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This thesis describes the long-term effects of enhanced inputs of ammonium and sulphate (NS) in a spruce stand in SW Sweden on the accumulation and fluxes of nutrients in above and below ground biomass, soil chemistry and leaching of nutrients. Ammonium and sulphate were added annually at a rate of 100 kg N and 114 kg kg S ha^{-1}, which was five to six times higher than the deposition rate of the study area. The main nutrients studied were N, P, K, Ca, Mg and S. Other important parameters were pH, NH_4, NO_3 and Al in soil, soil solution and deposition.

The addition of NS decreased the pH in the mineral soil by 0.4 units and in the soil solution by 0.3 units. The increased acidity of the soil was almost totally buffered by dissolution of solid aluminium compounds (gibbsite). The input of inorganic nitrogen by deposition was totally retained in the ecosystem, as the stand was unsaturated with respect to nitrogen. The high additional input of nitrogen soon turned the stand into a nitrogen-saturated system. About 40% of the Mg was leached from the humus layer. The NS treatment increased the leaching of all nutrients except P and K from the root zone and the water soluble concentrations of all nutrients except NH_4 and SO_4 increased in the rhizosphere soil. The amount of fine roots (<2mm) decreased in the humus layer but increased in mineral soil and was unaffected overall when both humus and mineral soil were taken into consideration. The uptake of Ca and Mg by fine roots was blocked by ammonium in the forest floor and by ammonium and aluminium in the mineral soil. The concentrations of these nutrients decreased in the fine roots and also in the needles. The annual accumulation of N during the first six years (1988-1993) in the above and below ground biomass increased by a factor of 9 compared to control (C) plots. However, the accumulation of P, K, Ca, Mg and S was less than double the C level. During the six year treatment, the above ground biomass increased by 47% relative to C plots. During the following years (until 1998) the yearly basal area increment in NS plots decreased and in 1997 it was lower than in C plots. Changes in the nutrient concentration in needles indicated that deficiency of P, K and later Mg could be the reason for the growth decline.

It is suggested that high NS addition may increase biomass production in a short-term perspective, although not without negative effects on soil and soil solution. In a long-term perspective, it will lead to a strong disturbance both of the stand and its environment in the form of acidified soils and high leaching rate of nutrients and aluminium to groundwater.

Key words: Acid deposition, ammonium, sulphate, base cations, biomass, fine roots, macro nutrients, soil acidification.

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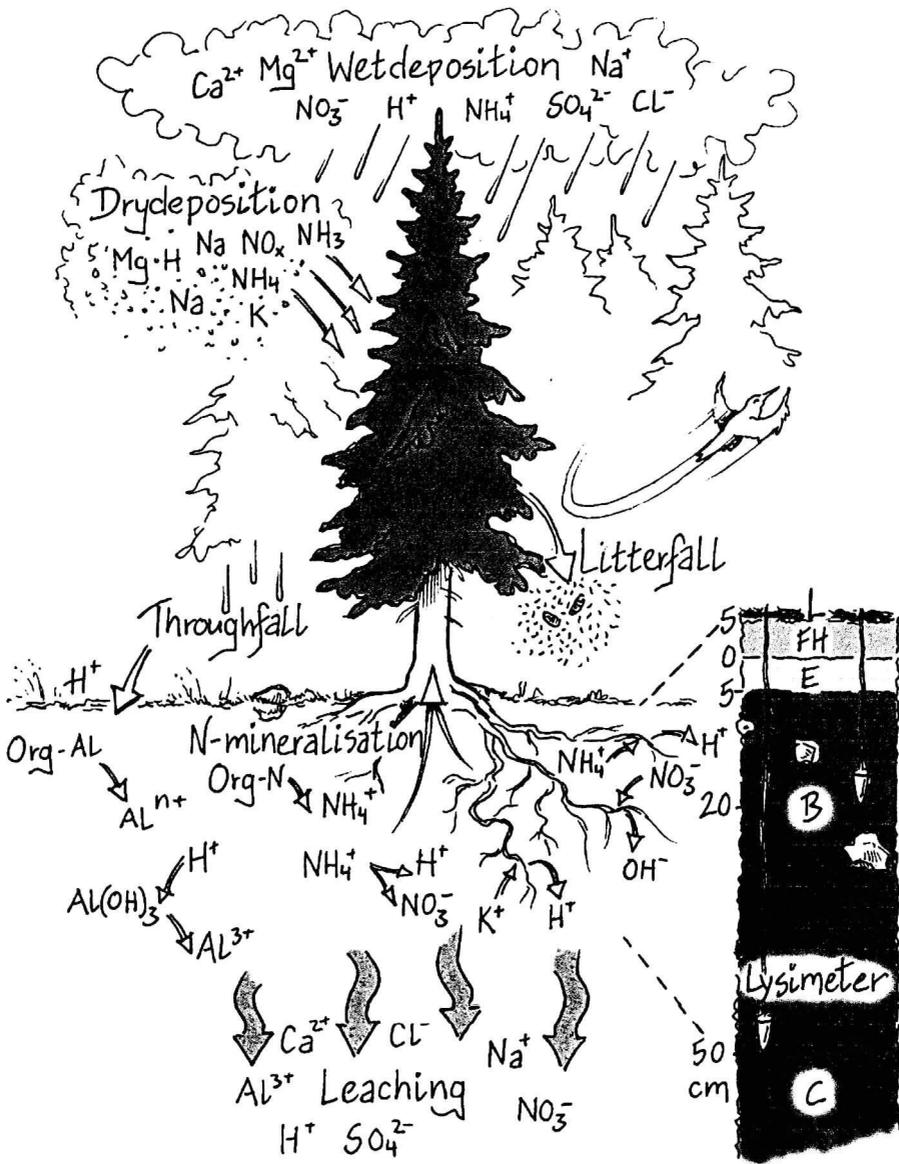ISSN,   ISBN   .

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Ca^{2+} Mg^{2+} Wetdeposition Na$^+$

NO$_3^-$ H$^+$ NH$_4^+$ SO$_4^{2-}$ CL$^-$

Drydeposition

Mg·H Na NO$_x$ NH$_3$

Na NH$_4$

K

Litterfall

Throughfall

H$^+$

N-mineralisation

Org-AL

Org-N NH$_4^+$

AL^{n+}

NH$_4^+$ H$^+$

NO$_3^-$

OH$^-$

H$^+$

AL(OH)$_3$

NH$_4^+$ H$^+$

AL^{3+}

NO$_3^-$ K$^+$ H$^+$

Ca^{2+} CL$^-$

Na$^+$

AL^{3+} Leaching

H$^+$ SO$_4^{2-}$

NO$_3^-$

5

0

5

FH

E

B

20

Lysimeter

50

cm

C

Contents

Appendix

Papers I-V

The present thesis is based on the following papers, which will be referred to in the text by their Roman numerals:

I.   Bergholm, J., Jansson, P-E., Johansson, U., Majdi, H., Nilsson, L.O., Persson, H., Rosengren-Brink, U. and Wiklund, K. 1995. Air pollution, tree vitality and forest production - the Skogaby project. General description of a field experiment with Norway spruce in South Sweden. In: L.O. Nilsson, R.F. Hüttl, U.T. Johansson and P. Mathy (eds.) Nutrient Uptake and Cycling in Forest Ecosystems. European Commission. Ecosystems Research Report 21. ISBN 92-826-9416-X. p. 69-88.

II.   Bergholm, J., Berggren, D. and Alavi, G. 2001. Soil acidification induced by ammonium sulphate addition in a Norway spruce forest in Southwest Sweden. Submitted to Water, Air, and Soil Pollution.

