

# Soil and surface water acidification in theory and practice



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# Soil and surface water acidification in theory and practice

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# Introduction



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To start with, I would like to give you a few perspectives on questions that we will be discussing during the next two days. As you are well aware of, Svante Oden initiated the acidification discussion in 1967 through his intelligent way of linking knowledge from different environments: air, soil and water. I was born in the most acidified areas of southwestern Småland and I can remember how the farmers drove out onto the ice-covered lakes to spread lime. That was in the early 1950s. This leads me to believe that they must have noticed that the fishing had become poorer. Their reasoning was presumably that if they limed their arable fields in order to improve production, then they could do the same with the lakes.

In my work I am accustomed to look at environmental questions through the eyes of the users. Then it is natural to think in different decision-making arenas, where formulations are made of applied needs of knowledge. In the present context we can distinguish three such important arenas:

1. The LRTAP Convention (Long-Range Transboundary Air Pollution. This is handled by UN-ECE. A decisive agreement was

reached in Göteborg in 1999. Revision of this agreement will be made in 2005/2006. If research is to be involved and be able to influence the decisions then processing and reporting of results must be adapted to this time plan. Otherwise we will have to wait another 10 years.

2. The EU with the so-called “ceiling directive” and the Clean Air for Europe (CAFE) programme. Proposals on measures will be processed until 2005 and subsequently a political process will continue until 2005–2006. We have good opportunities to influence the direction of the decisions that will be reached if we act in close contact with the process within EU.
3. National requirements, mainly concerning work dealing with environmental goals, where a revision will take place in 2004, together with strategies and measures concerning forest- and energy policy (bioenergy, etc.).

Acidification is an exciting field as regards the links between research and environmental monitoring in this sector. I believe that administrators and researchers in Europe are in

agreement that this field is the best example of how research results and researcher competence have made a break-through with regard to decisions on direction and extent of long-term measures in the environmental sector.

I would also like to say a few words about ongoing research and environmental monitoring in this sector. During the 1980s there was a research programme into acidification in most countries in northern Europe. Today, only Sweden has an all-embracing programme (ASTA). Naturally, individual projects on acidification and eutrophication are in progress in other countries, e.g., a nitrogen programme in England.

I have chosen to report on the ongoing R&D work in Sweden in four blocks:

## Environmental monitoring

Monitoring of acidification is included as an integrated part of environmental monitoring. Soil surveys concentrate on soil sampling, where about 1800 test plots are sampled annually. Integrated monitoring is ongoing within small catchment areas, where the flux of different substances are followed in the system from the atmosphere to the water. Lakes and waterways are covered by a national inventory (2000–4000 lakes) every fifth year. Studies are also made of reference waters (about 200 annually).

## Research at universities, individual projects

Here there is a relatively limited extent and the work is directed at individual processes, such as natural acidification, sulphur dynamics in the soil, podsol processes and nitrification.

## The ASTA programme

MISTRA funds a research programme for 8 years with a total budget of 59 million SEK. This programme is directed at feeding in knowledge into the above-mentioned arenas and is adapted to their respective time plans. The programme organised a workshop at Saltsjöbaden in 2000 where guidelines were drawn up for the above-mentioned negotiations within LRTAP and EU.

## Research into liming and return of ashes

The National Board of Forestry finances a follow-up programme in a number of catchment areas, where the links between soil and water are studied. In addition, a number of dosing experiments are being studied. The National Energy Board also has projects in this sector.

Before I hand over the microphone to those who have more facts to talk about, I would like to mention a few of my personal reflections on what we will be facing during the next couple of days. I am looking for a constructive and open discussion, where we try to respect each others views.

I have not fully understood the wording in the invitation to this workshop: "The results thus are in conflict with the previously prevailing theory that surface water chemistry reflects the soil chemistry status". In my opinion, there is good agreement between the map and the terrain. It will be interesting to see the result of your deliberations. With regard to the group work programmes that will be done, I have two messages: 1) It is the processes, not the status, that are most decisive for what happens; 2) The spatial variation is large. Water moves in different directions. Thus, we cannot make simple comparisons between the situation in the soil and what is happening in the surface water. We must have a dynamic approach.



# Summary



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## Soil and surface water acidification in theory and practice – conclusions from a KSLA-workshop

### Background and aims of the workshop

One of the scientific theories within the field of limnology states that water quality mirrors the soil status in the drainage basin, if the water is not affected by direct discharge of any substance. According to this soil and surface water linkage theory, generally accepted by the scientific society, soils acidified by acid precipitation would cause more acidic surface waters. The reverse would be true if acid deposition decreases and the surface waters exhibit recovery.

Since the middle of the 1980's, the deposition of acidifying compounds has decreased substantially and it is today at the same level as in the early 1950's in Central Sweden. The decreased deposition of sulphur can be ob-

served in many streams and lakes in the forested landscape, demonstrated by reduced sulfate concentrations, increased buffer capacity (ANC and alkalinity) and increased pH (SEPA 2000). In Norway, reduced concentrations of inorganic aluminium are documented as well (Skjelkvåle et al. 1996). Unfortunately, long-term time series on inorganic aluminium are not available from Sweden.

According to the theory, the acid status of the soils should also have improved parallel to the surface water recovery. However, recently published (SEPA 2000) soil data and model simulations indicated a continuous soil acidification during the 1990's down to the B-horizon (increased exchangeable Al) and that the acid soil status should not be expected to improve (base saturation and ANC) during the forthcoming decades in the

most acid sensitive areas of Southwest Sweden, respectively. In the perspective of one decade, the results from the soil and surface water assessments were obviously in conflict with the theory of surface waters acting as a mirror of the soil status. Questions arose whether the theory is too simple, if our conclusions have been based on different definitions of acidification/recovery of soil and water or if data and/or mathematical models are non-representative and not comparable with each other.

This scientific workshop was initiated in order to answer those questions and to define important issues for future research related to acidity transfer from soils into surface waters in forested, Swedish catchments dominated by podzolic soils.

## Organization of the workshop

The workshop was opened with six state of the art presentations focussing on processes important for the soil acidity status (Ulla Lundström), flow paths of water in forest soils (Allan Rodhe), measured soil acidity status (Erik Karlton), MAGIC modeled soil and surface water status (Filip Moldan), processes important for the surface water acidity status (Hjalmar Laudon) and measured surface water acidity status (Anders Wilander). Summaries of these presentations are published in this volume.

Thereafter, the participants were split into four groups for the discussions. The chairman of each group (Allan Rodhe, Jan Seibert, Kevin Bishop and Gunnar Jacks) presented their conclusions before a final discussion took place. Jan Nilsson acted as chairman throughout the workshop.

The most important conclusions presented below have been formulated together with the participants. Therefore, the conclusions of the workshop are expressed in consensus.

## Results and conclusions from the workshop

### *The relevance of the soil and surface water linkage theory*

Based on time series from the Swedish surface water monitoring, which comprise data from through June 2002, Anders Wilander (this volume) showed that the recovery from surface water acidification is proceeding. It can be measured as reduced sulfate concentrations and increased concentrations of ANC and alkalinity as well as an increased pH (Wilander and Löfgren this volume).

Erik Karlton (this volume) presented an assessment of changes in soil status between the last two Swedish Forest Soil Surveys, which mainly represent trends from 1983 through 1998. The assessment was based on almost twice as many soil samples as were used in the SEPA evaluation (SEPA 2000). The larger data set shows that the changes in soil acidity have been less pronounced than described in the SEPA report. No statistically significant trends can be observed concerning  $\text{pH}_{\text{H}_2\text{O}}$  in the O-horizon, while a significant, but low increase is indicated for  $\text{pH}_{\text{H}_2\text{O}}$  in the B-horizon. Exchangeable base cations (BC) have remained fairly constant in the O- and B-horizons. The total acidity as well as exchangeable Ca and Mg have increased in the O-horizon in the whole country, while there has been a significant increase of exchangeable Al and tendencies of reduced Mg and increased Ca concentrations in the B-horizon. Organic carbon (C) shows a net accumulation in O horizons in Southwest Sweden, while no such trend can be detected for the rest of the country.

The presentations by Wilander and Karlton gave valuable up to date information about the soil and surface water status in Sweden, and modified the current view established before the workshop (c.f. Background chapter). The current trends are only partly consistent with the soil and surface water

linkage theory. One main discrepancy is for instance a reduced surface water acidity combined with a less uniform or less significant soil improvement. This problem was thoroughly discussed at the workshop and three main explanations were brought forward.

Firstly, Filip Moldan (this volume) showed, based on data from the Swedish reference lakes, the Swedish Forest Soil Survey and the estimated acid deposition during the period 1850–2040, that the MAGIC model could simulate the surface water acidity in fairly good agreement with measured values. He also stressed that the simulations for all objects (132 of which 64 are considered acid sensitive) gave similar trends in the future regardless of original acid status and location in the country. The main explanation to this was mainly the long time needed for rebuilding the exchangeable BC pools in the soils. He therefore concluded that one should expect a much slower response in soils compared to surface waters. He also pointed out, that even though the lakes are currently improving, without a soil recovery the lakes would never return to their pre-acidification status. The accumulation of BC is highly dependent on the mass balance including BC weathering rates (c.f. Lundström and Hees this volume), BC deposition, BC uptake by the vegetation and BC leaching.

Secondly, the decreasing sulphur deposition has caused a decline in the ionic strength in the soil solution. This might have changed the ion exchange equilibria favoring an increased accumulation of exchangeable  $Al^{3+}$  combined with an excess loss of BC to surface waters, resulting in a maintenance of high soil acidity but an improved surface water quality. The question was raised whether the high and variable marine salt ( $Na^+$  and  $Cl^-$  ions) deposition determines the ionic strength variability in the soil solution in Southwest Sweden, overshadowing the influence by the anthropogenic sulphur deposition. This region exhibits the same recovery

trends in surface waters as the rest of the country, indicating that the ionic strength as such might be of less importance. However, the relatively higher contribution of sulfate to ionic strength compared to  $Cl^-$  and the fact that sulfate deposition has decreased over time, while the  $Cl^-$  deposition is assumed to have remained at the same level, makes the ionic strength effect to an open question that should be analyzed further. The leaching of mobile anions, expressed as the sum of sulfate, nitrate, chloride and organic anions, was put forward as the most important factor for the BC losses.

Finally, the soils sampled by the Swedish National Forest Soil Survey mainly represent dry and mesic sites situated in groundwater recharge areas. However, soil properties and water flow paths in the groundwater discharge areas (Fig 1, Rodhe this volume), to a very great extent influence the water chemistry (c.f. Laudon this volume). Hence, the acid trends in surface waters do not necessarily have to be the same as shown by the Swedish National Forest Soil Survey. The temporal variation might be disparate between the two media due to unequal kinetics in different compartments of the catchment. The heterogeneous properties of soil and hydraulic activity, with important acid-base processes occurring in moist discharge areas, might create the observed discrepancies.

**The most important conclusion on this issue was that the acid trends observed in the Swedish soil and surface water surveys are consistent with the prevailing soil and surface water linkage theory. However, the results from the soil and surface water surveys are not fully comparable due to different spatial and temporal scales caused by disparate hydraulic and soil properties in different compartments of the catchment. There are theoretical explanations for why the soils should have a slower recovery rate in terms of increased pools of exchangeable**

### base cations than should the surface waters in terms of increased ANC.

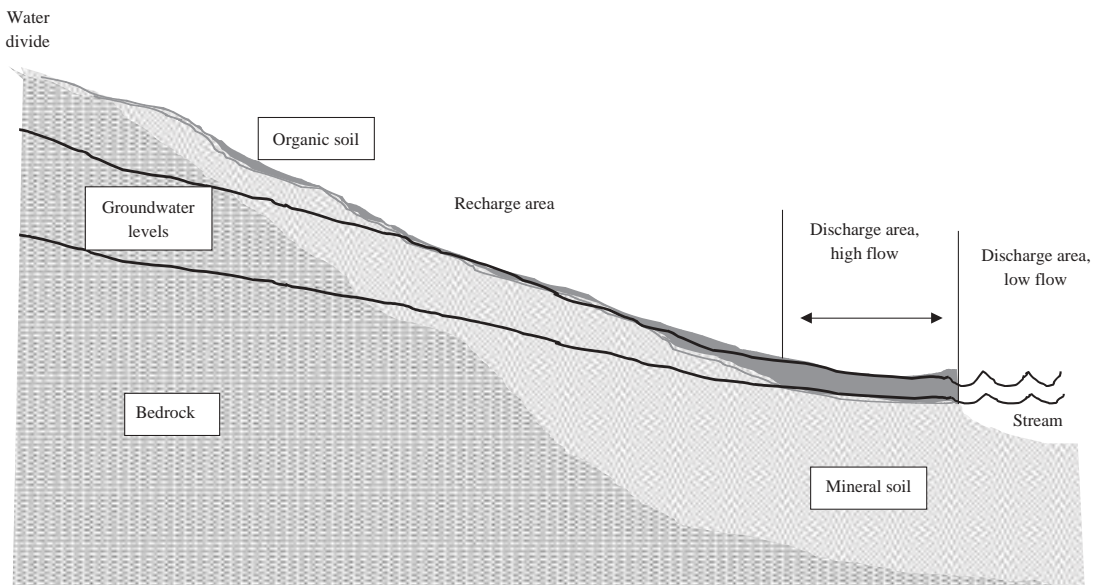
#### *Key issues for future research*

Throughout the workshop a large number of questions were put forward as being of scientific interest for the understanding of the relations between soil and surface water acidification. Many questions were of an applied nature, e.g. coupled to the planned forest soil liming program or to improvements of the models used as political decision support tools, while other questions were of a more theoretical nature. However, the participants clearly defined two scientific key issues that were important from both theoretical and practical points of views.

Firstly, the horizontal and vertical heterogeneity in groundwater flow paths in forested catchments, described by Allan Rodhe (Fig. 1, this volume), demonstrates that different parts of a catchment are unequally involved in the stream water generation. Hjalmar Lau-

don (this volume) complemented this picture by showing the importance of BC and thereby ANC dilution and TOC leakage from discharge areas for generating stream water acidity in Northern Sweden. The acid-base properties of surface waters are obviously greatly influenced by the groundwater flow paths in the catchment and by the soil properties in the discharge areas. However, integrated, scientific studies of acid-base processes in the different compartments in forested catchments are extremely rare both nationally and internationally. Generally, information is lacking on either hydraulic, soil physical and/or soil chemical properties in the discharge areas characterized by upward groundwater flow components in the deeper soil layers and mainly lateral groundwater flow paths near the soil surface. The best available information in Sweden is from 4 forested reference catchments (Integrated Monitoring) and some few (<5) forestry influenced catchments.

**Figure 1. Hypothetical slope in a drainage basin.**



**We therefore recommend that a comprehensive research program should be initiated directed towards detailed studies of processes in discharge areas being expected to have significant influence on the acid-base status of surface waters. The research program should include intensive hydrological and biogeochemical studies of watersheds and development of catchment based mathematical models, taking into account hydraulic and chemical processes in both the recharge and discharge areas. It would be advantageous if the studies were located at monitoring and research areas already in use and partly mapped and equipped for these purposes.**

**By improving the knowledge about processes in discharge areas we expect the research program to generate results important for the implementation of the EU water framework directive (acid reference conditions), for the development of acidification remedial measures (silviculture practices, liming etc.) and for improving the estimates of future surface water acidity.**

Examples of research issues of special interest for the acid-base status in discharge areas are:

- catchment based three dimensional quantification and simulation of groundwater flow and stream water generation,
- the effects of soil physics and soil chemistry in discharge areas on groundwater and stream water acidity,
- processes controlling DOC generation in discharge areas,
- the effects of redox processes in discharge areas, e.g. S(II)/(VI), N(III)/(V), Fe(II)/F(III) and Mn(II)/M(IV), on groundwater and stream water acidity,
- assessments of the Al-chemistry in discharge areas, including effects of ionic strength and development of Al-fractionation techniques suitable for dilute and humic surface waters,

- the influence of groundwater quality in recharge areas on the groundwater quality in discharge areas,
- the effects of mixing of groundwater originating from discharge areas of different character, e.g. organic or minerogenic soils, on stream water acidity (generation of permanent or episodic acid events),
- the effects of climatic variation (drought, flood etc.) on riparian processes,
- the effects of vegetation (tree species composition, buffer strips etc.) on riparian processes,
- the effects of microbial activity on important redox processes, e.g. mineralization and oxidation of organically bound sulphur, nitrogen etc.,
- development of three dimensional dynamic models linking hydrology and chemistry,
- catchment based three dimensional quantification and model simulation of acid-base fluxes in groundwater and stream water.

