



*Recovery from Acidification in
the Natural Environment*

Present Knowledge and Future Scenarios

Editors

Per Warfvinge

Ulla Bertills

*Recovery from Acidification in
the Natural Environment*

Present Knowledge and Future Scenarios



Editors
Per Warfvinge
Ulla Bertills

ENVIRONMENTAL ASSESSMENT DEPARTMENT
ENVIRONMENTAL IMPACTS SECTION
CONTACT: Ulla Bertills, telephone +46 8 698 15 02

The authors assume sole responsibility for the contents of this report,
which therefore cannot be cited as representing the views of
the Swedish Environmental Protection Agency.
The report has been submitted to external referees for review.

PRODUCTION: MARGOT WALLIN
TRANSLATION: MARTIN NAYLOR
COVER PHOTOGRAPH: LAKE STORA IDEGÖLEN IN THE RAIN
PHOTOGRAPHER: JAN SCHÜTZER/N

Most of the illustrations in this report have been redrawn
by JOHAN WIHLKE

PHOTOGRAPHS PAGE 38: PER WARFVINGE, PAGE 50: PER HÖRSTEDT

ADDRESS FOR ORDERS:
Swedish Environmental Protection Agency
Customer Services
SE-106 48 STOCKHOLM, SWEDEN
TELEPHONE: +46 8 698 12 00
FAX: +46 8 698 15 15
E-MAIL: kundtjanst@environ.se
INTERNET: <http://www.environ.se>

ISBN 91-620-5034-6
ISSN 0282-7298

This report is also available in Swedish ISBN 91-620-5028-1

© Swedish Environmental Protection Agency
PRINTED BY BERLINGS SKOGS, TRELLEBORG, 2000
EDITION: 1 000 copies

PREFACE

This report is a summary and synthesis of the information and knowledge currently available concerning the nature of the recovery process that may be expected to result from reduced atmospheric deposition of acidifying compounds. It is one of the final reports on the project area Acidifying Substances and Tropospheric Ozone, which was established in 1993 as part of the research programme of the Swedish Environmental Protection Agency. Funding for the final phase of this research has been provided by the Swedish Foundation for Strategic Environmental Research (MISTRA).

A number of individuals, most of whom received research funding through the project area, have been involved in writing this report. It should be noted, though, that many of the results and much of the knowledge on which it is based stem from the efforts of fellow researchers beyond the immediate circle of the authors. We would like to emphasize our appreciation of the patient, long-term and high-quality work they have undertaken in this field.

The present report is intended for readers who already have some understanding of the causes and effects of acidification. The aim is that the synthesis of knowledge which it contains will provide a basis for measures, decisions and policies, while also laying a foundation for future research. For a more in-depth scientific discussion of the issues involved, we refer to the publications cited.

PER WARFVINGE AND ULLA BERTILLS
LUND AND STOCKHOLM
9 OCTOBER 1999

CONTENTS

EXECUTIVE SUMMARY	6
1 INTRODUCTION	9
1.1 Acidification of soil and water	9
1.2 International agreements	10
1.3 Chemical and biological recovery	12
1.4 Gaps in current knowledge	13
1.5 Monitoring data, field experiments and models	14
2 DEPOSITION TRENDS IN SWEDEN	15
2.1 Why, where and how is deposition measured?	15
2.2 pH of precipitation has risen	16
2.3 Sulphur deposition is decreasing	17
2.4 Only gradual decline in nitrogen deposition	18
2.5 What is happening to base cation deposition?	20
3 WHAT PROCESSES GOVERN RECOVERY?	23
3.1 Reversible and irreversible soil processes	23
3.2 Studies of catchments and soil profiles	24
3.3 Ion exchange	25
3.4 Weathering	26
3.5 Sulphur fluxes in soil and water	27
3.5.1 Sulphate adsorption	28
3.5.2 Organic sulphur	29
3.5.3 Sulphide oxidation and bacterial sulphate reduction	29
3.6 Aquatic chemical equilibria – ANC and pH	30
3.7 Nutrient uptake and leaching of nitrogen	32
3.8 The importance of land use	33
3.9 Spatial variation within catchments	34
3.10 The dynamics of acidification and recovery	34
4 EXPERIMENTAL STUDIES IN SWEDEN	37
4.1 The Gårdsjön Roof Project	38
4.1.1 Why was the roof built?	41
4.1.2 Benefits and limitations of the roof project	41
4.1.3 Higher ANC and lower aluminium levels when deposition decreases	42
4.1.4 Soil sulphur dynamics – important and uncertain	43
4.1.5 Base cations – concentrations falling despite lower acid deposition	46
4.1.6 Many questions still to be answered	47
4.2 Diatoms as a biological pH meter	49
4.2.1 Lake Örvattnet, Värmland	50
4.2.2 Lakes around the Falun copper mine	51

5	RECOVERY OF SURFACE WATERS AND FOREST SOILS IN SWEDEN	53
5.1	Recovery of lakes – indications in individual lakes	53
5.2	Trends in the water chemistry of the time series lakes	54
5.2.1	Sulphate concentrations falling	54
5.2.2	Slow rise in alkalinity and pH	55
5.3	National lake surveys	57
5.4	The Integrated Monitoring programme – recovery of catchments	58
5.5	Changes in soil chemistry – Survey of Forest Soils and Vegetation	59
5.5.1	How is the pH of forest soils changing?	60
5.5.2	How does growth affect changes in pH?	61
5.5.3	Exchangeable base cations, acidity and aluminium	63
5.6	How is chemical recovery affecting biota?	65
6	INTERNATIONAL EXPERIENCE	67
6.1	Roof experiments within the EXMAN project	68
6.2	The RAIN project	69
6.3	Studies in the Netherlands	71
6.4	Sudbury, Canada	71
6.5	Monitoring programmes under CLRTAP	72
7	PROSPECTS FOR THE FUTURE	74
7.1	Future deposition trends	74
7.2	Interpretation of the roof experiment – modelling	78
7.3	Modelling of forest sites in southern Sweden	80
7.4	Regional assessments	82
8	SYNTHESIS	85
8.1	What do we know?	85
8.2	What do we believe?	87
8.3	What problems lie ahead?	87
8.4	What knowledge gaps remain?	89
8.5	Concluding remarks	90
9	REFERENCES	91
	AUTHORS' ADDRESSES	96

EXECUTIVE SUMMARY

Acidification of air, soil and water has had highly detrimental effects on the environment of Europe and North America. In Sweden, the ecological value of many lakes, rivers and streams has been greatly undermined, and vital nutrients have been leached from forest soils. Cultural assets such as rock carvings and architectural features have been affected. Over the last decade or so, however, emissions of acidifying pollutants have decreased. It is hoped, therefore, that the natural environment will recover, to a state similar to that prevailing before the acidification of the past century.

International negotiations to reduce pollutant emissions in Europe and North America have taken place under the Convention on Long-Range Transboundary Air Pollution (CLRTAP). The 1994 protocol now in force is based on the principle that the difference between current sulphur deposition levels and critical loads must be reduced by 60%. In December 1999 a 'multi-effect, multi-pollutant' protocol was signed. This agreement lays down new emission ceilings for sulphur dioxide, nitrogen oxides, ammonia and volatile organic compounds (VOCs). Within the European Union, the Commission has drawn up an Acidification Strategy which includes several proposals for directives aimed at achieving substantial emission reductions.

Recovery from acidifying deposition comprises both a chemical and a biological component. Chemical recovery means that certain critical chemical variables return to an original state, for example pH values rise and aluminium concentrations in surface waters fall. In aquatic environments, biological recovery occurs when key organisms have resumed their role in the ecological system by re-establishing viable populations; the organisms concerned may for instance be zooplankton, benthic animals or a characteristic fish population.

At the end of the 1980s, the average pH of precipitation in the southern Swedish county of Blekinge was between 4.0 and 4.2. By 1997, the figure had risen to 4.5. Roughly the same trend has been observed in other parts of southern and central Sweden.

Atmospheric deposition of sulphur has decreased considerably, while deposition of nitrogen has exhibited relatively little change since 1990. Deposition of sulphate-sulphur in bulk precipitation has fallen by 30%;

deposition to spruce forests (in throughfall) has on average shown a larger decrease, of about 45%. The downward trend in sulphur deposition is relatively strong, and similar throughout Sweden. Emissions of nitrogen in Sweden and the rest of Europe have not abated to the same extent as sulphur emissions in recent years, which explains the differing deposition trends.

Acidification and recovery from acidification are processes which extend over many decades. The time-scale is governed primarily by chemical processes in the soil, such as chemical weathering, cation exchange and sulphate adsorption. The most important surface water parameter in biological terms, pH, is determined by aquatic chemical equilibria. As deposition falls, soils will tend to bind base cations and release sulphate, delaying recovery. The risk of forest soils generally beginning to leach nitrogen in the form of nitrate, which would have an acidifying effect, is small.

In Sweden, recovery has been investigated experimentally in the Gårdsjön Roof Project and through palaeolimnological studies. In the Lake Gårdsjön area, a roof was built over a 0.6 ha catchment and polluted precipitation was replaced with water corresponding to natural rain and snow. After 7 years of this experimental treatment, concentrations of sulphate, inorganic aluminium and base cations in runoff have fallen by 50–60%. The buffering capacity (acid neutralizing capacity, ANC) of runoff has increased at the same rate as aluminium levels have fallen. There has been only an insignificant rise in pH, as the increased buffering capacity of the water has served to reduce the concentration of aluminium.

A palaeolimnological study of Lake Örvattnet in Värmland has shown how chemical recovery, from pH 4.7 to 4.9, has coincided with biological recovery, e.g. of the lake's perch population.

According to a study of the water chemistry of the 'time series lakes', which are sampled regularly, sulphate concentrations in these lakes have fallen by around 2 $\mu\text{eq/l/yr}$ since 1983. Concentrations of base cations have also declined, limiting the increase in buffering capacity (measured as ANC). In most of the lakes that have had positive alkalinity, alkalinity has increased since the beginning of the 1980s. The general picture remains the same, whether the data are drawn from studies of the time series lakes, lakes included in national surveys, small streams covered by the Integrated Monitoring programme, or studies outside Sweden. There are clear signs of recovery even in areas where critical acid loads are still exceeded. Over a 10-year period, the median pH of the time series lakes increased by 0.1 units.

Analyses of soil chemistry carried out as part of the National Survey of Forest Soils and Vegetation have shown that the pH of forest soils fell by

an average of 0.1 units between the mid-1980s and the mid-1990s. The decrease was particularly marked in inland areas of southern Sweden, north-west central Sweden and Västerbotten. In the B horizon of the mineral soil, concentrations of exchangeable magnesium fell and concentrations of exchangeable aluminium rose throughout the country. Since more recent data are not available, we do not know whether soil acidification has been halted in the last 4–6 years, following the substantial reduction in sulphur deposition.

Future levels of acid deposition are dependent on what undertakings the countries of Europe make within the EU and CLRTAP. Several different future deposition scenarios are therefore conceivable. By 2010, sulphur deposition is expected to be 65–75% lower than in 1990. The reduction of nitrate-nitrogen will be 50–60%, while deposition of ammonium-nitrogen will decrease by only about 15%. Compared with 1980, the reduction in sulphur deposition will be 80–85%. The largest relative decreases in sulphur and nitrate-nitrogen will occur in the southern counties of Sweden.

A simulation of the recovery process in the Gårdsjön roof experiment suggests that sulphate concentrations in runoff will stabilize within the next 20 years. Runoff concentrations of base cations will continue to decline, as will levels of inorganic aluminium. Even after 30 years with no acidifying deposition, however, aluminium concentrations will still be elevated and ANC will remain below 0, although the pH will have risen somewhat. Modelling of developments at 17 forest sites in southern Sweden shows that the base saturation of the soil will not be restored, and that ANC will not reach estimated pre-industrial levels at any of the sites concerned. The most marked recovery in terms of pH and ANC will occur in soils with relatively high buffering capacities and high weathering rates. Modelling of 147 sites included in the National Survey of Forest Soils and Vegetation reinforces the picture of very slow recovery of the soil system, and shows that acidification is not entirely reversible, even over a period of 50 years. The results of these model calculations are particularly discouraging when it comes to the most sensitive and most severely acidified areas.

The report underlines the importance of environmental monitoring and experimental scientific research being guided by a long-term view, with the aim of further enhancing our understanding of recovery processes.

1. INTRODUCTION

PER WARFVINGE AND RICHARD F. WRIGHT

Acidification of air, soil and water has had highly detrimental effects on ecosystems across Europe and caused extensive damage to cultural assets and materials. After about a decade of decreasing emissions of acidifying pollutants, we now expect the natural environment to recover and conditions similar to those prevailing prior to the acidification of the past century to be achieved within a reasonable period of time.

The favourable developments now being seen are the result of abatement measures brought about in the framework of international environmental conventions. To achieve the long-term aim of sustainable development, deposition of acidifying compounds must be reduced to critical load levels.

1.1 ACIDIFICATION OF SOIL AND WATER

Since the industrial revolution of the 19th century, emissions of acidifying pollutants have risen very substantially. The pollutants concerned are sulphur and nitrogen compounds, arising from the burning of fossil fuels, extraction of metals from ores and a wide range of other industrial activities. The historical development of atmospheric deposition of sulphur closely mirrors the expansion of industrialism (figure 1).

Acidifying pollutants disperse via the atmosphere and return to the earth's surface by deposition, in the form of gases or airborne particles or dissolved in rain or snow, far away from their emission sources. Over large areas of northern and central Europe and eastern North America, many decades of acid deposition have caused extensive damage to the environ-

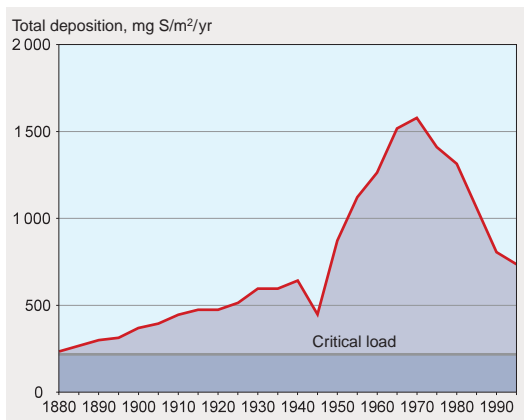


Figure 1. Estimated levels of sulphur deposition in an area of Småland, southern Sweden, 1880–1995. After Mylona 1993.

ment. Thousands of lakes, rivers and streams have suffered damage to their ecosystems; above all, populations of salmonids have been lost. Acidification of forest soils has resulted in losses of mineral nutrients, and in chemical conditions in the soil which could have adverse effects on the forests growing there. In addition, high concentrations of acidifying compounds, combined with oxidizing substances, have caused widespread damage to buildings and other structures.

As a result of its geographical location and its natural susceptibility, Sweden is one of the countries of Europe where the ecological damage arising from acid deposition has been most apparent and most serious. Because of this, together with the fact that 80–90% of the acidic deposition to which Sweden is exposed originates beyond its borders, the country has since the 1970s pursued a very active policy aimed at reducing emissions. It has pressed for far-reaching undertakings by the states of Europe, invested heavily in research on acidification, and allocated billions of kronor to direct measures such as liming of lakes and watercourses.

Acidification of soil and water is a complex phenomenon. On a very long time-scale, for example since the last ice age, it is a natural process. Natural acidification is caused by such factors as a gradual decrease in the rate of weathering of soil minerals. However, as more and more land has been brought into cultivation over the last one thousand years, the pH of many southern Swedish lakes appears to have risen (Renberg *et al.* 1993a, 1993b), probably as a result of swidden (slash-and-burn) agriculture and other land use.

Around the turn of the century, acidification accelerated as a consequence of acid deposition. This factor has had many times the effect of natural acidification, and has more than offset the effect of agriculture. As a result of this ‘recent acidification’, therefore, soils in many areas have effectively aged by thousands of years in the course of a single century. Acid deposition has consumed the buffering capacity of the soil. This has manifested itself first of all in heavy leaching of mineral nutrients from the soil, and subsequently in falling pH and elevated aluminium concentrations in lakes and running waters. Leaching of aluminium is the direct reason why several sensitive plant and animal species have disappeared from acidified waters.

1.2 INTERNATIONAL AGREEMENTS

Thanks to national and international efforts, there has now been a marked decrease in acid deposition. The highest levels of deposition occurred

some time in the 1970s or early 1980s. Since then, deposition of sulphur has fallen by more than half.

In the last few decades, considerable energy has been devoted to reducing atmospheric emissions of acidifying compounds. International negotiations on emission reductions in Europe and North America have been conducted under the Convention on Long-Range Transboundary Air Pollution (CLRTAP). The first result of these negotiations was a protocol entered into in 1985, in which the signatory states pledged a 30% cut in sulphur emissions by 1993, compared with 1980 levels. A second protocol on sulphur was signed in 1994. If the undertakings made in that agreement are honoured, emissions in Europe could be halved by the year 2000, from 1980 levels. The 1994 protocol is based on the principle that the difference between current sulphur deposition levels and critical loads must be reduced by 60%.

A summary of the agreements entered into under CLRTAP is presented in table 1.

Table 1. Summary of agreements reached under the Convention on Long-Range Transboundary Air Pollution (CLRTAP).

PROTOCOL	UNDERTAKING(S)	BASE YEAR	TARGET YEAR	RATIFIED
First Sulphur Protocol 1985	30% reduction of emissions in all countries	1980	1994	1987 (21 states)
NO _x Protocol 1988	Emissions to be frozen at base year level, and negotiations to continue	1987	1994	1991 (26 states)
VOC Protocol 1991	30% reduction of emissions by 1999	1984-90, at discretion of signatories	1999	1997 (17 states)
Second Sulphur Protocol 1994	Different emission cuts in different countries, to reduce the difference between actual deposition and critical loads by 60%	1990	2000; for some countries 2010	1998 (22 states)
POP Protocol 1998	Bans or restrictions on 16 persistent organic pollutants			
Heavy Metals Protocol 1998	Reduced emissions of cadmium, lead and mercury from industrial, energy and waste incineration plants			
Second Nitrogen Protocol, multi-pollutant, multi-effect, 1999	Further reductions in emissions of SO ₂ , NO _x and VOCs	1990	2010	

Work is also in progress in the CLRTAP framework to reduce emissions of oxidized nitrogen, NO_x . An initial agreement to freeze NO_x emissions at 1987 levels by 1994 was reached in 1988. In 1999, a ‘multi-effect, multi-pollutant’ protocol was signed in Göteborg. This agreement defines emission ceilings for sulphur dioxide, nitrogen oxides, ammonia and volatile organic compounds (VOCs).

Within the European Union, an Acidification Strategy has been developed and a proposal has been put forward for a directive on national emission ceilings for the air pollutants mentioned above.

The primary aim of these agreements is to slow the pace of acidification and, in the long term, to reduce deposition to, and preferably below, the relevant critical loads. Only when these levels have been reached can a gradual return to natural chemical conditions be expected (Lövblad & Bertills 2000).

1.3 CHEMICAL AND BIOLOGICAL RECOVERY

What, then, is meant by ‘recovery’? We distinguish in this report between *chemical recovery* and *biological recovery*.

The term *chemical recovery* refers to abiotic processes – usually in the soil system – which influence biological recovery. The chemical aspect of recovery is sometimes referred to as *reversibility* or *reversal* (see for example Dise *et al.* 1994). Chemical recovery does not necessarily mean that all chemical variables return to their original values. In acidified soil systems, it may involve an increase in the pool of base cations (calcium, magnesium and potassium) present in the soil. In lakes and running waters, recovery occurs if the pH rises and aluminium levels fall, for example. These changes are strongly linked to an increase in the acid neutralizing capacity (ANC) of the water.

The term *biological recovery* relates to biotic processes. (Some writers refer to this simply as *recovery*; see Dise *et al.* 1994.) In aquatic environments, biological recovery occurs when a number of key organisms have resumed their role in the ecological system by re-establishing viable populations (Dise *et al.* 1998). Key organisms in standing and running waters may consist of sensitive phytoplankton, zooplankton, benthic animals or a characteristic fish population.

A prior condition for the biological recovery of a lake or stream is that chemical recovery has begun. How quickly organisms return then depends on their rate of reproduction, but above all on their powers of dispersal. An aquatic system in which acidification has not progressed very

far, and in which small populations of the original organisms still remain, is better placed to recover in biological terms when its chemical status improves. In severely damaged freshwater systems, organisms with a strong dispersal ability are expected to be the first to return.

Just as acidification has been a protracted process, so it will take a long time for the beneficial effects of reduced deposition to become evident in lakes and watercourses. The critical chemical processes occur in the soil, since virtually all air pollutants are transferred to and pass through the soils of catchment areas before entering surface waters. Depending on the circumstances, it will subsequently take varying periods of time for ecological communities to re-establish themselves; in certain cases, important species may have to be reintroduced.

1.4 GAPS IN CURRENT KNOWLEDGE

Although deposition, particularly of acidifying sulphur, has decreased, many important questions still need to be answered. These include:

- Will we actually achieve chemical recovery within a reasonable time on the basis of the agreed deposition reductions, and in which areas will it be most rapid?
- Assuming that chemical recovery does take place, how will ecological communities develop?
- How should Sweden's lake liming programme be designed in the future, as recovery progresses?
- Is it necessary to begin large-scale liming of soils in order to prevent further soil acidification, speed up the recovery process and protect surface waters?
- Will increased extraction of biomass for energy purposes affect recovery, and is it compatible with agreed environmental quality objectives?
- Does the nature of the recovery process mean that Sweden should in any way modify its line of reasoning and its negotiating position in international efforts to reduce air pollution?
- What economic costs to society will acidification entail in the future?

Three different approaches can serve to shed light on the recovery process: analysis of time series of chemical and biological data, experiments involving radical reductions of deposition, and mathematical modelling. All of these approaches have been used by Swedish acidification researchers.

1.5 MONITORING DATA, FIELD EXPERIMENTS AND MODELS

The empirical data obtained from environmental monitoring in Sweden include measurements of water chemistry from around a hundred lakes and watercourses. These measurements have been performed since the beginning of the 1980s, and therefore we lack data from the actual acidification phase, which makes the interpretation of any trends more difficult. However, analyses of diatom remains in lake sediments provide information about when and to what extent lakes have been acidified. Diatoms are also important when it comes to tracking biological recovery, since they are expected to show a rapid response in terms of species composition when the chemical status of surface waters improves. Evidence of changes in soil chemistry is provided by the National Survey of Forest Soils and Vegetation (*Ståndortskarteringen*), in which soil chemical parameters are measured at some 2000 sites around the country. To date, conditions at each site have been recorded twice, in the 1980s and the 1990s. Measurements of deposition, carried out through regional, national and international networks, are of course another key source of data. In Sweden, monitoring of deposition chemistry began as early as 1955.

Experimental studies include the important roof project in the Lake Gårdsjön catchment, near the west coast. This is an example of a large-scale experimental manipulation involving very substantial reductions of sulphur and nitrogen deposition. Similar studies have previously been conducted in several parts of Europe, but the Gårdsjön project is one of the few covered catchment experiments still in progress.

Acidification models have been used to shed light on the chemical recovery that may be expected in soils and waters under different scenarios of sulphur and nitrogen deposition. Similar biogeochemical models have served as a tool in the estimation of critical loads of acidifying compounds, which have in turn provided a scientific basis for international negotiations under CLRTAP.

Each of these approaches has its limitations. However, a combination of controlled experiments, regional databases and mathematical forecasting tools offers the greatest potential for answering the questions set out above. This report presents the results of a number of studies, most of them funded by the Swedish Environmental Protection Agency. Its aim is to elucidate the recovery process, but also to document Swedish research in this area and to set it in its international context.

2. DEPOSITION TRENDS IN SWEDEN

OLLE WESTLING AND GUN LÖVBLAD

As a result of the industrial revolution, atmospheric deposition of sulphur increased as early as the closing decades of the 19th century. This increase accelerated after the Second World War, primarily owing to a sharp rise in the combustion of oil. Deposition peaked in the 1970s, and is expected to have fallen considerably by the year 2010 as a result of emission reductions achieved on the basis of international agreements. Emissions of nitrogen from fossil fuel use increased at a later stage than those of sulphur, as a consequence of growth in road transport. Deposition of nitrogen oxides culminated around 1990, and a slight decline can now be seen. Nitrogen deposition resulting from agricultural emissions of ammonia reached its highest level in the middle of the 20th century and has since decreased. These deposition trends are illustrated by figure 2, which shows wet deposition of sulphate at a monitoring station in southern central Sweden.

2.1 WHY, WHERE AND HOW IS DEPOSITION MEASURED?

The purpose of deposition measurements is to quantify pollutant loadings both to open sites, such as land with low vegetation and lake surfaces (bulk, or wet deposition), and to forests (throughfall, reflecting total deposition).