III. Bergholm, J. and Majdi, H. 2001. Accumulation of nutrients in above and below ground biomass in response to ammonium sulphate addition in a Norway spruce stand in Southwest Sweden. Water, Air, and Soil Pollution 130, 1049-1054.

IV.   Majdi, H. and Bergholm, J. 1995. Effects of enhanced supplies of nitrogen and sulphur on rhizosphere and soil chemistry in a Norway spruce stand in SW Sweden. Water, Air, and Soil Pollution 85, 1777-1782.

V.   Bergholm, J. and Majdi, H. 2001. Spruce forest ecosystem response to six years of ammonium sulphate addition in Southwest Sweden. Submitted to Forest Ecology and Management.

Introduction

Historical aspects of soil acidification

The increasing acidity in precipitation and its effects on streams, lakes and fish in Sweden and Norway was recognised by Odén (1967). Odén (1968) published a comprehensive report in which the acidification of rain and its causes and the effects of acid rain on lakes and rivers, soil, vegetation, forestry, fisheries, materials and buildings was discussed. However, the acid rain problem had already been recognised in the mid 19th Century by Smith, 1852 (cit. Cowling, 1982) who in a study of the chemical composition of rain in Manchester and its surroundings found a quite different composition of the rain in the city compared to the surroundings. Twenty years later (1872) the term 'acid rain' was used for the first time by Smith who discussed several principal ideas of our present understanding about acid precipitation problems. Already when Carl Linnaeus travelled through the town of Falun in 1734, he noticed problems with high sulphur concentrations in the air. The Falun area was highly polluted as a result of the copper production industry. Linneus claimed that 'Sulphur smoke rises and poisons the air far and wide so one cannot without pains go there. The smoke corrodes the earth, and no plants can grow around' (von Linné, 1889 cit. Ek et al., 2001).

The basis and start of the past 50 years of Swedish acid rain studies was the installation of a network of atmosphere chemistry stations in Sweden for analysis of air and precipitation. In the early 1960s, there were about 25 stations in Sweden and another 130 stations in Western Europe (Odén, 1968). Later on, the number of stations was reduced and new stations were set up as part of the EMEP, European Monitoring Evaluation Programme.

In 1985, a protocol signed by 21 European countries called for a reduction in their sulphur emissions by at least 30% between 1980 and 1993. It was subsequently recognised that it was not enough to just reduce sulphur emissions, as the emissions of nitrogen oxides were also gradually increasing, so a new protocol was signed in 1999 with the target of reducing the emissions of sulphur, nitrogen, ozone and particulate matter. The 1999 protocol suggested a reduction in Europe by 2010 of sulphur emissions by 63%, nitrogen oxides by 41% and ammonium by 17%, all compared to the 1970 level (UN-ECE, 2000). Behind the targets for nitrogen and sulphur, there was research to establish permissible deposition levels that did not cause harmful effects on ecological systems (Nilsson, 1986). These 'critical load' values were defined as 'The highest load that will not cause chemical changes leading to long-term harmful effects on the most sensitive ecological system'.

Soil acidification

Proton producing processes

Soil acidification is defined as the decreasing acid neutralizing capacity (ANC) of the inorganic fraction of the mineral soil (van Breemen et al., 1984) or more popularly, as increasing input of hydrogen ions, protons (H^+), in the soil. The ANC is defined as the sum of basic components minus the sum of strong acid components. Different processes which produce protons may be involved (Table 1). Normally, soil acidification is associated with the deposition of free protons together with sulphate and nitrate, 'acid rain'. Another process is the uptake of NH_4^+ and base cations (K^+, Mg^{2+} and Ca^{2+}) by plants and microorganisms in exchange with protons from the root, which are released to the soil solution. Nitrifying microorganisms in the soil may oxidise NH_4^+ to NO_3^- and two protons are produced. If NO_3^- is taken up, one proton is neutralised by the released OH^- ion and if NO_3^-, is not taken up, both protons contribute to the acidity of the soil and soil solution. If plants or microorganisms take up equal amounts of NH_4^+ and NO_3^-, the protons are neutralised and there is no net soil acidification.

The sulphate ion acts as a proton buffer in the soil. When sulphate is desorbed (released) from iron or aluminium oxides and hydroxides, two protons together with the sulphate ion are released to the soil solution. The opposite process operates when sulphate is adsorbed to the soil particles (see *Proton consuming processes*).

Other proton producing processes in the soil are the production of weak acids (organic acids) during decomposition of complex organic molecules. When organic matter is decomposed or when roots and microorganisms respire, CO_2 is released to the soil and soil solution and CO_2 dissolves in water, resulting in the weak acid H_2CO_3, which dissociates at pH >5.6 into HCO_3^- and H^+. The dissociation of protons from different organic acids is pH dependent, and the protons are released when the pH of the soil solution increases. The reverse process happens when pH decreases.

In southern Sweden, with the heaviest acid deposition in the country, the acidification of the soils has been progressing for several decades (Hallbäcken and Tamm, 1986; Falkengren-Grerup, 1987).

Proton consuming processes

Nitrogen is involved in different proton consuming processes (Table 1) such as ammonification of organic nitrogen compounds, uptake of nitrate by plants and microorganisms and denitrification. Ammonification is the opposite reaction to uptake of NH_4^+ and a proton is consumed. The uptake of NO_3^- and other anions (SO_4^{2-} and $H_2PO_4^-$) results in a release of OH^- from the roots and a proton is neutralised. Denitrification is not so common in well-aerated Swedish forest soils. This process occurs in wet conditions, where the oxygen supply is reduced.

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Table 1. *Proton producing and proton consuming processes in the soil.*

Proton-producing processes
(R denotes a carbon atom in an organic molecule, M denotes mineral, metal oxide or a metal hydroxide and CH_2O denotes an organic molecule)

Uptake / immobilisation of NH_4^+
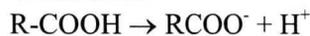$R-OH + NH_4^+ \rightarrow R-NH_2 + H_2O + H^+$

Nitrification
$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$

Sulphate desorbtion from Fe- and Al-oxides and hydroxides
$M-SO_4^-H^+ + H_2O \rightarrow M-OH + SO_4^{2-} + 2H^+$

Uptake / assimilation of base cations (Na^+, K^+, Ca^{2+}, Mg^{2+})
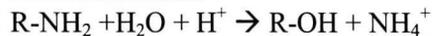$K^+ \rightarrow H^+$; $Mg^{2+} \rightarrow 2H^+$

Weak acids
$R-COOH \rightarrow RCOO^- + H^+$

Proton-consuming processes
Ammonification
$R-NH_2 + H_2O + H^+ \rightarrow R-OH + NH_4^+$

Uptake / assimilation of NO_3^-
$R-OH + NO_3^- + H^+ + 2CH_2O \rightarrow R-NH_2 + 2CO_2 + 2H_2O$

Denitrification
$4NO_3^- + 5CH_2O + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O$
$4NO_3^- + 3CH_2O + 4H^+ \rightarrow 4NO + 3CO_2 + 5H_2O$
$2NO_3^- + 2CH_2O + 2H^+ \rightarrow N_2O + 2CO_2 + 3H_2O$
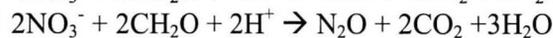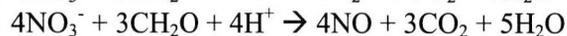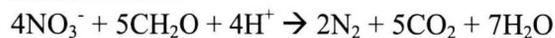
Sulphate sorption to Fe- and Al- oxides and hydroxides
$M-OH + SO_4^{2-} + 2H^+ \rightarrow M-SO_4^-H^+ + H_2O$
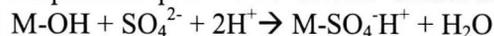
Uptake/ assimilation of anions (Cl^-, SO_4^{2-}, $H_2PO_4^-$)
$Cl^- \rightarrow OH^-$; $SO_4^{2-} \rightarrow 2 OH^-$

Weathering (e. g. anortite to caolinite)
$CaAl_2Si_2O_8 + H_2O \rightarrow Ca^{2+} + Al_2Si_2O_5(OH)_4$
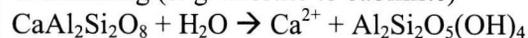
When SO_4^{2-} is adsorbed to aluminium and iron oxides and hydroxides in the minerral soil, two protons are withdrawn from the soil solution. Protons are also consumed by weathering of mineral particles in the soil. However, this process is relatively slow in most Swedish forest soils because of the low weatherability of the dominating minerals, which makes our soils sensitive to acidification.