**At a national level, we also recommend intensive monitoring of the soil status in discharge areas, allowing coordinated and improved assessments of forest soil and surface water surveys. Long-term monitoring data on soil and water are of utmost importance for future assessments.**

Secondly, the historical, large-scale environmental changes related to land-use, fire frequency, tree species composition etc. have obviously influenced the acid-base status of many forested catchments in Sweden. Processes such as weathering and carbon accumulation, potentially influencing the BC- and TOC-leakage to surface waters, might have changed tangibly during the past centuries. An improved knowledge about the relations between past large-scale environmental changes and acid-base status in soil and surface water may help us to identify complementary remedial measures within silviculture, be-

sides reduced emissions of acidifying substances, reduced biomass harvesting, or liming for achieving efficient soil and surface water acidity recovery.

**We therefore recommend that a comprehensive research program should be initiated directed towards (i), assessing the effects of historical, large-scale environmental changes on the acid-base status in soil and surface water and (ii) identification and development of remedial silviculture practices. The research program should include historical, paleolimnological, hydrological and biogeochemical studies as well as development of mathematical models, taking into account the quantitatively most important effects of these historical changes.**

Examples on research issues of special interest related to land-use and silviculture practices are:

- in representative catchments, perform detailed historical reconstruction of land-use change (land-use practices in dry and moist areas, drainage and burning techniques etc.), with special emphasize on forestry and agricultural development during the 20<sup>th</sup> century,
- in the above catchments, perform paleolimnological studies, reconstructing vegetation, land-use, fire regimes, surface water pH, color etc. since the last glaciation, with special emphasize on forestry and agricultural development during the 20<sup>th</sup> century,
- based on the above information develop catchment based proton budgets for the natural state without human influence ("baseline") and the most important time periods with different land-use,
- based on the above information develop catchment based model simulations of acid-base fluxes in stream water,
- identification of land-use key factors for the acid-base status in surface waters,
- experimental testing of land-use key factors of relevance for development of remedial forestry practices,
- evaluate ongoing and establish new field experiments concerning silviculture measures affecting soil and surface water acidity.

## Acknowledgement

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## References

- SEPA (2000). Recovery from acidification in the natural environment – present knowledge and future scenarios. Swedish Environmental Protection Agency report 5034, 96 pp.
- Skjelkvåle, B.L., Henriksen, A., Faafeng, B., Fjeld, E., Traaen, T.S., Lien, L., Lydersen, E., Buan, A.K. (1996) Regional lake survey 1995. A water chemical survey of 1500 Norwegian lakes. The national monitoring programme for long-range transported air pollutants. Norwegian State Pollution Control Authority, Report 677/96, 73 pp.

# Implications of anthropogenic acidification on forest soil processes in Sweden



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## Abstract

By anthropogenic acidification the soil forming process, podzolisation, will be perturbed. The organic acids in soil solution will form complexes with aluminium to a less degree and inorganic aluminium will be leached from the illuvial horizon. The soil acidification has not resulted in declined coniferous forest growth, which might be explained by mycorrhizal activity promoting nutrient uptake direct from minerals. Liming and wood ash applications on forest soil might enhance CO<sub>2</sub> evolution, increase DOC concentrations and might also initially decrease pH and increase Al concentrations in soil solution.

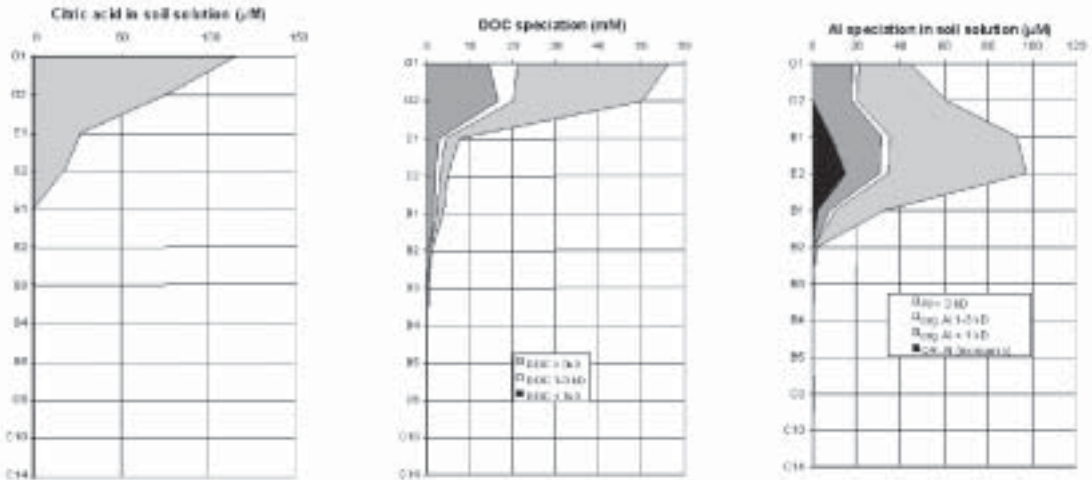
## Soil forming processes

In northern Europe and N. America, where the climate is humid and the soil is of medium

to coarse texture, coniferous forest soils are often podzolic. Weathering in these soils is promoted by organic compounds forming complexes primarily with the trivalent ions Fe and Al released from primary minerals. Thereby the nutrients Ca, Mg and K are released mainly as free ions. It has been shown in laboratory experiments that soil solutions containing organics and solutions of synthetic organic acids enhance the dissolution rate of primary minerals by a factor of 2–4 times compared to water with the same inorganic content of ions (Lundström and Öhman, 1990; van Hees *et al.*, 2002).

Formation of complexes generally had a greater impact on the dissolution rate than pH (van Hees *et al.*, 2002). Citrate (50–250 µM), acetate (50–175 µM), formate (0–200 µM), fumarate (1–5 µM) and oxalate (3–15 µM) were found in soil solution from the mor layer of a coniferous forest in north Sweden (van Hees *et al.*, 2000a) (Fig. 1). In the deeper

**Figur 1.** a) Average concentration of citric acid ( $\mu\text{M}$ ,  $n=6$ ) in soil solution of Nyänget profile.  
 b) Average concentration of DOC (DOC<1000D, DOC 1000-3000D, DOC>3000D) (mM,  $n=6$ ) in soil solution of Nyänget profile.  
 c) Average Al (QR Al (inorg), orgAl<1000D, Al<3000D-(orgAl<1000D)- QRAI ( $\mu\text{M}$ ,  $n=6$ )) in soil solution of Nyänget profile.



horizons these concentrations decreased. Many of these acids have high complex forming ability with Al. It has been shown by size exclusion chromatography and equilibrium calculations that these compounds bind about 30% of the Al in soil solutions of forest soils (van Hees *et al.*, 1996, 2000b), while about 50–60% is bound to high molecular weight compounds and the rest is inorganic Al. This suggests that complex-formation is important during the process of mineral weathering.

From observations on thin-section microphotographs and scanning electron micrographs of soil mineral particles, Jongmans *et al.* (1997) found that fungal hyphae are able to etch weatherable minerals in the upper soil. Mycorrhizal fungi have been shown to produce organic acids (Ahonen-Jonart *et al.*, 2000; Leyval and Berthelin, 1991) and siderophores (Holmström *et al.*, unpubl; Watteau and Berthelin, 1994). Siderophores are much stronger complex-formers than the acids and have recently been found in the mor soil solution

from a coniferous forest (Holmström *et al.*, unpublished). The concentrations of organic acids and siderophores surrounding hyphal tips are likely to be much higher than those in the bulk soil solution. Thus weathering may be greatly enhanced and a significant proportion of the released Al may be bound by these complex-formers. These low molecular weight organics will be easily decomposed in the soil solution (van Hees *et al.*, 2003), and thus Al might be complexed by high molecular weight organic substances to a higher extent.

The main immobilization process in the uppermost B horizon for Al and Fe, being transported as organic complexes, might be microbial decomposition of the organic ligand in solution releasing ionic Al and Fe to precipitate as imogolite type material and ferrihydrite, which could also form following degradation of adsorbed organic Al and Fe complexes (Lundström *et al.*, 2000). Rapid evolution of CO<sub>2</sub> from the soil is evidence for high microbial activity.



## Soil acidification processes

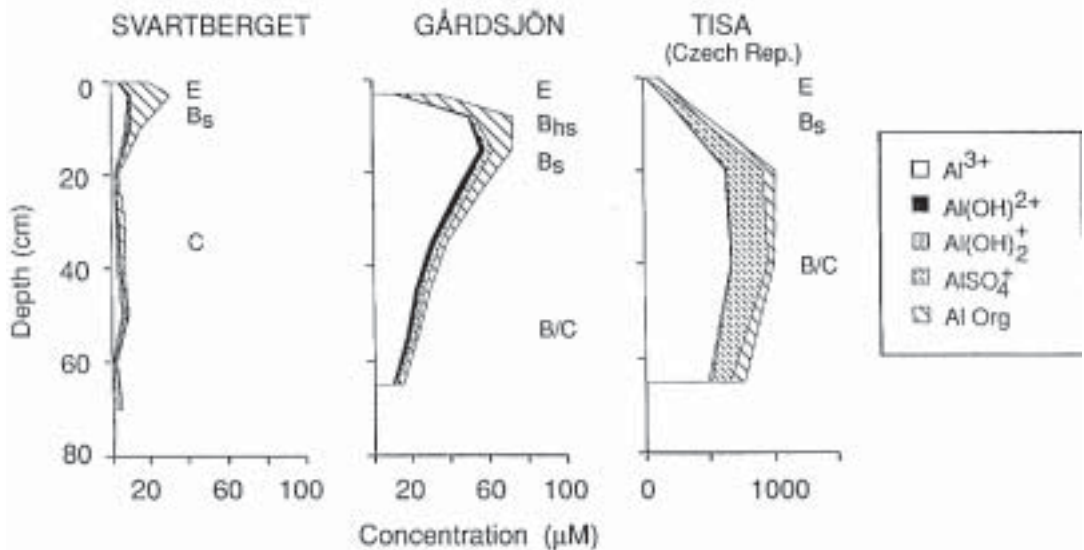
As a result of increasing acidification the proportion of organically complexed Al in soil solution will decrease due to equilibrium conditions: the complex-forming acids become protonated at low pH. In addition, as a result of lower pH inorganic Al will be released from the illuvial horizon where it was formerly bound. Combined these indirect effects of acidification may disrupt the processes of weathering and soil formation.

The sites Svartberget, Gårdsjön, and Tisa are exposed to different acidic load (Lundström *et al.*, 1995). From Svartberget being almost unaffected to Tisa being in the most affected area in Europe. The different degrees of perturbation of the soil forming process are demonstrated by the aluminium speciation in soil solution in the profiles (Fig. 2). At Svartberget there are low concentrations of total aluminium (<40  $\mu\text{M}$ ) mainly present in the upper soil. About 80% of the aluminum is organically bound. These relations show that a normal soil forming process is going on,

where the organic acids promote weathering, aluminium is complexed and immobilized in the illuvial horizon. At Gårdsjön these processes are affected. The total concentration of aluminium is higher, the part being organically bound is lower and obviously inorganic, mainly trivalent aluminium, is leached from the illuvial horizon but seems to be immobilized deeper down. At Tisa the total concentration of aluminium is high (>600  $\mu\text{M}$ ) in the deep soil and almost all is as inorganic aluminium, mainly trivalent and aluminium sulfate complex. This aluminium distribution shows that the soil forming process is perturbed with a great leakage of inorganic aluminium. The pH and sulfate concentrations in these profiles support this conception. The pH in the profile of Svartberget is about one pH unit higher than at Gårdsjön, which in turn is about a half pH unit higher than at Tisa. The sulphate concentrations in the profiles, which relate to the deposition was much higher at Tisa.

At high concentrations of trivalent Al and hydrogen ions, a large proportion of the pool

Figur 2. Aluminium speciation with depth at Svartberget (Umeå), Gårdsjön (Göteborg) and Tisa (Czech Republic).



of exchangeable cations will be comprised of these ions and the part composed of the base cations will be less, resulting in low base saturation.

## Soil acidification and tree growth

In laboratory experiments inorganic Al in soil solution has been shown to interfere with the growth of the roots of young seedlings (Rost-Siebert 1983, 1985). Increased concentrations of inorganic Al, resulting from acidification, have been assumed to affect tree growth particularly if the concentrations of Ca are low. The molar ratio  $(Ca+Mg)/Al_{inorg}$  has been used to estimate critical loads. It has been suggested that where this ratio is less than 1, tree growth will be reduced (Sverdrup *et al.*, 1992). In addition, the lower base saturation resulting from acidification has been suggested to decrease tree growth as a result of nutrient deficiencies leading to a non-sustainable forest. However, there is little field evidence that soil acidification leads to a decline in forest growth.

An extensive investigation was made in the county Värmland on soil chemistry and tree growth (Lundström *et al.*, 1998; Nyberg *et al.* 2001). The deposition of sulphate in the south of the county is 2.5 times higher than in the north. In Värmland pH in soil solution in the upper B-horizon was about 5.5 in the north and about 4.7 in the south of the county. In the deeper horizons the pH's were about 0.8 lower throughout the profiles in the southwest of the Värmland than in the north of Värmland.

In the southwest of Värmland the concentrations of total aluminium and inorganic aluminium were generally higher than in the north of Värmland (Fig. 3). Also the part of total Al being inorganic was higher in these areas, sometimes as high as 50% in the upper B-horizon and on average 30%. In the north,

inorganic Al made up a smaller part. Aluminium concentrations in the north of Värmland were comparable to those found in Svartberget, while the concentrations in the south of Värmland were lower than in Gårdsjön.

The base saturation in the mor layer was high (>60%) and no distribution pattern for Värmland could be recognized. In the illuvial horizon the base saturation was lower, with the lowest values in the southwest of Värmland.

Principal Component Analyses made on soil solution composition and exchangeable cations and additional parameters demonstrated the availability of pH and the concentrations of total aluminium and inorganic aluminium in soil solution as indicative parameters.

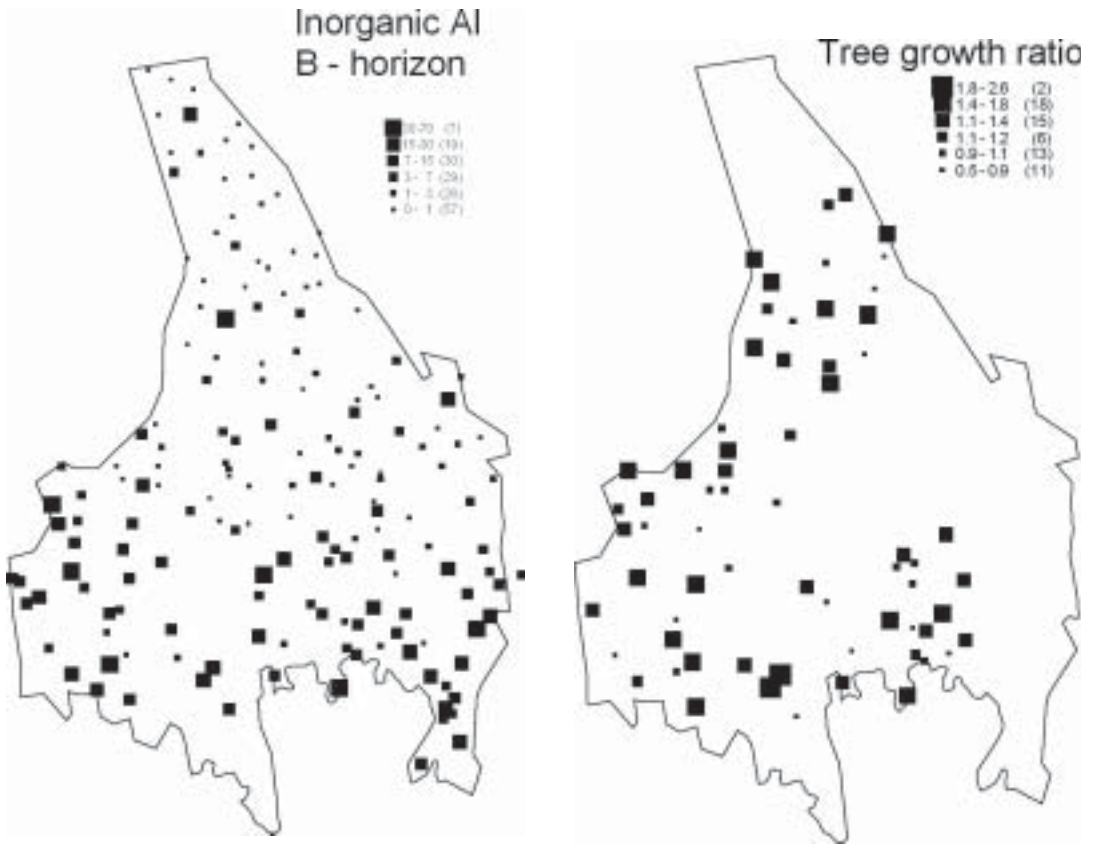
An evaluation on the tree growth including 80 sites, did not suggest any correlation between soil acidification and forest growth (Nyberg *et al.*, 2001). All over Europe forest biomass production is greater than ever before (Kauppi, 1992).

