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# Long-term changes in acidification and recovery at nine calibrated catchments in Norway, Sweden and Finland

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## Abstract

International agreements to reduce the emissions of acidifying pollutants have resulted in major changes in deposition of sulphur and nitrogen in southern Scandinavia over the past 25 years. Long-term monitoring of deposition and run-off chemistry over the past 12–25 years at nine small calibrated catchments in Finland, Norway and Sweden provide the basis for analysis of trends with special attention to recovery in response to decreased sulphur and nitrogen deposition in the 1980s and 1990s. During the 1980s and 1990s sulphate deposition in the region decreased by 30 to 60%, whereas inorganic nitrogen deposition showed very little change until the mid-1990s. Deposition of non-marine base cations (especially calcium) declined in the 1990s most markedly in southern Finland. Run-off response to these changes in deposition has been rapid and clear at the nine catchments. Sulphate and base cations (mostly calcium) concentrations declined and acid neutralising capacity increased. Occasional years with unusually high inputs of sea-salt confound the general trends. Trends at all the catchments show the same general picture as that from small lakes in Scandinavia and in acid-sensitive waters elsewhere in Europe.

**Keywords:** acidification, recovery, Scandinavia, catchment, trend analysis

## Introduction

For more than 100 years, acid deposition resulting in acidification of freshwaters and damage to fish populations has been a major environmental problem in southern Scandinavia. Research aimed at discovering the causes of acidification and the terrestrial and aquatic processes governing the rates of acidification and recovery has made use of small calibrated catchments (e.g. Moldan and Cerný, 1994). Careful measurements of fluxes of water and chemical components into and out of catchments reveals processes in soils and water controlling acidification and information on dose-response relationships. The strength of such small catchments in environmental research has been shown by such work as the pioneering investigations at, for example, the Hubbard Brook Experimental Forest (Likens *et al.*, 1977).

Calibrated catchments have become integral parts of acidification monitoring programmes in Finland, Norway and Sweden. These national programmes are carried out under the auspices of the Finnish Environment Institute, the Norwegian State Pollution Control Authority and the Swedish Environmental Protection Agency. They also provide input data for international networks such as the International Co-operative Programme on Integrated Monitoring (ICP-IM), a programme of the United Nations Economic Commission for Europe's (UN-ECE) Convention on Long-Range Transboundary Air Pollution (LRTAP).

Systematic monitoring of inputs and outputs at small calibrated catchments in southern Scandinavia began in 1973–74 in Norway (three catchments), in 1981–1985 in Sweden (four catchments) and in 1988 in Finland (two catchments). Together, these nine catchments cover a large

geographic area and represent a diversity of natural physiographic regimes of precipitation, vegetation, soils and geology.

International agreements to reduce the emissions of acidifying pollutants (UN-ECE, 1994; UN-ECE, 1998; UN-ECE, 1999) have resulted in major changes in deposition of sulphur (S) and nitrogen (N) over the past 25 years in southern Scandinavia (Barrett *et al.*, 2000). These reductions are intended to stop the acidification trend and allow recovery from acidification in terrestrial and aquatic ecosystems. The long-term records from the nine calibrated catchments provide a robust dataset for evaluation of trends in recovery. Harmonised analysis and synthesis of the data has been undertaken as part of projects of the Nordic Council of Ministers and the European Union (RECOVER:2010) (Ferrier *et al.*, 2001), as well as the national programmes.

Here, trends in deposition and run-off chemistry at these nine calibrated catchments are investigated with special attention to the recovery in response to decreased S and N deposition during the 1980s and 1990s.

The work complements and adds to the work of Skjelkvåle *et al.* (2001) who conducted a similar analysis on small lakes in the same region. The lakes were sampled much less frequently (1–4 times per year) but data from many more sites (344) are available. The catchment data presented in this study are from more frequent sampling (usually weekly),

which allows calculation of input-output budgets and flow weighting of annual concentrations.

The Nordic data from calibrated catchments (this paper) and from small lakes (Skjelkvåle *et al.*, 2001) comprise part of a large European-wide assessment of trends in acidification and recovery. The European overview is given by Evans *et al.* (2001a), trends in S are given by Prechtel *et al.* (2001) and trends in N are given by Wright *et al.* (2001).

## Sites and methods

The data used in this work are from national monitoring programmes in Finland, Norway and Sweden (Johannessen, 1995; Forsius *et al.*, 1995; Wilander, 1998). The sampling and analytical methods are similar in the three countries. Site descriptions for the Norwegian catchments are from Lydersen (1994). Key catchment parameters are summarised in Table 1.

### THE SITES

#### Norway

The Birkenes catchment is located in southernmost Norway, about 15 km north of Kristiansand (Fig. 1). The catchment area is 0.41 km<sup>2</sup> and altitude ranges from 200–300 m.



Fig. 1. Map of southern Scandinavia showing locations of the nine calibrated catchments.

