Abstract

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Atmospheric deposition of air pollutants has been a severe threat to terrestrial and forest ecosystems for several decades. In Sweden sulphur deposition has caused acidification of soils and runoff, while nitrogen deposition only had a minor or local impact on runoff quality so far. During the last three decades, emission control has caused a decline in sulphur deposition, whereas nitrogen deposition on the other hand, has continued to increase to a rate several times above the natural background level. Long term changes in runoff acidity and nitrogen chemistry after these changes in deposition are of great concern. Monitoring of small, well-defined catchments including hydrochemistry of precipitation, soil and runoff, is a valuable tool for addressing this concern. When interpreting runoff data from such sites, the near-stream zone has been identified to be of crucial importance.

The main objective for this thesis was to explain how catchment processes were related to short-term variation and long-term trends in the hydrochemistry of forest stream water. The field work was conducted on the strongly acidified and nitrogen limited Kindla catchment, with a special emphasis on the relationship between the near-stream zone and both stream acidity and nitrogen leaching. Furthermore, time series of hydrochemistry in forest stream water from 13 catchments were analysed for changes in acidity and nitrogen leaching. In three of these sites, soil water from E- and B-horizons was also analysed with regards to these questions.

The investigations revealed that the near-stream zone was a net source of acidity in runoff at Kindla due to leaching of organic acids, although this contribution was overshadowed by sulphate from upland soils and deposition. The near-stream zone was also the main source for both organic nitrogen and nitrate to the stream, but the leaching rate was low, especially for inorganic nitrogen. In the 13 reference streams, sulphate concentrations declined in all cases. In the five most acidified streams, a recovery from acidification was detected, although at a low rate. Sulphate mobilisation and decreased leaching of base cations probably delayed the recovery. Similar trends of declining sulphate concentrations and a tendency for decreasing acidity were also found in soil water in two of the southern sites. The possibilities of a continued acidification of the soil with a concurrent recovery of runoff was discussed and indicated at one site as a decrease in the Ca/H^2 ratio. Leaching of inorganic nitrogen did not show any general trends in the reference streams, but a significant decrease of TOC/TON in most streams indicated a change in the quality of the organic matter in runoff.

Key words: acidification, near-stream, nitrogen leaching, recovery, soil water, stream, Sweden, trends

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“*Det finns vattnet som är kallt och tätt som stenen, du kan icke dricka det, och det finns vattnet som är så tunt och svagt att det icke hjälper att du dricker det och det finns vattnet som darrar då man dricker det så att man får frossan, och det finns vattnet som är bittert och smakas svetten, och en del vatten är liksom dött, vattuspindlarna sjunker rätt nergenom det som om det vore luften. Jo, vattnen är såsom sanden på havets strand, dem är oräkneliga.*

Så att det här papperet som ni i länsstyrelsen har skickat oss för att vi ska tala om huru det är med vattnet, det är odugligt, vattnet ryms icke oppå två rader, om man har levat i sjutti år som jag har gjort då vet man så mycket om vattnet att länsstyrelsen skulle kunna dränkas i denna kunskap.

Så jag säger icke allt.”

(Ur “Vatten” i “Merabs skönhet” av Torgny Lindgren)

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Appendix

Papers I-IV

The present thesis is based on the following papers which are referred to by their Roman numerals.

I. Fölster, J., 2001. Significance of processes in the near-stream zone on stream water acidity in a small acidified forested catchment. *Hydrol. Process.* 15, 201-217.

II. Fölster, J., 2000. The near-stream zone is a source of nitrogen in a Swedish forested catchment. *J. Environ. Qual.* 29, 883-893.

III. Fölster, J. and Wilander, A. Recovery from acidification in Swedish forest streams. Submitted.

IV. Fölster, J., Bringmark, L. and Lundin, L. Temporal and spatial variations in soil water chemistry at three acid forest sites. Manuscript.

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Introduction

Sulphur deposition in Sweden has declined to less than half of what it was around 1970, while the nitrogen deposition has continued to increase (Figure 1). For sulphur we are approaching a level where no harmful effects on biota occur according to calculations of critical loads (Posch et al., 1999), and signs of recovery of surface water from acidification are reported (Stoddard et al., 1999; Wilander and Lundin, 2000). In Sweden the effects of nitrogen deposition has not been as serious as for sulphur. Only at a few sites in south western Sweden, the deposition is high enough to cause a high leaching of nitrate from forest soils to surface waters (Wiklander et al., 1991; Dise and Wright, 1995). The long term effect of a nitrogen deposition several times higher than the natural background level, however, is not known. Further restrictions in emissions of sulphur and nitrogen are probably still needed, but will be more expensive than the measures already done, and have to be justified. Thus, more refined methods for estimating the proper targets for a decrease in deposition have to be found (Rapp, 1998). To achieve this, a better knowledge of the processes controlling surface water acidity and nitrogen content are needed. Monitoring of small, well defined catchments including hydrochemistry of precipitation, soil and runoff, is then a valuable tool. Although most principal processes are well known, their relative importance at different scales in time and space have to be better understood. An important issue is then the near-stream zone as a control for runoff chemistry, both concerning episodic acidity and nitrogen leaching (Bishop, 1991; LaZerte, 1993; Cirmo and McDonnell, 1997). To understand the recovery form acidification, the soil processes buffering against acidification, such as sulphate retention and cation exchange, are in focus. These are now being reversed and delays the recovery.

Objectives for the thesis

The main objective for this thesis was to explain how catchment processes were related to short-term variation and long-term trends in hydrochemistry of forest stream water. The field work for this study was conducted on the strongly acidified and nitrogen limited Kindla catchment, with a special emphasis on the relationship between the near-stream zone and both stream acidity and nitrogen leaching. In addition, time series of stream and soil water hydrochemistry at forested reference sites were analysed for changes in acidity status and nitrogen leaching. The main questions to be answered by the studies were:

- Is the near-stream zone a buffer against acidification or is it the main source of acidity to the stream by leaching of natural organic acids?

- Is the near-stream zone a source of nitrogen due to high rates of mineralisation, nitrification and leaching of organic matter, or is it a sink for inorganic nitrogen due to denitrification?

- Are Swedish forest streams recovering from acidification after three decades of reduced sulphur deposition?

- Are forest soils recovering from acidification as well, or is the base saturation of the soil still deteriorating?

- Is nitrogen leaching from forest soils increasing, due to the continuing high nitrogen deposition?

Background

Deposition history

Modern anthropogenic emissions of sulphur and nitrogen compounds to the air started during the industrialisation at the end of the 19th century and accelerated after the second world war (Mylona, 1996). The combustion of fossil fuels containing sulphur causes emission of sulphur dioxide that sooner or later converts to sulphuric acid in the atmosphere. Disastrous effects of the acid sulphur deposition on biota in surface water were noticed in the late 1960, and the measures for reducing the emissions of sulphur started. This resulted in that atmospheric deposition started to decline in Sweden after reaching a maximum around 1970 (Figure 1). The steepest trend in deposition decline was during the 1990s, due to implementation of international agreements to reduce sulphur emission as well as structural changes of industry in Eastern Europe.