Mycorrhizal activity has important implications for the weathering process. The potential direct access by the trees, via their mycorrhizal fungi, to Ca, Mg and K in soil minerals means that the base saturation of the exchangeable pool may be less important than previously thought for the nutrient supply of the tree. This may explain the failed impact of acidification on forest growth and may have implications for the treatment of forest soils.

## Ash and lime applications

In the south of Sweden two ash/lime treated sites were investigated (Lundström *et al.*, 2003a). At Horröd 3.3 ton/ha of dolomite and 4.3 ton/ha of wood ash and at Hasslöv two doses of dolomite, 3.5 ton/ha and 8.8 ton/ha were applied. The exchangeable pool as well as the base saturation in the mor layer were

Figur 3. Inorganic aluminium concentration in soil solution from the upper illuvial horizons and tree growth ratio (expected growth/ measured growth).



increased after treatment. Also the concentration of base cations in the mor layer solution was enhanced after treatment.

At Horröd 4 years after treatment there were tendencies of lower pH and increased concentration of inorg Al in soil solution (Geibe *et al.*, 2003). This might have been induced by the increased exchangeable pool and the exchange of  $H^+$  for Ca and Mg. At Hasslöv 15 years after treatment on the other hand the pH was higher and the Al concentration in soil solution lower than in the control. At both sites DOC concentrations were increased and at Hasslöv the respiration was up to 37% higher at treated areas, which might be due to higher microbial activity de-

pleting the C storage (Holmström *et al.*, 2003; van Hees *et al.*, 2003). The increased respiration may play a role for the forest as a sink or source for carbon. At Hasslöv after application of the high dose of dolomite the concentration of  $NO_3^-$  was high and leached from the profile, which might eutrophicate surface waters. All these findings are in accordance with other studies on lime and ash treatments as reviewed by Lundström *et al.* (2003b). In addition most studies report declined or unchanged forest growth. Liming and ash application on forest soils have been proposed with the aim to remediate soil processes, promote forest growth, protect surface waters, and for wood ash for recycling. However, at

present acid surface waters in Sweden are limed directly, and this might be preferable. To recognize processes involved in the interaction between soil, ground and surface water further studies are needed.

## Conclusions

The soil forming process, podzolisation, is perturbed by acidification resulting in low pH and leaching of inorganic aluminium to soil solution and surface waters. These effects of acidification, in addition to low base saturation, do not imply declined forest growth probably because the weathering process is induced by mycorrhizal activity delivering mineral nutrients. Treatments with lime and wood ash of forest soils may induce negative effects as increased CO<sub>2</sub> evolution, higher DOC concentrations, initially lower pH and higher Al concentrations in soil solution. The interaction between soil, ground and surface water is not well recognized.

## References

- Ahonen-Jonnarth, van Hees, P.A.W., Lundström, U.S. and Finlay, R.D. 2000. Production of organic acids by mycorrhizal and non-mycorrhizal *Pinus sylvestris* L. Seedlings exposed to elevated concentrations of aluminium and heavy metals. *New Phytologist* 146, 557–567.
- Geibe, C., Holmström, S., van Hees P.A.W., and Lundström U.S. 2003. Impact of lime and ash applications on soil solution chemistry of acidified podzolic soils. *Water, Air and Soil Pollution, Focus*
- van Hees, P.A.W., Andersson, A-M. & Lundström U.S. 1996. Separation of organic aluminium complexes in soil solution by size exclusion chromatography in combination with HPLC determination of low molecular weight organic acids. *Chemosphere* 1951–1966.
- van Hees, P.A.W., Lundström, U.S. and Giesler, R. 2000a. Low molecular weight acids and their Al-complexes in soil solution – Composition, distribution and seasonal variation in three podzolized soils. *Geoderma* 94, 173–200.
- van Hees, P.A.W. and Lundström, U. 2000b. Equilibrium models of aluminium and iron complexation with different organic acids in soil solution. *Geoderma* 94, 201–221.
- van Hees, P.A.W., Lundström, U.S. and Mörth, C-M. 2002. Dissolution of microcline and labradorite in a forest O horizon extract: the effect of naturally occurring organic acids. *Chemical Geology* 189, 199–211.
- van Hees, P.A.W., Jones, D.L., Lundström U.S. and Godbold D.L. 2003. Biodegradation of low molecular weight organic acids in limed forest soils. Accepted *Water, Air and Soil Pollution, Focus*.
- Holmström, S.J.M., Lundström, U.S., Finlay, R.D. and van Hees, P.A.W. Siderophores in soil solution and their production by an ectomycorrhizal fungus. Submitted.
- Holmström, S., Riise, G., Tau Strand L., Geibe, C., van Hees P.A.W. and Lundström U.S. 2003. Effects of lime and ash treatments on DOC fractions and low molecular weight organic acids in soil solutions of acidified podzolic soils. *Water, Air and Soil Pollution, Focus*.
- 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., and Olsson, M. 1997. Rock-eating fungi. *Nature* 682–683.
- Kauppi, P.E., Mielikainen, K. and Kuusela, K.: 1992, 'Biomass and carbon budget of European forests, 1971 to 1990, *Science* 256, 70–74.
- Leyval, C. and Berthelin, J., 1991. Weathering of mica by roots and microorganisms of pine. *Soil Sci. Soc. Am. J.*, 55: 1009–1016.

- Lundström, U. & Öhman, L-O. 1990. Dissolution of feldspars in the presence of natural, organic solutes. *J. Soil Sci.* 41, 359–369.
- Lundström, U.S & Giesler, R. 1995. Use of aluminium species composition in soil solution as an indicator of acidification. *Ecological Bulletins* 44, 114–122.
- Lundström, U.S., Nyberg, L., Danielsson, R., and van Hees, P.A.W. 1998. Forest soil acidification: Monitoring on the regional scale exemplified by Värmland, Sweden. *Ambio* 27, 551–556.
- Lundström, U.S., van Breemen, N., Bain, D.C., van Hees, P.A.W., Giesler, R., Gustafsson, J. P., Ilvesniemi, H., Karlton, E., Melkerud, P.-A., Olsson, M., Riise, G., Wahlberg, O., Bergelin, A., Bishop, K., Finlay, R., Jongmans, A.G., Magnusson, T., Mannerkoski, H., Nordgren, A., Nyberg, L., Starr M., and Tau Strand, L. 2000. Advances in understanding the podzolization process resulting from a multidisciplinary study of three coniferous forest soils in the Nordic Countries. *Geoderma*. 94, 335–353.
- Lundström, U.S., Bain, D.C., Taylor, A.F.S., van Hees, P.A.W., Geibe, Ch.E., Holmström, S.J.M., Melkerud, P.-A., Finlay, R., Jones, D.L., Nyberg, L., Gustafsson, J.P., Riise, G. and Tau Strand L 2003a. Effects of acidification and its mitigation with lime and wood ash on forest soil processes in southern Sweden. A joint multidisciplinary study. Accepted *Water, Air and Soil Pollution, Focus*.
- Lundström, U.S., Bain, D.C., Taylor A.F.S. and van Hees P.A.W. 2003b. Effects of acidification and its mitigation with lime and wood ash on forest soil processes. A review. *Water, Air and Soil Pollution, Focus*
- Nyberg, L., Lundström, U., Söderberg, U., Danielsson, R. and van Hees, P. 2001. Is there no impact of soil acidification on coniferous needle composition and tree growth? *Water, Air and Soil Pollution, Focus*. 1, 242–263
- Rost-Siebert, K.: 1983, "Aluminium-Toxizität und – Toleranz an Keimpflanzen von Fichte (*Picea abies* Karst.) und Buche (*Fagus sylvatica* L.)", *Allgemeine Forstzeitung* **38**, 686–689.
- Rost-Siebert, K.: 1985, "Untersuchungen zur H- und Al-ionen-toxizität an Keimpflanzen von Fichte (*Picea abies* L.) und Buche (*Fagus sylvatica* L.) in Lösungskultur", Berichte der Forschungszentrums Waldökosysteme/Waldsterben. Univ. Göttingen, Band 12.
- Sverdrup, H., Warfvinge, H., Frogner, T., Håøya, A.O. and Johansson, M.: 1992, "Critical loads for forest soils in the Nordic countries", *Ambio*, **21:5**, 348–355.
- Watteau, F. and Berthelin, J., 1994. Microbial dissolution of iron and aluminium from soil minerals: efficiency and specificity of hydroxamate siderophores compared to aliphatic acids. *Eur. J Soil Biol.*, 30: 1–9.



# Flow paths of water in Swedish forests



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Stream runoff can quite well be calculated mathematically without a detailed knowledge of flow processes in the catchment. The catchment can be regarded as a black box with precipitation as input and runoff (and evapotranspiration) as output. By using data from a period with observed precipitation and runoff, a good fitting between observed and calculated runoff dynamics and volume can be obtained by tuning parameter values in a set of more or less complicated mathematical transformations. Such a model may give good results as long as the catchment remains unchanged with regard to the conditions for the water flow. But when we want to estimate the catchment response under changed conditions we need more knowledge of the hydrological processes in the catchment (or a new calibration period). Furthermore, when we want to understand the chemical changes taking place in the water we have to open the black box and look more closely at the water fluxes and storages:

- Which flow paths does the water follow on its way through the catchment?

- To what extent has the discharging water been flowing through mineral soil and organic soil respectively?
- How long time is the water remaining in various biogeochemical environments?
- Are there important effects of by-pass mechanisms such as macropore flow or overland flow?

These questions will be briefly commented in my presentation.

## The medium in which is the water flows

Most of the Swedish forest area is dominated by sandy-silty till soils deposited on fractured granite or gneiss bedrock. The soil cover is comparatively thin, in many areas less than a few meters thick and with rock outcrops frequently occurring in elevated parts of the landscape. Mires, i.e., wetlands with organic soils, are common in low-lying and flat areas.

As is evident from the fact that much of the water supply in the countryside is based on

wells drilled into the bedrock, the fracture system in the bedrock may be quite conductive for water. The role of water flowing through these fractures in the runoff process is little known. It is probably of minor importance for the runoff dynamics, but it may affect the chemical composition of stream-water.

## What we know about the water flow

### *Shallow groundwater*

The groundwater table is typically shallow, with a depth of a few meters in elevated areas and it gradually approaches the ground surface when going down the hillslopes. The groundwater zone is continuous laterally and vertically, with streams and mires representing local low points for the groundwater surface. The depth to the groundwater table is determined by ability of the ground to conduct water (the hydraulic conductivity of the soil and bedrock and the slope of the ground surface) and the rate of groundwater recharge. With considerable groundwater re-

charge, a bedrock of fairly low conductivity and a thin soil cover with low conductivity in its deeper parts, the groundwater zone has to reach close to the ground surface in order to transmit all groundwater recharged uphill.

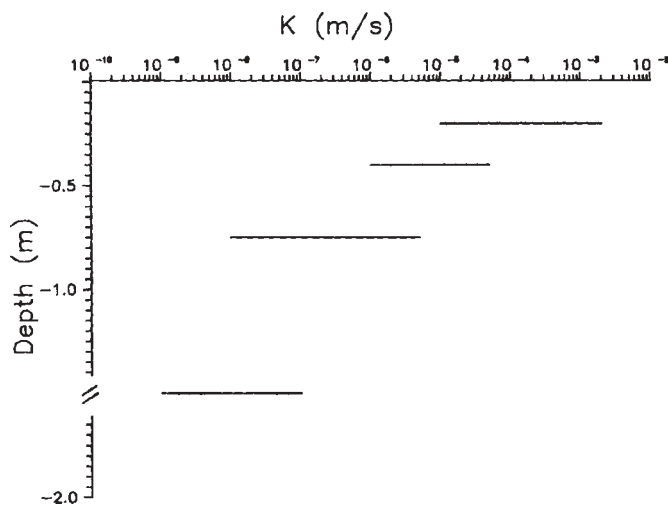
### *Most rainwater and snowmelt infiltrates into the soil*

The infiltration capacity of the till soil is normally larger than the rainfall or snowmelt intensity. Overland flow is therefore of little importance on unsaturated areas (recharge areas for groundwater), but it may be an important flow process on saturated areas (discharge areas). The extent of the discharge areas is dynamic, with the extent increasing with increasing groundwater level. Overland flow can of course also occur on rock outcrops, but this water probably infiltrates in fractures or in the soil downhill.

### *The hydraulic conductivity of till soil decreases with depth*

Several investigations have shown that the hydraulic conductivity of Nordic till soils decreases rapidly with depth (Figure 1). Soil processes such as biological activity, chemi-

Figure 1. Observed hydraulic conductivity in Nordic till soils. From Lundin (1990).





cal weathering and soil freezing and thawing all contribute to develop a structure giving a high hydraulic conductivity in the upper meter of the soil. Soil compaction in the deeper till contributes to the low conductivity at depth.

*Runoff events in streams are dominated by pre-event water*

Although it is evident that storm runoff in a stream is initiated by rainfall or snowmelt just prior to or during the event, a large number of isotope investigations have shown that the discharging water is dominated by pre-event water, i.e. water that was stored in the catchment before the event. A simplified interpretation of the isotopic hydrograph separation shown in Figure 2 is that the "pre-event water" is groundwater discharged as a response to groundwater recharge by rainfall infiltration, whereas the "event water" is rainwater that has reached the stream directly as saturated overland flow on saturated discharge areas.

*The mean transit time for water in headwater catchments is on the order of a few months to years*

Isotopic hydrograph separation separates the discharging water into two age classes, event and pre-event water. By following the isotopic input and output to a catchment over a longer time period, a mean transit time for the discharging water can be estimated. In this way mean transit times ranging from a few months to a few years have been estimated for a few Swedish catchments. It should be noted that those numbers are estimated long-term mean transit times. The mean transit time of the water that is discharging at a certain moment is highly variable over time (Figure 3). Each such mean transit time further represents a mean value of a transit time distribution with transit times ranging from minutes (water falling directly on the stream) to several years (water with the deepest groundwater flow paths towards the stream).

*The topography gives a general picture of the wetness pattern in the catchment*

Soil wetness and depth to the water table show large variations within a catchment, giving different pre-conditions for the water flow and storage. The topography gives valuable information on the wetness distribution. For a location with a large local catchment area (large groundwater flow to be transmitted downhill) and small slope of the ground surface (little ability for the ground to transmit the groundwater downhill) we can expect a shallow water table and wet soil.