Nitrogen saturation

Most coniferous forest ecosystems in the temperate and boreal regions of the world are considered nitrogen limited (Aber et al., 1989). When nitrogen deposition increases in highly polluted areas, there is a risk that ecosystems might be nitrogen saturated. Because of this, several investigations were started to determine the effects on the ecosystems and the environment, *e.g.* the EXMAN and NITREX projects (Beier and Rasmussen, 1993; Wright and Rasmussen, 1998).

The concept of nitrogen saturation includes different definitions. Nilsson (1986) defined nitrogen saturation as an 'ecosystem where the production by primary producers will not be further increased by an increase in the supply of nitrogen'. Aber et al. (1989) used almost the same definition, 'a saturated ecosystem is a system where the availability of ammonium and nitrate are in excess of the total demand of plants and microorganisms in the ecosystem'. Ågren and Bosatta (1988) focus on the nitrogen balance of the whole ecosystem and define nitrogen saturation as 'when the losses of nitrogen approximate or exceed the input of nitrogen'. In this thesis the definition of nitrogen saturation by Aber et al. (1989) is used, because the leaching of ammonium or nitrate is a first indication of coming environmental effects.

Aber et al. (1989) described three stages of response to increased nitrogen addition by deposition or fertiliser. This is a generalised picture of ecosystem behaviour and there may be different responses in different stands.
1. The nitrogen limiting stage, where the primary production is controlled by the rate of nitrogen mineralisation. Nitrogen is preferentially taken up as ammonium. Later studies indicate that nitrogen may also be taken up as simple organic compounds (Näsholm and Persson, 2001). In this stage the retention of nitrogen in the ecosystem is high.
2. The second stage is indicated by increased nitrogen concentration in the needles followed by increase in needle biomass, which in turn results in increasing tree growth. The mineralisation rate increases due to the more nitrogen-rich litter. The added nitrate by enhanced deposition or fertilisation is assimilated and nitrogen retention in the ecosystem is still high.
3. In the third stage, nitrification increases and nitrate starts to leach from the root zone. The needle biomass may start decreasing, followed by a decreasing net production. Nitrogen concentrations in needles increase due to storage of amino acids and the fine root mass decreases.

The Skogaby project

During the 1970s and early 1980s, there were several reports concerning forest decline, mainly in Germany and Eastern Europe (Nihlgård, 1985; Schulze, 1989; Hüttl, 1990). Similar patterns of forest decline were also reported from North-East America (McLaughlin, 1985). About 20% of European forests were classified as moderately or severely damaged. The main symptoms were increased needle loss, yellowing of the needles and increased tree mortality. There were several hypotheses about the causes, such as drought, gaseous pollutants (sulphur dioxide, nitrogen oxides and ozone), cation leaching from soil by acid deposition with subsequent soil acidification and increased aluminium concentrations in soil solution, nutrient deficiency of magnesium on acid soils and potassium on limestone soils manifested by yellowing needles (Schulze, 1989). These hypotheses were based on field observations.

In 1983, symptoms of forest decline as indicated by increased needle loss were observed in southern Sweden. Scientists and the Swedish Environmental Protection Agency were concerned about this problem, and a country-wide assessment of needle loss or crown thinning on coniferous trees was started (Anon., 1986). Later in the 1980s, it was hypothesised that needle loss in Swedish forests was being indirectly caused by air pollutants, such as nitrogen, sulphur and acidity, via the soil. This could only be tested by forest experiments.

Nitrogen deposition was expected to increase tree growth in areas with nitrogen deficiency, which could increase the demand for exchangeable base cations and lead to nutrient imbalances in areas with acidified soils with low base saturation (Nihlgård, 1985). Further enhanced nitrogen deposition could cause nitrogen saturation, resulting in nitrate leaching and negative environmental effects. The question arose as to whether it was possible to increase the growth and vitality of trees by adding phosphorus and base cations in areas with high nitrogen deposition. Another question was how the trees were affected by water stress in the form of summer drought.

These different stress factors were taken into consideration when the Skogaby project was planned. To investigate effects of nitrogen, sulphur and acidity on trees and soil, an area with high deposition of these compounds was selected (Jansson, 1990). The area contained a relatively young and healthy Norway spruce stand on a soil that was not extremely acid or poor in exchangeable base cations.

The general objectives of the Skogaby project which started in 1987 were 'to find out which climatic and nutritional conditions result in positive or negative effects of air pollutants on spruce forest growth and vitality' (Jansson, 1990). Nilsson (1991) reformulated the objectives: 'to quantify stores and fluxes of nutrients in forest stand and soil; to estimate the risk for future forest injuries or

decreased forest production due to air pollutants; and to investigate the relation between nutrient uptake, tree growth and tree vitality'.

In the Skogaby project, seven treatments including the control were set up, with the focus on controlling nutrient and water stress in trees (Figure 1).

Objectives

The general objective of this work was to study the long-term response of a Norway spruce (*Picea abies* (L) Karst.) stand, the soil and the soil solution to the addition of high doses of ammonium sulphate.

The specific objectives were:
1. To describe the experimental design, soil physical and chemical characteristics, and above and below ground biomass and nutrients prior to the treatments (Paper I).
2. To study the effects of annual addition of nitrogen and sulphur on acidification of soil and soil solution, including proton producing and proton consuming processes and nutrient leaching (Paper II).
3. To estimate the accumulation of nutrients in above and below ground tree biomass (Paper III).
4. To study the effects of nitrogen and sulphur on rhizosphere soil chemistry (Paper IV).
5. To estimate pools, accumulation rates and fluxes of nutrients in the tree and soil system during a six year treatment with nitrogen and sulphur (Paper V).

Materials and methods

Experimental site (Papers I-V)

The Skogaby experimental site was established in 1987 and six treatments controlling nutrient and water stress on trees were begun in 1988. This thesis discusses the results from the control (C) and the ammonium sulphate treatment (NS). The experiment had a randomised block design with four blocks. The plot size was 45x45 m^2 with a net area of 12.5x12.5 m^2 (Figure 1).