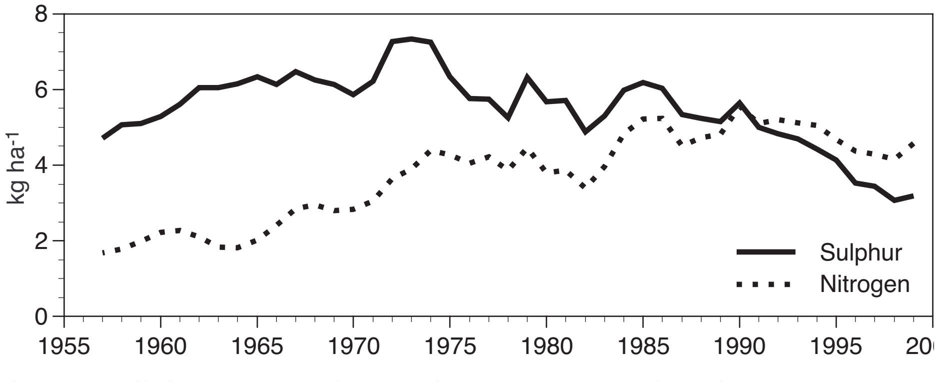

Figure 1. *Bulk deposition of Sulphur and Nitrogen in Central Sweden (moving average of three years). Data from IVL/MISU.*

For nitrogen, the deposition shows another pattern. Deposition of inorganic nitrogen has increased in Sweden at least until 1990 (Figure 1) with about equal amounts of nitrate and ammonium. During the 1990s, the nitrogen deposition levelled out and even showed tendencies to decline. Oxidised nitrogen compounds are formed during combustion by oxidation of elementary nitrogen in the air. In solution, oxidised nitrogen is found mainly as nitrate. Ammonium on the other hand is emitted from agriculture

Acidification history

Acidification of freshwater is a natural process that has been going on in Scandinavia since the last glaciation. Much of the buffering alkalinity of surface water originates from weathering of minerals in the soil within the catchment. As the most easily weathered minerals are consumed over the millennia, the weathering rate in the soil decreases, and pH and alkalinity in runoff decline. This trend is reinforced by the build up of the soil humus layer that leaches natural organic acids to the runoff water which lowers the pH. The evolution of surface water acidity can be studied by paleolimnological studies of sediments in lakes. Alkalinity and pH in a lake are reflected in the species composition of diatoms, a group of microscopic algae. By studying the silica cell walls of diatom species left in the sediment, the development of pH and alkalinity over time can be reconstructed. Results from 20 lakes in southern Sweden show how pH declined from about 6.8 to 5.5 after the last deglaciation until about 2000 years ago (Renberg et al., 1993). By then changes in land use started to impact runoff acidity. Forestland was turned to fields for grazing and agriculture which caused the pH to increase by about 0.7 units. When the land was afforested about 100 years ago, now with conifers, the pH declined below the pre-agricultural level, since conifers produce a more acid humus than the original deciduous forests. Further the acidification was strongly reinforced by industrial acid deposition, with detrimental impacts on fish and other living organisms. In lake Örvattnet in central Sweden, for example, diatom reconstruction of pH shows a decrease from about 6 to below 5 pH units during the 1960s (Ek et al., 1995).

There are however, only few examples where water chemistry time series are available that provide direct evidence of acidification during the 1960s (Bernes, 1991; Nyberg, 1995) since long term monitoring of acid sensitive waters started much later. Besides paleolimnology, another indirect way to investigate acidification is to use dynamic acidification models, such as MAGIC (Cosby et al., 1985), that models time series of water chemistry from present water chemistry, soil characteristics as well as the history of land use and atmospheric deposition. An application of the MAGIC model to 20 soil plots in southern Sweden suggested a varied response to anthropogenic acidification; from a negligible change up to a decrease of 2 pH units (Moldan, 1999). While there is good evidence of a severe impact from anthropogenic acidification in many surface waters in Southern Sweden, the effect in Northern Sweden has been less dramatic due to a lower deposition and a higher sulphur adsorption capacity (Karltun, 1995). For example, the diatom reconstruction of pH in lakes showed that there has been no regional pH decrease since pre-industrial times in the two northernmost counties in Sweden (Korsman, 1999). At present, only a minor influence of anthropogenic acidification in streams in northern Sweden has been detected during spring flow episodes (Laudon, 2000) though this might have been higher in the 1970s, when deposition was higher. Acid episodes during spring flow are a natural phenomenon caused by dilution of alkalinity by melt water and an increased content of organic acids due to a change in hydrological flow paths. The natural pH depression is, however, reinforced by anthropogenic acidity in the melt water (Bishop et al., 2000).

After the increasing trend of sulphur deposition peaked around 1970 (Figure 1) and deposition started to decline, there was no sign of recovery from acidification for a long time, with few exceptions (Forsberg et al., 1985; Bernes, 1991; Ek et al., 1995). Although the sulphate concentration decreased in surface waters, pH and alkalinity continued to decline. It was not until the 1990s that a large-scale recovery could be detected in the Nordic region (Stoddard et al., 1999; Wilander and Lundin, 2000; Skjelkvåle et al., 2001). The rate of recovery was very low, however, suggesting a recovery period extending over several decades. Predictions by the MAGIC model also indicated that only a minor improvement of water quality will take place in Southern Sweden during the following decades, even with further reductions in deposition (Moldan, 1999).

Nitrogen leaching

Nitrogen leaching causes eutrophication in coastal areas (Rosenberg et al., 1990) and may have affected oligotrophic lakes as well (Smith, 1982; Wilander, 1995). The dominant sources of nitrogen to the sea in Sweden are leaching from arable land, direct deposition on the water surface and point sources while leaching from forest soils is a minor source, and usually dominated by less available organic forms (Olsson and Löfgren, 1990; Lepistö et al., 1995). Only to the Bothnian bay, where other sources of nitrogen are small, forestland is a major source. Most focus has been put on NO_3 leaching since it is easily bioavailable and highly mobile in the soil. Nitrate leaching also contributes to acidification. In the 1980s warnings were raised that forest decline due to acidification would induce high rates of nitrogen leaching from Swedish forest soils (Fleischer and Stibe, 1989). This scenario was however not realised. There is no evidence of a negative effect on forest growth due to acidification in Sweden, and the forests are strictly nitrogen limited, with a few exceptions in south west Sweden (Binkley and Högberg, 1997). High rates of NO_3 leaching, > 3kg ha^{-1} yr^{-1}, in European forests has only been found at deposition levels above 9 kg N ha^{-1} (Dise and Wright, 1995), which in Sweden is exceeded only on the southwest coast. Still there might have been smaller increases in nitrate leaching due deposition in boreal forests with lower rates of nitrogen deposition (Lepistö, 1995). The long term effects of a nitrogen deposition several times above the natural background level on the forest ecosystem is, however, not known. Recently also the role of organic nitrogen for coastal eutrophication has been given attention. Organic nitrogen is generally considered recalcitrant, but recent studies has shown that the bioavailability of organic nitrogen in streams is greatly variable and higher than previously thought (Stepanauskas et al., 1999).

The history of surface water monitoring in Sweden

The Swedish monitoring program for surface waters started in the mid 1960s with the main focus on eutrophication and only comprised larger streams and Lake Mälaren. The catchments of the monitored rivers were large and included various types of land use. Since runoff from arable land has concentrations of alkalinity and nitrogen often several orders of magnitudes larger than runoff from forest soils, any changes in hydrochemistry of runoff from forest soils was masked by runoff from arable land. Hence there is no long term monitoring data of forest runoff during the period with the highest atmospheric sulphur deposition. It was not until 1983 that a network of regularly measured reference lakes was set up, today including 188 lakes distributed over Sweden (Wilander, 1997). In 1985 a program was initiated of hydrochemical and biological monitoring of small catchments not affected by agriculture or forestry in the recent past. The monitoring program was intended to generate information about the impact of long range transported air pollution on the whole ecosystem (Bernes, 1990). The program, called PMK 5, originally comprised 18 sites, but the number of parameters differed between the sites. Soil water for example, was only sampled at three sites. In the 1990s, dynamic modelling of catchment hydrochemistry became common. It then appeared that the Swedish reference sites were too large and complex to be suitable for such purpose. The monitoring of the reference sites were shut down in 1995 and replaced by a program for Integrated Monitoring (IM), presently including four sites with a much higher sampling intensity. Monitoring of stream hydrochemistry and bulk deposition, however, continued in about half of the PMK 5 sites. Both the PMK 5 and the IM programs are parts of International Co-operative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems (Pylvänäinen, 1993; ICP IM Programme Centre, 1998)

Importance of the near-stream zone

One aspect not considered in the PMK 5 program was the importance of the spatial variation within the catchment in relation to stream hydrochemistry. In this context the soils adjacent to the stream, or the near-stream zone, have been identified as an important control of runoff chemistry (Bishop et al., 1990; Cirmo and McDonnell, 1997). Although there is a general agreement on the importance of the near-stream zone, the influence on runoff chemistry is highly variable between catchments. In northern forested areas, near-stream zones have been found to be both natural sources and sinks for acidity and nitrogen (Bishop, 1991; LaZerte, 1993; Norrström, 1995; Hill and DeVito, 1997; Andersson and Lepistö, 1998; Lundin, 1998). The variable findings are, however, not surprising since these areas are hydrologically and biogeochemically complex. In the near-stream zone, water flowing along different pathways mixes and continues through soil layers with a high organic content where microbial activity and redox conditions vary significantly both in time and space. The geomorphology and the hydrological flow paths are likely to be crucial for the function of the near-stream zone, as well as the upslope conditions, deposition history and stage of acidification/recovery.