## What we believe about the water flow

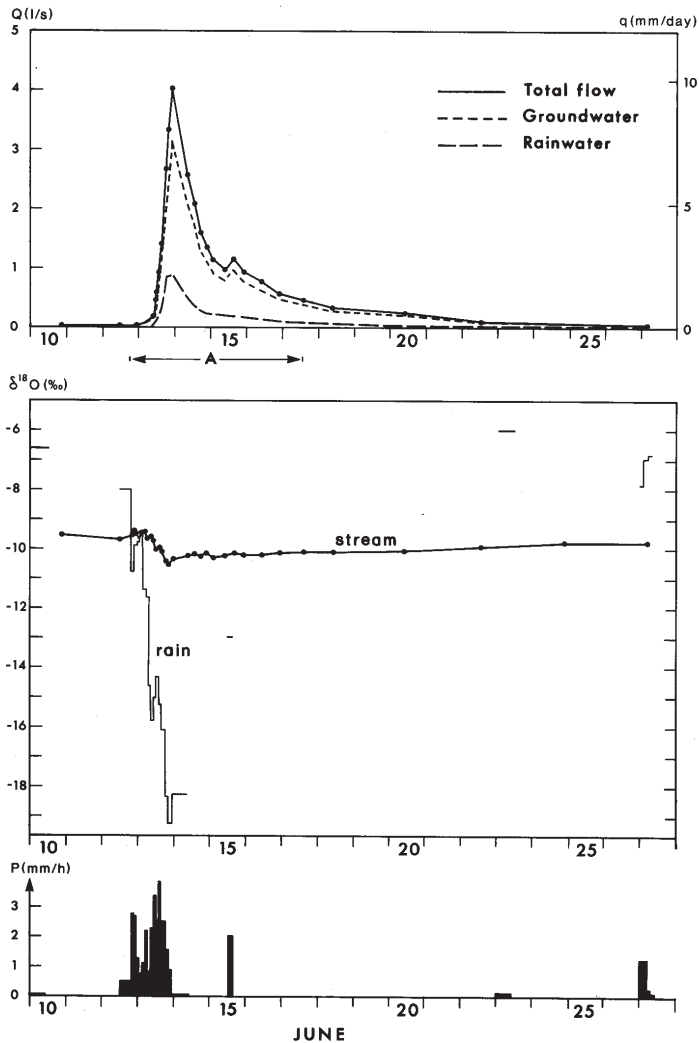
*Lateral unsaturated flow is of little importance*

The lateral subsurface flow feeding the discharge areas and the streams takes place in the groundwater zone. There are no indications of an important lateral flow in the unsaturated zone.

*Preferential flow in macropores is probably of little importance in the unsaturated zone below the root zone*

High rates of water input to the ground may under certain conditions give rapid flow and transport in large interconnected pore systems in the surface layer. A pre-condition for such a flow is that the rate of water input to the pores is large as compared with the hydraulic conductivity of the soil matrix. Otherwise the larger pores will be emptied by suction from the surrounding pores. With the low rainfall intensities and the comparatively coarse till soil in Swedish forest areas, preferential flow in unsaturated soil is probably of little importance except in the topmost layer of the soil. In the groundwater zone, on the other hand, large pores or coarse soil layers will, when they exist, greatly contribute to the flow since they are always water filled.

**Figure 2. Isotopic hydrograph separation of a rainfall generated runoff event. Catchment F2 at Lake Gård-sjön, Sweden, 1980. From Rodhe (1987).**



*Groundwater discharge to streams increases drastically when the shallow, highly conductive layers become saturated*

The main mechanism of stream flow response to infiltration in till soil is that the water table rises so that superficial layers with high hydraulic conductivity become saturated (Figure 4). In this way the transmissivity of the ground increases drastically and the groundwater flow feeding the stream can be

multiplied, although the slope of the groundwater table may remain essentially constant. One effect of this event related saturation of the shallow layers is that the lateral flow at a certain shallow depth may be intermittent, with lateral flow taking place only during periods of saturation. Such intermittent lateral displacement in shallow layers has been observed in tracer experiments.

Figure 3. Mean transit time of the discharging water as estimated from catchment runoff using information obtained from a step shift in the  $^{18}\text{O}$  input. Catchment G2 at Lake Gårdsjön, Sweden, October 1990 to April 1994. From Rodhe et al. (1996).

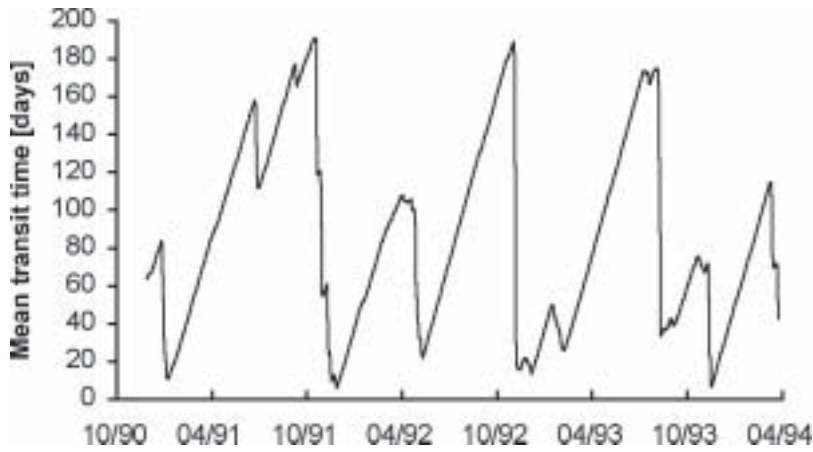
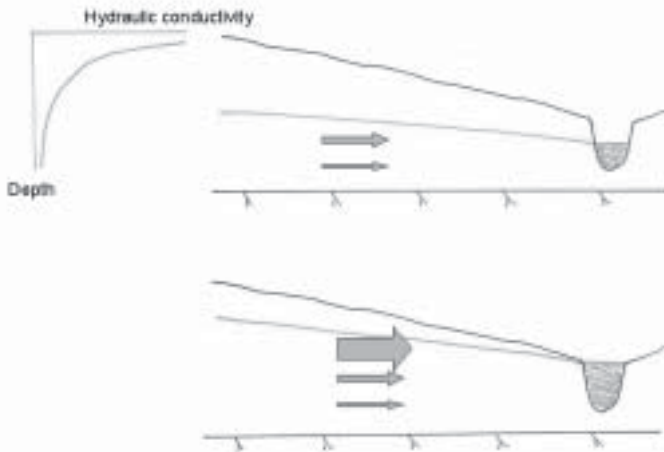


Figure 4. Large increase of groundwater flow in the soil profile due to saturation of superficial highly conductive layers.



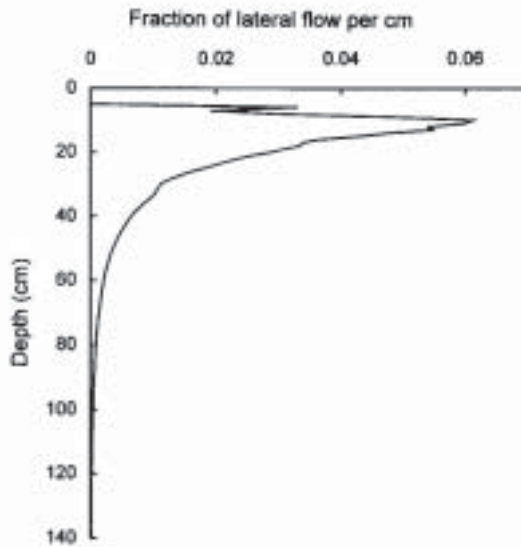
*On a long-term basis, the largest volumes of lateral flow go through superficial layers*

Although the superficial layers are saturated only during a small fraction of the total time, the flow in these layers dominates the total lateral flow in the soil profile. The high hydraulic conductivity of these layers more than compensates for the short time of saturation with lateral flow. (Figure 5).

*Soil frost has little influence on the magnitude of the spring flood*

Isotope studies have shown that also spring floods are dominated by pre event water, and attempts to introduce the effects of soil frost in runoff modelling did not improve the modelling of the spring flood. These findings might be surprising, since we could expect the infiltration capacity of the soil to be

**Figure 5.** Vertical distribution of the annual lateral groundwater flow calculated from an observed hydraulic conductivity profile and the frequency distribution of groundwater levels. Catchment G1 at Lake Gärd-sjön, Sweden. From Seibert (1993).

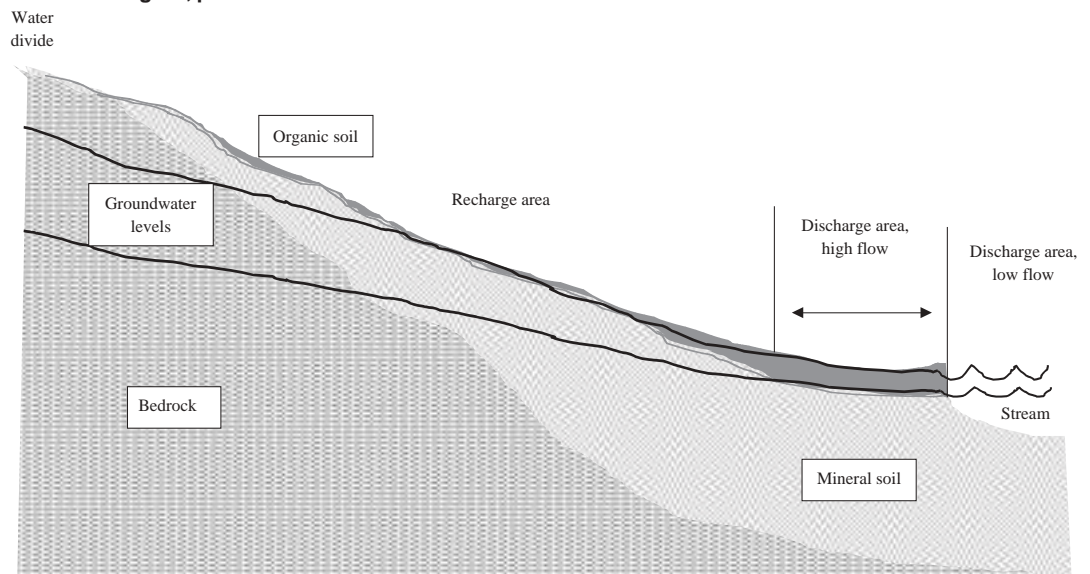


strongly reduced by soil frost. Factors tending to give infiltration excess and overland flow during snowmelt are high soil moisture content when the freezing starts, thick frozen layer, continuous soil frost over the area and large snow pack with rapid melting. One reason for the lack of a significant effect of soil frost on overland flow might be that some of these factors are counteracting each other. A large snow pack, for instance, reduces surface cooling and frost growth. It is also probable that the soil frost is laterally discontinuous in many forest soils.

### We must have a simplified conceptual picture of the flow paths

In order to understand the chemical processes taking place in the water and to identify processes that need further research we must have a picture of the flow path of water through the catchment. Obviously for each individual catchment, local geological, topo-

**Figure 6.** A hypothetical hillslope with groundwater discharge through organic soil. Modified after Stefan Löfgren, personal communication 2002.



graphical, climatological factors and effects of land use and man's activities in the catchment, such as forest draining, have to be taken into consideration. The above discussed knowledge, however, allows drawing a generalized picture, see for instance Figure 6. Such a picture can help to understand the relations between hydrological and chemical processes and should guide further model development.

## References

- Lundin, L., 1990. Saturated hydraulic conductivity of Nordic till soils. Hydrogeological properties of till soils, *NHP Report 25*, 51–55.
- Rodhe, A. 1987. The origin of streamwater traced by oxygen-18. *Uppsala Univ., Dept Phys. Geogr., Div. Hydrol., Report Series A 41*, 290 pp, Appendix 73 pp. (Doctoral thesis)
- Rodhe, A., Nyberg, L. and K. Bishop, 1996. Transit times for water in a small till catchment from a step shift in the oxygen-18 content of the water input. *Water Resources Research*, 32(12):3497–3511.
- Seibert, J., 1993. Water storage and flux in a micr catchment at Gårdsjön, Sweden. Thesis paper (Examensarbete 20 p), Dept of Earth Sciences, Hydrology, Uppsala University.



# Acid-base status and changes in Swedish forest soils



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## Introduction

It is now more than fifteen years since Hallbäck & Tamm (1986) and Falkengren-Grerup *et al.* (1987) showed an increase in the acidity and a decrease in pH in southern Sweden. They repeated sampling of previous studies and could by comparing the acid-base status of the older soil samples with the newly sampled detect a significant decline in pH of Swedish forest soils over the middle part of last century. In other studies (Eriksson *et al.*, 1992; Karlton, 1994) the geographical pattern of acid-base status over Sweden was revealed. There was a strong correlation between deposition of acidifying substances and the acidity of the soil profiles. This confirmed that the soil acidification showed the same geographical distribution as the lake acidification with south-west Sweden as the most acidified area. Just around 1990 the deposition of acidifying substances started to decline quite rapidly. This was a combination

of air-pollution protocols coming into effect and the collapse of the eastern bloc economy. Surface waters have responded positively to this decrease in deposition with increasing pH and ANC (Stoddard *et al.*, 1999; Skjelkvale *et al.*, 2001).

Another factor that may have affected the acid-base status of the soil are the growing forests. We have had a continuous increase in standing biomass in the Swedish forests over the last 20 years. This increase has resulted in an input of acidity to the soils, a process that might have counteracted the effect of the decreased deposition. In this paper we use data from the Swedish National Survey of Forest Soils and Vegetation (NSFSV) to evaluate the present acid-base status of forest soils to try to answer the following questions. Which role do anthropogenic and biological acidification play for the present acid-base status of the soil profile? What is the present acid-base status of Swedish forest soils and how large areas may be considered as severe-

ly acidified? Do the current tendencies in soil acid-base status correspond with the positive development in surface waters?

## Materials and methods

### *Data material*

The recent status of the forest soils were evaluated using data from the second inventory sampled between 1993 and 1998. The dataset contained data for the O horizon from 7535 plots, for the B horizon from 2178 plots and for the C horizon from 1738 plots.

The possible changes in soil status were evaluated using data from the first inventory 1983 to 1987 and the second inventory 1993 and 1998. All paired plots where the same humus form (O horizon) or soil type (B horizon) has been recorded in both inventories. For pH there were 3007 paired plots and for base cations and acidity there were 525 plots that fulfilled the selection criteria.

The following variables were used; pH(H<sub>2</sub>O), total acidity (TA) determined in 1M ammonium acetate extract, exchangeable acidity (EA) determined in 1M KCl and exchangeable Ca and Mg determined in 1M ammonium acetate extract. Base saturation was calculated using the sum of exchangeable base cations plus the total acidity as the cation exchange capacity.

### *Statistics*

When data is presented as a mean it is the area-weighted mean where each plot is weighted by a factor which size is determined by the forest area that the plot represent, i.e. the forest area of a region divided by the number of plots in that region. They area-weighted means are calculated as

$$\bar{V}_i = \frac{\sum_i AF_i \cdot V_i}{\sum_i AF_i}$$

where V is the analyzed variable and AF the area factor. The area-weighted means are used because the plot density is different in different regions. Uncertainty is given as 95% confidence intervals. The changes between inventories on paired plots were analysed by ANOVA using time as the main factor.

### *Systematic error compensation*

After re-analyzing samples from the first inventory to check for comparability systematic differences between the inventories has been detected for some variables. The differences were compensated for before doing the ANOVA analysis. The compensation is described in Bertills (2003).

## Results & discussion

### *Biological contra anthropogenic acidification*

The effect of a growing stand on the acidity of the soil is more likely to be most pronounced in the part of the soil where the uptake of nutrients is highest. In figure 1 we have plotted the pH for O, B and C horizon versus the stand age in 10 year classes. The pH in the O horizon shows a strong negative trend with stand age. The negative trend for the B horizon is weaker but still significant while there is no trend for the C horizon. Thus, the stand development affect primarily the acidity of the O horizon while the mineral soil is less affected. When the same variable is plotted against latitude, as in figure 2, there is no relationship for the O horizon. In the mineral soil samples, however, there is a positive correlation between latitude and pH. This positive correlation is most pronounced in the C horizon. This observation is consistent with earlier studies which showed that the regional differences in acid-base status, allegedly caused by differences in deposition, are more pronounced at deeper levels of the soil profile where the effect of biological acidification is small (Karlton, 1995).



Figure 1. pH(H<sub>2</sub>O) in the O, B and C horizons as a function of stand age.