The experimental site is situated 26 km SE of Halmstad and 16 km from the coast in Southwest Sweden. The annual mean precipitation is 1100 mm. In spite of the high annual amount of precipitation, drought may occur in May and early June. The growing season lasts for 200 days, starting in early April and ending in early November. The annual bulk deposition rate of sulphur and nitrogen prior to the start of the treatments (June 1987 to May 1988) was 12 and 13 kg ha^{-1} yr^{-1}, respectively and the mean soil pH was 4.4 in the upper B-horizon (10-20 cm) in

the mineral soil. In 1998, at the end of the deposition measurement period, the nitrogen deposition was similar to that at the start of the period (13 kg ha^{-1}), while the sulphur deposition had decreased to 9 kg ha^{-1} yr^{-1}. Data on soil chemistry prior to the experimental treatments are given in Paper II.
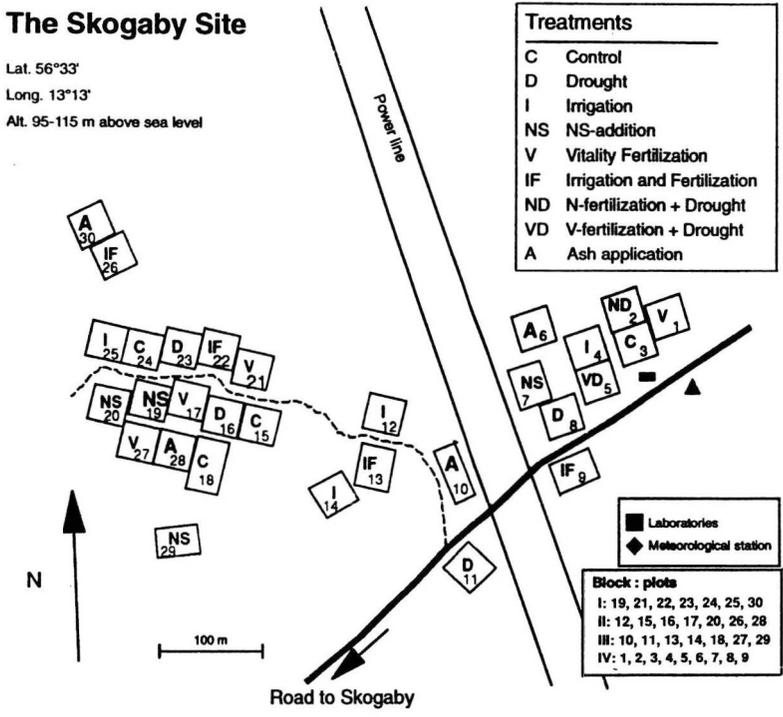

Figure 1. The Skogaby experimental site.

Ammonium sulphate (NS) was added annually to the soil surface and the fertiliser was spread manually in three portions each year, in May, June and July. The application rate was 100 kg N and 114 kg S ha^{-1} yr^{-1}. This is about six times more N and S than was added by deposition. The treatment has continued and the NS-plots have received 1 400 kg N and 1 596 kg S ha^{-1} by fertilisation up to the year 2001.

Samplings

Deposition, stemflow and soil solution (Papers I-V)

The sampling of bulk and throughfall deposition started in January 1989 and ended in 1998. Bulk deposition was sampled weekly from four collectors in an open area and throughfall deposition was sampled from six collectors per plot randomly placed inside the net area on C plots. NS-plots were sampled during two periods (1989-1990 and 1993-1994). The throughfall samples were collected

every fortnight during the summer period and every 4-6 weeks during the rest of the year. Stemflow measurements were performed during 1990 on two trees in C plots and on three trees in NS plots. The dry deposition was not measured directly but calculated by different methods.

Soil solution was sampled by suction lysimeters (ceramic cups of P80 material, Ceramictech). The lysimeters were installed at 20 and 50 cm depth with six cups per level and plot. The lysimeters were operated at a transient vacuum during one week using an initial tension of about -70 kPa. The deposition and soil solution samples were stored in a freezer (-18 °C) prior to chemical analyses.

Soil (Papers I-V)

Soil samples were taken prior to the treatment from all plots in October 1987 and after treatment in October 1990, 1993 and 1997. A volume based composite sample (n=40) using cores (5.6 cm in diameter) was taken from the forest floor (FF; in 1987 and 1990). The FF consists of a litter layer (L) on top of a humus layer (FH), and these layers were sampled separately in 1993 and 1997. Mineral soil was sampled (n=20) in five 10 cm layers down to 50 cm depth using cores (2.8 cm in diameter). The samples were sieved fresh and one part was stored at +5 °C before analyses. The other part was dried at 40°C. The volume of stones (>2 mm) was estimated from twelve pits (0.5x0.5 m^2) spread over the whole experimental area in combination with values of stoniness in the upper 30 cm of the mineral soil measured in each plot by the rod method (Viro, 1952) and the mean bulk density from a separate measurement (n=8).

Rhizosphere soil was sampled from 0-10, 10-20 and 20-30 cm depth in mineral soil in October 1992. The samples were stored in a freezer (-18 °C) and in a refrigerator at +4 °C before root sorting. Root fragments with attached soil were carefully picked out by hand and the attached soil (0-2mm) was separated from the root surface by shaking the root fragments gently in a plastic container. The rest of the soil was considered as bulk soil.

Above ground and coarse root biomass (Papers III and V)

Data on above ground biomass and nutrient content in different biomass compartments (1987, 1990 and 1993) and litterfall biomass and nutrient content (1990, 1993) were taken from Nilsson and Wiklund (1992; 1994; 1995) and provided by L.O. Nilsson (pers. comm).

Coarse roots (2-20 mm) were sampled from 8 of the biomass sample trees in 1990 (2 from each C plot) by Persson et al. (1995). The roots were excavated from a 0.5 m deep pit with a 0.5 m radius centred in the middle of the stump. Roots with a diameter of 2-5 mm were sampled (n=10 per plot) between trees by cylindrical soil cores (7.2 cm in diameter) in the forest floor and (4.5 cm in diameter) in the

mineral soil, in three 10 cm layers to 30 cm depth in 1989 and 1992 (Majdi and Persson, 1993; 1995). The root samples were dried at 85 °C to constant weight.

Coarse root biomass was estimated by establishing a logarithmic equation with stem volume (d^2h) as independent and coarse root biomass as dependent variable (log y=0.88*log d^2h+0.93), where (y) denotes coarse root biomass (kg tree^{-1}), (d) tree diameter at 1.3 m above ground in cm and (h) tree height in m. For this purpose we used coarse root (2-20 mm) data from 8 excavated trees in 1990 (Persson et al., 1995) and soil core data on 2-5 mm size roots (Majdi and Persson, 1995) sampled in 1989 and 1992 from the study site. The total root biomass was estimated by adding the calculated coarse root biomass for the plot and the 2-5 mm roots of the area between trees that was not already covered by the coarse root calculations. The equation was then used for all trees at the small area to calculate the coarse root biomass per ha.

Fine root biomass (Paper V)
Fine roots (<2 mm) were sampled in September 1987, 1989, 1990 and 1992 from forest floor and from three 10 cm layers down to 30 cm depth of the mineral soil (n=10 per plot and soil layer) using soil cores (7.2 cm in diameter for FF and 4.5 cm for mineral soil). The samples were stored in a freezer (-18 °C) and in a refrigerator at +4 °C before root sorting (Majdi and Persson, 1993; 1995).

Measurements and chemical analyses
The deposition and soil solution samples from each plot and sample occasion were pooled by volume weight and by equal amounts, respectively. The pooled samples were analysed according to the main constituents, Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Al_{tot} (soil solution only), NH_4^+, NO_3^-, Cl^-, PO_4^{3-} and SO_4^{2-}. On one occasion (November 1997) the concentration of Al_{qr} (quick reacting Al) was analysed on each soil solution sample. Dissolved organic nitrogen (DON) was analysed during a two year period (1994-1995) and dissolved organic carbon (DOC) from 1994 onwards.

All soil solution samples from 20 and 50 cm depths taken on one occasion (November 1997) were analysed for inorganic aluminium (Clarke et al, 1992) and the Al^{3+} was calculated according to the programme ALCHEMI (Schecher and Driscoll, 1987).

The pH in soil samples was measured in distilled water and 0.01 M $CaCl_2$ in a soil:solution ratio of 1:1 by volume. The soil samples were extracted freshly using 1 M NH_4Cl for analysis of exchangeable base cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) and 1 M KCl for analysis of exchangeable H^+ and Al^{n+}. A percolation method was used, and 2.5 g of soil was intermittently extracted by 100 ml of solution during a total of 5 h. Exchangeable SO_4^{2-} was extracted from dried mineral soil samples with 0.01 M $CaH_4(PO_4)_2$ in a soil:solution ratio of 1:5.