Table 1. Catchments characteristics

	Country	Latitude N	Longitude E	Altitude m.a.s.l.	Area (ha)	Precipitation(mm)	Runoff (mm)	Temperature (°C)
<b>Birkenes</b>	Norway	58°23′	8°15′	200-300	41	1530	1170	5.4
<b>Storgama</b>	Norway	59°01′	8°32′	580-690	60	1210	950	5.1
<b>Langtjern</b>	Norway	60°22′	9°39′	510-750	480	860	610	3
<b>Hietajärvi</b>	Finland	63°10′	30°43′	170-210	464	630	400	2
<b>Valkeakotinen</b>	Finland	61°14′	25°04′	150-190	30	650	200	3.1
<b>Gårdsjön F1</b>	Sweden	58°03′	12°01′	120-140	4	1100	550	6.3
<b>Lommabäcken Nedre</b>	Sweden	58°42′	14°38′	190-230	104	660	540	5.6
<b>Pipbäcken Nedre</b>	Sweden	57°03′	12°47′	80-170	93	1010	514	6
<b>Ringsmobäcken</b>	Sweden	58°59′	11°45′	180-250	112	780	320	5.4

	Forest/vegetation	Geology	Soil type	Mean soil depth (m)	Data periods	Key reference
<b>Birkenes</b>	Mixed coniferous	Granite	Podzols	0.4	1974-1999	Lydersen (1994)
<b>Storgama</b>	Individual trees, heather, moorgrass	Granite	Rankers and Podzols	0.32	1975-1999	Lydersen (1994)
<b>Langtjern</b>	Mixed coniferous	Gneiss	Podzols, bedrock outcrops	0.4	1974-1999	Lydersen (1994)
<b>Hietajärvi</b>	Pine/spruce	Granitoides	Podzols, Histosols	0.85	1988-1999	Forsius <i>et al.</i> , (1995),
<b>Valkeakotinen</b>	Pine/spruce/birch	Gneis	Dystric Cambi- sols and Histosols	1.5	1988-1999	Forsius <i>et al.</i> , (1995),
<b>Gårdsjön F1</b>	Spruce/pine	Gneissic granodiorite	Podzols	0.43	1981-1999	Moldan (1999)
<b>Lommabäcken Nedre</b>	Pine/spruce	Granite	Histosols, bedrock outcrops	0.02	1985-1999	Löfgren and Kvarnäs (1995)
<b>Pipbäcken Nedre</b>	Mixed coniferous deciduous forest	Gneiss, amphibolite	Histosols, Podzols	0.69	1985-1999	Löfgren and Kvarnäs (1995)
<b>Ringsmobäcken</b>	Pine/spruce	Gneiss	Histosols, bedrock outcrops	0.01	1986-1999	Löfgren and Kvarnäs (1995)

Bedrock is biotite granite. Overburden is a thin layer of ground moraine upon which podzols and peaty podzols have developed. The vegetation is predominantly mature mixed coniferous forest of Norway spruce (*Picea abies* L.) and Scots pine (*Pinus sylvestris* L.) with some birch (*Betula pendulosa* L.). The ground vegetation consists primarily of heather (*Calluna vulgaris* L.) and blueberry (*Vaccinium myrtillus* L.). The station for precipitation and air sampling is located about 500 m north of the catchment. The site was instrumented in 1972 as part of the Norwegian SNSF-project (Overrein *et al.*, 1980).

The Storgama catchment is located in southernmost Norway about 50 km north of Arendal (Fig. 1). The catchment area is 0.6 km<sup>2</sup> and altitude ranges from 580–690 m. Bedrock is granitic. Overburden is a thin layer of ground moraine upon which podzols and peaty podzols have developed. About 20% of the catchment is exposed bare rock and 20% of the catchment covered by peat > 30 cm in depth. The vegetation is predominantly sparse unproductive forest of Scots pine (*Pinus sylvestris* L.) and some birch (*Betula pendulosa* L.). The ground vegetation consists primarily of heather (*Calluna vulgaris* L.). The weir at the

bottom of the catchment is at the outlet of a small pond. The station for precipitation and air sampling is located about 6 km east of the catchment at Treungen. The site was instrumented in 1974 as part of the Norwegian SNSF-project (Overrein *et al.*, 1980).

The Langtjern catchment is located in southeastern Norway about 100 km northwest of Oslo (Fig. 1). The catchment area is 4.8 km<sup>2</sup> and altitude ranges from 510–750 m. Bedrock is biotite gneiss and granite. Overburden is a thin layer of ground moraine upon which podsoles and peaty podsoles have developed. About 16% of the catchment is exposed bare rock, 16% of the catchment covered by peat > 30 cm in depth and 5% is ponds and small lakes. The vegetation is predominantly mixed forest of Norway spruce (*Picea abies* L.), and Scots pine (*Pinus sylvestris* L.) and some birch (*Betula pendulosa* L.). The ground vegetation consists primarily of heather (*Calluna vulgaris* L.) and blueberry (*Vaccinium myrtillus* L.). The weir at the bottom of the catchment is at the outlet of the lake Langtjern (0.26 km<sup>2</sup>; water retention time about two months). Until 1995 the station for precipitation and air sampling was located about 6 km east of the catchment at Gulsvik and then was moved a short distance to Brekkebygda. The site was instrumented in 1974 as part of the Norwegian SNSF-project (Overrein *et al.*, 1980).

Since 1980, the Birkenes, Storgama and Langtjern catchments have been part of the Norwegian Monitoring Programme for Long-Range Transported Air Pollutants (Johannessen, 1995).

