching enzyme. A chorion thickening, probably a protein denaturation due to the surrounding low pH, and a reduced activity of the embryo inside the egg (reduced mechanical breakdown) due to the low pH of the perivitteline fluid, enforces these negative effects.

Daphnids, ventilate their brood pouch so that developing embryos are exposed to the external medium before their are released. Hence, many die within the brood pouch if conditions are unfavorable.

ALEVIN STAGE

An increasing negative influence of Al with age occurs after hatch (Baker and Schofield 1982, Wood and McDonald 1982). The reason for this is still unclear, but it might have something to do with the changes that take place in the respiratory system/organ. Alevins shortly after hatch still respire through their skin but gradually gills become the primary organ of gas and ion exchange. The sensitivity related to the gill as a target organ thus gradually develops in the alevin. This might therefore explain the gradual importance of Al as a toxicant after hatch.

Al and pH are known to interfere with whole body mineral content and skeletal calcification at the embryo and fry stage (Sayer et al. 1991). Recent studies on strain of brown trout having different sensitivity to acidic waters seem to indicate differences in calcification rate at the alevin stage (Dalziel et al. 1995). In spite of a comparable total body Ca, the most resistant strains had the lowest calcification rate of finrays and skeletal. This phenomenon might thus indicate an important resistant mechanism for embryo survival before swimup, giving priority to a high plasma/serum Ca to ensure Ca and electrolyte homeostasis. Development of screening techniques to investigate strain tolerance in fish based on early calcification rate, is under way in the ReFish project (Dalziel et al. 1995).

A reduced metabolism, indicated by an increased number of degree-days from fertilization to hatch and through the yolksack period, have been suggested as a mechanism of resistance. By increasing the period until swimup, the chance to avoid acid episodes in the stream habitats will be reduced, thus enhancing the chance to survive (Rosseland 1986).

4. Conclusions

What really causes the loss of fishes and invertebrates in acidified water is probably a sum of a variety of disturbances of which we know but a few. Laboratory studies and field studies, at the subcellular to the ecosystem level, spanning a broad set of dynamic water chemistry challenges and including sensitive stages of an organisms life-cycle have been conducted. Many of the early studies focused on the physiological effects of acid and aluminum in softwater environments. Information regarding environment heterogeneity and the presence of both refugia as well as toxic episodes and mixing zones has improved our understanding of the subtle factors controlling the presence and absence of species in a particular environment. In the future scientists will deal with even more subtle factors of competition, and predator-prey interactions and their role in influencing species composition, population biomass, and community structure as lakes either continue to acidify or begin to recover as they have in parts of North America and Scandinavia.

To link the toxic substances involved to the ecological effects observed, calls for cooperation between chemists, geologists, atmospheric scientists, ecophysiologists, and ecologist. And to link ecological effects with regulation, legislation, and management strategies requires even broader cooperation between scientists and policy makers.

It seems that the observations and theories of the effects of acid deposition on aquatic systems formulated by Developed Countries will soon be tested in Developing Countries as their use of and dependence on fossil fuels increase.

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REGIONAL LAKE SURVEYS IN FINLAND, NORWAY AND SWEDEN -1995 COORDINATION AND DESIGN

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Abstract. Regional lake surveys have previously been carried out in the three Nordic countries, Finland, Norway and Sweden. Finland carried out their first survey in 1988 comprising 987 lakes. Norway started already in the mid 70's, and followed up with an extensive regional survey in 1986 (1005 lakes). Sweden has carried out several lake surveys, the most extensive one in 1990 (4018 lakes). The Finnish and Swedish latest surveys were based on statistical selection of lakes from their national lake registers, while the Norwegian survey was based on subjectively selected lakes within each topographic map located in areas with geology giving lakes sensitive to acidification. The three Nordic countries plan to carry out new national lake surveys in their respective countries in the fall of 1995, and based on statistical selection of lakes . The purpose of these surveys will, among other goals, be to establish a new baseline of chemical data to follow up the future effects of the new sulfur protocol that was signed in Oslo in June 1994. The Effect Group of the Nordic Council of Ministers supports the joint planning and reporting of the three surveys. The poster will present the common lake registers, lake size distributions, purpose of the surveys, descriptions of the sampling strategies, analytical methods, quality control routines etc.

Key words: Lakes, water chemistry, acidification, monitoring, critical loads, lake survey, long-term trends.

CRITICAL LOADS OF ACIDITY FOR SURFACE WATERS - Can the $\text{ANC}_{\text{limit}}$ be considered variable?

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Abstract. The critical load of acidity for surface waters is based on the concept that the inputs of acids to a catchment do not exceed the weathering less a given amount of ANC. The Steady State Water Chemistry (SSWC) Method is used to calculate critical loads, using present water chemistry. To ensure no damage to biological indicators such as fish species a value for $\text{ANC}_{\text{limit}}$ of 20 µeq/l has been used to date for calculatiing critical loads. The SSWC-method is sensitive to the choice of the $\text{ANC}_{\text{limit}}$. In areas with little acid deposition the probability of acid episodes leading to fish kills is small even if the $\text{ANC}_{\text{limit}}$ is set to zero, while in areas with high acidic deposition fish kills may occur at this value. Thus, the $\text{ANC}_{\text{limit}}$ can be a function of the acidifying deposition to the lake, nearing zero at low deposition and increasing to higher values at higher deposition. A formulation for such an $\text{ANC}_{\text{limit}}$ has been worked out, and we have tested the effect of the $\text{ANC}_{\text{limit}}$ as a linear function of the deposition, assuming $\text{ANC}_{\text{limit}} = 0$ at zero deposition with a linear increase to 50 µeq/l at a deposition of 200 $\text{meq.m}^{-2}.\text{yr}^{-1}$. For areas with high deposition the effect of a variable $\text{ANC}_{\text{limit}}$ is small, while in areas with low deposition the effect is significant. For Norway the exceeded area decreases from 36 to 30% using a variable $\text{ANC}_{\text{limit}}$ instead of a fixed value of 20 µeq/l.

Key words: critical load, acidity, water acidification, soil acidification, fish, empirical models, sulphur deposition, acid episodes,

1. Introduction

In recent years large areas of Europe and eastern regions of North America have suffered from acid precipitation resulting in the acidification of surface waters, increased fish mortality and other ecological changes. The concept of critical load has come into wide use in connection with international negotiations on reducing emissions of nitrogen and sulphur compounds. It was first put into practical use in Canada in the last part of the 70's in relation to the problem of lake acidification. It was further developed by working groups established by the the Nordic Council of Ministers in 1985 and used in the Scandinavian countries as a method for quantifying the extent and spatial dimension of the acidification problem. Since then it has been developed on a European basis by a number of international cooperative programmes and activities under the United Nations Economic Commission for Europe's Convention on Long Range Transboundary Air Pollution, signed in 1979.

2. The Steady State Water Chemistry Method

The critical load of acidity for surface waters can be estimated on the basis of present water chemistry by means of a simple steady-state method. The critical load of acidity is calculated as:

$$CL(Ac) = Q*([BC*]_0 - ANC_{limit}) \quad (1)$$

where Q ($m \cdot yr^{-1}$) is the runoff, $[BC*]_0$ the pre-industrial seasalt corrected base cation concentration and ANC_{limit} is the selected critical ANC (Acid Neutralization Capacity) threshold (Henriksen *et al.* 1993).

The Acid Neutralization Capacity is used as the chemical criterion for sensitive indicator organisms (usually fish) in surface waters. ANC is defined as the difference between base cations and strong acid anions. Including present-day nitrate leaching the present exceedance of the critical load of acidity is defined as:

$$Ex(Ac) = S_{dep} + N_{le} - BC*_{dep} - CL(Ac) \quad (2)$$

where S_{dep} is the total S deposition and $BC*_{dep}$ is the non-marine base cation deposition (Henriksen *et al.* 1993). N_{le} is present nitrate leaching from the lake and its catchment, which is estimated from yearly runoff and present lake nitrate concentration minus an estimated background concentration of nitrate in lakes not affected by acid deposition (which for Norway has been estimated as 4 µeq/l, (Kämäri *et al.* 1992).

In order to calculate the critical load of acidity to surface waters a value for the ANC_{limit} is needed. This value has been derived from the information on water chemistry and fish status obtained from the 1000 lake survey carried out in Norway in 1986 (Henriksen *et al.* 1988, Lien *et al.* 1992). The Scandinavian countries have so far used ANC_{limit} = 20 µeq/l as the critical chemical value for fish in surface waters (Henriksen *et al.* 1990). The natural ANC in lakes can, however, be equal or less than 20 µeq/l in areas with granitic and gneissic bedrock with thin soil cover. For such lakes the ANC_{limit} has so far been set to the original ANC-value of the lake. The critical load for acidity will thus be zero for such lakes. For Norway 163 (16%) of the lakes included in the 1000-lake survey in 1986 have "negative" critical loads using ANC_{limit}.= 20 µeq/l. The corresponding figures for Sweden and Finland are 18 (0.4%) out of 4015 and 4 (0.3%) out of 1450, respectively (Henriksen *et al.* 1993). The much higher percentage of lakes with negative critical loads in Norway is due to the larger number of lakes with low base cation concentrations. These Norwegian lakes are all located in areas where the bedrock consist of granites and gneisses and the soil covers are thin, as is also the case for the Swedish and Finnish lakes.

The critical load is thus sensitive to the choice of the ANC_{limit}. For Norway, a value of ANC_{limit} = 0 µeq/l will give a critical load exceedance in 25% of the area of Norway, whereas an ANC_{limit} = 20 µeq/l will result in an exceeded area of 36%. In this paper we suggest a variable ANC_{limit} that adresses some of the shortcomings of a fixed value.

3. Fish and ANC

The value of 20 µeq/l for ANC_{limit} was chosen to ensure no toxic episodes during the year. In areas with little acid deposition, however, the probability of acid episodes leading to fish kills is small even if ANC is close to zero, while in areas with high acidic deposition fish kills may occur at this value. Thus, the ANC_{limit} could be considered variable, e.g. a function of the deposition to the lake, nearing zero at low critical loads and increasing to an upper limit at higher critical loads. There are good biological arguments for considering ANC_{limit} as a variable: The pH-range 5.5 to 6.0 is regarded as safe under natural conditions for most fish species. One of the first attempts on setting a critical level for effects of acidification on aquatic systems was made in a Swedish case study (1971). The study used a critical limit of pH = 5.5 for salmon fish species. The toxicity of inorganic Al was unknown at this time (Schofield 1977). The toxicity of Al in the pH range 5.5 to 6.0 depends on the concentration and chemical form of Al, the concentration of Ca as well as temperature (Brown 1982; Rosseland and Hindar 1991). In areas with higher critical loads, deposition of sulphur to acidified forest soils causes leaching of Al. This will result in the presence of inorganic Al-forms in lakes and streams also at deposition levels of sulphur at the critical load as long as the soils remain dominated by Al and H^+ (Hultberg 1988). Inorganic Al causes toxic effects on young life stages and to adults of many fish species and other aquatic animals also at low concentrations (salmonid fishes ≥ 30 to 50 µg/l; lake plankton 100 µg/l) in the pH-range 5.5 to 6.0 (Fivelstad and Leivestad 1984; Henriksen *et al.* 1984; Hultberg 1988).

In lakes roach (*Leuciscus rutilus*) and Arctic char (*Salvelinus alpinus*) are two of the most sensitive fish species. Crayfish species in lakes (*Astacus astacus and Pacifastacus leniusculus*), glacial relicts of crustaceans as well as molluscs (*Margaritana margaritifera*) and mayfly species (*Ephemera sp.*) among the insects are very sensitive to acid episodes and inorganic Al (Hultberg 1977; Nyberg *et al.* 1986). In streams with sea-running brown trout (*Salmo trutta*) and rivers with Atlantic salmon (*Salmo salar*) draining of upstream acid lakes or soils, later running into areas with non-acid soils with resulting high pH (5.5 to > 6.0) in the water are still affected by low survival of overwintering young year classes as well as fish kills of adult fish (Rosseland *et al.* 1986; Degerman *et al.* 1986). This is caused by inflow of water with inorganic Al into water with higher pH and ANC of 20 to ≥ 50 µeq/l at periods with high waterflow and low temperatures. Liming of such upstream acid areas results in decreased transport of inorganic Al which in turn has caused dramatic increases in survival of overwintering young year classes of sensitive fish populations as well as invertebrates in the non-acid downstream parts of the water system (Nyberg *et al.* 1986). Decreased concentrations of inorganic Al was caused by precipitation of Al in lakes, wetlands and headwater streams in upstream limed parts of the catchment. Inflow of inorganic Al from acid catchments into limed lakes and streams may result in toxicity to fish at high pH in the mixing zone (Dickson 1978, 1983; Skogheim *et al.* 1984; Rosseland *et al.* 1992; Poleo *et al.* 1994).

The acidification recovery process at critical load will be slower for soils than for surface waters. Fish populations and other aquatic biota in lakes and rivers may therefore be exposed to toxic Al-forms also at very low sulphur load. In areas with higher critical loads ANC-values up to 50 µeq/l are necessary to avoid negative effects on fish and other aquatic fauna. The ANC_{limit} of 20 µeq/l was set to the reaction of brown trout, the most abundant fish species in Norway. In other countries other species are more abundant and thus a variable ANC_{limit} seems to be required to protect most aquatic organisms.

4. Method

In order to develop an equation for a variable ANC_{limit} we can rewrite the critical load equation (equation 1) in the following way:

$$[BC^*]_0 - CL(Ac)/Q = ANC_{limit} \tag{3}$$

which can be visualized by intersecting the line $y = [BC^*]_0 - x/Q$ with the horizontal line $y = ANC_{limit}$, where y is the concentration-axis and the x-axis is the deposition axis. The x-coordinate of the point of intersection of these two straight lines is the critical load.

This way of deriving the critical load can be generalized for an ANC_{limit} which depends on the deposition, i.e. x. Then $y = ANC_{limit}$ is no longer a horizontal line, but a function of the deposition. The critical load is then computed by intersecting the line $y = [BC^*]_0 - x/Q$ with the curve $y = ANC_{limit}(x)$ (see Figure 1). As argued above, the ANC_{limit} can be low in areas with low deposition (backround areas) and should be higher in areas with high depostion. the simplest way to express this is to assume a constant ANC_{limit} below and above given deposition values and a linear dependence between those limits:

$$ANC_{limit} = \begin{array}{ll} A_1 & \text{for } Ac_{dep} \le Ac_1 \\ k^*Ac_{dep} + d & \text{for } Ac_1 < Ac_{dep} < Ac_2 \\ A_2 & \text{for } Ac_{dep} \ge Ac_2 \end{array} \tag{4}$$

where $k = (A_2 - A_1)/(Ac_2 - Ac_1)$ and $d = A_1 - k^*Ac_1$. If $A_1 > 0$, it must be ensured that $[BC^*]_0 > A_1$. Depending on $[BC^*]_0$ and Q we have three cases, and for each of them we can derive explicit formulae for the critical load and the ANC_{limit} (see Figure 1):

(a) $Q^*([BC^*]_0 - A_1) \le Ac_1$:
Then we simply have: $CL(Ac) = Q^*([BC^*]_0 - A_1)$ and $ANC_{limit} = A_1$ (5a)

(b) $Q^*([BC^*]_0 - A_1) > Ac_1$ and $Q^*([BC^*]_0 - A_2) < Ac_2$:
In this case we obtain after a few calculations:
$CL(Ac) = Q^*([BC^*]_0 - d)/(1 + k^*Q)$
and $ANC_{limit} = (k^*Q^*[BC^*]_0 + d)/(1 + k^*Q)$ (5b)

(c) $Q^*([BC^*]_0 - A_2) \ge Ac_2$:
Again, one simply gets: $CL(Ac) = Q^*([BC^*]_0 - A_2)$ and $ANC_{limit} = A_2$ (5c)

The critical load, i.e. the deposition obtained by solving equation 3 after inserting the ANC_{limit} given by equation 4, depends on the parameters of the ANC-function (Ac_1, A_1, Ac_2 and A_2, see equations 5a-c), which have to be derived from biological criteria i.e. the (fish) species to be protected. The expression for the ANC_{limit} is not restricted to the broken linear function as defined in equation 4, but any monotonously increasing function, e.g., a S-shaped curve, could be chosen. However, in such a case equation 3 would become non-linear, and the critical load would have to be computed by an iterative method.

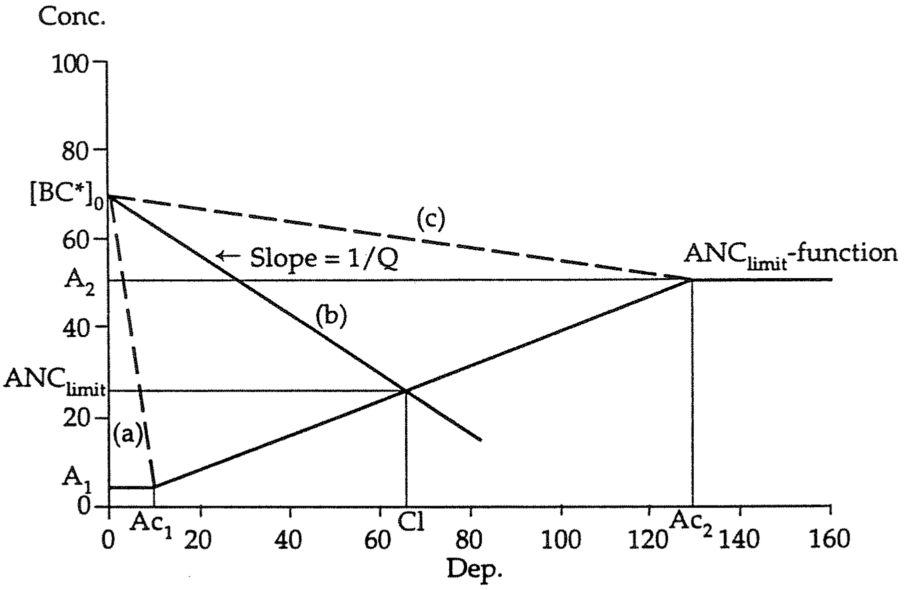

Figure 1. Determination of the critical load for a deposition dependent ANC_{limit} (equation 4). Three cases are possible, depending on the parameters of the function (Ac_1, A_1 and Ac_2, A_2), $[BC^*]_0$ and the runoff Q (see text).

It should be noted that, although now ANC_{limit} is not a fixed value for all lakes, each lake will have its own value for all depositions, given by the characteristics of the lake ($[BC^*]_0$ and Q).

5. Results

To test the concequences of a variable ANC_{limit} for the critical loads in Norway, Sweden and Finland we used $A_1 = 0$ for $Ac_1 \leq 0$, and $A_2 = 50$ for $Ac_2 = 200$. Using the critical load databases for Finland, Norway and Sweden (Henriksen et al 1990), we have calculated the critical loads and their exceedances (Table 1).

Table 1. Percent of area (Norway) and percentage of lakes (Finland and Sweden) for which critical loads of acidity is exceeded for a variable ANC_{limit} and a fixed ANC_{limit} (20 µeq/l).

Country	Fixed ANC_{limit}	Variable ANC_{limit}	Difference
Sweden	30,2	28,6	1,6
Finland	17,2	14,3	2,9
Norway	36,0	30,0	6,0

The effect of a deposition dependent ANC_{limit} is larger in Norway than in Sweden and Finland, because the number of sensitive lakes are highest here, as pointed out above. Using a fixed ANC_{limit} = 20 µeq/l, the critical load of present acidity for surface waters is exceeded in 36% of the area of Norway. The variable ANC_{limit} (0-50µeq/l) reduces the exceeded area to 30%, and most of these areas receive little acididic deposition (central and northern Norway). The distribution of areas where the critical load of acidity is presently exceeded using the variable $\mathrm{ANC}_{\mathrm{limit}}$ corresponds better to those where fish populations are damaged than using the fixed $\mathrm{ANC}_{\mathrm{limit}}$ (Henriksen and Hesthagen, in prep.).

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CRITICAL LOADS OF ACIDITY TO SURFACE WATERS -
How important is the F-factor in the SSWC-model?

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Abstract. The critical load of acidity to surface water is based on the condition that the inputs of acids to a catchment do not exceed the weathering rate less a given amount of ANC (Acid Neutralizing Capacity). The Steady State Water Chemistry (SSWC) Method is used to calculate critical loads of acidity, using present water chemistry. To calculate the weathering, the so-called F-factor is used to estimate the part of the base cation flux that is due to soil acidification. The F-factor has been estimated empirically from historical data comparisons from Norway, Sweden, U.S.A. and Canada and is considered to be a function of the base cation concentration by the formula: $F = \sin(BC^*/S)$, where BC^* is the present base cation concentration and S the base cation concentration at which $F = 1$. At higher values for BC^* F is set to 1. For Norway, Sweden and Finland S has been set to 400 µeq/l (ca. 8 mg Ca/l), giving F-values in the range 0.05-0.2. The importance of the F-factor in the calculations of the critical loads of acidity for Nordic surface waters was tested by calculating the magnitude of the area where the critical load of acidity is exceeded in Norway for different values of S. Similar calculations were carried out for the Finnish and Swedish lake data. Varying S from 100 µeq/l to 1200 µeq/l, the exceeded area in Norway decreases from 31,9 to 28,3%. For $F = 0$ ($S = \infty$, i.e. assuming no soil acidification), the exceeded area is reduced to 27,2%. For Finland and Sweden the the percent of lakes exceeded are reduced from 16,6 to 12,9% and 30 to 23,6%, respectively. For $F = 0$ the percent of lakes exceeded are reduced to 11,4 and 16,4, repectively. These results indicate that the F-factor is not of great importance for calculating critical load and critical load exceedances in Norway, Finland and Sweden.

Key words: Critical load, acidity, water acidification, soil acidification, empirical models, base cation fluxes

1. Introduction

The critical load of acidity to surface water is based on the condition that the inputs of acids to a catchment do not exceed the weathering rate less a given amount of ANC. The Steady State Water Chemistry Method (SSWC) (Henriksen *et al.* 1992) is used to calculate critical loads of acidity to a lake, using its present water chemistry. To calculate the weathering rate, the so-called F-factor is used to estimate the part of present base cation flux that is due to soil acidification (Henriksen 1984, Brakke 1990). The F-factor expresses the fraction of base cations in runoff that has been ion exchanged in the soil, and thus the effect of soil acidification on the runoff water. The F-factor has been critisized in connection with use for calculations of critical load of acidity for surface waters, and considered to be the most uncertain element in the SSWC-method (i.e. Sullivan *et al.* 1990). We have tested the importance of F in the calculations of the critical loads of acidity to Norwegian, Swedish and Finnish surface waters by varying the variables in its equation.

2. Method

The F-factor is defined as the ratio of change non-marine base cation concentration (denoted by asterisk) due to changes in strong acid anion concentrations, and is calculated as follows (Brakke *et al.* 1990):

$$F = \Delta[BC^{*}]/(\Delta[SO_4^{*}] - \Delta[NO_3$$

$$= ([BC^{*}]_t - [BC^{*}]_0)/(([SO_4^{*}]_t - [SO_4^{*}]_0) + ([NO_3]_t - [NO_3]_0)) \qquad (1)$$

where the subscripts t and 0 refer to present and background concentrations of non-marine base cations($[BC^{*}]$), non-marine sulphate ($[SO_4^{*}]$ and nitrate ($[NO_3]$), respectively (Henriksen *et al.* 1992).

From equation 1 the non-marine background, or preacidification, base cation concentration can be derived:

$$[BC^*]_0 = [BC^*]_t - F(([SO_4^*]_t - [SO_4^*]_0) + ([NO_3]_t - [NO_3]_0)) \qquad (2)$$

The critical load of acidity to a lake is then calculated by the formula:

$$CL(Ac) = Q \cdot ([BC^*]_0 - [ANC]_{limit}) \qquad (3)$$

where Q is the runoff ($m \cdot yr^{-1}$), $[BC^*]_0$ the original seasalt corrected base cation concentration and $[ANC]_{limit}$ is the selected critical ANC threshold (Henriksen *et al.* 1992, Henriksen *et al.* 1995). The unit is $meq/m^2/yr$.

If F=1, all incoming H+ is neutralized in the catchment (only soil acidification), at F=0 none of the incoming H+ is neutralized in the catchment (only water acidification). Since extensive water acidification has been documented in many areas of the world F must be <1 in those areas. The F-factor was estimated empirically to be in the range 0.2-0.4 based on historical data comparisons from Norway, Sweden, U.S.A. and Canada (Henriksen 1984). Brakke et. al. (1990) suggested later that the F-factor should be considered to be a function of the base cation concentration by the formula:

$$F = \sin(\Pi/2 \cdot [BC^*]/S) \qquad (4)$$

where $[BC^{*}]$ is the present base cation concentration (μeq/l) and S the base cation concentration (μeq/l) at which F = 1. For $[BC^*] > S$ the ratio $[BC^*]/S$ is set to 1.

For Norway S has been set to 400 μeq/l (ca. 8 mg Ca/l) (Brakke *et al.* 1990). For acidified lakes in Norway calculated F-values lie in the range 0.05-0.2.

In equation 4 present base cation concentration is used for practical reasons. Posch et al (1993) suggested a non-linear relationship between F and the original base cation concentration$[BC^*]_0$:

$$F = 1 - \exp(-[BC^*]_0/B) \qquad (5)$$

where B is a scaling factor estimated to be 131 μeq/l fra paleolimnological data from Finland (see Posch *et al.* 1993). Inserting this expression into Equation 3 gives a non-linear equation for $[BC^*]_0$ which can be solved by an iterative procedure.

The two expressions for F, equations 4 and 5, in fact give similar results when applied to calculation of critical loads for surface waters in Norway. Figure 2 show the cumulative distribution functions of $[BC^*]_0$ one computed with equation 4 and one computed with equation 5, indicating that either of the equations can be used for calculation of critical loads. For simplicity, all critical load calculation using the Norwegian database has been carried out using equation 4.

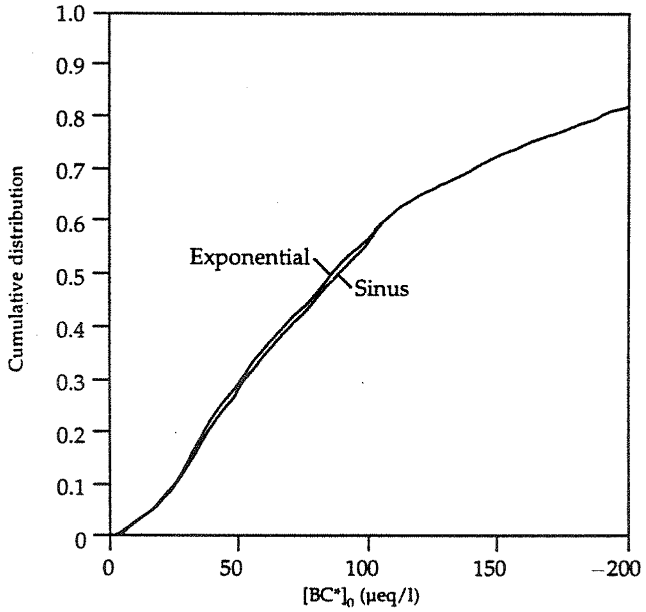

Figure 1. Cumulative distribution functions of $[BC^*]_0$, once computed with equation 4 (lower line) and once computed with equation 5 (upper line) in equation 2 for 2305 lakes in Norway.

3. Results

To test the importance of the F-factor in the calculations of the critical loads of acidity to Nordic surface waters, we have for Norway calculated the magnitude of the area where the critical load of acidity is exceeded for different values of S (Table 1). Similar calculations have been carried out for the Finnish and Swedish lake data bases used for the critical load calculations (Henriksen *et al.* 1990) (Table 1). Varying S from 100 μeq/l to 1200 μeq/l (Table 1), the exceeded area in Norway decreases from 31.9 to 28.3%. For $F = 0$ ($S = \infty$, i.e. assuming no soil acidification), the exceeded area is reduced to 27.2%. For Finland

and Sweden the the percent of lakes exceeded are reduced from 16.6 to 12.9% and 30 to 23.6%, respectively. For F = 0 the percent of lakes exceeded are reduced to 11,4 and 16.4, repectively.

TABLE 1.

Percent of area (Norway) and no. of lakes (Finland and Sweden) for which critical loads of acidity is exceeded for some values of S in equation 4. S=400 µeq/l has been used to calculate the critical load databases for Finland, Norway and Sweden.

S-value	**Exceeded area Norway**		**Percent of lakes exceeded**	
µeq/l	km^2	Percent	*Finland*	*Sweden*
100	102158	31.9	16.6	30.0
200	99715	31.1	16.6	30.0
300	97333	30.4	16.2	29.9
400	*95148*	*29,7*	*15.4*	*29.6*
600	92623	28.9	14.4	28.3
800	91248	28.5	13.7	26.5
1200	90644	28.3	12.9	23.6
∞ (F=0)	87308	27.2	11.4	16.4

These results, considering the large range of S-values tested, indicate that the F-factor is not of great importance for calculating critical load and critical load exceedances in Norway, Finland and Sweden.

As pointed out above, S=400 µeq/l has empirically been chosen for the calculations of critical loads in the three Nordic countries. Data from the Risdalsheia site of the RAIN-project (Reversing Acidification in Norway), where the acid rain was removed, showed that the F-factor for the 8-year period the experiment lasted was 0.18, not very different from the calculated value of 0.10 (Wright *et al.* 1993). The measured value should be expected to exceed the calculated one, because Risdalsheia has not yet reached steady state. At the Sogndal site of the RAIN-project, wher acid rain was added over an 8-year period the experimental F-value was found to be 0.35. Here also, the calculated value was 0.10. The Sogndal site, also, has not reached equilibrium. With further soil acidification, the measured F is expected to decrease (Wright *et al.* 1993). The results from these large scale, long term experiments indicate strongly that the measured and calculated values for F are within an acceptable range, confirming the empirical values used to calculate F according to equations 4 and 5.

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FRESHWATER LIMING

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Abstract. Operational liming of surface waters is part of Sweden and Norway's strategy to counteract freshwater acidification caused by air pollutants. Smaller scale liming efforts are performed as research or experimental programs in other countries. Yearly, approx. 300,000 tons of fine-grained limestone ($CaCO_3$) is spread in lakes and streams and on wetlands to raise the pH in surface water at a cost of approximately 40–50 million $US. The chemical target is set by the biological goals and objectives. A total of over 11,000 lakes and streams are treated on a continuing basis. Dose calculations consider pH, inorganic monomeric Al, dissolved organic matter and the necessary buffering. Lake liming, limedosers at streams and terrestrial liming are used. A mix of different liming techniques is often preferred to get an optimal result. The vast majority of changes are desirable and expected. Undesirable effects may appear and damaged wetlands are probably the most serious ones. Cost-benefit analysis show that liming may be profitable for the society. Recovery of the systems can take up to 10–20 years. Liming will in the long run restore the ecosystems but will not make them identical to what may be the original ones. In some cases, complementary measures, e.g. facilitation of recolonization, are necessary to enhance recovery. Reduced emissions of acidifying pollutants according to signed protocols will decrease the need for liming, but still liming is needed for several decades in large regions to preserve biodiversity.

1. Introduction

Acid deposition has changed the natural water chemistry, and thereby has affected the biological community in 50,000–100,000 lakes and watercourses in Europe and North America (e.g. Brodin, 1995a). Aquatic biodiversity is affected as well as the possibility for human use of natural resources. The accumulation of heavy metals like mercury in top carnivores is a latent threat to animal species and human health.

The deposition of sulphur has been reduced in Europe during the last 15 years, but further reductions are needed. Although many European countries have agreed upon a sulphur reduction of 70–80 % by the year 2010 relative to 1980 (UN, 1994), acidification will still be a problem for many decades in large areas (Henriksen and Hindar, 1993; Brodin, 1995a). No large scale reductions in nitrogen deposition have been achieved and acidification due to nitrogen compounds seems to be more important relative to sulphur in the future.

One way of counteracting acidification of freshwaters is to add neutralizing agents to the water. Sweden and Norway have chosen large-scale liming as a national strategy in order to preserve species threatened by acidification (e.g. Baalsrud *et al.*, 1985; Hindar and Rosseland, 1991; Henrikson and Brodin, 1995a; Romundstad and Sandøy, 1995; Svensson *et al.*, 1995). Smaller scale liming efforts, mainly as research or experimental projects, have been conducted in several other countries, e.g. Canada, Finland, the United Kingdom (Wales and Scotland) and USA. In Sweden, liming has also been used to reduce the content of mercury in fish in acidified lakes (Meili, 1995).

In this paper, we present an overview of the need of countermeasures and the experiences of liming in different countries. Earlier surveys on liming and effects of liming have been presented by Brocksen and Wisniewski (1988), Weatherley (1988), Olem (1991), Olem *et al.* (1991), and Henrikson and Brodin (1995a).

2. Acidification status and the critical load concept

Aquatic organism status is correlated to a set of water quality parameters, such as pH, dissolved inorganic aluminium (Al) and calcium (Ca) (Økland and Økland, 1986; Wood and McDonald, 1987; Brown and Sadler; 1989; Rosseland *et al.*, 1990; Herrmann *et al.*, 1993; Brodin, 1995a). Ca may ameliorate the toxic effects of Al in acidic water and dissolved organic matter forms complexes with Al and thereby reduces the inorganic concentrations. Iron and manganese have been shown to form toxic species in Sweden (e.g. Nyberg *et al.*, 1995).

Aquatic species are subjected to sublethal and lethal effects at different pH/Al-levels. Differences have been found between fish species, fish strains, invertebrate and phytoplankton species (e.g. Almer *et al.*, 1978; Eriksson, *et al.*, 1983; Engblom and Lingdell, 1984; Raddum and Fjellheim, 1984; Brett, 1989; Kroglund *et al.* 1992; Lien *et al.*, 1992). The critical chemical value of pH or a combination of pH, Al or other components may therefore vary from species to species. Regional differences in pH/Al-tolerance may be found due to differences in the natural water quality and climate.

Fish status, although related to the direct toxic effects of pH and Al, is well (and better) correlated to acid neutralizing capacity (ANC) (Lien *et al.*, 1992; Bulger *et al.*, 1993). Lien *et al.* (1992) found that intact Brown trout *Salmo trutta* populations in most cases corresponded to ANC values higher than 20 $\mu eq\ L^{-1}$. Exceedance of the critical load is reflected by lower ANC than 20 $\mu eq\ L^{-1}$. A variable ANC_{limit} has recently been introduced to take into account the very low (even lower than 20 $\mu eq\ L^{-1}$) naturally occurring ANC-levels in parts of Norway (Henriksen *et al.*, 1995). Exceedances and thereby anticipated damage to aquatic life due to acidification are manifest in large areas of Scandinavia (Henriksen *et al.*, 1992).

Biodiversity is the variation at genetic, species, and ecosystem level, and the ecological processes of the ecosystem. All levels of aquatic biodiversity are affected by acidification. Genetic unique populations of the Salmonidae family have been damaged (Appelberg and Degerman, 1991; Bergquist, 1991; Hesthagen and Hansen, 1991; Snucins *et al.*, 1995). The total number of species is lower in acidified compared to non-acidified waters (e.g. Brodin, 1995b) even though some tolerant species may be favoured and colonize acidified waters (e.g. Henrikson and Oscarson, 1981; B.-I. Henrikson, 1988). Although biodiversity is affected at species level we only know of one species, the Spring-spawning Cisco *Coregonus trybomi*, that may be threatened on a global or national scale (cf. Henrikson and Brodin, 1995b). On a regional and local scale several species may be considered as threatened, e.g. European Roach *Rutilus rutilus*, Freshwater Pearl Mussel *Margaritifera margaritifera* but also semi-aquatic species like Red-throated Diver *Gavia stellata* (Eriksson, 1987; Brodin, 1995b; Henrikson, unpubl. data). Changes at the ecosystem level are manifested by altered community structure as well as ecological processes, e.g. retarded breakdown of leaves (e.g. Appelberg et al., 1993). If the acid deposition decreases the biodiversity will increase (e.g. Keller and Gunn, 1995; Raddum and Fjellheim, 1995).

3. Liming as a countermeasure

3.1 EXTENT, OBJECTIVES AND TARGETS

Yearly, approximately 300,000 tons of fine grained limestone is spread in lakes and streams and on wetlands in different countries to raise the pH in surface water at a cost of approx. 40–50 million $US. A total of over 11,000 lakes and streams are treated on a continuing basis in Sweden and Norway including a maximum of 150 in other countries. The liming in Norway and Sweden is financed either in large part or in total by the respective governments.

At the start of operational liming of acidified surface waters in the 1970's, the main motive was the concern of fish populations for recreational fishing. Now, the aim and direction have been broadened and are focused on the preservation or recovery of biodiversity, but also human health. In Sweden (cf. Svensson *et al.*, 1995) the official aims of today are: (1) The biological aims are to detoxicate the water for the continued existence or recolonization of natural flora and fauna, (2) The chemical aims are to raise the pH above 6.0 and alkalinity above 0.1 meq L^{-1}. In Norway (Romundstad and Sandøy, 1995) the aims are (1) to improve conditions for recreational fishing and (2) to preserve biological diversity. The chemical targets vary according to the biological target. In Norwegian salmon rivers the chemical target is differentiated at an annual basis. Target pH is higher (pH 6.5) during February–June than during the rest of the year (pH 6.2–6.3) due to the extreme sensitivity of salmon smolt.

3.2 LIMING AGENTS AND DOSES

Many kinds of deacidification agents, such as carbonates, oxides, hydroxides and industrial waste products, have been used to neutralize acid waters (Dickson and Brodin, 1995). Calcium carbonate ($CaCO_3$) as finely grained dry powder may stabilize pH at intermediate levels (pH 6–8), is cheep and easy to handle, has low content of contaminants, and is therefore most widely used (>95 %).

Dose calculations may be on a theoretical basis and consider the concentrations of H^+, inorganic monomeric Al, dissolved organic matter and the necessary buffering. A more direct approach is titration analyses. Common doses are 5–30 mg $CaCO_3$ L^{-1}. The reactions with dissolved inorganic Al result in a change of Al-species from a mixture of inorganic monomeric species to longer chains of inorganic and organic complexes. Temperature and the concentrations of ligand-forming compounds may affect the kinetics and reaction products of these reactions (Lydersen, 1990).

Carbonates dissolve as a function of pH, dissolved carbon dioxide, powder size distribution and time and conditions for dissolution (Sverdrup, 1985). These variables are taken into account, together with the fraction of carbonates in the powder, in mathematical models for both dose calculations and simulation of lake reacidification after liming. However, run-off regimes other than the average may result in longer or shorter duration of the liming intervals than expected. Long-term dissolution of sedimented limestone powder may contribute significantly to the liming effect, stabilizes the water quality and may therefore increase the duration in some lakes. Limestone doses for rivers may be even more difficult to calculate due to the variability in water quality and run-off both within and between years. Doses for wetland liming depend on pH, the limed area relative to total catchment area and liming frequency. Common doses are 0.3–1 ton ha^{-1} catchment area corresponding to 3–25 tons ha^{-1} limed area.

A model based on calculations of the critical load exceedance has been developed for dose calculations on a catchment or regional scale (Henriksen and Hindar 1993; Hindar and Henriksen, 1995). Both present and expected future sulphur and nitrogen deposition data are used and scenarios for future liming have been estimated.

3.3 LIMING METHODS AND STRATEGIES

Both lake liming, limedosers and terrestrial liming may be used (Rosseland and Hindar, 1988; Dickson and Brodin, 1995), but a mix of different liming techniques is often preferred to get an optimal result. Increased knowledge and experience may result in changes in the liming strategy over time (cf. Alenäs *et al.*, 1995).

Lake liming is most common, but often insufficient because of severe acidification of the littoral zone during snow melt (Abrahamsson, 1993), which may affect sensitive littoral species (Henrikson, 1988; Barlaup and Åtland, 1995). To avoid this, lake liming should be supplied with other techniques, such as liming of the littoral area, wetland liming or doserliming of inlet streams.

Terrestrial liming techniques such as whole-catchment liming or wetland liming have several advantages compared to lake liming. Most important is terrestrial retention of Al and deacidification of melt water (Traaen *et al.*, 1995; Hindar *et al.*, 1995; Gubala and Driscoll, 1991; Dalziel *et al.*, 1992). Although the pH-increase in streams after forest soil liming may be small (Brahmer, 1992; Westling and Skärby, 1993) forest soil liming programmes may be coupled to aquatic liming strategies because both pH and Ca increase, Al decreases and because a more stable water quality may be achieved (Hindar *et al.*, 1995).

Dosers for dry limestone powder or slurried powder are used in both small streams and large rivers. The most advanced are equipped with automatic dosing control based on pH upstream or downstream and water flow (Hindar and Henriksen, 1992). Close-downs may be detrimental, especially to salmon populations if no other liming measures are included.

Adequate water quality, with elevated pH and low concentrations of inorganic monomeric Al, is necessary to reach the biological targets. Al must have time to reach more stable forms when pH increases to avoid mixing zones, which may be even more toxic than the acid water itself (Rosseland and Hindar, 1991; Rosseland *et al.*, 1992). Mixing zones are probably especially significant in salmon rivers due to the extreme sensitivity of salmon smolts. Acid, Al-rich tributaries of some size should therefore be limed, although the biological targets in these particular rivers may be insignificant.

3.4 ECOLOGICAL EFFECTS OF LIMING

Generalizing about the ecological effects after liming is difficult, partly because of a lack of data records. Long-term biological changes have been documented 16 years after liming (Appelberg, 1995) but such changes may be related to delayed re-colonization of extinct species rather than liming itself. Expected effects related to the chemical and biological targets may be considered as desirable, others as undesirable.

The experiences from large scale liming in Sweden and Norway as well as liming in USA and Scotland are that the vast majority of chemical, biological and ecological changes are desirable (Baalsrud *et al.*, 1985; Porcella, 1989; Hindar, 1992; Howells and Dalziel, 1992; Henrikson and Brodin, 1995b).

3.4.1 Desirable effects

The primary effects on water quality are increases in pH, alkalinity, ANC, Ca content and decreases in toxic metal species (cf. Wilander *et al.*, 1995). Biologically most important, together with elevated pH, is the decrease of the toxic species of Al and other metals like iron and manganese.

In polyhumic lakes the content of dissolved organic substances (water colour) decreases, whereas increases as well as decreases can occur in waters of lower humic content. Such changes may secondarily affect the light climate of the water. Immediately after liming there is an increased turbidity and a transient decrease in transparency. In the long term the transparency may increase as well as decrease, which may be related to the phytoplankton production and the occurrence of humic substances.

Short-term studies show a transient elevation of the phosphorus (P) content, probably due to phosphorus in the liming agent and release of P bound in the sediments or in decaying plants due to increased mineralization. Also, decreased P after liming, probably due to adsorption to the carbonate particles, has been measured (Blomqvist *et al.*, 1993). Long-term studies indicate unchanged or decreased contents. However, the accessibility of phosphorus to algae may increase. In the few studies of nitrogen, both increases or decreases have been documented.

The most obvious desirable biological effects after liming are successful fish reproduction, increased density of sensitive species and re-colonization of eradicated species (Appelberg, 1995; Bergquist, 1995; Degerman *et al.*, 1995; Larsson, 1995). Another desirable effect is the decrease or elimination of species favoured by acidification.

In figure 1 important factors and processes for the biological development after liming are illustrated. The abiotic changes are the triggers for all other changes but in the long run biotic mechanism, i.e. competition and predation, will determine the community structure.

The community structure will stabilize within the new abiotic limits set by the mix of liming techniques used. The community will be more complex, as seen by increased species number and trophic levels (Appelberg, 1995). Ecosystem processes like decomposition will become more normal (Gahnström, 1995; Gahnström and Andersson, 1995). Ecosystems severely damaged by acidification will experience the most profound changes in the community after liming (Henrikson *et al.*, 1985; Degerman *et al.*, 1995).

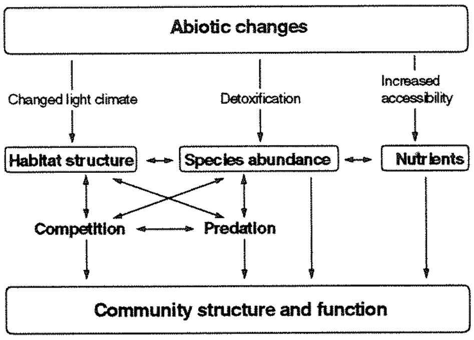

Fig. 1. Schematic illustration of important factors and processes for the biological development after liming. The direct action of altered water quality will affect species abundance, nutrient conditions and habitat structure. The detoxification will facilitate the fish reproduction and populations increase for fish and other sensitive organisms and the recolonization of eradicated species. This will affect the species abundance. The accessibility of the important plant nutrient phosphorus will increase when the Al content decreases or less toxic species of Al is formed, which will favour the production of algae. If the transparency is decreased, the habitat structure is changed, which may affect visual dependant predators like birds. The decrease of *Sphagnum* mat will change the habitat for benthic species. The primary changes caused by the new abiotic environment will release further biotic changes caused by competition and predation. The result is a "new" structure of the organisms community. As a consequence of changes in community structure also the functions within the ecosystems are changed. One example is increased breakdown of leaves due to increased number of shredders.

3.4.2 Undesirable effects

The overwhelming desirable effects of liming must be weighted against undesirable effects which also have been documented after liming. Undesirable effects may be divided into terrestrial and aquatic effects.

Direct damage to terrestrial vegetation after wetland or whole-catchment liming are probably the most severe of the undesirable effects. Terrestrial liming, especially wetland liming, is rather widely used as liming technique in Sweden. Death of *Sphagnum* mosses (Mackenzie, 1992; Hindar *et al.*, 1995; Larsson, 1995) changes the bog surfaces on the short term and probably alter both structure and function of bogs after some decades of repeated liming. More frequent use of smaller doses, coarser liming material and introduction of Mg-containing dolomite may reduce these unwanted effects.

In some lakes in Norway and Sweden increased expansion of *Juncus bulbosus* and *Myriophyllum alterniflorum* after liming has occurred (Brandrud and Roelofs, 1995; Dickson *et al.*, 1995; Larsson, 1995; Roelofs and Brandrud, 1995). This may have great impact on littoral flora and indirectly on littoral fauna and thereby on lake ecology. Increased availability of inorganic carbon in the littoral sediments as a result of carbonate addition may stimulate the increased growth.

3.5 SOCIO-ECONOMIC EFFECTS

Cost-benefit analysis in Norway and Sweden show that liming may be profitable (e.g. Navrud, 1990, 1993a, b; Krokan, 1992; Bengtsson and Bogelius, 1995). In these studies the cost of liming and fishery management has been related to benefit expressed as recreational value, i.e. the willingness to pay for fishing. The people around a limed Finnish lake was willingly to contribute to the costs of liming even if the lake only was used for outdoor recreation (Iivonen *et al.*, 1995). However, this kind of analysis only recognize a part of the economic aspects, not the value of e.g. preserved biodiversity.

Bengtsson and Bogelius (1995) also state that liming practices contribute to enhance environmental awareness among the people.

4. Synthesis

4.1 LIMING TO RECREATE PREVIOUS WATER QUALITY AND RESTORE ECOSYSTEMS?

Successful liming operations will lead to improved water quality and increased number of species susceptible to acidification, but do the ecosystems recover completely? Several difficulties must be considered. First of all, nobody knows the exact structure and function of the ecosystems before they were influenced by the anthropogenic acidification. Second, all ecosystems experience a developmental process and a certain degree of unstability between years even if the external conditions remain more or less constant (cf. Brink *et al.*, 1988).

Well aware of the uncertainties, we state that if the chemical target is met liming in the long run will restore the ecosystems but will not make them identical to what may have been original (Figure 2) (cf. Degerman *et al.*, 1995; Henrikson and Brodin, 1995b; Lingdell and Engblom, 1995; Wilander *et al.*, 1995). That the ecosystems are not completely recovered is not specific for liming but also for other attempts to repair disturbed habitats of aquatic as well as terrestrial systems (cf. Brink *et al.*, 1988; Cairns, 1988).

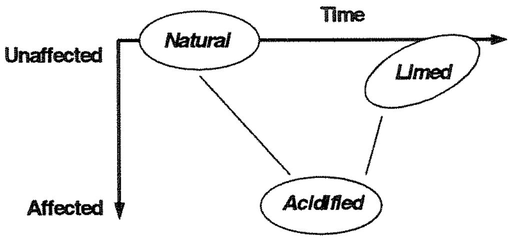

Fig. 2. Generalization of changes occurring in freshwater ecosystems influenced by acidification and liming. Acidification results in decreased ecosystem complexity. Successful liming entails a "normalization", i.e. the complexity and function of the ecosystem will be largely similar to unaffected ecosystems, yet the ecosystems will not become identical and liming alone might not bring back completely natural conditions. However, with time the similarity with unaffected waters will increase.

There may be several reasons why the limed waters differ from waters unaffected by acidification (cf. Appelberg, 1995; Degerman *et al.*, 1995). The most common reason is probably that the chemical target is not met due to insufficient planning or severe practical difficulties. Limed waters may become rather unstable if acidified waters continuously are discharged into the lakes and streams. Toxic water and the variable environment will affect the normal competition relations, favouring non-competitive "opportunistic" species. Also, changed nutrient availability and slow recolonization may affect the result of liming. Improved liming strategy and complementary measures may improve the success of liming.

Complementary measures are a part of the Swedish liming programme. Bergquist (1995) defined two categories of "biological restoration": (1) measures aimed at facilitating natural re-colonization and re-establishment of species which have been eliminated, and (2) direct reintroduction of species by man. Examples are; elimination of migration obstacles, biotope reconstruction, and replenishment of individuals for species occurring in restricted numbers. Supply of nutrients, especially phosphorus, is another complementary measure in order to restore the productivity of limed waters. Hitherto, such measures have been taken only in a few research projects (Blomqvist *et al.*, 1993) and more experience is needed before these measures can be operational.

4.2 PERSPECTIVES ON LONG-TERM LIMING

As a consequence of deposition scenarios according to the commitments of the UN sulphur protocol (UN, 1994) liming in Norway will be reduced to one third some time after year 2010 (Henriksen and Hindar, 1993). Numbers in Table I are based on the introduction of a variable $\mathrm{ANC}_{\mathrm{limit}}$ (Henriksen *et al.*, 1995).