Study sites

This thesis present results from a field study of the near-stream zone in an acidified catchment. Further, time series of hydrochemistry in stream water and soil water at forested reference sites was analysed. In the following section, short descriptions of the study sites are given.

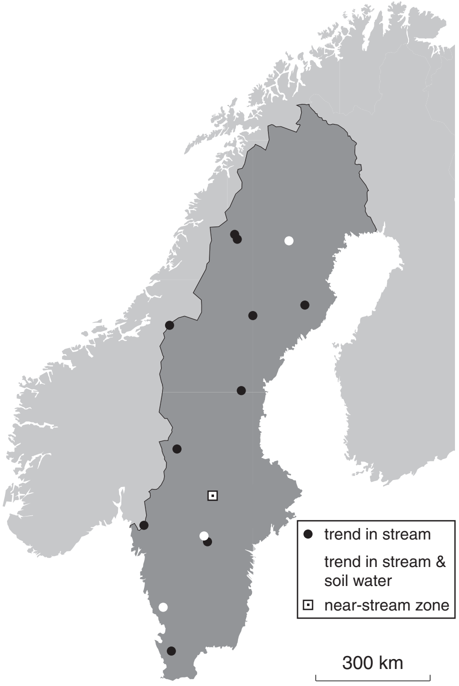

Figure 2. *Map over Sweden with locations of study sites.*

The study of the near-stream zone

The near-stream zone study (Papers I and II) was performed within the Kindla catchment in central south Sweden (Figure 2). This is a site within the International Co-operative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems, (ICP IM Programme Centre, 1998). The main study area was located along a stream, bordered with riparian peat and running from a small poor fen (0.2 ha). The mineral soil is a sandy silty till with low boulder frequency. Podzols are the dominant soil type of the catchment, but close to the stream there are dystric gleysols and histosols. No forestry activities have been carried out in the area during the last 100 years. Soil water and groundwater were sampled from 2-5 depths at a total of 21 locations. The locations were distributed along 4 transects aligned downslope towards the stream, perpendicular to the contour lines, at 4-5 distances from the stream.

Table 1. *Catchment area and median pH for study areas ordered from north to south. A comparison of the median pH during autumn 1995 in stream water was compared to 603 streams not affected by liming in the Swedish National Survey of Streams 1995 (RI95) and the result is presented as percentile value.*

Stream	Catchm. area km^2	pH median	pH percentile of RI95
Lillbäcken	2.17	7.17	69
Raurejukke	10.52	7.16	73
Laxtjärnsbäcken/Reivo	10.9	6.82	58
Svartberget	0.5	5.07	6
Höjdabäcken	4.9	6.06	11
Lilltjärnsbäcken	0.52	6.71	50
Stormyrbäcken	3.21	6.27	17
Lillfämtan	5.83	4.57	0.3
Kindla (near-stream zone)	0.19	4.53	0.3
Ringsmobäcken	1.4	4.31	0
LommabäckenN/Tiveden	1.04	4.28	0
Bråtängsbäcken	7.49	4.55	0.4
PipbäckenN/Berg	0.93	4.55	0.4
Tostarp	1.67	6.08	10

Trend studies

The study of trends in streams (Paper III) included 13 catchments distributed over Sweden (Figure 2) draining forested headwater catchments with areas varying from 0.52 to 10.9 km^2 (Table 1). In three of the catchments, Reivo, Tiveden and Berg, time trends of soil water was studied in one plot at each site with a well-developed podzol (Paper IV). All sites except one, Höjdabäcken, were included in the PMK 5 program (see above). No forestry activities have been performed within the catchments for several decades and all streams are natural except Svartberget, which has been ditched. Swedish forests are in general used for forestry, but most reference sites are located in areas unsuitable for forestry due to poor soils or steep and stony terrain. Hence, the representativity of the sites is biased with respect to Swedish forested areas in being more sensitive to acidification than forested areas in general. This can be illustrated by comparing the stream water pH of the reference sites to 603 randomly selected streams within the National Surface Water Survey not affected by liming (Wilander et al., 1998). The comparison shows that the majority of the reference streams are among the most acid streams in Sweden with a pH value below the 20th percentiles (Table 1). Only Lillbäcken and Raurejukke have relatively high pH values. If those sites are compared only to sites in Northern Sweden however, their pH are close to the median.

Results and discussion

Summary of papers

Papers I and II. Studies of the near-stream zone

In papers I and II the results from a study on temporal and spatial variability of the hydrochemistry in the near-stream zone of the small, forested Kindla catchment are presented. Groundwater and soil water were sampled using piezometers and ceramic cups respectively. During 1997, 24 locations were sampled three times. The piezometers were used for measuring groundwater levels, hydraulic potential and hydraulic conductivity. Stream water was sampled biweekly at two gauges located upstream and downstream from the study area. A more intensive sampling of stream water was performed during a spring flow episode. Stream flow was recorded continuously at the gauges. Bulk deposition and throughfall were sampled monthly and the results were used to set up an element budget for the catchment.

Both hydrological data and hydrochemistry showed that runoff was dominated by superficial groundwater. An upward flow component, measured as an increase in hydraulic potential with depth, was only measured occasionally in a few points, and there was no area of permanent upward flow. Furthermore, the concentrations of base cations and silica found in groundwater in upper soil layers in the near-stream zone were close to what was found in the stream. The concentrations in groundwater at 1 m depth however, were much higher. Thus the contribution from this flow path must have been negligible, presuming that there was no retention of silica as the groundwater moved towards the stream.

Paper I. Acidity control by the near-stream zone

The Kindla catchment was heavily affected by acidification with a stream water pH between 4.4 and 4.6 and an acid neutralising capacity (ANC) of -84 – -21 μeq L^{-1}. Sulphate was the dominant anion, which means that sulphuric acid is probably the major source of acidity. The sulphur transport out of the catchment, 70 meq m^{-2} yr^{-1}, was more than twice as high as the input with throughfall, 30 meq m^{-2} yr^{-1}, showing that there must have been an internal source of sulphate. Since the sulphate concentration decreased slightly in the groundwater along the transects towards the stream, this source for sulphate was rather located in upslope areas than in near-stream zone.

The tendency for a decrease in sulphate as the groundwater moved down the slope, and a correlation of low sulphate concentrations with anoxic conditions, implied microbial reduction of sulphate to sulphide in the near-stream zone. The sulphate concentration was positively correlated to calculated groundwater flow velocity, which was interpreted as an indication that sulphate reduction was more significant in locations that made smaller contributions to stream flow. A comparison of sulphate concentrations in groundwater with stream water also suggested that the influence of sulphate reduction was of minor importance for stream water chemistry.

There were no indications of buffering by cation exchange in the near-stream zone, except during a spring flow episode, and then at a small rate. A small peak in calcium concentration at the beginning of the episode could have been due to buffering of acidity by cation exchange in the near-stream zone. However, the influence on stream water acidity was then only c. 0.02 meq L^{-1}.

The near-stream zone was a source for organic acids, but these were overshadowed by sulphate during base flow. During the episode, though, the impact of organic anions became more pronounced. The sulphate concentration during the episode decreased due to dilution of groundwater with melt water and precipitation lower in sulphate, while the concentration of organic anions increased due to flushing of organic matter. At the flow peak, the concentration of dissociated organic acid anions was equal to that of sulphate anions.

Paper II. N-control by the near-stream zone

Concentrations of inorganic nitrogen in groundwater and soil water were generally low. In the upslope locations no inorganic nitrogen was found in groundwater at all. In near-stream locations, nitrate only occurred occasionally and locally, usually when the groundwater level was lowered. Furthermore, nitrate was predominantly found in locations with relatively high pH and high concentrations of dissolved oxygen. In the stream, nitrate only occurred temporarily and mainly at concentrations below 50μg N L^{-1}. It was concluded that the near-stream zone was a source for nitrate, although at a low level. During spring flow, however, negligible nitrate concentrations were interpreted as a possible retention by denitrification.