#### Finland

The Valkeakotinen catchment is located in southernmost Finland, about 140 km north of Helsinki (Fig. 1). The catchment area is 0.30 km<sup>2</sup> and altitude ranges from 150 to 190 m. Bedrock is gneiss and granitoids. Overburden is glacial drift upon which dystic cambisols have developed with some peatlands (histosols). There is a small lake within the catchment and vegetation is predominantly mature mixed coniferous forest of Norway spruce (*Picea abies* L.) and Scots pine (*Pinus sylvestris* L.) with some birch (*Betula sp.*).

The Hietajärvi catchment is located in southeastern Finland, about 80 km northeast of Joensuu (Fig. 1). The catchment area is 4.64 km<sup>2</sup> and altitude ranges from 170 to 210 m. Bedrock is granitoids and gneiss. Overburden is glacial drift with some small eskers upon which orthic podsoles have developed. There are also some peatlands (histosols) and two small lakes in the catchment. The vegetation is predominantly mature mixed coniferous forest of Norway spruce (*Picea abies* L.) and Scots pine (*Pinus sylvestris* L.) with some birch (*Betula sp.*).

At both sites the atmospheric deposition and run-off have been monitored, since 1988, by the Finnish Meteorological Institute and the Finnish Environment Institute as a part of the Finnish ICP-IM Programme (Bergström *et al.*, 1995).

#### Sweden

The Gårdsjön catchment F1 is located in southwestern Sweden, about 50 km north of Gothenburg (Fig. 1). The catchment area is 0.04 km<sup>2</sup> and altitude ranges from 115 to 135 m. Bedrock is gneiss and granodiorite partly overlain by glacial till upon which podsoles, and in the valley bottom, histosols, have developed. The vegetation is predominantly mature mixed forest of Norway spruce (*Picea abies* L.), birch (*Betula pendula* and *B. pubescens.*) and Scots pine (*Pinus sylvestris* L.). The ground vegetation consists primarily of blueberry (*Vaccinium sp.*), grass (mainly *Deschamsia flexuosa*), abundant mosses (mainly *Dicranum maius*) and lichens (*Hypogymnia physodes*, *Lepraria incana*). The site was instrumented in 1979 and has been continuously operated by IVL Swedish Environmental Research Institute since 1980 (Andersson and Olsson, 1985).

The Pipbäcken Nedre catchment is located in southwestern Sweden, about 25 km northeast of Falkenberg (Fig. 1). The catchment area is 0.93 km<sup>2</sup> and altitude ranges from 75 to 165 m. Bedrock is gneiss and amphibolite overlain mainly by moraine upon which podsoles have developed. The vegetation is mature mixed forest of spruce (*Picea abies*), pine (*Pinus sylvestris*), beech (*Fagus sylvatica*) and oak (*Quercus petraea*). About 31% of catchment is covered by peatland (Löfgren and Kvarnäs, 1995). The catchment was established as a part of the Swedish National Environmental Monitoring Programme (Aastrup *et al.*, 1996) and the continuous data on precipitation and run-off are available since 1986. The catchment is operated by the Swedish University of Agricultural Sciences.

The Ringsmobäcken catchment is located in southwestern Sweden, about 160 km north of Gothenburg in the Stora Tresticklan area (Fig. 1). The catchment area is 1.12 km<sup>2</sup> and altitude ranges from 180 to 245 m. Bedrock is gneiss and about 80% is bedrock outcrop. The rest of the catchment is covered by peatland and a small lake. The vegetation is sparse consisting mainly of heather (*Calluna vulgaris*) and a thin pine forest (*Pinus sylvestris*). The catchment was established as a part of the Swedish National Environmental Monitoring Programme (Aastrup *et al.*, 1996) and continuous run-off data are available since 1985. Precipitation data were available for only four complete years (1983, 1984, 1988 and 1989) and were complemented by measurements at Gårdsjön catchment. The catchment is operated by the Swedish University of Agricultural Sciences.

The Lommabäcken Nedre catchment is located in the Tiveden national park about 20 km northeast of Karlsborg in southern Sweden (Fig. 1). The catchment area is 1.04 km<sup>2</sup> and altitude ranges from 190 to 230 m. Bedrock is granite and about 85% of the catchment area is bedrock outcrop. A small lake and peatland cover about 11% of the catchment area and the rest is covered by thin organic soil. The vegetation is dominated by blueberry (*Vaccinium myrtillus*) and thin mixed forest of pine (*Pinus sylvestris*), spruce (*Picea abies*) and birch (*Betula sp.*) (Löfgren and Kvarnäs, 1995). The catchment was established as a part of the Swedish National Environmental Monitoring Programme (Aastrup *et al.*, 1996) and continuous run-off data since 1985 are available. Precipitation was monitored at nearby station Sjöängen. The catchment is operated by the Swedish University of Agricultural Sciences.