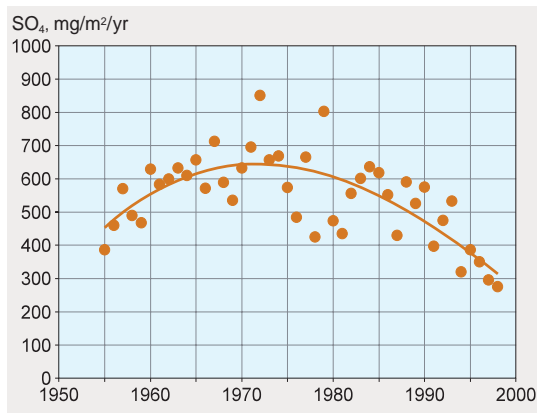


Figure 2. Wet deposition of sulphate in southern central Sweden.
Unpublished data from Department of Meteorology, Stockholm University.

The data thus collected can show whether the emission reductions decided on in Europe are in fact leading to lower levels of deposition, and also provide a basis for modelling. Models can be used to predict deposition trends over the next few decades, on the basis of expected future emissions of air pollutants across Europe. For this purpose, the 'EMEP model' is used.

In Sweden, wet deposition has been measured since the mid-1950s, but to date total deposition has only been monitored over a 10-year period. In recent years, deposition measurements have been performed at more than a hundred sites in Sweden, using methods that are employed throughout Europe. These measurements are carried out by the Swedish Environmental Research Institute (IVL) on behalf of the Environmental Protection Agency, county administrative boards and local authorities. In addition, the results are reported to European databases. Monitoring has been in progress for varying periods of time, but for several counties relatively long runs of data are available, showing trends over at least 10 years (Hallgren Larsson *et al.* 1995).

Studies of pollutants in precipitation in open countryside primarily provide information about the wet component of deposition, incorporated in rain and snow. Deposition to forests is measured by means of studies of throughfall at permanent sample plots in representative forest stands. Throughfall contains both the wet and the dry components of deposition and thus indicates the total atmospheric loading of substances, such as sulphate-sulphur, sodium and chloride, which are not affected by processes in the forest canopy. Concentrations of nutrients such as nitrogen, calcium, potassium and manganese increase or decrease in throughfall as a result of uptake, leaching or transformation on the surfaces of needles or leaves.

2.2 pH OF PRECIPITATION HAS RISEN

One of the early signs of acidification was low pH values in precipitation. For several years in the late 1980s, the average pH of bulk precipitation at a number of monitoring stations in Blekinge in the south of Sweden was between 4.0 and 4.2 (figure 3). Even lower pH values, below 4.0, were recorded in throughfall over a period of several years. In the early 1990s, measurement programmes were started in many parts of the country, and, with some variations between years, the pH of precipitation has generally risen. In the far north of Sweden pH values were higher than elsewhere when measurements began, and the same trend has subsequently been observed there as in central and southern Sweden.

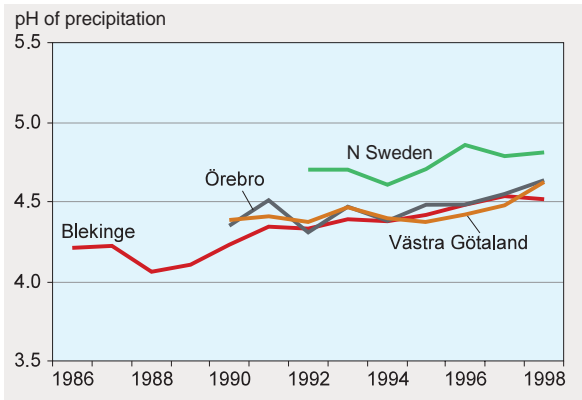


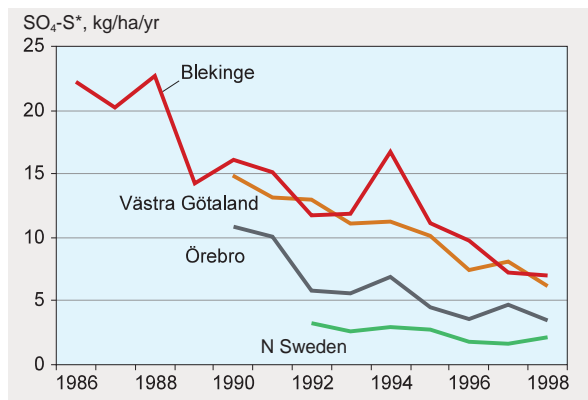
Figure 3. Annual mean pH of precipitation (volume-weighted) at open sites in different counties/regions: Blekinge (South-east Sweden), Örebro (Central Sweden), Northern Sweden, Västra Götaland (South-west Sweden). Data: IVL.

2.3 SULPHUR DEPOSITION IS DECREASING

The principal reason why precipitation and throughfall pH are rising is that European sulphur emissions have been reduced. In the county of Blekinge, for which the longest run of data is available, average deposition to spruce forests dropped from over 20 kg/ha/yr to around 8 kg/ha/yr between 1988 and 1998 (figure 4). Deposition of anthropogenic sulphur to forests has fallen in the other counties/regions included in figure 4, too.

In northern Sweden, where deposition was low to begin with, only a slight decrease has been observed. The data presented do not include the natural sulphur in deposition, from marine salts. In southern and central areas of the country, it is above all the dry component of deposition, in the form of gases and particles, that has abated. On sites where wet deposition predominates, a smaller reduction has occurred.

Figure 4. Deposition of anthropogenic sulphur to forest sites in different counties/regions. Data: IVL.



In the counties of Blekinge and Västra Götaland, the difference between sulphur deposition to forests and to open sites in the late 1980s was substantial, owing to the large quantities of dry deposition intercepted by trees. Figure 5 shows sulphur deposition in Blekinge, where there is a clear trend in deposition to forests.

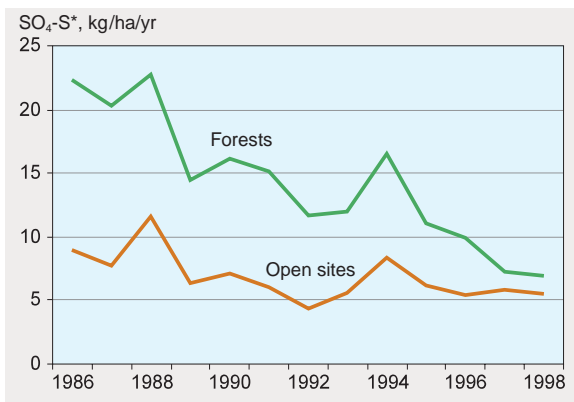


Figure 5. Deposition of anthropogenic sulphur to forests and open sites in Blekinge. Data: IVL.

The temporary increase in 1994 was a result of the special weather conditions prevailing that winter, which gave rise to a large influx of particulate pollutants into eastern Sweden from neighbouring countries in the southern Baltic Sea region.

The trend for bulk deposition of sulphur is not as clear, since it is influenced more by between-year differences in precipitation.

Deposition of sulphur still exceeds critical loads over much of Sweden, despite the substantial decrease (Warfvinge & Sverdrup 1995). In the south of the country, the target level is exceeded by a factor of between two and four. In large areas of central and northern Sweden, deposition is currently close to the critical load. Northern areas, however, face particular problems after the spring snowmelt, when the large quantities of precipitation accumulated during the winter can give rise to short-term acid surges in streams and rivers, despite moderate annual deposition.

Table 2 shows how sulphate-sulphur concentrations in bulk precipitation and sulphur deposition to spruce forests have changed in different parts of the country since 1990.

2.4 ONLY GRADUAL DECLINE IN NITROGEN DEPOSITION

Emissions of nitrogen in Sweden and the rest of Europe have not fallen by as much as sulphur emissions in recent years; in Sweden, the decrease between 1980 and 1997 was 30%. This is reflected in a relatively small decline in deposition of nitrogen in the last few years. Trends may be partly masked by year-to-year variations, due primarily to fluctuations in the

weather. Deposition of nitrogen to forests is difficult to measure, since nitrogen is transformed and taken up by trees before it can pass through the forest canopy. The highest levels of nitrogen deposition in Sweden are found in parts of Halland and Skåne in the south, often exceeding 10 kg/ha/yr on open sites and 15 kg/ha/yr in forests. Over much of northern Sweden, deposition is less than 3 kg/ha/yr. Nitrogen deposition has both a fertilizing and an acidifying effect, depending on to what extent and in what forms it is taken up by organisms in the ecosystems concerned.

Table 2. Estimates of trends in sulphate-sulphur concentrations in bulk precipitation (open sites) and sulphur deposition to spruce forests, for different counties where measurements were performed between 1990 and 1997. Estimated concentrations and depositions are based on the linear regression calculated for the period from the reference year 1990 to 1997. The correlation coefficient (r) expresses the strength of the association between the number of years after 1990 and the change in the concentration or deposition.

COUNTY	SULPHUR CONCENTRATION IN BULK PRECIPITATION			
	mg/l, estimated		Reduction	
	1990	1997	%	r
Skåne	1.11	0.72	35 %	-0.783
Blekinge	1.05	0.76	28 %	-0.675
Jönköping	0.95	0.55	42 %	-0.903
Västra Götaland	0.87	0.66	24 %	-0.765
Kronoberg	0.84	0.58	32 %	-0.838
Örebro	0.93	0.64	32 %	-0.887
Östergötland	0.97	0.53	46 %	-0.850
Södermanland	0.86	0.64	25 %	-0.849
Värmland	0.79	0.51	36 %	-0.858
4 counties in northern Sweden	0.53	0.35	34 %	-0.848
COUNTY	TOTAL DEPOSITION OF SULPHUR, SPRUCE FORESTS			
	kg/ha, estimated		Reduction	
	1990	1997	%	r
Skåne	19.2	10.7	44 %	-0.792
Blekinge	16.1	8.9	45 %	-0.780
Jönköping	15.3	6.9	55 %	-0.963
Västra Götaland	14.6	7.6	48 %	-0.966
Kronoberg	11.2	7.3	35 %	-0.766
Örebro	9.8	3.2	67 %	-0.869
Östergötland	9.8	5.3	45 %	-0.649
Södermanland	9.2	5.0	45 %	-0.709
Värmland	8.0	4.1	48 %	-0.940
4 counties in northern Sweden	3.9	1.8	54 %	-0.907

Figure 6 shows average deposition of nitrogen in throughfall in spruce forests and in precipitation at open sites in Skåne. In areas with heavy deposition, there is often more nitrogen in throughfall than in precipitation, owing to high levels of dry deposition and relatively limited uptake and transformation. As the diagram makes clear, the difference between forests and open sites varies widely from one year to another, but there is a clear downward trend in deposition. In 1998, however, precipitation was around 50% higher than normal, which explains the high level of deposition to open sites.

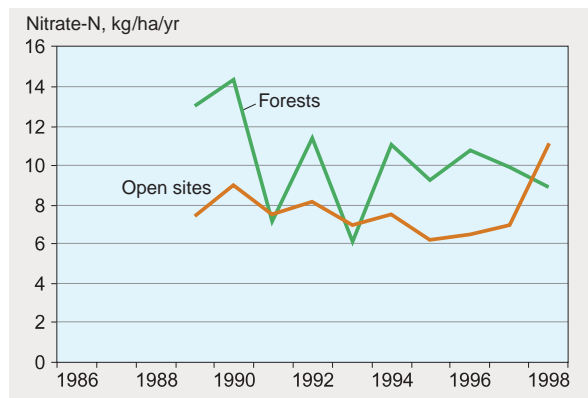


Figure 6. Deposition of nitrate-nitrogen to forests (as throughfall) and to open sites (bulk precipitation) in Skåne. Data: IVL.

2.5 WHAT IS HAPPENING TO BASE CATION DEPOSITION?

Atmospheric deposition of base cations is another important element in the process of acidification and recovery. These ions have both natural and anthropogenic origins. Natural sources include marine salts, dust and biogenic aerosols (e.g. pollen), while important anthropogenic sources are the burning of wood and coal and certain industrial processes (Lövblad *et al.* 2000).

Atmospheric deposition and weathering are the only mechanisms which offset the leaching of base cations from soils that is caused by acid deposition. Base cations can also play a direct neutralizing role if they are associated with alkaline anions such as carbonate or hydroxide.

Deposition of base cations is generally difficult to estimate, and varies widely from one site to another. Deposition of marine salts, for example, shows a strong gradient from coastal to inland areas. The base cations produced by combustion and industrial processes are associated with particles of varying size, which have shorter or longer lifetimes in the atmosphere. In the vicinity of emission sources, elevated deposition of base cat-

ions is observed, often combined with high pH. This local effect further complicates the task of mapping deposition over large areas in a way that is reasonably representative of the ecosystems concerned.

Existing monitoring networks only measure wet deposition of base cations. Estimates of deposition trends can be made by reviewing these measurements and studying how emissions have varied over time.

As industry has developed over the past century, emissions and deposition of base cations have changed considerably (figure 7).

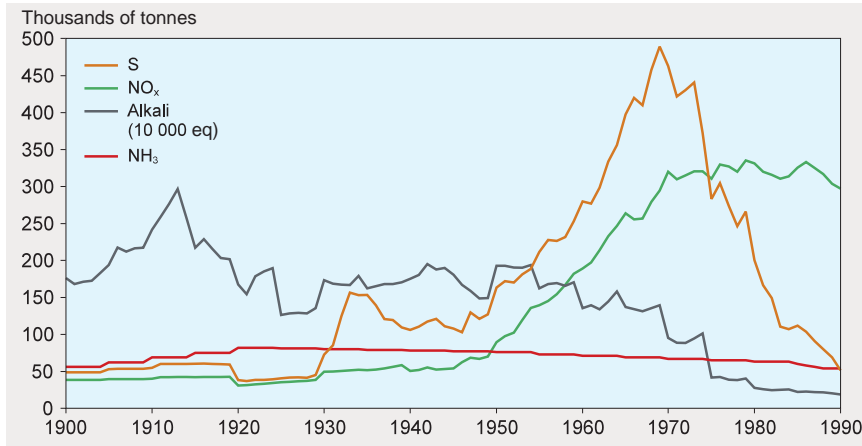


Figure 7. Total annual emissions of sulphur dioxide, nitrogen oxides, alkaline dust and ammonia in Sweden, 1900–1990. After Kindbom *et al.* 1993.

Even before the industrial era, some deposition of base cations occurred as a result of small-scale burning of wood. The scale of this deposition is difficult to estimate, since there were probably substantial local and seasonal variations in atmospheric emissions. With the installation of equipment to control particulate emissions at many sources from the mid-1970s on, in Sweden as in the rest of western Europe, and with more widespread use of oil instead of fuels such as coal and wood, which give rise to alkaline ash, emissions and deposition of base cations were reduced along with those of other pollutants. Such reductions were observed both in Sweden and in other parts of Europe, primarily in the 1970s and 1980s (Hedin *et al.* 1994).

A further decline in base cation deposition has been noted in some parts of Europe (Germany, the Netherlands and Finland) since 1990. This is assumed to be due to the closure of combustion plants and factories in the

wake of the economic changes in eastern Europe. As yet, no such trend has been observed in monitoring data from Sweden. Any trend that does exist will be revealed by the trend study of Swedish environmental monitoring results currently in progress.

As far as forest soils are concerned, a decline in base cation deposition means that the rate of recovery will be slowed somewhat, though not to such an extent as to offset the beneficial effects of the abatement measures introduced.

3. WHAT PROCESSES GOVERN RECOVERY?

PER WARFVINGE,
MAGNUS MÖRTH AND FILIP MOLDAN

3.1 REVERSIBLE AND IRREVERSIBLE SOIL PROCESSES

A host of different processes, substances and phases in the soil interact to determine how critical soil and surface water variables such as pH and concentrations of base cations and aluminium are affected by atmospheric deposition of acidifying compounds. The parameters influencing these quantities vary widely from one area to another. This means that any given chemical or physical process will assume differing importance in different ecosystems, even though it operates in fundamentally the same way in every ecosystem. This variability is one of the reasons why it is very difficult to assess the prospects of recovery from acidification in any particular area.

In order to analyse and explain how soil and water undergo and recover from acidification, it is important not only to study the responses of entire ecosystems to reduced levels of deposition, but also to investigate the chemical, biological and geochemical processes that take place in the soil. Without a grasp of the individual processes involved, it is impossible to gain the understanding needed to assess the future prospects of recovery, assuming different deposition rates, land use scenarios etc.

Soil processes can be reversible or irreversible, rapid or slow, and may be governed to a greater or lesser degree by biological factors.

Reversible processes include mechanisms buffering against changes in pH. If the input of acidifying compounds increases, cation exchange and sulphate adsorption in the soil, for example, will initially make a positive contribution to the buffering capacity of the soil solution and surface waters. This will counteract the pH-lowering effects of the acid deposition. If the pollutant loading is reduced, such reversible processes will slow down recovery by offsetting the effects of the decrease in deposition.

Of the irreversible processes, chemical weathering is particularly important. This process always increases the buffering capacity and base cation concentrations of soil water. The rate of weathering depends on a wide range of chemical, geological and biological factors, and can vary enor-

mously from one area to another. This variation is due to, among other things, differences in temperature and in the mineral composition of the soil.

These reversible and irreversible processes are affected by and interact with biological processes such as uptake of nutrients by trees, field-layer vegetation and micro-organisms, and decomposition of organic matter and smaller organic molecules. Complete decomposition results in the formation of CO_2 , NO_3^- , NH_4^+ and H_2O . Many biological processes influence the pH of the soil and release or immobilize substances in such a way as to affect abiotic processes, and vice versa.

3.2 STUDIES OF CATCHMENTS AND SOIL PROFILES

Acidification and recovery processes can be studied on many different scales in terms of time and space. The molecular scale is relevant to our understanding of the forces driving individual chemical and physical processes. In other cases, the regional scale may be relevant, e.g. when it comes to developing control strategies at a policy level. In the great majority of cases, however, the *catchment* (watershed) and the *soil profile* are suitable scales for studies of acidification and recovery.

The water leaving a catchment can be regarded as the combined result of the biogeochemical processes occurring in the soil in the area, which are driven by a range of factors including deposition of air pollutants. By comparing the chemical composition of the runoff from different catchments, and analysing how it varies geographically and over time, it is possible to obtain a great deal of information about the biogeochemical and hydrological properties of individual catchment areas.

This report refers to several examples of catchment studies, such as the research being conducted near Lake Gårdsjön and the analysis of chemical changes in Sweden's lakes.

As water passes down through a soil profile, chemical reactions occur which determine the composition of the runoff. At the same time, different substances are redistributed in the soil, resulting, on a time-scale of a few centuries, in the formation of distinct, chemically homogeneous layers, or horizons. It is of course important to be able to distinguish natural soil formation processes from changes caused by air pollution.

A particularly important type of soil system is the podzol, which is Sweden's commonest soil type in areas with till deposits, and which is also characteristic of areas susceptible to acidification. A podzol has several easily recognizable layers: an organic horizon nearest the surface, followed

by an eluvial (leached) layer of mineral soil, an illuvial (enriched) layer (known as the B horizon), and finally a layer of relatively unaltered parent material. The properties of a podzol in terms of the release, adsorption and desorption of ions depend on the characteristics of these different horizons, and concentrations of different substances therefore vary with depth.

Some of the processes with particularly marked impacts on biogeochemical cycles and hence on the recovery of acidified ecosystems are illustrated in figure 8.

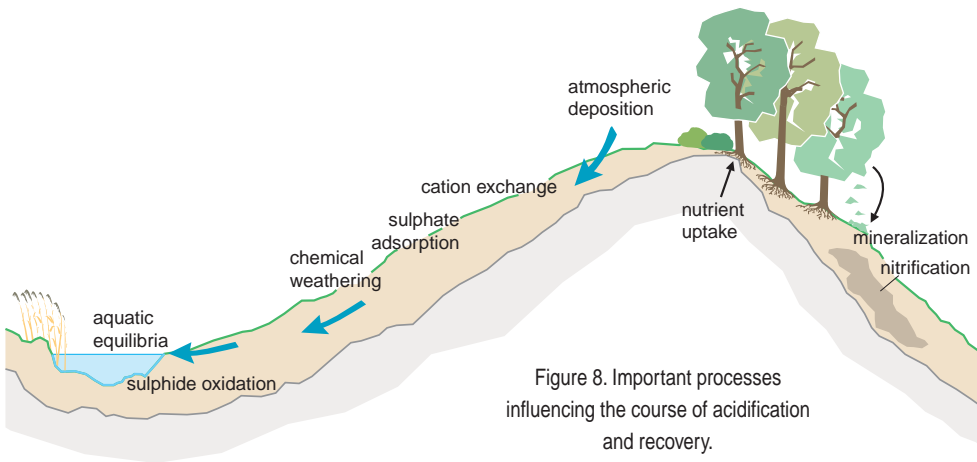


Figure 8. Important processes influencing the course of acidification and recovery.

3.3 ION EXCHANGE

Cation exchange is one of the most important processes for acidification and recovery from acidification. This is because it acts as a buffer against both acidification and recovery, and thus regulates the pH and buffering capacity of soil water and runoff. Usually, a very large pool of exchangeable cations is available, compared with the annual deposition of acid.

Exchangeable cations are bound electrostatically to charged soil particles. Cation exchange is a rapid and reversible process. It occurs on colloids which have negative charges on their surfaces, e.g. clay minerals and partially decomposed organic solids. The total exchangeable pool is referred to as the *cation exchange capacity*.

The cation exchange capacity of a soil varies with depth (horizon). In contrast to sulphate ions, which are mainly adsorbed in the B horizon,

cations are adsorbed most strongly in upper layers of the soil, owing to the abundance there of organic compounds to which metals can bind. Around Lake Gårdsjön, about 70% of calcium, for example, is found in the top 15 cm of the soil and the remaining 30% at greater depth. Most of the other base cations have similar distributions.

As a consequence of acidification, base cations have been displaced from soil particles by aluminium and hydrogen ions through the process of cation exchange. There has thus been a reduction of the 'base saturation' of the soil. In south-west Sweden, an estimated 2000–10 000 meq of base cations have been displaced per square metre of soil, resulting in higher concentrations of these ions in the soil solution. As this water drains from the soil as runoff, base cations are thus removed from the system.

The process of recovery from acidification entails aluminium and hydrogen ions on exchange sites being replaced by base cations, resulting in a higher base saturation. In the long term, this raises the pH of the soil water, reducing the solubility of aluminium and hence the concentrations of this metal found there.

3.4 WEATHERING

Chemical weathering involves the dissolution of minerals present in the soil, such as feldspars, quartz and mica. The reactions take place at the interface between the minerals and the water surrounding them, and the dissolved reaction products enter the soil solution. The rate of weathering depends to a certain extent on the chemical composition of the soil solution, but primarily it is determined by the properties of the minerals themselves. Chemical weathering differs in many respects from ion exchange, since it is irreversible and kinetically controlled and the quantities of minerals occurring in soils do not change on a time-scale of many centuries.

Weathering includes more than just chemical weathering. Wind, water and ice affect the physical structures of the rocks constituted by the different minerals. In addition, the hyphae of mycorrhizal fungi can bore into and dissolve mineral particles (Jongmans *et al.* 1997).

Dissolution of minerals adds buffering capacity to the soil. This occurs at a relatively constant rate, from a very large pool. Consequently, chemical weathering is the process that determines a soil's long-term resistance to acidification. Together with atmospheric deposition of base cations, it is also the chemical process which ensures a long-term supply of mineral nutrients in all soil ecosystems.

The rate of weathering in Swedish forest soils is normally estimated at somewhere in the range 20–100 meq/m²/yr. Thus, in many areas weathering has been appreciably slower than deposition of acidifying compounds. In the Gårdsjön area, the quantities of base cations released by weathering correspond to roughly 30% of the atmospheric deposition of sulphate, i.e. only 30% of this deposition is buffered by weathering. The rate of weathering is decisive to how rapidly the soil pool of exchangeable cations can be replenished.

3.5 SULPHUR FLUXES IN SOIL AND WATER

Soil contains large amounts of sulphur, bound in organic matter and adsorbed onto minerals. This means that processes which affect the cycling of these solid substances can potentially have a major impact on the flow of sulphur through the soil. The quantity of bound sulphur is several orders of magnitude larger than the amount of sulphur in soil water.

The most stable form of sulphur is sulphate, which is the most important inorganic form of this element in soil and water (Krouse & Grinenko 1991). In certain environments sulphides also occur, which can be a significant problem, causing acid surges or more permanent acidification. In the absence of sulphides, however, most of the sulphur in soils is found in organic compounds. In the Gårdsjön area, around 85% of the sulphur pool consists of organic sulphur compounds, while 15% is available as adsorbed sulphate (Torssander & Mörth 1998). These figures are not unusual, even in a global perspective.

Figure 9 shows how a number of processes interact in the soil sulphur cycle.