The ammonium concentrations showed a totally different distribution pattern compared to nitrate, both in time and space. In the groundwater, ammonium was found at stable concentrations between 100 and 400 μg L^{-1} in a few locations within the near stream zone with low oxygen concentrations. Since no ammonium was found in the stream, with the exception of the spring flood, it is possible that the ammonium rich locations were primarily soils with low hydraulic conductivity that made a small contribution to runoff. During the spring flood, an ammonium concentration up to 90 μg N L^{-1} was detected.

The near-stream zone was concluded being the main source for organic nitrogen since concentrations increased progressively as the groundwater moved down the slope. In the stream, the C/N ratio was close to the ratio in the transition zone between organic and mineral soil in the near stream soil profile. Hence, this soil layer was probably the main source of organic matter during base flow. During the spring flow there was a peak in organic nitrogen with a relatively low C/N ratio which was interpreted as a flush of fresh, microbially derived, organic matter.

Paper III. Trends in stream water chemistry indicating recovery

Paper III presents time trends of water chemistry between 1985 and 1998 in 13 forest streams. In nine of the catchments, bulk deposition was measured as well. During this time, bulk deposition of sulphate decreased at all sites. This was accompanied by somewhat weaker declines of sulphate concentrations in stream water. The catchments were either in balance with respect to sulphate or had a net loss. The strength of the sulphate trends in both deposition and stream water became stronger from north to south, following a gradient of increasing anthropogenic influence. Five chronically acidic sites in the southern half of the country showed weak signs of recovery from acidification in terms of increasing concentrations of ANC and decreasing concentrations of hydrogen ions, corresponding to annual increases of 0.01 pH units. Changes in stream discharge and concentrations of marine salts and organic acids could not explain the observed decline in acidity. The results were thus interpreted as recovery from anthropogenic acidification. For the northern half of Sweden, changes in water chemistry could be attributed to natural variation in climate and marine influence, and the effect of anthropogenic acidification was negligible.

Paper IV Temporal and spatial variation in soil water chemistry.

Paper IV presents 8-11 years of soil water chemistry from E- and B-horizons in three acid forest soil plots within monitored catchments. Five years of sampling also included the B/C-horizon. The soil water was sampled by ceramic cup suction lysimeters, with 3 – 7 replicates at each level. Any sign of recovery from acidification was investigated along with indications of sulphate mobilisation and soil acidification.

The sulphate concentration declined in soil water at most sites and levels with the steepest decline in the E-horizons where it was 3-4% annually. The decline in the E-horizon was smaller compared to changes in deposition, which was interpreted to indicate mineralisation of organic sulphur form the superimposed soil layer. In the most acidic site, Tiveden, the sulphate concentration was higher in the B/C horizon compared to the B-horizon, which may indicate desorption of sulphate. The decline in soil water sulphate was to a large extent matched by decreases in Ca and Mg. Still there were tendencies of an improving acid status in the soil water at Tiveden and Berg in terms of increasing ANC and decreasing H^+. In Tiveden, the ratio $Ca/(H^+)^2$ showed negative trends in both E- and B-horizon, which was interpreted as continuing acidification of the soil. A high influence of sea-salt around 1990 was found at all sites, with the largest impact at Tiveden. Here the sea-salt pulse caused a peak in H^+ in the soil water. The soil water generally showed faster response to changes in deposition of sulphate and sea-salt compared to stream water.

Hydrology of the near-stream zone

The groundwater flow pattern in the near-stream zone varies greatly, depending on the geomorphology of the catchment (Hill and DeVito, 1997). In deep aquifers with highly permeable soils, deep flow paths are important and close to the stream a discharge area with upward flow can be found. In the till soils covering most of the Scandinavian forests however, there is a marked decrease in hydraulic conductivity with increasing soil depth. This results in predominantly lateral flow in superficial groundwater (Lundin, 1982; Bishop et al., 1990) while the vertically upward flow is less important for the total discharge (Bishop, 1994). This was also the case at Kindla where no area of permanent discharge was found in the near-stream zone, being defined as the area adjacent to the stream where the groundwater level was found in the organic soil at some time during the year.

The wet conditions in the near-stream zone favour the growth of *sphagnum* mosses and formation of peaty soils. The depth, extent and hydraulic properties of the peat influence the flow pattern of the groundwater through the near-stream zone. The peat cover can be divided into a superficial layer consisting of living and undecomposed dead vegetation and an underlying anaerobic layer of more humified peat. The superficial layer is usually thinner and has a higher hydraulic conductivity compared to the underlying layer. Groundwater may flow either in the mineral soil under the peat layer or through the superficial peat layer (Figure 3). The latter flow path can be expected to become more important when the groundwater level is elevated. Flow through the deeper humified peat layer is usually low but may be enhanced by macropores (Norrström, 1995). An

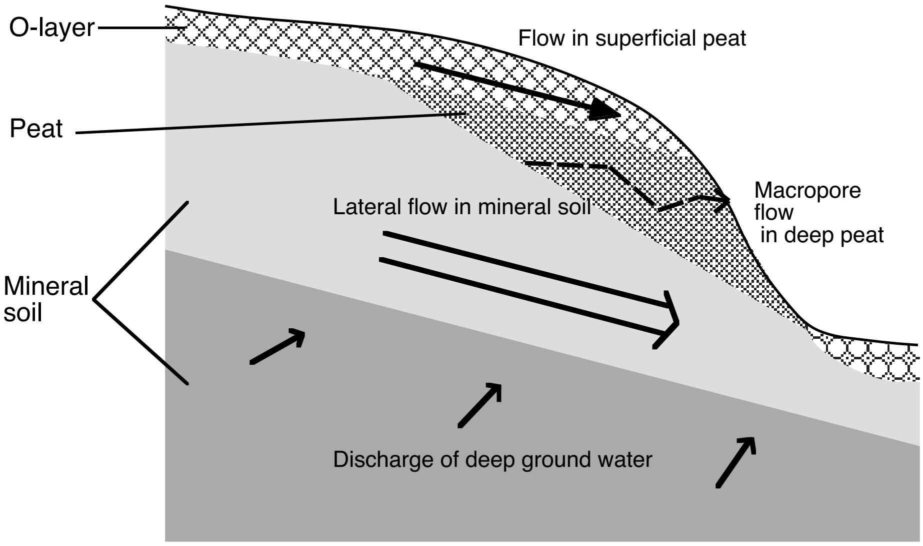

Figure 3. *Possible hydraulic flow paths in the near-stream zone in Scandinavian till soils with lateral flow in the superficial mineral soil as the dominating path.*

intermediate layer between the peat and the mineral soil with a high hydraulic conductivity and organic content has also shown to be an important flow path (Bishop et al., 1995). In Kindla, the groundwater table was close to the ground surface even at base flow (Paper I). Here the highly conductive superficial peat may have been a significant flow path, especially during flow peaks. A comparison of the C/N ratio in the dissolved organic matter in the stream water and groundwater at different levels, indicated however that the intermediate layer below the peat was the most important flow path. These results could however, also have been caused by a higher leaching rate of organic matter in the intermediate zone.

Since different biogeochemical processes dominate in different soil layers, the flow pattern in the near-stream zone is crucial to its influence on discharge chemistry. There are however, few studies that integrate hydraulic measurements with biogeochemical studies. Such studies are difficult to perform because of the large spatial variability. Instead the important flow paths can be pointed out by comparing the chemistry in groundwater from different locations in the near-stream zone, with the chemistry in stream water (Fiebig et al., 1990; Norrström, 1995)

Influence on acidity by the near-stream zone

The near-stream zone has been argued to act both as a natural buffer against acidification by cation exchange (Norrström, 1995) and as a natural source of organic acidity (Bishop et al., 1990). The organic-rich soils offer a large pool of cation exchange sites and the base saturation has been found to be higher in downslope wetlands compared to upland soils (Norrström, 1995; Giesler et al., 1998). At an earlier stage of acidification, hydrogen and aluminium ions in groundwater from upland areas may be exchanged with base cations in the near-stream zone, then acting as a buffer against acidification (LaZerte, 1993). As the acidification of the soil continues, the base cation supply in the near-stream zone becomes exhausted and the acidification of the runoff increases.