## METHODS

Non-marine fractions of sulphate (SO<sub>4</sub><sup>\*</sup>) and calcium (Ca<sup>\*</sup>) are calculated under the assumptions that all chloride (Cl) is of marine origin (cyclic sea-salts) and is accompanied by other ions in the same proportions as in sea water. Acid neutralising capacity (ANC) is defined as the equivalent sum of base cations (Ca + magnesium (Mg) + sodium (Na) + potassium (K) minus the equivalent sum of strong acid anions (SO<sub>4</sub> + Cl + nitrate (NO<sub>3</sub>)) (Reuss and Johnson, 1986). As a consequence of the ion balance (SO<sub>4</sub> + Cl + NO<sub>3</sub> + bicarbonate (HCO<sub>3</sub>) + OA) = (Ca + Mg + Na + K + hydrogen (H) + aluminium (Al)), ANC can also be expressed as the equivalent sum of (HCO + OA) - (H + Al). OA is organic anions. Aluminium is the sum of positively-charged Al species.

Trend analysis for each stream and each relevant variable were analysed with a non-parametric Seasonal Kendall tau (SKT) test (Hirsch *et al.*, 1982). One limitation of the SKT is that it detects only monotonic trends; trends need not be linear, but they must proceed in only one direction (increasing or decreasing) to be detectable.

In brief, the SKT analyses the data within blocks, and compares the rank value for a single observation to the rank values of subsequent data from that same season. The signs (indicating whether the second observation in each pair-wise comparison is higher or lower than the first) for all pair-wise comparisons within each block are summed and a Z statistic calculated as the ratio of the sum of signs divided by the standard deviation in the signs. The SKT does not estimate the slopes of trends, but it has become customary to associate slopes calculated according to the method of Sen (1968), which estimates the slope by calculating the median of all between-year differences in the variable of

interest. The trend analysis are performed on SO<sub>4</sub><sup>\*</sup>, NO<sub>3</sub>, Ca<sup>\*</sup>, ANC and H.

## Results

### DEPOSITION

Deposition of SO<sub>4</sub><sup>\*</sup> has declined at all sites, with significant decreasing trends in the 1980s and continuing in the 1990s (Fig. 2). In the 1990s, the period for which data are available for the entire region, SO<sub>4</sub><sup>\*</sup> deposition declined from 21% at Treungen, Norway, to 37% at Sjöängen, Sweden, relative to the average levels during the 1980s. Data from before 1980 are available only from the three Norwegian sites; these show no changes prior to 1980. Dry deposition of S has probably declined commensurately, as concentrations of sulphur dioxide (SO<sub>2</sub>) gas have also declined in the region during the 1980s and 1990s (Barrett *et al.*, 2000).

Deposition of inorganic N compounds has changed very little in Norway and Sweden whereas in Finland it has declined during 1990s (Fig. 2). Concentrations in bulk precipitation have been relatively constant during the 1980s and show only about 20% decline, mostly as NO<sub>3</sub>, during the late 1990s at some sites (Barrett *et al.*, 2000). Deposition of non-marine base cations has decreased strongly in the late 1980s and early 1990s in Finland, and to a much lesser extent in Sweden and Norway.

The magnitude of trends in precipitation concentrations was separately analysed for three periods; 1974–1980, 1981–1990 and 1991–1999. The changes of the average slope over these three periods showed clear differences. During the 1970s, only the Norwegian sites were monitored. Non-marine sulphate and Ca<sup>\*</sup> increased at two out of three sites, and inorganic N increased at all three. In the 1980s, Norwegian and Swedish sites were monitored. Non-marine sulphate decreased at all sites as did, with one exception, Ca<sup>\*</sup>. Nitrate did not show any consistent pattern. In the 1990s there was a pronounced decrease in the SO<sub>4</sub><sup>\*</sup> concentrations at seven of the eight sites for which deposition data are available. Inorganic N decreased at all sites whereas Ca<sup>\*</sup> did not show any consistent pattern (Fig. 2).

### RUN-OFF

The long records from the three Norwegian catchments show that SO<sub>4</sub><sup>\*</sup> concentrations were high (peak) in late 1970s and early 1980s (Fig. 3). Non marine sulphate concentrations began to decline in the 1980s and the decline accelerated in the 1990s (Table 2). This pattern is seen at all the nine catchments. The overall decrease since 1980 in Norway has

**Table 2.** Average slopes in runoff trends divided into decades (1970s = 1974-80; 1980s = 1981-90; 1990s = 1991-1999) and slope for the whole period, where only trends significant at  $p < 0.05$  level are given. na= data not available for whole period. NS= no significant trend detected. Units:  $\mu\text{eq L}^{-1} \text{yr}^{-1}$ .