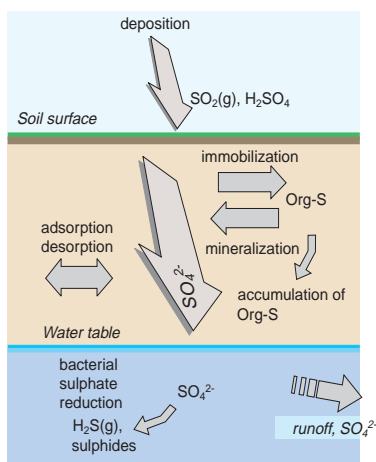


Figure 9. Cycling of sulphur in soil. A reduction of sulphur deposition results in sulphate being released from the soil pool until a new balance is achieved. Net mineralization of organic sulphur can appreciably prolong the recovery process.

3.5.1 SULPHATE ADSORPTION

In the part of the soil in which secondary minerals have formed, the B horizon, sulphate can bind to surfaces by adsorption. Upper soil layers on the other hand, which consist predominantly of organic matter, have a low capacity to adsorb sulphate. In the Lake Gårdsjön area, 96% of all adsorbed sulphate is to be found in the B horizon (Torssander & Mörth 1998).

A state of equilibrium exists between the amount of sulphate in solution and the amount adsorbed. This means that sulphur will tend to be released by desorption when atmospheric deposition decreases. When one equivalent of SO_4^{2-} is adsorbed, one equivalent of H^+ is consumed at the same time at the mineral surface. Sulphate adsorption thus buffers the soil solution against acidification, whereas desorption buffers it against recovery. We also know that the adsorption–desorption process is rapid and that the whole of the adsorbed quantity of sulphate is available and participates in the reaction (Karlton 1994). The latter has been shown by isotope studies in which researchers have tracked sulphate with differing isotopic compositions. There is no reason to believe that a desorption curve looks any different from an adsorption curve. The process would thus appear to be completely reversible.

How much sulphate can be adsorbed depends to a large extent on pH. A fall in pH enables the soil to adsorb more sulphate.

Karlton and co-workers carried out extensive studies of sulphate adsorption in podzols, in which they performed measurements along three transects across Sweden (table 3, Karlton 1995). Along the southern transect, soils appeared to be saturated with sulphate. In this region, therefore, sulphate adsorption will not buffer the soil against further acidification, but it will, when sulphur deposition falls, delay recovery by several decades. The amount adsorbed, 2800 meq/m², corresponds to some 50 years of sulphur deposition at the current, relatively low level.

Table 3. Adsorbed sulphate in Swedish forest soils (after Karlton 1995).

TRANSECT	No. of sites	Adsorbed Capacity meq/kg		Amount, 0–80 cm meq/m ²
Southern: Hallandsås–Västervik	10	2.8	2.8	2800
Central: Dalsland–Sundsvall	9	3.5	4.7	2000
Northern: Gällivare–Boliden	6	2.0	4.5	900

Isotope studies carried out as part of the Gårdsjön roof experiment show that, even after several years of minimal sulphur deposition, all the sulphate in runoff consists of 'old' sulphur, and that recovery is thus delayed by the adsorption–desorption process (Mörth & Torssander 1995).

3.5.2 ORGANIC SULPHUR

The majority of the sulphur in soil occurs in the form of organic sulphur compounds, which include amino acids and enzymes. The most important properties of organic sulphur compounds are how stable they are, and how rapidly they are turned over in the soil.

Studies in the Gårdsjön area using stable isotopes show that some 50% of the sulphate deposited from the atmosphere is converted into organic sulphur compounds in upper soil horizons (Torssander & Mörth 1998). In other words, this sulphate is not leached from the soil directly, but does a 'detour' via organic compounds. In deeper layers of the soil, organic sulphur compounds can subsequently be immobilized and accumulate in stable forms (Johnson & Mitchell 1998).

Microbial processes consequently have a major influence on how much sulphur is leached from a soil profile. Some of the organic sulphur in upper soil layers has low stability, and studies have shown that a dynamic equilibrium prevails between the amounts of sulphate that are immobilized and mineralized. Net mineralization corresponding to just a few per cent of the soil pool of sulphur can appreciably prolong the entire recovery process. This mineralization could be caused by reduced sulphur deposition, a higher temperature, or modified cycling of nitrogen.

3.5.3 SULPHIDE OXIDATION AND BACTERIAL SULPHATE REDUCTION

There are also processes in the sulphur cycle which are not directly linked to the soil profile. Two examples are reduction of sulphate in wetlands, and oxidation of sulphides in wetlands or in conjunction with changes in the water table. Sulphur reduction consumes H^+ ions in the surrounding water, while oxidation liberates H^+ .

The reduction of sulphur and its resultant accumulation as sulphides in wetlands is a natural process. The rate of accumulation has probably increased as a result of generally higher fluxes of sulphur in ecosystems. During dry periods, a small proportion of this sulphur can be oxidized, temporarily lowering the pH of streams draining the wetlands concerned.

There is nothing to suggest that the reduction or oxidation of sulphur in wetlands and groundwater is increasing or decreasing as a result of re-

duced deposition. However, these processes could become more important in conjunction with climate change. There is therefore every reason to keep an eye on what is happening to the sulphur retained in wetlands and other ecosystems.

3.6 AQUATIC CHEMICAL EQUILIBRIA – ANC AND pH

As was emphasized above, the chemical composition of soil water and surface water depends not only on the scale of deposition, but also on the interaction between soil and water within the soil profile and within the catchment, respectively. Once water has passed through the soil, the pH values and aluminium concentrations found in runoff are determined by its total content of dissolved substances.

Changes in the buffering or *acid neutralizing capacity* (ANC) of a given body of water are often used as measures of acidification and chemical recovery, in both surface waters and soil water. ANC is a further refinement of the alkalinity concept which enables other weak acids than carbon dioxide to be taken into account, and which in addition allows the buffering ability of very acidic waters to be calculated.

ANC can be defined in two ways. According to one definition, it is the difference between the total concentrations of base cations (BC) and strong acid anions (SAA):

$$\text{ANC} = \text{BC} - \text{SAA}$$

where

$$\text{BC} = [\text{Na}^+] + [\text{K}^+] + [\text{Ca}^{2+}] + [\text{Mg}^{2+}]$$

$$\text{SAA} = [\text{Cl}^-] + [\text{NO}_3^-] + [\text{SO}_4^{2-}]$$

The concentrations are expressed in equivalents per unit volume, e.g. $\mu\text{eq/l}$. A shift towards a lower ANC results in more acidic water.

Using the ANC concept, it is possible to see directly how different processes in soil contribute to or counteract acidification or recovery. For example, we can see that a process which releases base cations, i.e. increases BC, but does not affect SAA, leads to a higher ANC. One such process is chemical weathering. Conversely, a process which liberates sulphate ions but does not affect BC results in a lower ANC and hence a lower pH. One example of this is the desorption of adsorbed sulphur, another deposition of sulphuric acid.

The balance of charges in the water is also used to arrive at the other definition of ANC, which is the difference between anions of weak acids and cations of weak bases:

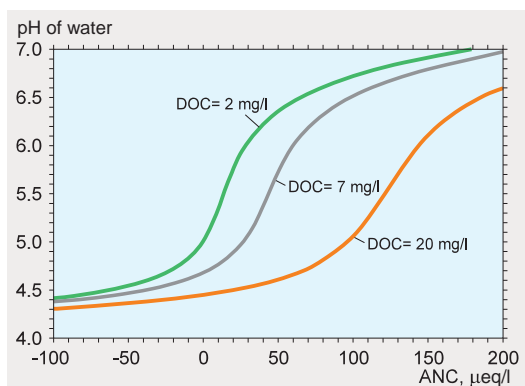
$$\text{ANC} = [\text{HCO}_3^-] + [\text{A}^-] - [\text{H}^+] - [\text{Al}^{n+}]$$

where A^- denotes anions of organic acids and Al^{n+} all forms of positively charged aluminium ions. In acid-sensitive waters, all other ions can normally be disregarded. This equation is used to calculate the pH for any given ANC, but also to analyse the causes of low pH in a particular body of water.

Severely acidified waters often have an $\text{ANC} < 0$. Such waters have low pH (normally below pH 5.3) and significant concentrations of inorganic aluminium. Waters with high levels of organic acids can have low pH values, without having a low ANC or being acidified.

With the help of chemical equilibrium relationships, it is also possible to construct diagrams showing the effects of, for example, dissolved organic acids, measured as dissolved organic carbon in the water. An example is shown in figure 10. This diagram illustrates, among other things, how a higher concentration of organic acids results in a lower pH, for a given ANC.

Figure 10. Model calculation of the pH of water as a function of ANC, for three different concentrations of dissolved organic carbon (DOC). The diagram refers to water with twice as much dissolved CO_2 as would be present if the water were in equilibrium with the atmosphere. After Warfvinge 1997.



The second definition of ANC also shows that an increase in ANC must result in a combination of lower aluminium concentrations in the water and higher pH. For the theory concerning how ANC and pH are linked to concentrations of dissolved substances and to chemical buffering systems in water, readers are referred to Warfvinge 1997.

3.7 NUTRIENT UPTAKE AND LEACHING OF NITROGEN

In the great majority of Swedish forest ecosystems, nitrogen is the limiting nutrient for primary production. This means that virtually the entire input of nitrogen from the atmosphere is taken up in the ecosystem, either in the soil, in the field layer or by trees.

Nitrogen undergoes deposition in two forms. Oxidized nitrogen is emitted as NO_x and deposited as NO_3^- . Reduced nitrogen is emitted as NH_3 and deposited as NH_4^+ .

Uptake of cations, such as NH_4^+ and base cations, results in H^+ ions being added to soil water. Uptake of anions, e.g. NO_3^- , causes OH^- ions to be released into the water. Where there is a balanced uptake of NO_3^- and base cations, growth as such thus does not entail any acidification of soil water. However, harvesting of trees means that base cations are not returned to the soil, which in the long term contributes to a declining base saturation.

Nitrogen deposition has an acidifying effect if nitrate is leached from the soil, or if the nitrogen has a fertilizing effect which leads to a greater uptake of base cations. Whether or not nitrate is leached is thus determined by how much nitrogen is needed as a nutrient. It is normally said that a state of nitrogen saturation has been reached if the atmospheric deposition exceeds the net uptake, which results in nitrate leaching and acidification.

Deposition of nitrogen is not expected to decrease as rapidly as that of acidifying sulphur. Any recovery brought about by a lower level of sulphur deposition could, if the worst came to the worst, be slowed down if nitrate begins to be leached from soils.

How great, then, is the risk of nitrate leaching? Soils have a low capacity to adsorb nitrate, and there is therefore no pool of nitrate that can be directly mobilized. Leaching of inorganic nitrogen seems to be closely related, rather, to how unstable the organic nitrogen in the soil is. A measure of the stability of the nitrogen compounds present is the C:N ratio, i.e. the ratio of organic carbon to organic nitrogen in the soil.

Figure 11 shows the relationship between the C:N ratio and leaching of nitrogen, primarily in nitrate form, in a number of forest ecosystems in Europe. A lower C:N ratio indicates that decomposer organisms in the soil have access to nitrogen in forms more readily available than organically bound nitrogen. The diagram shows that the higher the proportion of nitrogen in relation to the carbon it is bound to (i.e. the lower the C:N ratio), the greater is the risk of nitrate leaching. When the C:N ratio is below 25, there is a high risk of nitrogen being leached.

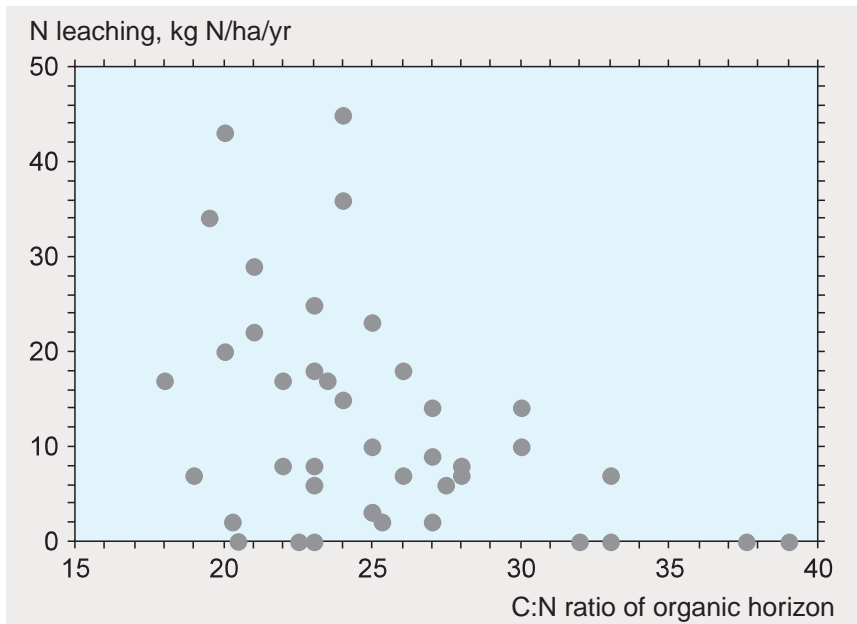


Figure 11. Relationship between the C:N ratio of the soil and leaching of inorganic nitrogen, primarily nitrate. Based freely on Dise *et al.* 1998.

In areas which experience nitrogen leaching, it normally decreases as soon as deposition is reduced. In Swedish forest ecosystems from which nitrate is not being leached, the ‘safety margin’ is probably quite wide. We therefore do not expect an increase in nitrogen leaching, provided that climate change does not result in greater net mineralization of soil organic matter. In the Gårdsjön area, where the C:N ratio is 35, large quantities of nitrogen have been applied experimentally to the soil, with no long-term effects on nitrate leaching (Wright & van Breemen 1995).

3.8 THE IMPORTANCE OF LAND USE

Land use will also influence the rate at which recovery takes place. In the timber production forests of today, large quantities of nitrogen and base cations accumulate in wood and needles and are subsequently removed from the ecosystem when the trees are harvested. It is difficult to precisely quantify the acidifying effect of forestry; it depends on how forests’ uptake of nitrogen is assessed in relation to their uptake of base cations. What is clear, though, is that the removal of base cations from forest ecosystems

has an acidifying effect. If there is a trend in forestry towards a higher extraction of biomass, without compensatory measures such as recycling of wood ash, recovery from acidification will be held back. Whole-tree harvesting is also a potential threat to recovery. It is particularly important not to remove the nutrient-rich needles.

Liming or nitrogen-free ‘vitality fertilization’ of forest soils is a way of rapidly restoring the base cation pool of upper soil horizons, thereby repairing to some extent the changes in soil chemistry caused by acidification. However, it takes several decades for liming to have a significant effect on deeper layers of soil.

3.9 SPATIAL VARIATION WITHIN CATCHMENTS

Closer studies of catchments often reveal considerable spatial variation in soil characteristics, even within small drainage areas. The soil is usually thinner and drier on hillsides than down in the valleys, in the vicinity of rivers or streams. The processes shaping the chemical and physical development of a soil are generally linked to water availability, and differences in soil moisture are therefore of great importance.

Runoff represents an integrated outflow of water and substances from an entire catchment area, but the soil cover in different parts of the catchment affects its composition to differing degrees. Areas far away from the stream or river may be of limited significance for runoff chemistry, since at times there may be no hydrological link between these areas and the watercourse. Consequently, soil processes occurring in recharge zones may be less important for the composition of runoff than those taking place in the discharge zone adjacent to the watercourse, even if the latter zone covers only a limited area. This mechanism affects different substances to differing degrees.

3.10 THE DYNAMICS OF ACIDIFICATION AND RECOVERY

The above discussion of processes in the soil system can be summarized by dividing the acidification and recovery process into four phases:

- Prior to acidification
- During acidification
- Acidified state
- Early stages of recovery

There is much to suggest that we are now at the beginning of the fourth of these phases.

Prior to acidification, a state of equilibrium prevailed between the production and consumption of ANC and the most important dissolved constituents in the soil system, and hence also in catchments. The degree of base saturation was therefore stable. The concentration of base cations in runoff corresponded to the difference between weathering plus deposition on the one hand and net uptake by vegetation on the other. A stable soil chemistry produced an even and high ANC, and often a high runoff pH, if the effect of organic acids was limited.

When acid deposition – chiefly in the form of acidifying sulphur – increased around the turn of the century, this steady state was disturbed. Via the mechanism of ion exchange, the elevated acid input to the soil system resulted in a reduction of the pool of exchangeable cations. This led to higher concentrations of base cations in the soil solution and losses of these ions from the soil system. As yet, there had been no appreciable fall in soil pH, and concentrations of inorganic aluminium were therefore still low. A certain proportion of the sulphate deposited was adsorbed, delaying the acidification process.

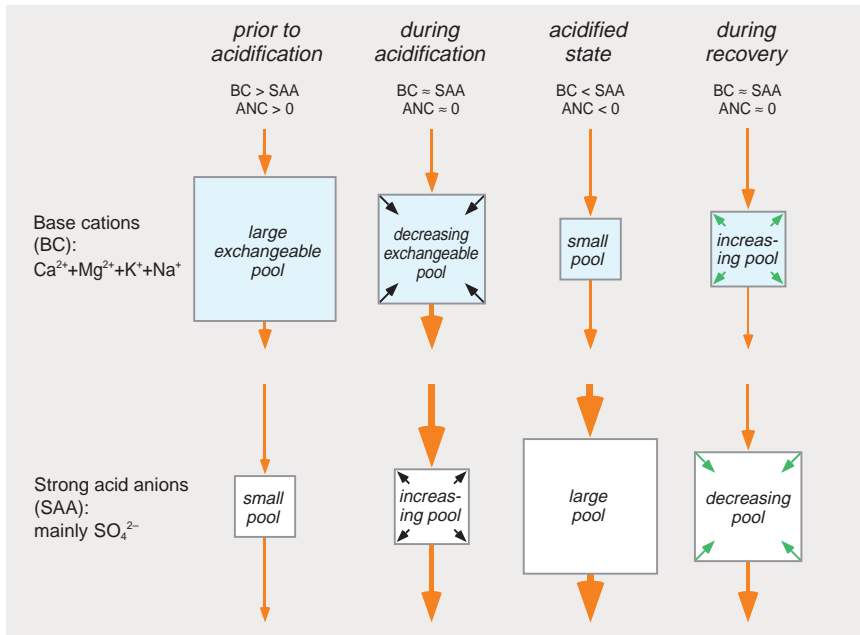


Figure 12. Illustration of how processes which buffer soil and soil water against acidification also buffer them against recovery when deposition decreases.

An acidified state is reached after a long period of high deposition. At this stage, the buffering capacity of the ion exchange pool declines and the system moves towards a new equilibrium. As buffering ion exchange reactions abate, soil and runoff pH fall rapidly to stable low levels. Concentrations of base cations in runoff decrease, while aluminium levels in soil water and runoff increase. The anion exchange sites in the soil are saturated and unable to adsorb any more sulphate. Streams and lakes show signs of chronic acidification, with ANC values below zero.

When deposition decreases, the process of recovery begins in the soil. This process is delayed by desorption of sulphate, and by replenishment of the pool of exchangeable base cations. Both these processes result in H^+ ions being released into soil water from solid material in the soil, and there is also a decrease in base cation concentrations in the soil solution and runoff. Since the annual rate of weathering is low in relation to the pools of exchangeable cations and adsorbed sulphate, this phase will be very protracted. What is more, deposition of acidifying compounds is expected to remain above pre-industrial levels for the foreseeable future, and it will take a very long time for pools of exchangeable base cations to return to their original levels. Consequently, only partial chemical recovery will occur. However, the biological benefits of this limited chemical recovery may be considerable.

This dynamic process is illustrated in figure 12 (see previous page).

4. EXPERIMENTAL STUDIES IN SWEDEN

FILIP MOLDAN AND ANNA EK

The links between air pollution and acidification of soil and surface waters can be regarded as relatively well known and well established. We have a more limited understanding, though, of how natural ecosystems recover as deposition of acidifying compounds abates, and of the processes governing their recovery. This is partly because recovery from acidification is a relatively recent phenomenon. Considerable reductions of acid deposition have occurred over large areas of Sweden in the last decade or so, but prior to that no recovery was possible.

When environmental monitoring data reveal signs of recovery in certain lakes and watercourses, it is possible to study this important process in greater detail. On the basis of field measurements, theories about the recovery process can be developed and tested and forecasting models can be elaborated. Many of the geochemical processes in soil and water which play a crucial role in the context of acidification (sulphate adsorption and ion exchange on soil particles, fluxes of CO₂, mobilization of aluminium, buffering of organic acids etc.) are well known and have been investigated throughout the 20th century, but it is only now that we can apply this knowledge to the recovery of acidified soils and lakes.

Underlying the calls for reductions of acidifying air pollutant emissions is a conviction that, when those emissions fall, there will be a return to more natural conditions in soils, running waters and lakes. That environmental improvements (defined, for example, as better conditions for biological life in lakes and streams) will occur if levels of acidifying pollutants are reduced is something most researchers take for granted. But it is far more difficult to predict *how far-reaching* such improvements will be and *how long* they will take. The only way of finding answers to these questions is to draw on our understanding of the mechanisms underlying acidification and recovery and to use the results of environmental monitoring and field experiments to develop and test theories and models relating to these processes.

4.1 THE GÅRDSJÖN ROOF PROJECT

The roof built as part of the Gårdsjön project consists of a timber frame covered with thin, but rigid, transparent plastic. It stands at a height of a few metres in a mature forest of Norway spruce. Each of the mature trees grows



through a hole cut in the plastic. The roof is divided into a number of sections which slope so as to follow the terrain below. Precipitation collected on the roof is led from the covered area by a system of gutters. It is replaced with the same quantity of clean artificial precipitation, by means of an irrigation system installed under the roof. This artificial rain consists of deionized water with certain additions, primarily sea water and potassium. The sea water replaces the marine salts that occur naturally in precipitation in the Lake Gårdsjön area. Potassium has to be added to make up for the quantities of this element that are normally recycled within a forest. Large amounts of potassium are taken up by tree roots and returned from the forest canopy to the ground in throughfall. Since here the roof intercepts this throughfall, potassium has to be applied with the irrigation water. For the same reason, i.e. to maintain the natural internal cycling of different substances in the forest, the litter falling onto the roof is collected from time to time and scattered on the ground below.

The roof covers the whole of a small, naturally shaped catchment with an area of 6300 m². The monitoring programme includes regular sampling of runoff at the lowest point in the roofed area. This is a very important feature of the experiment, since the chemistry of the runoff collected reflects the conditions and changes occurring in the catchment. This also means that the data gathered can be used for mass balance calculations.

The south-west of Sweden is the most severely acidified region in the country. This is because of high levels of acidifying deposition over the last hundred years or more, combined with the low capacity of forest ecosystems in the area to counteract this deposition. The latter can in turn be attributed to the fact that the bedrock here contains little calcium carbonate, the soil cover is thin, and intensive forestry has been carried on over large areas. Lake Gårdsjön is situated some 15 km from the west coast of Sweden, 50 km north of Göteborg. The area was chosen as a location for acidification research because it exhibited most of the common symptoms of acidification, e.g. acidified lakes that had suffered losses of fish populations (these lakes now include both limed and unlimed waters), acidified catchments supporting mature spruce forests, acidic runoff with high aluminium levels, and thin, depleted podzol soils. At the same time, the terrain permitted the selection of a large number of small, well-defined catchments that could be used for experiments and monitoring.

The Gårdsjön project was launched in 1979, with studies of small catchment areas as its main strategy. A monitoring programme in a reference area (referred to as F1) was started that year, and measurements of runoff and deposition have been made continuously since then. In the 1980s and 1990s a succession of experiments to explore various aspects of the acidification problem were set up. The individual small catchments were subjected to treatments such as fertilization, liming, felling, and applications of elemental sulphur and neutral sulphur salts. Each experiment was conducted in a hydrologically delimited catchment area, on a scale of a few hectares. Throughout the project, the reference area F1 has served as a basis for assessing the effects of the different treatments. The roof (see box) was completed in 1990, and the roof experiment began in 1991.

As the project has progressed, the data obtained from the reference area, which now span almost twenty years, have become increasingly interesting in their own right. They reflect the changes in deposition that have occurred in the 1990s (figure 13) and the beginnings of a subsequent recovery process (figure 14). The clearest change is a reduction of sulphur deposition, followed by lower sulphate concentrations in runoff. Although a decrease in sulphate levels in runoff does not, per se, constitute chemical recovery, it is a sign that the chemistry of surface waters is beginning to change in a favourable direction. Only when the flux of sulphate (and in certain cases nitrate) through the catchment has fallen sufficiently can we expect an increase in the base saturation of the soil, together with improved alkalinity, lower aluminium concentrations and higher pH values in runoff.