The results from Kindla did not show any influence from ion exchange in the near-stream zone on stream water acidity in the present acidified state, but there may have been a buffering effect at earlier stages of acidification (Paper I). The near-stream zone at Kindla was rather a source for acidity from leaching of natural organic acids which is in accordance with many other studies (e.g. Bishop et al., 1990; LaZerte, 1993). The influence of organic acids was, however, overshadowed by sulphuric acid. It was only during the spring flow episode that organic acids became important (Paper I). In low acid deposition areas as in Northern Sweden however, the organic acids are the main source for acidity, especially during flow peaks (Laudon and Bishop, 1999).

Dissimilatory microbial redox reactions of inorganic sulphur compounds can also have an impact on the acidity of the discharging groundwater. In the water-saturated organic soil near the stream, anaerobic conditions easily develop resulting in microbial reduction of sulphate into sulphide (DeVito, 1995). The process is hydrogen consuming and hence microbial sulphate reduction may be a sink for acidity. However, the process is reversible, so that during dry conditions when the water table is low, sulphide is oxidised as the soil is aerated. This has an acidifying effect on the soil solution. In riparian peat the hydraulic conductivity is highly variable, and the sulphate concentration has been found to be lowest in locations with the lowest permeability (Paper I and Norrström, 1995). The results indicate that sulphate reduction has the largest impact on the sulphate concentration in stagnant locations with a low contribution to runoff. In Kindla this may however be contradicted by seasonal pattern in stream water chemistry with decreasing SO_4 concentrations during summer and high concentrations during autumn (Paper I). A study with stable isotopes of S in SO_4 in the IM reference catchment F1 at Gårdsjön could show that dissimilatory SO_4 reduction caused a decline in SO_4 during summer, and that oxidation of the earlier reduced compounds caused a peak in SO_4 when the groundwater level was raised in autumn (Mörth et al., 1999). Hence it is likely that dissimilatory redox processes are responsible for the observed seasonal variation in SO_4 concentration in Kindla.

Nitrogen dynamics in the near-stream zone

Nitrogen cycling in forest ecosystems

In most parts of Sweden, the forest ecosystem is markedly nitrogen limited and any available nitrogen is instantly utilised by plants and micro-organisms (Binkley and Högberg, 1997). A large portion of nitrogen deposition on forests is already taken up in the canopy. This can be seen in a lower nitrogen flux in throughfall compared to bulk deposition measured in open field, although the total deposition in a forest is higher due to dry deposition (Paper II, Hallgren et al., 1997). The remaining nitrogen is then assimilated in the upper soil horizons, so that inorganic nitrogen is rarely found in the mineral soil in most parts of Sweden. The nitrogen in deposition only stands for a smaller part of the nitrogen demand of the trees. While the atmospheric deposition ranges between 0.2–1.0 g m^{-2} yr^{-1}, the internal circulation of nitrogen is in the range of 0.5–10 g m^{-2} yr^{-1} in Scandinavian forests (Löfgren, 1991). The internal cycling includes litterfall, mineralisation and plant uptake. Microbial nitrogen fixation is generally low, >0.1 g m^{-2} yr^{-1}, in Scandinavian forest ecosystems. The magnitude of the nitrogen fluxes can be compared to the vast pool of organic nitrogen, which is between 30 and 1000 g m^{-2} (*op. cit.*). Organic nitrogen is primarily mineralised to ammonium, that can be further transformed into nitrate through nitrification. Measurements of gross nitrification using ^{15}N dilution has shown both high (Stark and Hart, 1997) and low (Tietema, 1998) nitrification rates in coniferous forest soils. The competition for available nitrogen is high in the boreal forest ecosystem which is shown by the fact that both trees and shrubs in this type of ecosystem can take up organic nitrogen and thus bypass the mineralisation step in nitrogen cycling (Näsholm et al., 1998).

The near-stream zone as a source for nitrogen

A high pH and base saturation generally favour nitrogen cycling processes. Since downslope areas with the groundwater level close to the ground surface, such as near-stream zones, have a relatively high pH and base saturation, the nitrogen turnover is expected to be high (Lahti and Väisänen, 1987; Giesler et al., 1998; Högberg, 2001). These areas have the potential to be either sources or sinks for inorganic nitrogen in runoff. Budget studies have shown on both cases with differences depending on hydrological flow paths and concentrations of nitrogen in the groundwater coming from upland areas (Hill and DeVito, 1997; Lundin, 1998). At Kindla nitrate was only found in near-stream sites with relatively high pH and high concentrations of dissolved oxygen. Since nitrification is an oxygen demanding process and favoured by high pH, the findings suggested that the nitrate found in the soil originated from nitrification coupled to mineralisation of organic matter in the soil. Hence, the near-stream zone was a source of nitrate to runoff at Kindla. In the stream water, nitrate was found during periods of increasing silica concentrations. This further supported the hypothesis that nitrate in the stream had a microbial origin, and not originating from precipitation passing directly to the stream. A high contribution of precipitation would give a decrease in silica concentration, which was found during a spring flow episode when no nitrate was found in the stream water. The importance of flushing of pre event nitrate from areas close to the stream for high peak concentrations of nitrate has also been found for other forested catchments in the Nordic region (Andersson and Lepistö, 1998) and Canada (Creed and Band, 1998). It is possible that the near-stream zone being the main source of nitrate in nitrogen limited forest catchments is a general phenomena in Fennoscandia, which was indicated by a regional study of correlation between catchment characteristics and nitrogen leaching from 20 catchments in Sweden and Finland (Lepistö et al., 1995). Nitrate export was then related to a high stream density, i.e. stream length/area, which should be related to a high occurrence of near-stream areas.

A general feature of near-stream zones is that they are more or less sources for organic nitrogen (Hill and DeVito, 1997; Lundin, 1998). The organic matter however, mostly consists of humic substances that are not easy available for algal growth and hence have a low eutrophying effect. During the spring flow episode however, there was a peak in organic nitrogen with a decrease in the C/N and Abs/TOC ratios that indicated a release of fresh microbial carbon that is more available compared to humic substances (Paper II). A change in the quality of organic nitrogen during spring flow episodes was also found in two forest streams in Northern Sweden (Stepanauskas et al., 2000).

The near-stream zone as a sink for nitrogen

Although most nitrogen in runoff may originate from near-stream areas, this does not mean that they are net sources for inorganic nitrogen. Internationally, near-stream zones are recognised as important nitrogen retention sites, especially in areas with a high nitrate leaching (Haycock et al., 1993). Several processes may be involved (Figure 4), but denitrification is the process that has been paid most attention since it removes available nitrogen from the system whereas other processes such as plant uptake and microbial immobilisation only transform mobile forms into less mobile forms. Denitrification is the microbial reduction of nitrate into gaseous compounds such as dinitrogen oxide and elementary nitrogen. The process occurs under oxygen free conditions and is thus favoured by both the water-saturated conditions (Davidson and Swank, 1986; Ambus and Christensen, 1993) and the high content of organic matter in the near-stream zone (Federer and Klemedtsson, 1988). In most forests in Sweden, however, denitrification is not likely to be important during most time of the year because of the low concentrations of nitrate in the soil. During events with temporarily elevated nitrate concentrations however, denitrification may be important. Further, after clear-cuts, when high nitrate concentrations are found (Vitousek et al., 1979) denitrification in downslope wetlands and near-stream zones may also be important (Rosén and Lundmark-Thelin, 1986; Jacks et al., 1994). In the near-stream zone at Kindla, denitrification was probably limited by the low concentration of nitrate. During the spring flow however, a high retention of nitrate from the snow pack and precipitation might have been caused by denitrification. Nitrogen retention in the near-stream zone during snowmelt events was also indicated at two sites in Sweden and Finland (Andersson and Lepistö, 1998).