TABLE I.

Effects of decreased exceedance of the critical load in southern and northern Norway according to the commitments of the UN (1994) protocol for sulphur deposition reductions. Figures are based on a variable $\mathrm{ANC}_{\mathrm{limit}}$, see Henriksen *et al.* (1995). (Data from A. Henriksen.)

	AREA EXCEEDED percent		AMOUNT OF LIME tons $\mathrm{yr.}^{-1}$		COST mill. NKR	
	Today	Year 2010	Today	Year 2010	Today	Year 2010
South of Norway	55.0	21.2	390,000	149,000	312	120
North of Norway	6.4	1.2	22,000	5,600	23	4.3
Norway	29.7	10.8	412,000	155,000	335	124

Decreased exceedance of the critical load will probably result in decreased Al concentrations and to a decrease in the frequency and magnitude of acid episodes. Target-pH for liming may therefore be lower in this improved environment, thus reducing the liming costs further.

We are not yet able to estimate the exact timing of water quality improvements to given levels after future deposition reductions. Dynamic models, such as MAGIC (Wright *et al.*, 1988), have been used but lack of long data records during recovery makes the forecasts uncertain. Due to the time lags liming operations may probably be longer lasting than recognized from sulphur deposition scenarios, i.e. several decades.

Metals like Al may polymerize and eventually be precipitated as humic–metal complexes after liming (Egeberg *et al.*, 1995). Some has argued that easily available Al from such sediments could represent a threat to aquatic life during reacidification after liming and after close-downs of lime dosers. However, both theoretic considerations and monitoring data show that precipitated Al does not represent an additional Al-source of any significance for aquatic life during these circumstances (Hindar and Lydersen, 1995).

Wetland liming and whole-catchment liming may stimulate the decomposition of organic matter. A high carbon/nitrogen relation of the organic matter may reduce this stimulating effect and increased decomposition may therefore be less pronounced under humic/low-temperature climate as in Scandinavia. Nevertheless, liming for decades will probably change the structure and function of bog surface and the humic layer of e.g. forest soils. Knowledge of the quality and speed of these changes is needed.

Long-lasting liming obviously results in accumulation of undissolved minerals on lake bottoms and stream beds. So far, research activities have focused on the suitability of limed sediments as habitat for invertebrates and as spawning sites for fish. The ecological effects have not been studied.

In spite of increasing knowledge it is important to point out the short-comings and lack of scientific knowledge. We highlight the following (see also Henrikson and Brodin, 1995b; Kroglund *et al.,* 1995):

- long-term ecological effects, i.e. more than 20 years,
- concentrations and accessibility of nutrients,
- primary production,
- the structure and function of limed wetlands,
- re-colonization and reintroduction of species,
- strategies and methods to eliminate harmful effects of acidic episodes,
- improvements of liming techniques to reduce harmful effects in limed wetlands,
- identification of measurable biological targets others than fish and invertebrates.

5. Concluding remarks

We state that liming of acidified freshwaters preserves biodiversity and improves conditions for recreational fishing. Undesirable effects have been documented. Although further sulphur emission reductions are expected, acidification will still be a serious environmental problem and liming will be needed for several decades to come.

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EXTREME ACIDIFICATION OF THE AFFORESTED SVELA CATCHMENT ASSOCIATED WITH A SEA SALT EPISODE

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Abstract. Episodic acidification of streams and lakes may be due to a combination of acidic deposition and natural processes. The "sea salt effect" is a natural process in which episodic input of sea salt-rich precipitation to acidified soils can cause episodic acid runoff. The salt effect, which is reflected in "negative" non-marine Na concentrations, may temporarily reduce the acidity of the soil due to Na retention, but increase acidity and Al-concentration and thereby the toxicity of the runoff. A sea salt episode occurring during heavy storm events in January 1993 in coastal areas of southwestern Norway created extreme acidification in an afforested catchment. Stream water chloride increased sharply to eight times the normal concentration and the non-marine Na concentration was calculated to 208 μeq L^{-1}. The retained Na was largely compensated by an increase in Al and also H^+. The concentration of inorganic monomeric Al increased from 200 to 2000 μg L^{-1} and pH decreased from 4.90 to 4.45. Due to low pH and the dramatic increase in inorganic monomeric Al the water toxicity for aquatic organisms increased. Acidification associated with the storm was also seen in other small catchments and in large rivers at the Norwegian southwestern and western coast, but the potential toxicity never reached the levels of the afforested catchment. Afforested catchments in acidified catchments seem to be especially vulnerable to the sea salt effect because of their ability to retain larger amounts of sea salts than other areas. Afforestation may thus enhance the harmful effects of acidification in vulnerable areas.

Key words: sea salts, precipitition, episodes, afforestation, acidification, stream water quality, ion-exchange, aluminium.

EXTREME ACIDIFICATION IN SMALL CATCHMENTS IN SOUTHWESTERN NORWAY ASSOCIATED WITH A SEA SALT EPISODE

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Abstract. During heavy storm events in January 1993 in the coastal areas of south-western Norway, a sea salt episode created extreme acidification in the afforested Svela catchment. Stream-water chloride increased sharply to eight times the normal concentration and the non-marine Na concentration was calculated to -208 µeq L . Negative values indicate that Na was retained in the soil profile. By ion-exchange processes this was largely compensated by an increase in stream-concentrations of Al and H^{+}. Concentrations of inorganic monomeric Al increased from about 20 to 200 µeq L^{-1} and pH decreased from 4.90 to 4.45. Due to the low pH and the dramatic increase in inorganic monomeric Al the water toxicity for aquatic organisms increased. Acidification associated with the storm was also observed in a forested and a non-forested catchment, but never reached the levels of the afforested catchment. The extra vulnerability of afforested catchments may be due to their ability to intercept larger amounts of sea salts than areas less dominated by dense tree stands. Although both pH and Al went back to normal levels for the area after 3-4 months the Na/Cl-relationship in cumulated transport values indicated a long-lasting effect (> 2 years) on the soil profile. Reloading the soil profile with Al and H^{+} back to prestorm values will affect the catchments ability to mobilize these ions during future sea salt episodes. More frequent episodes will probably result in less acid and Al-rich stream-water during the episodes than documented here due to incomplete reacidification of the soils.

1. Introduction

The sea salt effect (Wiklander 1975) is ascribed to cation exchange processes in the soil, involving mainly exchange of Na with H^{+} and Al and/or base cations. Cl acts as a mobile anion (Skartveit *et al.* 1980, Norton *et al.* 1987, Wright *et al.* 1988) and passes through the soil relatively unaltered. The salt effect may thus temporarily reduce the acidity of the soil due to Na retention, but increase the acidity of the runoff (Wiklander 1975). Empirical evidence for the sea salt effect comes from concentrations of Na relative to Cl; when the equivalent ratio of Na/Cl is less than that of seawater (that is, the concentration of non-marine Na is negative), it can be assumed that ion exchange in the soil has occurred.

A prerequisite for a sea salt episode to be toxic for aquatic organisms is acidified soils in combination with high sea salt deposition in relation to normal deposition, or a period of large amounts of dry fall out followed by rain (Heath *et al.* 1992). In January 1993 the weather in south-western and western Norway was characterized by strong winds from south and south-west, relatively high temperatures and high precipitation amounts as rain. The storms resulted in a sea salt episode that temporarily increased the acidification of lakes, rivers and small catchments (Hindar *et al.* 1994). In this paper we focus on the storm effects in three catchments, a non-forested, a naturally forested and an afforested catchment in south-western Norway.

2. Materials and methods

The interinstitutional research programme "Nitrogen from mountains to fjords" includes detailed studies in the Bjerkreim River catchment in south-western Norway (Hessen and Henriksen 1994). Measurements of air and precipitation chemistry is performed by the Norwegian Institute for Air Research. Runoff from both non-forested, forested and afforested catchments and major tributaries is monitored. Volume-weighted water samples are collected every second week for five calibrated catchments. All samples have been analysed according to standard procedures at the Norwegian Institute for Water Research.

The sea salt effect in the streams was estimated as a negative non-marine sodium concentration ($Na^* < 0$) due to deviation from the original Na/Cl balance of sea salts;

Na^* (μeq L^{-1}) = Cl • (Na_{sea}/Cl_{sea})

Negative values indicate Na-adsorption in the soils and is compensated by other cations such as Ca^{2+}, Mg^{2+}, H^+ or positively charged Al-species.

Concentration of Al is expressed in μeq L^{-1} regarding all inorganic monomeric aluminium (Al_i) is Al^{3+}. The average charge of Al is close to 3+ at pH 4.5-5.0 and low temperatures but decreases at higher pH. Calculated Al concentrations may thereby be slightly too high at pH around and higher than 5.0.

Three small catchments (100-500 m.a.s.l.; two with forest cover, one without) in the Bjerkreim River were strongly affected by the storms. The **non-forested catchment** of Longa (0.80 km^2) is located only 7 km from the coast and consists of barren rocks, patchy soils, heather vegetation and five small ponds. The **afforested catchment** of Svela (0.51 km^2) is located 13 km north of Longa and 20 km from the coast. Svela is partly covered with very dense stands of Norway spruce (*Picea abies*) and sitka spruce (*Picea sitchensis*). The **forested** catchment of Högmoen (0.45 km^2), about 30 km from the coast, is covered with mixed and less dense stands of mainly Scots pine (*Pinus silvestris*) and birch (*Betula* spp.).

3. Results

In January 1993, both Cl-concentration in air (daily mean of 12 μg Cl m^{-3} at the representative monitoring station Skreådalen) and Cl-wet deposition reached the highest levels ever registered since routinely sampling and analysis was initiated in 1977. At Lista monitoring station 60 km south-east of the Bjerkreim catchment, the total wet deposition of Cl during this month was of the same order of magnitude as the normal annual deposition (SFT 1994).

Fig. 1. Concentrations in µeq L^{-1} of Cl, non-marine Na, H^+ and Al in the streams of Longa, Svela and Högmoen catchments in the period February 1992 to end of December 1994, including the storm events in January 1993.

Before the storm, Cl-concentrations in runoff from the three catchments were about the same (Fig. 1). A dramatic increase in Cl concentrations in runoff was measured after the storm especially in the afforested Svela catchment. Concentrations of Cl in precipitation in the period after the storms were not higher than normal but the Cl-concentrations in the streams remained high for about one year. Chloride may thus be less mobile than generally considered or subject to delayed retention because of slow dilution of the surface water (Longa) and soil water.

Concentrations of calculated non-marine Na was -208 μeq L^{-1} and -150 μeq L^{-1} in the runoff from the afforested and the forested catchments, respectively. This loss of Na, which was probably due to adsorption in the soil, was largely compensated by a corresponding increase in Al and H^+ (Fig. 1). The inorganic monomeric concentration of Al (Al_i) in the runoff from the Svela and Högmoen catchments increased tenfold during the sea salt episode, to about 200 and 130 μeq/l, respectively, and pH decreased from above 5.0 to 4.45 and 4.70. Stream-water was thus highly toxic to fish and other aquatic organisms. The stream from the non-forested Longa catchment responded much less ($Na^* = -22$ μeq L^{-1}; pH from 5.17 to 4.78; Al_i from 3 to 10 μeq L^{-1}) to the storm events than the two forested catchments, partly because of absence of the intercepting effect of forest canopies, and probably later also (Fig. 1) because of a longer hydrologic retention time due to the five ponds in the catchment.

Fig. 2. The Na/Cl relation in cumulated transport values (based on concentrations in μeq L^{-1} and runoff) of the Høgmoen, Longa and Svela streams starting before the sea salt episode in January 1993. Dotted line indicates Na/Cl-ratio (equivalent basis) in seawater.

Although a dramatic increase in stream ion transport was associated with the storm, the relative proportion between most of the cations remained unchanged. However, the relative proportion of Na increased after the episode. Also, a change in dominating anion from SO_4 to Cl was found. The relationship between Na and Cl in stream water was close to 1.0 before the storm event indicating significant Na-sources in the catchment. Stream-water Na/Cl decreased during the storm probably due to adsorption of Na in the soil profile, but subsequently returned towards an equilibrium value. However, the Na/Cl-relation of cumulated transport values increased remarkably slow and had not reached the pre-storm situation after two years (Fig. 2).

4. Discussion

Sea salt episodes are believed to be of little long-term significance, since the yearly input/output ratio of Na is normally close to 1.0 in calibrated catchments (Skartveit *et al.* 1980, SFT 1992). However, results presented here indicate that the effect on runoff may last for more than two years. This is probably due to a slow reloading (reacidification) of the soil profile with H^+ and Al. Reloading the soil profile with Al and H^+ back to prestorm values will affect the catchments ability to mobilize these ions during future sea salt episodes. More frequent episodes will probably result in less acid and thereby less toxic stream-water due to incomplete reacidification of the soils.

Afforestation may increase the negative effects of acid rain by 1) increasing the uptake of base cations from the soil, 2) scavenging air pollutants, 3) increasing the evaporation and thus concentrating pollutants (Jenkins *et al.* 1990). Also, afforested catchments, as Svela, may be especially vulnerable to the sea salt effect because of their ability to intercept larger amounts of sea salts than areas less dominated by dense tree stands, as the forested watershed Høgmoen.

Toxic water with elevated concentrations of inorganic monomeric Al and low pH lasted for 3-4 months in the three calibrated catchments. Dramatic effects on aquatic organisms should be expected in the stream itself and also when entering larger streams. Highly toxic mixing zones are believed to be of significance when acid, Al-rich water enters water with more favourable pH due to the unstable Al chemistry (Rosseland and Hindar 1991; Rosseland *et al.* 1992).

In less acidified areas, base cations were released during the storm rather than Al and H^+ (Hindar *et al.* 1994). Heath *et al.* (1992) indicates that soil acidification was a prerequisite for the sea salt effect to occur.

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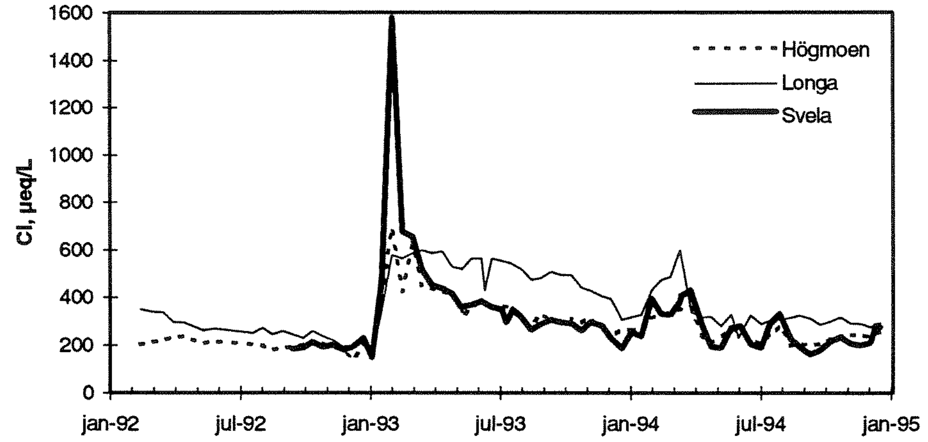
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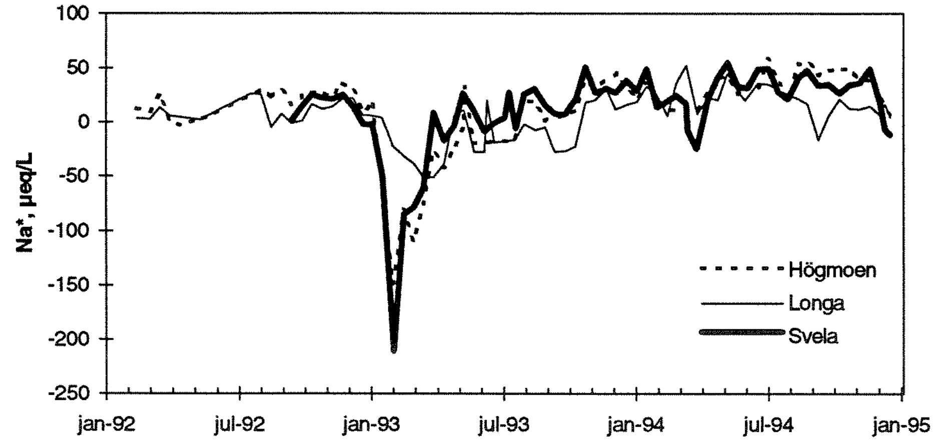
Högmoen
Longa
Svela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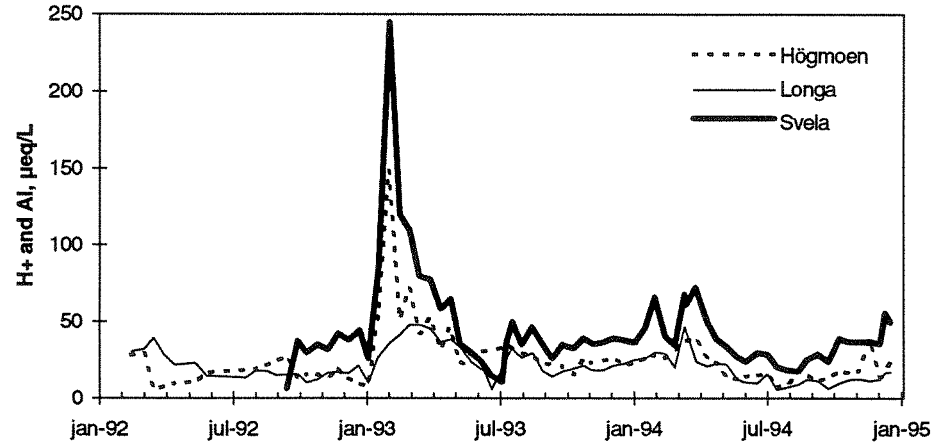
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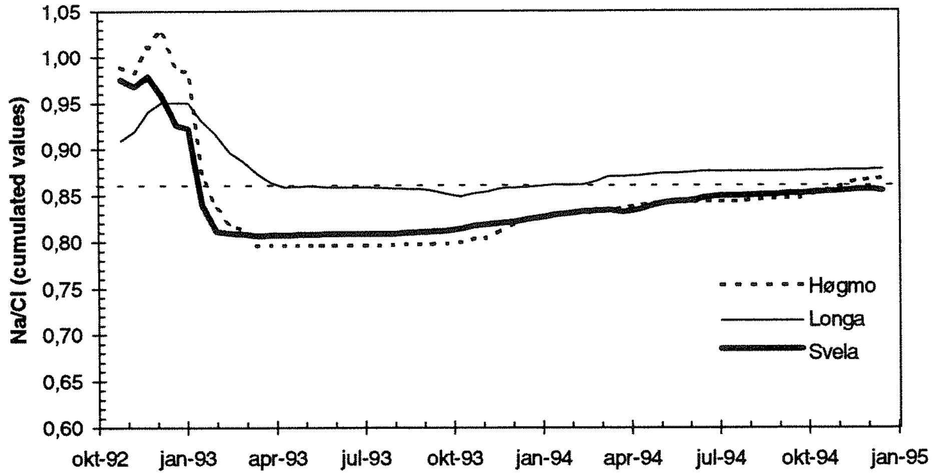
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0,80
0,75
0,70
0,65
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apr-93
jul-93
okt-93
jan-94
apr-94
jul-94
okt-94
jan-95
Høgmo
Longa
Svela

ACIDIFICATION AND FISH KILLS ASSOCIATED WITH A SEA SALT EPISODE IN SOUTHWESTERN NORWAY

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NAT17

Abstract. In a period with unusually strong winds and heavy precipitation in southwestern Norway in January 1993, deposition of very large amounts of sea salt both in precipitation and as dry deposited material led to profound changes in the chemical composition of runoff water. Fish kills were reported in both rivers and lakes. The deposition of sea salts by precipitation reached 300-600 meq m^{-2} on a monthly basis at sites 20-50 km from the coastline. The affected rivers had elevated Cl concentrations (up to 5 times the normal) and many of them had a "negative" non-marine Na concentration of 30-70 μeq L^{-1} due to soil ion-exchange effects. A significant linear relationship for the whole dataset between the relative Cl increase and the Na deficit was found ($R^2 = 0.81$, $N=15$). Areas 50-100 km from the coast were thus especially vulnerable, since heavy sea salt deposition here is rare. Acidified catchments apparently responded to Na adsorption by increased runoff H^+ and Al, whereas slightly and moderately acidified catchments responded by increases in base cations or by base cations together with H^+ or Al or both. Afforested catchments seemed to be especially vulnerable. Sea salt episodes were also found in areas that receive moderate amounts of atmospheric pollutants. This is of importance because rivers that are only slightly affected by acidification also may be vulnerable. Increased Al-concentrations associated with sea salt episodes may be the first signs of increasing acidification in areas along the coast. These data have to be considered in the context of critical loads.

Key words: sea salts, precipitation, episodes, acidification, fish kills, rivers, lakes, ion-exchange, critical loads.

NITROGEN FROM MOUNTAINS TO FJORDS. RETENTION OF ATMOSPHERIC DERIVED NITROGEN IN TERRESTRIAL AND AQUATIC ECOSYSTEMS OF THE BJERKREIM RIVER BASIN

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NUT06

Abstract. To approach the problems connected to increased nitrogen inputs and to the leaching of nitrogen from Norwegian ecosystems, an inter-institutional five-year project: "**Nitrogen from Mountains to Fjords**" was established in 1992. The project considers both the atmospheric and terrestrial contributions of nitrogen to freshwaters and the sea, and the transformations of nitrogen in soil and freshwater. Total N deposition (both wet and dry; about equal amounts of NO_3-N and NH_4-N) in the Bjerkreim river basin in southwestern Norway was 14 and 12.5 kg ha^{-1} yr^{-1} in 1992 and 1993, respectively. Very small seasonal and between stations variations in both NO_3-N and total N concentration have been found in the run-off of the upper two thirds of the 693 km^2 river basin. Specific N transport ranged from 4.7 to 7.7 kg ha^{-1} yr^{-1} in 1993 for three monitoring stations located in different parts of the catchment. The ratios between N transport and N deposition of 0.4-0.6 indicate low N retention. In 1992 a ratio of 0.7 was found for the upper two thirds of the catchment. Both high specific runoff (90 L s^{-1} km^{-2}) and exceedance of N uptake capacity are most likely important factors for the low N retention. There was insignificant N retention in the 240 m deep, ultra-oligotrophic (2-3 μg L^{-1} total P) Lake Ørsdalsvatn, the largest lake (surface area = 12.3 km^2) in the basin. The low N retention in both terrestrial and aquatic ecosystems is probably representative for southwestern Norway. Impacts on both acidification and nutrient status may be expected.

Key words: nitrogen, deposition, runoff, transport, retention, terrestrial, aquatic, acidification, nutrient.

LIMING OF WETLANDS IN THE RØYNELANDSVATN CATCHMENT - EFFECTS ON STREAM WATER CHEMISTRY AND POTENTIAL TOXICITY FOR FISH

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LIM26

Abstract. In August 1990, 20 tons ha^{-1} of fine powdered limestone was spread by helicopter on wetlands constituting 5 % of the 1.2 km^2 catchment of Lake Røynelandsvatn in southern Norway. Before liming the stream water chemistry at four stations was characterized by low pH, Ca and ANC and high reactive aluminium (RAL) concentrations (pH = 4.0 - 4.6; Ca = 38-57 $\mu eq\ L^{-1}$; ANC = -47 - -77 $\mu eq\ L^{-1}$; RAL = 320-400 $\mu g\ L^{-1}$). After liming, pH, Ca and ANC increased immediately and the concentration of Al declined both in the inlet and outlet stream. Three years after liming the Ca concentration in the inlet and outlet stream was still high (165 and 130 $\mu eq\ L^{-1}$) and ANC still positive. Due to significant Al retention in the catchment, RAL was still 50 % lower than preliming values. In the period after liming the stream-water chemistry was remarkably stable. Al-rich runoff during periods with ice cover, as regularly seen after ordinary lake liming, was never recorded. Elimination of such episodes increases the possibility of aquatic organisms to survive both in the littoral zone of lakes and in streams. Application of limestone powder on the bogs resulted in massive death of *Sphagnum* mosses. However, although this death should imply increased mineralization, no significant stream water increase in the concentrations of NO_3^- or total organic carbon was observed. Thus, in spite of some unwanted terrestrial effects, wetland liming may have ecological advantages.

Key words: liming, catchment, wetlands, stream-water, water quality, aluminium, acid episodes, fish toxicity, ecology.

LIMING OF WETLANDS IN THE RØYNELANDSVATN CATCHMENT- DEACIDIFICATION DYNAMICS AND CAPACITY

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LIM27

Abstract. In August 1990, 20 tons ha^{-1} of fine powdered limestone was spread by helicopter over 5.1 ha *Sphagnum* dominated wetlands in the 1.2 km^2 catchment of Lake Røynelandsvatn in Southern Norway. Before liming the stream water chemistry was characterized by low pH, Ca and ANC and high reactive aluminium (RAL) concentrations (pH = 4.0 - 4.6; Ca = 38-57 $\mu eq\ L^{-1}$; ANC = -47 - -77 $\mu eq\ L^{-1}$; RAL = 320-400 $\mu g\ L^{-1}$). A rapid increase in pH, Ca and ANC and a decrease in RAL was seen both in the inlet and in the outlet stream after liming. Both deacidification due to lime and dissolved CO_2 obviously played an important role for the variation in runoff pH. pH increased with increasing water flow and significant hysteresis effects were found. Regularly flooded bogs and the seepage bogs contributed with the highest amounts of dissolved lime relative to the dose. The long-lasting liming effect corresponded to an apparent residence time of 2-3.5 years compared with the actual residence time of one month. Based on stream-water Ca and monitored water flow a total of 45 % of the added limestone powder had been transported out by the end of 1993. The transport in 1993 contributed only 7 %, indicating rapidly decreasing liming effects. Terrestrial liming may be a useful approach to neutralizing acidic runoff because of the long-lasting effect on the water quality and the inherent deacidification capacity during storm flows and snow melt.

Key words: liming, catchment, wetlands, stream-water, deacidification, capacity, dynamics, water quality, aluminium, acid episodes, duaration.

COUNTERACTIONS AGAINST ACIDIFICATION IN FORESTS ECOSYSTEMS.
EFFECTS ON STREAM WATER QUALITY AFTER DOLOMITE APPLICATION TO FOREST SOIL IN GJERSTAD, NORWAY

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Abstract. The deposition of strong acids is one of many threats to forest ecosystems and viable forestry. Several counteractions against acidification have been launched, e.g. changes in forestry management and the introduction of chemicals. The inter-institutional programme "**Counteractions Against Acidification in Forest Ecosystems**" was established in 1993 to evaluate existing knowledge and run experimental and full-scale field experiments. A total of 240 metric tons of coarse dolomite powder was spread by helicopter in September 1994 on 84 ha forest catchment dominated by pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*). Potential desirable and undesirable effects after this carbonate application may be less pronounced than recorded at other sites due to the relatively moderate dose (3 tons ha^{-1}). Pre-liming stream water quality (mean values for May 1993-September 1994) was as follows: pH 4.8; Ca 1.13 mg L^{-1}; reactive Al (RAl) 248 µg L^{-1}; inorganic monomeric Al (Al_i) 72 µg L^{-1}. The reference station was slightly higher in Ca and slightly lower in both RAl and Al_i. Dolomite application resulted in a significant increase in pH to 5.7 as mean value for the post-liming period (September 1994-April 1995). Both Ca and Mg increased significantly after liming, and both RAl and Al_i declined significantly. The rapid detoxification of stream-water may be explained by dissolution of dolomite particles in both streams and catchment, a resulting pH increase and change in Al species composition. Retention of Al in the catchment probably explains the reduction in RAl. No increase in NO_3, total N, total P or TOC was recorded the first seven months.

1. Introduction.

Several counteractions against forest soil acidification are available for forest management practices. Counteractions can be devided into silvicultural measures and application of chemicals. The first group involves strategies like use of broadleaved trees, both in pure stands or mixed within conifer stands. The second group involves application of lime, dolomite, ash and use of different commercial fertilizers. Liming has already been used on a practical scale for a long time, e.g. in Germany (Hüttl and Zöttl 1993). Fertilization with the goal of revitalization of forest stands suffering from nutrient deficiencies has prooved successful (Hüttl 1991).

The question whether liming should be launched on a practical scale in Norwegian forestry or not, has dominated the discussion in the last decade. Due to lack of integrated studies on soil, water and vegetation under Norwegian conditions, a watershed study with dolomite application was initiated. The purpose of this experiment is to study the effects of dolomite application to a forested area on soil water and runoff water chemistry, soil chemistry, tree growth and vitality and changes on vegetation and mychoflora. The study is a part of a multidisciplinary research programme "Counteractions Against Acidification in Forest Ecosystems" dealing with several possible counteractions (Nilsen 1994).

Forest soil liming may have both desirable and undesirable effects on both aquatic and terrestrial ecosystems. Of special interest is the expected detoxification of stream water from limed areas and thereby the relevance of the treatment for aquatic organisms. Detoxification arises if pH and concentrations of base cations increase and toxic aluminium species decline. Unwanted aquatic effects may include increased nitrate concentration due to increased mineralization and nitrification and increased leaking of organically bound heavy metals such as iron and lead due to increased decomposition of organic matter.

We present a brief description of the experimental design and short-term effects on runoff water chemistry and potential toxicity for fish.

2. Materials and methods

Two catchments in Gjerstad in South Norway (59°, 53' N, 9°, 00' E) were choosen for the investigations. The catchments are forested with a mixture of mainly Norway spruce and Scots pine stands. A relatively small amount of broadleaved trees are mixed within the conifer stands. The forest consists of old mature stands and with a certain amount of newly regenerated areas (less than 15 years). Some main figures for the two catchments are presented in Table I.

TABLE I

Areas (ha), standing volume (m^3), mean age (yr) and area distribution according to tree age classes and impediment.

	Size (ha)	Standing volume Total	Spruce	Pine	Mean age	Middle aged and old forest	Regenerated areas	Imp.
Limed	84.4	9900	3400	4500	67	70 %	17 %	13 %
Control	40.8	6000	1600	3600	77	84 %	9 %	7 %

In september 1994 240 tons of coarse-grained dolomite were applied. The dolomite was evenly spread over the whole catchment by helicopter. This gives approximately 3 tons ha^{-1}. The grain-size distribution was 5 % < 0.2 mm, 0.2 mm < 90 % < 2.0 mm and 5 % > 2.0 mm. The Ca, Mg and water content was 43, 12 and 1 %, respectively.

Waterflow is recorded at two stations in the limed catchment and at one in the reference catchment. Volume-weighted streamwater samples were collected biweekly at these stations, and ordinary samples biweekly at another two stations in the limed catchment. Chemical analyses of all major ions were carried out according to Norwegian Standard (NS) procedures. Aluminium was analysed by the pyrocatecolviolet method before (reactive Al=RAl) and after (organic monomeric Al) ion exchange (Driscoll 1984) of the sample. The difference (inorganic monomeric Al=Al$_i$) is supposed to be toxic to aquatic organisms.

Registration of ground vegetation, mychoflora, tree growth and vitality is carried out on ten subjectively selected (25 m x 30 m) in each catchment. Soilwater is sampled from three depths in the mineral soil at regular intervals on three of the plots. Soil chemistry is analysed on soil samples from both humic and mineral soils. Humic samples are also analysed for root mychorriza. Results from these parts of the programme will be presented elsewhere.

Data presented here are from the outlet of the limed and control catchments before (May 1993-September 1994) and after (September 1994-April 1995) treatment (Table II, Figure 1).

3. Results

Prior to liming the stream water in both catchments was chronically acidified. pH was generally between 4.5 and 5.5 and mean concentrations of reactive aluminium (RAl) were 248 µg L^{-1} and 192 µg L^{-1} in the two catchments (Table II). About 30 % of the Al was inorganic monomeric (Al$_i$). The relatively high organic Al-fraction can be related to the generally high concentration of total organic matter in the streams (6-8 mg TOC L^{-1}).

Application of dolomite resulted in significant changes of the stream water quality (Table II, Figure 1). pH increased to 5.5-6.0. Mean concentrations of calcium (Ca) and magnesium (Mg) increased from 1.13 to 1.46 mg L^{-1} and from 0.36 to 0.69 mg L^{-1}, respectively. Acid neutralizing capacity (ANC) increased from 9 to 39 µeq L^{-1}.

TABLE II

Mean stream water chemistry with standard deviation in the limed and in the control catchment before (May 1993-Sept.1994) and after (Sept. 1994-April 1995) treatment. RAl=reactive aluminium; Al$_i$=inorganic monomeric aluminium; ANC=acid neutralizing capacity.

		pH	Ca *mg L^{-1}*	Mg *mg L^{-1}*	RAl *µg L^{-1}*	Al$_i$ *µg L^{-1}*	ANC *µeq L^{-1}*
Limed	before (n=19)	4.8±0.19	1.13±0.29	0.36±0.08	248±69	72±19	9±12
	after (n=13)	5.7±0.22	1.46±0.12	0.69±0.11	185±26	19± 9	39±16
Control	before (n=19)	4.8±0.20	1.27±0.32	0.37±0.08	192±55	34±14	22±17
	after (n=13)	4.9±0.15	1.28±0.18	0.40±0.06	190±16	41±10	15±14

Reactive aluminium (RAl) decreased to 185 µg Al L^{-1} and the toxic inorganic monomeric fraction (Al$_i$) decreased from 72 to 19 µg Al L^{-1}. TOC, nitrogen fractions, total phosphorus and heavy metals were not significantly affected. The water quality in the control catchment (not limed) was not significantly different in the period April

Fig. 1. Ca, Mg, pH and Al_i in stream water in the limed and control catchments. Dolomite application is indicated by arrow.

1993 to September 1994 compared to the period September 1994 - April 1995 (Table II).

4. Discussion

Desirable short-term effects after the dolomite application were increased pH, Ca and Mg, reduced reactive Al concentrations and a change to non-toxic Al species. These effects are supposed to be caused both by dissolution of dolomite in the streams and in the terrestrial part of the catchment.

Undesirable effects, such as increased NO_3 leaking in areas with high N deposition (Westling and Skärby 1993; Kreutzer 1995) and increased mobility of organically complexed heavy metals, such as Fe, Pb, Cu (Kreutzer 1995), may be expected after forest soil liming. So far, none of these effects have been documented in Gjerstad, probably due to the expected long-lasting dissolution of the coarse-grained dolomite and the moderate dose. Also, a high C/N ratio of the forest soil may reduce the stimulating effect on decomposition of organic matter caused by liming and thereby reduce the unwanted effects.

Experiments from Sweden with moderate limedoses (3-4 tons ha^{-1}) showed only minor effects on pH and Al concentration in stream water during a three-year period (Westling and Skärby 1993). Also in Germany only minor effects in stream water quality were registered after liming with 3-4 tons ha^{-1} (Brahmer 1992). Liming of the Tjønnstrond-catchment in Norway with a similar dose of calcite powder, however, resulted in a rapid increase in both pH and Ca and a more than 50 % reduction in reactive Al (Traaen et al. 1994). Steep slopes, thin soils (< 50 cm) and high precipitation in both Gjerstad and Tjønnstrond promote a rapid response due to good contact between runoff and the neutralizing material.

Several investigations have documented that even small water quality changes or differences may be of significance for the survival of fish (Kroglund et al. 1992) and invertebrates (Raddum and Fjellheim 1984). Decreased concentrations of the toxic inorganic Al-species are important and increased concentration of Ca may ameliorate Al toxicity (reviewed by Wood and McDonald 1987; Rosseland et al. 1990).

Whole-catchment liming has certain advantages compared to more traditional (in Norway) methods, such as lake liming and lime dosing. The Al transport from the acidified catchment to watercourses will be reduced, and a more stable water quality is achieved throughout the year. Moderate doses of coarse-grained dolomite will probably minimize the undesirable effects on both water quality and terrestrial vegetation. Forest liming, although relatively expensive, may therefore represent an interesting supplement to other liming methods. A longer data record is needed, however, because such conclusions also should be based on long-term effects.

5. Conclusions

Liming of forest soils by coarse-grained dolomitic limestone resulted in immediate short-term changes of the water quality. These changes were positive for the survival of aquatic organisms. However, a longer datarecord and results from other parts of the research programme are needed before this method can be recommended.

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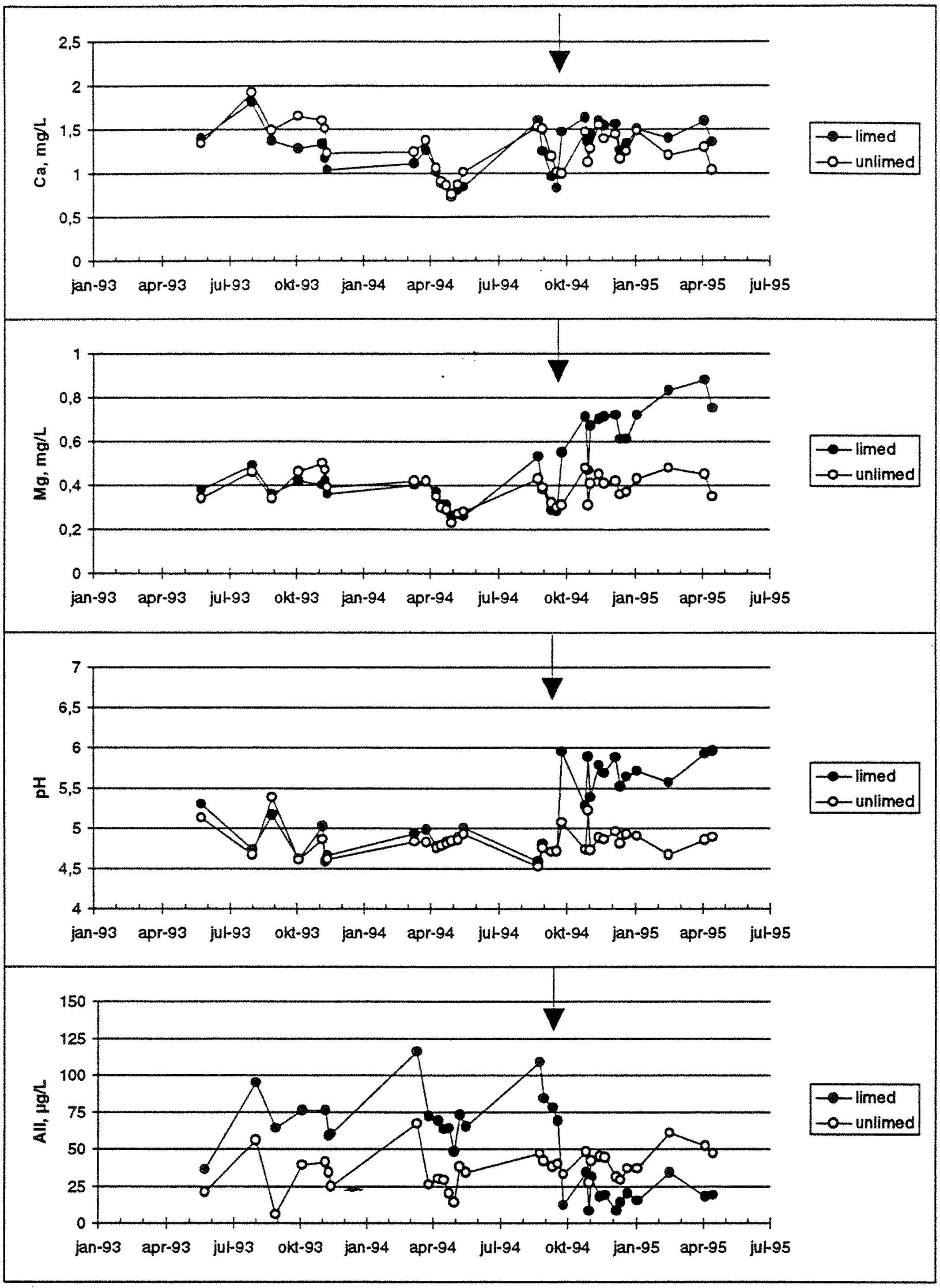
2,5
2
1,5
1
0,5
0
Ca, mg/L
limed
unlimed
1
0,8
0,6
0,4
0,2
0
Mg, mg/L
limed
unlimed
7
6,5
6
5,5
5
4,5
4
pH
limed
unlimed
150
125
100
75
50
25
0
AlI, µg/L
limed
unlimed
jan-93
apr-93
jul-93
okt-93
jan-94
apr-94
jul-94
okt-94
jan-95
apr-95
jul-95

Fig. 1

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

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LAK59

Abstract. The International Cooperative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes has been designed to establish the degree and geographic extent of acidification of surface waters. Further, to collect information in order to evaluate dose-response relationships, and to define long-term trends and variations in aquatic chemistry and biota attributable to atmospheric pollution, particularly to acidic deposition. Twenty countries of Europe, Russia, and North America have representatives in the Programme. Data from more than 200 sites in 16 countries are available in the database. Sites included in the Programme are monitored by each country individually, although the monitoring methods used have been standardised across participants, and intercalibration studies are completed each year. The programme has delivered data, reports and results for use to the Working Group on Effects of the ECE/UN. The Programme Centre and the Programme database are located at the Norwegian Institute for Water Research (NIVA).

The unique possibility to evaluate water quality in catchments across boundaries has been performed based on available data of the programme data base. Long-term trend analysis on the ICP dataset is the first attempt, as far as we know, to try to discover regional patterns both in Europe and North America in long-term changes in surface water chemistry, due to changes in deposition. Decreases in surface water sulfate and calcium concentrations were common among European sites, in both river and lake sites. Decreases in nitrate concentrations were observed in many of the European sites. Decreases in surface water sulfate predominated at the U.S. sites, although these were not accompanied by any specific trend patterns in other variables. At the Canadian sites, decreases in sulfate were common, and were accompanied by increases in pH. Concomitant increases in alkalinity were noted in some of these sites, but not all.

Key words: monitoring, rivers, lakes, long-term trends, sulphate, nitrate.

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ECOSYSTEM EFFECTS OF SULPHATE AND NITROGEN DEPOSITION TO A HUMIC LAKE: THE INFLUENCE OF SURFACE MICROLAYERS.

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LAK13

Abstract. Humic substances (HS) significantly affect the response of surface waters to acid precipitation. The HUMEX project was started to study the role of HS in acidification and the role of the acidification on the biological properties of HS. HUMEX entails the artificial acidification of a whole catchment to the dystrophic, humic lake Skjervatjern, western Norway. The lake was divided into two basins by a plastic curtain. One basin and its catchment area are treated with a mixture of H_2SO_4 and HNO_3 while the other functions as control.

The physiochemical state of the surface microlayers was distinct for each basin, in spite of small differences in bulkwater chemistry as a result of the treatment. Biological shifts were observed in the bulkwater, resulting in changes in SM chemistry.

SM of the acidified basin contained a greater percentage of particulate organic carbon (POC) than the non-acidified SM. The organic solutes also differed. Molecular sizes of the dissolved organic carbon (DOC) constituents in the acidified basin SM were smaller than those in the control basin SM. Free hydroxyl groups were more predominant in the DOC of the acid SM, indicating decomposition of the acidified basin organic macromolecules. Particulate and dissolved organic nitrogen were enriched in the SM of both basins, but the presence of NH_4-N in SM of the acidified basin also pointed to decomposition of high molecular weight organic solutes. The higher bioavailability of the DOC in the acidified SM possibly has an impact on primary production in the lake, in spite of the lower transparency. Higher transparency in the non-treated basin did not increase overall primary production due to nutrient limitations. The SM in the acidified basin functions as a micro-reactor in the turnover of organic solutes, possibly due to faster exchange rates between SM and bulkwater phases as a result of particle formation.

Key words: acidification, DOC, humic lakes, surface microlayer, HUMEX.

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WATER QUALITY REQUIREMENT OF ATLANTIC SALMON IN WATER UNDERGOING ACIDIFICATION OR LIMING

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LAK12

Abstract. The mean annual catch of Atlantic salmon in 9 rivers along the southern coast of Norway was reduced from 50 tons in 1890 to 10 tons in 1920. During the 1960s, catches were reduced to almost zero. Calculations show that the critical load (based on ANC_{limit} = 20 μeqv/L) for these rivers was exceeded already in 1880. Another 32 rivers along the south-western and western coast are today regarded as threatened by acidification. The critical load is exceeded for the region, but the rivers generally have high pH-levels (pH $\geq$ 6.0) and low concentrations of labile Al (<50 μg LAl/L). Since the smolt is the most sensitive life stage, the smoltification period in freshwater is of utmost importance for successful migration and osmoregulation in the sea. Water quality criteria for this stage has been estimated from both laboratory and *in situ* experiments in rivers. The water qualities tested range from pH 5.6-6.7, containing 0-50 μg LAl/L. Different methods have been used to determine the smolt quality in relation to fresh water chemistry. Seawater tolerance was characterized on basis of a seawater (34 ppt) challenge test. Salmon smolts have been found to be extremely sensitive to aluminium (10-20 μg LAl/L), especially in non-equilibrium Al-waters (mixing zones). Even where no effects have been observed in freshwater, seawater tests have demonstrated reduced tolerance. These new threshold values supports the theory that the reduced catches observed in several rivers today are caused by an ongoing acidification. These new threshold values may also necessitate revaluation of water quality criteria used in setting critical loads.

Key words: Atlantic salmon, acidification, water quality, critical load, aluminium, iono-regulation, gill histology, seawater tolerance, ecology.

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HAVE STRAINS OF ATLANTIC SALMON ORIGINATING IN ACIDIC RIVERS DEVELOPED INCREASED TOLERANCE TO ACID WATER?

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LAK24

Abstract. In Norway, 25 populations of Atlantic salmon (*Salmo salar*) have been lost due to acidification, and 32 populations are threatened by acidification. Strain difference in tolerance to acid water has been demonstrated for freshwater fish. Similar traits in anadromous fish have received less attention. Alevins, fingerlings, parr, presmolts and smolts from four strains of Atlantic salmon (two strains originating from acidic and two from non-acidic rivers) were exposed to natural acidic brook water (BW; pH 4.6-5.8; 0.8-1.0 mg Ca/L; 50-90 μg labile Al/L), BW plus H_2SO_4 (BW-pH) to reduce the pH to 4.3, or BW added $AlCl_3$ (BW-Al) to increase the Al concentration by 100 μg Al/L. Measurements included water chemistry, gill histology, iono-regulation and gill enzymes. For testing of seawater tolerance, a 24 hour seawater challenge test (34 ppt) was performed. Genetic analyses using electrophoresis confirmed that the four strains belong to discrete populations. The strains differed in tolerance to acidic water in the early freshwater life stages, but differences in tolerance were low for the smolt stage. In contrast to brown trout, Atlantic salmon from non-acidified rivers exhibited the highest tolerance to acidic water. Since the smolt stage is considered to be the most sensitive, and since there was no clear difference in strain tolerance to acidic water at the smolt stage, our results imply that critical water quality limits for Atlantic salmon in acid and limed waters are independent of strain.

Key words: Atlantic Salmon, acidification, strains, aluminium, critical load, iono-regulation, gill histology, seawater tolerance, ecology.

INCREASED PERIPHYTON-GROWTH IN REMOTE NORWEGIAN WATERS MAY BE DUE TO AIRBORNE NITROGEN DEPOSITION.

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LAK48

Abstract. In recent yeas there have been an increasing number of reports in Norway, of increased periphyton growth in small remote lakes and streams not affected by local pollution. A nation-wide interview survey was carried out in 1992 to identify recent developments of periphyton/attached algae. Of 592 questionnaires, 57% reported increasing peripyton-growth in small watersheds, located in remote areas and at high altitude, regions not previously recognised to be influenced by any kind of pollution. Primary production in high altitude watersheds is influenced by: Long days in summer, combined with high solar and UV-radiation. UV-B can have both biotic (reduced grazing pressure from chironomids and other benthic grazers) and abiotic (UV-B liberate recalcitrant compounds like phosporus) effects. Although primary production (P) is low due to the low temperatures prevailing at high altitudes, it seems to be counterbalanced by low respiration-rates (R). High P/R-ratios enable substantial accrual of periphyton over time. A second factor may be N deposition. In Norway, nitrogen runoff has increased the last decade, also in mountain areas. Due to thin soil- and vegetation-cover and high specific runoff, this type of catchment has low retention capacity, and the nitrogen uptake capacity may be exceeded. Recent studies show that both stagnant and running water have increased periphyton growth when additional nitrate is added to water of natural high nitrate content. It therefore might be hypothesized that the observed increase of periphyton-growth in small remote watersheds in Norway is connected to an increasing nitrogen input, primarily from airborne pollution.

Key words: periphyton, nitrogen deposition, UV-radiation, primary production/respiration rates.

FACTORS CONTROLLING PERIPHYTON GROWTH IN ACIDIFIED HUMIC WATER. EXPERIMENTS WITH NUTRIENT DIFFUSING SUBSTRATES IN THE HUMIC LAKE SKJERVATJERN

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LAK49

Abstract: The aim of the Humic Lake Acidification Experiment (HUMEX) is to study the role of humic substances in the acidification of surface waters and the impacts of acid deposition on chemical and biological properties of humic water. During the first year of acidification (sulphuric acid and ammonium nitrate), an extensive growth of filamentous green algae occurred in the acidified half of the lake. Periphyton accrual on nutrient diffusing substrates (clay flowerpots filled with nutrient diffusing agar) have been used, to study algae growth in the two basins. By using nutrient diffusing substrates, additions of both NH_4 and NO_3, bicarbonate, as well as a parallel-release of phosphate have been tested. So far, chlorophyll and chl/dry weight values have been consistently higher in the acidified basin (A). This suggests that regardless of additional nutrient input, the acidification has induced a significant enhancement of periphyton growth conditions. Persistently high chlorophyll values on nitrate-added pots suggest that periphyton has high potential of nitrate uptake and turnover, and input of nitrate to humic water of previously high nitrate content, will probably enhance periphyton accrual. In early summer, the highest chlorophyll and dry weight values in the controlbasin (B), were measured on nitrate-added pots. This suggests nitrogen to be primarily limiting in the control basin at this time. The acidified basin (A) seemed to be primarily P-limited. This is supported by analysis of elemental carbon, nitrogen and phosphorus. C/N ratios between 15 and 20 in basin B and 10-12 in basin A, indicate N-limitation in B, but not in A. N/P ratios between 26 and 30, suggest P-limitation in both basins. The assumption that low availability of bicarbonate limits primary production in acidified humic water, was not confirmed. On the contrary, pots diffusing bicarbonate had low values of chlorophyll and the lowest chl/dry weight ratios. High content of benthic animals and faeces on bicarbonate pots, suggest increased grazing activity in the bicarbonate-added environment. Generally increased periphyton-growth combined with the particular ability to respond to nitrate, suggest that both acidification and increased nitrogen input affects the conditions regulating primary production in humic water.