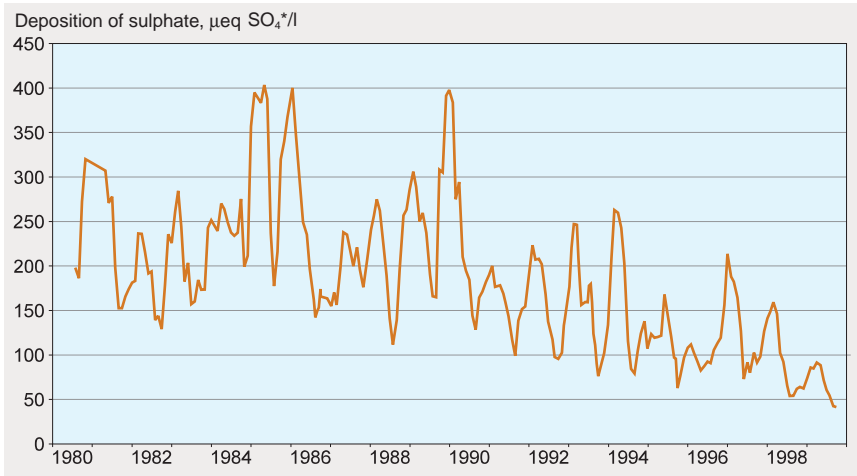


Figure 13. Non-marine sulphate concentrations in throughfall in the Gårdsjön reference area F1. The data shown are 5-month running means. Despite the relatively large temporal variations, there has clearly been a gradual decrease over the last 10 years, in which time sulphate concentrations have basically been halved. Data: IVL.

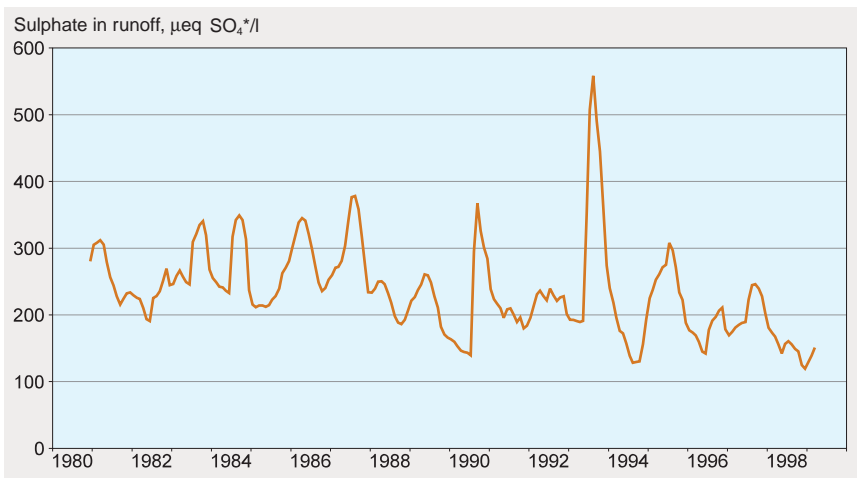


Figure 14. Non-marine sulphate concentrations (5-month running means) in runoff from the Gårdsjön reference area F1. The decrease in sulphur deposition has been followed by a somewhat slower decline in concentrations in runoff. The delay is mainly attributable to the desorption and release of sulphate previously retained in the soil. Data: IVL.

4.1.1 WHY WAS THE ROOF BUILT?

The main issues addressed by the roof project can be summarized as follows:

- How rapid will recovery be?
- How far-reaching will it be?
- How much must emissions be reduced to achieve the desired degree of recovery?
- How rapidly and to what level will recovery take place, for a given reduction of deposition?

Predictions of all kinds have one weakness in common: it is only after the event that it is possible to determine whether or not they were accurate. The roof was built in order to make predictions about recovery from acidification in south-west Sweden as certain as possible, particularly in terms of the time-scale of the process. The basic idea was that, by reducing acid deposition by almost 100% in the area under the roof, i.e. a much larger decrease than is actually occurring in the surrounding countryside, it would be possible to 'fast-forward' the process by a few decades. Thus, by looking at what is happening in the roofed area, researchers can study now later stages in the recovery process, which in other areas will not occur for another twenty or thirty years, or even further into the future.

4.1.2 BENEFITS AND LIMITATIONS OF THE ROOF PROJECT

Many different aspects of the acidification problem and the recovery process have been studied within the roof project. In addition to chemical monitoring of soil water, groundwater and runoff, studies have been made of the toxicity of the runoff to fish, and of the state of the forest, including effects on roots and fungi in the soil. Several other issues with a bearing on acidification have also been investigated, such as soil sulphur dynamics (using isotopic techniques) and the impacts of 'clean' precipitation on the cycling of mercury, methyl mercury, trace metals and persistent organic pollutants. By bringing together several research groups under one roof (literally and metaphorically), it has been possible to interpret experimental results in a broader perspective, to the mutual benefit of all the constituent projects (Hultberg & Skeffington 1998).

The roof project is an unreplicated study, i.e. there is only one roof experiment in the Gårdsjön area and there is no other roof of a comparable type anywhere else in Sweden. Normally, findings from an experimental site are of course compared with the results of a statistical analysis of differ-

ences between that site and a reference area. Care must therefore be taken when it comes to generalizing and regionalizing results from the roof project.

4.1.3 HIGHER ANC AND LOWER ALUMINIUM LEVELS WHEN DEPOSITION DECREASES

Lake Gårdsjön is situated in an area of very severely acidified forest land. Before the roof was built, runoff had an annual mean pH of 4.2, an annual mean ANC of $-260 \mu\text{eq/l}$ and an annual mean concentration of inorganic aluminium of $230 \mu\text{eq/l}$. In tests of fish toxicity, 50% of young brown trout (*Salmo trutta*) died within 7–51 hours of being placed in tanks of runoff water.

This can be compared with what is regarded as a desirable water quality standard for runoff, which is an ANC of $+50 \mu\text{eq/l}$ and virtually no inorganic aluminium at all.

The application of unpolluted precipitation produced a rapid and pronounced beneficial effect in terms of the quality of runoff (figures 15 and 16). Within a few months of the beginning of the experiment in April 1991, it was possible to observe a reduction of sulphate concentrations in runoff, a decrease in toxic inorganic aluminium and an increase in ANC.

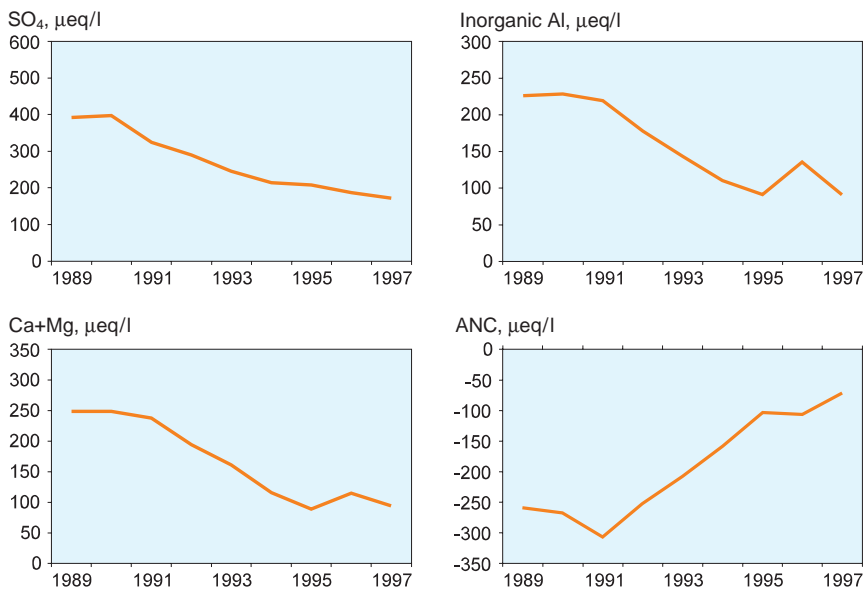
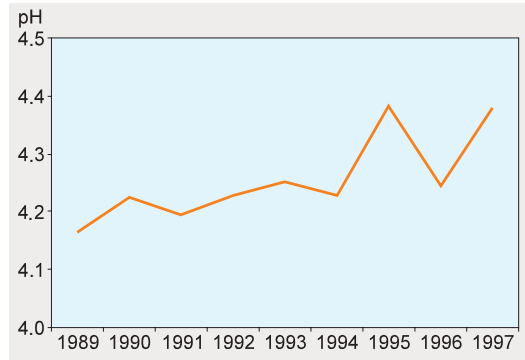


Figure 15. Annual mean concentrations in runoff from the roofed area, for the two years before and seven years after the roof was built. Sulphate, inorganic aluminium and base cations began to fall during the first year of treatment (1991). ANC (acid neutralizing capacity) rose appreciably during the seven years 1991–97, but is still well short of non-negative values. Data: IVL.

Figure 16.
The pH of runoff from the roofed catchment near Lake Gårdsjön had not risen appreciably after seven years without acidifying deposition. A slight upward trend can be discerned, however.
Data: IVL.



At the same time the concentration of base cations began to fall, suggesting that a smaller proportion of the available pool of these ions was being leached from the soil. This is a necessary change if the base saturation of the soil is to increase in the long term. Seven years from the start of the experiment, levels of sulphate, inorganic aluminium and base cations had fallen by 50–60%. ANC had risen at approximately the same rate as aluminium concentrations had fallen. All these changes can only be taken to mean that the chemistry of runoff from the area is beginning to improve. It has to be noted, though, that after 7 years with no acidifying deposition, the quality objective for runoff is still far from being achieved. The trends observed are pointing in the right direction, but so far they have not gone far enough.

At the same time as these favourable changes were observed, the pH of runoff showed relatively little improvement. The soil system is still chemically in a state of aluminium buffering and the pH is unlikely to rise until there is a further decrease in the concentration of inorganic aluminium.

4.1.4 SOIL SULPHUR DYNAMICS – IMPORTANT AND UNCERTAIN

The gradual change in runoff chemistry (in turn reflecting changes in soil chemistry) that has resulted from the gradual reduction of deposition is largely a consequence of the dynamics of sulphur in the soil. In somewhat simplified terms, it can be said that sulphur is present in soil in two forms: organic, i.e. sulphur bound to different forms of organic matter, and inorganic, the great majority of it in the form of sulphate ions adsorbed onto soil particles. In podzols in southern Sweden, organic sulphur normally accounts for over 90% of all the sulphur present, but adsorbed inorganic sulphur is the most important form as far as acidification is concerned.

Higher deposition of sulphuric acid or other sulphate-containing air pollutants increases the pool of adsorbed sulphate in the soil. This process delays leaching of base cations and hence acidification of the soil. When deposition falls, the adsorbed sulphate begins to be leached, with the result that improvements in runoff chemistry are also delayed.

The various pools and fluxes of sulphur in the Gårdsjön area are presented in figure 17. The mass balance shown has been calculated on the basis of mean values for the first five years of the roof experiment. Both the annual input in irrigation water and the output in runoff are relatively small compared with the amounts of sulphur stored in the soil. The soil pool of adsorbed sulphate-sulphur alone would be sufficient to keep the concentration in runoff from the covered area at the same level for another 15 years, even with the input reduced to natural, marine-derived sulphur only – provided that sulphate adsorption is in fact an entirely reversible process.

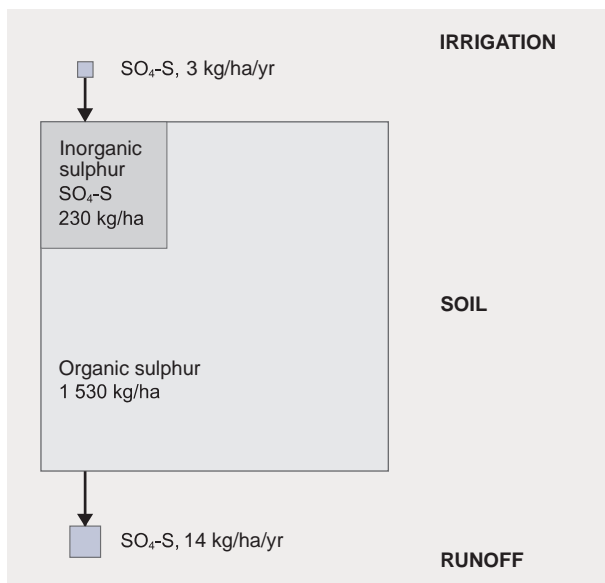


Figure 17. Relative sizes of soil pools and fluxes of sulphur in the Gårdsjön roof experiment. During the first five years of the experiment, leaching of sulphate-sulphur ($\text{SO}_4\text{-S}$) exceeded the input in irrigation by an average of $11 \text{ kg SO}_4\text{-S/ha/yr}$. The areas of the squares in the diagram are directly proportional to the sizes of the pools and fluxes. Data: IVL.

Further decreases in runoff sulphate concentrations are expected in the years ahead. This means that the soil pool of sulphate will diminish slowly, over several decades, rather than ‘just’ over the next 15 years. When sulphur is desorbed, hydrogen ions are also released in the soil. Leaching of desorbed sulphate will therefore cause leaching both of aluminium and hydrogen ions and of base cations.

Two principal conclusions can be drawn from this: the recovery of soils in severely acidified areas such as the Gårdsjön catchment will be delayed even if sulphur deposition falls rapidly, and a continuing high level of deposition will cause a further delay in sulphur leaching or an additional increase in the soil store of sulphur, thus pushing recovery even further into the future. Furthermore, if deposition of sulphur remains high, areas which are currently little affected could suffer acidification.

As figure 17 shows, there is roughly seven times as much organic as inorganic sulphur in the soil in the Gårdsjön area, a state of affairs which is not unusual in forest soils with a high organic content. The inorganic sulphur stored in the soil will very probably delay recovery. By contrast, the organic sulphur in soil is often regarded as stable, i.e. net changes in the amount of soil organic matter are small or not measurable on a scale of a few years. This is taken to mean that organic sulphur will not appreciably affect the course of acidification or recovery. In reality, however, there is a large turnover of organic matter in soil, even though the net changes are small, and relatively small changes in the net balance of organic sulphur can have major consequences for the sulphur budget.

Decomposition of humus may be affected by a reduced level of acidifying deposition and by other environmental factors, such as climate change. If net mineralization of organic sulphur occurs, this could increase the amount of mobile inorganic sulphur in the soil and thus further delay the recovery process. Measurements of soil sulphur pools in the roofed area have been performed using isotopic techniques which enable 'new' sulphur of anthropogenic origin to be distinguished from 'old', natural sulphur. The most recent measurements suggest that net mineralization of organic sulphur is occurring. It is too early to determine the scale of this process and hence its significance for the process of recovery below the roof. What is clear, though, is that soil sulphur dynamics may prove to have an important influence on the recovery of forest soils in southern Sweden.

The recovery process can be regarded as comprising two phases. The initial phase is characterized by rapid changes in fluxes of anions, above all sulphate, and by associated changes in soil and surface water chemistry. In the second phase, there is a gradual build-up of alkalinity in the soil, at best to pre-industrial levels.

The initial, rapid phase (corresponding roughly to the first 10 years of the roof project) is governed to a large degree by the dynamics of adsorbed sulphur in the soil. The early years of the roof experiment shed light on this phase. Data from other roof projects, above all in Norway

(the RAIN project), and environmental monitoring data from the early 1990s, when acid deposition began to fall sharply, confirm the findings of the Gårdsjön study, in terms of both governing processes and their time-scales. After a certain period in which sulphur dynamics are a dominant factor for runoff chemistry, the second, probably much slower stage of recovery begins.

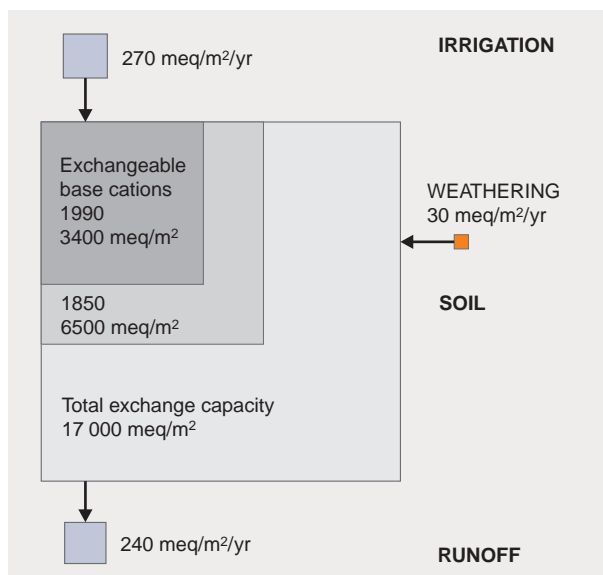
4.1.5 BASE CATIONS – CONCENTRATIONS FALLING DESPITE LOWER ACID DEPOSITION

During the period of acidification, exchangeable cations were lost from the cation exchange complex of the soil as they were displaced by hydrogen ions. In other words, the proportion of the soil's total exchange capacity made up of base cations, i.e. its base saturation, fell. Soil water is practically in equilibrium with the solid phase of the soil. Although the relationship between soil water and runoff can be highly complex, ultimately the base saturation of the soil is reflected in the composition of soil water, groundwater and, finally, runoff. Not until the base saturation has increased substantially can we expect runoff to regain a chemical composition resembling that found before the soil became severely acidified. This process of restoration could take a very long time.

In the roofed area of the Gårdsjön catchment, base saturation fell by roughly half between 1850 and 1990 (figure 18), according to the results of modelling of the acidification process. The pool of exchangeable cations in the soil decreased from 6500 meq/m² to 3400 meq/m². This can be compared with the current total input of 300 meq/m²/yr from weathering and the atmosphere (in the case of the roof project, simulated by irrigation) and leaching of 240 meq/m²/yr. The net increase in exchangeable base cations in the roofed area can thus be estimated at some 60 meq/m²/yr (irrigation + weathering – runoff). The estimates of deposition and weathering are uncertain, whereas leaching is measured with a satisfactory degree of accuracy. Even if the input of base cations is slightly underestimated, though, it is clear that, with a net input of less than 100 meq/m²/yr, it will take a very long time to rebuild the store of base cations lost since 1850, which according to the model estimates amounts to over 3000 meq/m².

Exactly how long it could take to raise the base saturation of the soil to a given level is very difficult to estimate. Apart from the uncertainties inherent in the estimates of deposition, weathering and leaching, all three processes are dynamic, and deposition and leaching in particular can vary

Figure 18. Relative sizes of the soil pools and fluxes of base cations in the roofed catchment near Lake Gårdsjön. During the first five years of the roof experiment, the input of base cations exceeded leaching by an estimated 60 meq/m²/yr. The areas of the squares in the diagram are directly proportional to the sizes of the pools and fluxes. Data: IVL.



considerably over time. However we attempt these calculations – with or without models, in a simple or more complex manner – there is no escaping the fact that the annual net input of base cations is relatively small compared with the soil pool. What is more, this net input is calculated as the difference between considerably larger quantities (deposition plus weathering, and leaching), each of which is somewhat uncertain.

These figures are not just applicable to the roof project; similar proportions between annual fluxes and exchangeable pools of base cations may be expected in most coniferous forest areas of southern Sweden. And an increase in the base saturation of the soil is a key issue in the context of acidification. Any predictions concerning the recovery of soils and surface waters which extend beyond the next 10, 20 or 30 years should therefore be treated with the utmost caution.

4.1.6 MANY QUESTIONS STILL TO BE ANSWERED

Even if future research confirms our present understanding of the processes important for recovery, namely sulphur adsorption, sulphur desorption and ion exchange in soils, there may be other processes which could prove decisive at a later stage. In 2000 the roof project is continuing into its ninth year, and a few more years of experiments are planned. It may be

noted that it is only now, with recovery in the roofed area entering the second, slower phase, that we can establish to what extent forest soils are able to recover and how long it may take.

Another factor that has to be taken into account if the results of the roof project are to be generalized to other areas is forestry. The net uptake and accumulation of base cations in the trunks and crowns of growing spruce trees in southern Sweden amounts to around 40 meq/m²/yr (averaged over an entire rotation). If felling is carried out without any steps whatsoever being taken to compensate for the loss of base cations, then more base cations will be removed from the forest soil than are added to it and recovery of the acidified soil will be further postponed by many decades.

Reports on findings from the Gårdsjön Roof Project frequently refer to data obtained from chemical monitoring of runoff. This is partly because runoff chemistry itself is important for aquatic organisms in downstream ecosystems, and partly because runoff reflects changes in the chemistry of the soil, which is an important habitat for both soil organisms and roots (although it can be discussed whether these data mirror changes in the catchment as a whole or primarily in the discharge zone). Another reason for focusing on runoff chemistry is that it reacts relatively quickly to changes in deposition; certain trends could be clearly observed within a few months of the roof being erected.

Various other effects of reduced deposition have been observed in the roofed catchment. There was, for example, an increase in the vigour of fine roots, compared with the reference area. In addition, production of fungal fruit-bodies increased, although the density and vigour of mycorrhizae below the soil surface did not change. Continuing increases in tree crown discoloration and needle thinning have been observed in both the covered and the reference area. In other words, no effect on the crown status of the trees can be attributed to the treatment. Nor has forest growth been affected. To sum up, it can be said that, after a few years of treatment, there have been few measurable effects on living organisms. As far as the trees themselves are concerned, this may be because this is an almost one-hundred-year-old forest which has a naturally slow growth rate. It may therefore take a long time for any differences between roofed and reference areas to become measurable. As for other factors, such as the toxicity of runoff to fish, the status of soil organisms or the degradation of organic matter, tests and studies will need to be repeated in later years of the project. This is necessary to ensure that slow processes and small changes are also detected, and not least to discern any trends in the natural variation that occurs in biological systems.

4.2 DIATOMS AS A BIOLOGICAL pH METER

Lake sediments are an invaluable environmental archive that can tell us a great deal about the history of lakes and their surroundings. Every day, year in, year out, new sediment is deposited on the bottom of a lake. This sediment consists of the remains of plants and animals that once lived in the lake, and also of material from its catchment (e.g. soil and plant parts). Pollutants which enter the lake via the atmosphere or via water flowing into it also end up in the sediment. By analysing the biological and chemical remains in the different layers of this sediment, we can trace the historical development of pollutant loadings, acidification, eutrophication and vegetation changes. Few environmental archives contain as much information as lake sediments. They can provide evidence of natural background conditions and the development of the environment over hundreds or thousands of years.

To study how lakes have been affected by acidification, we can make use of the diatoms found in their sediments. Diatoms, a type of microscopic algae, occur in large numbers in all types of lakes and are very sensitive to the pH of the water. This means that different species occur at different pH values. The main advantage of diatoms is that their silica cell walls, or frustules, are preserved in sediments, and it is therefore possible to analyse which species have lived in a lake and thus to reconstruct its pH, tens, hundreds or thousands of years ago. Diatoms serve as a biological pH meter, shedding light on the history of the lake.

In studies of recovery from acidification, diatoms can be used

- to gain a picture of acidification trends in a lake, i.e. when the lake was acidified, and to what extent,
- to establish whether the chemical state of the water is improving as acid deposition declines, and
- to answer the question: 'Recovery – to what?', i.e. to find the original pH, prior to acidification.

Analysis of the diatoms to be found in sediments is a good way of reconstructing the development of a lake's pH when frequent measurements of water chemistry from past periods are not available. In Sweden, diatom analysis has been used in two studies of recovery, which have shown:

- that there have been improvements, albeit very small, as a result of the recent fall in deposition (Lake Örvattnet, Värmland);
- that it is very important that forests and land are managed in ways which counteract acidifying deposition and help rather than hinder recovery processes when deposition is decreasing (lakes around the Falun copper mine).

Diatoms are small, unicellular algae with a cell wall, or frustule, of silica. They measure only 0.005–0.2 mm. They are common in all lakes, and hundreds of different species are found in Swedish fresh waters. When diatoms die, they accumulate in large numbers in lake sediments. Their microscopically small frustules are resistant to decay and can easily be identified, even if they have been buried in the sediment for thousands of years.

Diatoms are sensitive to the acidity (pH) of the water. This means that some species are only found in acid water, while others occur when the pH is high. To reconstruct the pH of a lake at different times in the past, a ‘transfer function’ is needed. This is a statistical model of the relationship between the diatom species present and the pH of the water, based on the composition of the diatom flora found in recent layers (i.e. the top centimetre) of sediment in a large number of lakes in which pH has been measured (Battarbee *et al.* 1999).



Tabellaria binalis

Cyclotella sp.

Brachysira vitrea

4.2.1 LAKE ÖRVATTNET, VÄRMLAND

Örvattnet is a lake that was acidified in the 1960s, from pH 6–6.5 to a pH of less than 5 (Ek *et al.* 1995). It is included in the environmental monitoring network and is what is known as a ‘time series lake’ (see section 5.2). When Örvattnet became acidified, its populations of brown trout (*Salmo trutta*) and minnow (*Phoxinus phoxinus*) disappeared, and the perch (*Perca fluviatilis*) that remained had difficulty reproducing. *Sphagnum* mosses covered the bottom of the lake. Analysis of the diatoms in the sediment shows that, as a result of acidification, species sensitive to low pH were replaced by other, more tolerant species. From the mid-1980s, the abundance of *Sphagnum* moss decreased, perch reproduction improved and the number of perch caught during sampling increased markedly. Diatom analysis reveals that, in the last few years, the proportion of acid-tolerant species has declined in favour of more sensitive species. If the

changes in species composition are converted into pH values (see box), they point to an increase in pH from 4.7 to 4.9 in the early years of the 1990s (figure 19). The improvement indicated by diatoms is reflected in measurements of the water chemistry of the lake, which show a corresponding rise in pH. Considerable improvements have occurred in biological terms, despite the limited extent of the improvement in pH.