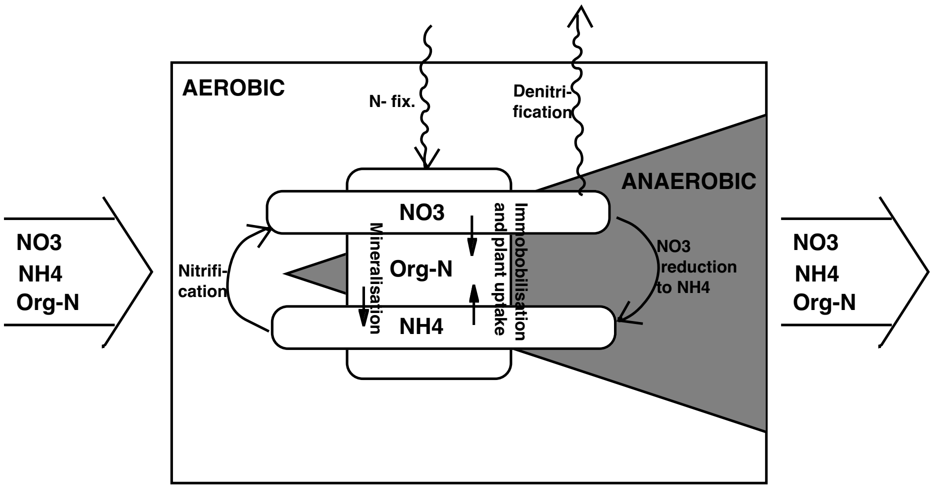

Figure 4. *A conceptual model of the nitrogen turnover in a riparian wetland with groundwater flowing through the soil. Closer to the stream anaerobic processes become more important.*

Statistical Implications of the Temporal Variation of Hydrochemistry

Fluctuations in groundwater level cause variability in stream water chemistry due to changes in transit time and alteration of flow paths (Lundin, 1982; Rodhe, 1987; Bishop, 1991). The stream water chemistry generally follows a seasonal pattern superimposed by episodes of high flow during snowmelt or rainfall. The natural variation of stream water chemistry causes time series with skewed distributions and a strong serial correlation and thus not suitable for linear regression. A commonly used method for detecting trends in such data is the non-parametrical Seasonal-Kendall method modified to correct for ties and serial correlation by Hirsch and Slack (1984). The method tests the significance of trends in ranked data, only comparing recordings from the same season. In paper III and IV we used a similar method called Seasonal-Kendall with Covariance Inversion, which also allows combined tests of many plots or sites (Loftis et al., 1991). A corresponding estimation of the slope is Theils slope on a seasonal basis, which is the median of between year changes in concentration (Helsel and Hirsch, 1992). For inorganic nitrogen the Seasonal-Kendall test may be less suitable, since most of the data are close to the detection limit. A small change in sample handling or analytical method could then introduce a trend, since the majority of near-null data is more important for the non-parametrical test compared to a few samples with high concentrations. This can be overcome by setting to zero all concentrations below a certain limit, where the analytical error is assumed to be the major source of variation.

Are there hazards for increased N-Leaching?

Although there are evidence for increasing nitrogen leaching from boreal forests due to nitrogen deposition at rates below 9 kg ha^{-1} yr^{-1} (Lepistö, 1995), this does not seem to be a general phenomena in Sweden. In a study of trends in flow normalised transport of nitrogen from 66 riverine sites in Sweden 1971-1994, upward trends in transport of nitrate and total nitrogen were only found downstream from lakes. This could be explained by a decreased retention due to reductions in sewage emissions of phosphorus (Stålnacke et al., 1999). In most of the reference streams, nitrogen leaching was low, <2.1 kg N ha^{-1} of Tot-N and <0.25 kg N ha^{-1} of inorganic nitrogen, i.e. nitrate and ammonium (Table 2). Only in the two southernmost sites, nitrate leaching was of relevance for acidification and eutrophication. The transport may, however, be underestimated since a high proportion of the transport often occurs during short episodes not detected by the biweekly sampling. In the stream at Kindla, for example, 72% of the ammonium and 30% of total organic nitrogen transport took place during a few days (Paper II). Due to the uncertainties in nitrogen transports from small catchments, a trend test was made on concentrations. To avoid effects of a change in detection level over time (see above) all values below 10 μg L^{-1} were set to zero. Although only few changes of high statistical significance were found, there was a tendency to an increased leaching of ammonium in northern Sweden. The only increasing trends

Table 2. *Average annual transport and p-value of trend in concentration (Seasonal-Kendall) of ammonium (NH_4), nitrate (NO_3) and total nitrogen (Tot-N) and p-value of trend for TOC/TON in forest streams. Preliminary results.*

	Years	Transport			Direction and p-value of trends			
		NH_4	NO_3	TotN	NH_4	NO_3	Tot-N *)	TOC/TON *)
		kg N ha^{-1} yr^{-1}			μg N L^{-1} yr^{-1}			yr^{-1}
Lillbäcken	1985-1998				+ 0.8	- 0.8	+ 0.001	- 0.003
Raurejukke	1985-1998	0.05	0.17	1.78	+ 0.1	+ 0.5	+ 0.001	- 0.006
Laxtjärnsbäcken/Reivo	1985-1998	0.02	0.07	0.99	+ 0.4	+ 0.02	+ 0.002	- 0.002
Svartberget	1985-1998				+ 0.8	- 0.6	+ 0.003	- 0.01
Höjdabäcken	1985-1998				+ 0.7	- 0.2	+ 0.004	- 0.02
Lilltjärnsbäcken	1985-1998	0.06	0.14	1.80	+ 0.05	- 0.2	+ 0.01	- 0.02
Stormyrbäcken	1985-1998				+ 0.5	+ 0.09	+ 0.2	- 0.02
Lill-Fämtan	1986-1998	0.04	0.09	1.58	+ 0.6	+ 0.9	+ 0.003	- 0.02
Ringsmobäcken	1985-1998	0.05	0.15	1.36	- 0.3	- 0.03	+ 0.003	- 0.009
LommabäckenN/Tiveden	1985-1998	0.10	0.15	2.06	- 0.1	- 0.6	+ 0.01	- 0.6
Bråtängsbäcken	1985-1998	0.04	0.15	1.83	- 0.4	+ 1	+ 0.002	- 0.1
PipbäckenN/Berg	1986-1998	0.15	0.87	2.74	+ 0.4	+ 0.001	+ 0.002	- 0.04
Tostarp	1989-1997	0.04	4.61	5.71	- 0.8	- 0.5	+ 0.8	- 0.2

*) Time series started 1987.

in nitrate concentrations with $p<0.05$ were found at Reivo and Berg, which also were the only sites where there was a significant downward trend in water discharge (Paper III). Elevated nitrate leaching might then have occurred through mineralisation of previously submerged organic matter when the groundwater table was relatively low. The annual change in concentration in Berg, however, was low, 0.6% of the median. For Reivo it is not meaningful to estimate the rate of change since almost 50% of the values were below 10μg L^{-1}.

More surprising are increaseing and highly significant trends for Tot-N throughout the country. Tot-N mainly consists of organic nitrogen and the increase in Tot-N could be due to an increase in leaching of organic matter. This however, only explained a smaller part of the changes, since only few significant increases in organic matter were found in the streams (Paper III). The highly significant negative trends in the ratio total organic carbon to total organic nitrogen, TOC/TON, indicate that it is the quality of organic matter that has changed over time, rather than the quantity. At present there is no explanation to this trend, but since the changes are most pronounced in northern Sweden where deposition is lowest, they are not likely to be related to deposition.

Recovery from Acidification

The trend tests of stream water chemistry presented in paper III showed a recovery in five chronically acidic sites in southern Sweden. Since those streams are among the most acidic ones in Sweden, the results indicate recovery in the most damaged surface waters. Recovery was earlier found in less acidic lakes, with measurable alkalinity (Wilander, 1997). There are few direct proofs of acidification in Sweden since the monitoring of acid sensitive water started when deposition already had passed its maximum level. The fact that acidity decreased in those streams as a response to decreasing SO_4, and that these changes could not be explained by natural sources of variation in stream water chemistry, however, can be seen as indirect evidence that these streams are anthropogenically acidified. The streams in northern Sweden did not show such a response. Here, anthropogenic acidification is small compared to the natural variation, at least during base flow.

Although there are now finally positive indications of a general recovery from acidification after three decades of decreasing sulphur deposition, the rates of recovery are very small, often in the range of a few μeq L^{-1} Yr^{-1} of H^+. The slow rate of recovery is partly due to the fact that the soil buffering processes that earlier protected runoff from acid rain now are reversed and prolonging the recovery phase. In the following sections some aspects governing the rate of recovery that were brought up by the results in papers III and IV will be discussed.