Key words: acidification, humic lake, nitrate, periphyton limiting factors, HUMEX.

LONG-TERM TRENDS IN SULFUR RETENTION IN THE HARZ MOUNTAINS, GERMANY

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LON31

Abstract. To describe accumulation of inorganic sulfur (S) in forest soils, SO_4 adsorption isotherms have been included in several process-oriented dynamic models, e.g., in MAGIC. The LB-Model is the first model used on the catchment scale containing solubility products for the hydroxosulfate minerals jurbanite and alunite.

By reconstructing the long-term acidification history (140 years) both models were successfully calibrated to a 14-year deposition, soil and streamwater data set at Lange Bramke (Harz Mountains), a 76-ha catchment with 47-year old spruce forest on spododystic cambisols and Devonian sandstone. According to MAGIC the present accumulation of SO_4 in 0 - 80 cm is 8.7 $mmol_c\ kg^{-1}$, while according to the LB-Model 10.2 $mmol_c\ kg^{-1}$ is stored as jurbanite. Both models predicted 4.5 $mmol_c\ kg^{-1}$ SO_4 in the bedrock layer, retained as alunite in the LB-Model. These values correspond to amounts measured in soil and bedrock samples, respectively.

With a 40% reduction in atmospheric sulfate input from 1988 to 1993, MAGIC forecasted continuously decreasing sulfate levels in the soil solution until 2030, but increasing concentrations in streamwater. The LB-Model showed a constant SO_4 soil water concentration until 1996, when the values fell stepwise within one year. This 'jump' was caused by the complete dissolution of jurbanite. Due to the dissolution of alunite in the bedrock layer the sulfate concentrations in streamwater decreased only slightly until 2030.

Although reductions in sulfur deposition up to 50% have been measured in many parts of Europe, stepwise changes in SO_4 concentrations in the soil solution have not been observed.
Simulation results showed that jurbanite and alunite were formed only at temperatures above 20 ^{o}C. Data and model simulations strongly suggest that hydroxosulfates are not important in controlling sulfate concentrations in soils and surface waters in forested catchments in Europe. Relatively slow modifications driven by adsorption processes are more likely.

Key words: sulfur retention, long-term acidification, sulfate adsorption, hydroxosulfate minerals, modeling, future scenarios.

THE CLIMEX SOIL HEATING EXPERIMENT IN SOUTHERNMOST NORWAY

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CLI08

Abstract. International measures to reduce sulfur and nitrogen emissions may be offset by global changes such as elevated atmospheric CO_2 which may lead to increasing temperature. To investigate possible effects, a soil heating experiment was established at EGIL, an entire forested catchment at the former RAIN site in Norway. The ambient acid precipitation from the EGIL roof is recycled beneath the roof without cleaning by means of an automatic sprinkling system. The experiment is part of the CLIMEX project.

EGIL consists of a shallow soil pocket on granite rock, with some birch and pine trees, and a ground vegetation dominated by heather (*Calluna vulgaris*). The catchment has an area of 400 m^2 of which about 250 m^2 are soil covered. To apply a controlled increase in temperature to the soil and near-soil environment, the lower 80% of the catchment are heated with resistance cables. The setup maintains a seasonally varying temperature differential between the control and heated areas of 5 °C in January and 3 °C in July. The upper 20% of the catchment are used as a control.

Soil warming began in June 1994. Data for the first several months show that the heating cables increase the temperature both in the soil and in the aboveground vegetation, although it cannot be raised to the full +5 °C above ambient during the late autumn and winter months. At EGIL and at control catchments, decomposition of plant litter, nitrogen mineralization, above- and belowground growth of the vegetation, and chemical composition of the dwarf shrubs are measured several times during the growing season. The carbon cycling and turnover in soils as well as changes in input-output fluxes of water, nutrients, and chemical components are measured.

Key words: global change, temperature increase, soil warming, whole-catchment experiment, CLIMEX.

THE HUMIC LAKE ACIDIFICATION EXPERIMENT (HUMEX): MAIN CHEMICAL RESULTS AFTER FOUR YEARS OF ARTIFICIAL ACIDIFICATION

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LAK05

Abstract. The HUMEX-project is a whole catchment manipulation experiment where the effects of addition of H_2SO_4 and NH_4NO_3 to a humic-rich lake and its catchment were studied to obtain information about the role of humic substances (HS) in acidification processes. Lake Skjervatjern, situated in an area receiving low inputs of strong acids, was divided into experimental and control halves. The present results cover 2 years before and 4 years after the experimental half was treated with H_2SO_4 (≈ 54 meq/L) and NH_4NO_3 (≈ 54 meq/L). The results show only minor changes in the inorganic chemistry between the two halves as a direct consequence of the division. The concentration of HS, however, changed due to the different ratios between lake volume and catchment area of the two halves. The treatment has so far lead to a 12% increase of ions (Cations+Anions), and sulphate has increased by nearly 100% of what present before the treatment. Nitrogen compounds have increased, total-N, NO_3-N, and NH_4-N are 1.5, 5 and 3.3 times higher than before treatment. Most of the increase in anions is compensated by mobilization of terrestrial derived base cations with only a slight decrease in pH. Qualitative but not quantitative changes have been observed regarding organic carbon in the two halves. Since summer 1994, lower transparency and more coloured water has been present in the treated half together with an extreme, and so far unexplainable increase in NH_4-N. There are tendencies of increasing concentration of organic-Al (ILAL) and decreasing concentrations of inorganic-Al (LAL) in both lake halves, but the decrease in LAL is smaller in the treated half.

Keywords: freshwater, acidification, lake-experiment, humic material, weak organic acids, strong acids, HUMEX.

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THE HUMIC LAKE ACIDIFICATION EXPERIMENT (HUMEX): MAIN PHYSICO-CHEMICAL RESULTS AFTER MORE THAN FOUR YEARS OF ARTIFICIAL ACIDIFICATION

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The HUMEX-project is a whole catchment manipulation experiment where the effects of addition of H_2SO_4 and NH_4NO_3 to a humic-rich lake and its catchment have been studied to obtain information about the role of humic substances (HS) in acidification processes and the interaction between strong inorganic acids and weak organic acids. Lake Skjervatjern, situated in an area receiving low inputs of strong acids, was artificially divided into experimental and control halves. 2 years after the division Basin A and its catchment were artificially acidified by H_2SO_4 ($\approx$ 54 μeq/L) and NH_4NO_3 ($\approx$ 54 μeq/L), concentration similar to what present in the more acidified southern Norway. Hydrological data, meteorology, precipitation and runoff chemistry collected during a 2 year pre-acidification period and a 4 year and 9 month post-acidification period are evaluated. Randomized intervention analysis (RIA) has been used to evaluate statistical significant differences between runoff chemistry from the two basins before and after the acidification. RIA showed significant higher concentrations of H^+, NH_4^+, NO_3^-, SO_4^{2-}, Al^{n+}, Ca^{2+}, RAL (total reactive Al) and LAL (labile Al) in Basin A compared with Basin B after treatment. The relative increases in Basin A compared with B were of 4.9 μeq/L, 3.0 μeq/L, 2.6 μeq/L, 18 μeq/L, 0.69 μeq/L, 2.1 μeq/L, 5.3 μg Al/L and 9.9 μg Al/L for H^+, NH_4^+, NO_3^-, SO_4^{2-}, Al^{n+}, Ca^{2+}, RAL and LAL, and a significant lower ANC (-9.8 μeq/L) in Basin A compared with B. After a very cold winter in 1993/94, an extreme NH_4^+ increase was observed in runoff water from Basin A from may 1994 with a maximum peak in October 1994. This increase was accompanied by increase in water color and UV-absorbency, without any increase in total organic carbon. The increase in NH4+ and the close relationships to color and UV-absorbency is also discussed in this article.

INTRODUCTION

The HUMEX-lake experiment is well described earlier in two special issues of Environmental International (Vol. 18, No. 6 (1992), Vol. 20, No.3 (1994), see specially Gjessing, 1992, 1994). The lake were divided in two lake halves (Basin A and B) by a plastic curtain in October 1988, and the water chemical effects of the devision were followed until October 1990, when Basin A and its catchment were treated by artificial rain, so that the average concentration of both sulphuric acid (H_2SO_4) and ammonium-nitrate (NH_4NO_3) in rain water were nearly 50 µeq/L. These concentrations are nearly the same as the concentration in rain water of the far more acidified Southern Norway. The main intention with the HUMEX-project was to study the impacts of this artificially additives on organic carbon in soil and surface water, both qualitatively and quantitatively, and to assess what portion of the acidity in water is due to strong acids in the precipitation and what portion is due to naturally occurring organic acids. This paper contains physico-chemical data from October 1988 until June 1995, which means two years of data before start of acidification and 4 year and 9 months of data from the acidification period. The statistical analysis only covers the two years before acidification and the first four years of acidification, because evaluation of fully years give the best statistical results .

MATERIAL AND METHODS

Runoff water from Basin A and B have been sampled almost weekly from October 1988. Discharge from A and B has been continuously logged since January 1991, and sun radiation, air and soil temperature as well as precipitation are logged since May 1991. Due to breakdowns during thunder whether the loggers have been out of work during several periods, especially the discharge logger. Besides other problems related to discharge logging, these data will unfortunately not be presented in this paper.

From January 1995 weekly samples of precipitation are analyzed regarding the major chemical compounds, e.g. pH, Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, SO_4^{2-}, Cl^-, NO_3^- and PO_4^{3-}.

The monthly and yearly additions of H_2SO_4 and NH_4NO_3 to Basin A and its catchment are presented in Fig.1 and Table 1, respectively.

Physico-chemical analysis

The pH was measured potensiometrically using a pH-meter, Orion Research 901 Ion Analyzer, with separate glass-electrode and reference-electrode. Calcium, magnesium and sodium were analysed by Induced Coupled Plasma atomic-emission spectrometry, while potassium was measured by flame-emission spectroscopy. Sulfate and chloride were measured by ion chromatography (IC), while total nitrogen, nitrate and ammonium were measured colourimetrically. Total-phosphorous and phosphate were also measured colourimetrically. Total organic carbon (TOC) was measured after oxidizing of organic material by peroxydisulfate and UV-radiation in a strongly acidic environment. The CO2 formed is then measured spectrometrically using an infrared (IR) gas analyzator. Both UV-absorbency and color were measured on Millipore filtered water (0.45 µm cutoff), UV measured at 254 nm, while color was measured at 410 nm, calibrated with a solution of potassiumhexachloroplatinum and cobalt chloride. Thus, the presented values are directly comparable with the traditional color term in mg Pt/L. Aluminum was analyzed by the colorimetric Pyrro-Catechol Violet PCV-method (Norwegian Standard, NS 4747), on both total and cationexchanged samples. The cationexchange procedure is described by Driscoll (1984). The total PCV-reactive Al is defined as RAL, while the Al present in the eluate is defined as non-labile Al (ILAL).The difference between RAL and ILAL is the labile Al-fraction (LAL), primarily representing the low molecular weight inorganic Al-species. Total Al was also measured by the same method after acidifying the samples by H_2SO_4 to pH $\approx$ 1 for at least 24 hr. To estimate the average charge of Al (ΣAl^{n+}), the ALCHEMI-Version 4.0 was used (Schecher and Driscoll, 1987, 1988), and both the inorganic and organic constants applied are the same as originally present in the ALCHEMI-Version 4.0. The organic Al-fractions are estimated on the basis of a triprotic acid with the given dissociation constants: $pK_1 = 6.86$; $pK_2 = 12.8$; $pK_3 = 14.9$, and complex-constants: Al + org = Al-org (pK = 8.38) and Al + Horg = AlH-org (pK = 13.1). In the present work, total organic carbon (TOC) is measured, while the program is based on dissolved organic carbon (DOC). In streamwater at the four sites, the differences between TOC and DOC is generally very small, so TOC should be acceptable as a substitute for DOC in the program. Total carbon and total nitrogen is also measured on filters after filtering the water through a glass fiber filter with cutoff $\approx$ 0.6-0.7 µm. and analyses by a HCN-analyzer after complete combustion of the solid material. Total fluoride was analyzed using an Orion Model 94-09 ion selective electrode, connected to an Orion research Microprocessor Ion Analyzer/901 with the Orion Model 90-01-00 as reference electrode. Iron and manganese were measured by Atomic Absorption Spectroscopy (AAS). Most of the analysis have been performed from the very beginning of the project, while colour and UV measurements started in June 1989, total phosphorous and phosphate in July 1991, filtered nitrogen and carbon in April 1993, iron, manganese and fluoride in November 1994

Statistical analysis

Randomized intervention analysis (RIA) is used to detect changes in the manipulated Basin A relative to the control Basin B. This method is well suited for statistical assessment of differences before and after a manipulation (Carpenter et al., 1989; Carpenter, 1993). RIA requires paired time series of data from both before and after manipulation (acidification), and is not affected by non-normal errors in the data. Monte Carlo simulation indicated that, even when serial autocorrelation was substantial, the true P value (i.e. from non-autocorrelated data) was < 0.05 when the P value from autocorrelated data was a 0.01 (Carpenter et al., 1989). RIA derived from the "before-after-control-impact" experimental design of Stewart-Oaten et al. (1986).

RIA begins with a series of parallel observations of experimental and reference ecosystems, paired in time, spanning periods before and after a manipulation. A time series of interecosystem differences is then calculated, and from these are calculated mean values fro the premanipulation and postmanipulation differences, $\overline{D}$(PRE) and $\overline{D}$(POST), respectively. The absolute value of the difference between $\overline{D}$(PRE) and $\overline{D}$(POST) is the test statistic. Its distribution is estimated by random permutations of the sequence of interecosystem differences. RIA is also used to estimate time trends by comparing the two first years of treatment with the two last years.

Definition of terms

In the charge balance (CB) of surface water (µeq/L):

$$CB = ([Ca^{2+}]+[Mg^{2+}]+[Na^{+}]+[K^{+}]+[H^{+}]+[NH_4^{+}]+[\Sigma Al^{n+}]) - ([SO_4^{2-}]+[Cl^{-}]+[NO_3^{-}]+[HCO_3^{-}]+[A^{-}])$$

$[A^-]$ is an expression for the amount of dissolved organic ions. Assuming all ions incorporated in the charge balance being measured, the amount of $[A^-]$ (µeq/L) can be estimated, so that charge balance is obtained. The concentration of ΣAl^{n+} is in the expression the sum of positively charged Al-ions, which can be estimated by the ALCHEMI-speciation program (Schecher and Driscoll, 1987,1988). By dividing the concentration of organic charges $[A^-]$ by the concentration of total organic carbon (TOC) measured in streamwater, a net charge (NC) per mg C is calculated. NC of organics is often called the charge density (CD) of organics, but because the $[A^-]$ is estimated on the basis of charge balance, it gives no information about the number of reactive sites present pr mg of carbon. Thus, NC pr. mg of carbon is a more distinctive term (Lydersen and Henriksen, 1994).

RESULTS AND DISCUSSION

Physical and morphological data of the two lake halves of Lake Skjervatjern is presented by Gjessing (1992).

Hydrology and meteorology.

The amount of precipitation at Skjervatjern has been continuously logged since May 1991. Most of the precipitation normally falls during September-March, which is typically for this region. In 1992, 1993 and 1994 annual amounts of precipitation were 2170 mm, 1890 mm and 1867 mm, respectively. Highest monthly precipitation (Fig. 3) was recorded in September 1991 (508 mm) and in January 1993 (488 mm). The weekly monitoring programme on precipitation chemistry, which started in January 1995, also included weekly recordings of precipitation. During the first 6 months of monitoring, the monthly relationship between weekly sampling (y) and continuously logging (x) of precipitation was: $y = 0.89x - 5.26$ ($r = 0.95$). As runoff data from lake Skjervatjern is reasonably useless, because of several technical problems, annual estimates of evapotranspiration are difficult to assess. However, based on a long termed monitored site (Kaarvatn) located some distance northwest of Skjervatjern (Lydersen, 1994), the annual evapotranspiration at Skjervatjern should be about 300 ± 100 mm.

Until the start of chemical monitoring of precipitation at Skjervatjern (January 1995), chemical data from the weather-station Nausta, located 18 km northwest of Skjervatjern, has been used to estimate the concentration of chemical compounds in precipitation at Skjervatjern. This weather-station is monitored by the Norwegian Institute for Air Research (NILU). Based on annual precipitation data at Skjervatjern from 1992, the precipitation there is 75 ± 9% of that annually precipitating at Nausta. During the 6 month of chemical monitoring of precipitation at Skjervatjern in 1995 (January-June), the concentrations of chemical compounds in precipitation at Nausta were 10-30% lower than the concentrations present at Skjervatjern (Table 2). Regarding fluxes of chemical compounds in wet deposition, however, Skjervatjern receives lower amounts of all ions (96-60% of Nausta), except for Ca^{2+}.

The higher amount of Ca^{2+} (111%) as well as relatively high amounts of other base cations (Mg^{2+}, Na^+ and K^+, 92%, 93% and 96%) compared with Nausta indicate slightly more inland influenced climate at Skjervatjern because more terrestrial influenced precipitation generally means higher amounts of terrestrial derived base cations, particularly Ca^{2+} and K^+.

As shown in Fig. 2, both strong acid episodes as well as seasalt episodes have been recorded during the first 6 months of chemical monitoring. From March 6 to March 13, the pH in the precipitation was 3.66 and 3.94 at Skjervatjern and Nausta, respectively, but the precipitation during this period was very low, i.e. 1.2 mm (Skjervatjern) and 13.4 mm (Nausta). The highest seasalt episodes were recorded during February 1 to February 6 (6 day's interval) and during February 27 to March 1 (3 day's interval), with Cl^- concentration of 242 µeq/L and 367 µeg/L at Skjervatjern and of 185 µeq/L and 264 µeg/L at Nausta. During the same two periods the amount of precipitation at Skjervatjern was 110 mm and 37 mm, while at Nausta 127 mm and 34 mm. Thus, the very acidic precipitation in March, have minor acidification impacts on the ecosystem because of very low water input, while the seasalt episodes are much more important events as long as high seasalt concentrations occur during heavy precipitation periods.

The highest air and ground temperatures (10 cm depth) normally occur within June-August, the lowest in January or February, which fit very well with the sun radiation (Fig. 3). Since start of monitoring, the most extreme and most important climatic period was the very long lasting cold period during the winter 1993/94. During this period, mean air temperature was < 0° C from November-March, lowest in February with a mean temperature of -9.2° C. During the same winter, soil temperature was < 0° C from November 6 (1993) to April 26 (1994). Soil temperatures < 0° C have never been recorded neither earlier nor later.

Runoff chemistry

As shown in Table 3, only minor water chemical differences were recorded between Basin A and B because of the lake division, regarding mean, maximum and minimum values during the two years following the division. There are a tendency of somewhat higher concentrations of chemical compounds in Basin B, which might be due to a higher catchment/lake ratio in this catchment (Gjessing, 1992).

After the start of treatment, there are still minor differences between Basin A and B regarding chemical parameters that is reasonably unaffected by the manipulation, e.g. like the seasalt derived as Na^+ and Cl^-. Regarding ions expected to respond to the manipulation, H^+, Ca^{2+}, NH_4^+, Al^{n+}, SO_4^{2-}, NO_3^-, generally higher concentrations are present in the manipulated lake half, Basin A, compared with the control Basin B, both regarding mean and maximum values, while ANC exhibits a decreasing trend related to the control half B.

Several ions exhibit seasonal variations. The pH is normally at lowest during late spring early summer with high peaks normally related to high runoff according to heavy rainfalls during autumn and winter, and during early snowmelt. The lowest recorded pH is observed during episodes of high seasalt inputs. During a hurricane in January 1993, concentration of Na^+ and Cl^- of 339 µeq/L and 423 µeq/L was recorded at the nearby weatherstation Nausta (SFT,1993). Accordingly the pH in runoff from Basin A and B was 4.35 and 4.25, the lowest values measured so far. During the same event the lowest ANC ever recorded was present in runoff from Basin B, -61.6 µeq/L, and a very low ANC was also recorded in Basin A, -40.6 µeq/L. The lowest ANC in Basin A so far, was measured one year earlier, in January 1992 (-57.8 µeq/L). The highest concentration of labile Al (LAL, i.e. the acute toxic Al-fraction) was also recorded during the seasalt episodes in January 1993, i.e. 162 and 160 µg Al/L in Basin A and B, respectively. Also very low pH's were recorded during springmelt 1994, after the very cold winter and a distinctive snowmelt. During this very rapid hydrologic peak, TOC concentrations fall from 8.2 to 2.3 mg C/L in Basin A and from 7.7 to 2,3 mg C/L in Basin B from March 6 to March 12, the initial period of snowmelt. Since the ground or soil temperature was still < 0° C, ionic poor melt water was the main reason for this dilution or decrease in TOC. pH was 4.44 in runoff from both Basin A and B, both March 6 and March 12.

Sulfate seems to be at lowest once during the winter, or during snowmelt, while the highest concentrations normally occur during summer. High summer concentrations are most likely related to low-flow and corresponding oxidation of sulphide stored in the bogs. However, there are no good relationship between sulphate and H^+ in neither Basin A nor B.

The concentrations of Ca^{2+} in runoff are normally at lowest during springmelt, and at highest once during the summer. However, as for H^+, the seasonal trend for Ca^{2+} is not very distinctive. Even though the runoff values are bad, their fluctuations are probably more related to hydrologic status, i.e. high-flow or low-flow, independent on time of the year.

NO_3^- and NH_4^+ are normally at the lowest during the growth season during spring and summer, and at the highest during springmelt or during winter related to high runoff. The very high concentration of NO_3^-, but particularly of NH_4^+ might be a direct effect of the very strong winter 1993/94 (the climate data are presented earlier). Reduced biological activity during the extreme cold winter with low runoff, may have caused a significant accumulation of those compounds, primarily within the bogs. The effect of temperature is earlier described by Fowler et al. (1991) and Proctor (1993). Proctor (1994) also showed that bogs are strong sinks fro NH_4^+. That the NO_3^- peak arose a couple of months earlier than NH_4^+ after this winter, might be due to a higher mobility of this ion. NH_4^+ on the other hand, should be tied up by organic anions, to a large degree by complexation reactions, and thereby leaving the bogs together with dissolved organic carbon. This might be one explanation to the very significant correlation between water color and NH_4^+ during the same period. The increase in UV-absorbency together with increase in color and NH_4^+ may also indicate that during cold winter with ground temperature < 0° C from early November to late April, the biological degradation of organic matter is substantially affected. Accordingly, more reduced dissolved organic material should be present after cold winter. This might be the reason for the high UV-absorbency and color in relation to dissolved organic matter observed several months after springmelt 1994. Another possibility for the qualitative change in TOC and concentration of NH_4^+ is the runoff pattern from the catchment. We have not been able to control this, but if major amounts of water is entering the lake from other soil/bog depths as a consequence of a precipitation poor cold winter, followed by a warm summer (Fig.3) more water feeds the lake from deeper soil/bog layers. The NH_4^+ relationship to aqueous organic parameters is discussed in more detail later. After the same cold winter the concentration of Tot-P was unusually high from the middle of June to early December.

Labile Al, Fe and organic parameters as TOC, UV-absorbency and color exhibit the most distinctive seasonal trends during the period of monitoring. TOC, UV-absorbency and color are always at their highest during autumn, probably as a direct consequence of degradation of organic matter produced during the latest growth season, while the lowest concentrations are present during late winter. As expected, this is also the typical seasonal pattern for Fe (Fig.7) and to a certain degree even for Mn. Regarding inorganic Al or labile Al (LAL, i.e. the primary acute toxic Al-fraction) the highest concentrations seem to occur during summer when the concentration of organic compounds are at average and pH is relatively low.

RIA-analysis

Randomized intervention analysis (RIA) has been used to test if significant differences (at 99% level) are established between the two lake halves after four years of acidification of lake half A and its catchment A.

Based on this statistical analysis, significant higher concentration of H^+, NH_4^+, NO_3^-, SO_4^{2-}, Al^{n+}, Ca^{2+}, RAL (total reactive Al) and LAL (labile Al) occur in Basin A in relation to Basin B (Table 4). Based on RIA-analysis, there have been a relative increase in Basin A compared with B of 4.9 µeq/L, 3.0 µeq/L, 2.6 µeq/L, 18 µeq/L, 0.69 µeq/L, 2.1 µeq/L, 5.3 µg Al/L and 9.9 µg Al/L in H^+, NH_4^+, NO_3^-, SO_4^{2-}, Al^{n+}, Ca^{2+}, RAL and LAL, respectively, as a consequence of the artificial treatment.

A significant lower ANC is also established in Basin A compared with B (i.e. ANC is on average 9.8 µeq/L lower in Basin A compared with B) after treatment compared with the two year before start of treatment. However, the mean ANC in Basin A during the two years before treatment (ANC = -12.9 µeq/L) was almost identical with the mean ANC during the 4 year and 9 month period of treatment (ANC = -11.5 µeq/L). During the same period, mean ANC in the Basin B increased from -11.9 µeq/L (average for the two years before treatment) to only -0.8 µeq/L as an average for the next 4 year and 9 month period. This means that a corresponding improving ANC should even have occurred in Basin A without any treatment. There are two main reasons for this improving ANC in Basin B, and almost unchanged ANC in Basin A:

1) The decreasing concentration of non-marine sulfate that is observed in most of western Europe due to reduced emissions of SO_2 and sulfuric acid from 1985.

2) Extreme seasalt episodes during the last years, because of higher mobility of the seasalt anion, Cl^- compared with the base cation counterion Na^+. This will initially cause a short-term acidification when Na^+ temporarily undergoes cationexchange with H^+ and Al, but the secondary effect is a more long term ANC improvement as Na^+ gradually leaves the catchment again due to a reverse cation exchange process.

Regarding the major organic compounds monitored, TOC, color and UV-absorbency, no significant differences between Basin A and B were found by this RIA-method. Despite the significant increases in color and UV from May 1994 until October 1994, the increases within this period were too small to obtain significant results by the RIA-analysis.

Time trends

The time series from the HUMEX-lake experiment is still too short to give satisfying statistical estimates of time trends. However, by the same RIA-method, we have tried to compare the two first years (October 1990-October 1992) of acidification with the two last years (October 1992-October 1994). By doing so (Table 5), we found significantly higher concentration of NH_4^+, NO_3^-, SO_4^{2-} and LAL the two last years of treatment compared with the two first years, which means there are significantly increasing concentrations of these compounds. Based on the RIA-analysis, the average concentration of NH_4^+, NO_3^-, SO_4^{2-} and LAL in Basin A compared with Basin B is 4.3 µeq/L (NH_4^+), 1.2 µeq/L (NO_3^-), 6.0 µeq/L (SO_4^{2-}) and 3.4 µg Al/L (LAL) higher during the two last years of treatment compared with the two first years.

The H^+ is the only chemical ion added to Basin A that have not increased significantly the two last years of treatment compared with the two first years. This is not unexpected due to the pH-buffering capacity of organic acids and the proton consuming Al-dissolving processes.

The water color

Due to the extreme increase in color, simultaneously with the NH_4^+ increase, the water color is evaluated in some more detail. Water color related to mg Pt/L (OD: 410 nm) is a normally used index of dissolved organic matter (Thurman, 1983), due to the strong existing correlation between brown organic color which is derived chiefly from peat and marsh detritus, and the amount of dissolved organic carbon in surface waters (Juday and Birge, 1933). Coloured water usually contains higher iron (III) concentrations. It is not yet certain whether such substances can really keep ferric iron in solution at the pH values of interest. It might be more probable that the coordinative products formed between the color bases, OH^-, and Fe (III) are insoluble and are present as highly dispersed colloids. The diameter of $Fe(OH)_3$ can be smaller than 100 Å (Stumm and Morgan, 1981).

In both Basin A and Basin B of Lake Skjervatjern, the best correlation exists between color and UV-absorbency (Fig. 8). This should also be expected since both analyses are performed spectrophotometrically at 410nm (color) and 254nm (UV) on filtered samples. There are also very significant correlation's between color and total organic carbon (TOC) and dissolved organic carbon (DOC). DOC is only measured since March 1993. Iron has only been measured since December 1994. However, as expected, significant correlation was found between color and iron (Fig. 9). In Basin B and before acidification of Basin A and its catchment, no correlation's were found between color and NH_4^+, but after the addition of NH_4NO_3 together with H_2SO_4 a significant correlation ($r^2 = 0.44$) was found in Basin A (Fig. 8). During the period when NH_4^+ really started to increase (May 1994) and up to June 1995 (the latest observation presented in this article), the correlation was far more significant, i.e. $r^2 = 0.83$ (Fig. 10). The relationship might have several explanations:

1) NH_4^+ might to a certain degree undergo complexation with organic anions which may lead to formation of color, and even the complexed NH_4^+ will be measured as free NH_4^+ ions in the analysis.

2) Both the color and NH_4^+ analyses are spectrophotometric methods, color analyzed at 410 nm, NH_4^+ at 630 nm. Thus, increase in NH_4^+ may to a certain degree interfere with color. So far, such studies have not been conducted, but should be done.

3) It is known from the literature that some aquatic fungus (e.g. *Aurobasidium pullulans*) has the ability of decompose large amounts of organic matter and exude yellow colored substances in freshwaters (Day and Felbeck, 1974) . Strains of similar fungi's are even common soil organism. By analyzing this exudates, they found characteristics consistent with previous research on color in freshwater (Midwood and Felbeck, 1968) and in humic substances (Felbeck, 1971). Thus, an increase in NH_4^+ in Basin A and its catchment might have stimulated such organisms to exude more yellow-colored organic complexes. However, no terrestrial or aquatic studies on fungi's have been conducted at Skjervatjern. Accordingly, it is nothing but a theoretical possibility, so far.

Since the NH_4^+ concentration really started to increase in Basin A (fig 4), from late April 1994 up today (June 1995), the very significant relationship between color and UV (Fig. 10) increased from $r^2 = 0.96$ to $r^2 = 0.98$ by adding NH_4^+ as the secondary explanatory variable, with the following regression equation: Color : $242.4\ UV + 0.069\ NH_4^+ - 8.74$. However, based on the linear regression between color (y) and NH_4^+ (x) from start of treatment up today, i.e. $y = 0.21x + 47.3$, NH_4^+ will not interfere or exhibit correlation with color at $NH_4^+ < \approx 50$ µg N/L.

FURTHER PLANS FOR THE HUMEX-PROJECT

Despite our last proposal to the Environment Research Programme of the European Commission (Environment and Climate) was rated A, which means excellent, our proposal was not funded. However, The Norwegian Institute for Water Research are now working with a national funded HUMEX-project in collaboration with The Norwegian Institute for Nature Research, eventually funded by the Norwegian Research Council. If so, our plans are to continue the acidification for three more years, followed by a three year recovery study. Without any further economic support, we have to end the project late 1995.

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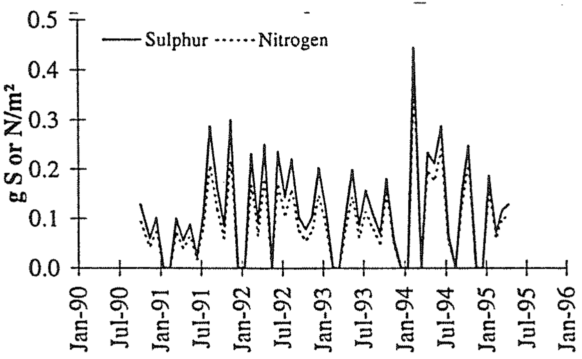
Year	**H_2SO_4** **g/m^2**	**S** **g/m^2**	**NH_4NO_3** **g/m^2**	**N** **g/m^2**
Oct 90/Oct 91	3.4	1.1	2.7	0.8
Oct 91/Oct 92	5.1	1.7	4.0	1.2
Oct 92/Oct 93	3.7	1.2	2.9	0.9
Oct 93/Oct 94	5.3	1.7	4.1	1.4
Total	17.5	5.7	13.7	4.3
Annual mean	4.4	1.4	3.4	1.1

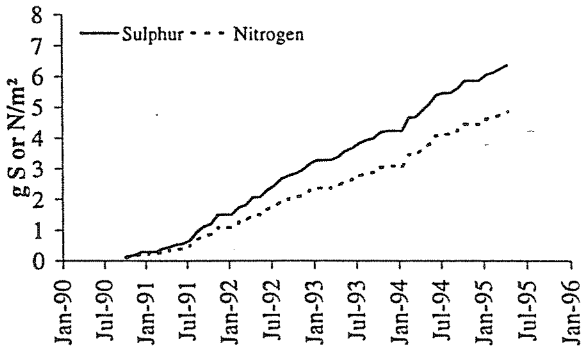
Parameter	Average concentration		Total flux	
	Skjervatjern	Nausta	Skjervatjern	Nausta
Precipitation			833	1189
H^+	14.8	13.2	10.3	14.7
SO_4^{2-}	25.8	21.2	18.2	22.7
Cl^-	79.2	60.7	84.8	94.3
NO_3^-	11.7	10.4	7.4	9.9
Ca^{2+}	6.2	4.2	5.7	5.2
Mg^{2+}	17.2	12.6	18.0	19.6
Na^+	71.9	52.7	75.8	81.9
K^+	2.2	1.6	2.0	2.1
NH_4^+	9.9	10.4	5.2	8.6

			Before			After	
	unit	mean	max	min	mean	max	min
H^+ (A)	µeq/L	26.3	41.7	15.5	29.1	46.7	10.7
H^+ (B)	µeq/L	28.2	45.7	17.4	26.5	56.2	7.1
Ca^{2+} (A)	µeq/L	10.0	16.5	5.0	12.6	40.4	2.0
Ca^{2+} (B)	µeq/L	10.4	16.5	5.5	10.8	28.9	1.0
Mg^{2+} (A)	µeq/L	24.7	51.8	13.2	27.9	83.1	1.7
Mg^{2+} (B)	µeq/L	24.9	44.4	16.5	25.1	94.6	2.5
Na^+ (A)	µeq/L	111.4	178.8	54.8	119.3	368.0	13.1
Na^+ (B)	µeq/L	115.5	179.7	67.0	121.6	392.4	20.4
K^+ (A)	µeq/L	3.4	5.1	1.5	3.8	8.2	0.8
K^+ (B)	µeq/L	3.7	5.9	2.1	3.3	9.2	0.2
NH_4^+ (A)	µeq/L	1.1	4.8	0.5	4.9	30.1	0.7
NH_4^+ (B)	µeq/L	1.2	2.6	0.4	1.1	6.2	0.2
Al^{n+} (A)	µeq/L	3.6	7.6	0.7	4.6	16.1	0.7
Al^{n+} (B)	µeq/L	4.4	5.5	0.7	4.5	14.1	0.6
SO_4^{2-} (A)	µeq/L	26.9	35.4	18.8	43.2	68.8	10.4
SO_4^{2-} (B)	µeq/L	28.2	43.8	16.7	26.8	64.6	10.4
Cl^- (A)	µeq/L	136.1	245.4	56.4	133.3	465.4	16.9
Cl^- (B)	µeq/L	138.5	231.3	62.1	135.1	521.8	22.6
NO_3^- (A)	µeq/L	0.6	4.5	0.1	3.3	17.5	0.1
NO_3^- (A)	µeq/L	0.8	6.4	0.1	0.8	5.9	0.1
ANC (A)	µeq/L	-12.9	18.6	-43.0	-11.5	40.9	-57.8
ANC (B)	µeq/L	-11.9	18.9	-41.6	-0.8	53.8	-61.6
Tot-P (A)	µg P/L	n.a.	n.a.	n.a.	6.6	25.0	1.0
Tot-P (B)	µg P/L	n.a.	n.a.	n.a.	5.3	16.0	2.0
Al_{tot} (A)	µg Al/L	n.a.	n.a.	n.a.	97	171	29
Al_{tot} (B)	µg Al/L	n.a.	n.a.	n.a.	90	182	41
RAL (A)	µg Al/L	64	127	10	81	223	10
RAL (B)	µg Al/L	78	120	12	87	214	10
ILAL (A)	µg Al/L	36	80	10	60	127	5
ILAL (B)	µg Al/L	44	84	10	70	139	10
LAL (A)	µg Al/L	29	61	0	21	162	0
LAL (B)	µg Al/L	34	49	2	16	160	0
Fe_{tot} (A)	µg Fe/L	n.a.	n.a.	n.a.	102	185	36
Fe_{tot} (B)	µg Fe/L	n.a.	n.a.	n.a.	101	195	50
Mn_{tot} (A)	µg Mn/L	n.a.	n.a.	n.a.	2.5	3.4	1.1
Mn_{tot} (B)	µg Mn/L	n.a.	n.a.	n.a.	2.2	4.0	1.2
TOC (A)	mg C/L	5.6	12.0	1.3	6.1	10.7	0.3
TOC (B)	mg C/L	6.3	13.1	2.7	6.8	11.6	0.7
UV (A)	OD_{254nm}	0.22	0.36	0.05	0.26	0.51	0.02
UV (B)	OD_{254nm}	0.26	0.43	0.04	0.30	0.52	0.03
Color (A)	mg Pt/L	51	83	14	62	149	3
Color (B)	mg Pt/L	58	112	20	70	119	8

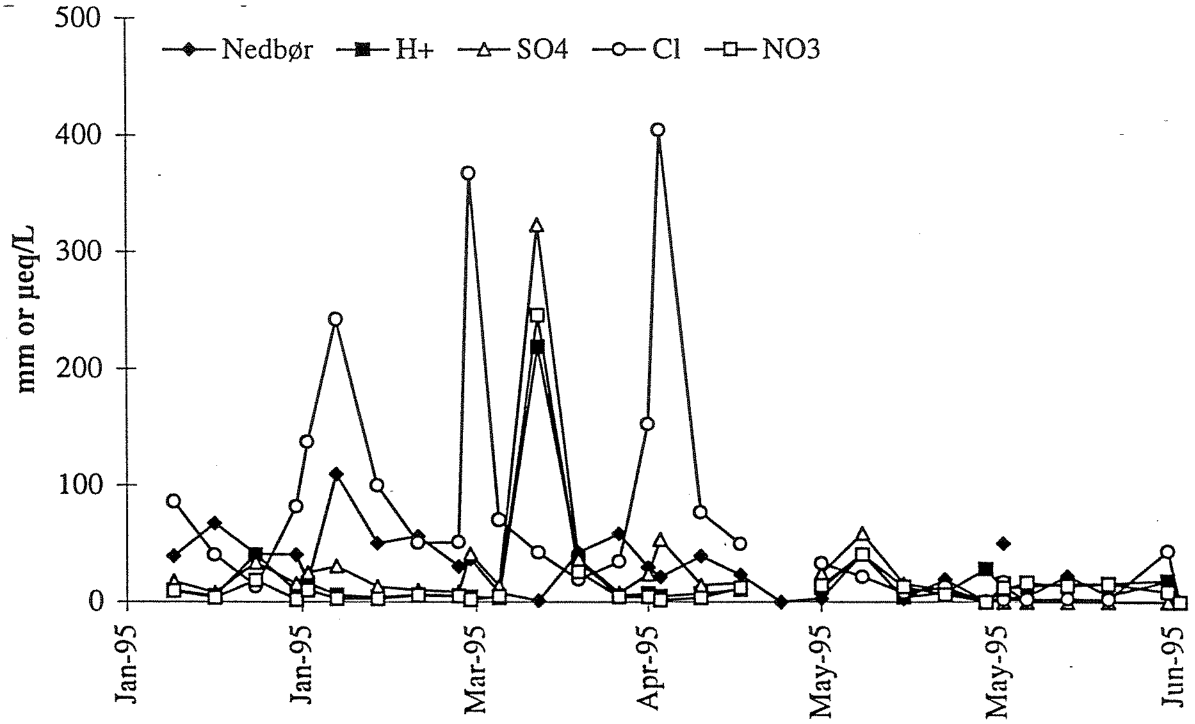
Parameter	unit	Dactual $\overline{D}_{pre}-\overline{D}_{post}$	P95%	P99%	
H^+	µeq/L	4.88	1.97	2.46	TRUE
NH_4^+	µeq/L	2.96	1.39	1.82	TRUE
NO_3^-	µeq/L	2.59	0.61	0.79	TRUE
SO_4^{2-}	µeq/L	17.9	3.71	4.61	TRUE
Al^{n+}	µeq/L	0.69	0.29	0.37	TRUE
Ca^{2+}	µeq/L	2.13	0.94	1.20	TRUE
ANC	µeq/L	-9.84	3.32	4.37	TRUE
RAL	µg Al/L	5.29	4.64	5.68	TRUE
LAL	µg Al/L	9.94	2.86	3.52	TRUE
TOC	mg C/L	-0.16	0.30	0.40	FALSE
UV	OD_{254}	-0.03	0.02	0.03	FALSE
Color	mg Pt/L	-4.46	5.14	6.69	FALSE

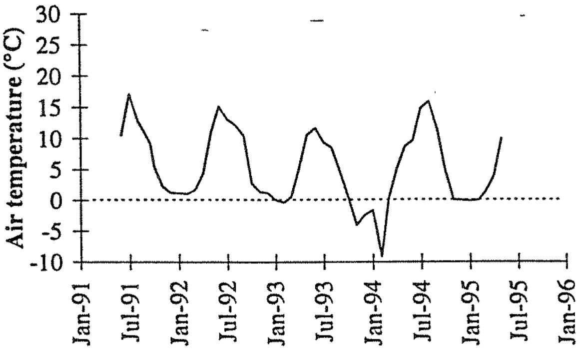
Parameter	**unit**	**Dactual** $\overline{D}_{first}-\overline{D}_{last}$	**P95%**	**P99%**	
H^+	µeq/L	0.39	2.00	2.54	FALSE
NH_4^+	µeq/L	**4.33**	**1.96**	**2.50**	**TRUE**
NO_3^-	µeq/L	**1.24**	**0.64**	**0.79**	**TRUE**
SO_4^{2-}	µeq/L	**5.95**	**3.76**	**4.91**	**TRUE**
Al^{n+}	µeq/L	0.27	0.30	0.38	FALSE
Ca^{2+}	µeq/L	0.36	1.00	1.28	FALSE
ANC	µeq/L	-2.07	3.53	4.59	FALSE
RAL	µg Al/L	6.22	**5.28**	6.52	FALSE
LAL	µg Al/L	**3.43**	**2.54**	**3.31**	**TRUE**
TOC	mg C/L	-0.16	0.30	0.40	FALSE
UV	OD_{254}	-0.03	**0.02**	**0.03**	FALSE
Color	mg Pt/L	-4.46	5.14	6.69	FALSE

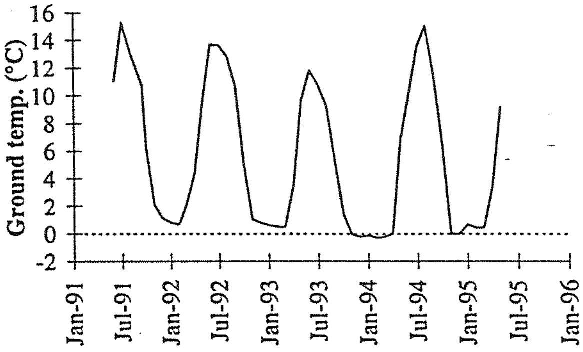

0.5
0.4
0.3
0.2
0.1
0.0
g S or N/m²
Sulphur
Nitrogen
Jan-90
Jul-90
Jan-91
Jul-91
Jan-92
Jul-92
Jan-93
Jul-93
Jan-94
Jul-94
Jan-95
Jul-95
Jan-96

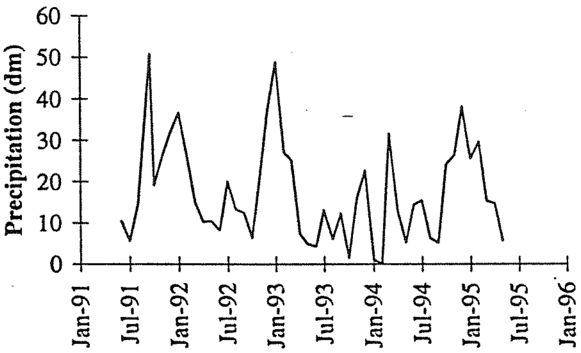

8
7
6
5
4
3
2
1
0
g S or N/m²
Sulphur
Nitrogen
Jan-90
Jul-90
Jan-91
Jul-91
Jan-92
Jul-92
Jan-93
Jul-93
Jan-94
Jul-94
Jan-95
Jul-95
Jan-96

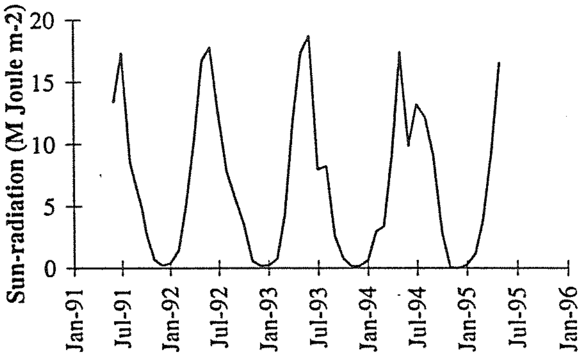
128

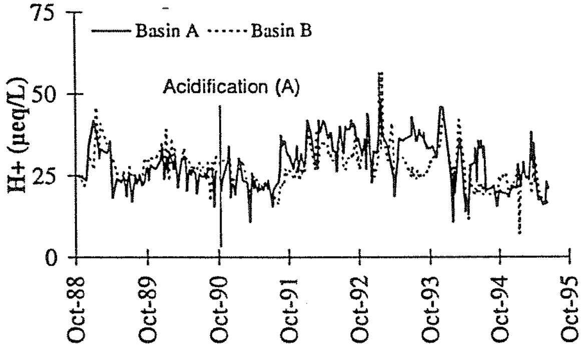

500
400
300
200
100
0
mm or µeq/L
Nedbør
H+
SO4
Cl
NO3
Jan-95
Jan-95
Mar-95
Apr-95
May-95
May-95
Jun-95

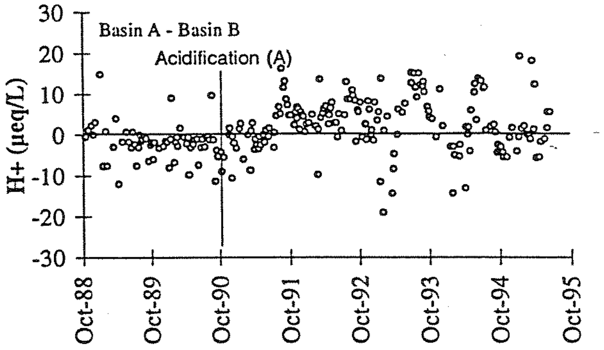

Air temperature (°C)
30
25
20
15
10
5
0
-5
-10
Jan-91
Jul-91
Jan-92
Jul-92
Jan-93
Jul-93
Jan-94
Jul-94
Jan-95
Jul-95
Jan-96

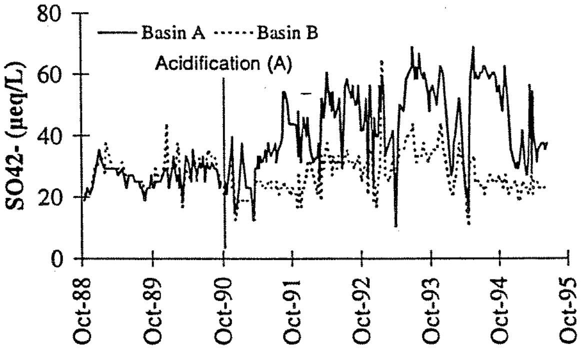

Ground temp. (°C)
16
14
12
10
8
6
4
2
0
-2
Jan-91
Jul-91
Jan-92
Jul-92
Jan-93
Jul-93
Jan-94
Jul-94
Jan-95
Jul-95
Jan-96

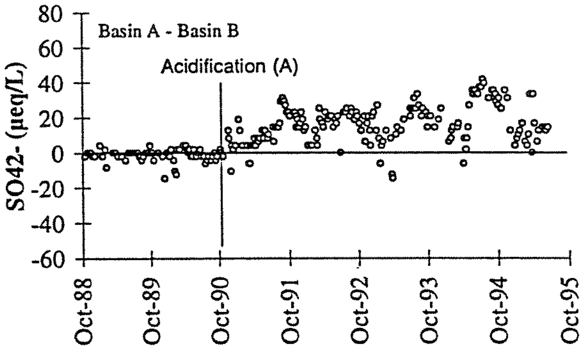

Precipitation (dm)
60
50
40
30
20
10
0
Jan-91
Jul-91
Jan-92
Jul-92
Jan-93
Jul-93
Jan-94
Jul-94
Jan-95
Jul-95
Jan-96

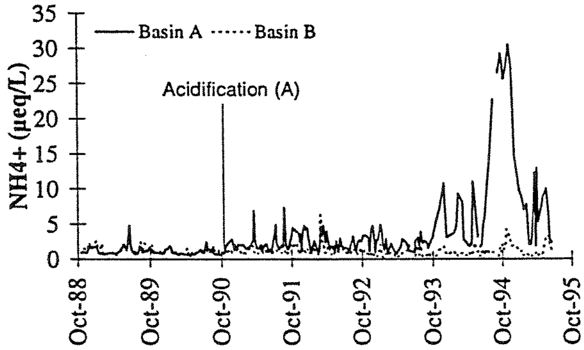

Sun-radiation (M Joule m-2)
20
15
10
5
0
Jan-91
Jul-91
Jan-92
Jul-92
Jan-93
Jul-93
Jan-94
Jul-94
Jan-95
Jul-95
Jan-96