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The rhizosphere and bulk soil was extracted with distilled water in a soil:water ratio of 1:2. The water addition was adjusted to the water content in the sample to reach an exact 1:2 relation (Majdi and Persson, 1993). The samples were shaken for 24 h and centrifuged at 10000 r. p. m. and the supernatant was filtered through a 0,45 μm Millipore filter. The solution was analysed for K, Ca, Mg, Al, NH_4, NO_3 and SO_4 and pH was measured.

The nutrient elements P, K, Ca, Mg and S in the soil, biomass and fine roots samples were extracted by wet digestion with nitric acid and perchloric acid (2.5:1) at 115 ^{o}C. Mineral soil samples from different levels in the 1 m deep pits in control plots were prepared and fused with lithium borate at 1000 ^{o}C and subsequently dissolved in nitric acid for geochemical element analyses.

The conductivity of deposition and soil solution was measured on a conductivity meter (Philips) and pH on a pH-meter (Radiometer PHM 93). The base cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) and Mn^{2+} were initially analysed by an atomic absorption spectrophotometer (AAS, Perkin Elmer 305) and later by ICP-ES (Jobin Yvon 70 plus). Total Al was initially analysed by flow injection analysis (FIA star, Tecator) and later by ICP-ES. NH_4^+, NO_3^-, DON and PO_4^{3-} were analysed by FIA and Cl^- and SO_4^{2-} by ion chromatography (IC, Dionex). H^+ and Al^{n+} in KCl-extracts were analysed by titration with 0.02 M NaOH with recording equipment (Radiometer, Tim 900). Total nutrient elements in extracts from soil, biomass and fine roots were analysed by ICP-ES and the geochemical samples were analysed by plasma-emission spectrometry (ICP-AES). DOC was analysed by a carbon analyser (Shimazu 5000) and organic N in above and below ground biomass and soil was analysed by elemental analyser (Carlo Erba NA 1500).

Calculations (Papers I-III and V)

Deposition, soil solution and biomass
The bulk and throughfall deposition and stemflow of H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+} NH_4^+, NO_3^-, Cl^-, SO_4^{2-}, DON and DOC was calculated by multiplying the amount of precipitation by the concentrations of these elements in respectively fraction.

The difference between bulk and throughfall deposition gave the dry deposition of Cl. By using the relationship between Mg and Cl in sea salt, the dry deposition of Mg was calculated. Dry deposition of K and Ca, which consists of sea salts and aerosols of other origin, was estimated to be almost similar to that in bulk deposition found by Ragsdale et al. (1992). The sum of NH_4^+, NO_3^- and DON in deposition by throughfall and stemflow was used as input of nitrogen to the plots. Phosphorus and SO_4^{2-} were treated in the same way. The deposition of K^+, Ca^{2+} and Mg^{2+} on the plot was calculated as the sum of bulk and dry deposition plus

the stem flow. The dry deposition of H^+ was calculated as the difference between throughfall and bulk deposition of NH_4^+, NO_3^- and SO_4^{2-} (Mulder et al., 1987). The deposition in 1988 was estimated from the bulk deposition prior to the treatments and from deposition data from nearby sites.

The vertical flow of soil water was simulated using the SOIL-model (Jansson, 1998). The main part of the model consists of two coupled differential equations describing vertical flow of water and heat in a soil profile. The profile is divided into a finite number of layers. The driving variables used here were daily sum of precipitation, daily average air temperature, air humidity, wind speed and global radiation. The thinning and the change in leaf area index (LAI) due to nitrogen fertilisation in NS were considered in the model.

The flow of nutrients at 20 and 50 cm depths was calculated as the simulated daily flow of water multiplied by the daily concentrations of nutrients, which was obtained from interpolation between the sampling occasions.

The amount of nutrients in above ground biomass was calculated as the sum of mean amount of biomass per ha times mean nutrient concentration in the different fractions. The amount of nutrients in fine roots (<2mm) was calculated by multiplying biomass and nutrient concentrations. The nutrient amount in coarse roots was calculated as the coarse root biomass times the biomass-weighted mean nutrient concentration of stem and living and dead branches.

Total proton load (Paper II)
The total proton load (TPL) to the soil was calculated using estimations of the atmospheric net proton addition (H_{NET}) and the most important proton producing and proton consuming processes in the soil (Table 1).

$$H_{NET} = H_{BD} + H_{DD} - H_{SS} \tag{1}$$
where BD denotes bulk deposition, DD dry deposition and SS soil solution.

$$N_{TR} = (NH_4^+ - NO_3^-)_{TF+SF+FE} + (NO_3^- - NH_4^+)_{SS} \tag{2}$$
where N_{TR} denotes nitrogen transformations, TF throughfall, SF stemflow and FE fertiliser.

$$SO_{4\,RET} = SO_{4\,SS} - SO_{4\,TF} \tag{3}$$
where $SO_{4\,RET}$ denotes sulphate retention.

$$BC_{AC} = BC_{BM} - A_{BM} \tag{4}$$
where BC_{AC} denotes base cation accumulation in biomass (BM).

The TPL is defined as the sum of these four equations:
$$TPL = H_{NET} + N_{TR} + SO_{4\,RET} + BC_{AC} \tag{5}$$

The retention of base cations BC_{RET} in the ecosystem was calculated as the difference between input and output of base cations:

$$BC_{RET} = BC_{BD} + BC_{DD} - BC_{SS} \qquad (6)$$

Statistical analyses

Statistical analyses were carried out using the SAS GLM procedure (SAS, 1996) with year, treatment and block as main factors. Tukey's HSD test ($p<0.05$) was used for assessing differences between means (n=4).

Results and discussion

Soil conditions in Skogaby (Paper I)

The soil chemistry analyses indicated that the soil was already acidic at the start of the project, in 1987. The mean pH of the forest floor (FF) and the upper mineral soil was 3.9 and 4.1, respectively, while it was 4.5 at 50 cm depth. The effective base saturation was 30% of the effective cation exchange capacity (CEC_e) in FF and between 7% and 12% in the mineral soil. Aluminium occupied between 66 and 76% of CEC_e in mineral soil. The site was heterogeneous and pH was significantly lower in the western part (Block I) than in the eastern part (Block IV).

The texture of the soil (<2mm) was homogeneous throughout the soil profile and contained 4% clay and 64% sand (0.06-2mm), and the till soil was classified a loamy sand soil. The porosity of the soil was about 70% in FF and decreased to 30% in the mineral soil. The total amount of plant-available water to 50 cm depth was around 100 mm. However, the water-holding capacity varied between plots. Alavi (1996) distinguished three types of plots with different water regimes: dry, normal and wet plots. The annual runoff was on average 18% lower from the wet plots than from the dry plots, which meant that the wet plots had more soil water available for tree growth.

The annual mean precipitation (P) reaching the canopy surface is shown in Figure 2. There were two rain-rich years (1994 and 1998) and two years with less precipitation than normal (1996 and 1997). On average for the period 1988-1998, 70% (760 mm) of the annual precipitation reached the forest floor in C plots as throughfall (TF). The rest (30% or 320 mm) was evaporated from the canopy. Of the 760 mm entering the FF, 55% (420 mm) passed through the root zone down to the ground water. The remaining 45% (340 mm) was mainly transpired by the trees and a minor fraction was evaporated from the soil.