	<b>SO<sub>4</sub>*</b>				<b>NO<sub>3</sub></b>				<b>Ca*</b>			
	1970s	1980s	1990s	all years	1970s	1980s	1990s	all years	1970s	1980s	1990s	all years
Birkenes	-2.9	-4.8	-4.9	<b>-4.3</b>	0.9	0.7	-1.1	<b>NS</b>	-1.2	-1.0	-1.7	<b>-1.3</b>
Storgama	-2.3	-1.5	-3.5	<b>-2.4</b>	0.9	-0.1	-0.4	<b>NS</b>	-2.0	-0.9	-1.0	<b>-1.2</b>
Langtjern	-1.1	-1.6	-3.6	<b>-2.2</b>	0.2	0.0	-0.1	<b>NS</b>	-2.3	-1.4	-1.5	<b>-1.6</b>
Valkeakotinen	na	na	-2.2	<b>-2.2</b>	na	na	-0.1	<b>NS</b>	na	na	-1.1	<b>-1.1</b>
Hietajärvi	na	na	-1.8	<b>-1.8</b>	na	na	-0.1	<b>-0.1</b>	na	na	0.2	<b>NS</b>
Gårdsjön F1	na	-5.8	-15.2	<b>-10.2</b>	na	-0.4	-0.1	<b>-0.3</b>	na	-2.0	-2.3	<b>-2.1</b>
Ringsmobäcken	na	-1.5	-17.3	<b>-11.0</b>	na	-0.2	-0.2	<b>-0.2</b>	na	-0.4	5.7	<b>NS</b>
Lommabäcken n.	na	-0.8	-26.5	<b>-16.2</b>	na	-0.4	-0.2	<b>NS</b>	na	-0.6	-3.4	<b>-2.3</b>
Pipbäcken n.	na	13.3	-28.3	<b>-10.1</b>	na	0.6	0.6	<b>0.6</b>	na	2.8	-3.3	<b>NS</b>

<b>ANC</b>				<b>H+</b>			
1970s	1980s	1990s	all years	1970s	1980s	1990s	all years
-1.1	1.3	4.4	<b>NS</b>	-1.4	-0.2	-1.8	<b>NS</b>
-3.0	0.2	3.1	<b>0.5</b>	-0.7	0.2	-1.6	<b>-0.7</b>
-2.7	0.4	1.4	<b>-0.1</b>	0.0	0.3	-0.8	<b>NS</b>
na	na	0.3	<b>NS</b>	na	na	0.7	<b>0.7</b>
na	na	2.4	<b>2.4</b>	na	na	0.0	<b>NS</b>
na	9.0	20.6	<b>14.5</b>	na	0.3	-3.4	<b>NS</b>
na	-4.9	20.7	<b>NS</b>	na	2.4	-2.8	<b>-0.8</b>
na	-4.5	22.1	<b>11.4</b>	na	3.9	-2.9	<b>-0.2</b>
na	-17.7	22.2	<b>NS</b>	na	3.5	-3.3	<b>NS</b>

been about 72% (27% in the 1980s and a further 45% in the 1990s). The records for Finland cover only the 1990s and here,  $\text{SO}_4^*$  declined by 28%. In Sweden, the decline was 24% in the 1980s and 50% in the 1990s.

Nitrate accounted for by far the largest portion of inorganic N in run-off;  $\text{NH}_4$  concentrations are negligible in streams draining non-agricultural catchments (data not shown). Most of the inorganic N in deposition was retained in the catchment. Nitrate is a minor acid anion compared to  $\text{SO}_4^*$ . Concentrations of  $\text{NO}_3$  in run-off at the nine catchments showed very few trends over time. The exception was Pipbäcken Nedre in southern Sweden, which had the highest absolute concentration of  $\text{NO}_3$  of the nine catchments and showed significant increases in concentrations during the 1990s (Fig. 3, Table 2).

The decreased concentrations of anions (mainly  $\text{SO}_4^*$ ) must be accompanied by decreased concentration of one or

more cation or compensated by increased concentration of another anion. Some of the decline in  $\text{SO}_4^*$  has been accompanied by decline in concentrations of base cations, mostly  $\text{Ca}^*$  (Fig. 3).

Increased ANC compensates for the rest of the decline in  $\text{SO}_4^*$ . The pattern is clearest at the three Norwegian catchments. Here, acidification continued until the early 1980s (declining ANC), at which time the decline stopped, turned around and ANC began to recover, with the largest increases in the 1990s. The changes in ANC are comprised of decreased Al, decreased H (in sites with substantial H, that is,  $\text{pH} < 5$ ), and increased  $\text{HCO}_3^-$  (at higher pH sites).

This general picture is confounded in part by year-to-year variations in sea-salt inputs. In southwestern Norway (Hindar *et al.*, 1994), and in Sweden (Gustafsson and Hallgren-Larsson, 2000) the winter of 1993 had unusually severe storms, with high inputs of sea-salts. As a result of