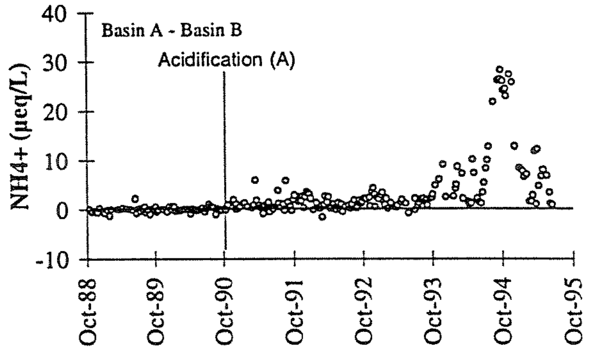

75
50
25
0
H+ (µeq/L)
Basin A
Basin B
Acidification (A)
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

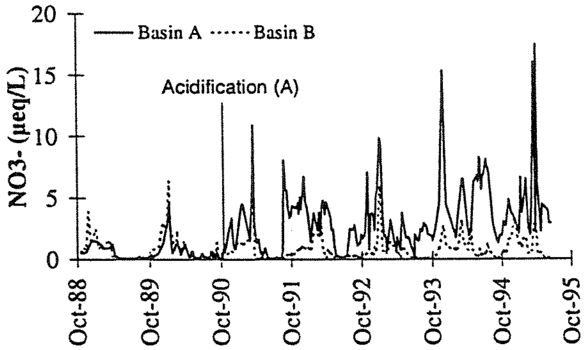

30
20
10
0
-10
-20
-30
H+ (µeq/L)
Basin A - Basin B
Acidification (A)
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

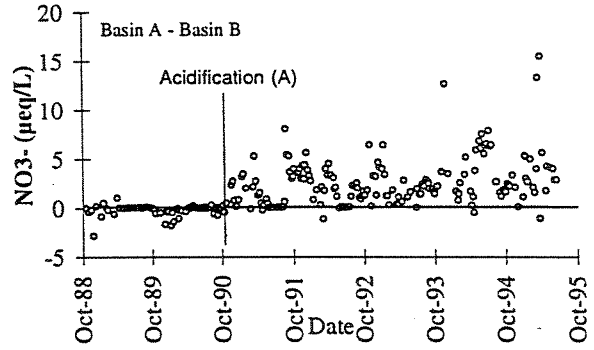

80
60
40
20
0
SO42- (µeq/L)
Basin A
Basin B
Acidification (A)
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

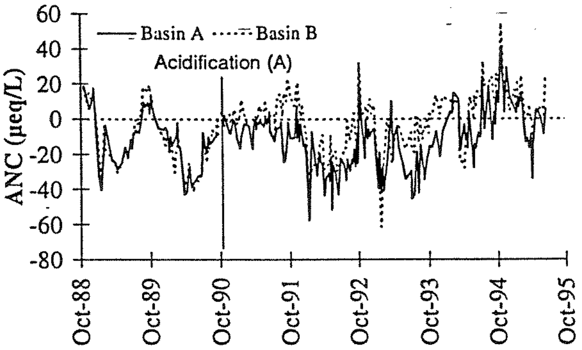

80
60
40
20
0
-20
-40
-60
SO42- (µeq/L)
Basin A - Basin B
Acidification (A)
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

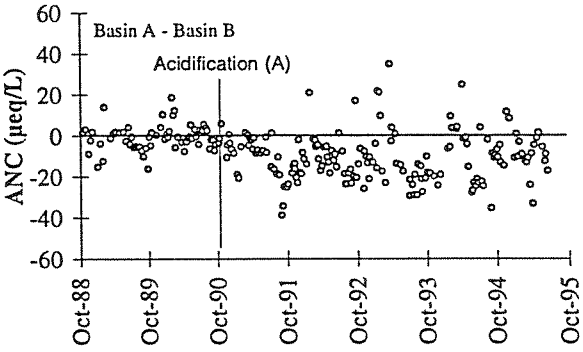

35
30
25
20
15
10
5
0
NH4+ (µeq/L)
Basin A
Basin B
Acidification (A)
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

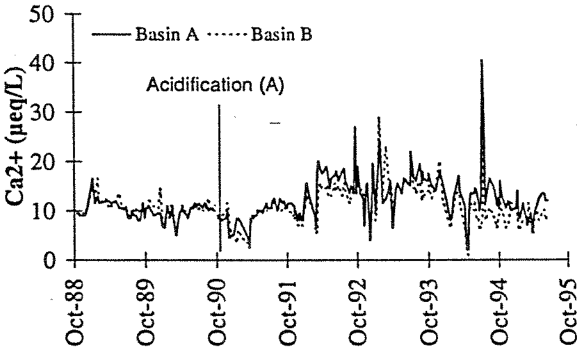

40
30
20
10
0
-10
NH4+ (µeq/L)
Basin A - Basin B
Acidification (A)
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

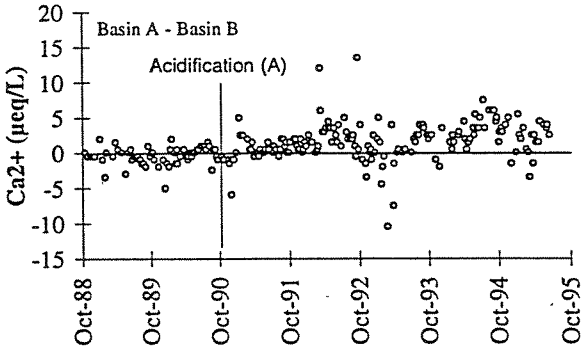

20
15
10
5
0
NO3- (µeq/L)
Basin A
Basin B
Acidification (A)
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

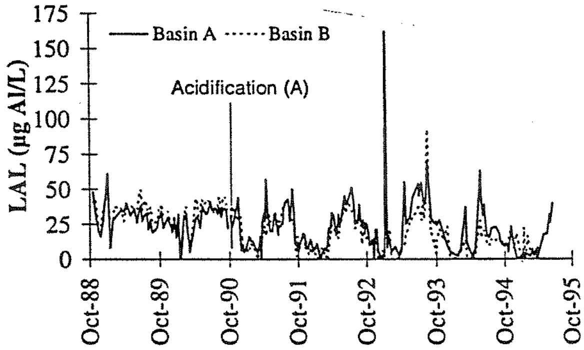

20
15
10
5
0
-5
NO3- (µeq/L)
Basin A - Basin B
Acidification (A)
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95
Date

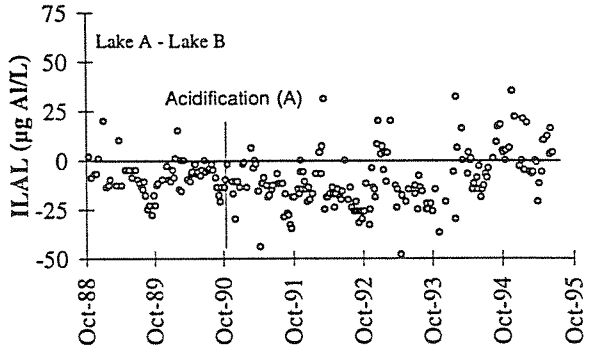

Basin A
Basin B
Acidification (A)
ANC (µeq/L)
60
40
20
0
-20
-40
-60
-80
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

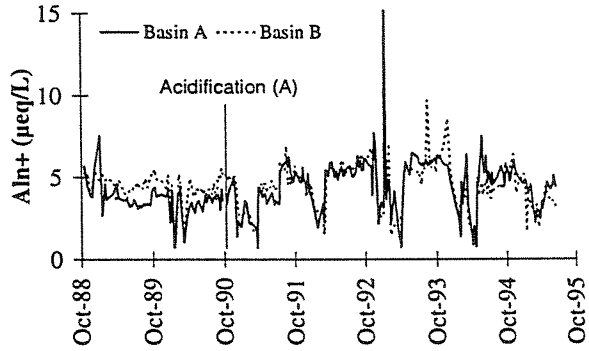

Basin A - Basin B
Acidification (A)
ANC (µeq/L)
60
40
20
0
-20
-40
-60
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

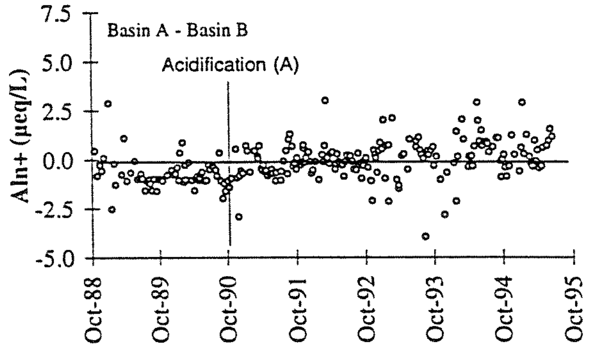

Basin A
Basin B
Acidification (A)
Ca2+ (µeq/L)
50
40
30
20
10
0
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

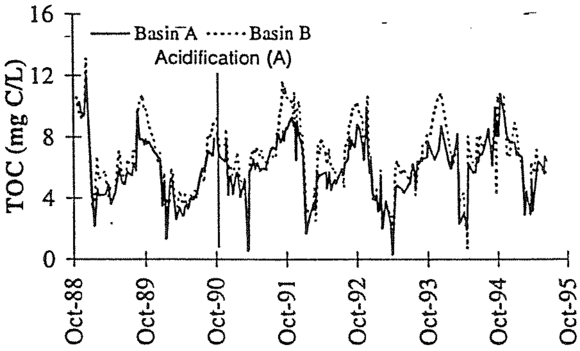

Basin A - Basin B
Acidification (A)
Ca2+ (µeq/L)
20
15
10
5
0
-5
-10
-15
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

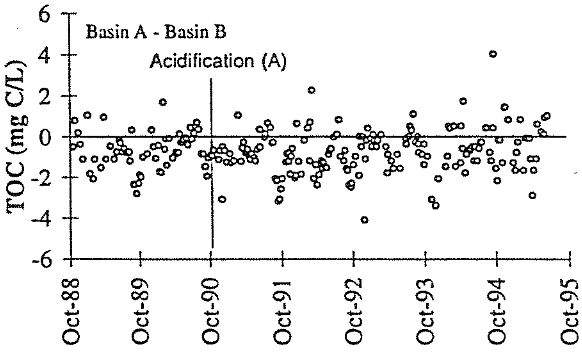

Basin A
Basin B
Acidification (A)
LAL (µg Al/L)
175
150
125
100
75
50
25
0
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

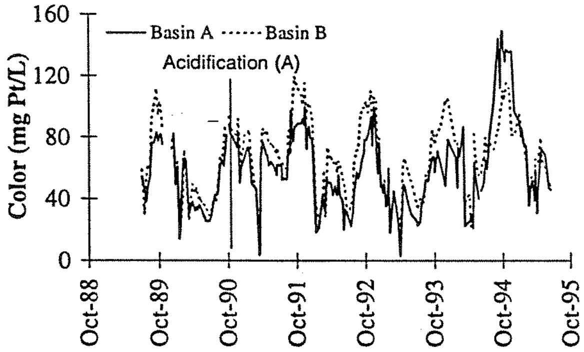

Lake A - Lake B
Acidification (A)
ILAL (µg Al/L)
75
50
25
0
-25
-50
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

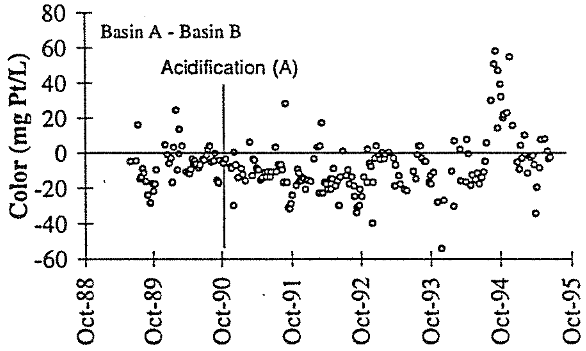

Basin A
Basin B
Acidification (A)
Aln+ (µeq/L)
15
10
5
0
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

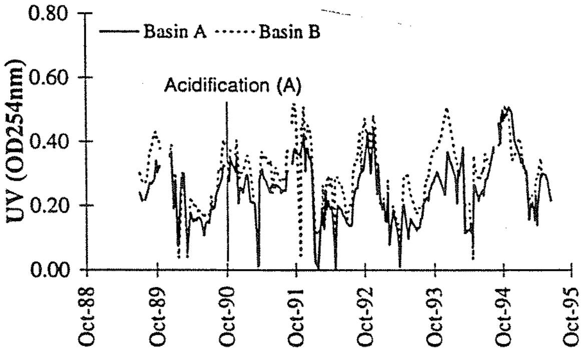

Basin A - Basin B
Acidification (A)
Aln+ (µeq/L)
7.5
5.0
2.5
0.0
-2.5
-5.0
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

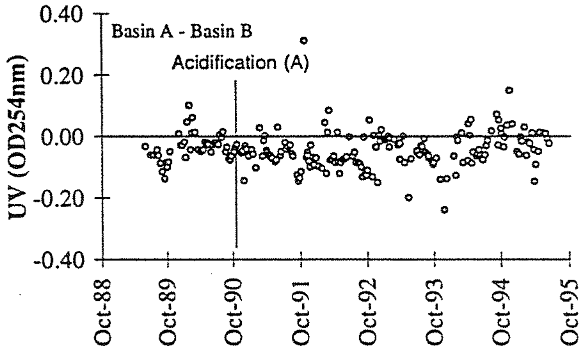

TOC (mg C/L)
16
12
8
4
0
Basin A
Basin B
Acidification (A)
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

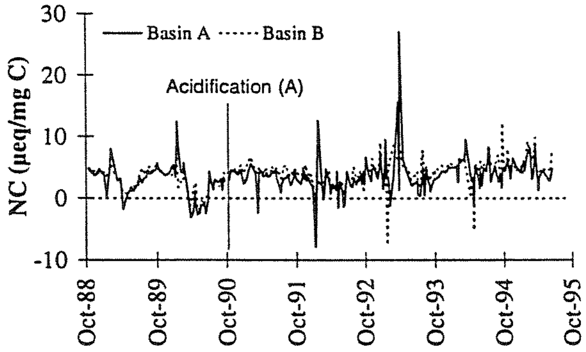

TOC (mg C/L)
6
4
2
0
-2
-4
-6
Basin A - Basin B
Acidification (A)
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

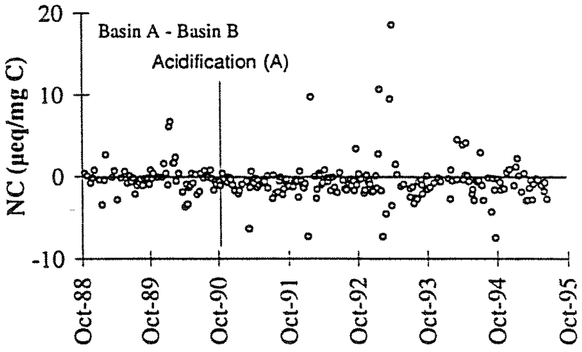

Color (mg Pt/L)
160
120
80
40
0
Basin A
Basin B
Acidification (A)
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

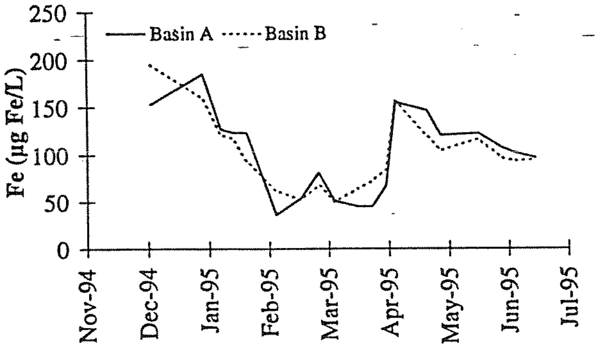

Color (mg Pt/L)
80
60
40
20
0
-20
-40
-60
Basin A - Basin B
Acidification (A)
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

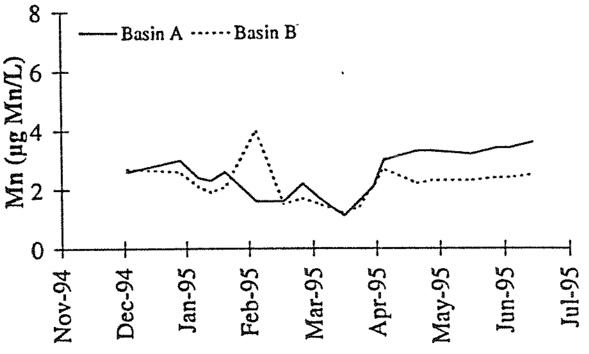

UV (OD254nm)
0.80
0.60
0.40
0.20
0.00
Basin A
Basin B
Acidification (A)
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

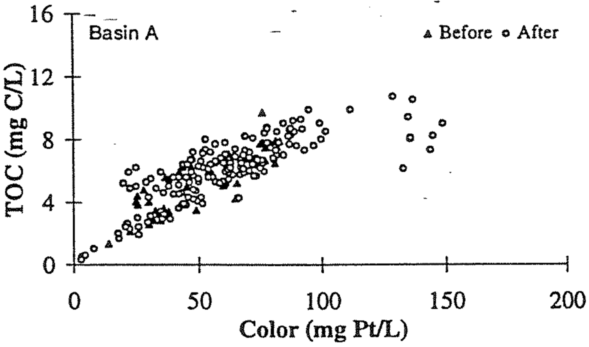

UV (OD254nm)
0.40
0.20
0.00
-0.20
-0.40
Basin A - Basin B
Acidification (A)
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

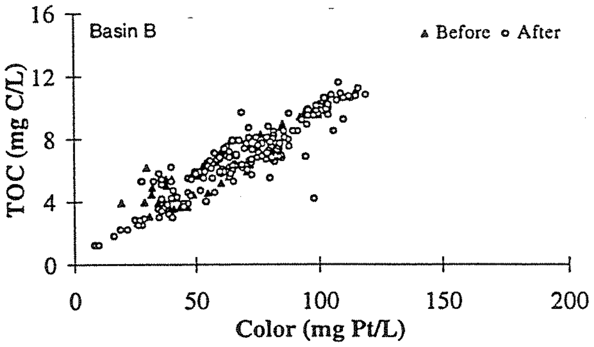

NC (µeq/mg C)
30
20
10
0
-10
Basin A
Basin B
Acidification (A)
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

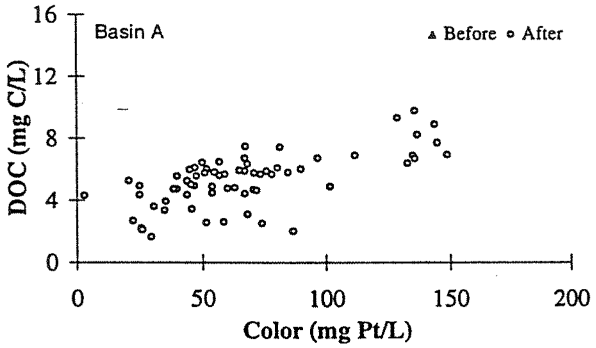

NC (µeq/mg C)
20
10
0
-10
Basin A - Basin B
Acidification (A)
Oct-88
Oct-89
Oct-90
Oct-91
Oct-92
Oct-93
Oct-94
Oct-95

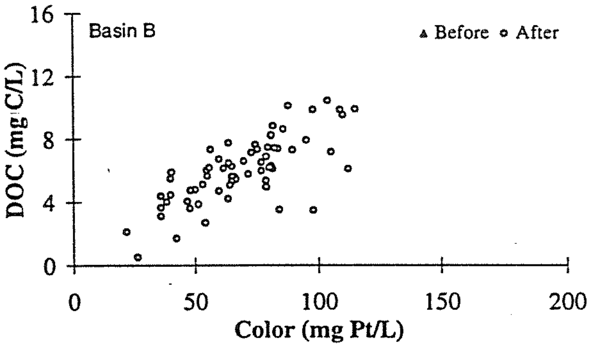

Basin A
Basin B
Fe (µg Fe/L)
250
200
150
100
50
0
Nov-94
Dec-94
Jan-95
Feb-95
Mar-95
Apr-95
May-95
Jun-95
Jul-95

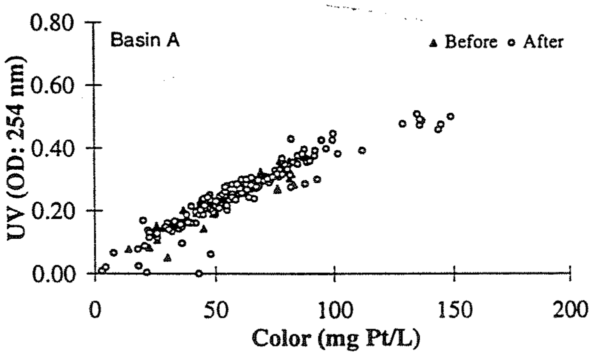

Basin A
Basin B
Mn (µg Mn/L)
8
6
4
2
0
Nov-94
Dec-94
Jan-95
Feb-95
Mar-95
Apr-95
May-95
Jun-95
Jul-95

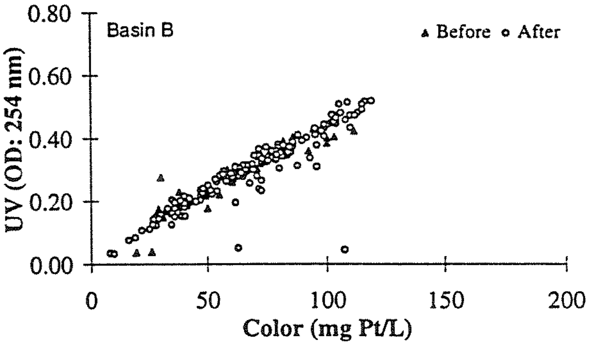

Basin A
▲ Before ○ After
TOC (mg C/L)
0
4
8
12
16
Color (mg Pt/L)
0
50
100
150
200

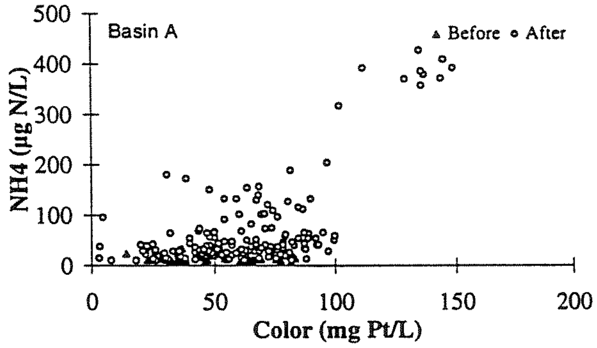

Basin B
▲ Before ○ After
TOC (mg C/L)
0
4
8
12
16
Color (mg Pt/L)
0
50
100
150
200

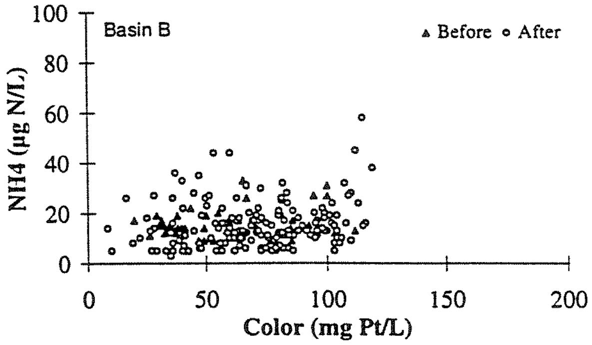

Basin A
▲ Before ○ After
DOC (mg C/L)
0
4
8
12
16
Color (mg Pt/L)
0
50
100
150
200

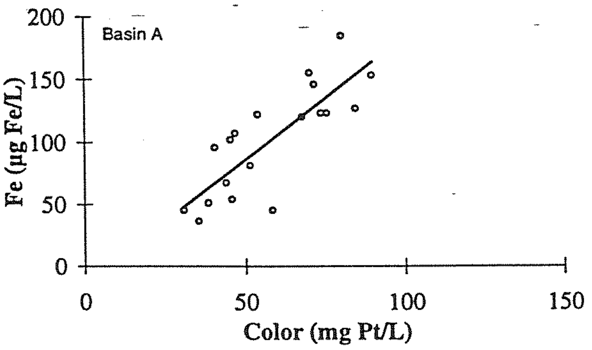

Basin B
▲ Before ○ After
DOC (mg C/L)
0
4
8
12
16
Color (mg Pt/L)
0
50
100
150
200

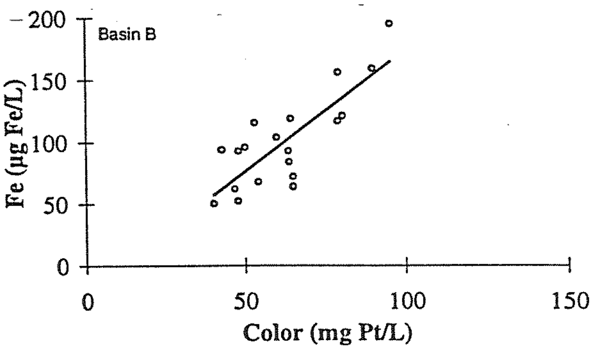

Basin A
▲ Before ○ After
UV (OD: 254 nm)
0.00
0.20
0.40
0.60
0.80
Color (mg Pt/L)
0
50
100
150
200

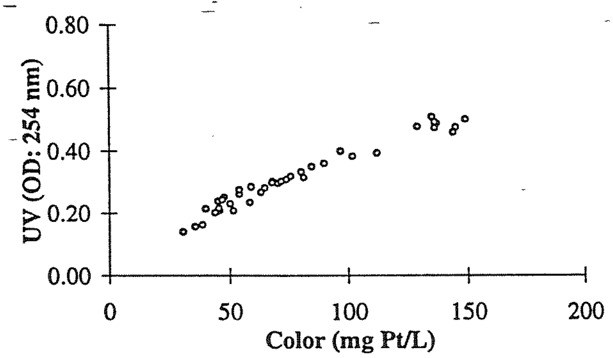

Basin B
▲ Before ○ After
UV (OD: 254 nm)
0.00
0.20
0.40
0.60
0.80
Color (mg Pt/L)
0
50
100
150
200


Basin A
▲ Before ○ After
NH4 (µg N/L)
0
100
200
300
400
500
Color (mg Pt/L)
0
50
100
150
200


Basin B
▲ Before ○ After
NH4 (µg N/L)
0
20
40
60
80
100
Color (mg Pt/L)
0
50
100
150
200


Basin A
Fe (µg Fe/L)
200
150
100
50
0
0
50
100
150
Color (mg Pt/L)


Basin B
Fe (µg Fe/L)
200
150
100
50
0
0
50
100
150
Color (mg Pt/L)


0.80
0.60
0.40
0.20
0.00
UV (OD: 254 nm)
0
50
100
150
200
Color (mg Pt/L)

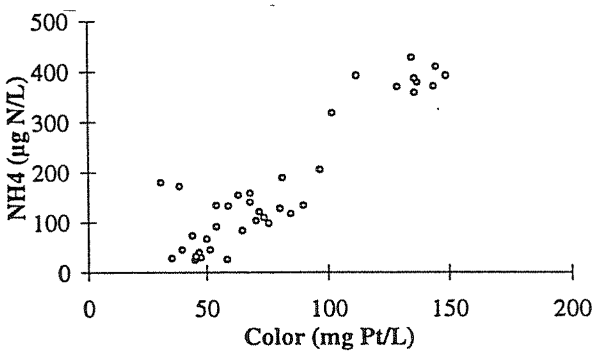

500
400
300
200
100
0
NH4 (µg N/L)
0
50
100
150
200
Color (mg Pt/L)

TABLE TEXTS

Table 1 Annual amounts of H_2SO_4 and NH_4NO_3 added to the terrestrial part of the catchment and to the lake surface (total 2.7 ha) during the 4 years of treatment. Additions are weekly in water equivalent to 10% of ambient precipitation.The pH of the artificial solution is between 3.0 and 3.2, which means that diluted with the natural amount of rain, the pH will be between 4.0 and 4.2.

Table 2 The amount of precipitation (mm), weighed average concentrations (meq/L) and total fluxes (meq/m^2) of chemical compounds from wet deposition at Skjervatjern (SK) and Nausta (NA) from 1 January 1995 to 1 July 1995 (sulfate only until 1 June).

Table 3 Mean, maximum and minimum concentration of major chemical compounds in runoff water from Basin A and B, based on two years before and 4 years and 9 months after acidification. n.a. : not analyzed.

Table 4 Mean values in basin A (artificially acidified) and B of 2 years before and of 4 years after start of acidification (almost weekly sampling), the relative actual differences ($D_{actual} = \overline{D}_{pre} - \overline{D}_{post}$), the 95% and 99% values based on Randomized Intervention Analysis (RIA). If the P95% or P99% values < absolute value of D_{actual}, there are a 95% or 99% probability that the changes due to the manipulation (acidification of basin A) are real. $N_{tot} = 146$, $N_{pre} = 53$.

Table 5 Mean values in basin A (artificially acidified) and B for the 2 first years and 2 last years of the acidification period, the relative actual differences ($D_{actual} = \overline{D}_{first} - \overline{D}_{last}$), the 95% and 99% values based on Randomized Intervention Analysis (RIA). If the P95% or P99% values < absolute value of D_{actual}, there are a 95% or 99% probability that the differences between the 2 first years of acidification and the 2 last years are real, i.e. time trends occur. $N_{first} = 79$, $N_{last} = 67$.

FIGURE TEXTS

Fig. 1 The monthly and cumulative amounts of sulfur (as H_2SO_4) and nitrogen (as NH_4NO_3) added to Basin A and its catchment from October 1990 to May 1995.

Fig. 2 Weekly precipitation (mm), and concentration of H^+, SO_4^{2-}, NO_3^- and Cl^- in precipitation at the local weather station at Skjervatjern since start of monitoring January 1995.

Fig.3 Monthly mean air and soil temperature (°C), precipitation (dm) and sun radiation (M Joule/m^{-2}). The photo sensor responds through the wave length range of 400-700 nm. The radiation is monthly values in Joule s^{-1} m^{-2} integrated over 24 h. Units: M Joule m^{-2}.

Fig. 4 Weekly concentrations of H^+, SO_4^{2-}, NH_4^+ and NO_3^- (meq/L) in runoff from Basin A and B, and the differences between lake A and B of Lake Skjervatjern from October 1988 to June 1995.

Fig. 5 Weekly ANC (acid neutralizing capacity), Ca^{2+}, LAL (labile or inorganic monomeric Al), and Al^{n+} (total average charge of Al) in runoff from Basin A and B, and the differences between Basin A and B of Lake Skjervatjern from October 1988 to June 1995.

Fig.6 Weekly TOC, Color (OD: 410 nm or mg Pt/L), UV (OD: 254) and NC (net charge organic in µeq/mg C) in runoff from Basin A and B, and the differences between Basin A and B of Lake Skjervatjern from October 1988 to June 1995.

Fig. 7 The concentration of Fe and Mn in runoff from Basin A and Basin B during the monitoring period, i.e. December 1994-June 1995.

Fig.8 The relationship between color and TOC, UV and NH_4^+ in Basin A and Basin B of Lake Skjervatjern during October 1988 to June 1995. Before: before acidification of Basin A and its catchment, i.e. from October 1988 to October 1990. After: After acidification of Basin A, i.e. from October 1990 to June 1995. **Before**: **Basin A**, TOC = 0.078*color + 1.35 ($r^2 = 0.71$); UV: 0.0037*color + 0.032 ($r^2 = 0.88$); NH_4 = 0.008*color + 14.0 ($r^2 = 0.007$). **Basin B**, TOC = 0.085*color + 1.19 ($r^2 = 0.84$); UV: 0.0038*color + 0.039 ($r^2 = 0.88$); NH_4 = 0.064*color + 11.6 ($r^2 = 0.07$). **After**: **Basin A**, TOC = 0.057*color + 2.57 ($r^2 = 0.64$); DOC = 0.033*color + 3.09 ($r^2 = 0.44$); UV: 0.0036*color + 0.039 ($r^2 = 0.89$); NH_4 = 2.09*color - 60.7 ($r^2 = 0.44$). **Basin B**, TOC = 0.085*color + 0.95 ($r^2 = 0.84$); DOC = 0.071*color + 1.12 ($r^2 = 0.55$); UV: 0.0040*color + 0.028 ($r^2 = 0.83$); NH_4 = 0.064*color + 10.7 ($r^2 = 0.03$).

Fig. 9 The relationship between Fe and color in Basin A and B during the period of monitoring, i.e. December 1994 -June 1995. **Basin A**: Fe = 1.96*color - 12.1 ($r^2 = 0.66$); **Basin B**: Fe = 1.96*color 21.9 ($r^2 = 0.65$).

Fig. 10 The relationship beween color and UV and NH_4^+ in Basin A of Lake Skjervatjern from May 1994 to June 1995. UV = 0.0029*color + 0.0893 ($r^2 = 0.96$); NH_4 = 3.39*color - 94.8 ($r^2 = 0.83$).

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The effects of ionic strength on the toxicity of aluminum to Atlantic salmon parr in dynamic Al-chemistry water.

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The major cause of fish death in acidic freshwaters, is the elevated concentration of inorganic aluminum (Al) forms. Since the toxicity is related to interactions between Al and the gill surfaces, the effects of ionic-strength variations have been studied, because ionic-strength is very important for the quality and quantity of diffuse electric double-layers present near all aquatic surfaces. In our studies, an acidic Al-solution was added to lake water of pH 6.5 (Ca ≈ 3 mg/L) to obtain a pH of 5.7-5.8 and a concentration of total monomeric Al between 400 and 600 µg/L (15-20 µmolar) in a continuous flow system. Thus, fish were exposed to a dynamic Al-chemistry water (mixing zone) that always occurs a certain time following such pH increases. Parallel experiments were run by adding neutral salts, $CaCl_2$, $MgCl_2$, and NaCl to the water. The addition of Ca was about 2 mg/L (50 µmolar), and NaCl and $MgCl_2$ were added so that correspondent ionic-strength increases were obtained. In all experiments, decreasing mortality was observed by time after the pH adjustments. In the experiments during spring, comparisons were made between $CaCl_2$ and NaCl additions. Both the solutions with elevated ionic strengths ameliorated the Al-toxicity significantly, and the ameliorating effect was strongest for Na. This was probably because 3 times more Na-ions have to be added to obtain the same ionic strength increase than by Ca. In the comparison studies conducted a few months later, almost no ameliorating effect was observed by increasing ionic strength by either $CaCl_2$ or $MgCl_2$. Several physico-chemical causes of these inconsistencies are discussed in this article.

Keywords: Freshwater, Acidification, Aluminium, Polymer, Toxicity, Fish, Ionic-strength

Introduction

There is little doubt that the toxicity of fish in natural acidic surface waters is primarily associated with the concentration of inorganic aluminum (1-2) and that aluminum primarily leach out from soils with low pH-buffering capacity, i.e. low dissolution rates of base cations. Accordingly these acid sensitive catchments to a large extent consist of slowly weatherable soils and rocks often with only a thin soil cover. Thus, the concentration of terrestrial derived base cations like Ca, Mg are normally relatively low and the release of aluminum by dissolution or exchange are therefore major pH-neutralizing processes (3-4). Because the ionic content of the surface water derived from these catchments are generally low, many scientist have observed that survival of fish at low pH can be affected by the ionic content of the water (5-10). The observed moderating effect of increased ionic strength of water has often been attributed to concentration increases of Ca per se (11-14). This is not surprising since Ca is important in stabilizing biological membranes, maintaining the integrity of cell to cell junctions, and controlling ion and water permeability across epithelial tissues (15-18). Surveys of moderate acidic lakes (pH 4.5-5.5) in southern Norway have indicated that Ca is as critical to fish population status as pH (19), while correspondent surveys made by Muniz and Walløe (20) and Baker et al. (21) gave no statistical significant correlations between Ca and fish population status. Ionic strength was not tested in any of these surveys. Toxicity of aluminum in oversaturated solutions has been reported back to 1978 (2). Lydersen (22) found that generally, for all later corresponding studies, the initial pH was always lower to what the fish were exposed to. Thus, he concluded that there has to be a subsequent history of lower pH for significant amounts of polymeric aluminum to be present, and that polymerization may be of major importance for the toxic response (23). Later studies have shown that the most extreme aluminum toxicity often is present soon after a pH increase in aluminum rich acidic waters, and that the extreme Al-polymerization/accumulation of Al on fish gills is the main physical-chemical mechanism (24-26). Since aluminium processes taking part on the gill surfaces seem essential for the understanding of mechanisms behind this extreme mortality, effects of ionic strength on Al-polymerization and the subsequent effects on fish toxicity have been studied in this paper.

Material and Methods

Theoretical background

The mucus on fish surfaces, including gill surfaces, consists of 95% water. The major organic compounds of mucus are glycoproteins (27) rich in sialic acid with a pK_a-value less than 3 (28), which means that at most fresh-water pH-values sialic acid is primarily negatively charged. Positively charged cations (counterions), including Al-species may therefore easily bind to the gill surface, and at water pH's where Al-hydrolysis and Al-polymerization occur (primarily between pH 5 and 7), the negatively charged sites present on fish gills may act as Al-polymerization nuclei.

Counterions are electrically attracted by the opposite charge solid phase, like the negative charge surface of fish gills. At the same time, however, these ions have a tendency to diffuse away from the surface toward the bulk of the solution, where their concentrations are lower. The net result of the two competitive tendencies is an equilibrium distribution of ions in which their concentration gradually decreases with increasing distance from the solid surface. Simultaneously, there is a deficiency of co-ions (anions) nearby the surface, since these ions are repelled because they have charges with the same sign as the surface of the particle/solid phase, but the concentrations of co-ions gradually increase by distance from the solid surface. This diffuse character of ions was recognized by Gouy (29) and Chapman (30), and is often referred to as Gouy-Chapman diffuse layer. Very close to the negative charge surface the cations are able to be present without their hydration shells (often termed the inner Helmholz layer), but to which extent depends to a certain degree of the ionic radii, i.e. small ions are less dehydrated than larger ions. By distance from the negative charge surface the cations will be more and more hydrated until they reach the hydration status as present in the bulk solutions. In the bulk solution there is electroneutrality. At a charged solid phase in a medium of low ionic strength the disturbance in the electroneutrality extends further into the solution than in the case of a solution with higher ionic strength. The centre of charge falls at a plane of distance $1/\kappa$, referred to as the double layer thickness, which depends of the electrolyte concentration. For water at 20°C:

$$\kappa^{-1} \sim \frac{2.8 \text{ x } 10^{-8}}{\sqrt{I}}(cm) \qquad \text{Equation I}$$

where I is the ionic strength (molarity) and defined as:

$$I = \frac{1}{2}\sum_i c_i z_i^2 \qquad \text{Equation II}$$

where c_i is the concentration of an ion in moles per kilogram of water, z_i is its charge, and the sum is taken over all ions in the solution.

Since all experiments are performed at nearly identical pH's, we assume that the numbers of negative charges per surface area of the gills are constant. Thus by increasing the concentration of ions by adding salts of basecations the Al-toxicity should be reduced because of :

a) Decreasing thickness of the double layer due to an increase in ionic strength

b) Increasing possibility of base cations to compete with Al as the cations present in the diffuse double layer.

c) At the base cation concentrations and pH level present (pH about 5.7-5.9) in the test solution, the base cations are only present as conservative monomeric pure dissolved ions, while Al to a large extend will be present as dynamic polymers that most likely increase in size and decrease in cationic charge by ageing. This is because Al derives from a very acidic solution where it is only present as Al^{3+}. The positive correlation between ageing of Al-polymers and reduced Al-toxicity to fish is earlier reported (25).

Experimental animals

Atlantic salmon (*Salmo salar L.*) parr from a local hatchery near Oslo, Norway, were brought into the fish holding department at the University of Oslo, where they were kept and acclimatized for two weeks before the experiments. In the experiments in April/May 1994 the fish in the Ca experiment (n = 249) varied from 0.4 to 3.1 g in weight (mean: 1.4 ± 0.5 g) and from 3.8 to 7.0 cm in total length (mean: 5.5 ± 0.6 cm), while in the Na experiment (n = 234) the fish varied from 0.5 to 3.0 g in weight (mean: 1.3 ± 0.5 g) and from 3.7 to 7.1 cm in total length (mean: 5.4 ± 0.6 cm). In the experiments in October/November 1994, the fish in the Ca/Mg experiment (n= 255) varied from 2.0 to 21.4 g in weight (mean: 5.8 ± 3.6 g) and from 6.0 to 13.3 cm in total length (mean: 8.3 ± 1.5 cm), while in the experiment with Al only, the fish (n = 52) varied from 1.8 to 21.4 g in weight (mean: 7.8 ± 5.5 g) and from 6.0 to 12.3 cm in total length (mean: 8.9 ± 1.9 cm).

Analytical methods

Aluminum was analyzed by the HQ/MIBK-extraction method described by Barnes (31), with an extraction time of 20 s. The extracts were stored at 4°C for at least 24 h, and thereafter at room temperature (20°C) for 2 h before absorbency measurements were carried out on a Shimadzu UV-1201 spectrophotometer at 395 nm (32-33). Absorbency was also measured at 600 nm in order to correct for iron interference (34). By direct extraction of water samples, the amount of total monomeric Al-species (Al_a) was determined (35). Water samples were also run through a column of Amberlite IR-120 as cation exchange resin prior to extraction. As recommended by Driscoll (35), the cation-exchange flow-rate was 3.8 ml min^{-1} ml^{-1} bed-volume. The resin was prepared by displacing some of the exchangeable hydrogen ions with sodium ions. When an eluant of comparable ionic strength to that of the water samples being analyzed was passed through the exchanger, the pH of the effluent should be similar to the pH of the sample. A volume of 60 ml 10^{-4} M NaCl was always used for conditioning the resin between runs of samples. For preconditioning purposes 60 ml of water were eluted before another 60 ml of eluate were collected for extraction. The aluminum present in the eluate was defined as non-labile Al. In natural fresh water this fraction is often defined as organic monomeric Al, termed Al_o (35). The concentration of labile or inorganic monomeric Al (Al_i) was calculated as the difference between Al_a and Al_o. Total aluminum (Al_r) was also analyzed by HQ/MIBK-extraction after acidifying water samples with HNO_3 to pH 1.0 for 24 h. The amount of colloidal Al (Al_c) was calculated as the difference between Al_r and Al_a The standard deviation of the Barnes/Driscoll method is assumed to approximate 1% of the mean (34). ALCHEMI-Version 4.0 was used to calculate the theoretical distribution of inorganic Al-species from the Ali-fraction (Schecher and Driscoll, 1987; 1988), assuming equilibrium of dissolved species and a carbonate buffering system open to the atmosphere. In the ALCHEMI program, the effects of temperature and ionic strength on the Al-chemistry are accounted for. The uncertainties in the concentrations of all species obtained from these calculations are considered to be low (36-37).

pH was measured using a Radiometer PHM-80 with a Radiometer GK-2401C combined glass-electrode. The pH readings were taken when the pH-meter drifted less than 0.01 pH unit per minute. The standard deviation of the measured pH was ± 0.01 pH unit. The conductivity was measured with a Radiometer CDM-80. The conductivity was read when three consecutive measurements were identical within one tenth of a unit (µS cm^{-1}). The pH and conductivity measurements as well as Al-extraction's were performed immediately after the water samples were taken.

Total fluoride (F^-) was analyzed according to Harwood (38) using an Orion Model 94-09 ion selective electrode, connected to an Orion Research Microprocessor Ion Analyser/901 with the Orion Model 90-01-00 as reference electrode. The precision of the ion selective fluoride electrode is expected to be ± 2% (38). Na^+, K^+, Ca^{2+} and Mg^{2+} were analyzed by Atomic Absorption Spectroscopy (AAS), SO_4^{2-} and Cl^- by ion chromatography (IC), NO_3^- by the indophenolblue method and total organic carbon (TOC) by a combined photochemical (UV) wet-chemical ($S_2O_8^{2-}$) oxidation method.

Test conditions

The experiments were performed in the fish holding department at University of Oslo. Three experimental follow-through channels (Fig. 1) were used for the exposures. The channels were 218 cm long, 42 cm wide, and 16 cm deep. The channels were divided into 5 chambers in which the fish were held during the exposures. The water-flow rate into each channel was approximately 3 L min^{-1}, and the residence time was about 20 min. The fish were sheltered by covers over the channels. In two of the channels, dynamic Al-chemistry water were prepared by adding a few ml of an artificially made acidic (nitric acid) Al-solution $Al(NO_3)_3$ to the alkaline raw-water (pH ≈ 6.5) to obtain a mixing pH of ≈ 5.8 and a total Al concentration of about 500 µg Al/L (18.5 µmolar). The pH of the artificial Al-solution added was very low (pH ≈ 2) to ensure that the total amount of Al was on the Al^{3+}-form when added. While equal amounts of $Al(NO_3)_3$ were added to the raw-water in the two experimental channels, different types of salts were added to one of them (either $CaCl_2$, NaCl or $MgCl_2$). The additions of the various salts were calculated to obtain identical ionic strength increases, corresponding to an addition of 2 mg Ca/L (as $CaCl_2$). In the third channel fish were exposed to untreated raw-water only (pH ≈ 6.5, Al_i: 0-28 µg Al/L), only for control purpose.

Water temperature, conductivity, and pH were measured daily throughout the experiment. The chemical dosages and water-flows into the channels were also controlled each day. Three or four times during the experiment, Al_r, Al_a, Al_o and Al_i were determined. We used about 25 fish in all 5 chambers of the A and B channels. In the control channel, however, we only used 10 fish. All experiments were run for 140 hours. Experimental water temperature in April/May was between 5-6° C, while during October/November 9-10° C.

Results

Calcium addition experiment

The toxicity comparison was made between a solution with only Al added and a solution with both Al and $CaCl_2$ added. Water temperature varied between 4.8-5.2°C. In the Al only solution, pH, Ca and the ionic strength were 5.76, 158.7 µeq/L and 4.76×10^{-4} molar, while the concentration of Al_r (total Al), Al_c (colloidal Al), Al_o (non-labile Al or ≈ low molecular weight organic-Al), Al_i (labile Al or ≈ low molecular weight inorganic Al), and Al^{n+} (total average charge of Al calculated by the ALCHEMI-Version 4.0 program) were 593 ± 36 µg/L, 165 ± 44 µg/L, 159 ± 14 µg/L, 269 ± 41 µg/L and 13.5 ± 1.5 µeq/L (Table II). The concentration of Al^{n+} in relation to total amount of monomeric Al present (Al_a) indicates an average charge of each monomeric Al-atom of 0.85 ± 0.03 ($Al^{+0.85}$). In the Al+Ca solution, pH, Ca and the ionic strength were 5.83, 253.0 µeq/L and 6.27×10^{-4} molar, while the concentration of Al_r, Al_c, Al_o, Al_i and Al^{n+} were 521 ± 39 µg/L, 175 ± 39 µg/L, 145 ± 14 µg/L, 201 ± 42 µg/L and 9.5 ± 1.5 µeq/L. The average charge of each monomeric Al-molecule was calculated to be 0.74 ± 0.07 ($Al^{+0.74}$). Theoretically the thickness of the diffuse double layer should be 1.28×10^{-6} cm in Al and 1.12×10^{-6} cm in Al+Ca, which means a decrease by 12.5% due to the addition of $CaCl_2$. While, on equivalent basis, Al constituted 4.2% of the total cationic pool in the Al only solution, Al in the Al+Ca solution only constituted 2.3%.

In the Al only, 100% mortality (Fig. 2a) was recorded after about 97 hrs in the uppermost compartment (A), i.e. the compartment closest to the chemical additions, which also means the shortest time after the pH adjustment of the acidic Al solution. At the end of the experiment (140 hrs exposure time) 78%, 48,%, 13% and 12% mortality were recorded in compartment B, C, D, and E, which means about 5, 10, 15 and 20 min after the addition of chemicals. In compartment A and B where more than 50% of the fish died during the 140 hrs exposure period, LT_{50} was about 35 hrs and 102 hrs respectively. Totally 50% of all fish exposed (n = 123) died during the 140 hrs time of exposure. No fish died in the control group that were exposed to the raw water only.

In Al+Ca, 100% mortality (Fig. 2b) was recorded after about 93 hrs in the uppermost compartment (A). This compartment was the only one with > 50% mortality during 140 hrs, and the LT_{50} was about 46 hrs. After 140 hrs 44%, 8%, 0% and 4% mortality were recorded in compartment B, C, D and E. Totally 31% of the fish exposed (n = 126) died during 140 hrs. Thus, the ionic strength increase (by $CaCl_2$) from 4.76×10^{-4} molar to 6.27×10^{-4} molar caused a reduced mortality of 36%.

Sodium addition experiment

The toxicity comparison was made between a solution with only Al added and a solution with both Al and NaCl added. Water temperature varied between 5.0-6.2°C In the Al only solution, pH, Na and the ionic strength were 5.71, 90.9 µeq/L and 4.49×10^{-4} molar, while the concentration of Al_r, Al_c, Al_o, Al_i and Al^{n+} were 573 ± 59 µg/L, 217 ± 29 µg/L, 151 ± 16 µg/L, 217 ± 29 µg/L and 10.2 ± 1.0 µeq/L (Table III). The average charge of each monomeric Al-molecule was calculated to be 0.74 ± 0.04 ($Al^{+0.74}$). In the Al+Na solution, pH, Na and the ionic strength were 5.72, 236.6 µeq/L and 6.23×10^{-4} molar, while the concentration of Al_r, Al_c, Al_o, Al_i and Al^{n+} were 602 ± 61 µg/L, 206 ± 61 µ g/L, 150 ± 13 µg/L, 245 ± 28 µg/L and 11.5 ± 1.0 µeq/L. The average charge of each monomeric Al-molecule was calculated to be 0.78 ± 0.03 ($Al^{+0.78}$). Theoretically the thickness of the diffuse double layer should be 1.32×10^{-6} cm in Al and 1.12×10^{-6} cm in Al+Na, which means a decrease by 15% after addition of NaCl. While, on equivalent basis, Al constituted 3.3% of the total cationic pool in the Al only solution, Al in the Al+Na solution only constituted 2.5%.