In general, the pH in the forest floor of coniferous stands on podsols is strongly buffered against changes due to the soil's high content of acidic functional groups and organic acids. The pH often varies by a few tenths of a pH unit around 4 and there are small variations between stands with low and high atmospheric acid deposition (Troedsson and Nilsson, 1984; Karltun, 1995). However, pH in the FF and uppermost mineral soil layer normally decreases with increasing stand age (Hallbäcken and Tamm, 1986). The mineral soil is more affected by environmental changes and several decades of acid deposition have acidified the mineral soils in southern Sweden. Hallbäcken (1992) estimated that about 50% of the acidification of the mineral soils in southern Sweden during the period 1927-1984 was caused by anthropogenic acid deposition and 50% by base cation accumulation in tree biomass. The soil at Skogaby is representative of the soils in the south-western part of Sweden (Karltun, 1995).
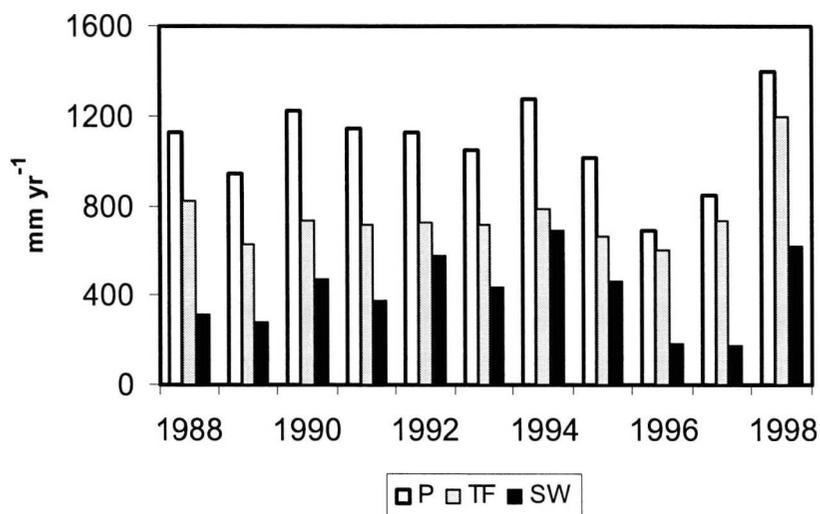
Figure 2. Amount of precipitation, throughfall and runoff of soil water (mm yr^{-1}) in control plots during 1988-1998. P=precipitation, TF=throughfall and SW=soil water.

Soil acidification (Paper II)

Deposition and soil solution

When all main constituents in deposition and soil solution are analysed, one should find a balance between the sum of cations and the sum of anions on an equivalent basis. The annual mean amounts of cations and anions in deposition and soil solution in C and NS plots during the period 1988-1998 are shown in Figure 3. In bulk deposition and throughfall, the sum of cations exceeded the sum of anions. The missing constituent was probably organic anions. Dissolved organic carbon (DOC) was analysed for some years (Paper II). Dividing the anion charge deficit by the mean annual amount of DOC resulted in 3.2 mmol$_c$ g^{-1} C for bulk deposition and 4.2 mmol$_c$ g^{-1} C for throughfall.
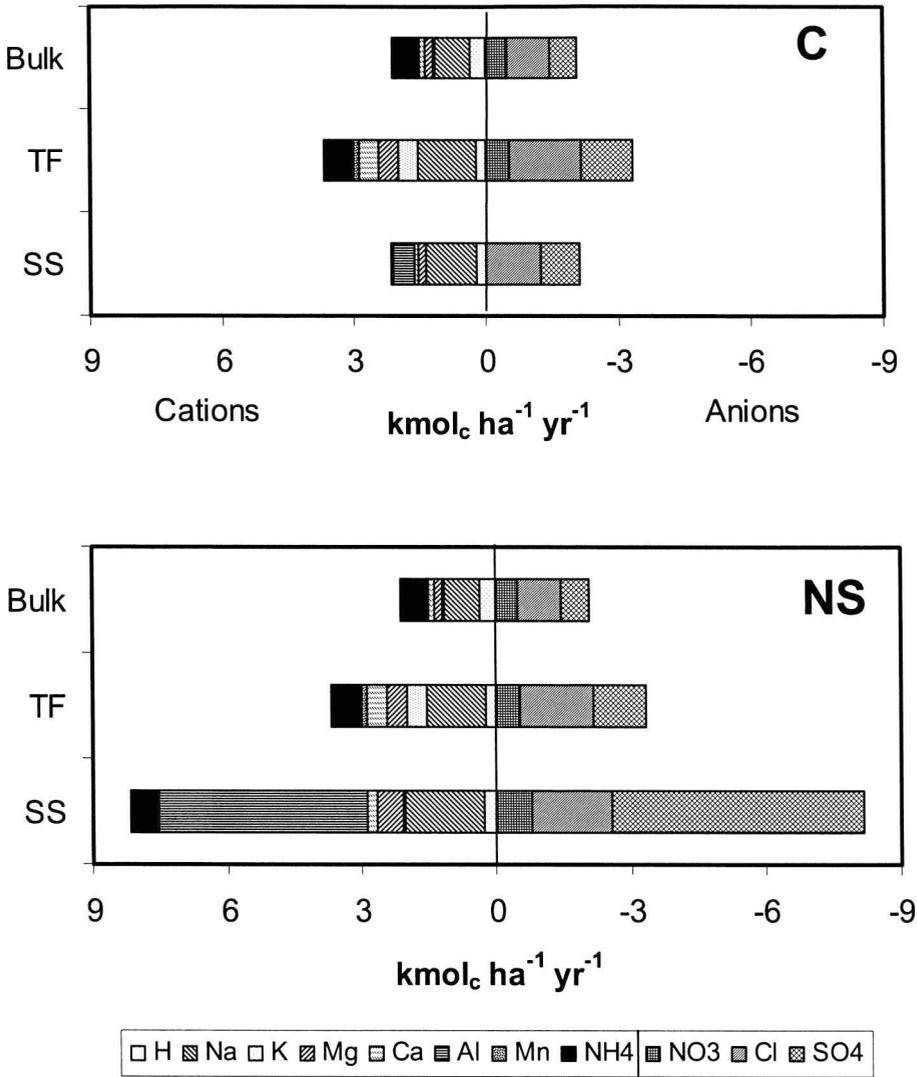
Figure 3. Ion balance in bulk deposition, throughfall and soil solution at 50 cm depth in C and NS plots. Mean for the period 1988-1998. Bulk=bulk deposition, TF=throughfall, SS=soil solution C= control plots and NS= ammonium sulphate treated plots.