Several studies of the diatom records of unlimed acidified lakes in southern Sweden (Ek, unpublished data) give no indication of improvements similar to that observed in Lake Örvattnet. A possible reason for this is that Värmland has enjoyed a longer period of reduced deposition, thanks to lower emissions inside Sweden's borders, whereas lakes in the south have been affected to a greater degree by emissions in other countries, where reductions began to be achieved at a later date.

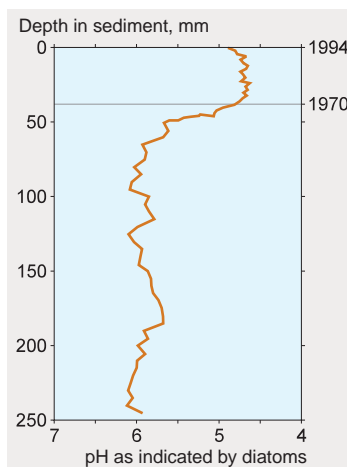


Figure 19. pH reconstruction for Lake Örvattnet, based on diatoms in the sediment (Umeå University).

4.2.2 LAKES AROUND THE FALUN COPPER MINE

The production of copper at the Falun copper mine has resulted in large quantities of SO₂ being released into the atmosphere. The mine is around 1000 years old, or more, so soils and lakes in the surrounding area have been exposed to deposition of acidifying compounds and metals over a very long period indeed. Emissions reached their highest levels in the 17th century, when copper production was at its peak, and have since fallen. Diatom analyses of a number of lakes show that pH values first rose somewhat owing to intensive agriculture, and have subsequently fallen from around 6.5 in the 17th century to the present figure of 6.0 (figure 20, Ek & Renberg 1998). Compared with Lake Örvattnet (see above) and the acidification that has occurred over the past century in the west coast region, this is not a large degree of acidification. Despite the fact that the estimated critical load has been exceeded for hundreds of years, then, only limited acidification has occurred (Falun kommun 1998). An important lesson to be learnt from these lakes is that appropriate land use can have beneficial effects on pH and thus offset acid deposition.

Nevertheless, despite a decrease in deposition over the last 300 years, the pH of these lakes has not risen; in certain cases, its decline has in fact continued to the present day. Why there has been no increase in lake pH is still unclear, however. Large quantities of sulphur remain in the soil around Falun, and leaching of this sulphur may be one reason why the pH has not risen. Another could be that the Falun area used to be sparsely forested, being used primarily for livestock grazing and arable farming. In the last 100 years, coniferous trees have been planted, and the growth of these trees is having an acidifying effect on soils. Our understanding of how this could affect the prospects of the soil recovering from acidification remains inadequate.

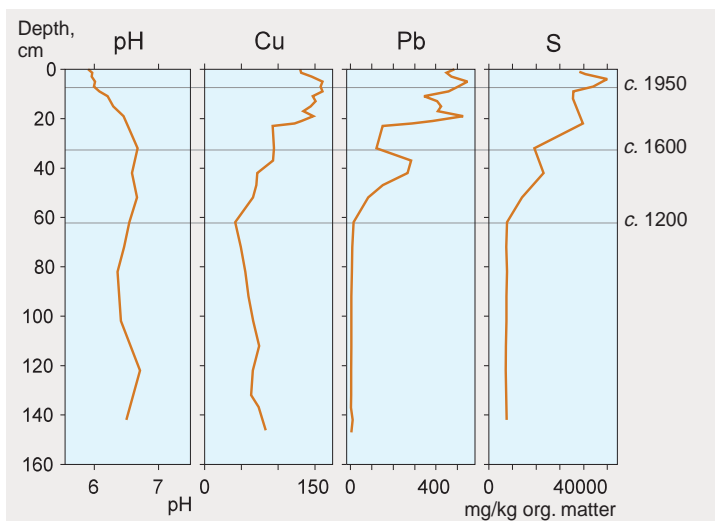


Figure 20. pH reconstruction for Lake Nästjärn, which is 4.5 km from the Falun copper mine. After a slight rise in pH resulting from agriculture, the lake was acidified from pH 6.7 to pH 5.9. Acidification can be seen as early as the 17th century. Copper, lead and sulphur emissions from the mining operations have also left their traces in the sediment (Umeå University).

5. RECOVERY OF SURFACE WATERS AND FOREST SOILS IN SWEDEN

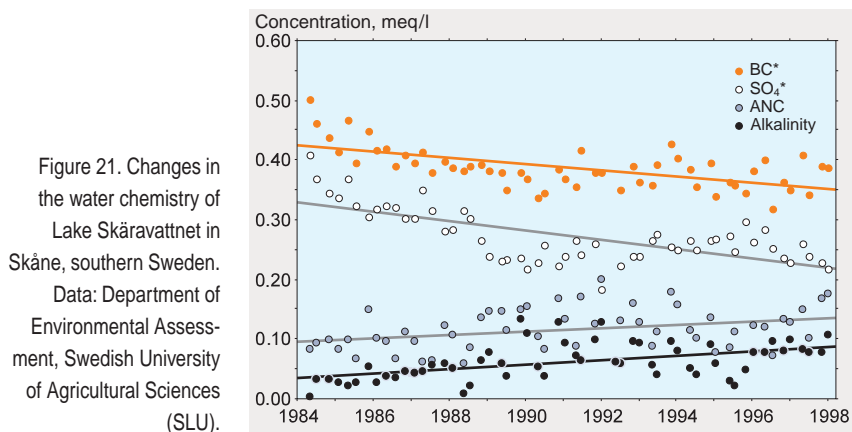
ANDERS WILANDER AND LARS LUNDIN

5.1 RECOVERY OF LAKES – INDICATIONS IN INDIVIDUAL LAKES

In southern central Sweden, atmospheric deposition of sulphur rose sharply until a few decades ago and has subsequently shown a gradual decline. Early indications of this decrease having affected the water chemistry of lakes were published in 1985 (Forsberg *et al.* 1985; Morling *et al.* 1985). These studies, covering a number of lakes to the south of Göteborg, showed that sulphate concentrations began to fall after 1976. In the case of three lakes, this decrease was accompanied by a gradual rise in pH. Hörnström and Ekström (1983) also demonstrated falling sulphate levels in several lakes near the west coast of Sweden, but observed no signs of a recovery in terms of pH.

The changes observed in one lake, Skäravattnet in the southern county of Skåne, are shown in figure 21. Here, the sulphate concentration decreased by 0.010 meq/l/yr over the period studied. This resulted in increases in alkalinity and ANC of 0.004 and 0.003 meq/l/yr, respectively.

At the same time, the concentration of base cations fell by 0.005 meq/l/yr. The alkalinity of the lake has changed from figures of less than 0.05 meq/l, qualifying it for state liming grants, to levels which, in 1996 and 1997 at least, have been constantly above that threshold.



5.2 TRENDS IN THE WATER CHEMISTRY OF THE TIME SERIES LAKES

The Environmental Protection Agency operates a sampling programme covering what are known as 'time series lakes' (sometimes referred to as 'reference lakes' or 'liming reference lakes'). At most, 190 lakes have been included in the programme, and all these lakes are sampled three to four times a year. In addition, since 1989, 26 of the lakes have been sampled more intensively, eight times a year.

Bernes (1991) evaluated the changes observed in these time series lakes and found that sulphate concentrations were decreasing throughout Sweden, and yet both alkalinity and pH were also falling. He attributed this to a reduction of the soil's capacity to neutralize acid deposition, due to the earlier high levels of deposition. At the same time, he pointed out that the data covered too short a period to provide unequivocal evidence of any effects of the reduced levels of deposition. All the studies mentioned above included measurements from only a short period following the downturn in sulphur deposition.

With access to longer runs of data, researchers are better placed to detect and interpret changes. Wilander (1997) was able to assess data spanning the period 1983–94. He found that sulphate concentrations were decreasing in 85% of the roughly 140 lakes studied and that alkalinity was increasing, albeit slowly, in 70% of them.

Changes in the chemistry of the time series lakes over the period 1983–97 have been analysed here using linear regression. Naturally, the trend estimates presented in this section cannot be extrapolated to provide forecasts of future rates of change, even if they do indicate the direction of the changes concerned.

In the same way as for Lake Skäravattnet, changes have been analysed for the entire group of time series lakes. The evaluation includes 137 lakes and covers the period up to and including 1997.

Distributions of the changes found for different acidification-related parameters in these lakes are shown in figure 22.

5.2.1 SULPHATE CONCENTRATIONS FALLING

Since 1983, sulphate concentrations in precipitation in southern central Sweden have decreased by about 0.002 meq/l/yr (Kindbom *et al.* 1993). Schematically, this corresponds to a decrease of 0.004 meq/l/yr in runoff, since the sulphate concentration of precipitation is increased by evapotranspiration. The reason why the whole of the decrease in deposition has not fed through into runoff is that retained sulphate is now being leached,

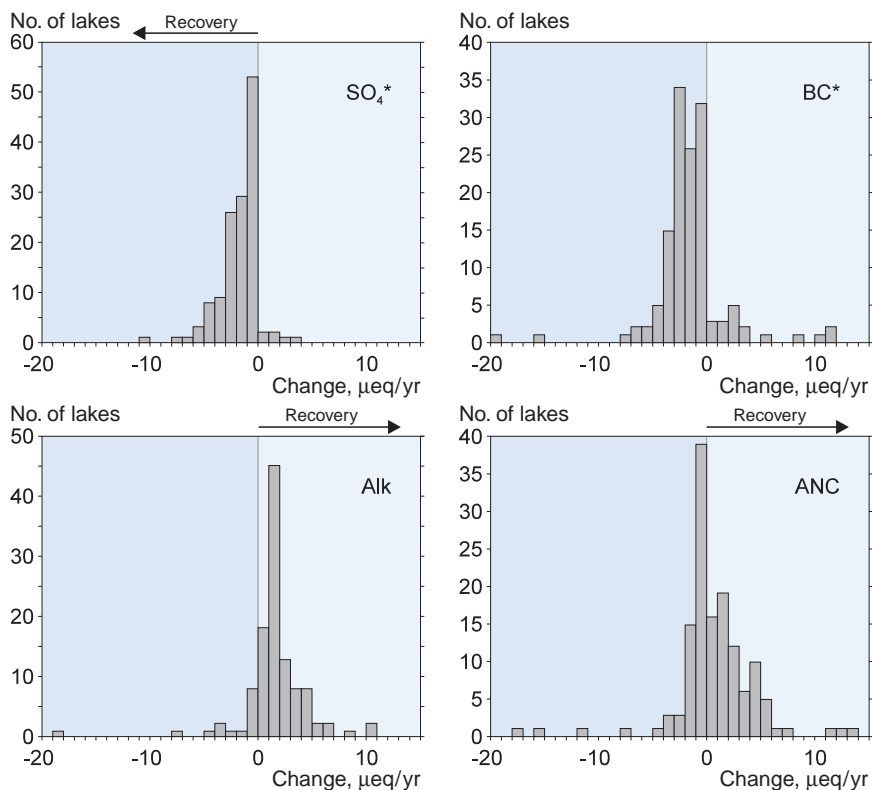


Figure 22. Changes in anthropogenic sulphate (SO_4^*), non-marine base cations (BC^*), alkalinity (Alk) and ANC in time series lakes sampled 1983–97. Data: Department of Environmental Assessment, SLU.

delaying recovery. Mass balance calculations for large catchment areas in Sweden also indicate ongoing leaching of previously deposited sulphur.

In 96% of the lakes, sulphate concentrations fell over the period studied. The median change was a decrease of 0.002 meq/l/yr.

5.2.2 SLOW RISE IN ALKALINITY AND pH

Sulphate concentrations have only an indirect effect on water quality from a biological point of view. More relevant chemical criteria for aquatic systems as habitats are alkalinity, ANC and pH.

In 87% of the lakes, alkalinity increased over the period analysed. The increase was small, 0.001 meq/l/yr, i.e. roughly half the decrease in sulphate. Trends in alkalinity can only be estimated for the 114 lakes that had alkalinity throughout the period in which measurements were made. It is therefore not possible to trace the development of alkalinity in lakes that had pH values below about 5.6.

Changes in ANC or pH, on the other hand, can be assessed for all the lakes. ANC, moreover, has the advantage of being independent of the effects of variations in organic acid concentrations. However, the method of calculating ANC, as the difference between strong base cations and strong anions, means that even small measurement errors give rise to uncertainties, and these will naturally affect any interpretation of the estimates.

ANC increased in only 53% of the lakes. The difference between the rates at which sulphate decreased and alkalinity increased is due to the fact that, at the same time, the concentration of base cations fell in 87% of the lakes. The median change in base cations was a decrease of 0.002 meq/l/yr.

These estimates also include the most acidic lakes. However, the relationship between the changes in ANC and sulphate concentrations does not differ between lakes with alkalinity and acid lakes (figure 23). In the case of the acidic lakes, the relationship is relatively simple, while in the case of the lakes with alkalinity a more irregular pattern emerges.

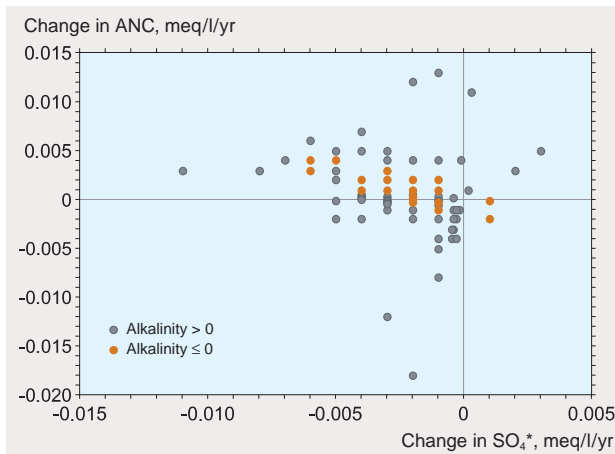


Figure 23. Relationship between changes in sulphate concentrations and ANC, in acidic and non-acidic time series lakes. Data: Department of Environmental Assessment, SLU.

Although a number of non-acidic lakes do not exhibit any recovery in the form of a rise in ANC, increases are occurring in many of the acidic lakes. It is important to point out, though, that these favourable chemical changes are not necessarily leading to biological recovery of the lakes concerned, i.e. to recolonization by acid-sensitive flora and fauna.

Changes in pH are often difficult to determine, since seasonal variations are relatively large and, in addition, the buffering properties of water give

rise to a certain resistance to change. The analysis performed indicates a pH rise in 85% of the time series lakes. Decreases occurred in 20 of the lakes. The median change in pH was an increase of 0.1 units over the 10-year period.

It was noted in chapter 3 that a reduced acid input can cause a decrease in base cation concentrations in runoff. This is due to ion exchange of H^+ and base cations in the soil, as a result of which the base saturation tends to increase at the expense of concentrations in runoff. In 87% of the lakes, base cation levels fell as expected. The median change was a decrease of 0.002 meq/l/yr, i.e. as much as the change in sulphate concentrations. This explains the insignificant change in ANC.

The considerable difference between the above assessments of recovery in terms of alkalinity and ANC may be due partly to changes in concentrations of humic substances in the waters concerned, and partly to the uncertainty involved in calculating ANC. A calculation of the correlation between changes in alkalinity and concentrations of humic substances, measured both as absorbance (water colour) and TOC, lends no support to the first of these possible explanations. In terms of median values, the change in absorbance was 0, while TOC increased by 0.017 mg/l. Concentrations of organic matter have thus, if anything, increased somewhat, rather than decreased, and are therefore not responsible for the increase in alkalinity.

5.3 NATIONAL LAKE SURVEYS

National surveys of lakes have been carried out in Sweden since 1972, with somewhat varying aims (see for example Bernes 1986). The earliest measurements thus relate to roughly the period in which sulphur deposition was at its peak. In all, five surveys have been undertaken, covering some 6000 lakes. Alkalinity was determined in each survey, probably using the same method. However, only 102 lakes unaffected by liming were studied in all five surveys.

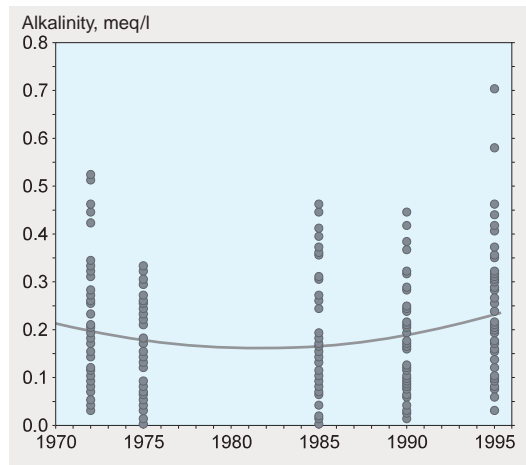
The data collected show that the median alkalinity fell from 1972 to 1975, before rising again (table 4). The 10th percentile values have also increased from a minimum in 1975. In 52 of the lakes the lowest alkalinity was recorded in 1975, while in 20 the minimum value did not occur until 1985. However, it is difficult to demonstrate a statistically significant degree of recovery. Significant increases in alkalinity, applying Kendall's test ($p < 0.1$), can be found for 27 of the 102 lakes included in the calculation.

Table 4. Frequency distribution of alkalinity (meq/l) in lakes sampled in five national surveys (n = 102).

YEAR	PERCENTILE VALUES OF ALKALINITY (MEQ/L)				
	10%	25%	50%	75%	90%
1972	0.061	0.100	0.170	0.260	0.330
1975	0.036	0.070	0.130	0.230	0.300
1985	0.060	0.090	0.150	0.250	0.353
1990	0.051	0.086	0.160	0.251	0.330
1995	0.083	0.108	0.191	0.266	0.338

There seems to be a geographical divide between northern and southern Sweden as regards the changes in lake alkalinity observed. In the northern lakes, there does not appear to have been a minimum during the period 1975–85, whereas this seems to have been the case in the southern lakes (figure 24). A trend change between falling values (acidification) and rising values (recovery) around 1990 has been noted in international studies (Lükewille *et al.* 1997).

Figure 24. Development of alkalinity in lakes in southern counties of Sweden. A quadratic equation has been fitted to the observations as a simple approximation. Data: Department of Environmental Assessment, SLU.



5.4 THE INTEGRATED MONITORING PROGRAMME

— RECOVERY OF CATCHMENTS

Under the Integrated Monitoring (ICP IM) programme, the chemical characteristics of runoff from a number of areas have been measured on a monthly basis since 1985. The resultant data thus have a higher temporal resolution than the data on the time series lakes. Each of the areas monitored consists largely of forest land and includes a lake, which discharges into the stream in which the measurements are performed. Several of them are in regions that have suffered acidification and are therefore suitable for studies to determine whether any recovery has taken place.

Fluxes of different substances through nine catchments have been calculated for the period 1985–96. In eight of these areas, the flux of sulphate decreased over this period, but an increase in ANC occurred in only four (figure 25). The increase in ANC was smaller than the decrease in sulphate transport, which was to be expected, since in most cases fluxes of base cations also fell.

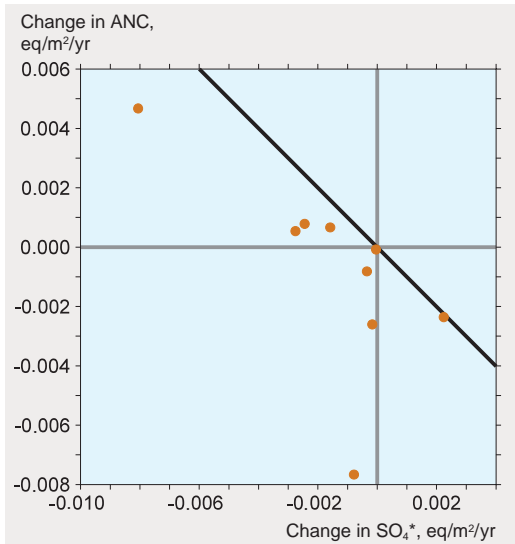


Figure 25. Relationship between the changes in fluxes of sulphate and ANC observed in streams sampled in the Integrated Monitoring programme. The line represents a ratio of 1:1. Data: Department of Environmental Assessment, SLU.

The changes, regarding both sulphate and ANC, appear to be somewhat greater in areas where the critical acid load, calculated using the Steady State Water Chemistry Model (Henriksen *et al.* 1992; Lövblad & Bertills 2000), is exceeded. If this is the case, it would mean that even areas which are still subject to deposition in excess of the critical load, thus calculated, are nevertheless showing a certain, albeit slight, degree of recovery. This is not a contradiction in terms: recovery from an acidified state can take place, even if deposition is not reduced right down to the critical load level.

The general picture remains the same whether the data are drawn from studies of the time series lakes, lakes included in national surveys, small streams monitored within the Integrated Monitoring programme or – as will be shown later – studies outside Sweden.

5.5 CHANGES IN SOIL CHEMISTRY – SURVEY OF FOREST SOILS AND VEGETATION

In chronically acidified areas, such as the till regions of south-west Sweden, acid runoff is a result of soils having lost their capacity to buffer acid deposition. We therefore have a great interest in monitoring any chemical recovery occurring in the soil.

The Swedish National Survey of Forest Soils and Vegetation studies the site conditions and soil chemistry of 23 500 plots across the country. Analyses of the pH of the humus layer are performed on some 20 000 samples, while the pH of the illuvial (B) horizon of the mineral soil is determined for around 2000 samples. Other analyses, e.g. of exchangeable cations, are limited to 500–1000 samples from each of these horizons.

This survey of Sweden's forest soils began back in 1963 with pH measurements of the humus horizon, which have since continued through four successive survey periods. The last two rounds of the survey, 1983–87 and 1993–2002 (in progress), have included a very ambitious programme of soil chemical analyses. The calculations presented below are based on data from all over the country, corresponding to 30–40% of all the sites covered in the latest survey.

The soil samples discussed here were collected from the humus layer and the top 5 cm of the B horizon. Since the surveys span a considerable period of time, the results are affected by the fact that methods of analysis have changed between survey periods.

5.5.1 HOW IS THE pH OF FOREST SOILS CHANGING?

The status of a forest soil in terms of acidity reflects a number of different factors, including the geology of the area, atmospheric deposition, the effects of nutrient uptake and harvesting of biomass. Changes in acidity are due chiefly to the last three factors.

In the humus horizon, pH values vary from 3.8 to around 5.5, with low values in the south-west of the country, north-western parts of central Sweden, and Västerbotten. Much higher values are found in eastern central Sweden, Gotland and Jämtland. B horizon pH varies along a gradient from the south-west to the north-east (figure 26). Low values of around 4.5 occur in the south-west, whereas in Norrbotten pH values of over 5 are found. The very lowest values can indicate a risk of leaching of aluminium into surface waters and groundwater.

The proportion of the total area of iron podzol forest soils with a B horizon pH of less than 4.4 increased from 8.8% to 9.1% between the 1983–87 and 1993–96 surveys. Increases in the areas with such low pH values were particularly marked in inland parts of southern Sweden, north-west central Sweden and Västerbotten.

The data also show that, in 1983–87, 71% of the area studied had a pH below 5.0 in the B horizon, whereas the corresponding figure in 1993–96 was 75%.

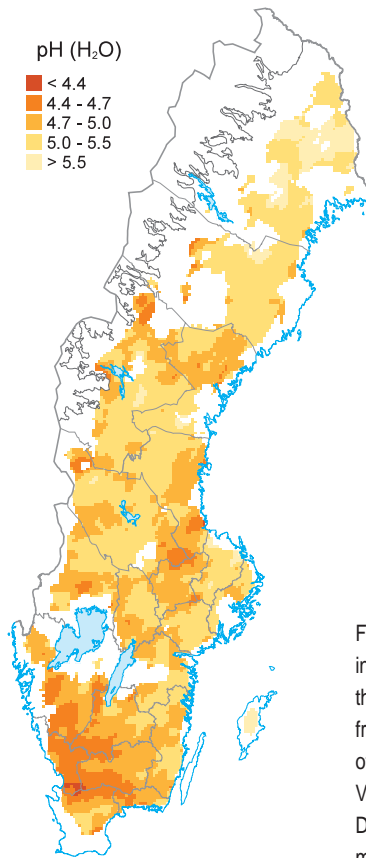


Figure 26. pH (measured in H₂O) of the B horizon of the soil, according to data from the National Survey of Forest Soils and Vegetation. Data: Department of Environmental Assessment, SLU.

5.5.2 HOW DOES GROWTH AFFECT CHANGES IN pH?

A separate analysis of pH changes between 1983–87 and 1993–96 has been carried out for southern Sweden (the counties of Halland, Västra Götaland, Kronoberg, Jönköping, Skåne and Blekinge). The analysis covers the commonest type of well-drained forest soil. Three types of calculations were performed:

- changes in pH for all plots, but limited to plots with trees aged 35–95 years;
- changes in pH against tree age, to study the effect of growth;
- changes in pH for plots with trees of the same age, to distinguish the effects of deposition.