In the Al only, 100% mortality (Fig. 2c) was never recorded, but 96% mortality was recorded in the uppermost compartment (A) during the 140 hrs of exposure. After 140 hrs exposure time, 75%, 32,%, 17% and 0% mortality were recorded in compartment B, C, D, and E. In compartment A and B where more than 50% of the fish died during the 140 hrs exposure period, LT_{50} was about 62 hrs and 134 hrs respectively. Totally 44% of all fish exposed to Al only died during the 140 hrs of exposure, which was almost the same as in the first experiment (Fig. 2a). No fish died in the control group.

In Al+Na, 100% mortality was never recorded (Fig. 2d) after 140 hrs of exposure even in the uppermost compartment (A). Compartment A was the only one with > 50% mortality during 140 hrs, i.e. LT_{50} was 135 hrs. After 140 hrs exposure time, 16%, 4%, 0% and 4% mortality were recorded in compartment B, C, D and E. Totally 16% of the fish exposed (n = 126) died during 140 hrs. Thus the ionic strength increase (by NaCl) from 4.49×10^{-4} molar to 6.23×10^{-4} molar caused a reduced mortality of 64%.

Calcium/magnesium experiment

After the calcium experiment was finished late April, we immediately ran the sodium experiment (spring experiments). Because we also want to compare ions with the same valence, a new toxic experiment was conducted in October/November (autumn experiments). In this experiment we wanted to compare the ameliorating effect of Ca^{2+} versus Mg^{2+}. The Al+Ca and Al+Mg experiments were performed simultaneously in the two parallel channels, while the Al only experiment was ran immediately after. Water temperature varied between 8.8-9.7°C. No analyses, except, pH and temperature were performed during the Al only experiments, but average pH was 5.72 ($[H^+]$: 1.91 ± 0.3 µeq/L, n = 14). The pH's in the Al+Ca and Al+Mg solution were 5.71 and 5.77 respectively. Because all three solutions were made from the same raw-water and the same acidic Al-solution, the good agreement in pH between Al only and Al+Ca and Al+Mg, indicates that the Al-concentration in the test solution of Al only should be very similar to the concentration of the other two solutions.

In the Al+Ca solution, pH, Ca and the ionic strength were 5.71, 235.5 µeq/L and 5.55×10^{-4} molar, while the concentrations of Al_r, Al_c, Al_o, Al_i, and Al^{n+} were 399 ± 41 µg/L, 158 ± 37 µg/L, 96 ± 4 µg/L, 145 ± 25 µg/L and 6.8 ± 1.0 µeq/L (Table II). The average charge of each monomeric Al-molecule was calculated to be 0.76 ± 0.06 ($Al^{+0.76}$). In the Al+Mg solution, pH, Mg and the ionic strength were 5.77, 132.9 µeq/L and 5.54×10^{-4} molar, while the concentrations of Al_r, Al_c, Al_o, Al_i and Al^{n+} were 380 ± 46 µg/L, 166 ± 37 µg/L, 91 ± 4 µg/L, 122 ± 25 µg/L and 6.2 ± 0.9 µeq/L. The average charge of each monomeric Al-molecule was calculated to be 0.78 ± 0.04 ($Al^{+0.78}$). Theoretically the thickness of the diffuse double layer should be 1.19×10^{-6} cm in both Al Al+Ca and Al+Mg. On equivalent basis, Al constituted 1.8% and 1.7% of the total cationic pool in the Al+Ca and Al+Mg solutions respectively.

In the Al only, 100% mortality (Fig. 3a) was only recorded in compartment (A) during 140 hrs. In A all fish were died after 43 hrs exposure. After 140 hrs exposure time, 73%, 60,%, 80% and 40% mortality were recorded in compartment B, C, D, and E. In the compartments where more than 50% of the fish died during the 140 hrs exposure, LT_{50} was 24 hrs (A), 80 hrs (B), 73 hrs(C) and 40 hrs (D). Totally 71% of all fish exposed (n = 52) died during the 140 hrs time of exposure.

In the Al+Ca solution, 100% mortality (Fig. 3b) was recorded in compartment A and B during 140 hrs, i.e. after 57 hrs (A) and 140 hrs (B). After 140 hrs exposure time, 56%, 32,% and 24% mortality were recorded in compartment C, D, and E. In the compartments where more than 50% of the fish died during the 140 hrs exposure, LT_{50} was 32 hrs (A), 33 hrs (B) and 85 hrs (C). Totally 62% of all fish exposed (n = 124) died during the 140 hrs time of exposure.

In the Al+Mg solution, 100% mortality (Fig. 3c) was never recorded in any compartment during 140 hrs, but more than 50% of the fish died i all compartment during the 140 hrs exposure, i.e. LT_{50} 25 hrs (A), 55 hrs (B), 63 hrs (C). 95 hrs (D) and 74 hrs (E). Totally 73% of all fish exposed (n = 131) died during the 140 hrs time of exposure. No fish died in the control group that were exposed to the raw water only.

Discussion

In the Ca and Na addition experiments performed during spring (Fig. 2), a significant decrease in toxicity was observed by distance from the chemical additions. In the Ca and Mg toxicity studies during autumn this tendency was less clear, even though the highest mortality was always present in the uppermost compartment, the lowest at the end of the channels (Fig. 3). This phenomena is earlier described and attributed to transformation processes of Al that occur when pH is raised in acidic Al-solutions (inorganic Al primarily present as Al^{3+}), i.e. a decrease in toxicity by ageing of Al-polymers (24-26). By ageing, the Al-polymers increase in size, which further means that their cationic charge is decreasing because Al-polymerization processes are deprotonation, dehydration reactions. Numerous cationic polymers are shown to be highly acute toxic to fish (39-41) and the physiological and pathological description of fish exposed to many different cationic electrolytes are identical to the description of Al-toxicity to fish exposed to dynamic Al-chemistry water (24-25). The cationic electrolyte studies conclude that the lowest molecular weight polymers (41) and the cationic polymers with highest positive charge densities (40) are the most toxic. The dynamic changes of Al-polymers by time and the subsequent reduced toxicity are therefore most likely due to the Al-transformation processes where the Al-complexes increase in size and decrease in cationic charge density. That, also flow through conditions are shown to be consistently more toxic than under static conditions when rainbow trout fingerlings were exposed to cationic polymers (41), may indicate that even known chemical polymers may undergo transformation processes by time as the Al-polymers.

The Ca and Na experiments during spring demonstrated very clear the hypothesized ameliorating effects of increased ionic strength. In the uppermost compartment the LT_{50} in the Al only solutions was 35 hrs (parallel to the Al+Ca experiment) and 62 hrs (parallel to the Al+Na experiment), while the LT_{50} in Al+Ca was 46 hrs and in Al+Na 135 hrs. Totally 44-50% of the fish died during 140 hrs exposure in channel with Al only, while 31% and 16% died in the channel with Al+Ca and Al+Na, respectively. The highest effect of basecation addition was obtained by addition of NaCl, even though the ionic strength increase was nearly the same in Al+Ca and Al+Na water. However, this does not necessarily mean that Na^+ more effectively ameliorate the Al-toxicity than Ca^{2+}, because, on equivalent basis, about 1.5 times higher amount of Na^+ is needed to obtain the same ionic strength increase as by Ca^{2+}. Assuming each ion being a point charge, 3 times more Na-ions are present compared with Ca-ions. It means that the possibility of a Na-ion to be present near the surface of a fish gill should be higher compared with Ca. However, Ca is a divalent ion and should therefore have better qualitative properties in the competition for cation exchange sites, like substituting Al present on negative charge sites at gill surfaces. But, cation exchangers exhibit low or moderate preference for one cation species compared to another (42), a preference that is further reduced when the temperature is low (43), as in these experiments. The ionic radii of Ca^{2+} and Na^+ is almost identical (0.99 A and 0.97 A, A = Ångstrom = 10^{-10} m), but Ca as a divalent ion will have a thicker hydration shell, which may prevent this ion to come as close to the gill surface as the Na-ion. All together this may explain why the Al-toxicity was lower in the Al-solution with addition of NaCl compared with $CaCl_2$. The toxicity differences between Al only, Al+Ca and Al+Na can not be revealed by any Al-fraction (Table II, III and IV), i.e. total Al (Al_r), colloidal Al (Al_c), inorganic monomeric Al (Al_i) or organic monomeric Al (Al_o), neither the saturation indexes (estimated by the ALCHEMI-Version 4.0) regarding known solid Al-phases, i.e. saturation with respect to synthetic gibbsite, natural gibbsite, micro-crystalline gibbsite, amorphous aluminum trihydroxide, jurbanite, kaolinite. imogolite or halloysite. However, all Al solutions seem to be close to saturation with respect to micro-crystalline gibbsite ($\log{}^*K_s = 9.35$).

In the Ca and Mg experiments conducted during autumn, lower concentrations of total aluminum were added compared with the Na and Ca experiments performed half a year earlier (Table II, III and IV), while pH were almost the same in all water types (pH = 5.7-5.8). While the total concentration of Al added was about 380-400 µg Al/L (≈ 14-15 µmolar) in the autumn experiments, it was 520-600 µg Al/L (≈ 19-22 µmolar) in the spring experiments. However, only 42-44% of the fish exposed to Al-only died in the spring experiment compared with 71% in the autumn experiment. While a significant lower toxicity was observed after addition of Na or Ca in the spring experiments, addition of Ca in the autumn experiments gave only a minor mortality reduction in the Al+Ca, while no change was observed after addition of Mg. The fact that no mortality change was observed in the Al+Mg water may be a result of a lower ionic radii of Mg^{2+} (0.66 Å) compared with Ca^{2+} (0.99 Å) which mean a thicker hydration shell, which subsequently means that Mg-ions are not able to come that close to the gill surface as the Ca-ions. Neither aluminium-fractions, Al-saturation indexes with respect to solid phases nor average charge of Al explain why the toxicity is higher in the autumn-experiments compared with the spring experiments. The only chemical explanation is that the cationic polymers produced in the autumn experiments have generally lower molecular weights and/or higher cationic densities, which is earlier shown to be decisive for the Al-toxicity (39-41). If the prevailing Al-polymers formed in the autumn experiments have higher cationic densities, the ionic strength increase in this experiments by addition of $CaCl_2$ or $MgCl_2$ might have been too low to obtain reduced toxicity. As long as there are cationic polymers bond to the gill surface, substitution by base cations at some of the negative sites involved in the Al-polymer bindings may be insufficient to "release" the Al-polymers from the gill surface. Thus, formation of Al-polymers with higher cationic density in the autumn-experiments compared with the spring experiments might be one reasonable explanation for the different toxicity and different toxicity response after addition of base cation salts. It is well known that it is more or less impossible to make identical polymerization conditions and Al-polymers, since the products formed may be influenced by factor as, pH, temperature, concentrations of reagents, kinds of anions present, and the manner in which the solutions are prepared (44). In addition one should neither ignore physiological differences between fish at spring compared with autumn. The fish is at different life stages and different weights, the latter means different ratio between gill surface area and body weight. In addition the different base cations are involved in different physiological mechanisms, including transport mechanisms, at or within the gill epithelium. This may also contribute to the observed toxicity variations after addition of base cations.

Tests showing that cationic polyelectrolytes will detoxify by addition of an anionic one are confirmed by at least a German patent (45). However, the concentration of anions including the estimate of negative charges of organics in the Al-toxicity studies can not explain the toxicity differences in the experiments (Table I). However, since the detoxifying effect of addition of anionic polymers to cationic polymers is also shown by Biesinger and Stokes (39), it means that both natural humic acids and clays (both anionic polymers) might be used for detoxifying cationic Al-polymers. Similar success should therefore be obtained by adding humic acids or clays to dynamic Al-systems as present when acidic Al-rich freshwaters are limed. Furthermore, to better interpret or understand the large difference in Al-toxicity at relatively uniform Al-levels, both the quality and quantity of cationic and anionic polymers should be better evaluated in the future. This is, however, a large scientific and analytical challenge.

It is important to underline that our studies are based Atlantic salmon parr only, and the test waters contain relatively high ionic strength strengths, Ca > 2 mg/L and dynamic Al-chemistry (pH 5.7-5.8). To which extent our studies are relevant for other salmonids or other fresh water fishes are relevant for more stable Al-chemistry at low pH's is difficult to say. Other published works related to corresponding problems are very contradictory. This means that more systematic ionic strength studies should be performed to better understand the fish toxicity and the physiological mechanisms behind. As long as the major effects of acute fish toxicity primarily are related to Al-accumulation on fish gills, both when fish are exposed to acidic stable Al-chemistry water and more dynamic Al-chemistry at higher pH's, ionic strength should play a key role because it is essential for the chemistry of all aquatic surfaces. If aluminum acts intracellularely on the microsomes and ATP-ase, the effects should develop more slowly than if the aluminum acts on the gill surface

Conclusions

The major conclusions from fish mortality studies in dynamic Al-chemistry water are:

- Mortality of Atlantic salmon parr is high when exposed to dynamic Al-chemistry water. Dynamic conditions are obtained by increasing pH in acidic Al-solutions to levels where Al-polymerization occurs, in this experiments to pH 5.7-5.8. The mortality decreases by ageing of the water, i.e. by time after the pH increase.

- Increased ionic strength (by addition of base cation salts) may significantly reduce the mortality. The unique ameliorating effect of Ca per se, hypothesized by many scientists, was not observed in these studies.

- Reduced mortality by base cation additions may not be explained by the ionic strength increase only. The lower mortality observed by addition of NaCl compared with $CaCl_2$ to obtain identical ionic strength increases, may also be a result of mass action because 3 times more Na-ions compared with Ca-ions are needed to achieve identical ionic strength increases. Thus, the possibility of a Na-ions to substitute for cationic Al bond to negative sites on fish gills is higher than for Ca-ions, even though Ca is a divalent ion.

- Lack of mortality reduction by addition of base cations might be because the cationic Al-polymers are bind to several negative sites. As long as there are cationic polymers bond to the gill surface, substitution by base cations at some of the negative sites involved in the Al-polymer bindings may be insufficient to "release" the Al-polymer from the gill surface. Thus, the base cation additions are too low.

- It is nearly impossible to relate the various ameliorating effects of base cation additions to differences in the thickness of their hydration shells, and to which extent the base cations are able to exist without their hydration shells. Regarding the cationic Al-polymers the thickness of the hydration shell and their possibility to exist without depends of their size and cationic charge density. However, these factors might be essential since the hydration radii is decisive regarding how close ions might come to a negative charge surface which again is important for the binding strength.

- Traditional aluminum analyses and Al-speciation program are not able to reveal the toxicity differences observed under dynamic Al-conditions. Despite that, the size and cationic charge density of the Al-polymers formed are probably the most important physico-chemical factors for the Al-toxicity and any eventually ameliorating effect of base cations. The Al-products formed are influenced by pH, temperature, concentrations of reagents, kinds of anions present, and the manner in which the solutions are prepared, as well as changes over time. Accordingly, it is very difficult to reproduce identical dynamic Al-solution and thus compare the toxicity results.

- Detoxification or reduced toxicity in dynamic Al-chemistry water should be possible by addition of natural anionic polymers as humic acids and clays, since Al-polymers, as other cationic polymers, should be detoxified by anionic polymers.

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		April		May		October/November	
		Al	Al+Ca	Al	Al+Na	Al+Ca	Al+Mg
H^+	µeq/L	1.7	1.5	2.0	1.9	2.0	1.7
Ca^{2+}	µeq/L	158.7	253.0	151.2	154.9	235.5	135.2
Mg^{2+}	µeq/L	45.3	45.3	43.6	44.0	37.8	132.9
Na^+	µeq/L	94.4	94.5	90.9	236.6	83.5	82.0
K^+	µeq/L	9.5	9.3	9.2	9.2	9.0	8.4
Al^{n+}	µeq/L	13.5	9.5	10.2	11.5	6.8	6.2
SO_4^{2-}	µeq/L	120.8	134.4	118.8	132.3	112.5	111.5
Cl^-	µeq/L	76.2	179.1	70.5	213.0	160.8	150.9
NO_3^-	µeq/L	87.9	79.3	64.6	83.9	80.0	74.3
Alk	µeq/L	9.0	11.7	17.5	10.5	12.3	13.8
TOC	mg/L	3.0	3.0	3.6	3.5	3.1	3.2
ΣCat	µeq/L	323.1	413.1	307.1	458.1	374.6	366.4
ΣAn	µeq/L	293.9	404.5	271.4	439.7	365.6	350.5
A^-*	µeq/L	29.2	8.6	35.7	18.4	9.0	15.9
NC*		9.7	2.9	9.9	5.3	2.9	5.0

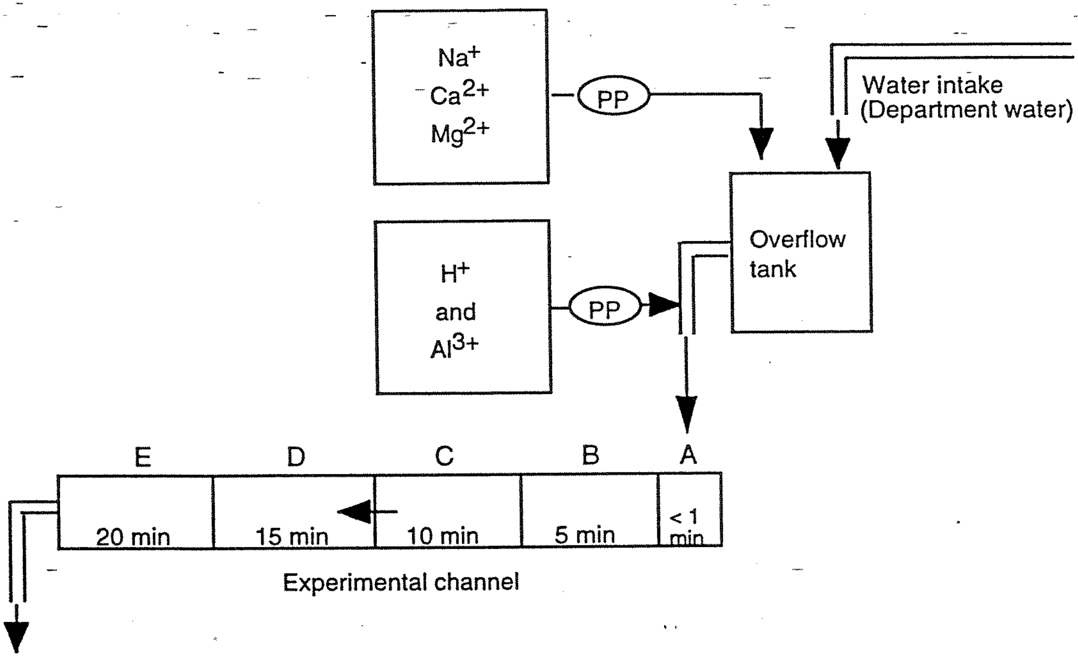
* A^-: Anion deficit, estimated as ΣCations-ΣAnions.

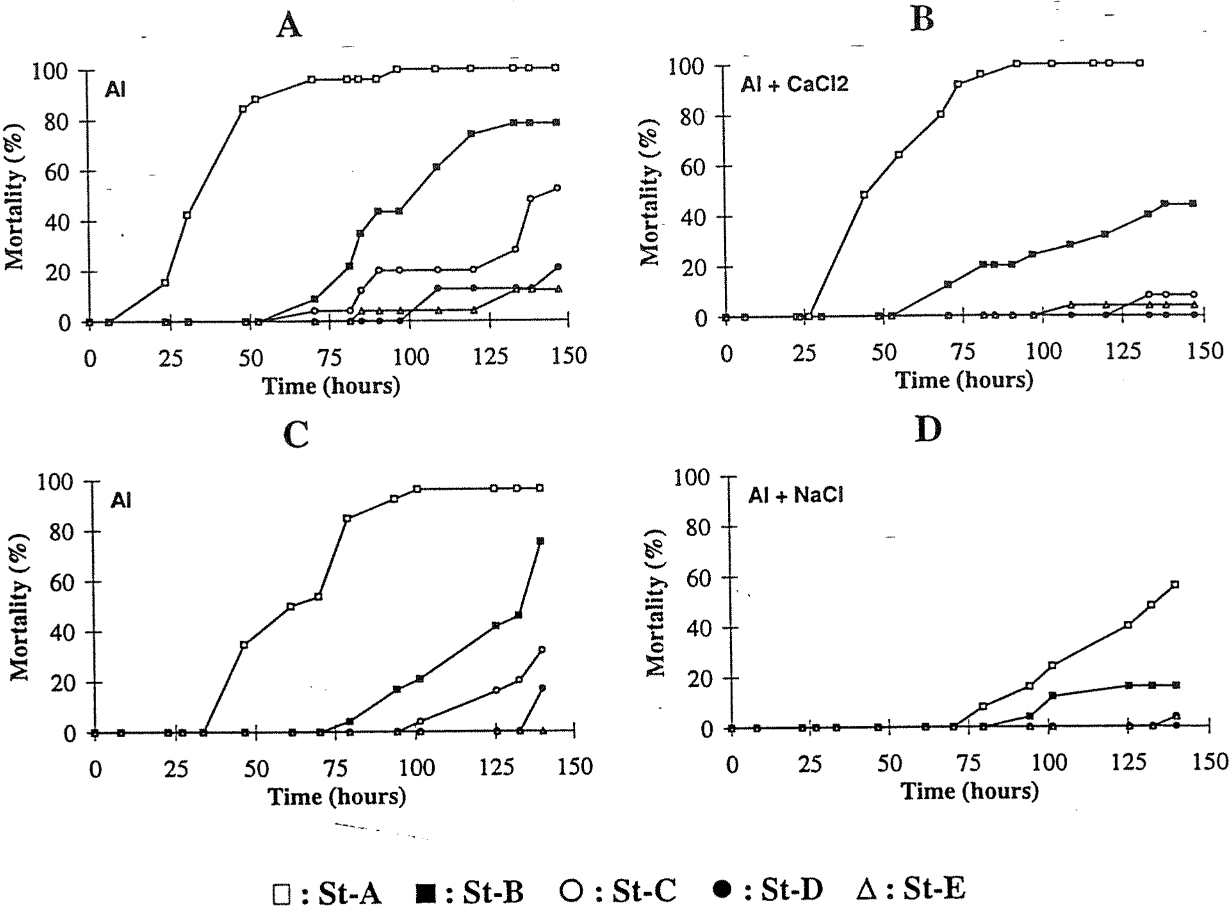
** NC: net negative charge of organics, estimated as A^-/TOC (µeq/mg C).

Water type	**Site**	**pH** -log(H+)	**I** 10^{-4} molar	**Al_r** µg/L	**Al_c** µg/L	**Al_o** µg/L	**Al_i** µg/L	**Al^{n+}** µeq/L
Al	A	5.77	4.77 ± 0.01	570 ± 40	111 ± 33	137 ± 13	321 ± 37	14.8 ± 1.3
	B	5.75	4.77 ± 0.02	608 ± 41	158 ± 24	163 ± 6	287 ± 38	14.5 ± 2.2
	C	5.75	4.76 ± 0.01	587 ± 69	160 ± 48	160 ± 7	266 ± 24	13.4 ± 0.9
	D	5.75	4.76 ± 0.01	609 ± 34	202 ± 20	165 ± 10	242 ± 8	12.5 ± 0.5
	E	5.75	4.76 ± 0.01	592 ± 9	195 ± 33	168 ± 12	230 ± 13	12.2 ± 0.9
Mean	**A-E**	**5.76**	**4.76 ± 0.01**	**593 ± 36**	**165 ± 44**	**159 ± 14**	**269 ± 41**	**13.5 ± 1.5**
Al+Ca	A	5.77	6.20 ± 0.17	497 ± 41	120 ± 11	131 ± 17	246 ± 52	11.2 ± 1.9
	B	5.84	6.28 ± 0.04	510 ± 25	157 ± 14	141 ± 13	212 ± 36	8.8 ± 1.4
	C	5.84	6.28 ± 0.04	561 ± 51	221 ± 11	146 ± 8	193 ± 47	9.4 ± 1.4
	D	5.85	6.28 ± 0.04	526 ± 25	199 ± 15	147 ± 9	180 ± 23	8.9 ± 0.7
	E	5.84	6.28 ± 0.04	512 ± 42	180 ± 26	158 ± 14	174 ± 20	9.1 ± 0.9
Mean	**A-E**	**5.83**	**6.27 ± 0.08**	**521 ± 39**	**175 ± 39**	**145 ± 14**	**201 ± 42**	**9.5 ± 1.5**
Control		6.51	4.71 ± 0.01	57 ± 3	39 ± 3	23 ± 6	0 ± 5	0.4 ± 0.02

Water type	Site	pH -log(H+)	I 10^{-4} molar	Al_r µg/L	Al_c µg/L	Al_o µg/L	Al_i µg/L	Al^{n+} µeq/L
Al	A	5.73	4.49 ± 0.01	520 ± 37	132 ± 18	130 ± 17	258 ± 12	10.7 ± 0.8
	B	5.71	4.49 ± 0.01	604 ± 65	225 ± 74	150 ± 13	229 ± 18	10.5 ± 0.9
	C	5.71	4.49 ± 0.01	614 ± 96	240 ± 99	158 ± 14	216 ± 20	10.3 ± 0.9
	D	5.70	4.49 ± 0.01	564 ± 28	215 ± 38	157 ± 6	192 ± 10	9.6 ± 1.0
	E	5.70	4.49 ± 0.01	562 ± 14	213 ± 25	160 ± 12	190 ± 10	9.7 ± 1.0
Mean	**A-E**	**5.71**	**4.49 ± 0.01**	**573 ± 59**	**217 ± 29**	**151 ± 16**	**217 ± 29**	**10.2 ± 1.0**
Al+Na	A	5.70	6.23 ± 0.11	537 ± 17	137 ± 21	134 ± 6	267 ± 40	11.8 ± 1.3
	B	5.72	6.23 ± 0.11	614 ± 54	222 ± 59	149 ± 12	244 ± 17	11.4 ± 1.0
	C	5.72	6.24 ± 0.11	662 ± 87	248 ± 64	155 ± 10	259 ± 29	12.2 ± 1.5
	D	5.73	6.23 ± 0.11	632 ± 80	231 ± 73	157 ± 10	244 ± 16	11.6 ± 0.2
	E	5.73	6.23 ± 0.11	595 ± 61	225 ± 62	158 ± 12	212 ± 13	10.4 ± 0.5
Mean	**A-E**	**5.72**	**6.23 ± 0.11**	**602 ± 61**	**206 ± 61**	**150 ± 13**	**245 ± 28**	**11.5 ± 1.0**
Control		6.48	4.39 ± 0.01	96 ± 2	36 ± 19	31 ± 14	28 ± 11	1.3 ± 0.4

Water type	**Site**	**pH** -log(H+)	**I** 10^{-4} molar	**Al_r** µg/L	**Al_c** µg/L	**Al_o** µg/L	**Al_i** µg/L	**Al^{n+}** µeq/L
Al+Ca	A	5.71	5.55 ± 0.14	395 ± 17	133 ± 10	95 ± 7	167 ± 11	7.4 ± 0.9
	B	5.71	5.55 ± 0.14	439 ± 82	174 ± 65	95 ± 4	169 ± 15	7.4 ± 0.3
	C	5.71	5.56 ± 0.13	383 ± 36	145 ± 46	98 ± 4	140 ± 13	6.7 ± 0.9
	D	5.72	5.56 ± 0.13	385 ± 22	165 ± 22	100 ± 1	120 ± 15	6.3 ± 0.9
	E	5.71	5.56 ± 0.13	391 ± 9	171 ± 31	94 ± 2	126 ± 23	6.3 ± 1.1
Mean	**1-5**	**5.71**	**5.55 ± 0.13**	**399 ± 41**	**158 ± 37**	**96 ± 4**	**145 ± 25**	**6.8 ± 1.0**
Al+Mg	A	5.70	5.53 ± 0.10	378 ± 14	138 ± 19	91 ± 5	149 ± 12	7.2 ± 0.2
	B	5.81	5.54 ± 0.10	402 ± 45	167 ± 27	91 ± 6	144 ± 14	6.6 ± 0.8
	C	5.77	5.54 ± 0.10	404 ± 72	194 ± 67	91 ± 5	119 ± 2	6.0 ± 0.2
	D	5.79	5.54 ± 0.10	365 ± 37	170 ± 30	91 ± 4	105 ± 14	5.6 ± 0.6
	E	5.80	5.54 ± 0.10	349 ± 55	162 ± 25	90 ± 5	97 ± 28	5.3 ± 1.0
Mean	**A-E**	**5.77**	**5.54 ± 0.10**	**380 ± 46**	**166 ± 37**	**91 ± 4**	**122 ± 25**	**6.2 ± 0.9**
Control		6.51	3.94 ± 0.05	45 ± 6	25 ± 7	18 ± 2	2 ± 3	0.5 ± 0.01


Na+
Ca2+
Mg2+
PP
Water intake
(Department water)
Overflow tank
H+
and
Al3+
PP
E
D
C
B
A
20 min
15 min
10 min
5 min
< 1 min
Experimental channel


A
Al
B
Al + CaCl2
C
Al
D
Al + NaCl
Mortality (%)
0
20
40
60
80
100
Time (hours)
0
25
50
75
100
125
150
□ : St-A
■ : St-B
○ : St-C
● : St-D
Δ : St-E

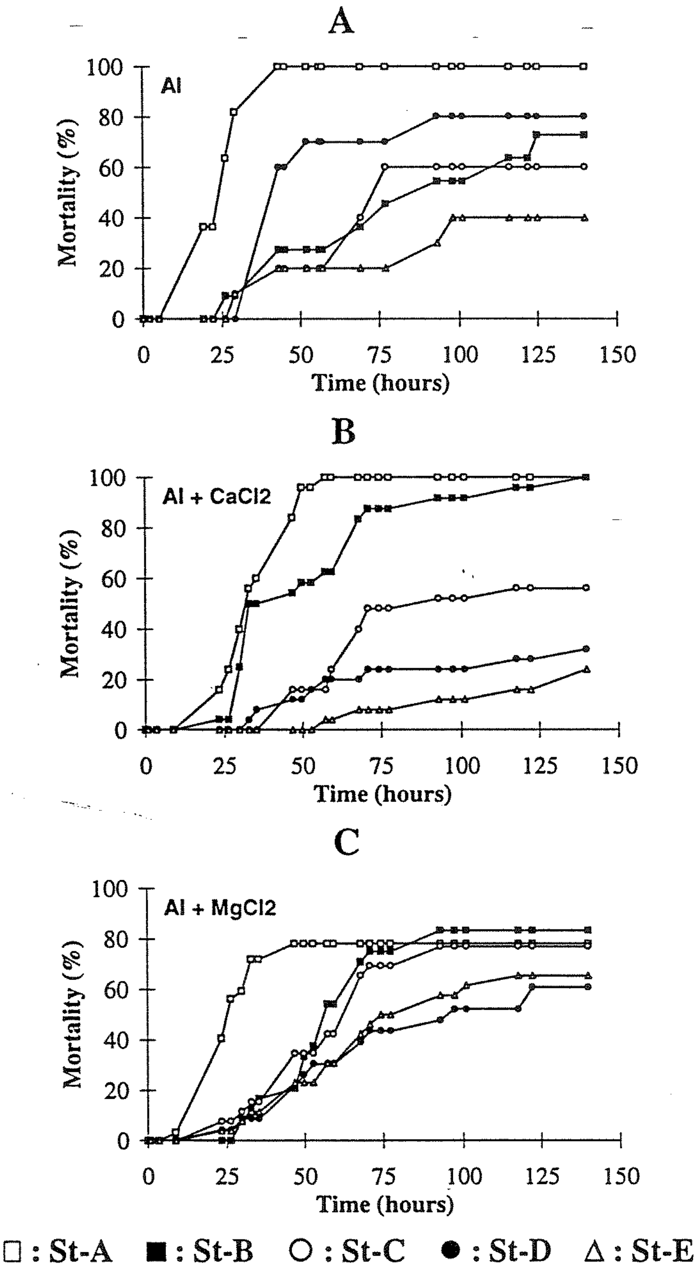

A
Al
Mortality (%)
100
80
60
40
20
0
Time (hours)
0
25
50
75
100
125
150
B
Al + CaCl2
Mortality (%)
Time (hours)
C
Al + MgCl2
Mortality (%)
Time (hours)
□ : St-A ■ : St-B ○ : St-C ● : St-D △ : St-E

Table texts

Table I Major chemical composition of the different water types used in the fish toxicity studies

Table II The pH, ionic strength, concentration of total Al (Al_r), colloidal Al (Al_c), organic monomeric Al (Al_o), inorganic monomeric Al (Al_i) and average charge of Al (Al^{n+}) in the water without and with addition of $CaCl_2$. At all sites $n = 3$, i.e. mean values $n=15$.

Table III The pH, ionic strength, concentration of total Al (Al_r), colloidal Al (Al_c), organic monomeric Al (Al_o), inorganic monomeric Al (Al_i) and average charge of Al (Al^{n+}) in the water without and with addition of NaCl. At all sites $n = 3$, i.e. mean values $n=15$.

Table IV The pH, ionic strength, concentration of total Al (Al_r), colloidal Al (Al_c), organic monomeric Al (Al_o), inorganic monomeric Al (Al_i) and average charge of Al (Al^{n+}) in the water after addition of $MgCl_2$ or $CaCl_2$. At all sites $n = 3$, i.e. mean values $n=15$.

Figure texts

Figure 1 The experimental set-up of the chemical dosing system and the fish exposing channel (A-E). Time (min) given for each fish compartment means time after addition of chemicals (by the peristaltic pumps: PP) to the department water. The experiments were always performed in two parallel channels, one with acidic Al addition (Al only) and one with both acidic Al and base cation additions (Al + base cation chlorides). The control fish exposed to raw water only were kept in a separate flow through channel.

Figure 2 Cumulative mortality (%) of Atlantic salmon exposed to aluminium, without (named Al) and with addition of $CaCl_2$ *and without (named Al) and with addition of NaCl at different station along the channel.* Station *A, B, C, D, and E means < 1 min, 5 min, 10 min, 15 min and 20 min after the pH adjustment of the acidic Al-solution to pH about 5.8.*

Figure 3 Cumulative mortality (%) of Atlantic salmon exposed to aluminium, without and with addition of $CaCl_2$ *or* $MgCl_2$*. A, B, C, D, and E means < 1 min, 5 min, 10 min, 15 min and 20 min after the pH adjustment of the acidic Al-solution to pH about 5.8.*

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AL:PE PROJECTS: WATER CHEMISTRY AND CRITICAL LOADS.

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LAK70

Abstract. Water chemistry, as the basis for all investigations in the AL:PE 1 (Acidification of Mountain Lakes: Palaeolimnology and Ecology) and 2 (Remote Mountain Lakes as Indicators of Air Pollution and Climate Change) projects, is available from 28 lakes in U.K. (Scotland), Italy, Norway and France (AL:PE 1) and from lakes on Svalbard (Norway), Ireland, Austria, Spain, Portugal, Poland, Slovakia and Russia (AL:PE 2). Water samples are analyzed for pH, conductivity, Ca, Mg, Na, K, chloride, sulphate, nitrate, fluoride, alkalinity, total organic carbon, reactive Al, non-labile Al, Cd, Pb and Hg by standard procedures for low ionic strenght waters at national laboratories, in co-operation with the chemical centres in Italy and Norway, which also organized intercalibration programmes. The results for AL:PE 1 show that in all the countries high sulphate concentrations are recorded in some mountain lakes. The distribution pattern of the nitrate concentrations among the sites differs from that of sulphate. A gradient from the north (Norway) to central Europe (via U.K. to Italy) was identified for acidification of the AL:PE lakes by means of multivariate data analysis. Critical loads and their exceedance are calculated, where sufficient information is available, both according to leaching of S, and of S plus N from the catchment. The pattern of critical load exceedance demonstrated increasing importance of nitrate from Norway via U.K. to Italy. For the lakes in the Italian Alps, leaching of N was of considerable importance to the acidification of the lakes. The projects receive financial support form the Commission of the European Communities.

Key words: water chemistry, remote lakes, critical loads, sulphate, nitrate, acidification.

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CRITICAL LIMITS OF ACIDIFICATION TO INVERTEBRATES IN DIFFERENT REGIONS OF EUROPE

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Abstract. The International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP-Water) started in 1987. The main aim of the programme is to establish degree and geographical extent of acidification of surface waters and evaluate dose/response relationships to aquatic biota attributable to acidic deposition. The sample frequency in each locality is from a few - to a large number every year. Samples of invertebrates are taken from 108 localities. One time samples as well as regularly seasonal samples over years exist in the database. The acidity score (Raddum index) is determined for the different sites and regions, and compared with the corresponding chemical data. The analysis show a strong relationship between water quality and fauna. Sensitive species/taxa are associated with high ANC and pH, while tolerant species/taxa are associated with low pH and ANC. The diversity of the fauna in less acidified areas varies from region to region depending on the native water quality and the adaptions of the fauna. In areas with strongly oligotrophic water, low in ionic strength, the sensitive fauna tolerate lower ANC and pH than in areas with originally high ionic strength and high pH. The critical load of ANC, 20 μeq/l, developed for the oligotrophic water in Norway, should therefore be increased in watersheds with high ionic strength. In Central Europe the data indicate a critical level of ANC $\approx$50 μeq/l.

Key words: Acidification, Freshwater , Invertebrates, Critical load, Adaptations

1. Introduction

The International Co-operative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP-water) has been designed to establish the degree and geographic extent of acidification of surface waters. Further, to collect information in order to evaluate dose-response relationships, and to define long-term trends and variations in aquatic chemistry and biota attributable to atmospheric pollution, particularly to acidic deposition. The programme is one out of five International Cooperative Programs presently at work under the frame of the United Nations, Economic Council of Europe (UN/ECE), Geneva Convention on Long Range Transboundary Air Pollution (LRTRAP). The number of participating countries has increased from 8, at the started of the programme in 1987, to 14 countries in 1994, represented by Russia, countries in Europe and North America. The Programme Centre and the Programme database are located at the Norwegian Institute for Water Research (NIVA) in cooperation with the Zoological Institute, University of Bergen.

The ICP-water sites are from national programmes, run in each participating country. The monitoring practice vary from county to country with respect to time series and type of studies. With regard to invertebrates, data exist for the whole period from some countries, while other have started later. The longest data series is from Norway, where monitoring of invertebrates started in 1981 (Johannessen 1995). Other countries with several years of invertebrate monitoring are Germany, Sweden and Ireland. In 108 of the sites, both biological and chemical data are available.

Invertebrate species respond on different compounds in the water. In acidified areas it is the toxic effect of low pH or pH in combination with aluminum which is the main cause for species reduction (Raddum 1979, Engblom & Lingdell 1984, Matthias 1983 and Herrman et al. 1993). The toxic effect is reduced by increased concentration of Ca and humic content (Lien et al. 1992). In this paper we will focus on data concerning critical limits of pH and ANC with respect to invertebrates in different regions of Europe.

2. Material and methods

AREA

The ICP-water localities are spread out in Europe and North America. In this presentation we will concentrate on data from sites in Europe where measurements of water quality and composition of invertebrates exists (Figure 1).

Figure 1. Location of monitoring sites in Europe.

The sites are mostly situated on bedrock highly to moderate sensitive to acidification. The buffer capacity is lowest in western Norway where yearly mean calcium concentrations vary from 0.3 to 1 mg Ca L^{-1}. In United Kingdom and Ireland the concentrations vary from 0.5 to 5.2 mg Ca L^{-1}, while in central Europe the variation is 0.4 to 17.2 mg Ca L^{-1}. The range in mean yearly pH of sites in Norway, United Kingdom and Ireland is 4.6 -7.2, in Sweden 4.4 - 6.9 and in Central Europe 4.0 - 7.4. Based on this each country or region contain a wide specter of localities with regard to sensitivity of the water and acidification. For more details about the water chemistry, see Skjelkvåle et al. (1994) and yearly data reports available from the Program Centre.

Annual total deposition of sulfur from all sources was in 1985 lowest in southern Scandinavia, Scotland and Ireland with about 1 g S m^{-2} . The highest deposition, 10 g S m^{-2}, was in areas on both sides of the border between Germany and the Czech Republic (Iversen et al. 1989). The deposition has decreased during the latest years, but the relative distribution is still the same as in 1985.

The ICP-water programme covers by this areas receiving low as well as high deposition of acidifying components, simultaneously as the areas contain sites with varying buffer capacity.

USE OF CHEMICAL DATA

When evaluating the effects of acidified water on invertebrates, the mean values of parameters are of low importance, since invertebrates usually is affected during episodes with high concentrations of toxic agents. Due to this we have selected chemical data from episodes instead of mean values. However, the most extreme data are not used.

USE OF BIOLOGICAL DATA

The acidification index, based on invertebrates, was determined after the method described by Raddum et al, (1988) and Fjellheim & Raddum (1990). The index discriminate between four levels of acidity, 0, 0.25, 0.5 and 1, based on the presence/absence of sensitive species. Level 1 indicate low or no acidification while level 0 indicate highly acidic waters. The species list and the acidification index of the species from the different countries, are presented in yearly data reports from the ICP-water Program Centre.

DATA QUALITY CONTROL

The data delivered from the different participants to the Programme Centre are harmonized through the use of recommended methods described in the manual for ICP-water (NIVA 1987). For further harmonizing and data quality control, intercalibrations have been performed on water chemistry, since 1988, and on biology since 1992. Examples of this work are given by Hovind (1992) and Raddum (1993).

3. Results

The lowest and highest number of species/taxa are recorded in Ireland and Germany with 104 and 223 taxa, respectively. From Norway and Sweden 161 and 219 taxa are noted. The distribution of sites with respect to acidification indexes is shown in Figure 2. Sites with index 1 were most frequent in Ireland and least frequent in Sweden and Germany. In Norway, the proportion of sites with index 1 and 0 were about equal, while sites with index 0.25 and 0.5 were relatively few. The mean pH and ANC at the different acidification indexes in Germany are shown in Figure 3 and 4. Sites with index 1 had a mean pH and ANC of 6.8 and 150 μekv L^{-1}, respectively, while the corresponding values for index 0 were 4.65 and - 32.4 μekv L^{-1}. At index 0.25 and 0.5 the mean pH values were 5.1 and 5.6, while the ANC values were -4.28 and 20.6 μekv L^{-1}. In Norway clear water sites with acidification index 1 and 0, had mean pH of 5.8 and 4.9 while ANC was 21 and - 21 μekv L^{-1} (Lien et al. 1992), showing that the range of both pH and ANC is much higher in the German sites than in the Norwegian. The number of species at the different acidification levels were different in Norway, Sweden, Ireland and Germany (Table 1). At index 1 the number was lowest in Norway and highest in Germany and Sweden. At index 0 the sites in Germany had the lowest occurrence of species. The relative decrease of species from index 1 to 0 was 28, 31, 60 and 81% for Ireland, Norway Sweden and Germany, respectively.

Figure 2.Distribution of samples at different acidification indexes.

TABLE 1.

Mean number of species recorded at different acidification indexes

Country/index	0	0.25	0.5	1.0
Norway	6.43 +/- 2.85 n = 53	9.0 +/- 2.06 n = 9	8.31 +/- 3.05 n = 16	9.33 +/-2,77 n = 60
Sweden	10.73+/-6.34 n = 11	14.86+/-5.15 n = 7	19.67+/-6.43 n = 12	26.83+/-9.56 n = 6
Irland	12.4+/-5.4 n = 6		16.5+/-4.7 n = 6	17.3+/-6.1 n = 32
Germany	4.83+/-2,57 n = 53	8.16+/-2.11 n = 18	14.47+/-6.48 n = 74	25.08+/-16.74 n = 63

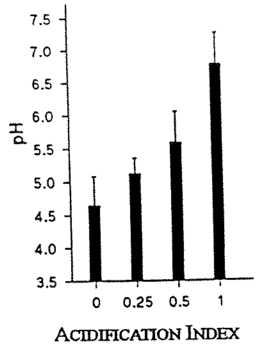

Figure 3. Acidification index against mean pH in Germany. Standard deviation is indicated

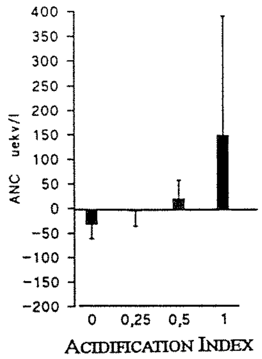

Figure 4. Acidification index against mean ANC in Germany. Standard deviation is indicated.

Discussion

The acid deposition is highest in central Europe and lowest in Scandinavia and Ireland (Iversen et al. 1989). Surface water acidification was low in Ireland (Skjelkvåle et al. 1994), which correspond with the high frequency of sites with acidification index 1. In Norway acidification is more extended due to very low buffer capacity in the watersheds, resulting in a high frequency of index 0 sites. The similar decline of species in Ireland and Norway, when comparing index 1 and 0 sites, could be that the exceedance of acidification level 0, pH <4.7, is relatively low (Lien et al. 1992, Skjelkvåle et al. 1994). Another factor is that naturally low ionic content of the water in these regions, restrict the occurrence of many species and generate a selection pressure for tolerance of oligotrophic water with low conductivity. This will favor euryecious species and reduce the difference in diversity between different acidification levels in Ireland and Norway.

The high number of species at index 1 sites in Sweden and Germany is due to naturally richer fauna in these regions than in Norway and Ireland (Illies 1978). One important reason for this is the normally higher content of calcium in the waters in these regions, which permits species like snails, mussels and others, which have critical limits with respect to lime (Økland 1986), to live in such areas. The highest concentrations of calcium were recorded in Germany (Skjelkvåle et al. 1994). High Ca gives also high pH, especially in absence of acid deposition. Due to this the selection pressure for water with low pH and conductivity have been low in Central Europe. This can be one moment for explaining the strong reduction in number of species at index 0 in Germany, compared with Norway. Another reason could be very strong acidification at level 0, since mean pH in some of the sites have been <4.0, single measurements as low as 3.2 (Skjelkvåle et al. 1994). This is much lower than in Ireland and Norway.

As indicated for Ireland and Norway, adaptations to different water qualities, seems to affect the acid tolerance of species in different regions. Support for this is obtained when comparing clearwater sites with index 1 in Norway, mean pH 5.8 (Lien et al. 1992), with the mean pH of 6.8 in German sites. The mean ANC was correspondingly 10 - and 150 μekv L^{-1} for the two countries. To protect fish and invertebrates in acidified water in Norway Lien et al. (1992) proposed an ANC $\leq$ 20 μekv L^{-1}. This limit is, however, much lower than the mean ANC for sites with index 1 in Germany and will probably not protect sensitive fauna in the region. It is, however, difficult to state the ANC limit in Central Europe, due to the high variation in the water chemistry data. The most sensitive fauna was on the other hand, very seldom found in water with pH $\leq$ 6. We therefore propose this pH as a critical limit for protection of the most sensitive species. From this we have determined the ANC limit based on correlation analyze between pH and ANC on the data from Germany (Skjelkvåle et al. 1994). The analysis show that pH 6 corresponds with ANC $\approx$ 50 μekv L^{-1} . For the moment, we think this to be the best suggestion for the critical limit of ANC in acidified areas of central Europe. We also feel that the ANC-limit in southern Sweden should be closer to ANC 50 μekv L^{-1} than ANC $\geq$ 20 μekv L^{-1}. The results of the monitoring underline that the critical limits of chemical compounds in surface water to invertebrates will vary in accordance with originally water chemistry and the adaptations of the fauna.

Acknowledgements

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THE EFFECT OF ACIDIFICATION, LIMING AND RE-ACIDIFICATION ON MACROPHYTE DEVELOPMENT, WATER QUALITY AND SEDIMENT CHARACTERISTICS OF SOFT WATER LAKES

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LIM21

Abstract. Rapid expansion of *Juncus bulbosus* L. and the concomitant suppression of isoetid plant species, such as *Lobelia dortmanna* L., *Littorella uniflora* (L.) Aschers and *Isoetes* species is often observed in acidifying shallow soft waters in Western Europe. Experimental studies have shown that this mass development of *Juncus bulbosus* was caused by changes in the carbon and nitrogen budgets in these ecosystems. Acidification leads to temporarily strongly increased carbon dioxide levels in the sediment when this is slightly calcareous and of accumulation of ammonium as a result of a reduced nitrification rate in acidifying waters.

Many acidifying Scandinavian soft water lakes, however, are in a good condition from a botanical point of view. It is suggested that this can be atributed to the non-calcareous character of the sediments. After liming, however, mass development of *Juncus bulbosus* and/or *Sphagnum* spec. has been observed in Swedish and S.W. Norwegian lakes. From field experiments it has become clear that part of the lime precipitates on the sediments leading to increased mineralisation, increased carbon dioxide production, decreased nitrate and strongly increased ammonium and phosphorus levels in the sediment pore water. These changes have also been observed earlier in acidifying West European waters. Rooted species like *Juncus bulbosus* can benefit from the higher nutrient levels in the sediment only when the carbon dioxide level in the waterlayer is relatively high as this species is adapted to carbon uptake by the leaves. It is shown that during winter and spring, when a lot of acid water from the catchments reaches the lakes, the carbon dioxide levels in the water becomes very high as a result of re-acidification leading to explosive growth of *Juncus bulbosus* and/or *Sphagnum* spec.

Key words: water acidification, liming, re-acidification, carbondioxide, aquatic macrophytes, isoëtides, *Juncus bulbosus*.