The amounts as well as the relationship between ions changed when the precipitation-soil solution passed through the soil profile down to 50 cm depth (Figure 3). Ammonium and nitrate were lacking from the soil solution in C plots, while aluminium was added. The amount of chloride was almost similar in throughfall and soil solution in C and NS plots, because chloride was neither taken up by the trees nor adsorbed in the soil in any substantial amounts. When ammonium sulphate was added to the NS plots, the sum of ions increased by
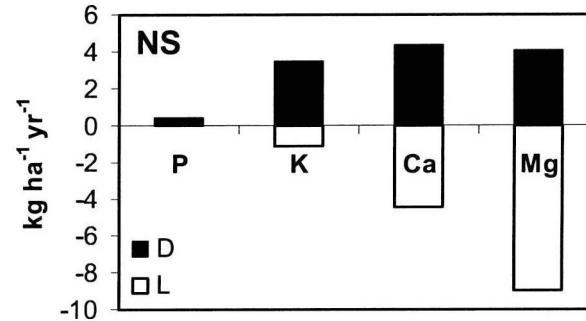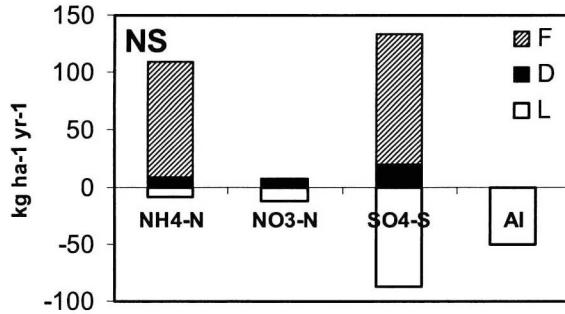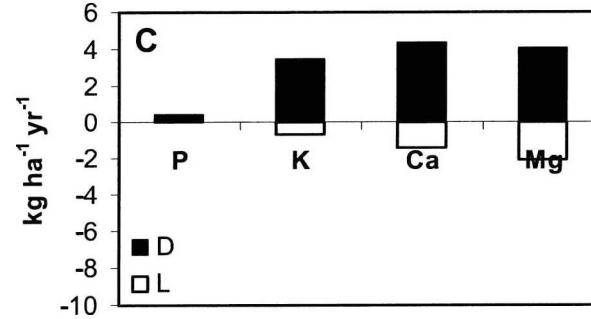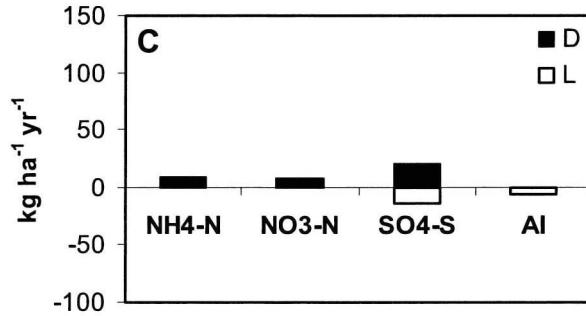
Figure 4. Mean annual flux of nutrients (kg ha^{-1}) into the ecosystem by deposition and fertiliser and from the ecosystem by leaching from 50 cm depth during 1988-1998. C=control, NS=ammonium sulphate addition, D=deposition (bulk+dry deposition), F=fertiliser addition and L=leaching.

almost a factor of 4 compared to that in the soil solution in C plots. These changes were mainly caused by increased amounts of ammonium, aluminium, nitrate and sulphate.

The mean inputs of different elements by deposition and fertiliser to the soil and the mean outputs by leaching at 50 cm depth between 1988 and 1998 in C and NS plots are illustrated in Figure 4. The inputs of ammonium, nitrate and phosphorus were totally retained in the ecosystem in C plots and the input was higher than the output for sulphate, potassium, calcium and magnesium. The addition of ammonium sulphate increased the leaching of aluminium, calcium and magnesium compared to C plots. In relation to the great annual input of ammonium of about 115 kg N ha^{-1} yr^{-1}, only a minor fraction was leached from the system, indicating that this ecosystem had a high capacity to retain the added nitrogen. The output of nitrate was similar to the input. The leaching of potassium increased only slightly compared to C plots. The added sulphate behaved differently from the ammonium because the trees only needed a small amount of sulphur. However, two thirds of added sulphate was retained in the ecosystem due to the capacity of the soil to sorb sulphate. The addition of ammonium sulphate increased the leaching of aluminium, calcium and especially of magnesium.

Total proton load

In general, four processes regulated the total proton load (TPL) to the soil at Skogaby. These were atmospheric net proton load (H$_{NET}$), nitrogen transformations (N$_{TR}$), sulphate retention (SO$_{4 \, RET}$) and base cation accumulation in the biomass (BC$_{AC}$).

H$_{NET}$ was the dominating source of protons in C plots, followed by base cation accumulation in the biomass (Figure 5). The input by H$_{NET}$ decreased during the study period. The contribution by N$_{TR}$ was almost negligible because the deposition contained almost similar amounts of ammonium and nitrate and the uptake of ammonium by trees and soil microorganisms was almost equal to the nitrate input by deposition since there was no leaching of inorganic nitrogen. SO$_4$ $_{RET}$ acted as a regulator of TPL. Sulphate was adsorbed in the soil and protons were withdrawn from the soil solution (1998-1992 and 1995-1997). In 1993, 1994 and 1998, sulphate and protons were desorbed and released to the soil solution. When the runoff in Skogaby exceeded about 600 mm, sulphate and protons were released to the soil solution and leached out from the root zone.

The sulphate concentration in throughfall decreased by 54% during the period 1988-1998. However, there was only a weak response to that decrease in the soil solution (Figure 6). The sulphur concentration at 20 cm depth decreased significantly ($p < 0.05$) by 24%, while the decrease at 50 cm depth (5%) was not significant. Magill et al. (2000) found a stronger response in the soil solution, both at 20 and 90 cm depth, of decreasing sulphate concentration in deposition in

Fichtelgebirge in Bavaria, Germany. They found that the sulphate concentration decreased proportionally to the throughfall levels at 20 cm, while the response was
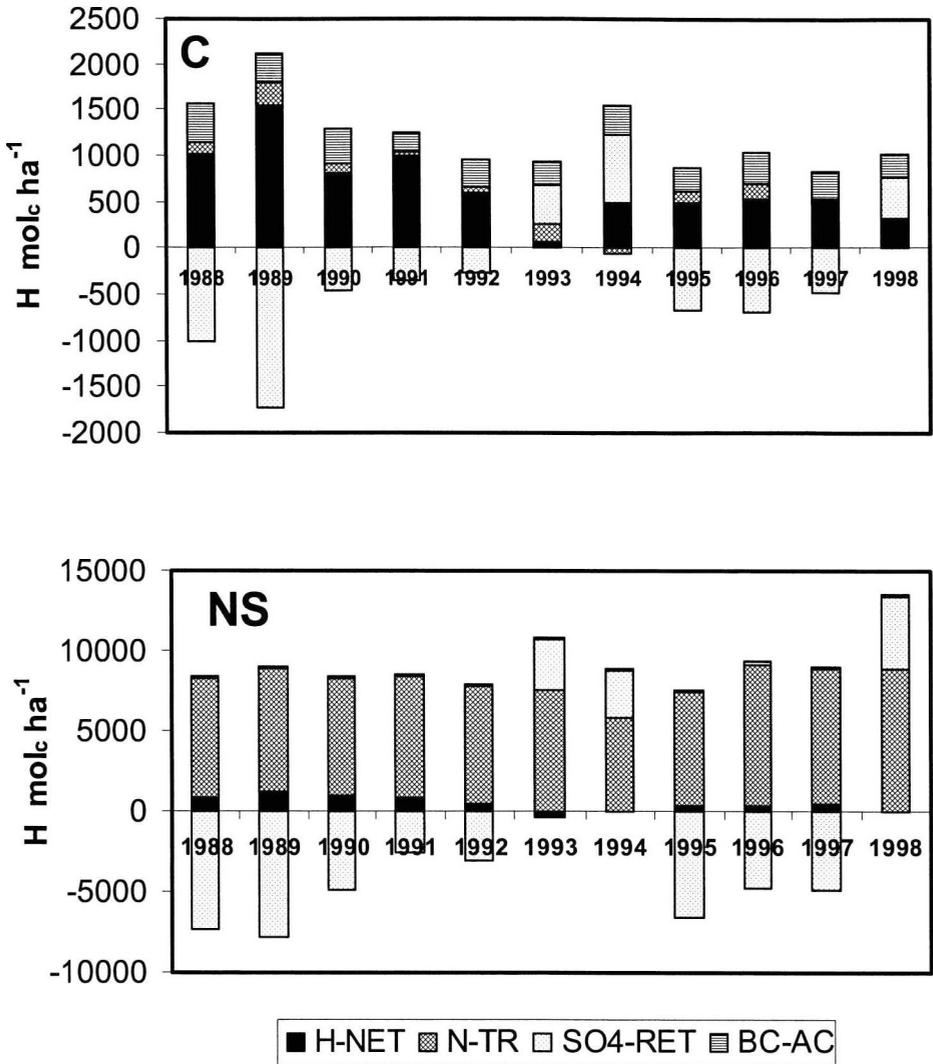