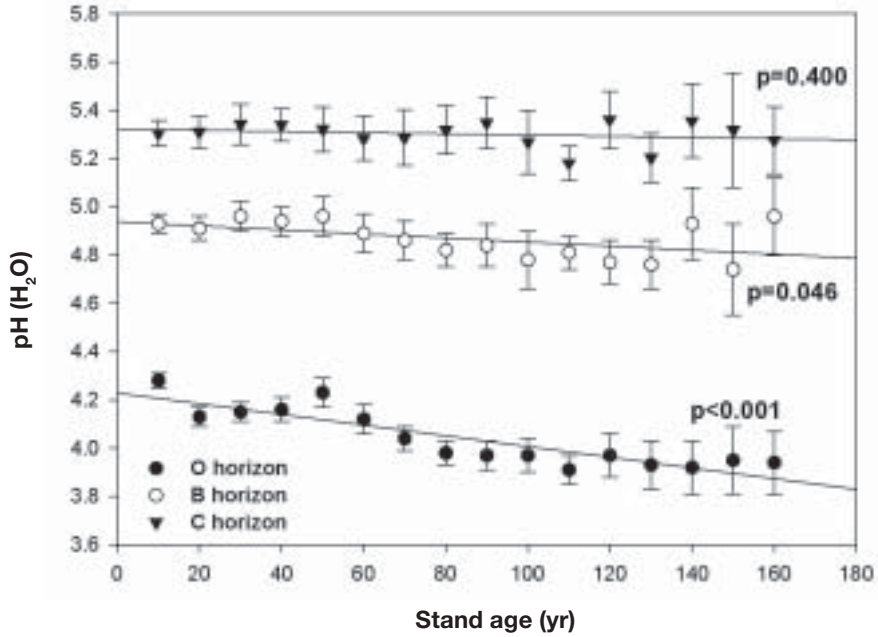
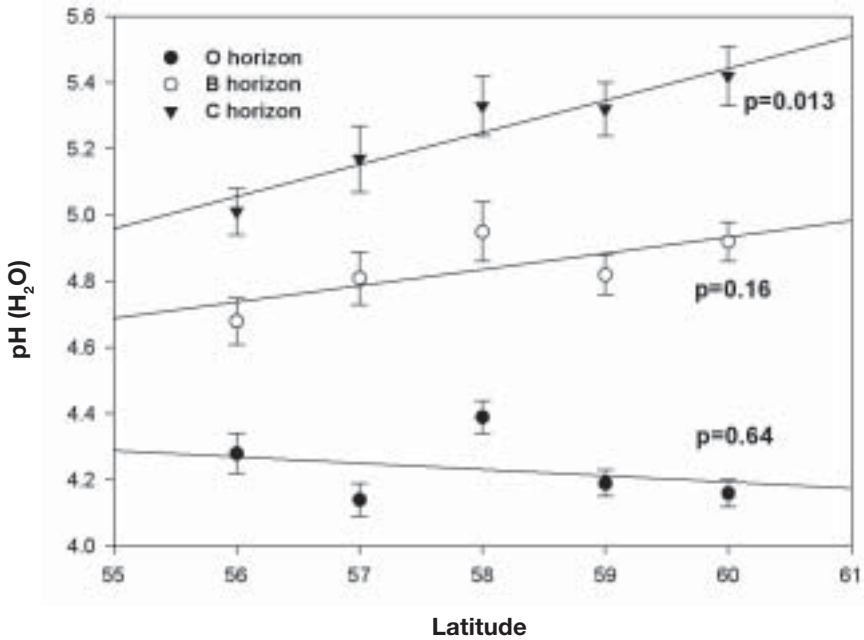


Figure 2. pH(H<sub>2</sub>O) in the O, B and C horizons as a function of latitude.



### Extent of acidification of Swedish forest soils

To determine how large areas that are severely affected by acidification is of course difficult. Since there are no obvious thresholds for soil acidification the determined area will be very much dependent on the criteria that is formulated for what is considered to be an acidified soil. In this presentation we used a classification published by the Swedish Board of Forestry (Gustafsson *et al.*, 2001) although we slightly modified it. In it's simplest version

the classification of acidified soils in the report from the Forestry Board is based on the pH of the B horizon (<4.5) or the pH of the C horizon (<4.75). We used a modified version where we used the above criteria but required both pH levels to be below the given values to consider the profile severely acidified. These requirements were applied to the NFSV database and the results are presented in table 1. Just above 6% or 1.4 million ha of Swedish forest soils fulfill the acidification criteria and of that area as much as 60% is located in Götaland, the southernmost geographical region. In Norrland, both the southern and northern part, the relative proportion of acid soils is much smaller and more likely to be the lower tail of the natural, normal variation in acidity among soil profiles.

**Table 1. Area of Swedish forests with a pH(H<sub>2</sub>O) <4.5 in the B horizon and a pH(H<sub>2</sub>O)<4.75 in the C horizon.**

Region	Area		
	ha	% of region	% of country
northern Norrland	123 000	2.0	0.54
southern Norrland	193 000	3.2	0.85
Svealand	259 000	4.6	1.10
Götaland	838 000	16.4	3.70

### Changes in acidification status between 1983–1987 and 1993–1998

The changes between the first and second inventories of NFSV were studied using ANOVA. The results are presented in Table 2.

**Table 2. Results from ANOVA analysis on the change in different variable describing the acidity between the first (1983–1987) and second (1993–1998) inventory of the NFSVS. Signs in brackets are results where the change is relatively large but still not significant**

Variable	O horizon	Average 1983–87	Average 1993–98	B horizon	Average 1983–87	Average 1993–98
PH	(-)	4.10	4.06	+ ***	4.73	4.85
Base saturation <sup>1</sup> (%)	no change	19.2	19.4	no change	6.41	6.31
Al <sup>3+</sup> (mmol/kg TS)	(+)	8.31	10.3	+ ***	5.81	8.12
Total aciditet (mmol <sub>c</sub> /kg TS)	+ ***	566	673	no change	77.3	75.8
Ca <sup>2+</sup> (mmol/kg TS)	+ ***	40.4	50.9	(+)	1.18	1.65
Mg <sup>2+</sup> (mmol/kg TS)	+ ***	11.0	13.2	- *	0.61	0.47

<sup>1</sup>) Base saturation using CEC<sub>pH7</sub>

The results in the O horizon and in the B horizon are quite different. In the O horizon the pH show a tendency to decrease while the total acidity is increasing. This may be interpreted as an increasing biological acidification. However, exchangeable  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are also increasing in the O horizon, which make this explanation more unlikely. The changes may also be an artifact caused by a slight change in the way the O horizon was sampled between inventories. We know that the C concentration of the O horizon has increased between the inventories, which indicates that a more pure organic part, i.e. less inclusion of mineral soil in the sample, of the O horizon has been sampled in the second inventory. Since the total capacity of the sample to hold acidity and base cations, the CEC, is much higher in organic matter than in mineral soil it can explain why both total acidity and exchangeable cations like  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  can increase. In the B horizon the pH is increasing significantly, in average about one tenth of a pH unit. Despite an increasing pH the exchangeable  $\text{Al}^{3+}$  is also increasing in the B horizon which is difficult to explain. Exchangeable  $\text{Ca}^{2+}$  show a tendency to increase while  $\text{Mg}^{2+}$  is decreasing so there is no general trend among the base cations. Thus, the discovered tendencies are neither easily interpreted nor mutually supportive. Some observations points at an increased acidification while others indicate improvements. It should be noted that the base saturation remains constant in both the O and B horizon which indicates that the changes in the acid-base status of the soils, in any direction, are rather small.

## Conclusions

Geographical differences in the acid-base status of Swedish forest soils are still large with most of the acidified soils found in the south of Sweden.

The geographical differences in acid-base status increase with depth and are most pronounced in the C horizon.

Even if some variables show statistically significant changes between the first and second NFSVS inventory there is no general, uniform trend towards increased or decreased acidification.

## References

- Bertills, U. (in press). Fördjupad utvärdering för Miljömålet Bara naturlig försurning. *Rapport*.
- Eriksson, E., Karlton, E. & Lundmark, J.E. 1992. Acidification of forest soils in Sweden. *Ambio* 21, 150–154.
- Falkengren-Grerup, U., Linnermark, N. & Tyler, G. 1987. Changes in acidity and cation pools of south Swedish soils between 1949 and 1985. *Chemosphere* 16, 2239–2248.
- Gustafsson, J.P., Karlton, E., Lundström, U. & Westling, O. 2001. *Urvalskriterier för bedömning av markförsurning*. Rapport. 11D, Skogsstyrelsen, Jönköping, 26pp.
- Hallbäcken, L. & Tamm, C.O. 1986. Changes in soil acidity from 1927 to 1982–84 in a forest area of south-west Sweden. *Scand.J.For.Res.* 1, 219–232.
- Karlton, E. 1994. Principal geographic variation in the acidification of Swedish forest soils. *Water Air Soil Pollut.* 76, 353–362.
- Karlton, E. 1995. *Acidification of forest soils on glacial till in Sweden*. Report 4427, Swedish Environmental Protection Agency, Solna, Sweden, 76pp.
- Skjelkvale, B.L., Mannio, J., Wilander, A. & Andersen, T. 2001. Recovery from acidification of lakes in Finland, Norway and Sweden 1990–1999. *Hydrology and Earth System Sciences* 5, 327–337.
- Stoddard, J.L., Jeffries, D.S., Lukewille, A., Clair, T.A., Dillon, P.J., Driscoll, C.T., Forsius, M., Johannessen, M., Kahl, J.S., Kellogg, J.H., Kemp, A., Mannio, J., Monteith, D.T.,

Murdoch, P.S., Patrick, S., Rebsdorf, A., Skjelkvale, B.L., Stainton, M.P., Traaen, T., van Dam, H., Webster, K.E., Wieting, J. & Wilander, A. 1999. Regional trends in

aquatic recovery from acidification in North America and Europe. *Nature* 401, 575–578.

# Modelling acidification and recovery of soils and surface waters



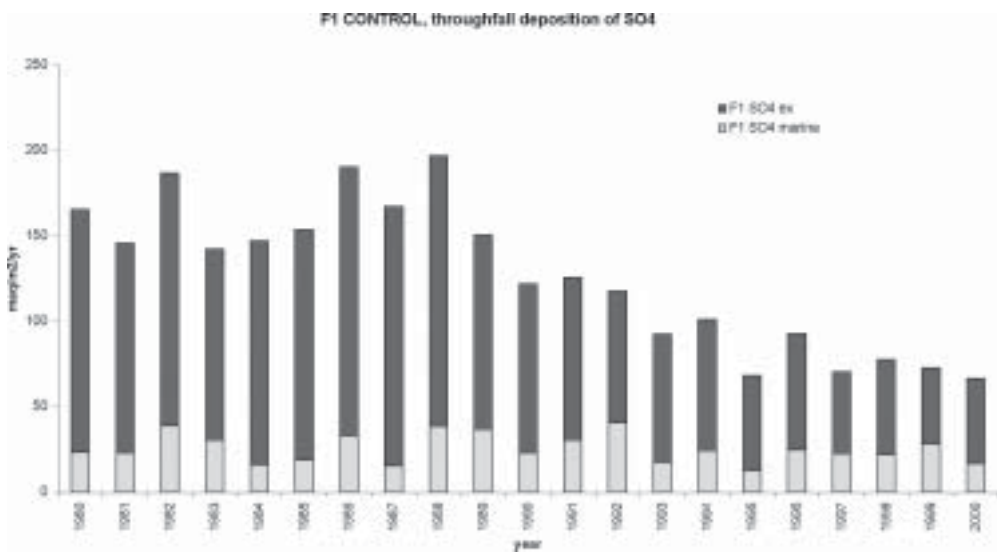
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## Introduction

Deposition of acidifying compounds has been decreasing in Sweden approximately since 1990. In particular the sulphur (S) deposition

is today only a fraction of the deposition in the late 1980ies. On the Swedish west-coast the decrease since 1990 was more than 50% (Figure 1).

Figure 1. Sulphur deposition measured in throughfall, Gårdsjön, 1980–2000.



There has been documented widespread signs of increasing lake water alkalinity (Wilander, 1997). The general pattern of lake water chemistry trends is declining sulphate ( $\text{SO}_4^{2-}$ ) accompanied partly by decreasing concentrations of base cations, partly by an increase of alkalinity. While these changes are readily observable, the development of acidified soils is much less well known. Changes in soils are typically slow compared to changes in surface waters and detection of trends in soils is further complicated by factors such as spatial heterogeneity or year-to-year variability of temperature and precipitation (Karl-tun et al, this volume).

However, long-term acidification of surface waters is to a large extent a consequence of soil acidification in catchments (Reuss and Johnson, 1986). In this paper we have used the acidification model MAGIC (Cosby et al, 1985, 2001) and data from several regional monitoring programmes in Sweden to estimate past, present and future development of soils and lake waters acidification. The main data which has been used were lake water chemistry at 143 intensively monitored lakes (SLU), data from soil monitoring (Ståndorts-kartering) at 23 500 plots (SLU) and MATCH model calculations of deposition on 20x20 km scale (SMHI/IVL).

## MAGIC calibration

The MAGIC model is a widely used medium complexity dynamic model. MAGIC consists of two major sections: an equilibrium section and a mass balance section, which are linked together.

The equilibrium section, in which the concentrations of major ions are simulated, are governed by:

- sulphate adsorption (Langmuir type of isotherm),
- cation exchange (Gains- Thomas expressions for monovalent and divalent cations),

- dissolution and precipitation of inorganic aluminium (equilibrium with aluminium hydroxide),
- dissolution of  $\text{CO}_2$  followed by dissociation of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ,
- organic anion dissociation (monoprotic, diprotic and triprotic organic anions).

The mass balance section, in which the flux of major ions to and from the soil are simulated, is assumed to be controlled by:

- atmospheric inputs,
- chemical weathering,
- net uptake and loss in biomass,
- runoff loss (sedimentation in the lake).

Data treatment, calibration procedure and results are described in Moldan et al. (submitted). The work has been done with the Swedish research programme ASTA (Abatement Strategies for Air Pollution).

In 133 cases the model successfully calibrated to soil and lake water chemistry measured in 1997 provided measured and/or estimated deposition and lakes and catchments characteristics. Also modelled and observed (Skjelkvåle et al., 2001) trends in lake water chemistry were compared and both magnitude and direction of lake water chemistry were in a reasonably good agreement (Moldan et al., submitted).

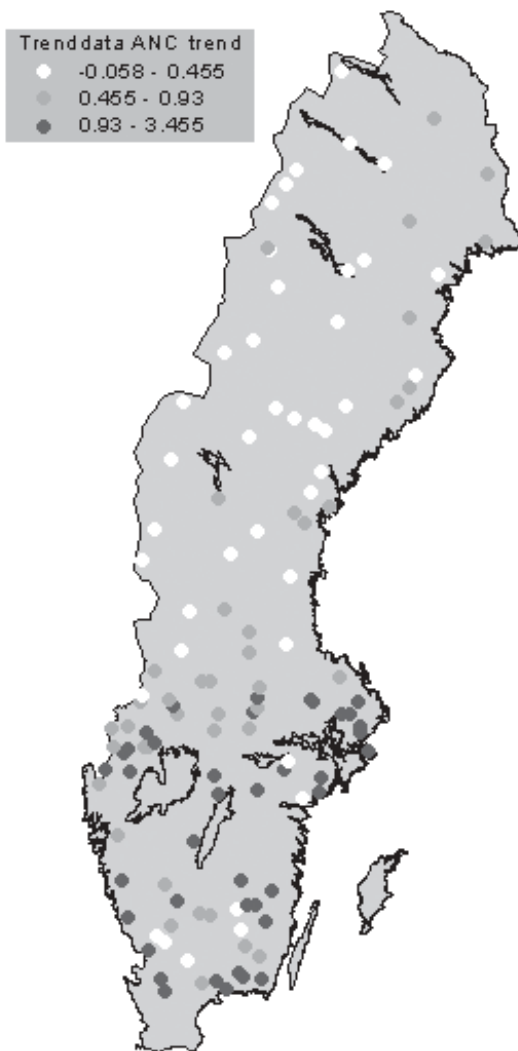
## MAGIC simulation results

The model predicted a countrywide increase in lake water ANC for a majority of the lakes. We have divided lakes into three categories according to magnitude of ANC changes. The largest increase was more frequent at the lakes in the southern compared to the northern part of the country (Figure 2).

The selection of modelled lakes included many lakes which were not particularly sensitive to acidification or which were in regions historically not much affected by acid depo-

sition. According to Swedish Environmental Protection Agency about 20% of all lakes in Sweden are classified as acidified or sensitive to acidification (Wilander, 1999). Using the same criteria (pH and alkalinity) about 50% of the modelled lakes are acidified or acid sensitive. Consequently about 50% of the modelled lakes probably never acidified and therefore also should not be expected to increase their

**Figure 2. Simulated annual ANC-change 1997–2010 ( $\mu\text{eq/l}$ , adapted from Munthe et al, 2002).**



alkalinity and pH when the acidifying deposition decrease.

For that reason we have divided the modelled lakes into two groups; acid sensitive and non-sensitive, using ANC in 1997 as a criteria. There were 63 lakes in the acid sensitive category. To present time series of lake water pH and ANC, we have calculated median, quartiles and 5% and 95% percentiles for each year (Figures 3 and 4).