AL:PE PROJECTS. FISH POPULATION STUDIES

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LAK72

Abstract. Within the AL:PE project ("Acidification of Mountain Lakes: Palaeolimnology and Ecology"), fish population studies and bioaccumulation of trace metals and organic micropollutants in fish have been studied. Of the 28 lakes in AL:PE, 17 contain fish of which the dominating species are Arctic charr (*Salvelinus alpinus*), brown trout (*Salmo trutta*) and rainbow trout (*Oncorhynchus mykiss*). Due to their high elevation, many lakes have been subjected to introduction and repeatedly stocking of fish. A test fishing programme using standard mult-mesh size nets (10 - 46 mm) and standard procedures for sampling and analyses, have provided comparative data on age composition, growth, etc. Mercury from fish muscle and cadmium and lead from fish liver have been analysed from most lakes, as well as organic micropollutants such as aliphatic, chlorinated and polycyclic aromatic hydrocarbons in fish muscle and/or liver. In some lakes, national programmes include physiological, biochemical and histological parameters. Because of differences in lake water chemistry and spawning facilities, the fish populations vary between good to sparse. The populations of Arctic charr have an age composition up to 30 years, whereas most brown trout populations are up to 6 years. Brown trout in all areas show a remarkable similarity in growth pattern. Some populations experience recruitment failure either due to water quality or lack of spawning facilities, and are thus dependent on stocking. Preliminary results from 9 lakes, show a positive correlation between concentrations of Hg, Cd and Pb and age. Site identity is the strongest controlling variable. Of the trace metals, only Cd (6 lakes) and Pb (1 lake) exceeded WHO standards for food consumption. Data on organic micropollutants will be presented.

Key words: Arctic charr, brown trout, rainbow trout, water quality, heavy metals, organic micropollutants, ecology.

DYNAMIC AL CHEMISTRY OF MIXING ZONES AND RELATED BIOLOGICAL AND ECOLOGICAL EFFECTS

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LIM02

Abstract. Liming is extensively used to restore fisheries of acidified lakes and streams. Field and laboratory experiments demonstrate that the chemical Al-transformation processes that occur when low pH/Al-rich waters are mixed with waters of higher pH induced negative biological responses. In a controlled channel experiment, natural acidic/Al-rich waters (pH = 5.3, Al_r = 379 μg/L) were confluenced with neutral water to form a well-mixed stream with constant pH of 6.2. Caged brown trout (*Salmo trutta* L.) experienced an acute mortality immediately after mixing; mortality was higher than in the acid inlet water, but decreased down the channel. No mortality was observed in the neutral water. Blood and tissue samples showed substantial physiological changes and damage to gills and skin from fish exposed to the mixing zone or to the acid water. The effects appeared faster and were more extensive in fish exposed in the upper part of the channel. Several *in situ* fractionation techniques were used to demonstrate for the first time the instantaneous polymerization of Al in the upper part of the mixing zone; transforming Al from low molecular weight forms to high molecular weight and less reactive forms. Of vital importance for a mitigation strategy, is that repeated experiments with presumably identical chemical exposure at other seasons, did induce stress but not with the same extreme toxicity in the mixing zone. The dynamic transformation processes influencing the Al-speciation and subsequent biological effects taken place in a mixing zone, are thus not yet fully understood.

Key words: Brown trout, acidification, water quality, aluminium, physiology, gill histology, ecology, liming

IN SITU FRACTIONATION TECHNIQUES FOR AL-SPECIATION IN DYNAMIC FRESH WATER SYSTEMS

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LAK14

Abstract. In natural fresh waters, Al may be present in different physico-chemical forms varying in size (molecular weight), charge (reactivity) and density properties. As mobility and biological relevance of Al depends on physico-chemical forms, information on transformation processes and kinetics is essential for assessing short and long-term consequences of Al-exposures. In mixing zones where waters of different qualities form a confluence, transformation processes influencing the Al-speciation occur. To follow transformation processes in mixing zones and to identify their biological relevance, controlled field experiments utilizing *in situ* fractionation techniques have been implemented. Waters from an Al-rich acidified lake and a neutral lake were pumped into a Y-shaped channel (30 m), forming a confluent stream having a constant pH of 6.2. Transformation processes and changes in the distribution of Al-species were followed *in situ* using hollow fibre ultrafiltration combined with HQ-MIBK extraction cation exchange chromatography. At the confluence, low molecular weight cationic Al hydrolysed immediately, forming Al-polymers. Metastable Al-species were formed and an increase in less reactive high molecular weight Al-species could be observed along the channel. Investigation of the biological relevance of these chemical changes indicated that the extent of the observed transformation processes could be correlated with acute toxicity to fish. The paper focuses on the applicability of in situ fractionation techniques for characterizing exposure, transformation processes and kinetics in stable water masses as well as dynamic fresh water mixing zones.

Key words: fractionation techniques, Al-speciation, mixing-zones, pH changes, transformation processes, kinetics.

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CHEMICAL WEATHERING RATES IN ECOSYSTEMS INFLUENCED BY ACID RAIN, ESTIMATED BY SR-ISOTOPE COMPOSITION

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SOI11

Abstract. Chemical weathering of minerals is the major long-term source of nutrient cations (Ca, Mg, Na and K) to the exchangeable pool in the soil, and is the only major process by which acidic deposition is neutralised on a time scale of decades or longer. Weathering rates is an important parameter in models which predict changes in soil and water chemistry due to changes in acid loading. Most methods for estimating chemical weathering rates have no possibilities to distinguish between cations mobilised by cation-exchange or released by chemical weathering. In this study we have used Sr-isotopes as a tool to evaluate quantitatively the two main neutralising processes in the soil: cation exchange and chemical weathering. The study is conducted in the CLIMEX (previously RAIN) catchments in southern Norway. The RAIN project is a 10 year study in which manipulations with whole catchments are conducted to determine the response of runoff chemistry to changes in loading of strong acids. The aim of the project is to (1) estimate present day weathering rates in the CLIMEX/RAIN catchments, with and without acid rain, (2) reconstruct the past 30-40 years weathering rates based on tree rings and (3) to map the internal fluxes of calcium in the ecosystem. Sr-isotope composition in precipitation and bedrock are significantly different in the CLIMEX/RAIN catchments and is therefore very appropriate for the Sr-isotope method. Preliminary results show that Sr-isotope ratios in runoff water are strongly influenced by residence time in the catchment and that Sr-isotope composition in lysimeter water directly reflects the Sr-isotope composition of the soil in the same depth.

Key words: weathering, sr-isotopes, calcium, cation exchange, runoff, soil water, fluxes, tree-rings.

ACIDIFICATION IN NORWAY - STATUS AND TRENDS
Surface and ground water

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Abstract. Surface and ground water monitoring in Norway is designed to give a regional coverage with most of the stations in areas with acidification and some stations in unpolluted areas that give background values. Surface water (weekly sampling) and precipitation (daily measurement) are monitored at 6 calibrated catchments, 5 located in southern Norway and 1 in northernmost Norway close to the Russian border. Ground water (weekly sampling) is monitored in 4 reservoirs in Southern Norway. 73 lakes located all over Norway are surveyed each fall. Nineteen rivers in western and southern Norway are monitored by monthly sampling. All sites are considered sensitive to acidification and are chosen to minimise the effects of anthropogenic catchment based impacts. Results from the monitoring over the period 1980-1994 show that there is a reduction of sulphate of about 25-35% in surface waters which is related to a 30-45% reduction in sulphate concentration in precipitation. An improvement in water quality as measured as increase in ANC has only been apparent since 1990. Due to heavy seasalt episodes in the most coastal catchments like Birkenes and the rivers in western Norway, there has been no improvement of ANC since 1980. Deposition of nitrogen has not changed over the last 10 years, and there is no change in the levels of nitrate in the monitored surface waters.

1. Introduction

Acidification of surface waters caused by long-range transported air-pollutants has caused severe environmental damage in Norway. The critical load of acidity in surface waters is exceeded in an area of 94,000 km^2 (Henriksen et. al 1995), and damage to fish is registered in an area of 86,000 km^2 (Hesthagen et al. 1995). In order evaluate the cause-effect relationships of acidification and the changes over time, a monitoring programme for long-range transported air pollutants covering deposition, surface- and groundwater, soil, fish populations and invertebrates was initiated by the Norwegian Ministry of Environment in 1980. The Norwegian Pollution Control Authority (SFT) is responsible for the overall co-ordination of the programme (Johannessen 1995). We present here the monitoring programme for surface and groundwater and the main results for the period 1980-1994.

2. The monitoring programme for surface waters

Surface and ground water monitoring in Norway is designed to give a regional coverage with most of the stations located in acidified areas, but also some stations located in unpolluted areas to give background values (Figure 1). All sites were chosen to minimize the effects of other kindspollution.

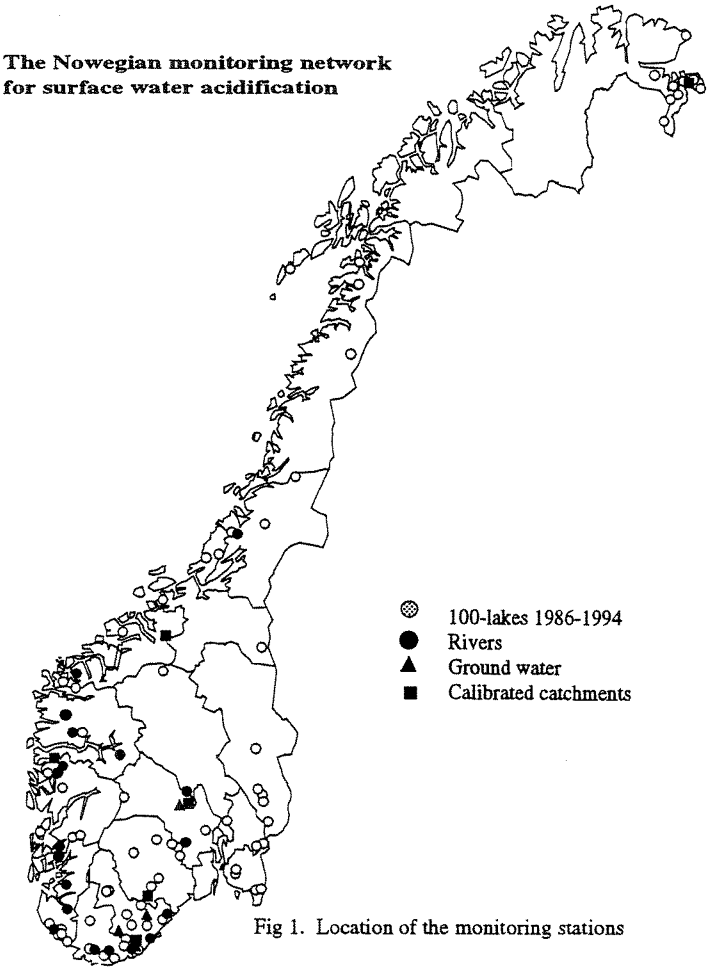

Fig 1. Location of the monitoring stations

CALIBRATED CATCHMENTS

Monitoring in 5 calibrated catchments was started in January 1980 to give detailed information about water chemistry. Birkenes, Storgama, Langtjern and Kårvatn were originally established during the years 1971-74 as a part of the SNSF project (Acid Precipitation - Effects on forest and Fish) (Overrein et al. 1981). In 1988 Dalelva catchment in northern Norway was added to detect effects of air pollution from the Kola peninsula (Russia). In 1994 the catchment Svartetjernet was established in the western part of Norway to cover effects of seasalt episodes (Hindar et al. 1993).

RIVERS

Monitoring of rivers started in 1980. The rivers are characterised by low ionic strength and good habitat for salmon and trout. 18 of the rivers are located in southern Norway and one in central Norway.

LAKES

After the "1000-lake survey" in 1986 (Henriksen et al. 1988), about 100 lakes were chosen to be followed up on a yearly basis. By the end of 1994 only 73 of the original lakes were left; the others had been limed.

GROUND WATER

Groundwater monitoring stations were established in connection with the calibrated catchments in 1980. In 1982, the station near Kårvatn in central Norway was replaced by Evje to give a better coverage of southern Norway.

At all sites samples are collected by local people and analysed by standard methods at the Norwegian Institute for Water Research (NIVA). pH is analysed potentiometrically, base cations by ICP, Cl and SO_4 by ion chromatography (IC), NO_3 by automated colorimetry (AA), alkalinity by potensiometric titration to pH 4.5, Al species by automated colorimetry and total organic carbon (TOC) by oxidation to CO_2 and detection by infrared. Groundwater is analysed for SiO_2 by photometry (FIA) and turbidity by nephelometry.

TABLE I

Norwegian monitoring programme for surface and ground water 1994

	Number of stations	Sampling frequency
Calibrated catchments	6	weekly
Rivers	19	monthly
Lakes	73	yearly
Groundwater	4	monthly

3. Results

Sulphate concentration in precipitation 1994 in Southern Norway have decreased by 30-45% from 1980 to 1994 (Figure 2) (Tørseth and Semb, 1995). Total deposition of sulphate does not, however, show the same tendency due to year-to-year variations in precipitation amounts.

Sulphate concentrations in all calibrated catchments and rivers also decrease during the same period by 25-35% (Figure 3). The lakes show a clear decrease in sulphate from 1986 to 1994 (Figure 5) (SFT 1994). This is clearly due to decrease in sulphate in precipitation. The changes in sulphate concentrations have been compensated by changes in base cations and ANC (Acid Neutralising Capacity). ANC is increasing in the calibrated catchments (Figure 4), rivers and lakes in southern Norway except for coastal areas, where the influence of seasalt episodes (Hindar et al. 1993) has counteracted the positive development of ANC (e.g. Birkenes). The same is true for the rivers in western Norway, and in this area there are no significant changes in ANC.

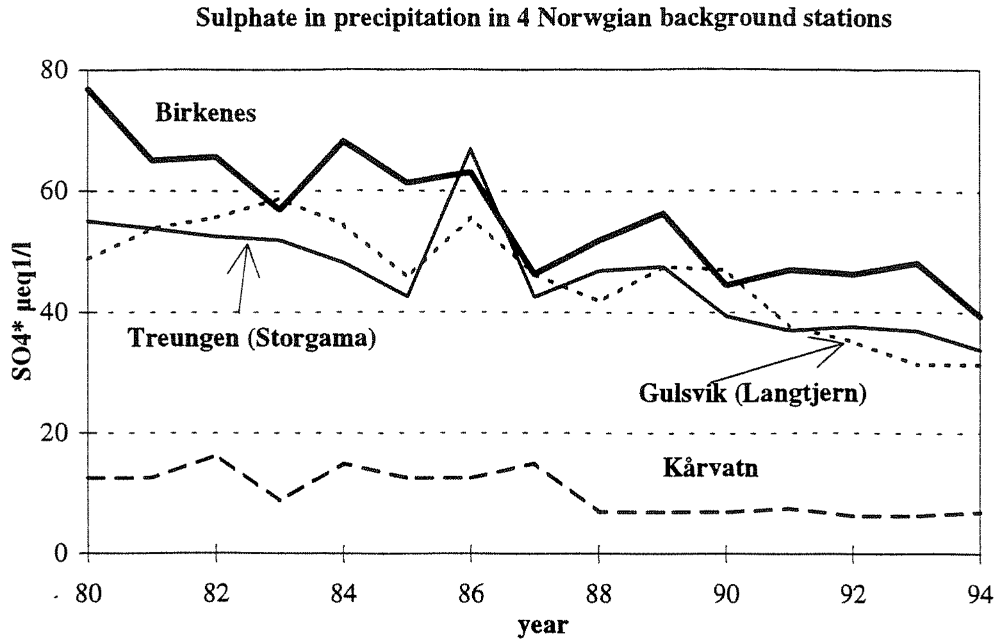
Sulphate in precipitation in 4 Norwgian background stations

Fig.2 Non-marine sulphate in precipitation from four background stations at Birkenes, Treungen (close to Storgama), Gulsvik (close to Langtjern) and Kårvatn 1980-1994. Data from NILU in SFT (1994).

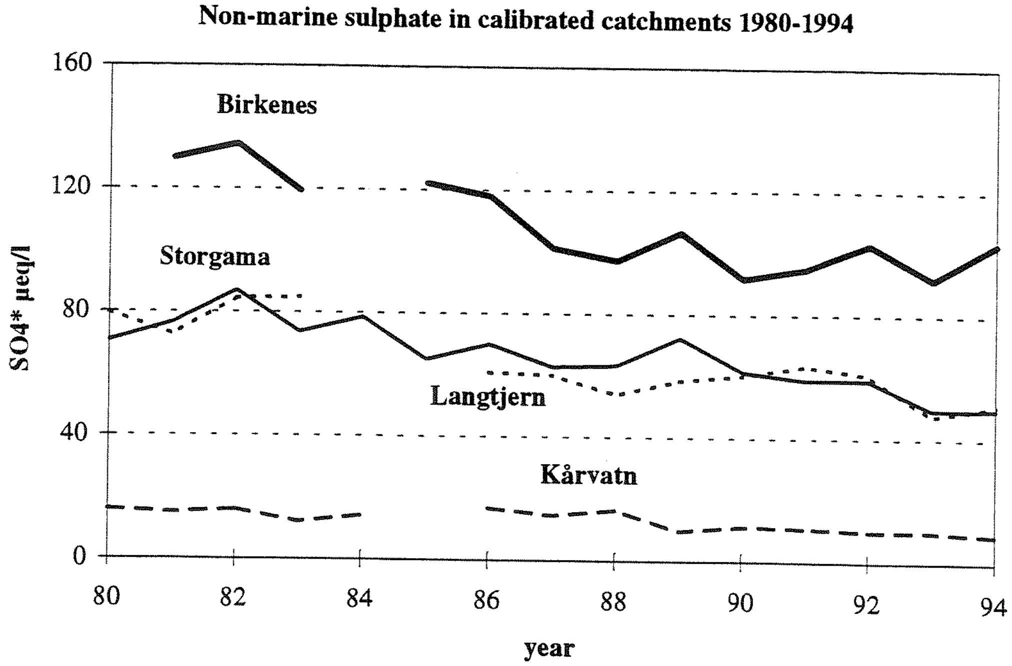
Non-marine sulphate in calibrated catchments 1980-1994

Fig. 3 Trends in non-marine sulphate for the calibrated catchments Birkenes, Storgama, Langtjern and Kårvatn. Data from NIVA in SFT (1994)

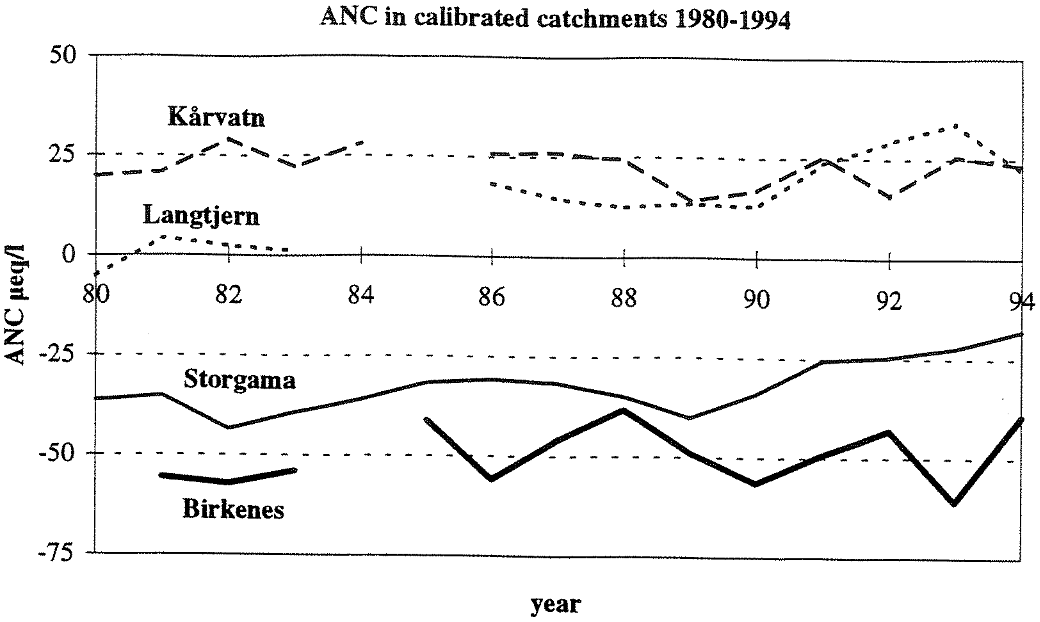

Fig. 4 Variations in ANC for the calibrated catchments Birkenes, Storgama and Kårvatn for the period 1980-1994. Data from NIVA in SFT (1994)

All groundwater stations show decreases in sulphate, and, except for Birkenes, increase in ANC. At Birkenes the groundwater is highly affected by seasalts, and the chloride concentrations are high and vary from year-to-year. From 1990 to 1994 chloride levels doubled as did reactive aluminium (Ral).

One of the main results from the "1000-lake survey" 1986 was the doubling of nitrate levels in lakes in southern Norway since 1974/75 (Henriksen et al. 1988). For 12 of the "100-lakes" there are data back to 1974/75.The data from 1986 to 1994 for these lakes show only small changes in the nitrate levels (figure 5), while there has been a decrease in sulphate and increases in pH and ANC.
There has been no significant change in the concentrations of nitrogen in deposition or surface waters during the period from 1980-1994. There is, however, a spatial correlation with high nitrate levels in runoff at sites with high N-deposition.

4. Conclusions

Long-term monitoring of acidification in surface water in relation to changes in acid deposition clearly show a close relationship to changes in deposition. Concentrations of sulphate have decreased by about 25-35% in in surface waters in southern Norway from 1980-1994. This parallels the 30-45% reduction in sulphate concentration in precipitation during the same time period (Tørseth and Semb, 1995).
Since 1990 ANC has increased and the water quality for fish and other aquatic organisms has improved in many areas. The positive development of ANC has been counteracted by severe seasalt episodes in the coastal catchments such as Birkenes and the rivers in

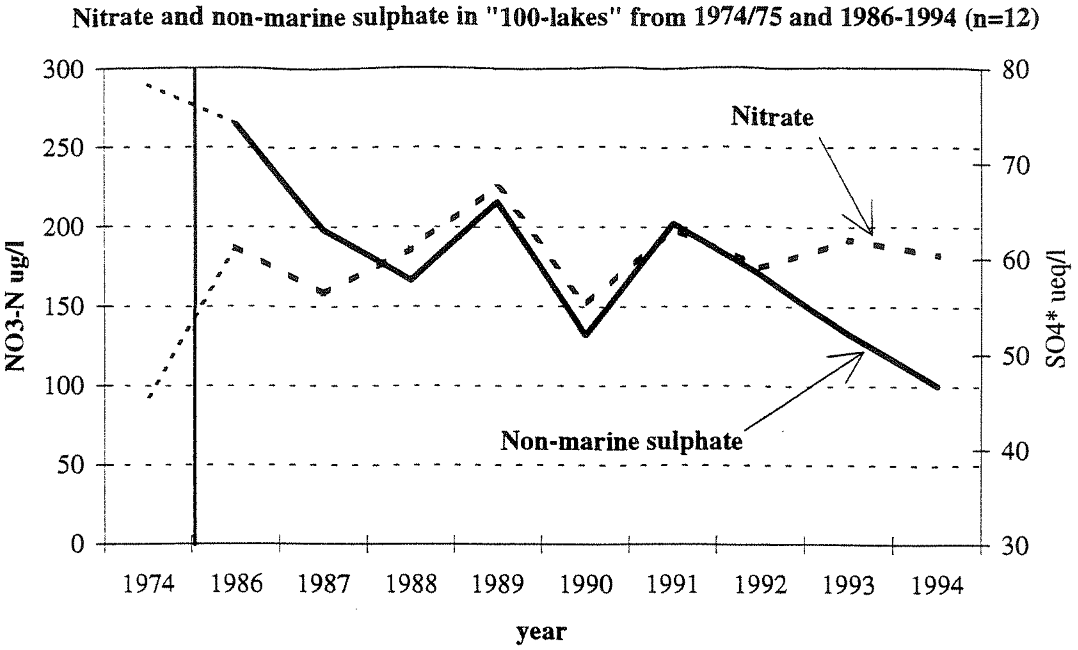

Fig. 5. Trends in non-marine sulphate and nitrate from 12 lakes with data from 1974/75 and 1986-1994. Data from NIVA in SFT (1994)

western Norway. Many of these catchments show either no or even negative change in ANC since 1980.

Concentration of nitrogen in precipitation has not changed over the last 10 years, and there are no changes in the levels of nitrate in surface waters. Sites receiving high N-deposition also have high concentrations of nitrate in surface waters.

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WATER QUALITY REQUIREMENT OF ATLANTIC SALMON (*SALMO SALAR*) IN WATER UNDERGOING ACIDIFICATION OR LIMING IN NORWAY

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Abstract. Atlantic salmon are severely affected by acidification in Norway. Water quality criteria for the salmon have to be based on the most sensitive stage, the smolt stage. The sensitivity to acidic water increases enormously during smolting, the seawater tolerance being especially vulnerable. Even moderately acidic water (pH about 6) with low inorganic monomeric aluminium (LAl) concentrations (<20 µg L^{-1}) and short-term episodes may be harmful. Mixing zones in limed or unlimed rivers may also represent a problem for seaward migrating smolts. In limed salmon rivers, the national liming goal has been increased to pH 6.5 during smolting (1 February to 1 July) and to 6.2 the rest of the year as a result of our experiments. In contrast to what has been found for brown trout, salmon strains originating from watercources undergoing acidification were not more tolerant than those from non-acidic watercourses. At the moment no such "tolerant" strains are available for restocking limed rivers in Norway.

1. The decline in Atlantic salmon populations: a need for better knowledge about effects of acidification

Atlantic salmon populations in southernmost Norway are severely affected by acidification. Recently, there has been a marked decline in catches in several rivers also in southwestern and western Norway. Because of the influence of marine fisheries and oceanic factors on salmon populations, several hypotheses have been raised. It is, however, reasonable to assume that acidification also has contributed to the decline since decreases in inland fisheries and exceedence of the critical load has been documented in these regions (Kroglund *et al.*, 1994).

At present no established definitions of acidic water quality criteria for Atlantic salmon exist. In the following, we give a preliminary short summary of a series of experiments in water undergoing moderate acidification, or liming, to get such data.

2. The anadromous life pattern make Atlantic salmon especially vulnerable for acidification

SENSITIVITY INCREASE DURING SMOLTING

Atlantic salmon is the most sensitive of the salmonids naturally present in Norway to acidic water, and is more sensitive during parr-smolt transformation than at other stages (Rosseland and Skogheim, 1984; Staurnes *et al.*, 1993a). Several months before fulfilled parr-smolt transformation the presmolts are very sensitive to acidic water (Henriksen *et al.*, 1984). However, during the few weeks when presmolts develop into seawater-tolerant smolts, they become extremely sensitive (Staurnes *et al.*, 1993a). A week's exposure to acidic water hardly affected presmolts in early April, but was detrimental to smolts in May (Figure 1).

Fig. 1. Survival and blood plasma concentration of Cl^- (mean with SD indicated, N=12) of smolting Atlantic salmon held in water of pH 6.3-6.5 (control) or pH 5 with 50 µg L^{-1} Al added (exposure) in the periods 11-18 April and 16-24 May. After Staurnes *et al.* (1993a).

THE VULNERABILITY OF SEAWATER TOLERANCE: EVEN MODERATE ACIDIFICATION AND SHORT-TERM EPISODES MAY BE HARMFUL

Water quality criteria for Atlantic salmon have to be based on the most sensitive life stage, the smolt stage. This makes the definition more complicated than it is for inland fishes: the criteria can not only be based on effects in freshwater, but they also have to account for possible effects on marine performance. This applies both to the migratory behaviour and seawater tolerance. While possible effects on behaviour are not easily studied (but certainly warrant future research), seawater tolerance can be tested in standard challenge tests.

Such challenge tests have demonstrated that acidic water exposure impairs seawater tolerance during smolting (e.g. Farmer *et al.*, 1989; Kroglund *et al.*, 1993; Staurnes *et al.*, 1993a; Rosseland and Staurnes, 1994). In experiments where smolts were released in an acidic and a neighbouring limed river in southern Norway, challenge tests demonstrated a strong impairment of the seawater tolerance after a short-term exposure in the acidic river, and the marine survival of smolts released in the acidic river was negligible (Staurnes *et al.*, in press). Seawater challenge tests may be indicative for the prospects of survival in sea (See Staurnes *et al.*, 1993b), and should therefore be used as a standard test procedure related to effects of acidic water on smolts.

Because of the enormous sensitivity increase during smolting, Staurnes *et al.* (1993a) and Rosseland and Staurnes (1994) suggested that even moderately acidic episodes of short duration may be critical to salmon smolts, and may possibly lead to reduction of salmon stocks even in rivers that are not chronically acidic and not normally regarded as being in danger of acidification. Therefore, we conducted several experiments to study the effects of such moderate short-term exposures. The results from one of these experiments are shown in Figure 2. Despite no ionoregulatory effects after 12 h exposure in water of pH 5.2 and about 30 µg LAl L^{-1}, the exposure caused a significant reduction in the seawater tolerance.

Fig. 2. Blood plasma concentration of Cl^- (mean with SD indicated, N=15) in freshwater or after 24 h in 35 ppt saltwater of Atlantic salmon smolts exposed 12 h in neutral water (control group) or acidic freshwater (exposed group). The fish were exposed to 5 or 31 µg inorganic monomeric aluminium (LAl) L^{-1} respectively.

MIXING ZONES MIGHT REPRESENT A PROBLEM FOR SEAWARD MIGRATING SMOLTS

When acidic water mixes with less acidic or limed water, it creates a zone of unstable Al chemistry. These "mixing zones", where inorganic Al goes from low to high molecular forms and polymerize, are especially toxic to fish. They are sometimes more toxic than the original acidic water, despite a higher pH and lower total Al concentration (Rosseland *et al.*, 1992).

Such mixing zones may be harmful for seaward migrating smolts (Rosseland and Staurnes, 1994). This is true not only in limed rivers receiving acidic water from tributaries, but also in unlimed semineutral rivers with major or minor acidified tributaries. The Vosso river in western Norway could be an example of such a watercourse. Over the last years, there has been a dramatic decline in the salmon catches in this river. Occasionally low pH (<6.0) has been measured in some of the tributaries. Fish kills were for the first time observed during spring 1993.

In an *in situ* experiment with hatchery-reared salmon smolts of the native population, marked differences in effects in freshwater, and especially on seawater tolerance, were observed for smolts exposed one to two weeks at different sites in the watercourse (Kroglund *et al.*, 1993). In the upper part of the River Strandaelva, the smolts behaved normally (Figure 3). In the lower part, both moderately acidic tributaries (e.g. River Teigdalselva) and less acidic tributaries drain into the main river. At all tested sites in this part of the main river, the smolts showed ionoregulatory disturbances in freshwater and low seawater tolerance, including an exposure site not far from the outlet of the river (River Bolstadelva). However, the water pH, LAl and Ca concentrations were not very much different from those measured in River Strandaelva, where the fish in freshwater had normal plasma concentration of chloride (Cl^-) and showed no mortality in seawater (Figure 3). Although there is no chemical evidence to support this, it could be hypothesized that the observed differences in effects are caused by unstable Al chemistry in the main river when acidic and more Al-rich water from tributaries drains into the river. This assumption is supported by the results from laboratory mixing zone experiments (unpubl. data). At the moment, however, the effects and importance of mixing zones for seaward migrating salmon smolts are not fully known, and therefore warrant future investigation.

Fig. 3. Survival and blood plasma concentration of Cl^- (mean with SD indicated, N=12) in freshwater or after 24 h in 35 ppt saltwater of Atlantic salmon smolts exposed one (River Teigdalselva) or two weeks in the upper part of the Vosso watercourse in western Norway (River Strandaelva), in an acidic tributary in the lower part (River Teigdalselva), or in the main river not far from the outlet (River Bolstadelva). Inorganic monomeric aluminium varied from 6 to 12 µg LAl L^{-1}. After Kroglund *et al.* (1993).

3. Mitigation strategies

If we are to manage Atlantic salmon stocks effectively it is important to establish the minimum water quality criteria that will ensure their existence.

IMPROVEMENT OF WATER QUALITY

In Norway, liming by fine powdered limestone added as slurry with automatic dosers is common. The liming goal is to yield a water quality good enough to ensure a self reproducing and healthy salmon population, but not more than necessary in order to minimize the costs. To attain this goal, it is obviously necessary to have the best possible information about water quality requirements of the fish. Since there always will be Al left in the water after liming of acidic Al-rich water, these requirements will not necessarily be the same as those of non-limed water, e.g. with respect to acidity.

To study these aspects, we conducted *in situ* experiments with hatchery-reared smolts in a river in western Norway (River Vikedalselva) that had been fullscale limed since 1987. The liming did not however bring about the expected increase in the salmon stock. During the smolting period, the river was limed to pH 6.2.

Compared to smolts held in water at pH>6.5, those held one to two weeks at pH<6.2-6.3 had suboptimal smolt quality, as shown by reduced blood plasma Cl^- concentration in freshwater, gill structural changes and Al accumulation, reduced gill Na-K-ATPase activity, and reduced seawater tolerance (Figure 4) (Kroglund and Staurnes, in press; Kvellestad *et al.*, 1995). The water qualities represented by pH values <6.2-6.3 were therefore suboptimal for the salmon smolts even though the concentration of LAl was as low as 15-20 μg L^{-1}.

Fig. 4. Survival and blood plasma concentration of Cl^- (mean with SD indicated, N=12) in freshwater or after 24 or 48 h in 35 ppt saltwater of Atlantic salmon smolts exposed two weeks in different water qualities in the limed River Vikedalselva in western Norway, made by liming the acidic water (Acid group) upstream the lime doser. Inorganic monomeric aluminium varied from 15 to 35 μg LAl L^{-1}. After Kroglund and Staurnes (in press).

STOCKING BY "ACID-TOLERANT" STRAINS

In affected rivers still holding fish, stocking is normally only allowed with fish from the native salmon population. When restocking limed rivers were the native population is extinct, however, use of salmon strains that are more resistant to acidic water could be a proper management strategy. For inland brown trout, the existence of such strains is well documented (Dalziel *et al.*, in press).

Therefore, a series of experiments were performed to investigate if strains more resistant to acidic water could also be found for Atlantic salmon (Kroglund *et al.*, 1995). Two or three generations of fish from several strains originating from non-acidic rivers and rivers undergoing early and, at present, still moderate acidification, were tested at different water qualities (pH 4.3-5.8, LAl 50-200 µg L^{-1}, Ca 0.8-1.0 mg L^{-1}), and at different stages (alevins, fingerlings, parr, presmolts and smolts). However, in contrast to what is found for brown trout, the tested salmon strains originating from the watercourses undergoing acidification were not more tolerant than those from non-acidic watercourses. These results do not preclude that such "acid-tolerant" strains of Atlantic salmon exist, but at moment no such strains are available for restocking in limed rivers in Norway.

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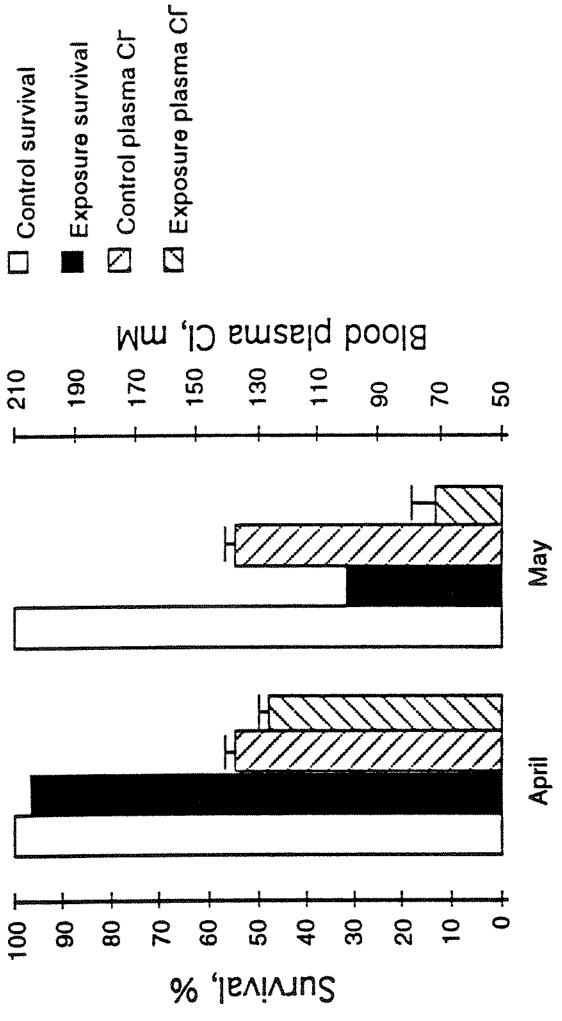

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Fig. 2

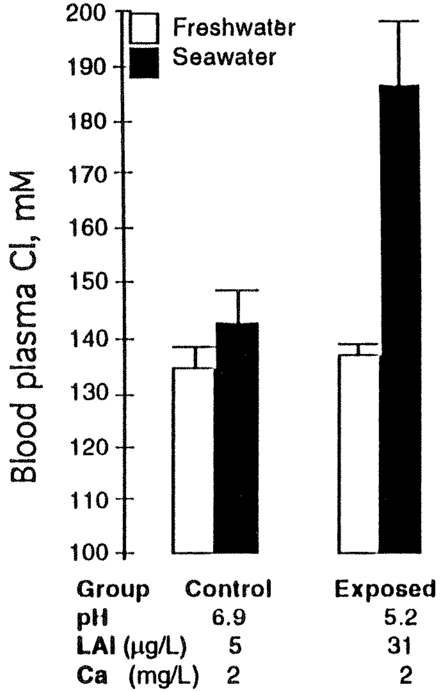

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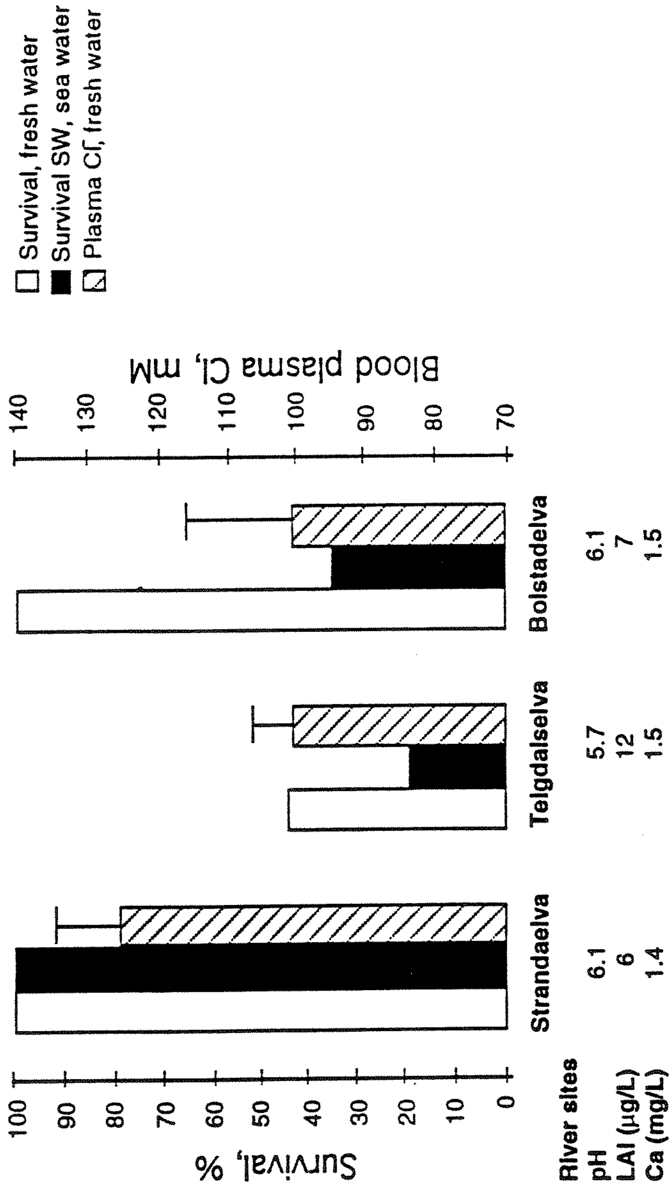
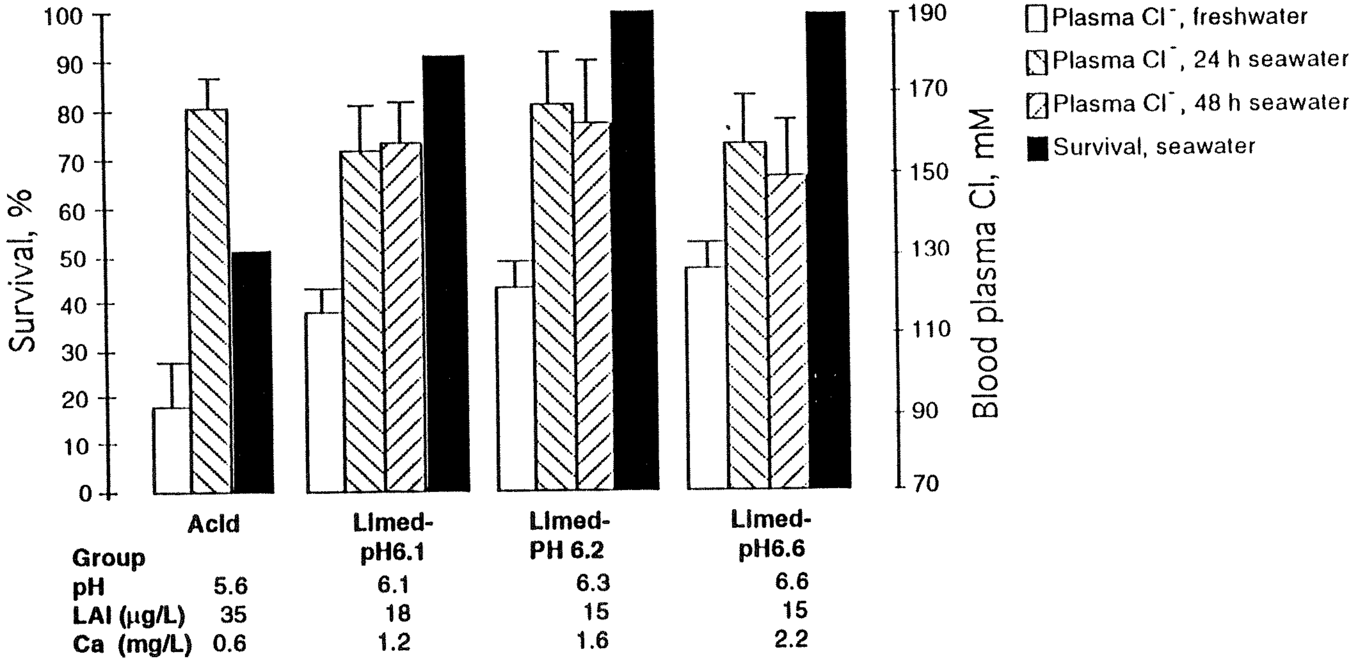
Fig. 3




100
90
80
70
60
50
40
30
20
10
0
Survival, %
190
170
150
130
110
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70
Blood plasma Cl, mM
Plasma Cl⁻, freshwater
Plasma Cl⁻, 24 h seawater
Plasma Cl⁻, 48 h seawater
Survival, seawater
Group
pH
LAl (µg/L)
Ca (mg/L)
Acid
5.6
35
0.6
Limed-pH6.1
6.1
18
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15
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2.2

NITREX: THE TIMING OF RESPONSE OF CONIFEROUS FOREST ECOSYSTEMS TO EXPERIMENTALLY-CHANGED NITROGEN DEPOSITION

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Abstract. In large regions of Europe and eastern North America atmospheric deposition of inorganic nitrogen (N) compounds has greatly increased the natural external supply to forest ecosystems. This leads to N saturation, in which availability of inorganic N is in excess of biological demand and the ecosystem is unable to retain all incoming N. The large-scale experiments of the NITREX project (NITRogen saturation EXperiments) are designed to provide information regarding the patterns and rates of responses of coniferous forest ecosystems to increases in N deposition and the reversibility and recovery of impacted ecosystems following reductions in N deposition.

The timing of ecosystem response generally followed a hypothesized "cascade of response". In all sites N outputs have responded markedly but to very different degrees within the first three years of treatment. Within this time significant effects on soil processes and on vegetation have only been detected at two sites. This delayed response is explained by the large capacity of the soil system to buffer the increased N supply by microbial immobilization and adsorption. We believe that this concept provides a framework for the evaluation and prediction of the ecosystem response to environmental change.

1. Introduction

NITREX is a consortium of European experiments in which nitrogen (N) deposition is drastically changed to whole catchments or large forest stands at 8 sites spanning a N deposition gradient (Dise and Wright, 1992; Wright and Van Breemen, 1995) (Figure 1; Table I). NITREX focuses on the impact of N deposition on forest ecosystems, in particular the factors and processes affecting N saturation. Nitrogen saturation is defined as the situation in which the supply of inorganic N exceeds the nutritional demand of biota and is operationally measured as increased leaching of N below the rooting zone (Aber *et al.*, 1989). At NITREX sites with low to moderate ambient N deposition (3-20 kg N ha^{-1} yr^{-1}) N is experimentally added to throughfall. At NITREX sites with high N deposition (>25 kg N ha^{-1} yr^{-1}) and significant leaching losses of N, N is removed from throughfall by means of roofs. Objectives of NITREX include measurement of the impact of changed N deposition on ecosystem functioning. Here we focus on the timing of the responses within three ecosystem components; water, soil and vegetation.

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TABLE I

Characteristics of the NITREX experiments

Site	Tree species	Ambient N flux in throughfall kg ha^{-1} yr^{-1}	Treatments	Experimental N flux in throughfall kg ha^{-1} yr^{-1}	Start Treatment	Key Reference
Sogndal	Alpine vegetation	3	add	8-24	1983	1
Gårdsjön	Norway spruce	12	add	49	1991	2, 3
Klosterhede	Norway spruce	27	add	61	1992-87	4
Alptal	Norway spruce	21	add	40	1994	
Aber	Sitka spruce	15	add	48-89	1990	5
Solling	Norway spruce	40	remove	0	1991	6
Speuld	Douglas fir	55	remove	0	1989	7, 8
Ysselsteyn	Scots pine	61	remove	0	1989	7, 8

1. Wright and Tietema (1995); 2. Moldan *et al.* (1995); 3. Stuanes *et al.* (1995); 4. Gundersen and Rasmussen (1995); 5. Emmett *et al.* (1995ab); 6. Bredemeier *et al.* (1995); 7. Boxman *et al.* (1995); 8. Koopmans *et al.* (1995).

2. Material and methods

As indicators of response we choose three key parameters; annual inorganic N input-output budget, net N mineralization rate in the organic layer, and the nutritional balance in newly-formed needles. Inorganic N inputs were measured as throughfall. The N output fluxes were calculated by multiplying concentrations in soil solution below the rooting zone or drainage water with simulated or measured water fluxes. Soil solution was sampled biweekly or monthly with lysimeters. Net N transformations were quantified with year-round *in situ* incubations of intact soil cores. As a measure of the nutritional balance of the needles, we used the K:N and Mg:N ratios in current year needles.

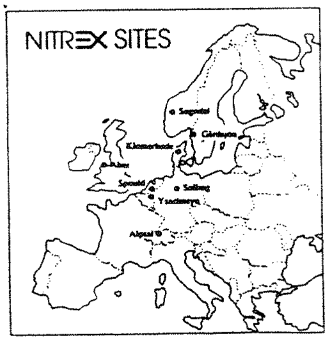

Fig. 1. Location of the NITREX sites.

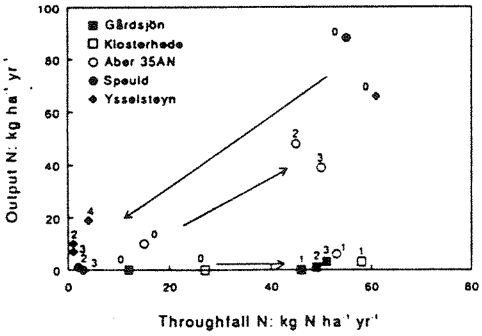

Fig. 2. Input-output budgets of inorganic N in the NITREX sites. The numbers indicate the treatment years; 0 refers to pre-treatment or control data.

Because for some of the sites time series of these parameters were not yet available, we have primarily used data from five of the seven forested NITREX sites, namely Gårdsjön, Klosterhede, Aber, Speuld and Ysselsteyn.

3. Results

The N input-output data from the NITREX sites are consistent with the general pattern of N fluxes from forest ecosystems in Europe (Wright *et al.*, 1995) (Figure 1). At annual inputs of less than about 10 kg ha^{-1} yr^{-1} nearly all the N is retained and outputs are very small. At inputs above about 25 kg ha^{-1} yr^{-1} outputs are substantial. In most sites changes in inorganic nitrogen output occurred during the first years after the start of the treatment (Figure 2). Changes were relatively low and slow at Gårdsjön and Klosterhede, sites previously not saturated; after two years N output has increased from zero to a maximum of 3 kg N ha^{-1} yr^{-1}. A fast and large response was found at Speuld and Ysselsteyn. Within the first two years of reduced input, N output decreased from about 80 to 10 kg N ha^{-1} yr^{-1}. The Welsh site Aber showed an intermediate response with no change in N output during the first year and a large increase (from 10 to 40 kg ha^{-1} yr^{-1}) during the second treatment year.

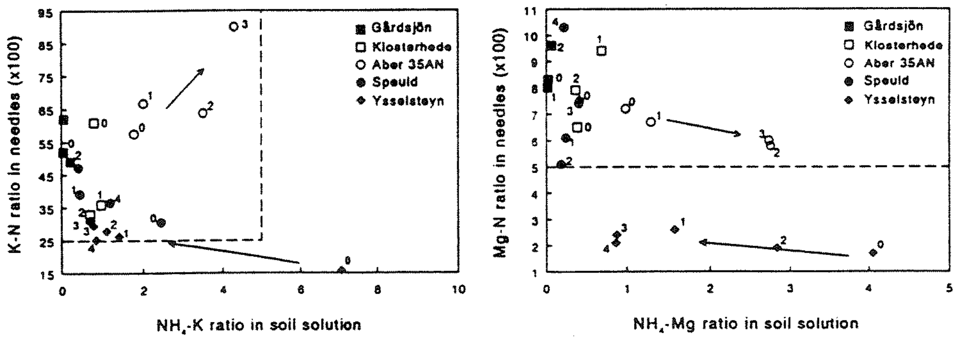

Fig. 3. Ratios between the total concentrations of K (left) or Mg (right) and N in current year needles as a function of the ratio of the concentrations (mol mol^{-1}) of NH_4 and K or Mg in soil solution (0-10 cm depth) in the NITREX sites. The dashed lines signify the levels of the ratios at which the supply of K and Mg becomes deficient (Boxman *et al*, 1995). The numbers indicate the treatment years; 0 refers to pre-treatment (Gårdsjön and Klosterhede) or control data (Aber, Speuld and Ysselsteyn).