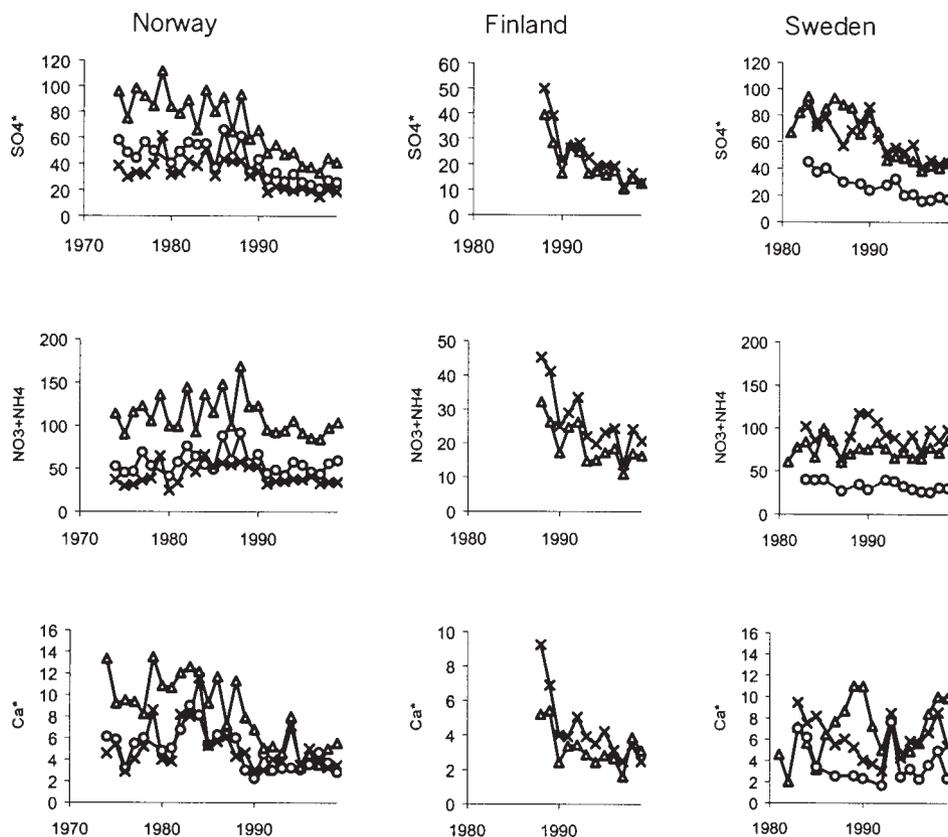


Fig. 2. Volume-weighted annual mean concentrations of  $SO_4^*$ , inorganic N ( $NO_3+NH_4$ ) and  $Ca^*$  in bulk precipitation sampled at three sites in Norway (data from Aas *et al.*, 2000), two in Finland and three in Sweden. Triangles: Birkenes, NO, Hietajärvi, FI, and Gårdsjön, SE. Crosses: Langtjern, NO, Valkeakotinen, FI, and Pipbäcken Nedre, SE. Circles: Storgama, NO, and Lomabbäcken Nedre, SE. Units:  $\mu eq L^{-1}$ .

this, run-off that year had abnormally high concentrations of Cl. Due to cation exchange in the soil, some of the base cations in this sea-salt input were exchanged with acid cations (H and Al) in the soil and caused a temporary decrease in ANC (Hindar *et al.*, 1994). In Sweden, the winter of 1989 was similar, with high inputs of sea-salts in the southwestern parts of the country (Hultberg and Grennfelt, 1992).

## Discussion

Sulphate concentrations and fluxes in run-off responded rapidly to the changes in S deposition at all sites. The catchment F1 at Gårdsjön illustrates well the role of the soil in delaying and modifying changes in deposition. The decline of  $SO_4$  concentrations in stream water output from F1 catchment was delayed relative to the decline in S deposition (Figs. 2 and 4). In terms of chemical budgets the deposition input is exceeded by the run-off output and there was a net release of previously stored  $SO_4$  from the catchment. Desorption of  $SO_4$  and mineralisation of

organically bound S from the catchment soils are two mechanisms which might cause a lag in the run-off response. In the relatively young soils in Scandinavia developed from parent material after the last glaciation, adsorbed  $SO_4$  is typically only a small fraction of the total S present in the soil. Most of the store of S is incorporated in soil organic matter (Mörth *et al.*, 1999).

The dynamics of the S release from the soil is an important factor that needs to be considered when predicting the future development of recovery of soils and surface waters from acidification. Desorption of  $SO_4$  involves release of acidity in nearly stoichiometric proportion (Gustafsson, 1995). Soils with large amounts of adsorbed  $SO_4$  might, therefore, remain acidified for years or even decades after a substantial decrease in S deposition (Beier *et al.*, 1995). Release of organically bound S from the soils might potentially prolong the lag in recovery in soils and surface water for decades (Löfgren *et al.*, 2001).

The delay in response due to the bleeding of "old" S from the nine Scandinavian catchments was generally less than about five years. This rapid response is characteristic for