For the acid sensitive lakes, the modelled pH generally decreased when the acid deposition increased in the middle 20th century, and increased sharply between 1990 and 2000 when the acid deposition decreased. The increase levelled off after 2010, when deposition stabilised on a new much lower level (Figure 3). The change was relatively smaller on lakes with either high or low historical pH. The pattern of ANC was similar to that of pH including generally slow increase of ANC after 2010 (Figure 4) in average by about  $4 \mu\text{eq/l}$  over 30 years from 2010 to 2040.

The modelled soil base saturation in the sensitive lakes' catchments declined for most of the catchments over practically the entire modelled period 1860–2040. In contrast to pH and ANC there was no increase of soil base saturation (Figure 5) in response to the acid deposition decline after 1990.

## Generalised European pattern of surface water recovery

The pattern of lake waters chemistry changes (both observed and modelled) is consistent with a general picture synthesised from a major European project on surface waters recovery RECOVER:2010 (Ferrier et al., 2001). Allowing for a certain degree of generalisation, the pattern in surface water across Europe was such that decreasing  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  led to an increasing ANC, but to an equal sized decrease of base cations (Evans et al., 2001), (Figure 6).

Figure 3. Simulated pH in 64 acid sensitive lakes 1860–2040.

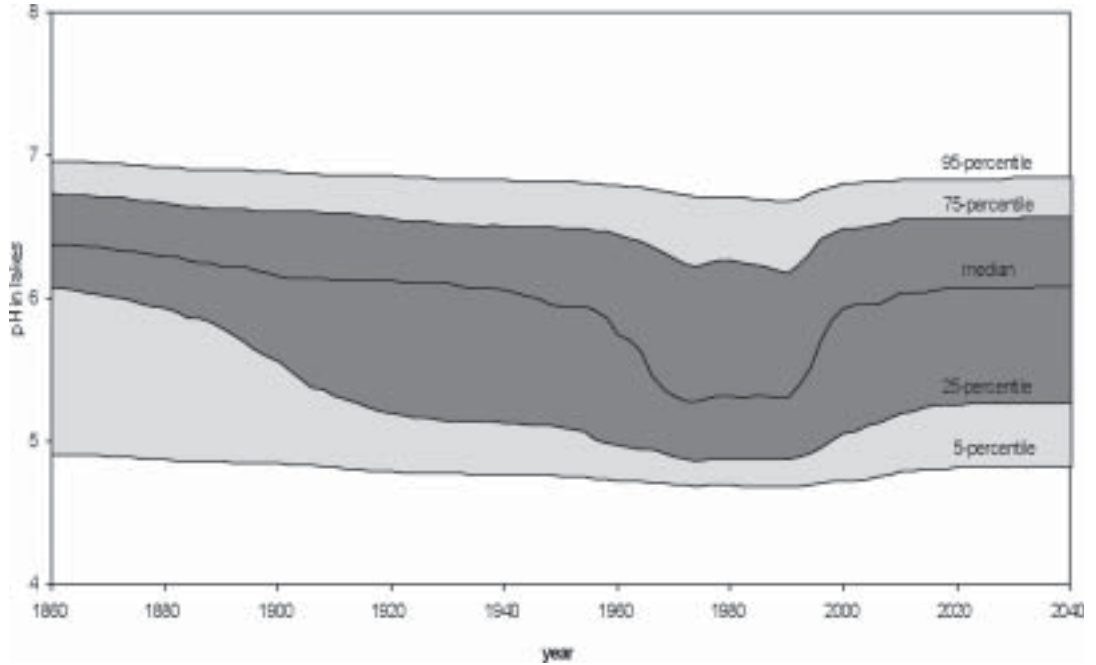


Figure 4. Simulated ANC ( $\mu\text{eq/l}$ ) in 64 acid sensitive lakes 1860–2040.

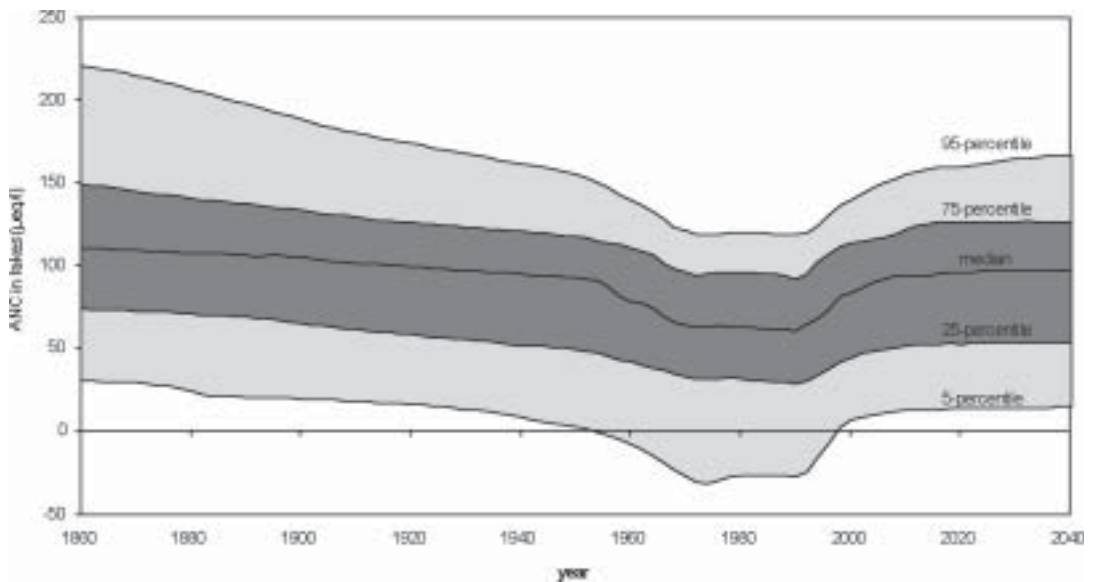




Figure 5. Simulated base saturation in the 64 acid sensitive catchments 1860–2040.

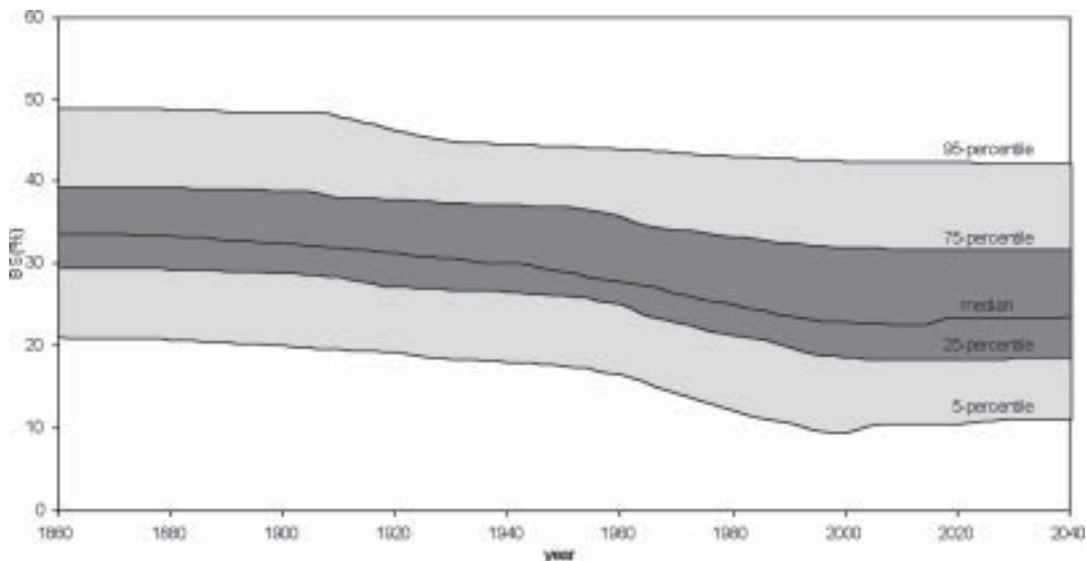
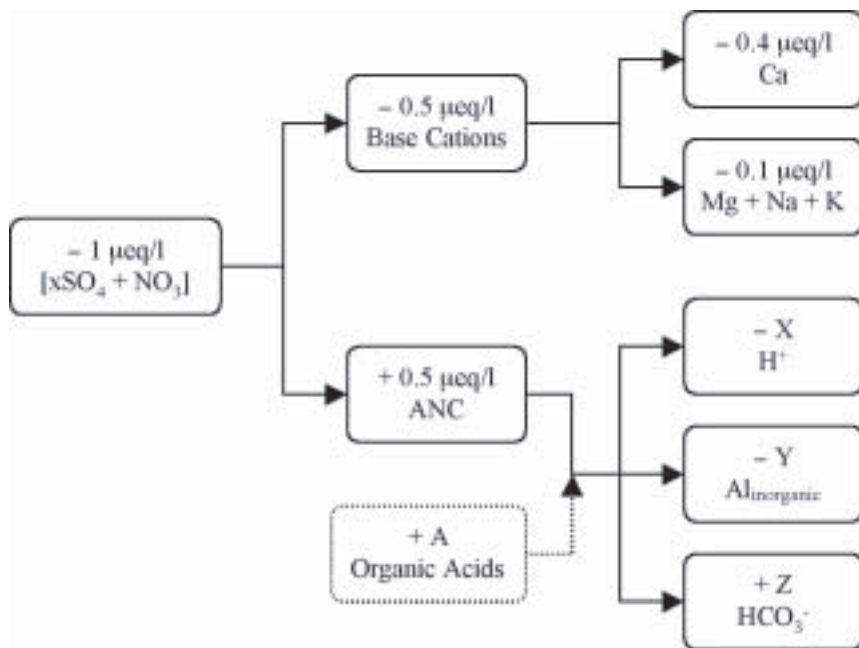


Figure 6. Generalised pattern of surface waters recovery from acidification observed across Europe. From: Evans et al, 2001.



## Conclusions

The MAGIC simulations indicate that:

- decreased deposition has a positive effect on both soils and surface waters,
- chemical recovery of soils takes much longer time than of lakes,
- surface waters can partly recover even if soils in the catchments continue to acidify,
- in many cases the soils will not recover by 2040 and
- in many cases the recovery of lakes will not be complete by 2040 unless deposition will decrease further.

## Acknowledgement

Erik Karlton (SLU) provided data and helped us with interpretation and data analysis of the soil inventory data, Anders Wilander (SLU) provided data and helped us with analysis of the lake inventory data and Jack Cosby (University of Virginia) has developed the MAGIC model and helped us with the regional calibration.

## References

- Cosby, B.J., Wright, R.F., Hornberger, G.M. and Galloway, J.N. 1985. Modelling the effects of acid deposition: assessment of a lumped parameter model of soil water and stream-water chemistry. *Water Resour. Res.* 21:51–63.
- Cosby, B.J., Ferrier, R.C., Jenkins A. and Wright, R.F. 2001. Modelling the effects of acid deposition: refinements, adjustments and inclusion of nitrogen dynamics in the MAGIC model. *Hydrol. Earth Syst. Sci.* 5: 499–517.
- Evans, C., Jenkins, A., Helliwell, R., Ferrier, R. and Collins, R., 2001. *Freshwater Acidification and Recovery in the United Kingdom*. Centre for Ecology and Hydrology, Wallingford, UK
- Karlton E., et al., this volume.
- Moldan, F., Kronnäs, V., Wilander, A, Karlton, E., and Cosby, B.J., submitted. Modelling acidification and recovery of Swedish lakes. Submitted to WASP.
- Munthe, J., Grennfelt, P., Sverdrup, H. and Sundqvist, G. 2002. New concepts and methods for effect-based strategies on transboundary air pollution. ASTA Synthesis Report. IVL Report B1495.
- Reuss, J.O. and Johnson, D.W., 1986. Acid deposition and the acidification of soils and waters. *Ecological Studies* 59, Springer-Verlag, New York, 119 p.
- Skjelkvåle, B.L., Mannio, J., Wilander, A. and Andersen, T., 2001. Recovery from acidification of lakes in Finland, Norway and Sweden 1990–1999. *Hydrol. Earth Syst. Sci.*, 5(3), 327–337.
- Wilander, A. 1997. Referenssjöarnas vattenkemi under 12 år; tillstånd och trender. (Reference lakes water chemistry under 12 years; status and trends.) Naturvårdsverket Rapport 4652. (in Swedish)
- Wilander, A. 1999. Surhet/försurning. In *Bedömningsgrunder för miljö kvalitet. Sjöar och vattendrag*. Red Wiederholm, T., Naturvårdsverket, Rapport 4920. (in Swedish)

# Processes affecting surface water acidity: Natural acid or anthropogenically acidified waters?



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The water quality of streams, rivers and lakes is affected by a number of processes in the landscape. Vegetation, geology, climate and natural atmospheric input of nutrients create the natural chemical conditions. Superimposed on this natural chemistry is the anthropogenic, human induced contribution, which can cause large perturbation in the natural chemistry and therefore produce severe conditions for many aquatic organisms.

Acidification, resulting from the emission of acid precursors to the atmosphere cause one of the most concerning anthropogenic effects on soils and waters in Sweden. Natural acid water environments are also common and ecologically important, especially in the northern forest ecosystem, called the boreal forest. Soils with low weathering capacity and an accumulation of organic material are a common feature of the boreal forest. Because the conditions of the soil environment to a large extent control the water quality, drain-

age water from these soils are often nutrient poor and acidic.

The term acidification suggests a development over time towards more acid conditions. Most natural acid ecosystems today have acidified over thousands of years since the last glaciation. In contrast, surface waters affected by anthropogenic acidification often experience a much more rapid transformation. Forest production and timber harvesting can also influence the acidity of soils, but the impact on surface waters is probably relatively unimportant compared to the role of acid deposition in most parts of Sweden.

Many lakes and rivers in south-western Sweden demonstrate serious biological damage caused by surface water acidification. In many of these waters it is clear that acid deposition have played a fundamental role in the pH decline the last decades. Acidification have in many locations gone so far that a new permanent acidified condition occurs, with

severely reduced base saturation of soils and constantly low pH values in surface waters. This can be called chronic acidification and implies low pH values and high concentrations of the inorganic (toxic) form of aluminum during the entire year despite changes in flow. In northern Sweden, with significantly lower levels of acid deposition, the largest risk of biological damage in aquatic environments, occur during high runoff periods associated with snow melt and heavy rain periods during summer and fall. These episodic pH declines often occur during short periods, lasting from days to weeks, but they can severely damage fish and other aquatic organisms. In northern Sweden the period between episodes during the winter or during dry summer periods, called base flow, is often not significantly affected by atmospheric deposition.

## What controls pH?

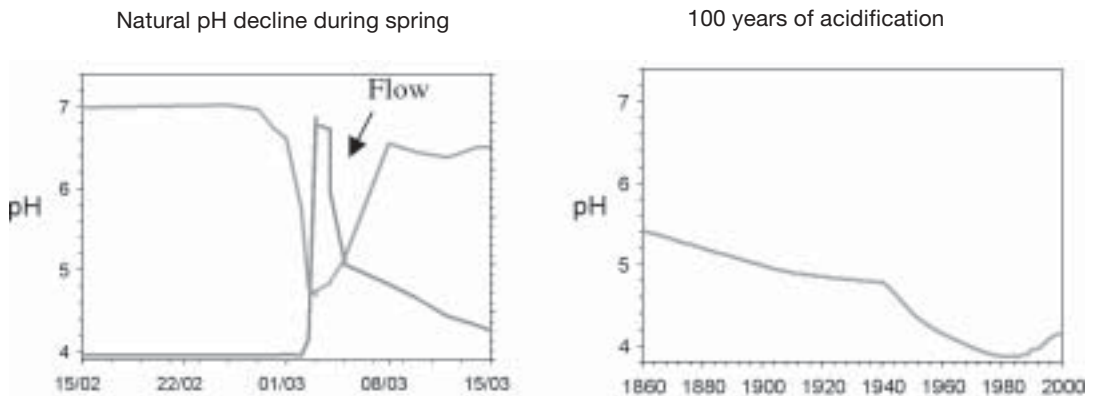
Negative effects caused by acidification are often described in terms of chemical parameters, such as low or declining pH values. In reality the main concern are the ecological consequences on fish and other aquatic organisms that are linked to the chemical changes. However, those ecological changes are much

more difficult to measure and predict. The pH of surface water (at a set partial pressure of carbon dioxide [ $p\text{CO}_2$ ]) is to a large extent determined by DOC (dissolved organic carbon) and ANC (Acid Neutralization Capacity). Despite the fact that the relationship between pH, DOC and ANC is mathematically complicated it can be described as figure 2.