Net mineralization rates changed significantly only at Ysselsteyn; in the low N deposition plot at Ysselsteyn the net mineralization rate decreased to about 4% of that in the high deposition plot (Koopmans *et al.*, 1995). Unpublished results indicated that at Gårdsjön a four-fold increase in net mineralization rate occurred during the third year of N addition; there was no response during the first two years (Kjønaas, unpublished data). At Klosterhede, Aber and Speuld net N mineralization did not change significantly due to N addition or removal (Gundersen and Rasmussen, 1995; Emmett *et al.*, 1995b; Koopmans *et al.*, 1995).

In all sites except Ysselsteyn, nutrient concentrations in the foliage after 2-3 years of treatment indicated no significant changes (Boxman *et al.*, 1995; Emmett *et al.*, 1995a; Gundersen and Rasmussen, 1995). This is illustrated by the relation between the K:NH$_4$ and Mg:NH$_4$ ratios in soil solution and in current year needles (Figure 3). At Ysselsteyn a significant change in the foliage ratios coincided with a large change in soil solution ratios. At Aber the NH$_4$:K and NH$_4$:Mg ratios in soil solution increased due to a increase in NH$_4$ concentration. The nutritional balance in the needles showed no significant change during the first three treatment years. At all other sites, both ratios in soil solution as well as in the foliage showed no significant changes during the treatment years.

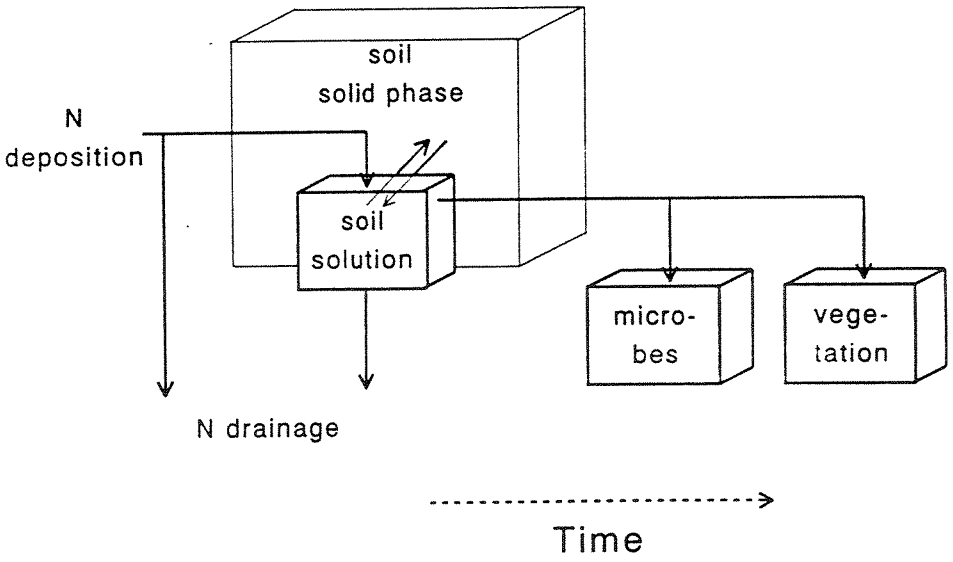

Fig. 4. Conceptual diagram of the hypothesized *cascade of response*. The diagram symbolizes the time sequence of ecosystem response in the ecosystem fluxes and compartments drainage, soil solution, microbes and vegetation, as a result of a change in N deposition.

4. Discussion

We hypothesize that the ecosystem response to the changed N input follows a temporal pattern which can be described as a *cascade of response* (Figure 4). Because the external change in the NITREX manipulation experiments affects the aqueous phase (precipitation and throughfall) and water is the principle transport medium, the response is expected first in the run-off or drainage. Depending on the physical properties of the soil

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compartment, soils may not fully interact with the incoming water. This will lead to a small fraction of the N signal passed through by runoff (or leachate) immediately. The next response will be in the soil; the signal is transmitted by way of the soil solution. Here major processes are microbial immobilization of N and adsorption. These processes generally proceed very rapidly and the soil represents a large pool for both processes; the soil will act as a buffer for the signal. As a result effects on soil solution and soil processes such as nitrogen mineralization will not appear until these pools have been altered significantly; i.e. the response will be delayed. Next to be affected will be the vegetation. Here the signal is passed through the soil solution, which in turn is influenced by the interaction with the soil.

At the NITREX sites the measured ecosystem response to experimentally-changed N deposition generally follows this cascade pattern. The behavior of each site can be explained within this theoretical pattern based on specific site characteristics such as tree species, soil type and degree of N saturation.

The non-forested NITREX catchment at Sogndal, Norway, is a good example of a site where the increased N input was followed by an immediate increase in inorganic N output in runoff (Wright and Tietema, 1995). High concentrations of NO_3^- in runoff were limited to periods during or immediately following N additions, and as the soil is thin and patchy in this site, this response was apparently solely hydrological. There were no measurable changes in soil or vegetation after the nine years of treatment (Wright and Tietema, 1995). At Gårdsjön inorganic N concentrations and fluxes in runoff have slightly but steadily increased during the 3 years of N addition (Moldan *et al.*, 1995). Here, the response of runoff is not simply hydrological; both frequency and magnitude of nitrate peaks in runoff increased during the first years of the experiment (Moldan *et al.*, 1995). In addition, the first results of the field incubation study showing the increased nitrogen mineralization rate three years after the start of the N addition (Kjønaas, unpublished data), indicates that the soil has responded without any response in vegetation. The non-saturated spruce forest at Klosterhede shows a response largely comparable to Gårdsjön; a steady but small increase of inorganic N leaching and no changes in nutritional balance of the needles (Gundersen and Rasmussen, 1995). However, in contrast with Gårdsjön, the observed increase in net mineralization rate was not significant. At Aber, increased N/NO_3 input resulted in increased N/NO_3 output of the same magnitude, whereas the increase in N/NH_4 input was retained in the system (Emmett *et al.*, 1995a). This indicates a limited N retention capacity at this site. No change in net mineralization rates nor in the nutritional balance of the vegetation was observed at Aber (Figure 3). The highly N saturated NITREX sites Solling in Germany and Speuld and Ysselsteyn in the Netherlands showed a very fast response of decreased inorganic N outputs due to decreased input; within a few months after the start of the treatment concentration in soil solution started to decrease (Bredemeier *et al.*, 1995; Boxman *et al.*, 1995). The other compartments in Speuld and Ysselsteyn showed a different response. At Speuld, no significant changes in net mineralization rates nor in nutritional balance of the needles was found, whereas at Ysselsteyn significant changes in net mineralization rates and nutritional balance in needles were found. These differences in response between Speuld and Ysselsteyn can be explained by a difference in the degree of nitrogen saturation. Despite excessive nitrate leaching in Speuld indicating nitrogen saturation, the Douglas fir trees grow reasonably well and the needles have normal N concentrations and N:Mg and N:K ratios above levels that are considered deficient (Boxman *et al.*, 1995). At Ysselsteyn, N concentrations in the needles are much higher than in Speuld and the nutritional balance of Mg and K relative to N has values below the deficiency level (Figure 3). From the fast response of the vegetation and soil processes in saturated Ysselsteyn compared to the delayed response in non-saturated Gårdsjön it appears that the soil pools are "one-way" in the response to changed N concentrations in soil solution. In non-saturated systems they are capable of rapidly removing large amounts of N from soil solution, but in saturated systems they do not release large quantities of N to soil solution.

The concept of cascade of response satisfactorily explains the observed ecosystem response to changed N deposition. The concept should be further verified by means of long-term field-scale manipulation experiments. We believe that it provides a framework for the evaluation and prediction of the ecosystem response to environmental change.

Acknowledgements

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ACIDIFICATION BY NITROGEN: NITROGEN LEAKAGE AND CLASSIFICATION OF NITROGEN SATURATION AT ICP ON WATERS CATCHMENTS.

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LAK16

Abstract. The increased nitrate leakage observed in several European and American regions in the 1980's has led to more attention on nitrogen as acidifying agent. In some regions increased nitrogen leakage has hampered improvement of water quality by reduced sulphur deposition.

Nitrogen data from sites in the International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP on Waters) have been assessed. More than half of 150 ICP catchments have yearly average nitrate concentration above 10 µeq/1 and 23% more than 50 µeq/l. Nitrate amounts to more than 10% of the non-marine acid anions at 64% of the catchments and more than 25% at 23% of the catchments. Due to the episodic pattern of nitrate concentrations at many catchments, the relative importance of nitrate in acidification may, in some seasons and especially during snowmelt, be 2 or 3 times greater than shown by yearly averages.

High nitrogen concentrations in the runoff were only found in catchments receiving high nitrogen deposition. The results confirm the observations from other studies that catchments have a treshhold value for nitrogen deposition above which severe nitrogen leakage occurs.

143 ICP catchments were classifed according to Stoddard's system of 4 stages (0-3) of nitrogen saturation. Half of the catchments had a high degree of nitrogen saturation (stages 2 or 3). At these sites nitrate leakage occur in all seasons. The results show that nitrogen is an important acidifying agent in many regions in Europe and North America.

Key words: nitrate, acidified lakes, nitrogen saturation, ICP.

WHOLE-CATCHMENT LIMING AT TJØNNSTROND, NORWAY: AN 11-YEAR RECORD

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Abstract. In June 1983 a whole-catchment liming experiment was conducted at Tjønnstrond, southernmost Norway, to test the utility of terrestrial liming as a technique to restore fish populations in remote lakes with short water-retention times. Tjønnstrond consists of 2 small ponds of 3.0 and 1.5 ha in area which drain a 25-ha catchment. The area is located at about 650-700 meters above sea-level in sparse and unproductive forests of spruce, pine and birch with abundant peatlands. A dose of 3 ton/ha of powdered limestone were spread by helicopter to the terrestrial area. No limestone was added to the ponds themselves. The ponds were subsequently stocked with brown and brook trout.

Liming caused large and immediate changes in surface water chemistry; pH increased from 4.5 to 7.0, Ca increased from 40 to 200 μeq/l, ANC increased from -30 to +70 μeq/l, and reactive-Al decreased from about 10 to 3 μmol/l. During the subsequent 11 years the chemical composition of runoff has decreased gradually back towards the acidic pre-treatment situation. The major trends in concentrations of runoff Ca, ANC, pH, Al and NO_3 in runoff are all well simulated by the acidification model MAGIC. Neither the measured data nor the MAGIC simulations indicate significant changes in any other major ion as a result of liming.

The soils at Tjønnstrond in 1992 contained significantly higher amounts of exchangeable Ca relative to those at the untreated reference catchment Storgama. In 1992 about 75% of the added Ca remains in the soil as exchangeable Ca, 15% has been lost in runoff, and 10% is unaccounted for.

The whole-catchment liming experiment at Tjønnstrond clearly demonstrates that this liming technique produces a long-term stable and favourable water quality for fish. Brown trout in both ponds in 1994 have good condition factors, which indicate that the fish are not stressed by marginal water quality due to re-acidification. The water quality is still adequate after 11 years and > 20 water renewals. Concentrations of H^+ and inorganic Al have gradually increased and approach levels toxic to trout, but the toxicity of these are offset by the continued elevated Ca concentrations. Reduced sulphate deposition during the last 4 years (1990-94) has also helped to slow and even reverse the rate of reacidification. The experiment at Tjønnstrond demonstrates that for this type of upland, remote terrain typical of large areas of southern Norway, terrestrial liming offers a suitable mitigation technique for treating acidified surface waters with short retention times.

Key words: acid deposition, liming, catchment, lake, water chemistry, fish, soil, model

1. Introduction

Liming is now widely used as a means to detoxify acidified surface waters such that fish populations can survive or be introduced (Olem *et al.*, 1991; Porcella *et al.*, 1991; Rosseland and Hindar, 1988; Thörnelöf and Degerman, 1991). Liming provides a temporary remedial measure in anticipation of permanent long-term reductions in deposition of acidifying compounds (Rosseland and Hindar, 1991). Liming of lakes commonly takes the form of direct addition of carbonates to lakewater. When properly carried out this technique offers the most complete use of the added carbonate. But direct addition is neither practical nor cost-effective for remote lakes with short water retention times, because additions must be repeated frequently and fish populations are in constant danger of damage by episodes of high discharge with acid, aluminium-rich water. At such sites continuous dosing as is used for running waters is called for (Hindar and Henriksen, 1992), but the lack of electricity and often also the lack of suitable inlet stream preclude installation of such equipment. Liming of the terrestrial catchment may in such cases provide the only suitable mitigation alternative.

Despite the widespread use of limestone to treat acidified waters, there have been few full-scale long-term experiments which focus on whole-catchment liming as a means. Best documented are perhaps the liming experiments conducted at Loch Fleet in southwestern Scotland, UK (Howells and Dalziel, 1992; Dalziel *et al.*, 1994). Similar experiments have been conducted at Gjerstad, Norway (Hindar *et al.* 1995a), Lynn Brianne in Wales, UK (Jenkins *et al.*, 1991), Woods Lake in the Adirondack Mountains of New York, USA (Gubala and Driscoll, 1991), and Lake Gårdsjön, Sweden (Hultberg and Grennfelt, 1986) (Table 1). At Lake Røynelandsvatn, Norway, wetlands constituting 4% of the lake catchment were limed (Hindar *et al.* 1995b).

In June 1983 as part of the Norwegian Liming Project a whole-catchment liming experiment was conducted at Tjønnstrond, southernmost Norway, to test the utility of terrestrial liming as a technique to restore fish populations in remote lakes with short water-retention times. We report here the effects of liming during the 11-year period 1983-94 on lake chemistry, soil chemistry, and fish populations, and evaluate the usefulness of MAGIC, a widely-used acidification model, in simulating the changes in soil and water chemistry.

2. Site description and methods

Tjønnstrond consists of 2 small ponds of 3.0 and 1.5 ha in area which drain a 25-ha catchment near Treungen, Telemark, Norway (Figure 1). The ponds are shallow (mean depth 1 m) and have short water retention time (about 2 months). The catchment is adjacent to Storgama, a calibrated research catchment now included in the Norwegian national environmental monitoring program (SFT, 1993). Measurements at both catchments were initiated in 1975 as part of the Norwegian SNSF-project (Acid Precipitation -- Effects on Forest and Fish) (Overrein *et al.*, 1980). The catchments are located at about 650-700 meters above sea-level in sparse and unproductive forests of spruce, pine and birch with abundant peatlands. The region receives moderate amounts (for Norway) of acid (mean non-marine sulphate deposition in the period 1982-88 of 69 meq/m^2/yr.). Prior to treatment the catchments and surface waters at both Tjønnstrond and Storgama were very similar (Johannessen and Joranger, 1976). The streams were highly acidified with pH about 4.5 with high concentrations of inorganic Al (Table 2).

Historically the two ponds at Tjønnstrond supported good populations of brown trout (*Salmo trutta*) which were dependent on regular stocking because of lack of spawning areas. From the 1960's and 70's the stockings failed due to increasing acidification. A stocking of brook trout (*Salvelinus fontinalis*) in 1982 yielded no recapture.

In June 1983, 73 metric tons of powdered limestone were spread by helicopter to the terrestrial area. No limestone was added to the ponds themselves. The dose of 3 ton/ha corresponds to 934 kg Ca/ha. Details of the liming and initial hydrochemical response are described by Traaen (1990). The ponds were subsequently stocked with brown and brook trout (L'Abée-Lund and Kleiven, 1987).

The effect of the liming was monitored by means of weekly water samples collected at the outlet to the lower of the 2 ponds at Tjønnstrond. Sampling began in June 1983. Samples are sent to the Norwegian Institute for Water Research for chemical analysis. The analytical program includes pH, electrical conductivity, major cations and anions, aluminium species, and total organic carbon. Weekly samples from Storgama receive the same procedure. Analyses are by conventional methods for soft waters and include atomic adsorption spectroscopy for base cations (ICP from 1993), automated colorimetry for strong acid anions (ion chromatography from 1985), and cation-exchange followed by colorimetry for Al-species (Røgeberg and Henriksen 1985).

Soils at both Tjønnstrond and Storgama were sampled in 1992 to evaluate the long-term impact of liming on soil chemistry. At Tjønnstrond samples were taken at 30 cross-points in a 80 x 80 m grid net over the catchment. At each point bulk samples consisting of 10-15 cores of 2.5 cm diameter split into 3 depths (0-5, 5-10 and > 10 cm) were taken. At Storgama samples were collected at three points with vegetation and soil characteristic for Tjønnstrond and Storgama catchments. Analyses were carried out at the Norwegian Forest Research Institute (NISK) by standard procedures and include bulk density, cation exchange capacity and amounts of exchangeable cations in unbuffered solution of 1M NH_4NO_3 . Results were mass-weighted by horizon and combined to obtain an aggregated value for each catchment (Table 3).

Since October 1983 summerold (0+) fish fry have been repeatedly stocked in both ponds to follow the biological effect of the liming (Table 4). Generally, brook trout were stocked in Øvre (upper) Tjønnstrond while brown trout were stocked in Nedre (lower) Tjønnstrond. This allowed evaluation of the relative success and growth of the 2 species under rather similar water-chemistry conditions. In addition migration between the 2 ponds could be easily detected. Test-fishing with two multi-mesh nets of the SNSF-series (Rosseland *et al.*, 1979) has been conducted yearly since 1984 except in 1986 and 1992. The brown trout stocked in 1983 and 1986 were of the lake spawning Byglandsfjord strain (Barlaup *et al.*, 1994). The brown trout stocked in 1993 was of the Stemtjønn strain.

The density of the 1983, 1986 and 1990 stockings are 83 brown trout ha^{-1} in Nedre Tjønnstrond and 42 brook trout ha^{-1} in Øvre Tjønnstond. The density of the 1993 stockings of the brown trout in both lakes are 67 and 33 brown trout ha^{-1}, respectively.

Several models have been used for constructing acidification history and predicting future acidification over time periods of decades. MAGIC (Model for Acidification of Groundwater In Catchments) (Cosby, 1985a; 1985b) is one of the more-widely used long-term process-oriented models operating at the catchment scale. MAGIC makes use of lumped parameters on a catchment scale and focuses on chemical changes in the soil caused by atmospheric deposition, vegetation, and leaching to runoff. We have tested the suitability of the MAGIC model to describe water quality after terrestrial liming.

MAGIC was first calibrated using the 3-year mean input-output data from Storgama for the period 1981-83 (Table 2). This procedure calls for a 140-year reconstruction of soil and water chemistry from 1842-1982 with changes driven by estimated long-term changes in acid deposition. A 2-box version of MAGIC was used, with the upper box corresponding to the organic A horizon (15 cm thickness) and the lower box corresponding to the aggregated B and C horizons (total 17 cm thickness). No flow routing was used; all water was assumed to move from the upper soil to the lower soil. Liming was simulated in the model by addition of the limestone to the upper soil box with complete dissolution during the year June 1983- June 1984. The carbonate added with the Ca was simulated in MAGIC by increasing the CO_2 partial pressure in soil air. Nitrate retention was decreased in the model for the first 2 years after liming. Details are given in Jenkins *et al.* (1994).

The model was then run for a 9-year post-liming period from June 1983 to June 1992. Measured precipitation volume and deposition chemistry data from the monitoring station at Treungen (Figure 1) were used to drive the model.

3. Results

3.1 WATER CHEMISTRY

Liming caused large and immediate changes in surface water chemistry at Tjønnstrond (Figure 2). pH increased from 4.5 to 7.0, Ca increased from 40 to 200 μeq/l, ANC increased from -30 to +70 μeq/l, and reactive-Al decreased from about 10 to 3 μmol/l (Traaen, 1990). None of the other base cations (Na, K, Mg, NH_4) exhibits large changes after liming. During the subsequent 10 years the chemical composition of runoff has decreased gradually back towards the acidic pre-treatment situation.

Concentrations of nitrate in runoff were higher the first and second years following liming at Tjønnstrond relative to earlier years and to Storgama (Figure 2). At both catchments nitrate exhibits a strong seasonal pattern of high concentrations during the winter and low levels during the summer. The increase in nitrate concentrations caused by liming resulted in higher concentrations both in winter and summer.

Sulphate concentrations in runoff are very similar at the two catchments. Sulphate levels exhibit a moderate general decrease over the 10-year period, especially in 1990-94. This decrease is typical for lakes and streams in southernmost Norway and reflects decreased deposition of sulphate in turn due to reduced emissions of SO_2 in Europe over the past decade.

There is a clear coherence between sulphate and calcium concentrations in the runoff, suggesting that the load of sulphate (and H^+) determine the the release of added calsium from the catchment. Even during snowmelt and autumn rainstorms the release of calcium is sufficient to avoid severe acid episodes with toxic aluminium.

3.2 SOIL CHEMISTRY

The soils at Tjønnstrond in 1992 contained significantly higher amounts of exchangeable Ca relative to those at Storgama (Table 3). Surface horizons show the highest differences. Fractions of the other base cations on the soil exchange complex are low and relatively similar at both catchments.

Mass-balance calculations indicate that during the first 9 years since liming about 15% of the added calcium was transported out of the catchment in runoff. Net transport of Ca relative to Storgama was about 150 meq/m2 the first year following liming (corresponds to about 3% of the Ca added in the limestone), and decreased gradually to about 30 meq/m2 in 1992-93. The Ca flux data and soils data indicate that in 1992 of the 4670 meq/m2 Ca added, about

3500 meq/m2 (75%) is in the soil as exchangeable Ca, 690 meq/m2 (15%) has been lost in runoff and the remainder of 500 meq/m2 (10%) unaccounted for. The fraction on the soils is obtained by comparing the 1992 exchangeable Ca on the soils at Storgama with that on the soils at Tjønnstrond. Because of large spatial variations in soil chemistry within each catchment, however, these estimates are uncertain.

3.3 FISH

Both brook trout and brown trout stocked following liming showed good survival and condition. In Øvre Tjønnstrond the recapture of brook trout was good, especially the first year after stocking (Table 4). Øvre Tjønnstond is a shallow habitat favourable for brook trout. Recapture in the first two years for the 1983, 1986 and 1990 brook trout stockings are 18%, 11% and 19%, respectively (Kaste *et al.*, 1993). The landowner's stocking in 1985 yielded no brook trout in the catches, but no test-fishing was conducted in 1986. However, one angler reported 21 brook trout from Øvre Tjønnstrond in 1987, where 13 specimens (29.0-34.0 cm) most likely originate from the 1985 stocking and 8 specimens (17.7-21.2 cm) from the 1986 stocking. This indicates total recapture of 22% for the 1986 stocking. The landowner's stocking of brook trout in 1988 in Øvre Tjønnstrond yielded 4 fish by test-fishing and 7 by an angler for a recapture figure of 11%.

In Nedre Tjønnstrond recapture of only a few brook trout indicates little migration from Øvre Tjønnstrond. Only 2 brook trout have been recaptured by test-fishing in Nedre Tjønnstrond, 1 each from the 1983 and 1990 stockings, respectively. In addition 4 are reported taken by local anglers. The low migration of brook trout is probably due to the favourable and relatively stable water quality.

The age frequency of brook trout in the test-fishing catches from 1984-1994 shows fish in the age groups 1+ to 2+ and one fish in age group 3+ (Table 4). Fully 88% of the brook trout have been caught as 1+. Largest brook trout caught was 1050 g. The mean condition factor for the brook trout catches has generally been high (1.10-1.40) with the exception for the year

1987 (0.99) (Table 5). The 1987 figure may be because of higher density due to fish stocking in both 1985 and 1986.

The recapture of brown trout stocked in Nedre (lower) Tjønnstrond has been very good especially of the 1986 cohort. Recapture figures of the 1983, 1986 and 1990 brown trout stockings, including catches of two anglers, are 23%, 45% and 15% respectively. The last brown trout stocking in 1993, of the Stemtjønn strain, yielded a recapture of 12% in 1994.

The age frequency of brown trout in the test-fishing catches from 1984-1994 shows fish in the age groups 1+ to 5+ and two fish in age group 7+. Fully 40% of the brown trout have been caught as 1+. The largest brown trout caught was 1100 g. The mean condition factor for the brown trout catches have been relatively good (0.99-1.13), with the exception of the year 1985 (0.87) (Table 5).

A few brown trout have been caught in both lakes which appear not to originate from any known stockings. This may be due to incorrect age classification, because only scales are available for this fish, or it may be due to reproduction in the system. The brown trout of the Byglandsfjord strain is known to spawn in lakes (Barlaup *et al.*, 1994), and stockings of this strain in the limed lake Store Hovvatn have resulted in lake spawning (Barlaup and Kleiven, 1994; 1995).

It was assumed that fish would not migrate up to Øvre (upper) Tjønnstrond, but some of the brown trout stocked in Nedre Tjønnstrond were also caught in Øvre Tjønnstrond prior to stocking there in 1993 (Table 4).

3.4 MODELLING

The major trends in concentrations of runoff Ca, ANC, pH, Al and NO_3 in runoff are all well simulated by MAGIC (Figure 3). The changes in Ca, ANC, pH, Al and NO_3 observed in the first year following liming as well as the subsequent 9-year gradual re-acidification are all reproduced by MAGIC. Neither the measured data nor the MAGIC simulations indicate significant changes in any other major ion as a result of liming.

Cation exchange is a key process in MAGIC. Conceptually the model is set up to account for the changes caused by the liming as follows. The limestone added at Tjønnstrond was assumed to dissolve completely within the first year with the Ca in the limestone assumed to participate fully in ion-exchange reactions with the uppermost 15 cm of soil. This would effectively raise the Ca saturation of the surface soil from about 10% to about 57% (Figure 3). During the following years the upper soil gives off Ca to soil solution. This Ca-rich solution then moves down through the lower soil where a portion of the Ca is removed from solution by ion-exchange with the more-acid soil. The net effect is to move Ca from the upper to lower soil, as well as result in elevated Ca concentrations in runoff. These are indeed the effects observed in the Tjønnstrond liming.

The major discrepancy between model and observed is the amount of Ca on the soil exchange complex. Whereas the measurements indicate about 23% Ca in the upper soil in 1992, MAGIC simulates about 40%. This discrepancy is largely due to the "missing" Ca in the liming budget. The MAGIC simulation assumes that all the limestone is dissolved and that the released Ca initially goes on to the exchange complex. The measured soil data indicate that about 10% of the added Ca is present in another form, perhaps undissolved free limestone in the soil.

The fact that none of the other base cations are affected by liming is due to the fact that although the high Ca concentrations in soil solution should displace these cations from the soil, the relative fraction of Ca on the soil has increased greatly at the expense of the acid cations, primarily Al. These offset each other such that no large changes in concentrations in other base cations are predicted by MAGIC, and indeed no changes are observed in the data.

3.5. COSTS

The cost-effectiveness of terrestrial liming at Tjønnstrond has to be weighted against the more traditional liming methods. Due to lack of inlet streams, liming by lime-dosers is not possible. The access to the area is difficult and the only practical way of spreading lime is by helicopter.

Liming directly on the lake surface twice a year may or may not result in acceptable water quality. During heavy rain and especially in winter-time when the shallow ponds are covered with ice most of the water body may be shifted out. The timing of reliming may therefore be essential and probably not always adequate for maintaining pH above 5.5-6.0.

At a cost of NOK 1200 (USD 200) per tonne and a lime-dose of 60 g/m^3 spread by helicopter twice a year lake-liming will cost NOK 6500 per year. At a similar cost per tonne and a dose of 3 tonnes/ha terrestrial liming lasting 10 years will cost NOK 9000 per year.

More frequent lake-liming than twice a year will result in more stable water quality, decreased annual addition of powdered limestone but increased spreading costs per tonne due to an anticipated lack of other helicopter jobs in the area. Reacidification of the shore-area with acid, Al-rich meltwater would still be a problem in periods with ice-cover.

5. Discussion

The whole-catchment liming experiment at Tjønnstrond clearly demonstrates that this liming technique produces a long-term stable and favourable water quality for fish. Test-fishing results from 1994 show that brown trout in both ponds have good growth condition factors, which indicate that the fish are not stressed by marginal water quality due to re-acidification. The higher condition factor for brook trout compared to brown trout may reflect the species differences in growth potential and, in some extent, also differences in stocking densities. The recapture figures for brook trout at Tjønnstrond (11 to 22%) are similar to those reported for 13 acidified and stocked lakes (pH 4.48-4.98; 5.5-140 ha) in southern Norway; here 11 lakes had recapture over a three-year period of 0-14.7%, and two lakes had recapture of 21 and 39%, respectively (Grande *et al.*, 1980). The water quality is still adequate 11 years and > 20 water renewals in the ponds after liming application. For brook trout the stable water quality has minimises downstream migration.

Three water quality factors H^+, inorganic Al, and Ca are of special importance for growth and survival of trout (Brown, 1983; Wood and McDonald, 1987; Rosseland *et al.*, 1990).

Liming at Tjønnstrond has changed the concentrations of all three towards more favourable levels. During the subsequent 11 years of reacidification, H+ and inorganic Al have gradually increased and approach levels toxic to trout, but the toxicity of these are offset by the continued elevated Ca concentrations. Reduced sulphate deposition during the last 4 years (1990-94) has also helped to slow the rate of reacidification. As a result pH and reactive-Al concentrations have not changed significantly 1990-94. Indeed the mean concentration of inorganic-Al has actually declined from about 35 µmol/l in 1990 to 10 µmol/l in 1993. Ca concentrations continue to decline, however, in part due to the decreased concentrations of sulphate, the major anion (Figure 2).

Because the water-retention time in the ponds is short (< 2 months), the water chemistry in the ponds reflects runoff chemistry from the terrestrial catchment; in-lake processes will have only a minor effect on water chemistry.

The results from Tjønnstrond and other experiments (see introduction) show that terrestrial liming in adequate doses produce favourable and stabile water quality in stream and lake water. Toxic episodes of acidic, Al-rich water are avoided because the acidity is neutralised in the soil. Of these experiments only the trial at Gårdsjön was unsuccessful, but this can be explained by the low dose (0.45 kg/ha) relative to the other experiments (3-23 kg/ha).

At Tjønnstrond as well as at several of the other sites referred to in the introduction, liming appears to cause an increased loss of nitrate to runoff. This increase persists for 1-2 years, and is probably due to increased mineralization of soil organic matter and damage to terrestrial vegetation such as *Sphagnum* mosses and lichens caused by higher pH. At Tjønnstrond the yellow-green lichen *Rhizocarpon geographicuna* was almost completely removed from rock surfaces. Damage to terrestrial vegetation appears to be the major negative effect of catchment liming.

MAGIC accounts for both the immediate and long-term trends in soil and runoff chemistry following liming at Tjønnstrond. The model indicates that the fate of the limestone can be largely explained by dissolution of most of the limestone during the first year following application, with the released Ca participating in cation-exchange reactions in the uppermost soil. Subsequently the upper soil releases Ca, again by cation exchange with predominantly acid cations in precipitation. Vertical movement of water from the upper to lower soil horizons will reduce the concentration of Ca in soil solution.

The quantitative description of this process by MAGIC first requires the specification of several important parameters. Among these are the fraction of limestone assumed to dissolve, the partial pressure of CO_2 in soil air to simulate the bicarbonate generated by dissolution of the limestone, and the increase in mineralization of N following liming. These parameters are difficult to predict for terrestrial liming, as there have been only a few large-scale terrestrial liming experiments in which effects on surface waters are included.

Given these shortcomings MAGIC offers a useful tool in accounting for the major changes in surface water chemistry following whole-catchment liming, and in particular as a tool for predicting the magnitude and duration of response. The liming at Tjønnstrond provides a new evaluation of the robustness of MAGIC.

The experiment at Tjønnstrond resulted in a relatively long-lasting effect and stable water quality. Especially important was the deacidification of meltwater and the retention of Al in the catchment. Thus, terrestrial liming provides a better protection against acid episodes than direct liming in the lake. For lakes with short retention times in this type of remote terrain, typical for large areas of southern Norway, terrestrial liming may offer the only practical mitigation technique. If more frequent lake-liming than twice a year is the only realistic alternative, terrestrial liming may also be relatively cost-effective.

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Figures

Figure 1. Topographic map (elevation in meters) of the catchment and 2 ponds at Tjønnstrond, southern Norway. Inserts: location of site in southern Norway and location of Tjønnstrond relative to Storgama.

Figure 2. Water chemistry at the outlet to Nedre (lower) Tjønnstrond pond and the untreated reference catchment at Storgama. The liming was conducted in June 1983. Data from Traaen (1990) and Traaen (pers. comm.). Asteriks (*) denotes sea-salt corrected values; Al-r = reactive Al; Al-l = labile Al; TOC = total organic carbon; ANC = acid neutralising capacity, defined as difference base cations less strong acid anions.

Figure 3. Results from the MAGIC simulations. Measured and predicted annual volume-weighted concentrations of Ca, ANC (acid neutralising capacity), pH, inorganic Al, and NO_3 in lake water and Ca saturation in upper and lower soil at Tjønnstrond (limed) and Storgama (untreated control). Soil data were measured only in 1992. Tjønnstrond was limed in June 1983. Observed data are from Traaen (1990) and Traaen (pers. comm.).

Tables

Table 1. Overview of several large-scale whole-catchment liming experiments which focus on effects on surface water quality.

Site	Catchment	Vegetation	Area (ha)	Dose (ton/ha)	Date applied	Reference
Tjønnstrond, Norway		sparse forest and peatland	25	3.0	June 1983	this study
Gjerstad, Norway		mixed forest	84	3.0	September 1994	Hindar *et al.* 1995a
Gårdsjön, Sweden	F2	Norway spruce	3.3	0.45	June 1984	Hultberg and Grennfelt, 1986
Loch Fleet, UK	IV	Sitka spruce	4.6	23.9	April 1986	Dalziel *et al.*, 1991
Loch Fleet, UK	VI	heathland	6.4	21.3	April 1986	Dalziel *et al.*, 1991
Lynn Brianne, UK	C15	Sitka spruce	33.4	9.0	September 1987	Jenkins *et al.*, 1991
Woods Lake, USA	BP	mixed forest	100	10.0	October 1989	Gubala and Driscoll, 1991
Woods Lake, USA	NI	mixed forest	100	10.0	October 1989	Gubala and Driscoll, 1991

Table 2. Volume-weighted mean precipitation and runoff chemistry 1981-83 at the acidified reference catchment Storgama. SBC = sum base cations; SSA = sum strong acid anions; ANC = SBC - SSA acid neutralising capacity. Al-l = labile Al, sum of inorganic positively-charged Al species calculated as difference reactive Al less non-labile Al and assuming average value of 2.7 µeq/µmole. Units: µeq/l;

	precipitation	runoff
H_2O (mm)	1060	966
H^+	48	31
Ca	7	34
Mg	5	13
Na	16	26
K	2	4
NH_4	33	2
Al-l	0	10
Cl	20	31
SO_4	55	76
NO_3	28	11
SBC	63	79
SSA	103	118
ANC	-40	-40

Table 3. Soil chemistry at Tjønnstrond and Storgama catchments sampled in 1992, 9 years after liming. B.D. = bulk density; CEC = cation exchange capacity; BS = base saturation.

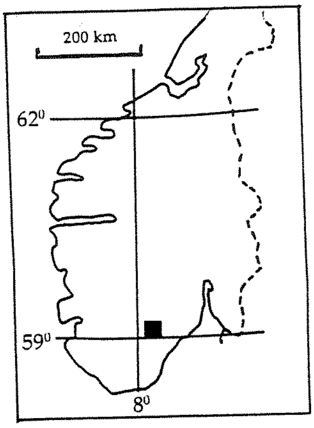
		Tjønnstrond		Storgama	
		A horizon	B+C horizon	A horizon	B+C horizon
depth	cm	15	17	15	17
B.D.	kg/m^3	220	590	180	430
CEC	meq/m^2	320	120	290	190
Exch.Ca	%	23	14	10	8
Exch.Mg	%	2	2	4	3
Exch.Na	%	1	1	1	1
Exch.K	%	3	3	6	4
BS	%	29	20	21	16

Table 4. Fish stocking of brown trout and brook trout and catch records from test-fishing for the two ponds Øvre (upper) Tjønnstrond (Ø.Tj.)and Nedre (lower) Tjønnstrond (N.Tj.) following catchment liming in June 1983. Angling catches (no systematic records) are in addition. Test-fishing is conducted each year prior to new stocking. Data from L-Abée-Lund and Kleiven (1987), Lande and Traaen (1989), Kaste *et al.* (1993) and Lande and Kleiven (in prep.).

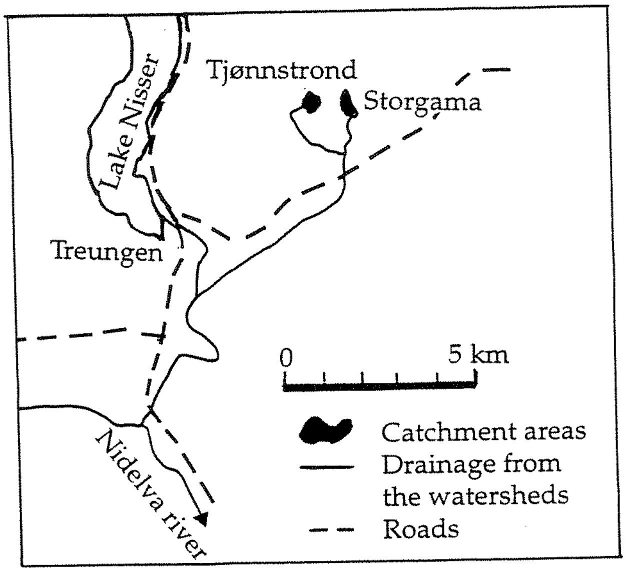
Pond/species	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994
Ø. Tj.												
brown: stocked											100	
caught		0	1		2	4	3	1	0		1	19
brook: stocked	125		140	125		50		125				
caught		17	5		12	2	4	0	23		1	0
N. Tj.												
brown: stocked	125			125				125			100	
caught		11	5		7	25	12	7	10		9	9
brook: stocked			60									
caught		1	0		0	0	0	0	1		0	0

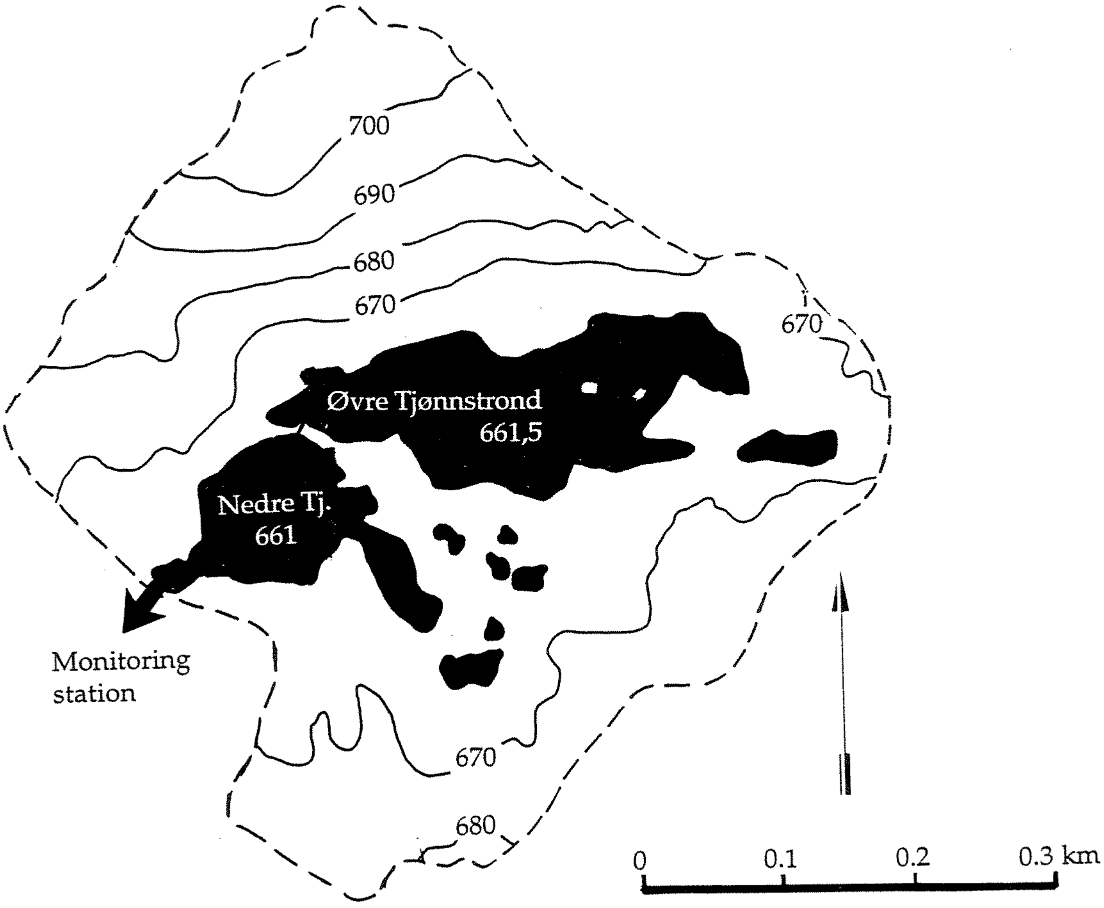
Table 5. Mean condition factors for brown and brook trout in the two ponds Øvre (upper) Tjønnstrond and Nedre (lower) Tjønnstrond following catchment liming in June 1983. Number of fish are given in Table 4.

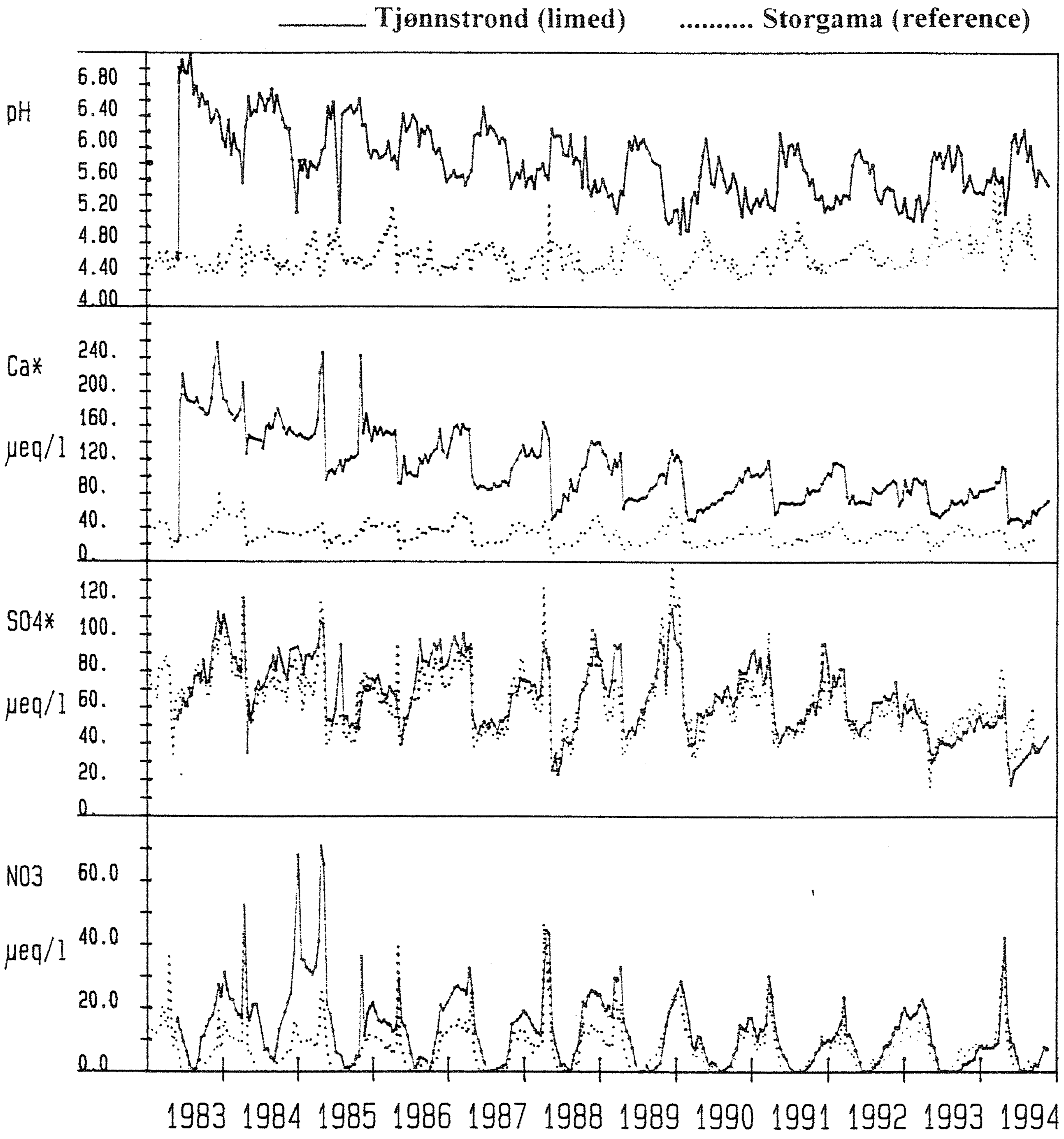
Pond/species		1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994
Ø. Tj.												
	brown		1.06		1.01	1.12	0.95	1.19			1.06	1.03
	brook	1.14	1.40		0.99	1.18	1.02		1.34			
N. Tj.												
	brown	1.05	0.87		0.99	1.03	1.00	1.13	1.03		1.07	1.03
	brook	1.22							1.10			



Southern Norway






Tjønnstrond (limed)
Storgama (reference)
pH
6.80
6.40
6.00
5.60
5.20
4.80
4.40
4.00
Ca*
µeq/l
240.
200.
160.
120.
80.
40.
0.
SO4*
µeq/l
120.
100.
80.
60.
40.
20.
0.
NO3
µeq/l
60.0
40.0
20.0
0.0
1983
1984
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994

2a

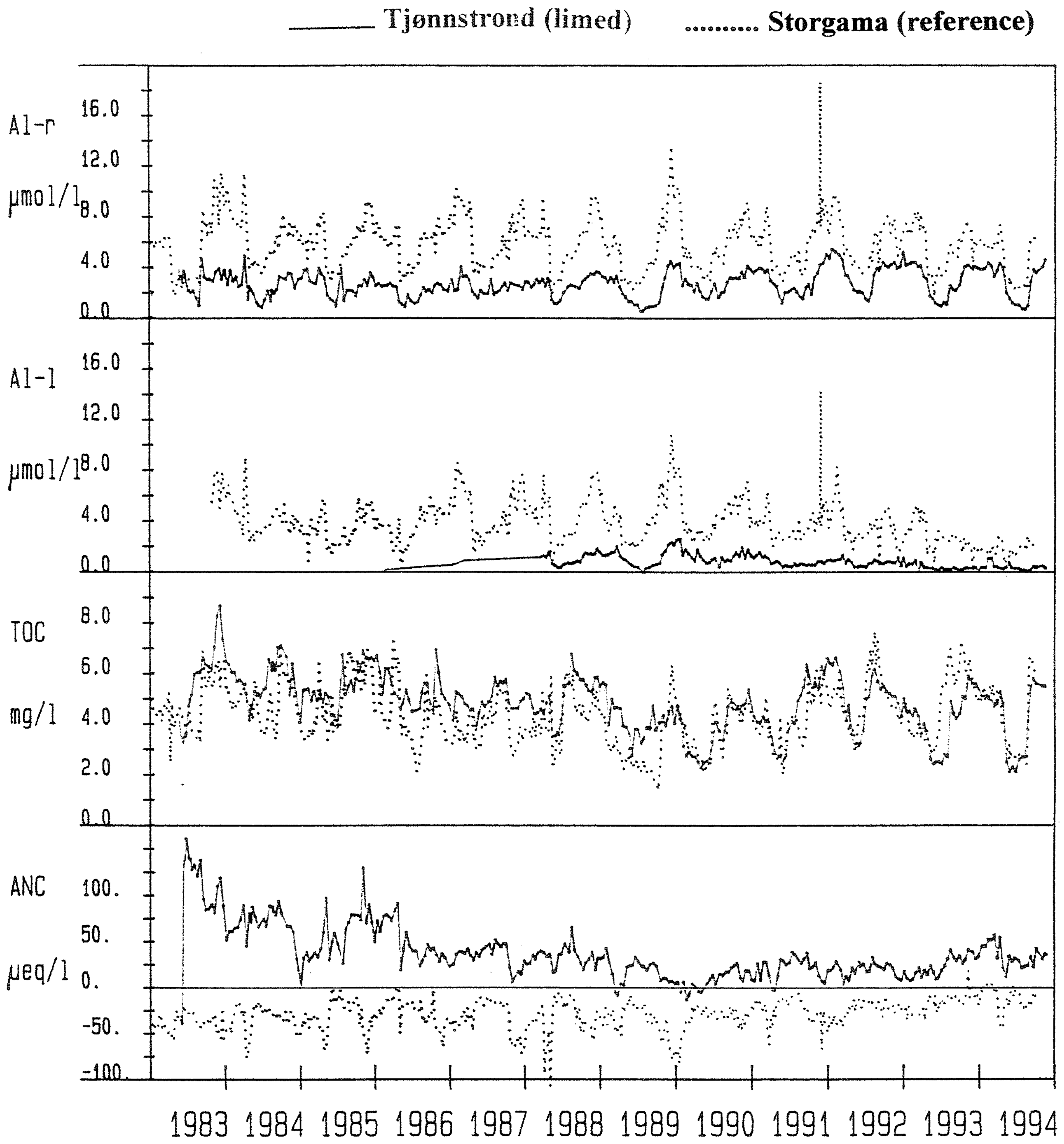
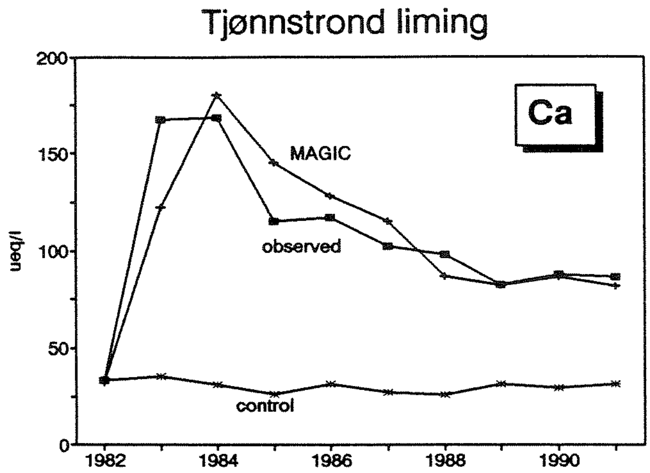
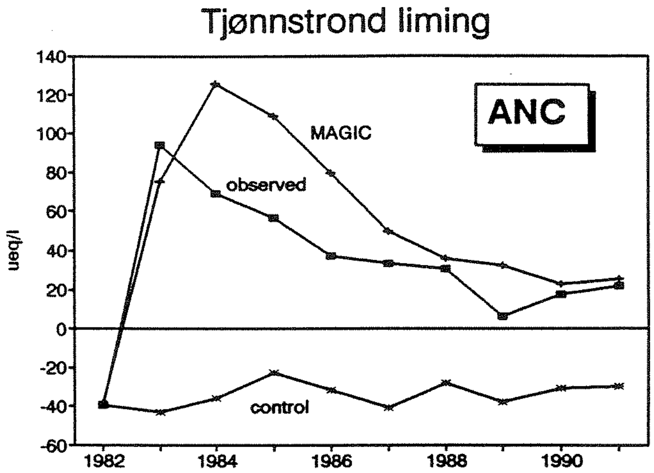

Tjønnstrond (limed)
Storgama (reference)
Al-r
µmol/l
16.0
12.0
8.0
4.0
0.0
Al-l
µmol/l
16.0
12.0
8.0
4.0
0.0
TOC
mg/l
8.0
6.0
4.0
2.0
0.0
ANC
µeq/l
100.
50.
0.
-50.
-100.
1983
1984
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994

Fig 2b


Tjønnstrond liming
Ca
MAGIC
observed
control
ueq/l
0
50
100
150
200
1982
1984
1986
1988
1990


Tjønnstrond liming
ANC
MAGIC
observed
control
ueq/l
-60
-40
-20
0
20
40
60
80
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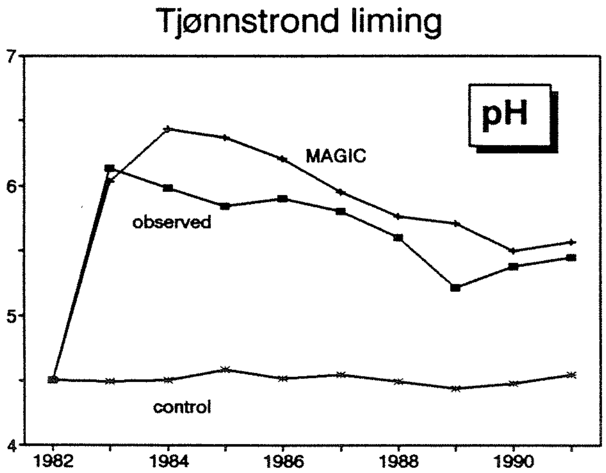
120
140
1982
1984
1986
1988
1990


Tjønnstrond liming
pH
MAGIC
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control
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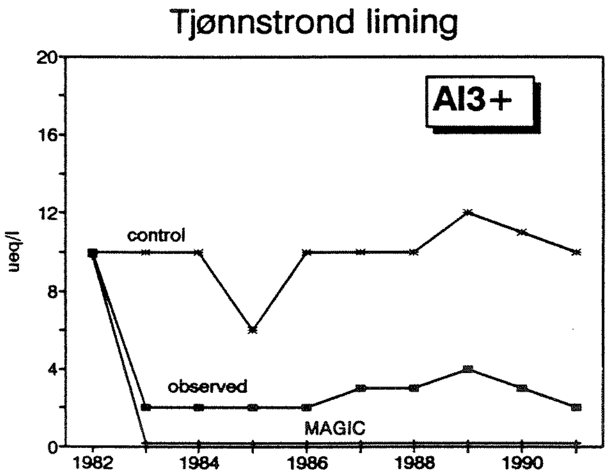
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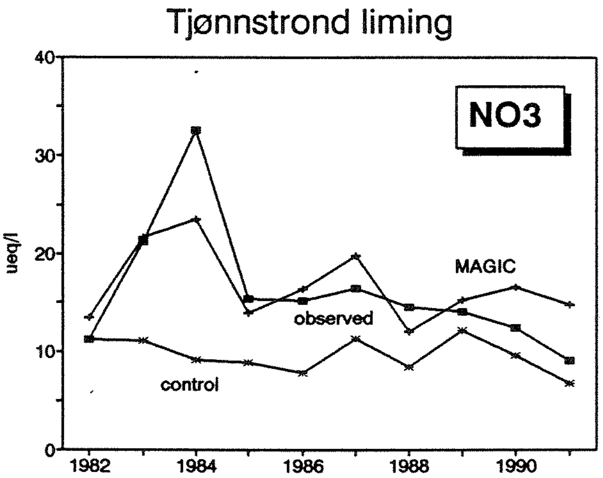
Tjønnstrond liming
NO3
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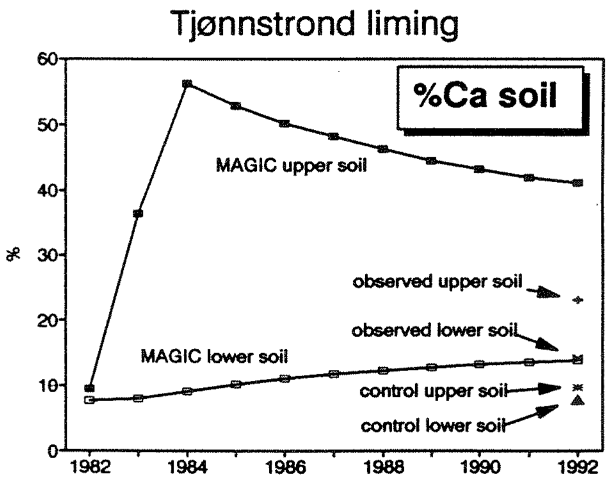
Tjønnstrond liming
%Ca soil
MAGIC upper soil
observed upper soil
observed lower soil
MAGIC lower soil
control upper soil
control lower soil
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1982
1984
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225

MIGRATION IN A TOXIC MIXING ZONE: EFFECTS ON BROWN TROUT (*Salmo trutta* L.)