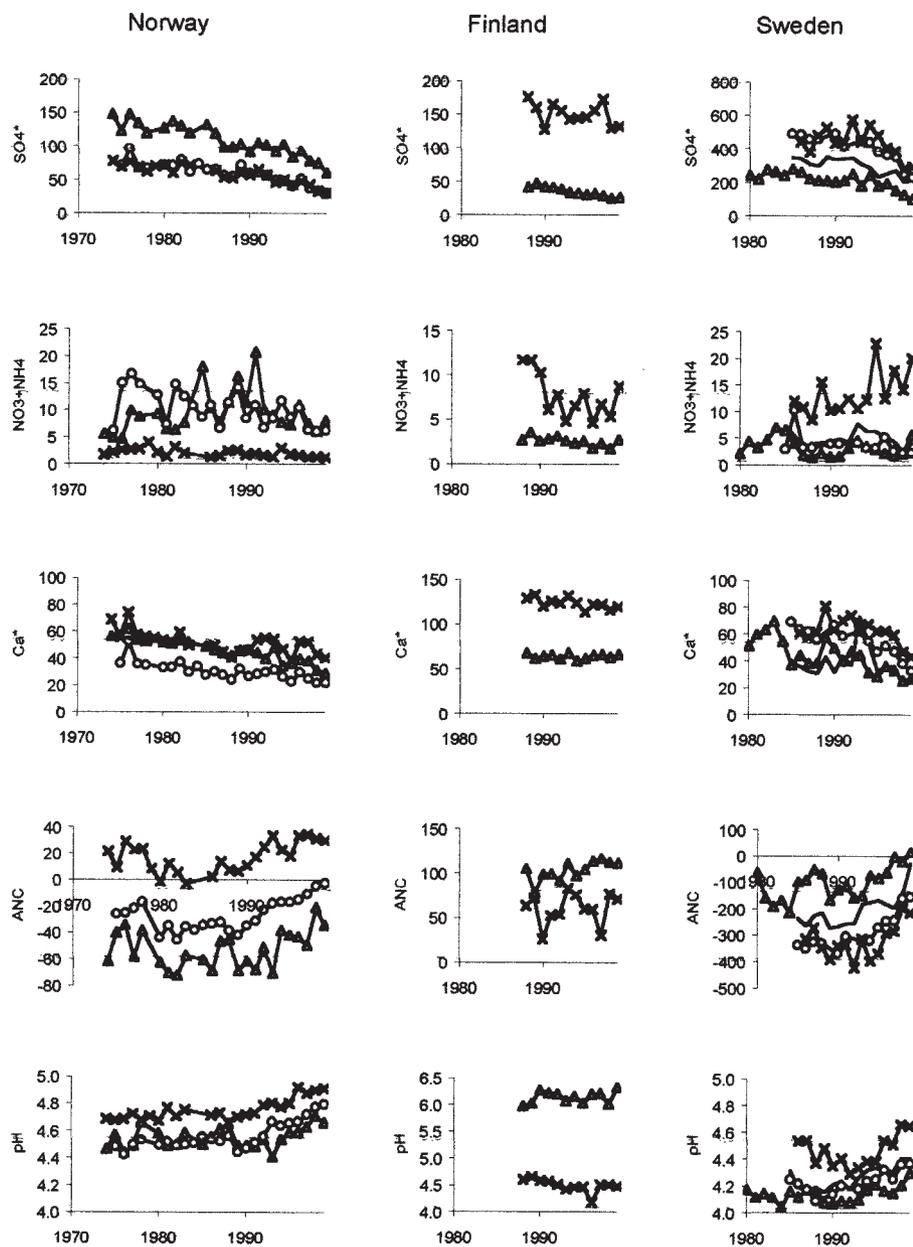


Fig. 3. Volume-weighted annual mean concentrations of  $SO_4^*$ , inorganic N ( $NO_3 + NH_4$ ),  $Ca^*$ , ANC and pH in run-off sampled at three catchments in Norway (data from SFT, 1998), two in Finland and four in Sweden. Symbols: Triangles: Birkenes, NO, Hietajärvi, FI, and Gårdsjön, SE. Crosses: Langtjern, NO, Valkeakotinen, FI, and Pipbäcken Nedre, SE. Circles: Storgama, NO, and Lommabäcken Nedre, SE. No symbols: Ringsmobäcken, SE. Units:  $\mu eq L^{-1}$  except for pH.

young and well-drained soils developed since the last glaciation; such soils have low  $SO_4$  adsorption capacity. In contrast, at sites with old and highly weathered soils the response in  $SO_4^*$  in run-off can be delayed by decades or more (Harrison *et al.*, 1989; Johnson, 1984; Johnson *et al.*, 1980).

The Scandinavian catchments examined here fit well into

the general picture of S response in the rest of Scandinavia. All catchments showed statistically significant decreases in  $SO_4^*$  concentration during the 1990s, as is also the picture shown by annual surveys of 344 small lakes in Finland, Norway and Sweden (Skjelkvåle *et al.*, 2001). Indeed, these trends have occurred in acidified surface waters generally in Europe (Prechtel *et al.*, 2001).

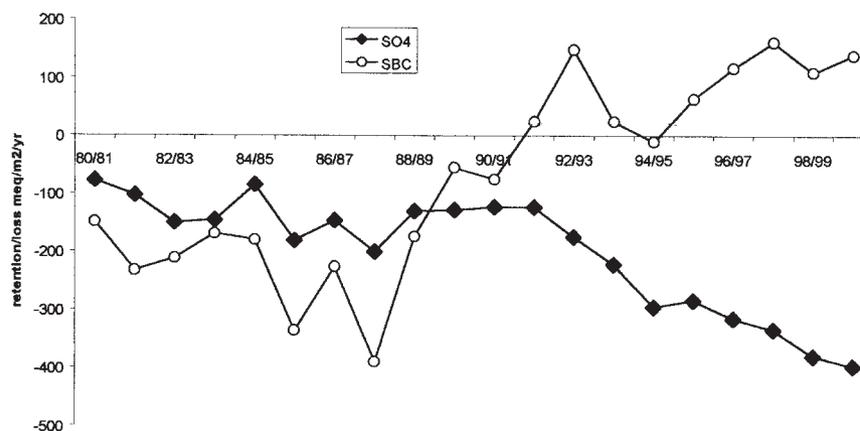


Fig. 4. Cumulative net flux of  $SO_4$  and base cations for F1 catchment at Gårdsjön, Sweden.