An illustration of how these calculations were carried out is given in figure 27.

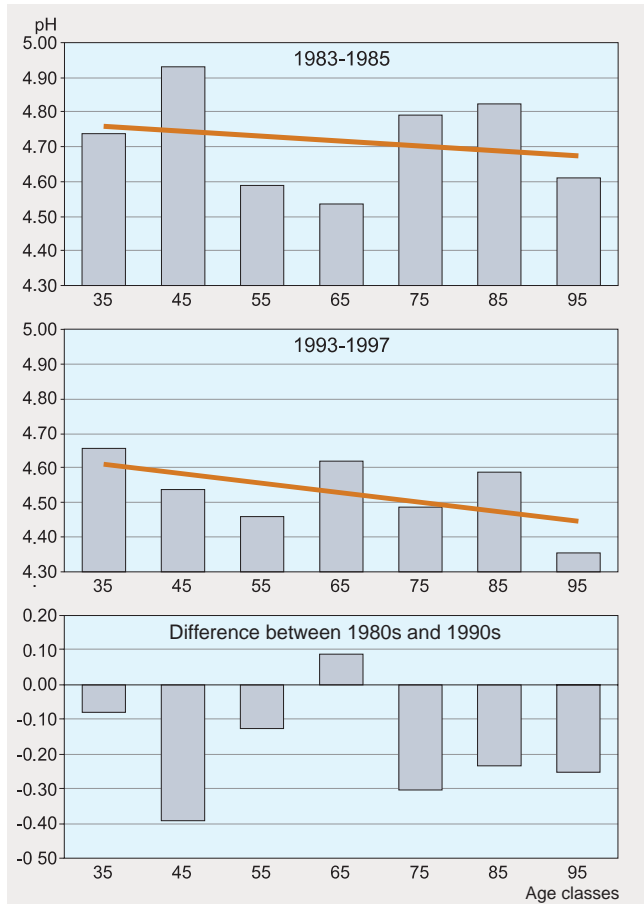
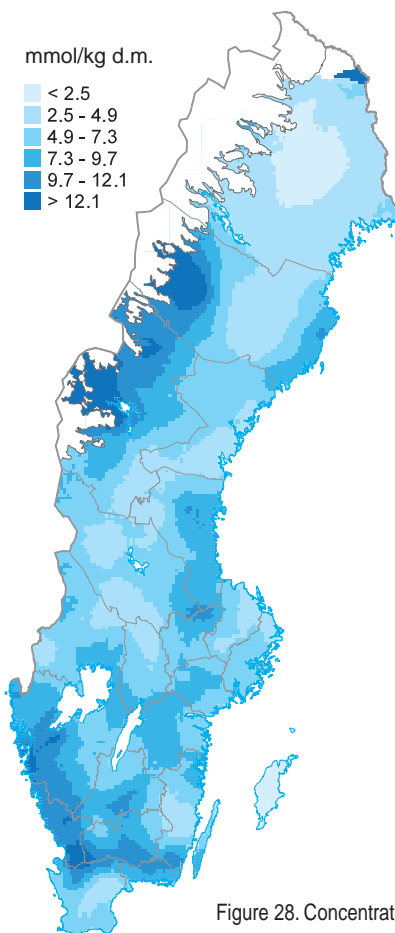


Figure 27. pH of the B horizon of forest plots with trees in age classes between 35 and 95 years, in 1983–85 (top) and 1993–97 (middle). The regression lines show the pH-lowering effect of growth. The comparison between the two survey periods (bottom) indicates a lower pH in the later period for all age classes except 65 years (i.e. the age range 60–70 years). Data: Department of Environmental Assessment, SLU.

The median humus horizon pH was 3.95 in the survey in the 1980s and 3.76 10 years later, i.e. a decrease of 0.2 pH units. The corresponding values for the B horizon were 4.74 and 4.54, again a difference of 0.2. If only sample plots with trees of the same age are compared – thereby eliminating the effect of forest growth and the associated uptake of base cations and release of H^+ – the differences are 0.13 and 0.21 units, respectively. If we choose to compare across different tree ages, we can see the influence of the trees’ uptake of nutrients and the resultant acidification. In this case, linear regression reveals a decrease of 0.02 units over a 10-year period.

It is suspected, however, that the pH determinations carried out in the 1983–87 survey overestimated the true values (Karlton 1998b). Reanalysis of samples and long-term regression over four survey periods, 1963–96, indicated that the values for 1983–87 were roughly 0.1 pH units too high. The divergences were clearly pH-dependent and, if they are allowed for, the pH changes in both humus and B horizons are reduced to around 0.1 units. Taking this factor into account, the preliminary conclusions are that

- forest growth combined with air pollution has caused *acidification* corresponding to a decrease in pH of around 0.1 units over a 10-year period;
- the acidifying effect of growth is responsible for one-tenth of the pH decrease observed.



5.5.3 EXCHANGEABLE BASE CATIONS, ACIDITY AND ALUMINIUM

The base saturation of the humus horizon varies from as little as around 10%, in the Småland highlands, to high values of almost 50% on Gotland and in eastern central Sweden. In the B horizon, the degree of base saturation varies over a wider range, but with a similar geographical distribution. The lowest values, around 5%, are found in the south-west. In southern Sweden there is a clear difference between the west and the east. Changes between survey periods are small (Karlton 1998a).

Concentrations of exchangeable aluminium in the B horizon vary from around 2 to 25 mmol/kg d.m. (d.m. = dry matter) (figure 28). High concen-

Figure 28. Concentrations of exchangeable aluminium in the B horizon, according to data from the National Survey of Forest Soils and Vegetation. Data: Department of Environmental Assessment, SLU.

trations, of over 10 mmol/kg d.m., have been recorded in south-west Sweden, Jämtland, and the montane forests of Västerbotten. The clearest changes are decreases in exchangeable magnesium and increases in exchangeable aluminium in the B horizon throughout the country. In this layer of the soil, magnesium concentrations were significantly lower in the most recent survey than in 1983–87, having fallen by 30% (Karlton 1998a). In the case of calcium, increases of about 0.1 mmol/kg d.m. may be noted in southern Sweden, with higher figures in the east than in the west, while in northern Sweden decreases of roughly the same magnitude can be seen. As for potassium, decreases of 0.02 mmol/kg d.m. have been recorded in south-eastern Sweden, and around 0.01 mmol/kg d.m. in the west (Karlton 1998a). Changes over the 10-year period since 1983–87 point to a median increase in aluminium concentrations from 8 to about 12 mmol/kg d.m., i.e. by around 4 mmol/kg d.m. This suggests that acidification has penetrated to greater depths in the soil during this period.

A qualitative summary of the trends in the data is presented in table 5.

Table 5. Summary of observed changes in concentrations of exchangeable ions in the humus horizon and B horizon between the 1983–87 and 1993–96 National Surveys of Forest Soils and Vegetation.

EXCHANGEABLE ION	TREND	
	Humus horizon	B horizon
Calcium	Increasing throughout Sweden	Increasing in the south Decreasing in the north
Magnesium	No change	Decreasing throughout Sweden
Total acidity (Al + H)	Increasing throughout Sweden	Decreasing throughout Sweden
Aluminium	–	Increasing throughout Sweden

5.6 HOW IS CHEMICAL RECOVERY AFFECTING BIOTA?

It is hoped that the recovery taking place in terms of water chemistry will result in surface waters being recolonized by species which disappeared or became less abundant when acidification was at its height.

It is quite well known that this happens in waters that are limed. But what about lakes and streams that recover naturally? Since 1986, studies of the littoral fauna (i.e. invertebrates inhabiting the littoral zone) have been carried out in a total of 34 lakes. In 20 of the lakes, improvements in this fauna have been observed, with statistically significant changes noted in 11 of the 20. In eight lakes, sampling has been limited to just five occasions, and these waters therefore cannot be included in the evaluation. Changes in biotic communities can be described in different ways; here, the Henrikson-Medin Acidity Index has been used (see box overleaf).

One lake in which recovery has taken place is Lake Fiolen, in the county of Kronoberg, southern Sweden. There, the biotic acidity index has increased markedly since the middle of the 1980s. Over the period in which measurements of the biota were made, the majority of chemical parameters also increased. Although the water chemistry of the lake was somewhat better in 1985 and 1986, this was not reflected in the biotic index for 1987 (figure 29).

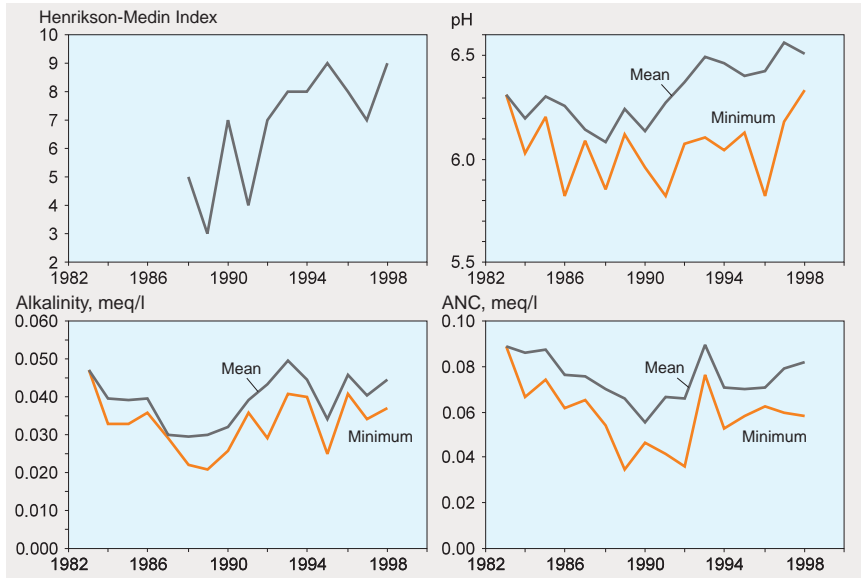


Figure 29. Recovery in Lake Fiolen. Changes in a littoral fauna-based acidity index and in chemical indicators of acidity.

Have significant changes in acidity status also occurred in the other lakes in which the acidity index points to an improvement? Several different criteria have been tested, including mean and minimum values of pH, alkalinity and ANC. Ten lakes show an improvement in terms of at least one of these variables. However, the data used to calculate the index and the chemical status of the lakes do not cover identical periods. The time series relating to biota must still be regarded as very short. In other words, there are still insufficient data to provide definite evidence of a link between development of the littoral fauna and changes in water chemistry. It is also important to note that, although the index was developed to reflect acidity, scores are also generally affected by nutrient levels. However, the results available suggest that biological recovery is taking place as a consequence of the improvements in water chemistry. This seems to be true even of lakes where the pH is still below 5.5.

Acidity index based on the littoral fauna

To reduce the significance attached to the presence of individual species, and to give as balanced a picture as possible, *biotic indices* are often used. Several such indices exist with regard to acidity. The earliest was designed by Gunnar Raddum in Norway. Later, Per-Erik Lingdell proposed a more elaborate index, and Lennart Henrikson and Mats Medin another. The Henrikson-Medin Index is the one recommended in the Swedish Environmental Protection Agency's environmental quality criteria for lakes and watercourses (Swedish Environmental Protection Agency Report 5050), and is also used here.

Acidity index proposed by Henrikson and Medin (1986):

The index is calculated as the sum of the highest scores obtained for each of the criteria I–V:

- I Presence of mayflies, stoneflies and caddis-flies with varying pH tolerance. Species can have indicator values between 0 and 3.
- II Presence of amphipods.
- III Presence of acid-sensitive groups such as leeches, gastropods and bivalves.
- IV Ratio between the number of species of mayflies of the genus *Baetis* and the number of species of stoneflies.
- V Number of taxa from a list that are present.

The index can vary from 0 to 14, the lowest value indicating a highly acidic and the highest a slightly alkaline environment.

6. INTERNATIONAL EXPERIENCE

ANDERS WILANDER, ANNA EK,
FILIP MOLDAN AND PER WARFVINGE

Research relating to acidification has to a very high degree been international in character. This has been reflected, for example, in the major scientific conferences that have been held every five years, with up to 1000 participants. Many international projects have been carried out, and a wide-ranging exchange of experience between countries has taken place. In Sweden's case, research with an international emphasis has chiefly been funded by the European Union and the Nordic Council of Ministers.

This international cooperation has been reinforced by the environmental monitoring programmes established under CLRTAP. As atmospheric deposition has abated, the question of recovery from acidification has come increasingly to the fore.

At the International Symposium on Acidic Precipitation in Muskoka in 1985 (*Water, Air and Soil Pollution* 30/31), however, only two papers on recovery were presented. Dillon, Reid and Girard (1986) dealt with changes in the area around Sudbury, Canada, where the effects of substantial reductions in emissions from a smelter, achieved in 1972, had been monitored. The other paper described the results of the first year of the RAIN (Reversing Acidification in Norway) project, in which acid rain was excluded from one of the catchments (Wright *et al.* 1986). Using the MAGIC model, Cosby and co-workers (1985) sketched out, among other things, what recovery from acidification might entail. They postulated that concentrations of base cations would continue to fall, but that in parallel with this alkalinity would increase, albeit slowly. Even at a workshop in Norway in 1986, which was devoted to acidification, but with a particular emphasis on recovery, only one paper on recovery and one on the early phase of the RAIN project were given (Barth 1987). Ten years later, at Acid Reign 1995 in Göteborg, some 25 papers were presented, many of which highlighted the need for long time series to enable reliable evaluations of changes to be made.

As part of the US National Acid Precipitation Assessment Program (NAPAP), several major syntheses of current knowledge in this field have been produced. According to NAPAP 1998, the conclusions to be drawn from the international literature can be summed up as follows:

- Further work is needed to improve scientific understanding of the effects of acid deposition on surface waters.
- Monitoring of lakes and watercourses must continue, to enable changes caused by changing levels of sulphur and nitrogen deposition to be quantified. Long-term measurement programmes are the only way of unequivocally determining what effects different alternative strategies and courses of action will have.
- Efforts to revise and apply acidification models should continue.

6.1 ROOF EXPERIMENTS WITHIN THE EXMAN PROJECT

EXMAN – Experimental Manipulation of Forest Ecosystems in Europe – was a major EC-funded project that was launched in the late 1980s. It included experiments involving different combinations of deposition reductions, fertilizer applications and induced drought (Beier *et al.* 1998).

Within the project, two experiments were carried out in which atmospheric inputs of sulphur and nitrogen were greatly reduced by the construction of roofs. At the two sites, Klosterhede in Jutland, Denmark, and Solling, near Göttingen in western Germany, sulphur deposition was reduced by 55% and 95%, respectively, and nitrogen deposition by 70% and 90%. The experiment at Klosterhede ran from 1989 to 1994, whereas the Solling study is still in progress.

The results of the EXMAN studies confirm that different ecosystems respond very differently to decreases in deposition. At Klosterhede, the reduction of sulphur deposition resulted in an immediate decrease in sulphate concentrations in soil water, whereas at Solling the effect was less marked. This is probably because at the Solling site there were large quantities of adsorbed sulphur in the soil, which began to be released when deposition was reduced. This is illustrated in figure 30, which shows that

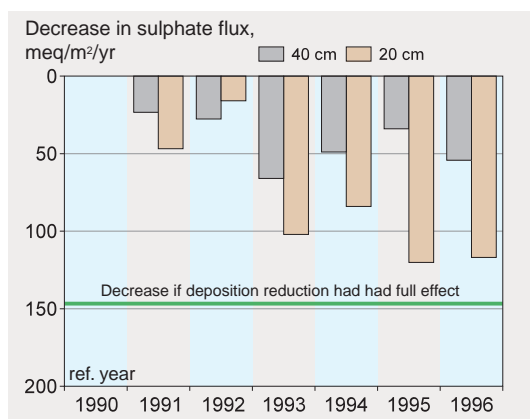


Figure 30. Decreases in the flux of sulphate at different depths below the 'clean rain' plot at Solling, Germany, compared with a control plot. The flux did not decrease as much as deposition at a depth of either 20 cm or 40 cm, showing that sulphur was being released from the soil. Data: Beier *et al.* 1998, Walse *et al.* 1998.

the flux of sulphate below the ‘clean rain’ plot decreased to a lesser extent than deposition.

For nitrogen, the converse was true: nitrate concentrations fell substantially at Solling; at Klosterhede they were low to begin with and remained unchanged. Retention of base cations increased to a certain extent, while there was some change in a favourable direction in aluminium concentrations and pH. Figure 31 shows that the pH rose and aluminium levels fell at a depth of 70 cm at Solling when deposition to the experimental site was substantially reduced. There was a small but clear increase in ANC.

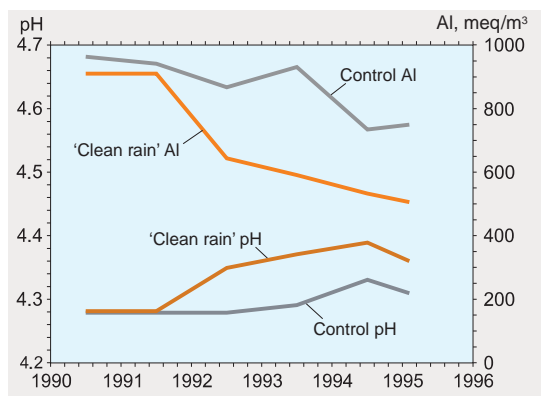


Figure 31. Increase in pH and decrease in aluminium concentrations (meq/m³) in soil water at a depth of 70 cm at Solling, Tyskland. After Walse *et al.* 1998.

It is difficult, then, to predict recovery processes with any certainty, even on the basis of the very ambitious experiments conducted within EXMAN. Different ecosystems react very differently to changes in deposition. It can also be noted that a soil’s ability to adsorb sulphate and immobilize nitrogen has a decisive impact on the response to reductions in deposition.

6.2 THE RAIN PROJECT

Risdalsheia in the south coast region of Norway was one of the sites included in the RAIN project. It is an area of rocky terrain situated high above sea level, with very thin soil cover (average depth 4–11 cm, organic matter) and 30–50% exposed rock. The experimental site at Risdalsheia was divided into several smaller, clearly demarcated catchments of around 500–1000 m². In 1984 roofs were built over two of these areas. One of the covered areas was irrigated with non-acidifying water, while the other was watered with unaltered precipitation and used as a control.

Before the experiment began, runoff from the area was acidic and had high levels of nitrate and a negative buffering capacity (ANC around $-100 \mu\text{eq/l}$). The treatment brought about a radical change, however. Nitrate concentrations showed a very rapid response, and within just a few weeks of the launch of the experiment leaching of this ion had basically ceased. The thin soil at Risdalsheia has a relatively limited capacity to adsorb sulphate. Nevertheless, it took almost 8 years to establish a new balance in the mass flux into and out of the experimental site. The cumulative total of sulphate in runoff up to that point corresponded approximately to the quantity adsorbed in the soil before the experiment began (Wright *et al.* 1993).

The change in pH over the entire period of the experiment was small, from pH 4.0 in 1984 to around 4.3 10 years later. Aluminium concentrations had decreased by about 80% after 10 years, the largest reduction having occurred in the first 2–3 years, followed by a further gradual decline. Base cation levels also fell, like those of sulphate. The combined decrease in sulphate and nitrate was not fully balanced by the decrease in base cation, aluminium and H^+ concentrations; the difference was accounted for by an increase in the concentration of organic anions. This is in fact normal if pH rises, but the scale of the increase was larger than expected. ANC rose very steeply during the first 5 years, from $-85 \mu\text{eq/l}$ to about $-20 \mu\text{eq/l}$. After that, it increased only slowly, and it did not reach positive values at any time during the 10-year period.

The conclusion that can be drawn from this, the first large-scale experiment on the reversibility of acidification, is that some recovery is possible and that appreciable changes can take place in the space of just a few years. Another lesson from the Risdalsheia study is that many areas may have been naturally acidic and that we should not expect too far-reaching changes in water chemistry when the acid load decreases. At Risdalsheia there are chemical systems, comprising organic acids and aluminium, which efficiently buffer runoff within the pH range 4–5.

The fact is that models used to make longer-term (100-year) forecasts of recovery at Risdalsheia have shown that the pH will not end up any higher than perhaps 4.6–5. It is debatable whether this site in fact ever was non-acidic, with a positive ANC. If it was, the results of these studies mean that acidification is not entirely reversible.

6.3 STUDIES IN THE NETHERLANDS

In 1989 another two roof projects were started, this time in the Netherlands as part of the NITREX project (Wright & van Breemen 1995). One roof was erected in a Scots pine forest at Ysselsteyn and another in a stand of Douglas fir at Speuld (Boxman *et al.* 1995). Compared with Sweden, both areas have very heavy pollutant loadings, with nitrogen deposition totalling up to 60 kg/ha/yr and sulphur deposition up to 40 kg/ha/yr. Owing to the high level of nitrogen deposition before the roofs were built, both of these forest ecosystems were nitrogen-saturated. Nitrogen leaching from the base of the illuvial horizon had been found to correspond to or even exceed the rate of deposition. The main question addressed by these roof projects was: Will a nitrogen-saturated and acidified ecosystem recover at all?

The total covered area was around 400 m², comprising two 100 m² plots for each experiment. One of each pair of plots was treated with purified throughfall that was virtually free of nitrogen and sulphur. The other served as a covered control plot and was treated with unaltered throughfall collected from the roof. In both cases, the treatment with clean throughfall brought about a rapid decrease in leaching of nitrate, sulphate and base cations from the soil. A few years into the experiment, various signs of recovery could be observed, such as lower nitrogen levels and better nutrient balance in needles, enhanced fine root vigour, increased forest growth (note that all these changes were a result of *reduced* nitrogen deposition), and an increase in mycorrhizal abundance (Boxman *et al.* 1998). The roof experiment at Ysselsteyn is now into its tenth year and, although the Speuld experiment was completed in 1995, the results of these two Dutch studies show that even forest ecosystems exposed to heavy deposition of acidifying compounds may be able to switch relatively rapidly from an ongoing process of acidification to recovery, in terms of soil, water and the trees themselves.

6.4 SUDBURY, CANADA

The abundant nickel and copper deposits at Sudbury, Canada, began to be mined towards the end of the 19th century. The high sulphur content of the ore, however, meant that its processing generated substantial emissions of sulphur dioxide, so large that in the 1960s Sudbury was the world's biggest single emitter of this pollutant. The effects of the site's emissions of sulphur dioxide and metals on vegetation, soil and water were devastating (Gunn & Keller 1990). In 1972, a combination of more strin-

gent legislation, closure of smelters and a taller chimney brought about an immediate 50% reduction of sulphur dioxide emissions. Today, emissions are only about 10% of their former levels.

The cut in emissions resulted in rapid chemical and biological improvements in a number of acidified lakes, particularly in the vicinity of the main emission sources. Sulphate concentrations fell and alkalinity and pH rose. These changes were accompanied by a recovery of phytoplankton, zooplankton, benthic fauna and fish (Gunn 1995). In one body of water, Baby Lake, the pH increased from 4.05 to 5.8 in just 12 years (Hutchinson & Havas 1986). Diatom analysis of the sediment of this lake shows that its pH is now back at its original level of just under 7 (Smol *et al.* 1998). These results have been important as evidence of how emission cuts can produce rapid beneficial effects.

In the majority of the lakes, however, chemical recovery is not yet complete. The rate of recovery is dependent on the acid sensitivity (weathering capacity) of the bedrock and the water residence time of the lake concerned (Mallory *et al.* 1998). So far, many lakes have shown only modest improvements.

6.5 MONITORING PROGRAMMES UNDER CLRTAP

Five environmental assessment and monitoring programmes have been established in the framework of the Convention on Long-Range Transboundary Air Pollution (CLRTAP). One of these, ICP WATERS, is tracking developments in lakes and rivers.

In 1995 an evaluation of nine years of studies at some 60 sites in Europe and North America was presented (Lükewille *et al.* 1997). This evaluation made use of statistical methods which took seasonal variations into account and also reduced the importance of extreme values.

It was found that the time series for most monitoring sites could be divided into two parts: the period before 1990, during which acidification was becoming increasingly severe, and the period after that date, in which recovery predominated. At 22 sites in the Nordic countries, pH and alkalinity increased significantly in the early 1990s, while concentrations of base cations fell slightly, but nevertheless significantly. More pronounced responses to the reduced pollutant load were observed in continental Europe, where the increase in alkalinity was 7.9 $\mu\text{eq}/\text{l}/\text{yr}$, compared with 2.5 $\mu\text{eq}/\text{l}/\text{yr}$ in the Nordic region. This favourable trend was not found in parts of North America (e.g. Adirondacks and Quebec), where, despite declining sulphate concentrations, no rise in alkalinity or fall in hydrogen

ion concentrations was recorded. By contrast, concentrations of base cations decreased almost universally. Improvements in the status of the aquatic invertebrate fauna have been reported from Norway and Germany.