The inertia of the soil sulphur pool delays recovery

When precipitation percolates through the soil, the acidity is partly neutralised by ion exchange and weathering. In the podzols dominating boreal forests, the cation exchange capacity in the organic matter of the O- and B-horizons is high, but the base saturation is low. In Sweden for example, the average effective base saturation is approx. 20% in the O-horizon and 4 % in the B-horizon (Karltun, 1998). Ion exchange is a relatively fast process, and the average cation content in soil water will be controlled by the exchangeable pool in the soil. Since soils in the boreal forest are naturally acid, only a part of the acidity in deposition will be neutralised. In the time range of at least a few years, the base saturation of the soil may remain largely unchanged and the instantaneous acidifying effect of sulphuric acid in deposition will be that SO_4 acts as a mobile anion (Reuss and Johnson, 1986). This mobile SO_4 transports a larger amount of acidity from superficial soil layers, compared to preindustrial conditions. The increased acidity will then consume a larger portion of the alkalinity supplied by weathering in the mineral soil resulting in a decline in pH and alkalinity in runoff. The mobility of SO_4, however, is not total and retention of SO_4 by assimilation, adsorption and dissimilatory reduction, associated by consumption of acidity, are important buffering mechanisms against acidification. When deposition declines, these processes may be reversed which will prolong the recovery process.

The first response observed in surface waters when sulphur deposition declines is that the SO_4 concentration decreases (Stoddard et al., 1999). The decrease of SO_4 in surface waters are, however, generally less compared to the deposition trend, which was exemplified in paper III. The reason for this is the reversal of SO_4 retaining processes. Being a macronutrient, SO_4 is assimilated by plants (Bringmark, 1977) and micro-organisms and incorporated into the organic soil pool from where it later can be mineralised (Mayer et al., 1995). Furthermore, the SO_4

ion can be adsorbed to Fe and Al oxides in the B-horizon in podzols (Karltun, 1995). As deposition declines, the soil may become a net source of SO_4 in the runoff, which was the case in four of nine catchments in paper III. Net release of SO_4 has also been found in other small Swedish forest catchments (Löfgren et al., 2001) as well as for catchments drained by large rivers (Wilander, 2001). At the sites Tiveden and Berg (paper IV), smaller declines of SO_4 in soil water in the E-horizon compared to deposition, along with decreasing concentrations and trends of SO_4 in soil water with depth, suggested that both mineralisation and desorption were important for delaying recovery from acidification. The importance of both processes was further exemplified in the experimental reversal of acidification at lake Gårdsjön (Moldan et al., 1998). There a whole catchment was covered by a roof and precipitation was replaced by water of assumed preindustrial composition, giving an 80% decrease in SO_4 deposition. The immediate response was a decrease in the SO_4 concentration in the A- and E-horizons, followed by a more gradual decrease in the B-horizon, (Giesler et al., 1996) and runoff (Moldan, 1999). This indicated a high influence of desorption and a minor source for SO_4 from mineralisation of the organic pool in the A-horizon. This was also confirmed by studies on stable isotopes in SO_4 (Torssander and Mörth, 1998). The relative importance of mineralisation may, though, increase over time as the adsorbed pool reaches a new equilibrium level. There seems to be a large variation in sulphur dynamics between sites, which can be illustrated by comparing the roofed Gårdsjö catchment with the Kindla catchment (paper I). Data from the Integrated Monitoring program at Kindla indicated that mineralisation in the O-horizon was a larger SO_4 source than deposition. The S-flux in the throughfall was only 0.46 g m^{-2} y^{-1}, compared to 1.19 g m^{-2} y^{-1} in the E-horizon. The contribution from desorption was probably small (Löfgren et al., 2001).

The influence of dissimilatory redox processes on SO_4 dynamics in runoff has been discussed above. The process is mainly a source of seasonal and between year variation but it will probably not delay recovery like mineralisation and desorption.

SO4 decrease is counteracted by BC decrease.

A commonly used parameter for the acidity status of surface water is the acid neutralising capacity, ANC, (Stumm and Morgan, 1981) which can be defined

$$\text{ANC} = (\text{Sum of proton acceptors}) - (\text{sum of proton donors}) \qquad (1)$$

In natural waters below pH 7, ANC can be simplified to:

$$\text{ANC} = \text{RCOO}^- + \text{HCO}_3^- - \text{H}^+ - \text{Al}^{n+} \qquad (2)$$

$RCOO^-$ stand for organic anions and all concentrations are in eq L^{-1}. Given charge balance considerations, ANC can also be calculated by the difference between cations and anions (Reuss and Johnson, 1986), without protolytic properties within the pH range of natural waters (2 > pKa > 12):

$$\mathrm{ANC} = \mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{K}^{+} + \mathrm{Na}^{+} - \mathrm{SO}_4^{2-} - \mathrm{Cl}^{-} - \mathrm{NO}_3^{-} \qquad (3)$$

The cations Ca^{2+}, Mg^{2+}, K^+ and Na^+ give a positive contribution to ANC according to eq (3), and are called base cations, BC. Recovery from acidification can be defined as an increase in ANC towards a pre-industrial value. In acidic waters were HCO_3 is negligible, recovery can also be defined as a decrease in H^+ or Al^{n+} by using eq (2) and assuming average $RCOO^-$ to be constant over long time periods.

When the SO_4 concentration decreases in runoff as S-deposition declines, an increase in ANC is expected (Eq 3). The SO_4 decrease is, however, often counteracted by a decrease in BC with a large regional variation depending on deposition history and site characteristics. In most regions in Northern America, a decrease in SO_4 was balanced by an equal or even larger decrease in BC, resulting in a constant or deteriorating alkalinity (Stoddard et al., 1999). In Norwegian surface waters, however, BC concentrations were almost constant and a decrease in SO_4 resulted in an improved ANC or alkalinity (Skjelkvåle et al., 2001). In the Swedish reference streams (paper III), there was a decrease in BC for most sites with a SO_4 trend $>1\mu$eq L^{-1} Yr^{-1}, but the BC decrease only partly counteracted the SO_4 reduction enabling a small recovery to take place.

The main reason for the decline in BC is that when the acid deposition goes down, the rate of ion exchange will also decrease. This can also be expressed by using the mobile anion concept. A decrease in SO_4 will be followed by an equivalent decrease in the sum of cationic charge (SCC) with the relative decrease in different cations depending on the composition of the exchangeable pool.

A decrease in SCC will also affect the recovery phase by changing the equilibrium between cations of different charge in the solute and the exchangeable phase (Matschonat and Vogt, 1998). In the mineral soil, the exchangeable acidity mainly consists of Al and the effect of SCC can be exemplified by the equilibrium of Al and Ca. The relations between cations in the soil solution and the exchangeable phase can be expressed with the Gaines-Thomas equation which for Ca and Al can be written:

$$\frac{\left[Ca^{2+}\right]}{\left[Al^{3+}\right]^{2/3}}\frac{\gamma_{Ca}}{\gamma_{Al}{}^{2/3}} = \frac{E_{Ca}}{E_{Al}{}^{2/3}} \cdot K_s \qquad (4)$$

where γ_ι, are the activity constants, E_i are the molar fractions of the exchangeable phase and K_s is a constant (Reuss and Johnson, 1986). The change in the ratio between γ_ι, is small at the low ionic strength of natural waters (Stumm and Morgan, 1981). A decrease in SCC, here Ca + Al, will then lead to an increase in the ratio Ca/Al and a decrease in the ratio E_{Ca}/E_{Al} to satisfy eq (4). This has also been shown both theoretically and empirically to be valid also when all major cations were included, at least when SCC was < 1 mmol L^{-1} (Matschonat and Vogt, 1998). In other words, this could mean that lowering the SCC will give an increase in ANC in the solution and a decreased base saturation of the soil. For the recovery process, this would imply that during decreasing SO_4 deposition, runoff may recover while soils will continue to get acidified.

Are the soils deteriorating while surface waters are recovering?