The lack of a statistically significant trend in  $NO_3$  concentrations and fluxes at eight of the nine catchments also is consistent with the results from small lakes in the region (Skjelkvåle *et al.*, 2001) and with trends in  $NO_3$  in surface waters elsewhere in Europe (Wright *et al.*, 2001). Therefore, there is no evidence of N saturation at these catchments (with the possible exception of Pipbäcken Nedre in southern Sweden) over the past 12-25 years, despite the fact that the catchments retained > 90 % of inorganic N inputs.

The decline in  $SO_4^*$  was accompanied in part by decline in base cations, mostly  $Ca^*$ . This is the same picture as found in the Nordic lakes (Skjelkvåle *et al.*, 2001) and in acidified surface waters in Europe in general (Evans *et al.*, 2001a). The response of base cations is most probably due to the “salt effect”; cations must decrease simply as a consequence of reduced anions (Reuss and Johnson, 1986). In southern Finland and, to a lesser extent, in southern Sweden, however, decreased deposition of base cations may be a factor contributing to declining run-off concentrations of base cations, as has been postulated at Hubbard Brook, USA (Likens *et al.*, 1996). The decrease in base cation deposition in Finland is related to the reduced emissions of dust and fly ash from cement factories and power plants in the Baltic countries and adjacent areas of Russia. Over decadal time frames, a gradual increase in base cation concentrations in run-off should occur as the pools of exchangeable base cations in soil are replenished by weathering in the “post-acidification” era of the future.

At catchment F1 (Gårdsjön, Sweden), the cumulative mass balances illustrate the general picture for  $SO_4$  and the sum of base cations (SBC) (Fig. 4). For  $SO_4$  every year the output (run-off) was subtracted from the input (throughfall) and the flux was accumulated. In the case of SBC, the output was run-off and estimated net uptake to the trees and the

input was estimated deposition plus weathering.

For the first ten years, the input and output were, for most of the time, in approximate  $SO_4$  balance (Fig. 4). From 1980 to 1990 about 100 meq  $m^{-2}$  of  $SO_4$  were lost from the soil, most of it in the first measured year. Since 1990, however, the catchment started to lose  $SO_4$  almost every year with exception of the extremely dry year of 1995. The total loss was about 250 meq  $m^{-2}$ . For the base cations, the picture is the opposite; up to 1990 a slight loss (*c.* 50 meq  $m^{-2}$ , even though there were some ups and downs). Since then, the soils retained about 250 meq  $m^{-2}$  of base cations (Fig. 4).

A fraction of the reduced  $SO_4^*$  concentration has been compensated for by increased ANC in run-off at the nine Scandinavian catchments. This is consistent with the pattern found in the Nordic lakes (Skjelkvåle *et al.*, 2001) and in acid-sensitive waters in Europe as a whole (Evans *et al.*, 2001a). For Europe generally about 50% of the decrease in  $SO_4^*$  was compensated by decreased base cations and about 50% by increased ANC.

The increased ANC means that water chemistry conditions have improved for aquatic organisms such as fish and invertebrates. Concentrations of toxic inorganic Al species have decreased and pH has increased. Again this is the same general picture as found in the lakes in Scandinavia (Skjelkvåle *et al.*, 2001) and in acid-sensitive waters in Europe generally (Evans *et al.*, 2001a).

The sea-salt-rich years of 1989 in Sweden and 1993 in southwestern Sweden and southern Norway confound the picture by causing temporary decreases in ANC thus delaying recovery. The sea-salt effect (temporary acidification due to episodic inputs of sea-salts) has been well-documented in Norway (Hindar *et al.*, 1994; Wright *et al.*, 1988) as well as in the eastern US (Heath *et al.*, 1992). These episodes of sea-salt inputs generate noise in the signal of long-term trends, and thus larger monotonic changes over

longer time periods are required to obtain statistically significant trends (Wright and Jenkins, 2001). Sea-salt deposition may be cyclic over several years, due to such things as regular changes of the North Atlantic Oscillation (Evans *et al.*, 2001b) and, therefore, any given period of several years might be influenced by consistently declining or increasing sea-salt, which also complicates the picture. For example, at the nine Scandinavian catchments the increase in ANC during the 1990s was often larger than the decrease in  $\text{SO}_4^*$  (Table 2) due to the decreasing Cl concentration in run-off (aftermath of the high sea-salt years early in the decade).

The present analysis of the nine catchments in southern Scandinavia extends in time previous trend analyses that have included surface waters in the Nordic countries. The patterns of recovery for the early 1990s documented by the ICP-Waters network (Stoddard *et al.*, 1999) (part of the UN-ECE LRTAP convention) have continued through the decade and are now quite clear and consistent at acid-sensitive surface water sites in Scandinavia and elsewhere in Europe. There have been no systematic trends in  $\text{NO}_3$  in run-off, strong decreases in  $\text{SO}_4^*$ , accompanied by decreases in base cations and increases in ANC. Continued long-term monitoring at these sites is essential to document that large investments in emission control pay off in terms of a better environment and that water chemistry returns towards ecologically acceptable levels as the protocols of the UN-ECE Convention on Long-Range Transboundary Air Pollution are implemented (UN-ECE, 1999).

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