DOC is a very important component in most Swedish surface waters. High concentrations and therefore often naturally low pH values are generally found in regions with large areal extent of wetlands in the boreal forest. The highest levels are found in the inland and coast of northern Sweden and south-central Sweden. The human impact on DOC is relatively marginal although forestry and ditching can have had some influence. The effect of climate on the concentration and dynamics of DOC in rivers and lakes has been explored in recent years. Today we know that temperature and precipitation affect the DOC export from nearby soils positively. Winter conditions such as temperature and snow amounts are also expected to strongly influence the concentration of DOC, especially during snow melt periods.

ANC expresses the capacity to buffer against acidifying protons. Surface water with a high ANC has a high ability to neutralize

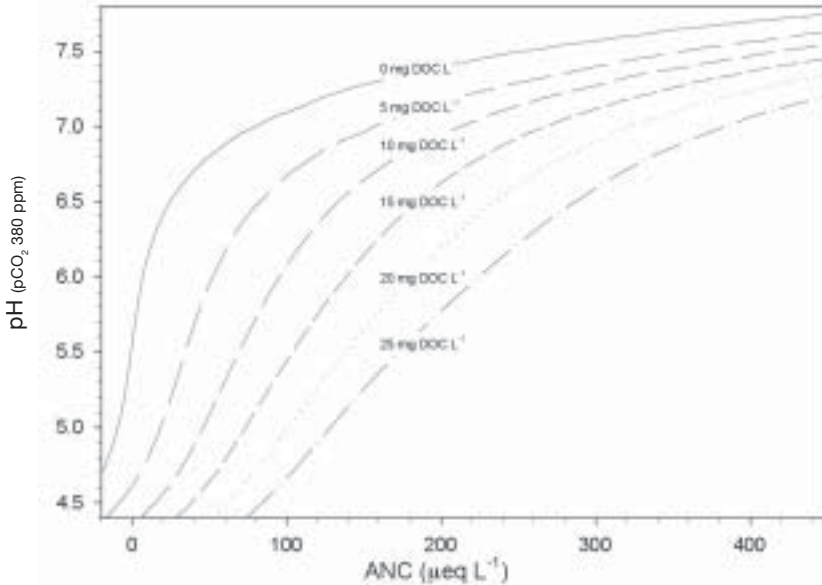
**Figure 1.** Example of a naturally driven pH decline during the spring flood (to the left) and a stream that has been acidified for over 100 years by acid deposition (to the right).



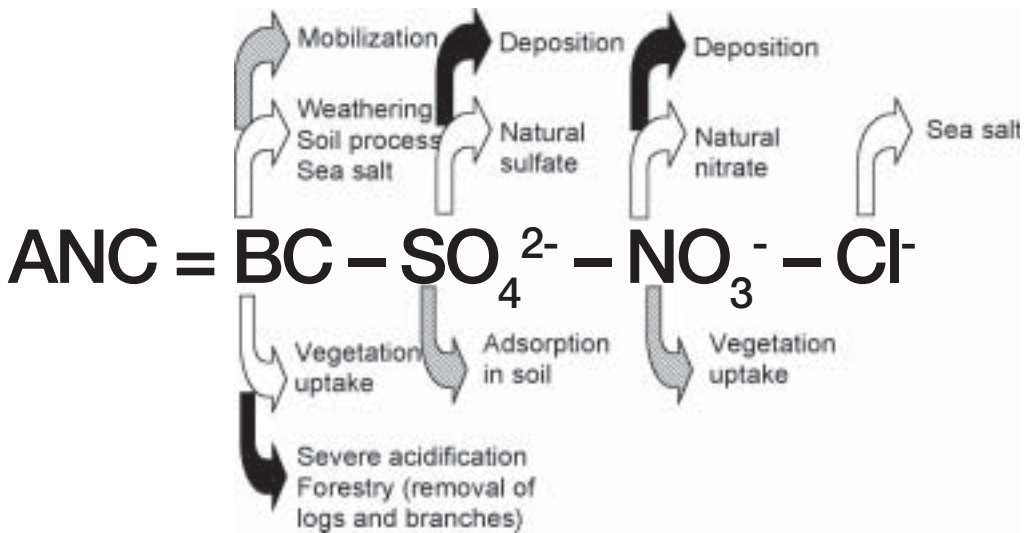
protons but the ability is reduced when acid is added. ANC is affected by a number of natural factors but is also the parameter that is most affected by acid deposition. ANC is not measured directly but is calculated from

standard water chemical analyses using base cations and strong acid anions. In figure 3 the calculation of ANC is presented along with natural and anthropogenic processes that affect ANC.

Figur 2. Relationship between ANC, DOC and pH at atmospheric partial pressure of CO<sub>2</sub>.



Figur 3. Calculation and factors that affect ANC. Arrows downwards indicate a declining concentration of the solute, whereas an upward arrow indicates an increasing concentration. White arrows represent a natural source/sink, a black arrow is anthropogenic source/sink and banded arrows indicate that an anthropogenic change is partly compensated by a change in uptake or mobilization.



Two other factors that affect pH are aluminum concentration and the partial pressure of carbon dioxide ( $p\text{CO}_2$ ). In surface waters the  $p\text{CO}_2$  is primarily high during the winter and can therefore have a pH decreasing effect on ice covered lakes. The  $p\text{CO}_2$  influence becomes important at pH values above 5.5 and has therefore a relatively unimportant effect on pH in the most acid surface waters. For aluminum the effect is the opposite. Aluminum, or rather the fraction of inorganic monomeric aluminum ( $\text{Al}_i$  which is the most toxic fraction of aluminum) buffers against pH decline (and at the same time produce higher concentrations of  $\text{Al}_i$ ). The importance of aluminum buffering for determining pH is in general limited as long as pH exceed pH 4.5.

## Acid episodes

In general, it is the same water chemical mechanisms that drive pH decline associated with high runoff episodes as controls pH during other periods of the year. The largest difference between an acid episode and chron-

ic acidification is in the importance of the transient change in hydrology, which influences both the decline and the recovery of pH during episodes. The two most important natural factors that affect the large pH decline (up to two units) during the spring flood in northern Sweden are an increase in DOC (often two to three times as high during peak flow compared to base flow figure 4) and a natural dilution of ANC (figure 5). Short pulses of anthropogenic sulfate from snow or rain during the episode will be superimposed on the natural decline of ANC and therefore further depress pH.

Episodic changes in the water quality are a natural feature of most aquatic ecosystems. Natural variation in water chemistry is of fundamental importance in the establishment of natural biodiversity. Organisms that survive these often toxic conditions gain competitive advantages in the ecosystem.

To conclude that a stream, river or lake is acid is rather straightforward, but to determine that anthropogenic acidification during the last century is responsible for that low pH is much more difficult. This task becomes

Figure 4. Example of DOC change during the spring flood in a small stream in northern Sweden. Note that DOC increases from  $7 \text{ mg L}^{-1}$  during baseflow to over  $20 \text{ mg L}^{-1}$  during peak runoff.

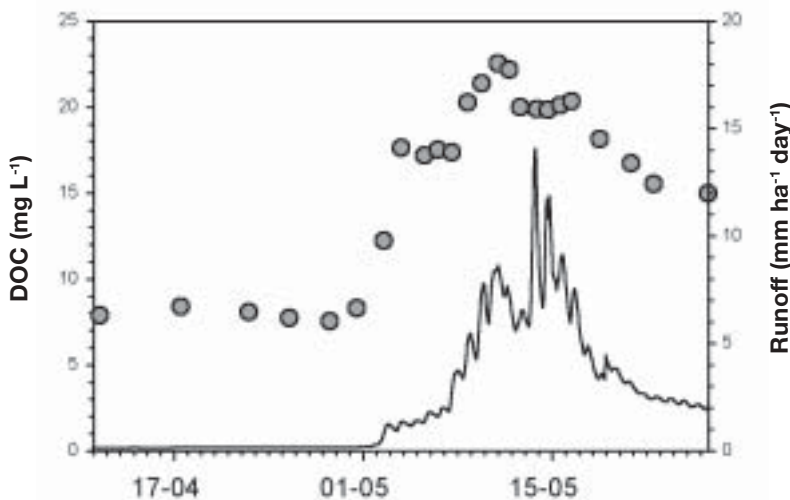


Figure 5. Natural dilution of ANC during an episode. When a base flow with a high ANC is diluted by snow melt water or rain water with a very low ANC, a dilution of both the base cations and the strong acid anions will occur.

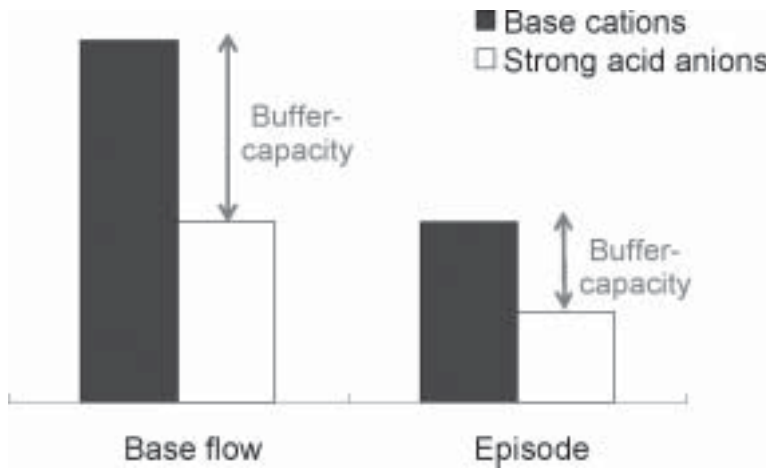
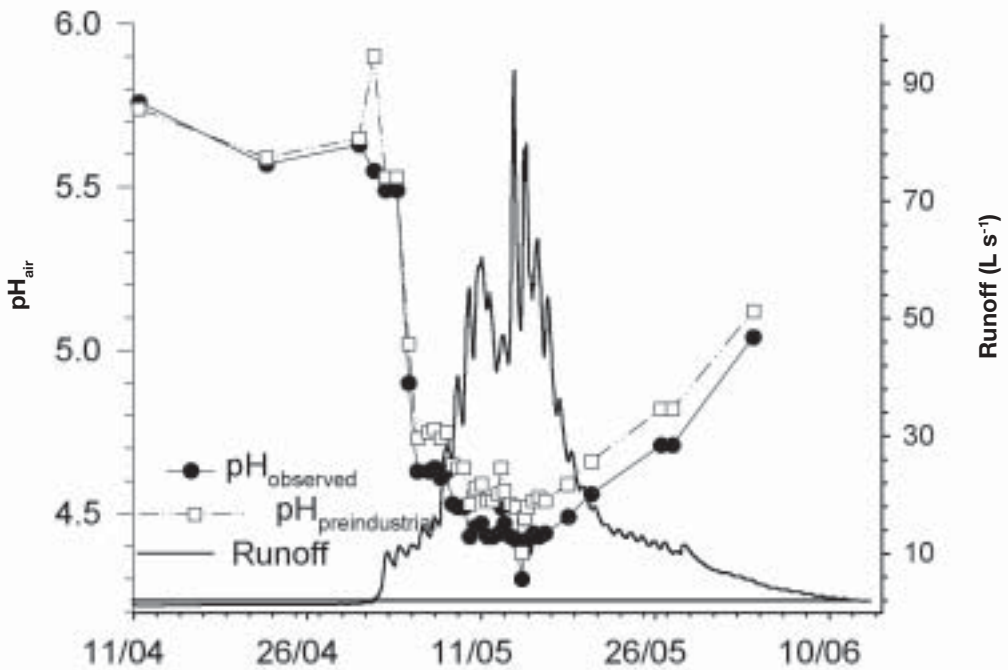


Figure 6. Observed pH decline and natural (preindustrial) pH decline in a small stream in northern Sweden. The difference between the observed (dark symbols) and the preindustrial pH decline (open symbols) depends on the anthropogenic deposition. The preindustrial pH decline is driven by a combination of natural increase in DOC and a natural dilution of ANC.



even more difficult when acidification is episodic and long time series of a water chemistry and aquatic biology is lacking. The biodiversity of many surface waters in Sweden have certainly been affected by acidification during the 20<sup>th</sup> century, but also by of destruction of spawning grounds, forestry practice, migratory restraints, introduction of new species and over-fishing. Without a proper process base understanding of how surface water chemistry is controlled we will never be able to understand and separate the anthropogenic influence on surface water acidity from natural variability.

## References

- Laudon, H., Westling, O., Vøllestad, L. A., & Poléo, A.B.S. (2001). *Naturligt sura och försurade vatten i Norrland*. 'Naturvårdsverket Rapport 5144, Stockholm. (In Swedish with English summary).
- Laudon, H., Westling, O., Löfgren, S. & Bishop, K. (2001). Modelling preindustrial ANC and pH during spring flood in Northern Sweden. *Biogeochemistry*, 54, 171–195.
- Laudon, H. and Hemond, H. F. (2002). Recovery of streams from episodic acidification in northern Sweden. *Environmental Science & Technology*, 36, 921–928.



# Recovery from acidification in Swedish lakes and streams



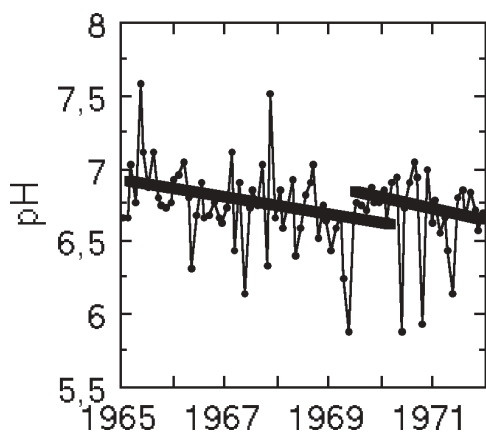
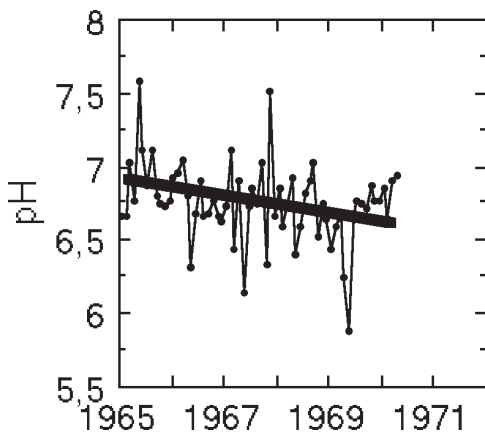
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## Introduction

In 1972 the first UN conference on the environment was held in Stockholm. One Swedish contribution dealt with air pollution across national boundaries (Bolin et al. 1971) presenting data from river monitoring as frightful

examples of effects of acid deposition (Figure 1a). Before the opening of the conference additional data were included. Svante Odén and Thorsten Ahl (1972) concluded that the upward step (Figure 1b) was caused by melt water from thawing snow infiltrating the soil, leading to a raised pH. They also wrote, “the

Figure 1. pH-value for River Klarälven as presented at the 1972 UN Conference. A) Data from the Case study (Bolin et al. 1971). B) Updated data (Odén and Ahl, 1972).



negative trend, if persistent in time, will change the situation drastically, within some 20 years". Other information such as increased acid deposition and observed fish kills supported their conclusion. Their prediction, fortunately, did not realise (figure 2).

In the following the recent changes with regard to recovery from acidification in Swedish lakes and streams will be elucidated.

## Material and methods

The latest national survey of lakes and streams was conducted in the autumn 2000 (Wilander et al. 2003). Only lakes >4 ha were included. The statistical stratification method used forced lakes in the southern, more acid deposition affected parts of the country as well as large lakes to be over-represented in the sub-sample of a population of about 60 000 lakes >4 ha.