Another conclusion which has been drawn is that recovery from acidification is often a slow process, and that long-term recovery (over more than 30 years) is affected more by the scale of the decrease in deposition than by the point in time at which it occurs.

An evaluation of trends in all the CLRTAP monitoring programmes has recently been carried out (UNECE 1999). It includes data from ICP Integrated Monitoring, too, but is based on a relatively short period of time. On the basis of the data as a whole, the same conclusions are drawn. Modelling suggests that slow recovery is taking place in many cases. Emphasis is also placed on the need for continued monitoring, to enable future trends to be quantified.

7. PROSPECTS FOR THE FUTURE

GUN LÖVBLAD,
MATTIAS ALVETEG AND FILIP MOLDAN

7.1 FUTURE DEPOSITION TRENDS

Future trends in atmospheric deposition will depend on the effectiveness of efforts to control and reduce air pollutant emissions. To assess how ecosystems will develop on a long time-scale, long-term emission forecasts are needed. At present, it is not possible to make reliable predictions beyond the year 2010.

Several agreements have been entered into since the end of the 1970s to reduce the long-range transport of air pollutants between the countries of Europe. The first steps towards establishing large-scale abatement strategies were taken as early as around 1970. With the adoption in 1979 of the Convention on Long-Range Transboundary Air Pollution (CLRTAP), under the auspices of the United Nations Economic Commission for Europe (UNECE), real progress could begin to be made in this direction.

A breakthrough in terms of reducing emissions occurred when it became possible to base strategies on reduced effects in the environment. Once the concept of 'critical load' had been defined, abatement strategies could be geared to narrowing the gap between actual and critical loads in different parts of Europe. Europe-wide monitoring made it clear that atmospheric deposition exceeded critical loads not only for sensitive Scandinavian ecosystems, but for a large proportion of ecosystems across Europe.

The various protocols that have been signed under the Convention are listed in table 1 (p. 11). The First Sulphur Protocol was implemented to a greater extent than expected, and several of the countries that undertook to cut their sulphur emissions by 30% were in fact able to reduce them by more than half. The Second Sulphur Protocol, signed in 1994 and ratified in 1998, is based on critical loads and is designed to reduce emissions to varying degrees in different countries by the year 2010, depending on the extent to which those emissions affect sensitive ecosystems. A new 'multi-effect, multi-pollutant' protocol was signed in December 1999.

The work now under way within the EU, partly as a result of Swedish initiatives, may be expected to bring about further steps in the right direction. An EU directive laying down 'national emission ceilings' for the member states could become a reality in the relatively near future.

At present, therefore, action to reduce emissions is being taken throughout Europe, with cuts both decided on and planned. The most vigorous measures relate to sulphur, but emissions of nitrogen oxides and to a certain extent ammonia are also to be reduced. On the one hand, countries that have signed the Second Sulphur Protocol have to honour the commitments which that entails. On the other, the EU member states have to meet the requirements which are already, and will be, imposed by directives relating to large combustion plants and the transport sector. Furthermore, countries which are applying to join the European Union are endeavouring to live up to EU environmental legislation, to demonstrate their readiness for membership. In addition, many countries and regions have defined emission targets of their own for the first decade of the 21st century. All these factors are expected to result in clear improvements in terms of acidification, eutrophication, oxidant formation and urban air quality in Europe.

On the basis of expected emission reductions, forecasts of future changes in deposition levels can be made with the help of EMEP model calculations (EMEP/MS-CW 1998). The emission cuts achievable by measures already decided on or planned, together with the action that will be required by the new 'multi-effect, multi-pollutant' protocol, will probably bring about appreciable improvements in terms of deposition in Sweden.

Table 6 shows the changes in deposition that are expected by the year 2010 under different deposition scenarios, compared with the situations in 1980, 1990 and other years. The scenarios concerned are:

- A reference scenario, REF, based on implementation of the Second Sulphur Protocol, combined with existing legislation and national plans already adopted.
- The WGS scenario, used as a basis for the 1999 'multi-effect, multi-pollutant' protocol to CLRTAP.
- HI, the scenario which at the time of writing is the main alternative underlying the EU's proposal for a directive on national emission ceilings.

Table 6. Estimated deposition levels (kg S/ha/yr and kg N/ha/yr, mean values over large areas) in different regions of Sweden in the year 2010, compared with earlier years. Predictions of deposition in 2010 are based on EMEP model calculations (EMEP/MSC-W 1998). The different scenarios are:

REF: 2nd Sulphur Protocol, existing legislation and national plans

WGS: Scenario used for negotiations on CLRTAP Multi-Effect Protocol

H1: Scenario currently serving as basis for negotiations within EU

SCENARIO	YEAR	BLE- KINGE	KRONO- BERG	WEST COAST	STOCK- HOLM	SOUTHERN NORRLAND	NORTHERN NORRLAND
		Deposition kg/ha/yr					
SO₄²⁻-S	1980	20.3	16.6	14.5	13.3	4.4	3.3
	1990	13.1	10.0	8.3	7.7	2.6	1.8
	1995	7.9	6.1	5.1	4.5	1.5	1.0
	1996	7.4	5.7	4.8	4.3	1.4	1.0
	1997	6.5	4.9	4.1	3.8	1.2	0.9
REF	2010	4.1	3.2	2.7	2.8	0.9	0.7
WGS	2010	3.7	2.8	2.4	2.9	0.9	0.8
H1	2010	3.6	2.7	2.3	2.6	0.8	0.7
NO₃⁻-N	1980	5.0	6.6	5.3	3.9	1.7	1.4
	1990	4.6	6.1	5.0	3.6	1.7	1.4
	1995	3.7	4.9	4.1	3.0	1.4	1.2
	1996	3.8	5.0	4.2	3.0	1.4	1.2
	1997	3.6	4.7	3.9	2.8	1.3	1.1
REF	2010	2.4	2.7	2.5	2.1	0.9	0.9
WGS	2010	2.4	2.6	2.4	2.1	0.8	0.8
H1	2010	2.4	2.4	2.4	2.0	0.9	0.9
NH₄⁺-N	1980	4.0	4.1	3.3	2.1	0.8	0.6
	1990	3.8	3.9	3.1	2.0	0.7	0.5
	1995	3.5	3.7	2.7	1.7	0.7	0.4
	1996	3.7	3.6	2.8	1.7	0.6	0.4
	1997	3.8	3.7	2.7	1.7	0.7	0.5
REF	2010	3.2	3.2	2.6	1.7	0.6	0.5
WGS	2010	3.4	3.4	2.6	1.7	0.7	0.5
H1	2010	2.8	3.0	2.4	1.6	0.6	0.4

By 2010, according to the reference scenario, deposition of sulphur in southern areas of Sweden is expected to be around 3–4 kg/ha/yr. This represents a decrease of about 70% compared with 1990 deposition levels. In northern Sweden (Norrland), deposition will fall to about 1 kg/ha/yr, a reduction of 60–70%. These figures are mean deposition levels over large areas with mixed land use. Actual deposition will therefore be somewhat higher on forest land, and somewhat lower in open countryside.

Deposition of oxidized nitrogen (nitrate) is also expected to decrease, but by a smaller percentage than deposition of sulphur. Deposition in 2010 is expected to be of the order of 2–3 kg N/ha/yr in southern parts of the country, and just under 1 kg N/ha/yr in the north. For southern Sweden, this represents a decrease of 50–60% from 1990 levels.

Deposition of reduced nitrogen (ammonia) is predicted to be around 3 kg N/ha/yr in the south and roughly 0.5 kg N/ha/yr in the north, i.e. a decrease of 15–20% in most areas compared with 1990.

The H1 scenario, currently the basis for negotiations within the EU, presupposes deeper cuts in emissions than the reference scenario. The difference corresponds to additional reductions of about 0.5 kg/ha/yr in both sulphur and total nitrogen deposition in southern Sweden by 2010.

Provided that the measures already decided on are implemented according to plan, therefore, the situation in terms of sulphur and nitrogen deposition will improve appreciably, and there will thus be a chance of ecosystem recovery.

Another factor with an important bearing on the future state of ecosystems is atmospheric deposition of base cations. Up to now, only rough estimates of this parameter have been possible (see for example Lövblad *et al.* 2000). The base cations present in deposition originate from both natural sources (marine salts, soil erosion, pollen etc.) and human activities (burning of wood and coal, industrial processes, agriculture). Natural emissions of base cations can probably be regarded as one of the basic factors affecting natural habitats, and as something that will not change dramatically over time. Anthropogenic emissions, on the other hand, do change over time, depending on the intensity of the human activities concerned. The scale of base cation deposition affects what reductions in acid loadings to ecosystems are necessary.

Reliable estimates of current deposition of base cations are not available. Equally, in the absence of a comprehensive inventory of sources, forecasts of future deposition levels have not been possible. Detailed surveys of emissions in Europe are virtually non-existent and, as things stand, estimates of dispersion of emitted particulates cannot be made using the EMEP model, either.

7.2 INTERPRETATION OF THE ROOF EXPERIMENT

– MODELLING

An important complement to experiments and long-term environmental monitoring programmes is the development and use of mathematical models for both the spatial and the temporal extrapolation of experimental results. The strength of models lies in the fact that it is relatively easy to change the parameters on which the calculations are based. Using a model, it is possible to study the effects of different deposition scenarios, felling and replanting of forests, liming etc., and also to predict future developments and geographical variations. Models are always limited, however, by the current state of knowledge about the processes concerned, in this case those governing acidification and recovery, which means that forecasts and predictions always have to be questioned and the uncertainties in the calculations discussed when modelling results are used.

Data from large-scale field experiments are an excellent means of testing the usefulness of models. Experimental treatments often dramatically change the biogeochemistry of an entire catchment. If model outcomes tally with field measurements and correctly predict different effects of experimental treatments, model-based predictions going beyond the temporal and spatial constraints of an experiment can be made with some degree of confidence, even though there may be little data by which to verify the model used.

The acidification model MAGIC (Model of Acidification of Groundwaters in Catchments, Cosby *et al.* 1985) has been used to model the future development of runoff chemistry in the roofed catchment at Gårdsjön. The model was calibrated on the basis of the hydrology of the area, a description of its soils and forests, and historical estimates of atmospheric deposition and land use going back 140 years and looking ahead 30 years, i.e. to the year 2020. It was calibrated so as to correspond to the measurements of runoff chemistry and soil base saturation made before the clean precipitation experiment was started in 1990. Once close agreement had been achieved between observed and simulated values, simulations of runoff and soil chemistry were run for a deposition scenario corresponding to the reduction of acid deposition brought about in the experiment (Moldan *et al.* 1998). Figure 32 shows modelled annual mean values of various runoff chemistry variables between 1980 and 2020, together with measured data from the two years before the roof was built in 1990 and the six years following the start of the treatment.

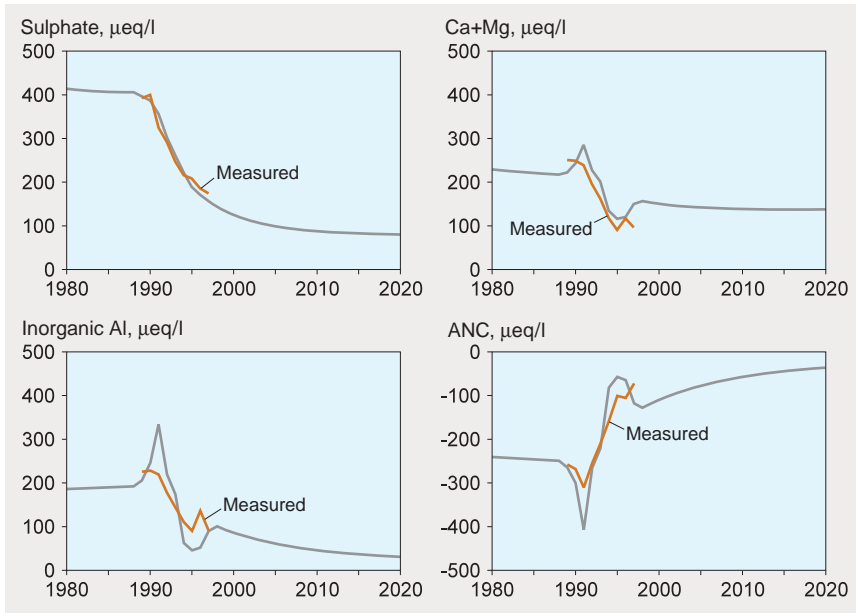


Figure 32. Measured values and model simulations of sulphate, base cations, inorganic aluminium and ANC (annual means) in runoff from the catchment near Lake Gårdsjön that has been covered since 1990. When deposition of acidifying compounds to the entire catchment had ceased, sulphate concentrations began to decline. At the same time, concentrations of base cations and inorganic aluminium also started to fall, balancing the sulphate reduction to a roughly equal extent in equivalent terms. Data: IVL.

Sulphate concentrations in runoff began to fall just a few months after all non-marine sulphur had been eliminated from the irrigation water. However, the decrease was gradual, in contrast to the practically instantaneous decrease in deposition. This was due to leaching of sulphur previously retained in the soil. By far the largest source of ‘old’ sulphur is sulphate adsorbed onto soil particles. There are also certain indications that net mineralization of organic sulphur (the dominant form of sulphur in soil) has made a contribution to the sulphate found in runoff in recent years (Mörth & Torssander 1998). How important that contribution is remains to be determined, but the roof project may eventually shed some light on the matter.

The gradual decline in sulphate concentrations was independent of factors such as hydrology or deposition of marine salts. This was in contrast to virtually all the other ions in runoff, which in the short term were strongly influenced by fluctuations in marine salt deposition. This effect could be observed with both base cations and aluminium (figure 32),

which, on top of the overall downward trend, showed marked fluctuations as a consequence of the fact that concentrations of marine salts in the irrigation water were high at the beginning of the experiment in 1991, moderately high in 1992–94 and low in 1995.

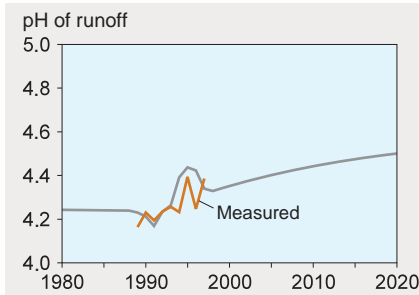


Figure 33. Measured values (annual means) and model simulation of the pH of runoff from the roofed catchment near Lake Gårdsjön. Data: IVL.

Concentrations of hydrogen ions have not fallen at all as rapidly as those of sulphate, and pH has thus risen only moderately since the roof experiment began (figure 33). Total acidity (hydrogen ions + inorganic aluminium), however, has fallen sharply. This means that ANC calculated on the basis of the balance of charges has risen appreciably (figure 32).

The model predicts that sulphate concentrations in runoff will stabilize at a new and much lower level, in balance with the reduced input of sulphur, within the next 20 years. Concentrations of base cations will also decrease and stabilize. Inorganic aluminium, on the other hand, will show a continuing gradual decline, but will still be elevated even after 30 years without acidifying deposition, if the model predictions prove correct. The pH will rise somewhat, but ANC will not reach non-negative values. Similar trends may be expected in other severely acidified areas, where the soil pool of base cations was depleted during the years of acidification and the pH of runoff is in a range in which the water is buffered by aluminium. In such circumstances, the pH is determined by the dissolution of aluminium hydroxides, and the supply of base cations to the soil from weathering and alkaline deposition is relatively small.

7.3 MODELLING OF FOREST SITES IN SOUTHERN SWEDEN

To investigate the possible development of the acidification situation in southern Sweden, the MAGIC model was applied to some twenty forest plots in that part of the country (Moldan *et al.* 1999). The sites chosen have widely varying soil properties and deposition levels. MAGIC was used to describe the historical development of acidification and to simulate future changes up to the year 2020. It was assumed that sulphur deposition will fall by around 70%, on the basis of full implementation of the

Second Sulphur Protocol. It was also assumed that no felling or replanting of forest stands will occur, even if stands are mature.

With few exceptions, the outcome obtained with this scenario is that there will be some improvement in the water quality of runoff from the forest plots. However, at most of the sites, the base saturation of the soil will continue to decline. The predicted improvement is therefore to be regarded as a new equilibrium between deposition and the state of the forest ecosystem, rather than a complete recovery in terms of the base saturation of these forest soils.

ANC will not reach its estimated pre-industrial levels at any of the sites for which the model was run. The most marked recovery in terms of pH and ANC will occur in soils with relatively high buffering capacities and high weathering rates. In more sensitive areas, the results are even less encouraging. The assumed scenario will reverse the acidification trend, but the positive trend will level off and previously acidified areas will remain acidified for a long time, even after the year 2020.

The pH and ANC values obtained from the model provide a good summary of the results. They are presented in figure 34, which shows the distributions of the simulated outcomes for the different sites.

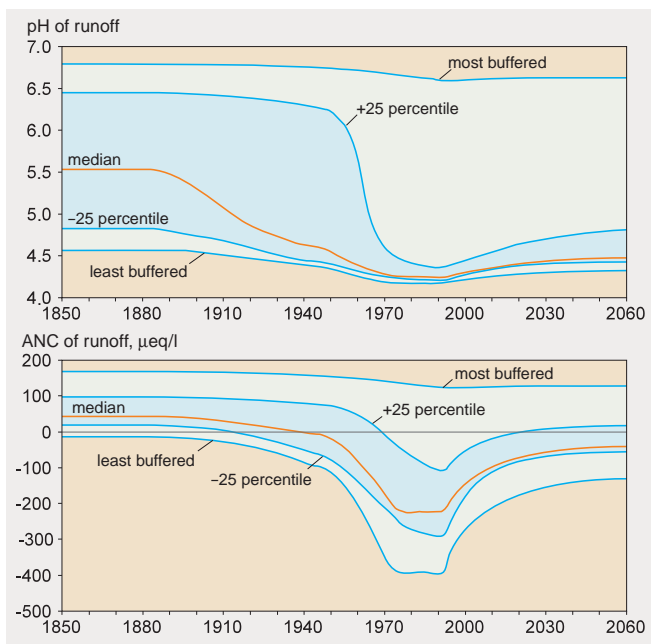


Figure 34. Distributions of pH and ANC of runoff from 17 sites, modelled using MAGIC. Data: IVL.

7.4 REGIONAL ASSESSMENTS

The largest nationwide soil chemistry database in Sweden consists of the data from the National Survey of Forest Soils and Vegetation. As was shown in section 4.6, these data can be used to analyse trends in forest soil chemistry. They have also formed the basis for an estimation of critical loads for forest soils, covering 1883 sites (Lövblad & Bertills 2000).

Preliminary calculations using a dynamic soil chemistry model (SAFE) have so far been performed for 147 sites from the Survey of Forest Soils and Vegetation database, to be compared with the 1883 sites just mentioned (Alveteg 1999). The reason why dynamic modelling has been applied to such a relatively small number of sites is that such models require a great deal of information, information which is not yet available for all 1883 candidate sites.

A simulation of the future chemical state of soils at these sites was performed for a deposition scenario based on the Second Sulphur Protocol. The results of the calculations were combined in three groups, covering sites in north-west Norrland ($n = 21$), central Sweden ($n = 66$) and south-west Sweden ($n = 60$). The diagrams below show median values for the sites in each region.

The preliminary findings regarding the long-term effects of the Second Sulphur Protocol on Swedish forest soils give cause for both optimism and concern. As figure 35 shows, very modest changes in base saturation are predicted over the period – despite the fact that the calculations assume that forests will simply be left to mature on site, resulting in a steadily decreasing uptake of base cations. At a few sites, there may admittedly be some recovery, but at others the trend will still be in the wrong direction, so the overall picture is a gloomy one. At a regional level, the chemistry of the soil will be largely the same in 2050 as it was in the 1970s. Some recovery in soil chemical terms should, though, have taken place compared with the early 1980s, when, according to the model, the situation was at its worst at many sites.

Although the chemical composition of runoff reflects that of soil water, it is not possible to translate these estimates of soil chemistry directly into forecasts of surface water chemistry. We can, however, see to what extent there will be a return to pre-industrial conditions. Figure 36 shows estimated ANC values at a soil depth of 0.5 m. The calculations indicate a fairly similar starting position throughout the country in pre-industrial times. Since then, there has been an appreciable decline in ANC in central Sweden, and a dramatic decrease in the south-west of the country. Simulated ANC values for deeper soil horizons indicate that the problem of

acidified watercourses may persist. In the year 2050, ANC will be below $-50 \mu\text{eq/l}$ at around 10% of the sites in northern Sweden, at some 50% of the sites in the central region and at virtually all the sites in the south-west. It is also predicted that the biggest changes will occur within a fairly short space of time. As this research continues, these results will be compared with time series of runoff chemistry data covering up to 30 years.

Figure 35.
Median base saturation in three regions of Sweden. The base saturation at each site has been calculated as a weighted mean for the entire rooting zone. Department of Chemical Engineering II, Lund University.

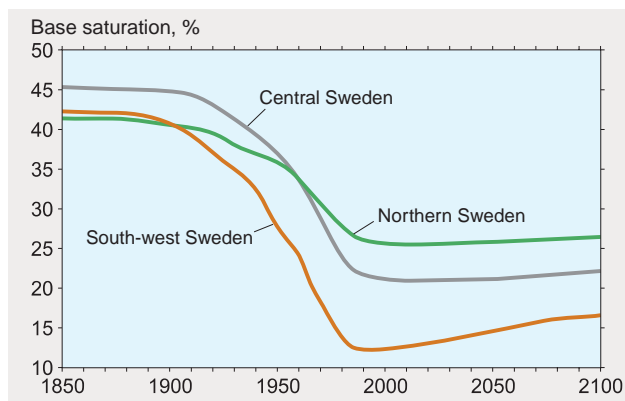
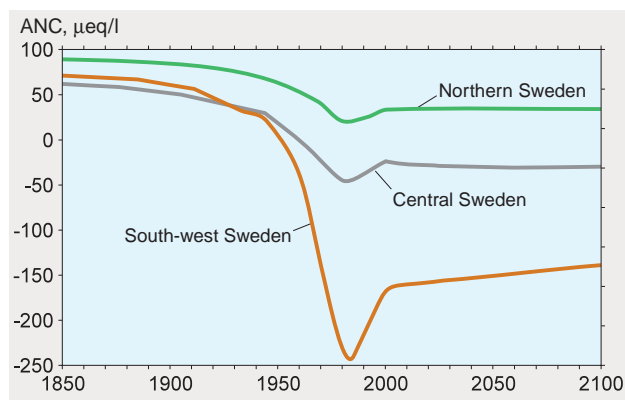
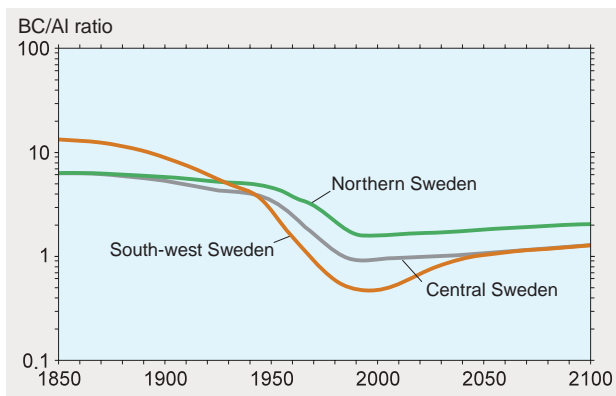


Figure 36.
Median values of ANC in the lowest soil horizon for the three regions. Department of Chemical Engineering II, Lund University.



In international negotiations on air pollution, the base cation/aluminium (BC/Al) ratio of the soil solution has been used as a chemical criterion. Northern Sweden differs from central and south-western areas of the country in that a much lower proportion of sites there have unfavourably low BC/Al ratios (figure 37). In the north, according to the prediction, some 10% of all forest land will have a BC/Al ratio of less than 1 at the end of the period modelled. The corresponding figure for central and south-west Sweden is 50%.

Figure 37. Median base cation/ aluminium ratios in the three regions. The lowest ratio found in the rooting zone has been chosen for each site. Department of Chemical Engineering II, Lund University.



Assuming that these results are correct, liming of forest land appears to be justified, *if* the aim is to restore the base saturation of the soil. Natural recovery processes are not sufficient for soil and water to ‘heal’ by themselves in the space of a couple of decades. For a number of reasons, recovery may prove somewhat slower than the preliminary findings suggest. The possibility of sulphate adsorption delaying the recovery process, for example, has not been taken into account.

Although certain inferences are possible on the basis of these preliminary modelling results, a great deal of time-consuming research still needs to be done before reliable predictions can be made. The quality of the databases used needs to be scrutinized more closely, and the models employed must be further developed and fine-tuned, for example to take account of the changes that have occurred in forestry in Sweden. In addition, the uncertainties involved in the use of the models need to be studied, as do the effects of different emission scenarios on the results. The large volume of information required for dynamic models also makes internal consistency all the more important, i.e. it must be ensured that contradictory assumptions have not been made when estimating different quantities and designing the models.