An acidification of the soil while runoff is recovering was suggested for Norwegian streams by Kirchner and Lydersen (1995). The recovery of surface water may then only be temporary as long as the SO_4 deposition is declining. Results from some sites in southern Sweden show that this might be the case there as well. At Tiveden, runoff pH increased (paper III) while decreases in the $Ca/(H^+)^2$ ratios in soil water indicated deteriorating base saturation of the soil (paper IV). The extreme conditions created by the experimental reversal of acidification at Gårdsjön also resulted in an increase in ANC in runoff and simultaneous acidification of the soil. In the adjacent reference stream however, there was no soil acidification, but a recovery in the stream took place (Moldan, 1999). The application of a dynamic acidification model (MAGIC) to the Berg catchment also suggested a decline in base saturation between 1985 and 1995 (Krám et al., 2001). Application of MAGIC to 17 forested sites in Southern Sweden predicted increasing ANC in runoff and continued soil BC depletion in half of the sites while the soil recovered in the other half (Moldan, 1999). Results from the Swedish National Survey of Forest Soils and Vegetation did not show on any significant changes in total acidity and saturation of Ca+Mg in the soil between c. 1985-c.1995 in any of the regions in Sweden (Karltun, 1998). The MAGIC-modelling, however, suggests the potential for a large variation in the development of soil acidity between sites.

Seasalt influence

Episodes of high deposition of sea salt can cause severe acidification in runoff from acid soils (Wiklander, 1975). The mechanism behind the salt effect is that cations, mainly Na, from seasalt is exchanged with H^+ and Al in the soil pool of exchangeable cations. The release of Al is reinforced by the effect of increasing SCC as described above. Dramatic episodes are reported from Norway, where intensive storms from the south-west in January 1993 caused elevated H^+ and Al concentrations in runoff resulting in severe fish death (Hindar et al., 1994). In Sweden episodes of high seasalt deposition also occur with a prominent spatial and temporal pattern (Gustafsson and Larsson, 2000). In January 1989 a pronounced episode of dry deposition of sea salt was detected for southern Sweden (Franzen, 1990). The acidifying effect on soil solution could, for example, be seen in the E-horizon in Tiveden as a peak in Cl and H^+ (paper IV). Although sea salt episodes might have a dramatic, but short-term effect on runoff acidity, there is no long term acidifying effect of such episodes (Andersen and

Seip, 1999). The peak in Cl concentration found in most of the reference streams during the early 1990s (paper III) might have delayed a statistical verification of a recovery for a few years, but should not have affected the overall trend (paper IV). In the case of Al though, the seasalt episode might have caused a small increase, prolonged over several years, which then could explain the upward trends in Al concentration found in soil water at the three reference sites.

Direct response of changes in sulphur deposition in surface waters

Although the acidity status of surface waters are mainly controlled by processes in the catchments, acidity in rain falling directly on surface water or on saturated near-stream areas, will have an instantly detrimental effect on the buffering capacity of the water. Lakes with small catchment areas compared to lake areas are thus the first to become acidified, but also the first where recovery is to be found as deposition declines. An example of that could be a perched seepage lake in the Adirondacks in eastern USA (Stoddard et al., 1998). In all other lakes in that region, a SO4 decrease was counteracted by an equal decrease of BC, resulting in no recovery in terms of increased ANC. In the seepage lake, however there was no change in BC and a relatively large, although not significant, increase in ANC.

A direct response to changes in deposition is also expected during snowmelt episodes. Acid episodes during spring flow are a natural phenomenon caused by dilution of base flow alkalinity by melt water and increased concentration of organic acids due to a change in flow paths (Laudon and Bishop, 1999). When precipitation is polluted by sulphuric acid, this will further depress pH and ANC during spring flow. The anthropogenic component of spring flow pH decline is strongly linked to the SO_4 content of the snowpack (Bishop et al., 2000). Thus when deposition goes down, a response would first be expected during spring flow. In the acidic streams in southern Sweden (paper III), this was indicated as larger declining trends in SO_4 for samples with the lowest pH of the year, compared to the corresponding trends in data for all seasons. In Northern Sweden we could not find any response in the winter/spring pH-min data. Regionalized modelling of the anthropogenic contribution to episodic pH decline has shown that at present 6% of the streams in northern Sweden are seriously affected by acid deposition during spring flood (Laudon, 2000). Since the reference streams in northern Sweden (paper III) were assumed to be relatively sensitive to acidification, we would have expected some response to the decrease in deposition in the spring flow data. The absence of such a response indicates, that the anthropogenic impact on acidity in these streams was too low to be detected in a response to changes in deposition, even during spring flow. It is also likely that the biweekly sampling during high flow failed to represent the transient changes in spring flow episodes. A specialised study of spring flood during the 1990's showed that the human impact on spring flood acidity declined consistently in response to declining S deposition, even though the impact was already small in 1990 (Laudon and Lindquist, 2001).

Can soil water monitoring be used as an early warning system?

The response in surface waters to a decline in acid deposition has been shown to be prolonged for decades after the peak in deposition (Stoddard et al., 1999). Soil solution in the uppermost soil horizons has been found to respond instantly to drastic decreases in deposition (Giesler et al., 1996; Marschner et al., 1998). In paper IV we thus wanted to examine if a recovery in soil solution could be used in monitoring to get an early indication of recovery as deposition declines. The SO_4 concentration in the soil solution of the B-horizon has been shown to be representative for runoff (Giesler et al., 1996) if there are no processes in the near-stream zone modifying SO_4 concentrations. We thus compared the trends of SO_4 in soil solution with those in stream water and found that trends of the same magnitude were found in Tiveden and Berg three years earlier in the soil solution. For the soil water, however 5–7 replicates were needed to get statistically significant changes. This may be seen as a high price for slightly earlier answers. In the E-horizon a larger response was found, but at the same time much larger trends were needed to get statistically significant changes compared to the B-horizon and stream water. More important than predicting changes in runoff quality, though, is the fact that soil water sampling gives insight into the soil processes controlling runoff quality. Sampling of different soil horizons helps demonstrate the importance of the mobilisation of both the organic and the adsorbed pool of sulphur. Furthermore, the trends in soil water could give indications of ongoing acidification of the soil, at least in Tiveden.

Future Perspectives

The latest protocol for control of emission of pollutants that was signed in Gothenburg in 1999 prescribed further reductions in Europe by 2010 of 60% for sulphur and 40% for nitrogen compared to 1990 emissions. If the countries that signed the protocol fulfil their commitments, deposition will continue to decrease and surface waters will show a further recovery from acidification, although at a very low rate. The possibilities for predicting the rate of recovery are restricted by lack of knowledge about two important factors: Changes in soil base saturation over time and microbial sulphur dynamics. Although data from the Swedish National Survey of Forest Soils and Vegetation did not show on any changes in base saturation, this might be found if the data is subdivided into relevant groups, since different development of the base saturation at different sites is expected. A deeper analysis of times series of surface water could also give indications of the development of the soil status. This can be done by looking at ratios between ions or by investigating the residuals from a multiple regression model of base cations by other hydrochemical variables as was done by Kirchner and Lydersen (1995). A trend in base cations after removing the effect of changes in ionic concentration and runoff is an indirect indication of changes in soil base saturation.

Sulphur leaching from the soil, on the other hand, cannot be studied in the sulphate dynamics in runoff, since at least three processes are involved: Mineralisation of organic sulphur in the O-horizon, desorption from the B-horizon and redox processes in the near-stream zone. Studies of stable isotopes of sulphate in soil solution including the spatial variability within the catchment as performed at Gårdsjön by Mörth et al. (1999) might be a useful approach, but need to be extended to several sites to get a more general understanding of sulphur dynamics. The intensively monitored IM-sites are suitable targets for such studies. Since two of the processes are microbial, and thus controlled by temperature and water content, the effects of any climate change on the long term rate of recovery from acidification is an important issue for future research.

Nitrogen leaching is also likely to be affected by climate change. The soil pool of organic nitrogen is huge. An increased mineralisation of organic matter could have a large impact on riverine nitrogen transport. Since the near-stream zone and adjacent soils are likely to be the most important sites for controlling nitrogen leaching, these sites need to be better understood. The tremendous spatial and temporal variation of nitrogen species is a great challenge for such studies, as well as for monitoring and modelling of small catchments. At present leaching of inorganic nitrogen mainly occurs after clear-cut and other disturbances. This makes it obvious that managed forests have to be included in monitoring programs, which is not the case in Sweden today. Reference sites will then be important for separating effects from forestry activities on runoff chemistry from natural variation. In the near-future, an elevated leaching of inorganic nitrogen is not likely to occur. For organic nitrogen, however, the situation is more uncertain and should be the object of further investigations. The increases in TON and decreases in C/N ratio found in the reference streams have to be further investigated, especially if this is connected to a change in the bioavailability of the organic matter.

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