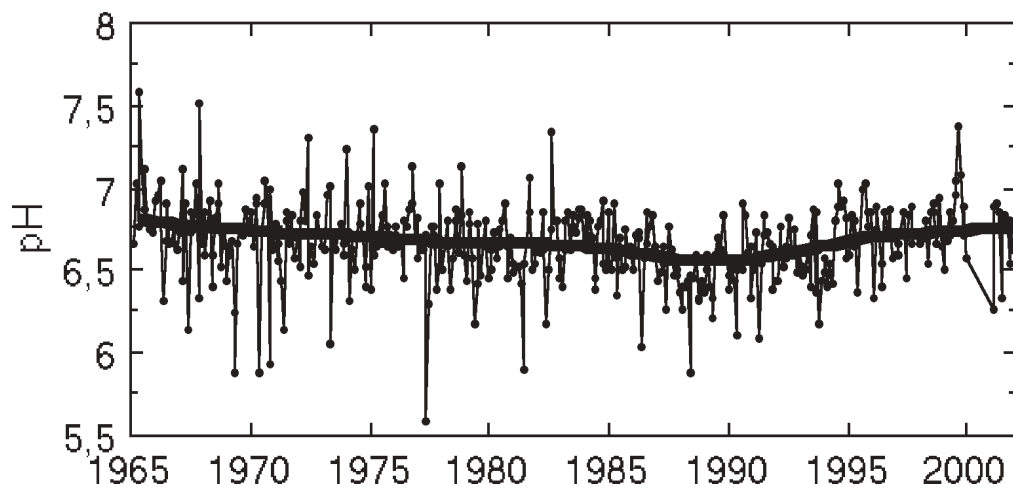
In addition two time-series programmes were initiated in 1983–84, covering about 100 forest lakes and about 50 streams. Emphasis was put on acid sensitive, clear water lakes, which makes the selection non-representative for the entire Swedish lake population.

The lakes are sampled 3–4 times a year, while the streams are sampled monthly and occasionally more frequently.

## Acid status according to the national lake and stream surveys in 1995 and 2000

Based on the lake survey in 2000 it was estimated the 6.2% of the lake population had an alkalinity <0.05 meq/l. When ANC is used as a measure of buffer capacity, the percentage is as low as 1.3%. In 1995, the corresponding figures were 6.2% and 2.4%, respectively. According to the ANC trend, a recovery from acidification occurred between 1995 and 2000. A small recovery was also indicated by the stream surveys (Wilander et al. 2003). Sulphate concentrations were substantially lower according to RI00 as compared to RI95 (table 1). This should lead to equivalent increases in alkalinity and corresponding raise in pH-values if the concentrations of base cations (BC) and humic substances (TOC) were constant. However, the BC concentrations were lower while the TOC concentrations were higher (table 1). Thus, there are two opposing

Figure 2. pH-values for River Klarälven from 1965 through 2002. Line fitted with LOWESS smoothing.



**Table 1. pH-value, buffer capacity (alkalinity och ANC), base cations (BC) total organic carbon (TOC) and sulphate (SO4) calculated for the lake population > 4 ha (about 58 000).**

Parameter	RI00			RI95		
	10	50	90	10	50	90
pH	5.53	6.57	7.24	6.01	6.79	7.31
Alkalinity ( $\mu\text{ekv/l}$ )	3	105	382	18	131	450
ANC ( $\mu\text{ekv/l}$ )	56	195	498	49	192	598
BC ( $\mu\text{ekv/l}$ )	99	275	795	99	291	950
TOC (mg/l)	2.0	8.7	18.7	2.0	8.4	13.2
SO4 ( $\mu\text{ekv/l}$ )	15	35	142	21	47	193

**Table 2. The share of sampled lakes with concentrations of inorganic Al > 25  $\mu\text{g/l}$  (toxic for the most sensitive species) and >75  $\mu\text{g/l}$  (toxic for less sensitive species). N=535.**

Parameter	Tolerance value	Share of sampled lakes %	
		1995	2000
Inorganic Al	>25 $\mu\text{g/l}$	17	26
	>75 $\mu\text{g/l}$	6	9
pH-value	< 6,0	18	32

signals on alkalinity and ANC between the two surveys, especially in low ANC lakes. The contribution of humic acids diminishing the alkalinity without affecting ANC is the cause of the different patterns.

Aluminium (Al) in inorganic form is strongly toxic for gill breathing organisms such as fish and many bottom-living invertebrates. More lakes had inorganic Al concentrations higher than 25  $\mu\text{g/l}$  in 2000 as compared to 1995 (table 2). This is a level where damage can be expected on salmon and roach (Lydersen et al 2002). One cause may be the lower pH-values in 2000 (table 2). The stream survey in 2000 sowed a mean total aluminium concentration of 79  $\mu\text{g/l}$ , which is 25  $\mu\text{g/l}$  higher than for the survey in 1995 (n=216 both years). However, the concentrations of inorganic Al were equal or 15  $\mu\text{g/l}$  both years. The concentrations of organically bound Al explain the difference in total aluminium. In

both lakes and streams, there was a negative relation between inorganic Al and pH and a positive relation between inorganic Al and TOC.

## Acid trends in reference lakes and streams

Monitoring of lakes and streams sensitive to acidification started in the beginning of 1980:ies. As a consequence we have little information about the acidification phase but a good coverage of the recovery. The recovery phase is exemplified with Lake Brunnsjön (figure 3).

Obviously there are no monotonous trends even though a decrease in sulphate is accompanied by a decrease in BC (figure 3a). Alkalinity is more or less unaffected by the sulphate level (figure 3b), but there is a signifi-

Figure 3: A) Time series for concentrations of non-marine sulphate (SO<sub>4</sub><sup>\*</sup>), non-marine base cations (BC<sup>\*</sup>), acid neutralisation capacity (ANC) and alkalinity for Lake Brunnsjön in southern Sweden (Kalmar county). Lines fitted with LOWESS smoothing. B) Relationship between non-marine sulphate (SO<sub>4</sub><sup>\*</sup>) and non-marine base cations (BC<sup>\*</sup>) and ANC. The line shows the ratio 1:1.

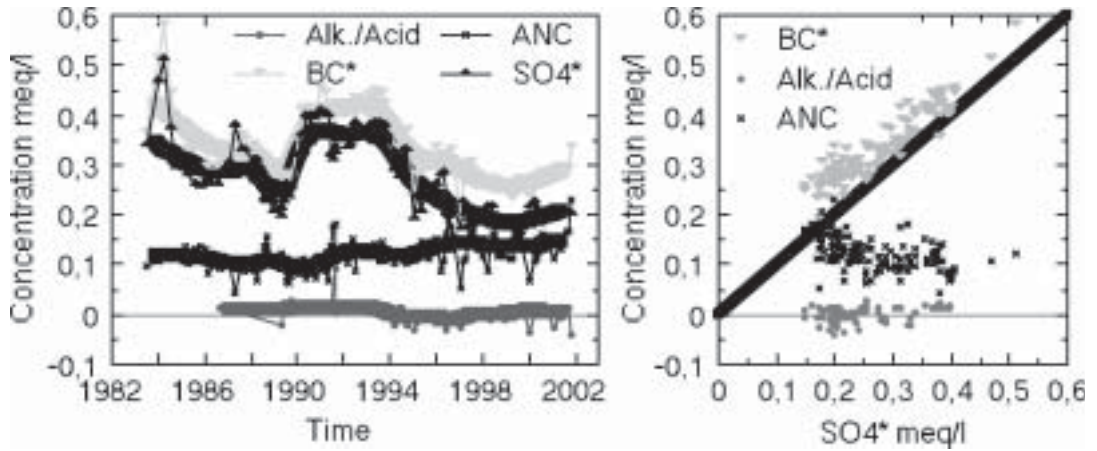
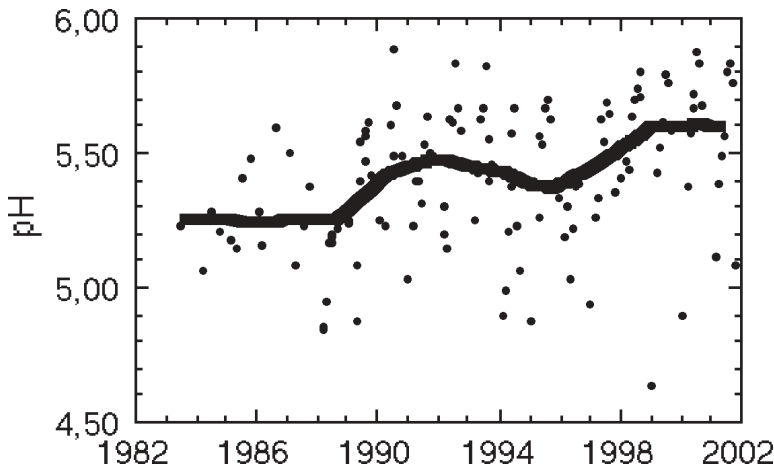


Figure 3. Changes in pH-value in the acidified reference lake Brunnsjön in southern Sweden (Kalmar county). Line fitted with LOWESS smoothing.

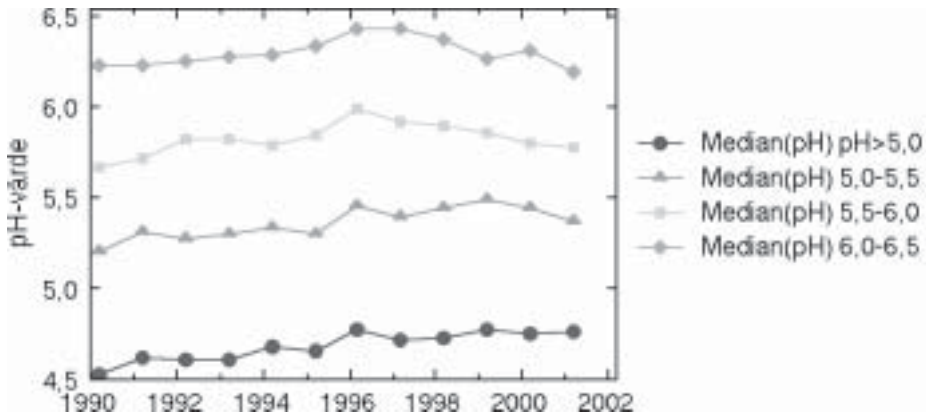


cant increase in ANC with decreasing sulphate concentration. The difference between the two parameters is partly due to increased humus concentrations, but it is also an effect of the BC/sulphate ratio, which increase at lower sulphate levels. This shows the positive effects on BC and ANC of the decreased acid deposition. The pH-values has increased

as well (figure 4). Similar behaviours are observed in most of the reference lakes in southern Sweden.

The pH-values increased with a mean of 0.2 units in the two groups of reference lakes with the lowest pH-values (pH<5.0, n=12 and 5.0<pH≤5.5, n=16). A proceeding increase of that magnitude can not be expected in the

Figure 4. Changes in pH-value (mean values) from 1990 through 2001 (n= 67) for four groups of reference lakes with different initial pH-levels.



future. Lakes with higher pH-values exhibit smaller changes as expected. ANC increased in all lake groups with the exception of the most acid one, which had the highest ANC during 1991–94. Model simulations indicate that the most acid lakes are natural acidic. Thus, they are very much influenced by TOC variations. The recovery during the period 1990–2001, measured as ANC, was as a mean 0.003 meq/l/year for lakes in the three highest pH-classes.

The trends for pH and alkalinity were similar for lakes in the entire country regardless of the very different S deposition. pH increased about 0.02 units/year, while alkalinity showed very small changes. ANC, however, increased about 0.003 meq/l, year in the most heavily polluted south-west part of Sweden and with about 0.002 meq/l, year in the remainder of the country. This indicates a more rapid recovery in the most acid deposition affected regions.

## Acidification classification of Swedish lakes

Based on data from RI00, the SSWC model (Rapp et al. 2002) and the Swedish quality

criteria for surface waters (SEPA 1999), the number of lakes acidified by acid deposition was estimated. Based on ANC, 3% of the lakes were acidified, while based on alkalinity, the same proportion was 10% (Figure 5). This highlights the difficulties in separating naturally acidic lakes from anthropogenically acidified lakes, when using alkalinity. This is because the alkalinity expression does not take the humus acidity into consideration.

Most acidified lakes are situated in south-west Sweden, while liming activities are common also in the central and northeast part of the country (Figure 5). This is partly caused by poor liming criteria (alkalinity and pH) and partly due to liming against acid episodes in northern Sweden during snowmelt, heavy rains etc. The latter are mainly of natural origin, but become more severe due to acid deposition (c.f. Laudon this volume).

## Conclusions

Swedish lakes and streams exhibit recovery from acidification since the late 1980's due to the decreased sulphur deposition. The recovery is shown as slow increases of ANC and pH and has been most pronounced in poorly

**Figure 5.** Lakes >4 ha classified as acidified based on ANC (left) and alkalinity (middle) according to Swedish Water Quality Guidelines (SEPA 2000) and limed lakes (all size classes, right). Data from the national lake survey 2000. Maps from Lars Rapp, SLU.

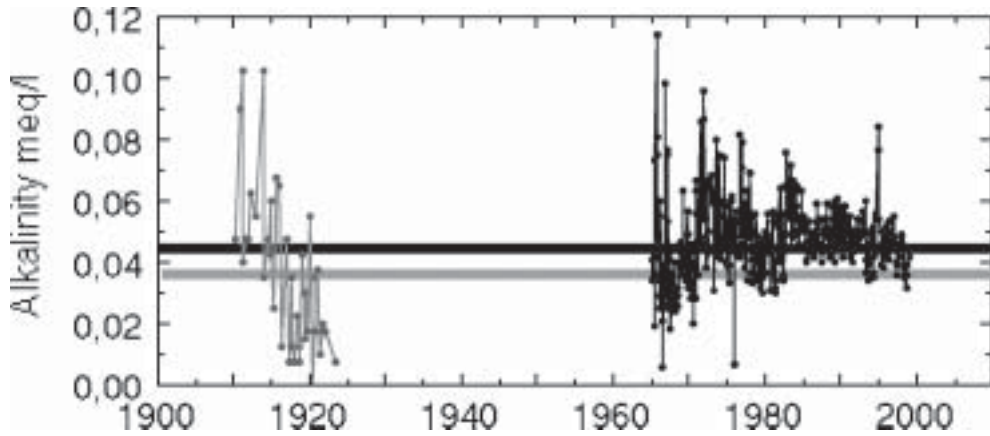


buffered, circumneutral waters. The ANC increase has been largest in the most severely polluted south-west parts of Sweden, corresponding to an annual increase of 0.003 mekv ANC/l. In central and northern Sweden, the annual increase has been around 0.002 mekv ANC/l. Naturally acidic or well buffered lakes and streams exhibits less pronounced recovery trends. Alkalinity exhibits no or very small changes with time. According to the officially used models and quality criteria for ANC, approximately 3% of the Swedish lakes larger

than 4 ha are still acidified by acid deposition. Most of those lakes are situated in south-west Sweden.

Turning back to River Klarälven, J.V. Eriksson (1929) studied the river in the beginning of last century. Fortunately, that time series (figure 6) was not used at the 1972 UN conference. A comparison with present data does not reveal any major difference. Extensive liming activities in the county of Värmland and in Norway influence the concentrations from 1990 and onwards.

Figure 6. Comparison of present time series for alkalinity with that given by J.V. Eriksson (1929) for River Klarälven.



## References

- Bolin, B. et al. (eds.) 1971. Air pollution across national boundaries. The impact on the environment of sulfur in air and precipitation. Sweden's case study for the United Nations conference on the human environment. Royal Ministry for Foreign Affairs. Royal Ministry for Agriculture.
- Eriksson, J.V. 1929. Den kemiska denudationen i Sverige. In Swedish with French summary. Medd. Statens Meteor. Hydrogr. Anstalt Band 5 N:o 3.
- Lydersen, E., Löfgren, S. & Arnessen, T. 2002. Metals in Scandinavian surface waters: effects of acidification, liming, and potential reacidification. *Crit. Rev. Environ. Sci. Techn.* 32(2&3):73–295.
- Odén, S. & Ahl, T. 1972. The long-term changes in the pH of lakes and rivers in Sweden. Paper referring to Section 5.2 of Sweden's case study for the United Nations conference on the human environment. (mimeographed report).
- Rapp, L. Wilander, A. & Bertills, U. 2002. Kritisk belastning för försurning av sjöar. In Bertills, U. & Lövblad, G. (eds) *Kritisk belastning för svavel och kväve. Naturvårdsverket Rapport 5174*. In Swedish.
- SEPA 2000. Environmental quality criteria. Lakes and watercourses. Swedish Environmental Protection Agency. Report 5050.
- Wilander, A. & Lundin, L. 2000. Recovery of surface waters and forest soils in Sweden. In Warfvinge, P. & Bertills, U. (eds.) *Recovery from acidification in the natural environment. Present knowledge and future scenarios*. pp 53–66. Swedish Environmental Protection Agency Report 5034.
- Wilander, A., Johnson, R.K. & Goedkoop, W. 2003. Riksinventering 2000. En synoptisk studie av vattenkemi och bottenfauna i svenska sjöar och vattendrag. *Inst.f. miljöanalys, SLU Rapport 2003:1*. In Swedish.





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