8. SYNTHESIS

PER WARFVINGE AND ULLA BERTILLS

In the introduction to this report, a number of important questions were discussed relating to recovery of the natural environment following the period of extremely high sulphur deposition to which we are now beginning to discern an end. These questions concerned the future course of recovery in temporal and spatial terms, the need for liming of forests and surface waters, the effects on biodiversity, the need for policy development and so on.

We have not been able in this report to give unequivocal and exhaustive answers to any of these questions. We are, though, beginning to discern a pattern in our knowledge, a pattern pieced together from environmental monitoring data, process studies, experimental manipulations and modelling.

8.1 WHAT DO WE KNOW?

Atmospheric deposition of sulphur and nitrogen to forests has by and large mirrored emission trends in Europe. Deposition of acidifying sulphur has thus fallen by 50% in Sweden, while nitrogen deposition has changed relatively little over the period 1985–97.

The downward trend in sulphur deposition is relatively strong, and similar throughout Sweden. Deposition to spruce forests has fallen by a larger percentage than concentrations in bulk precipitation. In southern and central Sweden, it is above all the dry component of deposition that has decreased.

The lower level of deposition has resulted in a reduction of sulphate fluxes in soil water and runoff. However, this reduction has been smaller than the decline in atmospheric deposition. This is because sulphate which has accumulated in the soil is gradually released when the external input falls. Reduced deposition of acidifying sulphur has led to an appreciable lowering of sulphate levels in surface waters, but also to a reduction of base cation concentrations. The reason for the latter is that acid-driven leaching of base cations abates and soils instead tend to bind these ions as the acid load decreases.

The key surface water parameter in biological terms, pH, has shown a marginal average change (about 0.1 units) in the time series lakes since the middle of the 1980s. In most of these lakes, alkalinity has risen since the early 1980s. The increase in ANC has been less significant.

Statistically significant chemical recovery of lakes has occurred even in areas where critical acid loads are still exceeded.

There are few signs of biological recovery of surface waters, largely owing to a lack of reliable time series. Recovery of the invertebrate fauna has been observed both in Sweden and in Norway and Germany.

Data from the National Survey of Forest Soils and Vegetation show that the pH of Swedish forest soils fell over the 10-year period between 1984–87 and 1993–96. The decrease was of the order of 0.1 pH units. The proportion of forest land with a mineral-soil pH of less than 5.0 increased from 71% to 75%.

Forest growth was responsible for a small part of the decrease in pH. This means that land use has to be taken into account in efforts to achieve environmental quality objectives of various kinds.

Changes in the quantities and distribution of exchangeable base cations over the 10-year period were small, but magnesium concentrations decreased and aluminium concentrations increased significantly in the B horizon.

The average base saturation in the humus layer fell from 13.2% to 12.8%, but the total pool of exchangeable cations increased. In the mineral soil, base saturation was largely unchanged, with a slight upward tendency.

There is little risk of nitrogen generally beginning to leach from forest soils and having an acidifying effect on soil and water.

The evidence of recovery that is provided by experiments and environmental monitoring data confirms that the principles underlying dynamic mathematical acidification models are correct. Despite the shortcomings of these models and the uncertainties attaching to predictions, they are an indispensable tool for gaining an overall picture of future states of the environment.

The data collected in environmental monitoring programmes will prove increasingly valuable in future analysis, modelling and assessment of the pace of the recovery process.

8.2 WHAT DO WE BELIEVE?

The conditions for biological recovery of Sweden's lakes, rivers and streams are improving, albeit slowly. Beneficial effects on biota are ex-

pected to become apparent over the next decade, and to be due primarily to reduced aluminium concentrations in runoff. It will take a long time for ecosystems to be restored, but our understanding of what ecological recovery will look like is still limited.

There is a large turnover of organic sulphur in soil, and some 50% of the input of sulphate-sulphur is converted into organic sulphur compounds in upper soil horizons. One hypothesis is that, if nitrogen deposition is reduced, turnover of this organic sulphur could increase still further and more sulphate could leach from the soil system.

Soil pools of nitrogen have increased in recent decades, which means that the soil has a large pool of relatively readily available nitrogen. Continuing high levels of nitrogen deposition consequently entail a risk of nitrogen leaching, not least if there is a general rise in temperature.

Modelling shows that in deeper soil horizons – and hence in runoff – ANC will not reach estimated pre-industrial levels at the rates of deposition that are expected. Base saturation will increase only slightly. In practice, therefore, acidification is not fully reversible.

The most marked recovery in terms of pH and ANC will occur in relatively unaffected soils. This means that only a limited degree of acidification will remain in central and northern Sweden, while soils in the south of the country could exhibit chronic acidification symptoms, even beyond 2020.

In the short term at least, recovery processes cannot be expected to restore waters to a chemical state that will permit full recolonization by acid-sensitive biota. Nor can the changes be expected to continue as straight-line trends.

8.3 WHAT PROBLEMS LIE AHEAD?

WHAT WILL THE SITUATION BE LIKE IN 2010?

- By 2010, deposition of acidifying sulphur will have fallen by about 80% from 1980 levels, as a result of the measures already agreed by countries negotiating within the EU and CLRTAP. However, since critical loads will still be exceeded in parts of Sweden, and since the recovery of acidified areas needs to be accelerated, further emission reductions are called for.
- The chemical status of forest soils will improve only marginally over the coming decade. The decrease in deposition, primarily of sulphur, will only bring about marginal improvements in soil pH and base saturation. On the other hand, aluminium concentrations in soil water will probably fall appreciably. Reasons for the slow pace of re-

covery include desorption of sulphate, but also the removal of base cations associated with active forestry.

- The quantity of adsorbed anthropogenic sulphur in the soil should have fallen by half compared with the situation in the 1990s.
- If present water quality trends continue, severely acidified lakes will only experience minor improvements in pH. On the other hand, leaching of aluminium will decrease appreciably, though not dramatically. Thanks to an increase in ANC of 2–3 $\mu\text{eq}/\text{l}/\text{yr}$, some less acidified lakes may not need to be limed.
- Waters which are now chronically acidified could instead suffer only periodical acid surges.
- Acid surges caused by acid deposition should have decreased in both frequency and amplitude.

WHAT WILL THE SITUATION BE LIKE IN 2050?

- By 2050, deposition of acidifying sulphur will have decreased by at least 95% from 1980 levels as a result of international agreements. To a large extent, these agreements will be shaped by the need to switch to renewable energy sources. Emissions of oxidized nitrogen will also be radically reduced, thanks to improved technology.
- In most areas, the chemistry of runoff will have returned to a state that permits considerable biological diversity in wetlands, running waters and lakes. Only a few freshwater systems in south-west Sweden will still be limed.
- Soils will not yet have fully recovered, since pools of exchangeable base cations will be considerably smaller than in pre-industrial times.
- Only small quantities of adsorbed anthropogenic sulphate will be present in the soil. A new equilibrium will have developed between inputs and leaching of sulphur. Unless climate change has resulted in an increased turnover of soil organic matter, leaching of nitrogen will be limited.
- Global climate change, however, is a very major source of uncertainty. If our worst fears prove correct, the situation could become considerably worse than expected. Increased mineralization of soil-bound carbon and nitrogen could be followed by heavy acidification pressure on soils and surface waters.

8.4 WHAT KNOWLEDGE GAPS REMAIN?

We have a poor understanding of biological recovery of aquatic ecosystems, mainly owing to inadequate funding for monitoring programmes. As a result, it is difficult to formulate optimum chemical criteria and objectives for the measures that are undertaken. Furthermore, we lack the tools we need to carry out carefully considered action in support of natural ecological processes. It is also alarming that we have a very limited national capability in the field of acidification-related limnology. Our society is simply not equipped to handle these issues scientifically.

We know very little about the soil chemistry of pre-industrial times, or even about the chemical status of Swedish forest soils only 20–30 years ago. Our understanding of what constitutes a natural state therefore has to be based on modelling, making it very difficult to define what recovery in soil chemical terms really is – and hence to set environmental quality objectives based on a return to a natural state.

Deposition of base cations is difficult to measure, and models of this process are very uncertain. In a situation in which deposition of acidifying sulphur is falling sharply, uncertainties about base cation deposition can have an appreciable impact on forecasts and assessments. A new generation of mathematical models for estimating deposition on the basis of local and regional emissions is being developed. These models could make it easier to calculate deposition to individual forest stands.

We lack sufficiently long runs of data to validate predictive models. This is true of both forest soil and surface water chemistry, but it is particularly the case when it comes to biological indicators. Continuity in environmental monitoring is thus of great importance, since monitoring is an indispensable instrument in the search for effective measures to safeguard aquatic biodiversity and the long-term productivity of forests.

Our understanding of acidification and recovery in mountain regions is inadequate. Developments over the next few years must be monitored very carefully, to give us a better understanding of the processes governing runoff chemistry. We do not know enough about the biological dynamics of mountain ecosystems to assess whether the expected decrease in deposition will be sufficient to allow recolonization by insects, fish etc.

Environmental monitoring has shown that concentrations of dissolved organic matter in Swedish waters have risen over the last decade. This phenomenon is probably due to intensified land use, but its causes and consequences should be studied more closely.

Very convincing arguments are needed to persuade the countries of Europe of the need for further reductions in emissions of acidifying com-

pounds. Existing mathematical models of acidification/recovery and the basic data used in modelling are too uncertain to convince decision-makers that further action is necessary. In the last few years, methods for handling these uncertainties in a policy context have been developed (Barkman 1998). However, it is important to apply a coordinated approach, involving the development of dynamic mathematical models, augmentation of environmental databases, and the development of new effects criteria that can form the basis for international emission abatement efforts.

8.5 CONCLUDING REMARKS

The data on which this report is based are the result of many years of acidification research in Sweden. If environmental research is to succeed, it requires continuity and a minimum critical mass, as has been shown, not least, by the pioneering Lake Gårdsjön project. It is important that Sweden should maintain the highest degree of scientific readiness to develop the knowledge needed in support of tangible environmental action and to retain the initiative in international decision-making bodies.

9. REFERENCES

- Alveteg, M. (1999). *Simulering av markkemisk återhämtning till följd av minskad aciditetsbelastning*. Lund, Avd. för Kemisk teknologi.
- Barkman, A. (1998). *Critical loads – assessment of uncertainty*. Chemical Engineering II. Lund, Lund University.
- Barth, H. (ed.) (1987). *Reversibility of acidification*. London, Elsevier.
- Battarbee, R. W., Charles, D. F., Dixit, S. S. & Renberg, I. (1999). Diatoms as indicators of surface water acidity. In E. F. Stoermer & J. P. Smol (eds.), *The diatoms: applications for the environmental and earth sciences*, pp. 85–127. Cambridge, Cambridge University Press.
- Beier, C., Blanck, K., Bredemeier, M., Lamersdorf, N., Rasmussen, L. & Xu, Y.-J. (1998). Field-scale ‘clean-rain’ treatments to two Norway spruce stands within the EXMAN project – effects on soil chemistry, foliar nutrition and tree growth. *Forest Ecology and Management* **101**: 101–123.
- Bernes, C. (1986). *Sura och försurade vatten*. Solna, Statens naturvårdsverk, Monitor 1986.
- Bernes, C. (1991). *Acidification and liming of Swedish freshwaters*. Solna, Swedish Environmental Protection Agency, Monitor 12
- Boxman, A. W., van Dam, D., van Dijk, H. F. G., Hogervorst, R. F. & Koopmans, C. J. (1995). Ecosystem responses to reduced nitrogen and sulphur inputs into two coniferous forest stands in the Netherlands. *Forest Ecology and Management* **71**(1–2): 7–29.
- Boxman, A. W., van der Ven, P. J. M. & Roelofs, J. G. M. (1998). Ecosystem recovery after a decrease in nitrogen input to a Scots pine stand at Ysselsteyn, the Netherlands. *Forest Ecology and Management* **101**: 155–163.
- Cosby, B. J., Hornberger, G. M., Galloway, J. N. & Wright, R. F. (1985). Modelling the effects of acid deposition: Assessment of a lumped parameter model of soil water and streamwater chemistry. *Water Resources Research* **18**: 51–63.
- Dillon, P. J., Reid, R. A. & Girard, R. (1986). Changes in the chemistry of lakes near Sudbury, Ontario following reduction of SO₂ emissions. *Water, Air and Soil Pollution* **31**: 59–66.

- Dise, N., Ahlf, W., Brahmer, G., Cosby, B. J., Fott, J., Hauhs, M., Jüttner, I., Kreuzer, K., Raddum, G. G. & Wright, R. F. (1994). Group report: Are chemical and biological changes reversible? In C. E. W. Steinberg & R. F. Wright (eds.), *Acidification of Freshwater Ecosystems: Implications for the Future*, pp. 375–391. Chichester, John Wiley & Sons Ltd.
- Dise, N. B., Matzner, E. & Gundersen, P. (1998). Synthesis of nitrogen pools and fluxes from European forest ecosystems. *Water, Air and Soil Pollution* **105**(1–2): 143–154.
- Ek, A., Grahn, O., Hultberg, H. & Renberg, I. (1995). Recovery from acidification in Lake Örvattnet, Sweden. *Water, Air and Soil Pollution* **85**: 1795–1800.
- Ek, A. & Renberg, I. (1998). *Faluns sjöar under 1000 år. Försurning och metallutsläpp från kopparframställningen*. Falun, Miljö och hälsoskydd, Falu kommun, MH 1998:9.
- EMEP/MS-C-W (1998). *Transboundary acidifying air pollution in Europe*. MS-C-W Status Report 1998. Oslo, Meteorological Synthesizing Centre – West, Norwegian Meteorological Institute.
- Falu kommun (1998). *Faluns historiska svavelbelastning. Tre rapporter om svavel och pH-värden i Faluområdet*. Falun, Miljö och hälsoskydd, Falu kommun, MH 1998:5.
- Forsberg, C., Morling, G. & Wetzel, R. G. (1985). Indications of the capacity for rapid reversibility of lake acidification. *Ambio* **14**: 164–166.
- Gunn, J. M. (ed.) (1995). *Restoration and recovery of an industrial region*. New York, Springer-Verlag.
- Gunn, J. M. & Keller, W. (1990). Biological recovery of an acid lake after reductions in industrial emissions of sulphur. *Nature* **345**: 431–433.
- Hallgren Larsson, E., Knulst, J., Malm, G. & Westling, O. (1995). Deposition of acidifying compounds in Sweden. *Water, Air and Soil Pollution* **85**: 2271–2276.
- Hedin, L. O., Granat, L., Likens, G. E., Buishand, T. A., Galloway, J. N., Butler, T. J. & Rodhe, H. (1994). Steep declines in atmospheric base cations in regions of Europe and North America. *Nature* **367**(6461): 351–354.
- Henriksen, A., Kämäri, J., Posch, M. & Wilander, A. (1992). Critical loads of acidity: Nordic surface waters. *Ambio* **21** (5): 356–363.
- Henrikson, L. & Medin, M. (1986). *Biologisk bedömning av försurningspåverkan på Lelängens tillflöden och grundområden 1986*. Aqualogerna. Rapport till länsstyrelsen i Älvsborgs län
- Hörnström, E. & Ekström, C. (1983). *pH-, närings- och aluminiumeffekter på plankton i västkustsjöar*. Solna, Statens naturvårdsverk, PM 1704.

- Hultberg, H. & Skeffington, R. (eds.) (1998). *Experimental reversal of acid rain effects: The Gårdsjön Roof Project*. Chichester, Wiley.
- Hutchinson, T. C. & Havas, M. (1986). Recovery of previously acidified lakes near Coniston, Canada following reductions in atmospheric sulphur and metal emissions. *Water, Air and Soil Pollution* **28**: 319–333.
- Johnson, D. W. & Mitchell, M. J. (1998). Responses of forest ecosystems to changing sulfur inputs. In D. G. Maynard (ed.), *Sulfur in the environment*, pp. 219–262. New York, Marcel-Dekke.
- Jongmans, A. G., van Breemen, N., Lundström, U., van Hees, P. A. W., Finlay, R. D., Srinivasan, M., Unestam, T., Giesler, R., Melkerud, P. A. & Olsson, M. (1997). Rock-eating fungi. *Nature* **389**(6652): 682–683.
- Karlton, E. (1994). The determination of adsorbed sulfate with isotopic dilution of ^{35}S as compared with $\text{Ca}(\text{H}_2\text{PO}_4)_2$ extraction. *Communications in soil science and plant analysis* **25**: 207–214.
- Karlton, E. (1995). *Sulphate adsorption on variable-charge minerals in podsolized soils in relation to sulphur deposition and soil acidity*. Department of Soil Sciences. Uppsala, Swedish University of Agricultural Sciences.
- Karlton, E. (1998a). *Basketjoner och aciditet i svensk skogsmark – tillstånd och förändringar*. Jönköping, SKS.
- Karlton, E. (1998b). *Systematiska avvikelser mellan analyserna i 1:a och 2:a ståndortskarteringen*. Uppsala, Institutionen för skoglig marklära, SLU.
- Kindbom, K., Sjöberg, K. & Lövblad, G. (1993). *Beräkning av ackumulerad syrabelastning från atmosfären till de svenska ekosystemen. Delrapport 1: Emissioner av svavel, kväve och alkaliskt stoft i Sverige 1900–1990*. Göteborg, Swedish Environmental Research Institute, IVL Report B 1109.
- Krouse, H. R. & Grinenko, V. A. (1991). *Stable isotopes. Natural and anthropogenic sulphur in the environment*. SCOPE 43. New York, John Wiley & Sons.
- Lövblad, G., Persson, C. & Roos, E. (2000). *Base cation deposition in Sweden*. Göteborg, Swedish Environmental Research Institute (in preparation).
- Lövblad, G. & Bertills, U. (2000). *Kritisk belastning för svavel och kväve*. To be published in the Swedish Environmental Protection Agency's report series.
- Lükewille, A., Jeffries, D., Johannessen, M., Raddum, G. G., Stoddard, J. L. & Traaen, T. S. (1997). *The nine year report: Acidification of surface waters in Europe and North America – Long-term developments (1980s and 1990s)*. Oslo, NIVA, ISBN 82-577-31951.

- Mallory, M. L., McNicol, D. K., Cluis, D. A. & Laberge, C. (1998). Chemical trends and status of small lakes near Sudbury, Ontario, 1983–1995: evidence of continued chemical recovery. *Canadian Journal of Fisheries and Aquatic Sciences* **55**: 63–75.
- Moldan, F., Andersson, I., Bishop, K. & Hultberg, H. (1998). Catchment-scale acidification reversal experiment at Gårdsjön, south-west Sweden – Assessment of the experimental design. In H. Hultberg & R. Skeffington (eds.), *Experimental reversal of acid rain effects: The Gårdsjön Roof Project*, pp. 85–108. Chichester, Wiley.
- Moldan, F., Westling, O. & Munthe, J. (1999). *Geochemical modelling of acidification and recovery in forest soils and runoff waters*. Göteborg, Swedish Environmental Research Institute, IVL Report B 1323.
- Morling, G., Forsberg, C. & Wetzel, R. G. (1985). Lake Änketjärn, a non-acidified lake in an acidified region. *Oikos* **44**: 324–330.
- Mörth, C.-M. & Torssander, P. (1995). Sulfur and oxygen isotope ratios in sulfate during an acidification reversal study at Lake Gårdsjön, Western Sweden. *Water, Air and Soil Pollution* **79**: 261–278.
- Mörth, C.-M. & Torssander, P. (1998). Sea water sulfate addition to a forested catchment: Results after five years of experimental treatment. In G. B. Arehart & J. R. Hulston (eds.), *Water–Rock Interaction*, pp. 63–66. Rotterdam/Brookfield, A. A. Balkema.
- Mylona, S. (1993). *Trends of sulfur dioxide emissions, air concentrations and deposition of sulfur in Europe since 1880*. Oslo, Norwegian Meteorological Institute, EMEP/MSC-W.
- NAPAP (1998). *National acid precipitation assessment program. NAPAP Biennial Report to Congress: An integrated assessment*. Silver Spring, Maryland, National Science and Technology Council.
- Renberg, I., Korsman, T. & Anderson, N. J. (1993a). A temporal perspective of lake acidification in Sweden. *Ambio* **22**: 264–271.
- Renberg, I., Korsman, T. & Birks, B. (1993b). Prehistoric increase in the pH of acid-sensitive Swedish lakes caused by land-use change. *Nature* **362**: 824–827.
- Smol, J. P., Cumming, B. F., Dixit, A. S. & Dixit, S. S. (1998). Tracking recovery patterns in acidified lakes: a paleolimnological perspective. *Restoration Ecology* **3**(4): 318–326.
- Swedish Environmental Protection Agency (2000). *Environmental Quality Criteria – Lakes and Watercourses*. Report 5050.
- Torssander, P. & Mörth, C.-M. (1998). Sulfur dynamics in the roof experiment at Lake Gårdsjön deduced from sulfur and oxygen isotope ratios in sulfate. In H. Hultberg & R. Skeffington (eds.), *Experimental reversal of acid rain effects: The Gårdsjön Roof Project*, pp. 185–206. New York, John Wiley & Sons.

- UNECE (1999). *Trends in Impact of Long-range Transboundary Air Pollution*. Technical Report prepared by the Bureau, the International Cooperative Programmes (ICP) of the Working Group on Effects, Geneva.
- Walse, C., Blanck, K., Bredemeier, M., Lamersdorf, N., Warfvinge, P. & Xu, Y.-J. (1998). Application of the SAFE model to the Solling clean rain experiment. *Forest Ecology and Management* **101**: 307–317.
- Warfvinge, P. (1997). *Miljö kemi – miljövetenskap i biogeokemiskt perspektiv*. Lund, KFS AB.
- Warfvinge, P. & Sverdrup, H. (1995). *Critical loads of acidity to Swedish forest soils*. Lund, Department of Chemical Engineering II, 1995:5.
- Wilander, A. (1997). *Referenssjöarnas vattenkemi under 12 år; tillstånd och trender*. Stockholm, Naturvårdsverket, Rapport 4562.
- Wright, R. F., Gjessing, E., Christophersen, N., Lotse, E., Seip, H. M., Sletaune, B., Storhaug, R. & Wedum, K. (1986). Project RAIN: Changing acid deposition to whole catchments. The first year of treatment. *Water, Air and Soil Pollution* **3**: 47–63.
- Wright, R. F., Lotse, E. & Semb, A. (1993). RAIN project – results after 8 years of experimentally reduced acid deposition to a whole catchment. *Canadian Journal of Fisheries and Aquatic Sciences* **50**: 258–268.
- Wright, R. F. & van Breemen, N. (1995). The NITREX Project: An Introduction. *Forest Ecology and Management* **71**(1–2): 1–5.

AUTHORS' ADDRESSES

MATTIAS ALVETEG
Dept. of Chemical Engineering II
Lund Institute of Technology
Lund University
Box 124
SE-221 00 Lund

ULLA BERTILLS
Environmental Assessment Dept.
Swedish Environmental Protection
Agency
SE-106 48 Stockholm

ANNA EK
Dept. of Ecology and
Environmental Science
Umeå University
SE-901 87 Umeå

LARS LUNDIN
Dept. of Forest Soils
Swedish University of
Agricultural Sciences
Box 7001
SE-750 07 Uppsala

GUN LÖVBLAD
IVL Swedish Environmental
Research Institute Ltd.
Box 470 86
SE-402 58 Göteborg

FILIP MOLDAN
IVL Swedish Environmental
Research Institute Ltd.
Box 470 86
SE-402 58 Göteborg

CARL-MAGNUS MÖRTH
Dept. of Geology and Geochemistry
Stockholm University
SE-106 91 Stockholm

PER WARFVINGE
Dept. of Chemical Engineering II
Lund Institute of Technology
Lund University
Box 124
SE-221 00 Lund

OLLE WESTLING
IVL Swedish Environmental
Research Institute Ltd.
Aneboda
SE-360 30 Lammhult

ANDERS WILANDER
Dept. of Environmental Assessment
Swedish University of Agricultural
Sciences
Box 7050
SE-750 07 Uppsala

RICHARD F. WRIGHT
Norwegian Institute for
Water Research
Postboks 173, Kjelsås
N-0411 Oslo

REPORT 5034

Recovery from Acidification in the Natural Environment

Present Knowledge and Future Scenarios

ACIDIFICATION OF AIR, SOIL AND WATER has had highly detrimental effects on Sweden's ecosystems. Over the last decade or so, however, emissions of acidifying pollutants have decreased, and we now expect to see signs of recovery in the natural environment. This report is a summary and synthesis of the information and knowledge currently available concerning the nature of the recovery process that may be expected to result from reduced atmospheric deposition of acidifying compounds. It describes deposition trends, soil chemical processes, the results of experimental studies and environmental monitoring, and different scenarios for the future. The report will, it is hoped, provide a basis for environmental policy decisions and measures.



ISBN 91-620-5034-6

ISSN 0282-7298

SWEDISH ENVIRONMENTAL PROTECTION AGENCY