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Abstract. Mixing of acid river water containing aluminium (pH 5.1, Al 345 $\mu g.l^{-1}$) with neutral water of a lake (pH 7.0, Al 73 $\mu g.l^{-1}$) resulted in water (pH 6.4, Al 245 $\mu g.l^{-1}$) with a pH (6.4) and Al concentration (245 $\mu g.l^{-1}$) expected to have low toxicity to fish on the basis of current Al toxicity models. However, under semi-field conditions the freshly mixed water (a few sec. after mixing) proved to be highly toxic to brown trout. The fish were exposed to the water at different places along a 30 m channel. At the beginning of the channel acid and neutral water were continuously mixed; the mixed water left the channel after 340 sec. The cells of the gills showed a highly increased rate of cell death by apoptosis and necrosis. Intercellular spaces were enlarged, and many leucocytes penetrated in these spaces. Mucus release was stimulated to depletion. Plasma chloride levels were hardly affected. There was a clear gradient in the deleterious effects on the fish along the channel. The fish at the beginning of the channel (about 12 sec. after mixing of the water), were severely affected, whereas the fish kept at the end of the channel (340 sec. after mixing) were only mildly affected.

In the natural situation fish will relatively quickly pass through a mixing zone. In our study we therefore focused on the effects on fish after a 60 min exposure to a mixing zone (5 sec after mixing), with subsequent recovery in a region downstream of the confluence and in neutral water with low Al. The recovery in the downstream area (at the end of the channel, i.e. 5 min after mixing) was clearly hampered when compared to the recovery in neutral water with low aluminium. Thus, a short exposure to the toxic mixing zone followed by a stay in water downstream of this zone, as may occur in nature, is detrimental to migrating trout. We conclude that freshly mixed acid and neutral water contain toxic components during the first seconds to minutes after mixing, that can not be explained by current models on aluminium toxicity.

Introduction

Fish mortality has been reported in areas where acid, Al-containing water mixes with neutral (limed water) even though the mixed medium typically has a pH above that known to produce toxic aluminium (Al) species (>pH 5.5; Muniz and Leivestad, 1980; Baker and Schofield, 1982; Howells et al., 1983, Verbost et al. 1992). In field experiments with Atlantic salmon and brown trout, higher mortality has been observed in the mixing zone (0-20 sec after mixing of water of an acid inlet with that of a neutral lake) than in the acid inlet, which has been attributed to transient products of Al-polymerization (Rosseland et al., 1992; Poleo et al., 1994). In this study we aimed to gain more insight in the toxic effects of such mixing zones on brown trout by electron microscopy of the gills in combination with measurements of plasma Cl⁻ levels and blood haematocrit. In an artificial channel neutral water and acid water, coming from two lakes, were mixed and led through the channel with a maximum water residence time of 340 sec. Brown trout were exposed for up to 72 h to the mixed water at different sites along the channel.

In addition to the long term exposure experiments intended to demonstrate the toxicity of the mixing zone, we studied a more natural situation where the fish relatively quickly pass through the toxic mixing zone. The fish are known to try to escape from toxic mixing zones if they can (Åtland and Barlaup, 1995). This field study focused on the effects of a relatively short exposure (60 min) of brown trout to a toxic mixing zone, with and without subsequent recovery in a region down stream of the toxic zone and in neutral water with low Al.

Materials and methods

Fish. Brown trout (*Salmo trutta*), 5 to 14 g in weight (8 ± 2 g, n=80), were obtained from the Oslomarkas Fish Administration (OFA) hatchery near Oslo, Norway. Fish were transferred to the experimental site (1 h by road) and were kept in a large tank until being used in the experiment.

Experimental design. The mixing zone experiments were performed in a Y-shaped channel (Fig. 1) in the respective arms of which water was pumped from lake Nepptjern (pH 5.1, Al 345 $\mu g.l^{-1}$, Ca 20 $\mu mol.l^{-1}$) and lake Gørja (pH 7.0, Al 73 $\mu g.l^{-1}$, Ca 160 $\mu mol.l^{-1}$), located in the Nordmarka area north of Oslo. From the point of confluence (where thorough mixing was assured resulting in water of pH 6.4, Al 245 $\mu g.l^{-1}$, Ca 77 $\mu mol.l^{-1}$) to the end, the channel was 30.5 m long. The channel was 20 cm wide and 15 cm deep, the flow rate was around 9 $cm.sec^{-1}$ corresponding with 340 sec residence time of the water. Fish were kept in cages at various intervals along the channel and protected from direct light by covers. Control groups were put in cages in the two inlet arms in front of the mixing zone. Separate cages, with fish that were not sampled, were used for determining mortality.

For the recovery experiment fish were exposed to the toxic mixing zone (5 sec after mixing) for 60 min and subsequently moved to either the far end of the channel (in water aged for 340 min, cage W) or to separate black tanks with neutral, unmixed water (from lake Gφrja) which provided optimal recovery conditions. As controls for the exposure and the handling, fish were held for 60 min in the neutral and acid water inlets and cage W, and subsequently transferred to either cage W or a black tank with water from lake Gørja.

Experiments were conducted in June 1994.

Electron Microscopy. Gill samples were obtained from the third gill arch on the left side. Tissues were fixed in 3% glutaraldehyde buffered in sodium cacodylate (0.1 $mol.l^{-1}$, pH 7.3), and post-fixed in 1% osmium tetroxide in the same buffer. Ethanol-dehydrated tissues were embedded in Spurr's resin. Ultrathin sections, collected on 150 mesh copper grids, were contrasted with uranyl acetate and lead citrate. They were examined in a Jeol 100 CXII transmission electron microscope.

Analytical techniques. Total acid reactive Al (Al_r) was measured after acidifying untreated water samples to pH 1.0 (HCl) for at least 24 h before the Barnes-Driscoll extraction-cation exchange method (Driscoll, 1984) was applied to measure Al.

Blood from samples collected from the caudal vessels after cutting the tails was partly used for determination of haematocrit (heparinized capillaries were filled, centrifuged and read). The other part was centrifuged in heparinized eppendorfs and plasma transferred to clean tubes. Plasma chloride was determined in the field (with a chloride titrator) and checked, with similar results in the laboratory (automated colorimetric method according to Zall et al., 1956).

Results

Plasma chloride and blood haematocrit

In fish from cage Ne, receiving water from the acid inlet from Lake Nepptjern, there was a progressive decrease in plasma Cl^-, apparent already after 1 h. All the other groups showed no significant changes in plasma Cl^- during the long exposure experiment except for group E (5 sec after mixing) after 24 h (Table 1).

Haematocrit increased in fish held in acid water for 24 h (cage Ne). In the recovery experiment fish were placed for 1 h in the toxic mixing zone (cage E), the end of the mixing channel (cage W), the neutral (Gϕ) or acid (Ne) inlet. Subsequently they were transferred to either cage W or to separate tanks with neutral water (GϕT) for 24 h. There was no

Table 1

Top: Effects on plasma Cl^- and haematocrit of brown trout of exposure for 1 h or 24 h to neutral, unmixed water with low Al (Gø; neutral inlet of channel), to acid water with high Al (Ne; acid inlet of channel), to the confluence of both water types (E; beginning of channel, 5 sec after mixing), or to mixed water 340 sec after mixing (W; end of channel).

Bottom: Effects on plasma Cl^- and haematocrit of recovery for 24 h (after 1 h exposure to water of the mixing zone, E) in tanks with neutral water from Lake Gørja (GøT) or to mixed water at the end of the channel (W).

	Gϕ	Ne	E	W
plasma Cl^- 1 h	121.0 ± 1.9	$114.4 \pm 0.7^*$	119.8 ± 0.9	122.2 ± 1.0
plasma Cl^- 24 h	126.5 ± 3.2	$99.0 \pm 1.6^*$	$114.2 \pm 3.5^*$	125.0 ± 4.1
haematocrit 1 h	37.3 ± 1.3	42.2 ± 1.9	39.3 ± 2.2	37.3 ± 1.5
haematocrit 24 h	42.8 ± 2.2	$60.6 \pm 1.9^*$	46.0 ± 3.3	37.8 ± 1.4
plasma Cl^-				
24 h recov. in GϕT	122.9 ± 3.0	116.9 ± 3.2	128.9 ± 2.7	125.9 ± 2.9
24 h recov. in W	113.9 ± 4.9	118.6 ± 3.1	$117.3 \pm 4.3^\#$	$114.1 \pm 4.1^\#$
haematocrit				
24 h recov. in GϕT	36.0 ± 2.2	37.3 ± 1.5	34.2 ± 1.3	33.5 ± 3.8
24 h recov. in W	38.8 ± 0.9	34.3 ± 2.2	36.8 ± 1.9	34.2 ± 2.7

* : significantly different from 'Gϕ group'
\# : significantly different from '24 h recov. in GϕT group'
n = 6, means ± SEM

mortality in the recovery experiments. Fish exposed to cage E restored their plasma Cl^- levels well in GϕT but not in cage W. Fish exposed to cage W maintained their plasma Cl^- in GϕT but showed a significant drop in cage W. Control fish kept in cage Gϕ reacted similarly to the W group but the decrease in Cl^- was just not significant. Fish kept in cage Nc for 60 min maintained their low plasma Cl^- levels in cage W and did not recover very well in GϕT (neither after 72 h, results not shown) in contrast to the Cl^- levels of the other groups. In the recovery experiment there were no significant differences in haematocrit between the different groups.

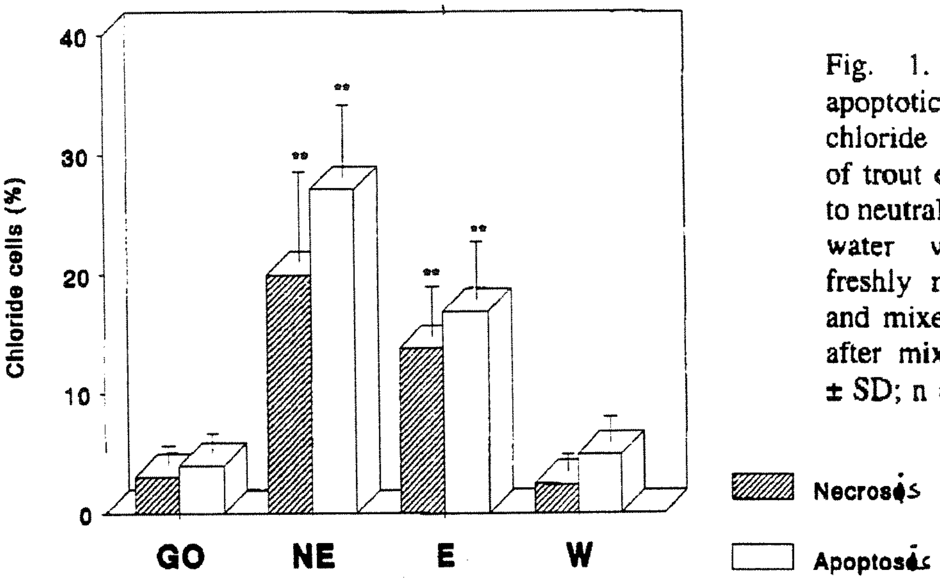

Fig. 1. Percentage of apoptotic and necrotic chloride cells in the gills of trout exposed for 24 h to neutral water (Gø), acid water with Al (NE), freshly mixed water (E) and mixed water 340 sec after mixing (W); means ± SD; n = 6.

Electron microscopy of the gills.

In fish exposed for 24 h to water from lake Gørja (cape Gø) the gills showed the normal ultrastructure known for brown trout, and no differences were observed with fish sampled at the hatchery (results not shown). Only few chloride cells (branchial cells specialized for ion exchange) showed signs of degeneration by necrosis or apoptosis (necrosis: accidental cell death, characterized by rupture of membranes and swelling of cell compartments; apoptosis: physiologically controlled cell death, characterized by cellular shrinkage and densification of nuclei, mitochondria and cytoplasm; Wendelaar Bonga et al., 1990). However, in fish from acid water (NE) and from the mixing zone (E) Al deposits on the branchial filaments and severe damage of the branchial epithelium were found. After 24 h the percentage of necrotic and apoptotic chloride cells was significantly increased (Fig. 1; $p<0.01$) when compared to the fish from water of lake Gørja. Also many respiratory cells, which form the epithelium covering the respiratory lamellae, showed highly increased percentages of necrotic and apoptotic cells. The intercellular spaces of the branchial epithelia were enlarged in many places, and many leucocytes (many macrophages, lymphocytes and some neutrophilic granulocytes) had left the blood and penetrated into these spaces. In mixed water 340 sec after mixing (W), hardly any Al deposits nor substantial damage were observed, and the percentages of necrotic and apoptotic chloride cells were not different from control levels (Fig. 1). After 1 h of exposure, the branchial damage of groups NE and E already was substantial, and hardly less than after 24 h. The percentage of necrotic cells was similar, although the percentage of apoptotic cells was 30-40% of that observed after 24 h in these groups. Al deposits were as dense as after 24 h, and enlargement of intercellular spaces and presence of leucocytes in these spaces were hardly less than after 24 h.

After 24 h recovery following 1 h of exposure to freshly mixed water (E), the strucutre of the branchial epithelium was substantially improved in fish that recovered in neutral lake Gørja water, and slightly improved in fish that recovered in cage W. Improvement was observed for all ultrastructural parameters mentioned.

Discussion

Our results show that freshly mixed acid and neutral waters are toxic to brown trout especially during the first minutes after mixing and this toxic effect can not be explained on the basis of current models on Al toxicity that predict no toxic effect of the metal above pH 6. The acidification was very mild in the mixed water (pH 6.4) compared to that in the acid inlet (pH 5.1). The reduction in plasma Cl^- levels is more drastic in fish kept in the acid inlet (cage Ne) than in the first meter of the mixing zone (cage E). However, fish in cages further downstream experienced the same pH as fish in cage E but did not show any reduction in plasma Cl^-. This observation and the microscopical results show that toxicity decreases rapidly with time after mixing. The EM analysis clearly showed that the structural damage to the gill epithelium (necrosis and apoptosis of chloride cells) and infiltration of leucocytes in fish kept in cage E (beginning of the mixing zone) were comparable to that seen in fish from the acid inlet (Ne).

When the fish were kept in the toxic mixing zone (cage E) and then moved to a more down stream area (cage W), thus mimicking a more natural situation of a short encounter with the toxic mixing zone, there was clearly a reduced capacity to restore the damaged gill tissue and plasma Cl^- levels when compared to fish recovering in neutral, unmixed water (GøT).

The mechanism for the toxicity of the mixing zone is unknown at present. In previous articles of our group reporting on the mixing zone phenomenon a causal relationship between the toxicity and the process of Al-polymerization has been suggested (Rosseland et al., 1992; Salbu et al., 1995). The proposed mechanism was a combination of suffocation by Al-precipitates on the gills and loss of plasma Na^+ and Cl^- by the acidification (Poleo et al., 1994). In this study we found further evidence for toxic effects of mixing zones of neutral and acid Al-containing waters that may have negative effects on the survival of migrating trout. It is likely that young trout on their seaward migration in spring will reach the ocean in a weakened state when they have to pass toxic mixing zones in a river system.

Acknowledgements

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AL:PE PROJECTS.

AL:PE 1. Acidification of Mountain Lakes: Palaeolimnology and Ecology

AL:PE 2. Remote Mountain Lakes as Indicators of Air Pollution and Climate Change

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LAK04

Abstract. AL:PE 1 was a 2 year project launched in April 1991 as a joint project between institutions in Italy, France, United Kingdom and Norway. The research programme covered the four subject areas "Lake sediments and diatoms", "Fish", "Invertebrates", and "Water chemistry". Main aim of the project was to understand the ecosystems of remote mountain lakes and the response of these lakes to varying levels of acid deposition. Some of the most interesting conclusions from the project concern the similarities of the sites in these different mountain regions of Europe. The similarities are obvious at all levels, water chemistry, palaeolimnology, invertebrates and fish. This reflects a similiar response of the biological communities to a specific chemical environment in these high altitude areas, and these lakes can thus act as indicators of future environmental changes. These ideas are being further developed in AL:PE 2. AL:PE 2, a 2,5 year project, was launched in January 1993. This project is a geographical extension and enlargement of AL:PE 1, assessing a wider range of long range transported air pollutants, including bioaccumulaiton of trace metals and organic micropollutants. Both AL:PE 1 and Al:PE 2 receives financial support from the Commission of the European Communities.

Key words: high mountain lakes, water chemistry, invertebrates, zooplankton, fish, sediments, diatoms, palaeolimnology.

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INTERACTION OF ACID RAIN AND GLOBAL CHANGES: EFFECTS ON TERRESTRIAL AND AQUATIC ECOSYSTEMS

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Abstract. Both acid deposition and changes in the global atmosphere and climate affect terrestrial and aquatic ecosystems. In the atmosphere sulphate aerosols tend to increase haze, altering the global radiation balance. Increased nitrogen deposition to N-limited systems such as boreal forests results in increased growth and increased sequestration of atmospheric CO_2, slowing the increase in CO_2 levels in the atmosphere. Future reduction in S and N emissions may result in a trade-off -- better with respect to some effects of acid deposition and greenhouse warming, but worse with respect to others.

Global warming may cause the incidence and severity of drought to increase. Mineralisation of N and oxidation of organic S compounds release pulses of SO_4, acid and Al to surface waters. Effects in lakes may include reduced deep water refugia for cold stenotherms, lower nutrient concentrations, and greater penetration of harmful UV radiation. Longer water renewal times cause declines in SO_4 and NO_3, due to increased *in situ* removal, but increases in base cations. The net result is increased internal alkalinity production.

In areas characterised by cold winters, global warming may result in a major shift in hydrologic cycle, with snowmelt episodes occurring during the winter rather than the typical pattern of accumulation in the winter and melting in the spring. Increased storm frequency predicted for the future will cause increased frequency and severity of sea salt episodes in coastal regions.

Predicting the interactions of regional and global environmental factors in the coming decades poses new challenges to scientists, managers and policy-makers.

1. Introduction

Interest in acid rain is now increasingly focused on the future. To what levels should emission of acidifying compounds be reduced, and over what period of time with the responses occur? Major changes in the global atmosphere and the resulting changes in global climate will occur at the same time as these future changes in acid deposition. Terrestrial and aquatic ecosystems will thus be subject to simultaneous change in several important environmental variables. In addition other regional and global air pollutants such as toxic metals and organochlorines may play an increasingly important role.

Here we present examples of the interactive effects of acid deposition and global change (1) in the atmosphere, (2) in terrestrial ecosystems, (3) at the terrestrial-aquatic interface, and (4) in aquatic ecosystems. While examples come largely from studies in North America and Europe, such interactive effects can be expected over the rest of the world as well.

2. Emissions of air pollutants

International agreements to reduce the emissions of sulphur compounds to the atmosphere have achieved substantial reductions in deposition in both North America and Europe, and the prognosis is for further reductions. The S pollution era reached its maximum in the 1970's and 1980's and is now on the wane (Figure 1). In contrast N emissions continue to increase (Figure 1), and binding international agreements for major reductions in N emissions have yet to be made.

Meanwhile in other parts of the world N and S emissions may increase by 3 to 4 -fold in industrialising and developing countries such as China (Galloway et al. 1994).

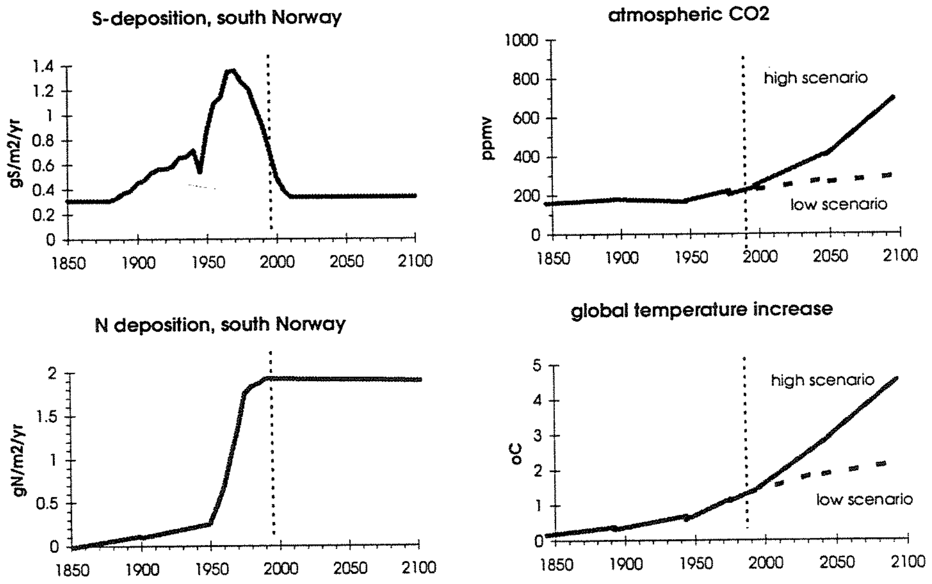

Figure 1. Historical and future trends in S and N deposition in southern Norway (as an example of region strongly affected by acidification) (left 2 panels), atmospheric CO_2 content (upper right panel), and global temperature increase (lower right panel). Sulfur deposition data are from Mylona (1993) with predictions based on the 1994 Oslo protocol. Historical N deposition data for southern Norway are lacking, but probably generally parallel European emissions of NOx; shown are emission estimates of NOx from 1950-85 (A. Semb, unpublished) scaled to measured deposition (wet and dry of oxidized and reduced N compounds) at Birkenes 1972-93 (SFT 1994), with future levels assumed constant. CO_2 and temperature data and predictions are from IPCC (1990). The CO_2 and temperature data predictions are for 2 scenarios of "business-as-usual" (high) and substantial reductions for greenhouse gases (low).

Emissions of other air pollutants are expected to lead to global change. Increasing CO_2, methane, chlorofluorocarbons (CFC's) and other gases from human activities will increase greenhouse warming, increase exposure to UVb radiation and induce a whole suite of climatic changes (Figure 1) (IPCC 1990). Many of these air pollutants affect ecosystems directly, and there will be interactive effects.

Emissions to the atmosphere of many toxic metals and organic substances continue to increase, and many toxins persist in the environment. Several toxic chemicals carried in the atmosphere such as lead, DDT, and toxaphene have been regulated in most first-world countries. For other toxins such as mercury and PCB's, however, re-emission from contaminated ecosystems has maintained elevated levels in deposition even in remote areas (Schindler et al. 1995a, Mackay and Wania 1995). In some third-world countries many of these toxicants are still produced and used. Reduction of many toxins in the atmosphere will be difficult to achieve for many decades to come.

3. Atmospheric interactions

Acidifying and greenhouse gases interact in the atmosphere. The S aerosol in the troposphere reflects solar radiation; S emissions thus tend to *decrease* the greenhouse effect by about one-third (Wigley 1989, Mitchell et al. 1995).

Emissions of N compounds also play a role in the greenhouse effect. N_2O is a greenhouse gas, and is estimated to account for about 6% of the anthropogenic greenhouse gas emissions (IPCC 1990). Nitrogen oxide emissions also act indirectly in their role as precursors to tropospheric ozone formation, and ozone is a greenhouse gas. Nitrogen emissions thus tend to *increase* the greenhouse effect.

4. Terrestrial ecosystem effects

Global change is predicted to significantly affect terrestrial ecosystems, in particular the temperate and boreal forest ecosystems of northern Europe and eastern North America that today are impacted by acid deposition (Boer et al. 1990). The interaction between the N deposition and the increased atmospheric CO_2 levels is central. Increased N deposition fertilises forest and marine ecosystems. Primary production increases in these environments and this results in increased sequestering of CO_2, slowing the build-up of greenhouse gases in the atmosphere (Kauppi et al. 1992, Schindler and Bayley 1993). The increased CO_2 also tends to increase primary production and thus demand for N by vegetation, leaving less available for leaching. Global change can thus slow the tendency of ecosystems to reach N saturation, a situation manifest by increased leaching of inorganic nitrogen from below the rooting zone (Aber et al. 1989), caused by chronic N deposition.

Future increases in temperature will further promote primary production as long as nutrients such as N and water are in sufficient supply (Pastor and Post 1988). A longer growing season with generally higher temperatures should result in increased growth in temperate and boreal forests.

Nitrogen supply appears to be one human-altered factor determining whether boreal ecosystems will be a net source or sink of CO_2 in the future (Rastetter et al. 1991). Nitrogen can be supplied externally through N deposition or released internally from the vast stores of N tied up in soil organic matter in most forest soils. Increased temperature can speed up mineralization and release N for potential plant growth. Experiments *in situ* with increased CO_2 and temperature in tussock tundra ecosystems show that with increased CO_2 alone, net carbon sequestration showed only a transient 1-2 year response, but with a combination of increased CO_2 and +4 ^{o}C temperature net carbon sequestration persisted (Oechel et al. 1994).

5. Terrestrial-aquatic interface

The combined effects of acid deposition and global change on terrestrial ecosystems cause changes in the quantity and quality of leachate, groundwater and streams. Impacts on surface waters thus begin in the terrestrial catchment.

Although external supply of N through acid deposition in the first instance fertilises and increases forest growth, chronic and excessive N deposition can be a contributing factor in forest decline (Ulrich 1989). Adverse effects can be direct by wet and dry deposition of N compounds on foliage, and indirect via soil acidification and nutrient imbalances. N deposition to coniferous forests in excess of about 10 kgN/ha/yr leads to increased leaching of nitrate (Dise and Wright 1995). In acid soils increased leaching of nitrate is often accompanied by acid cations such as H+ and inorganic Al, contributing to surface water acidification (Matzner 1989, Reynolds et al. 1992).

Global change exacerbates N saturation if increased temperatures lead to increased mineralization of soil organic matter with release of N in excess of that taken up by plants or immobilised in the soil. Such pulses of NO_3 can occur in the short term, as demonstrated by the now classic acid, Al-rich NO_3 pulses in soil leachate following warm and dry summers at Solling, central Germany (Matzner 1989). The effects of drought and increased temperature on NO_3 leaching to streams can also persist for several years, as was the case at Plynlimon, Wales, in the mid-1980's (Reynolds et al. 1992) (Figure 2). Increased loss of NO_3 can also come during unusually warm winters, such as the winters of 1989 and 1990 in Norway, although in this case the major effects appears to be a shift in the seasonal pattern, rather than an absolute increase in NO_3 release from the catchment (Lydersen 1995) (Figure 3).

It is as yet unknown whether a long-term increase in temperature due to global change will result in widespread increase in N leaching due to increased mineralization of soil organic matter. And it is also unknown whether increased leaching of N will be limited to those ecosystems that receive significant N deposition. Certainly the organic soils typical of the boreal region contain N stores equivalent to many decades of N

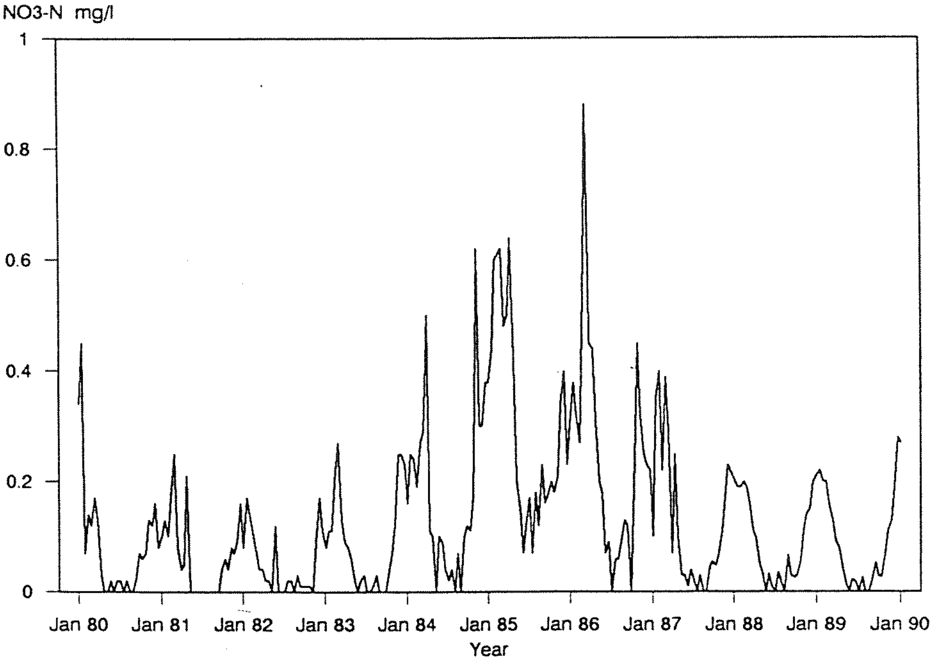

Figure 2. Nitrate concentrations in streamwater at C2 catchment at Plynlimon, Wales, UK. Concentrations were high for several years following the dry summer of 1984 (from Reynolds et al. 1992).

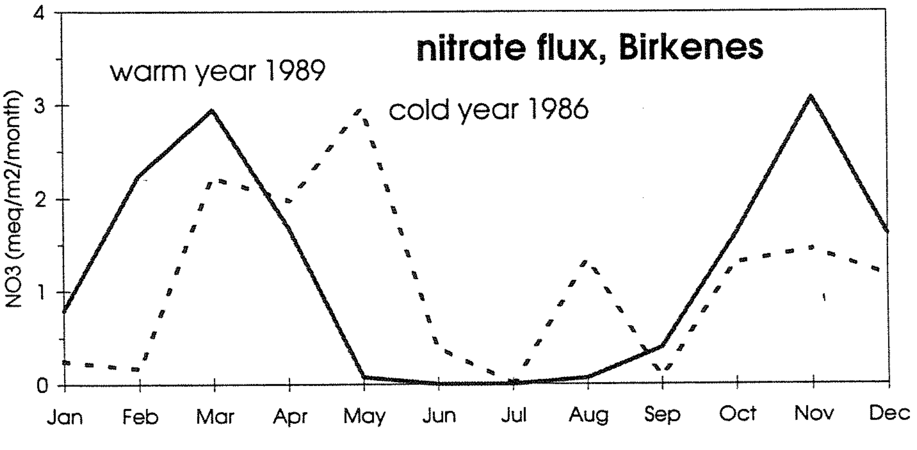

Figure 3. Monthly NO_3 flux in streamwater at Birkenes, Norway, for 1986 a year with relatively cold winter, and 1989 a year with relatively warm winter. During cold winters precipitation comes as snow, accumulates and melts in the spring; a large portion of the annual NO_3 transport comes with snowmelt. during warm winters, on the other hand, precipitation is often as rain and snow accumulation is minor; under these conditions NO_3 is transported during the winter (data from Lydersen 1995).

deposition, and loss of only a small fraction can cause significant effects on soils and waters (Hessen and Wright 1993). These questions are the focus of the ongoing CLIMEX project (Climate change experiment) in which 2 whole headwater catchments are being experimentally manipulated with increased CO_2 and temperature (Jenkins et al. 1993). Clearly much more is to be learned about the interactive effects of acid deposition and climate change on the N and C cycles in terrestrial ecosystems before the full impact on the receiving aquatic ecosystems can be assessed.

Sulphate has long been recognised as the major culprit in serving as mobile strong acid anion and vehicle for acid and inorganic Al in soil solution, runoff and surface waters. Short-term climatic events strongly affect the SO_4 concentrations in soil water and surface waters. Pulses of acidic, SO_4-rich water following drought have been reported from many acidified sites in both Europe and North America (Christophersen and Wright 1981, Hultberg 1985, LaZerte 1993, Bayley et al. 1992). These pulses are evidently caused by oxidation of previously-reduced S whose ultimate origin is atmospheric deposition. Sites which receive higher S deposition produce greater acid pulses in streamflow following drought (Figure 4).

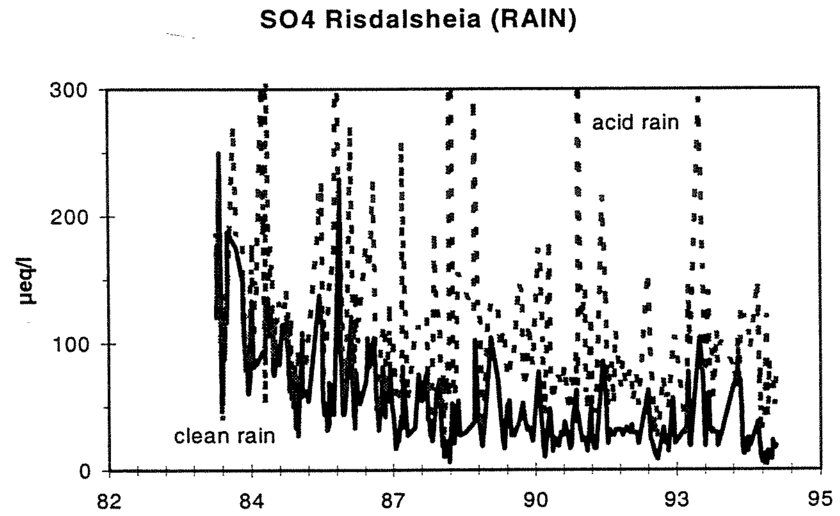

Figure 4. Sulfate concentrations in runoff from 2 experimental catchments at Risdalsheia, southernmost Norway (RAIN project). One receives ambient acid rain (upper panel) while the other experimentally "cleaned" rain (lower panel). Pulses of SO_4 occur during snowmelt and following drought (data from Wright et al. 1993).

For both N and S the store in organic-rich soils typical of temperate, boreal and arctic regions is equivalent to decades supply of strong acid anions. Acid exclusion experiments with roofs indicate that removal of acid deposition alone causes rapid and complete decline in both SO_4 and NO_3 in runoff and leachate (Wright et al. 1993, Beier et al. 1993, Bishop and Hultberg 1995, Boxman et al. 1995), and that there is little mobilisation from the large pool stored in soil organic matter (Beier et al. In review). The question is whether the organic N and S will be mobilised by the temperature and moisture changes likely in the future.

Chloride is the third mobile strong acid anion potentially affected by future global change. Increased frequency of storms may be one consequence of global warming and the need to transport larger quantities of heat from low to high latitudes (Bergström 1993). In coastal areas storms cause short-term high deposition of seasalts, either as aerosols or in precipitation. In areas with acid soils the incoming base cations can be exchanged for acid cations, and the results are acid episodes in streams and lakes (Norton et al. 1987, Hindar et al. 1994).

In areas such as the Experimental Lakes Area (ELA) in northwestern Ontario, Canada, where climatic warming causes evapotranspiration to exceed precipitation, streamflow declines. At the ELA small first-order streams that flowed continuously throughout the ice-free season in the 1970's were dry for up to 150 days in the late 1980's, when air temperatures were about 2 ^{o}C warmer and precipitation had declined by about 30% (Schindler et al. 1995b). These streams had decreased losses of strong acid anions, decreased weathering of base cations, and decreased losses of DOC, silica and nutrients. The ratio of strong acid anions to base cations increased with net acidification the result (Schindler et al. 1995b) (Figure 5). Thus climatic disruptions appear to aggravate acidification caused by acid deposition.

6. Aquatic ecosystems

In lakes and streams the effects of climatic warming modify the effects of acidification in several ways. Only few such interactions have yet been examined in the field. Decreased precipitation and streamflow cause increased water residence in lakes (Figure 5). Longer water residence times generally mean higher concentrations of conservative chemicals, and longer response times following changes in pollutant inputs. In-lake removal of SO_4 and NO_3 will increase (Kelly et al. 1987, Baker et al. 1988), as will retention of base cations (Schindler et al. 1995b). Such changes at ELA have caused increasing alkalinity in lakes (Figure 5). Climatic warming and drought have thus caused increased acidity in streams and decreased acidity in lakes at ELA.

The concentration of phosphorus in lakes at ELA has declined due to reduced inputs via streams, whereas N has increased (Schindler et al. 1995b) As expected, chlorophyll trends have followed P, indicating that climatic warming and drought will aggravate the oligotrophication of lakes (Schindler 1994).

There are also positive feedbacks of DOC losses on the DOC decline. Photolytic degradation of DOC appears to be the most important removal mechanism for DOC in lakes (Molot and Dillon, in press). This would be expected to increase as lakes become clearer. Both Dillon and Molot (in press) and Schindler et al. (in press) found that the residence time for DOC decreases in acidified lakes.

Declining DOC concentrations allow the penetration of UV light to increase, particularly in lakes with DOC concentrations below 300 μM. At low DOC concentrations, a decline of 10% in DOC will cause a many-fold greater increase in the UVb exposure of aquatic organisms than all of the changes expected to the stratospheric ozone layer combined. About 20% of the boreal lakes in Ontario and >80% of the lakes of Norway have low DOC levels. Alpine and arctic lakes are particularly vulnerable.

Other airborne pollutants may add additional stresses to aquatic communities in the years ahead. In particular, lipid-soluble substances such as organochlorines and mercury are of concern. While these are deposited in ecosystems at extremely low rates, bioaccumulation in food chains can reach factors of 10^7 to 10^8 (Cabana and Rasmussen 1994, Kidd et al. 1995). Both acidification and warming affect bioaccumulation, as is the case for mercury (Ramlal et al. 1985). So far, the interactions between acidification, climatic warming and other toxic pollutants are poorly documented.

7. Discussion

As a result of 10-20 years of international negotiations on reductions of sulphur emission to the atmosphere, the "sulphur era" is now on the wane in eastern North America and Europe. Acidified terrestrial and aquatic ecosystems already show signs of recovery in some areas. The ecosystem response to the long-term decline in S deposition will be complex, exhibiting both time lags and complex interactions with other perturbations.

At the same time these ecosystems will be subjected to continued and increasing deposition of N compounds. It has long been feared that improvements gained by reductions in S emissions may be offset by continued or even increased deposition of N compounds (NAS 1981).

As ecosystems respond to changes in acid deposition over the next several decades, the effects of global change will assume increasing importance. Warming, changed hydrological regimes, changed frequency of extreme climatic episodes, and increased CO_2 levels will all affect these same ecosystems. Many of these driving variables will impact the N cycle in terrestrial and receiving aquatic ecosystems. The critical load for N to terrestrial ecosystems may depend on the climate regime to which the ecosystem is exposed. Ongoing negotiations to reduce N emissions to the atmosphere will have to consider the possible implications of other concurrent long-term changes in environmental driving variables. The nature and intensity of the interactions is at present largely unknown.

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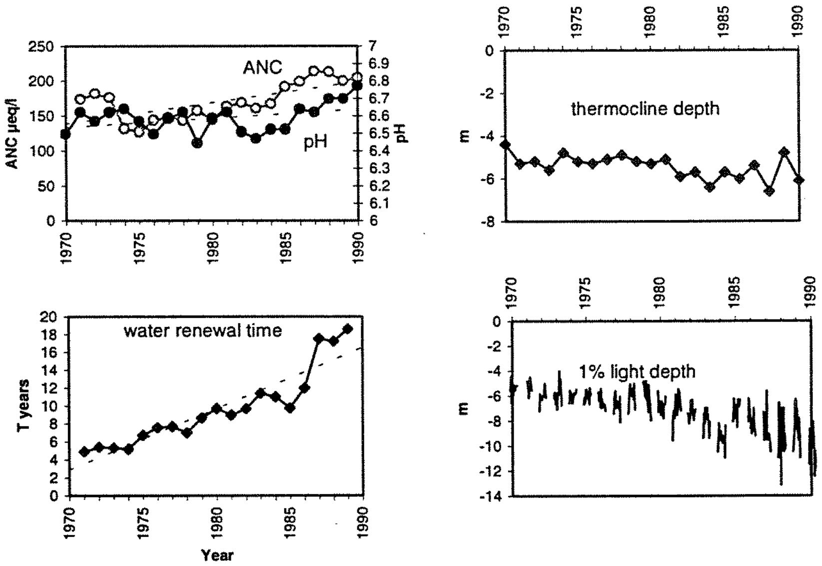

Figure 5. The changes caused by a 20-year period of climatic warming and drought in lake 239 at the Experimental Lakes Area (ELA), northwestern Ontario, Canada. Upper left panel: pH and acid neutralising capacity (ANC=BC-SAA). Changes are due to the relative differences in processes that produce and consume strong acid anions and base cations in catchments and lake sediments. Lower left panel: water residence time. Upper right panel: thermocline depth. Lower right panel: euphotic zone depth (assumed to be the depth of penetration of 1% of surface light) Similar changes have been observed in other small lakes (from Schindler et al. 1995b).

Many of these same interactive effects have been reported by Psenner and Schmidt (1992) at 2 alpine lakes in Austria.

Effects on seepage lakes, which receive most of their buffering from base cations in groundwater, can be even more complex. Webster et al. (1990, 1995) found that over several years of drought in northern Wisconsin, seepage lakes high in a poorly buffered aquifer became more acidic due to declining inputs of buffering groundwater, while those lower in the same aquifer became more alkaline because of increased contact time between inflowing groundwater and base-rich substrates.

Many interactions between acidification and climatic warming are mediated by dissolved organic carbon (DOC). Climatic warming and drought caused DOC in lakes in the ELA to decline by 20-25%. Acidification caused further declines up to 90% in DOC (Scully and Lean 1994). As a result the lakes became clearer, thermoclines and euphotic zones deepened (Figure 5), and summer habitat for cold stenotherms shrunk. Many of these species of cold stenotherms are sensitive to acidification, such as lake trout (*Salvelinus namaycush*) and the opossum shrimp (*Mysis relicta*).

Research and policy over the next few decades must take into account these interactions. For example reduced S emissions will lead to lower concentrations of aerosols in the atmosphere which results in increased greenhouse warming. Reduced N emissions may mean lower CO_2 uptake by forests and thus increased greenhouse warming. Increased greenhouse warming may lead to more frequent acid pulses and delayed recovery from acidification. Regional and global pollution by trace contaminants come on top of the driving variables associated with acid deposition and global change. Predicting the interactions of regional and global environmental factors in the coming decades thus poses new challenges to scientists, managers and policy-makers.

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REVERSIBILITY OF ACIDIFICATION DURING 10-YEAR5 OF EXPERIMENTALLY-REDUCED ACID DEPOSITION TO A WHOLE CAICHMENT IN SOUTHERNMOST NORWAY (RAIN PROJECT)

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Abstract. At Risdalsheia, an acidified area in southern Norway, a catchment-scale acid-exclusion experiment was conducted for 11 years (June 1984 - May 1994) as part of the RAIN project (Reversing Acidification In Norway). Acid precipitation was intercepted by means of a 1200-m^2 transparent roof, treated by ion-exchange, seasalts readded, and reapplied as clean rain beneath the roof. The chemical composition of runoff showed major changes. Concentrations of sulfate decreased from about 111 μeq/l in 1984-85 to 30 μeq/l in 1993-94 and nitrate from about 33 μeq/l to 2 μeq/l. Base cations decreased and alkalinity increased over the 10-year period from -88 to -8 μeq/l to compensate for this climate in strong-acid anions. Much of the alkalinity change is due to the increased role of organic anions. The results fit an empirical nomograph relating alkalinity, base cations and strong-acid anions; F-factor is 0.15. They also fit an empirical nomograph relating alkalinity, H^+, and TOC. The acid-exclusion experiment provides the first catchment-scale evidence for the reversibility of nitrogen saturation. The results for the acid-exclusion experiment of the RAIN project corroborate field observations of changes in surface water chemistry in response to reduced acid deposition as well as process-oriented, conceptual acidification models. The roofed catchments at Risdalsheia arc the longest-continuously running whole-ecosystem manipulations of this type. The enclosures have now been converted to accommodate whole-ecosystem experiments with climate change (CLIMEX).

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Key words:RAIN-project, catchment experiment, reversibility, acidification.

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