Figure 5. Annual mean contribution of protons to the total proton load (TPL) in C (above) and NS plots (below). Positive values indicate a surplus of protons and negative values indicate a retention of protons in the soil. H-NET=net atmospheric proton deposition, N-TR=nitrogen transformations, SO$_4$-RET=sulphate retention and BC-AC=biomass accumulation of base cations in excess of anion accumulation.

somewhat lower at 90 cm. In a five-year roof experiment at Gårdsjön, Sweden, a 95% reduction in the anthropogenic sulphur deposition resulted in a 45% reduction in sulphur output in stream water (Hultberg et al., 1998). The response to decreasing deposition of sulphur seems to be slow at Skogaby and Gårdjön

compared to that at Fichtelgebirge. Most of the sulphate in the soil is adsorbed to iron and aluminium oxides and hydroxides in the B-horizon (between 10 to about 50 cm depth). This layer, which in the case of Skogaby contains about 250 kg inorganic and about 400 kg organic sulphur per ha, buffers against long-term changes as in Figure 6 (different response at 20 and 50 cm depth). However, it also acts as a reservoir for short-time changes related to the discharge of soil water (Figure 5). According to the different responses to deposition changes in the upper and lower parts of the soil profile, one can expect a quicker response in stream waters in areas with shallow soils on hilly sites than on flat areas with deeper soil layers.
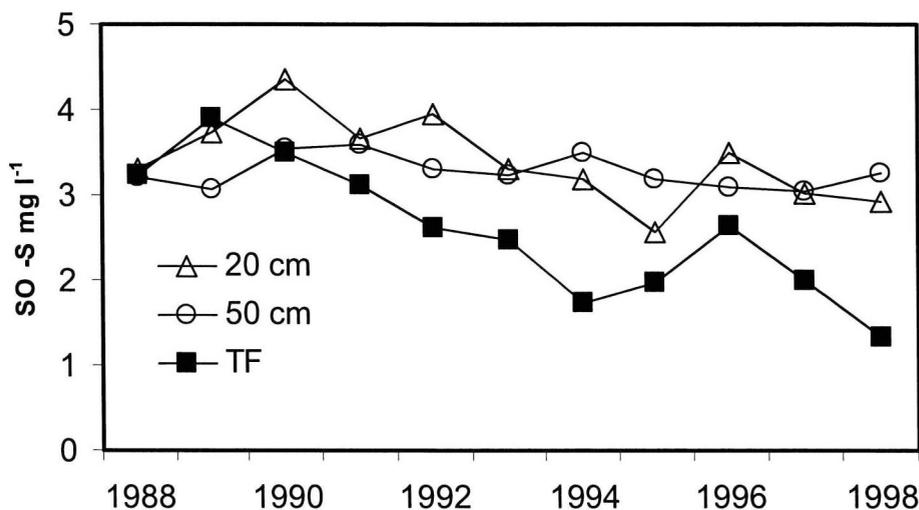
Figure 6. Annual mean concentration of sulphate in throughfall and soil solution at 20 and 50 cm depth in C plots during 1988 - 1998.

The NS treatment increased the TPL by nearly a factor of eight compared to C plots (Figure 5). The N_{TR} was the dominant proton source. The inputs of protons via H_{NET} and BC_{AC}, similar amounts as in C plots, were almost negligible in comparison with the proton input by N_{TR}. The uptake of nitrogen was high and more than 98% was retained in the ecosystem during the first three years. Low concentrations of nitrate were found in the soil solution during the period 1990-1992. Thereafter the nitrate concentration increased gradually and peaked in 1996 and 1997 (Paper II), indicating that the system had become nitrogen saturated (Aber et al., 1989). The long delay before the nitrate leaching became high was probably due to a combination of low pH in the soil and the presence of acid-sensitive nitrifiers that adapted slowly to the high concentration of ammonium. These effects contributed to an accumulation of ammonium in the soil profile of 8 kg ha^{-1} yr^{-1}. The pH in soil solution at 50 cm decreased by 0.3 and the pH in mineral soil decreased by 0.4 pH units (Paper II).
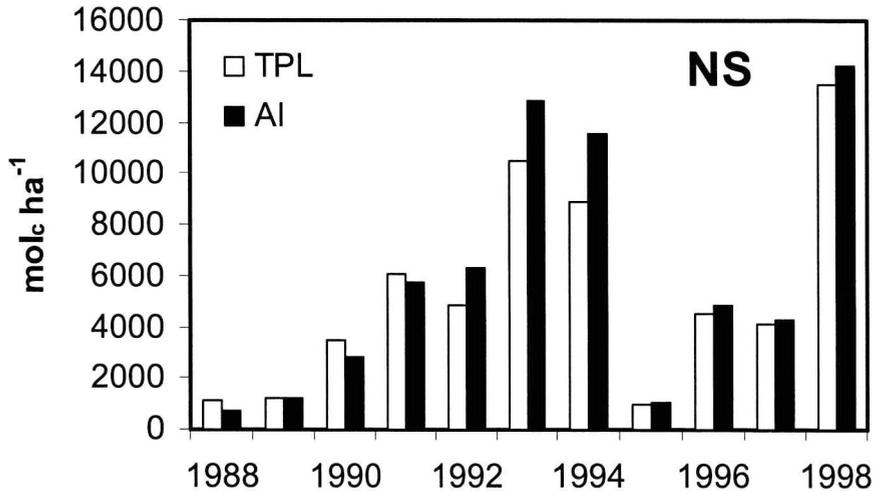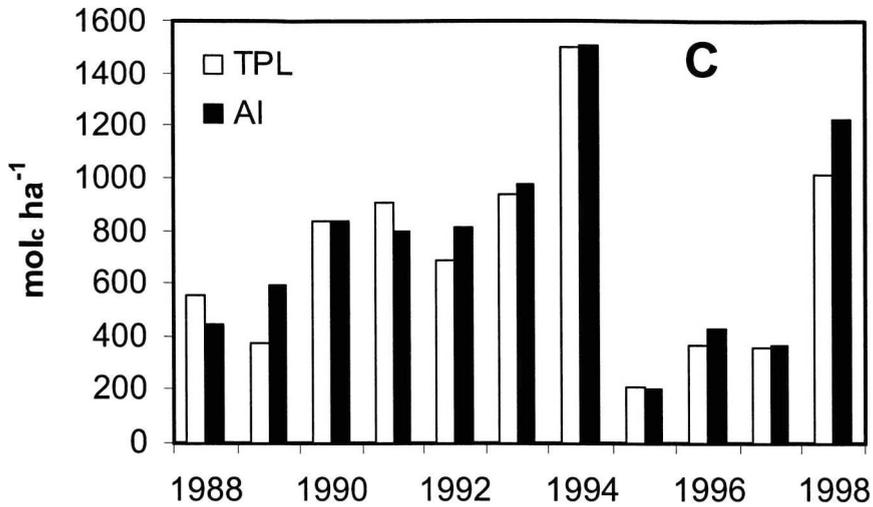
Figure 7. Mean total proton load (TPL) and amount of total aluminium (Al$_{tot}$, calculated as Al^{3+}) in soil solution at 50 cm depth during 1988-1998. C=control and NS=ammonium sulphate treated plots. Note different scales on the y-axis.

Sulphate acted as a proton buffer in both NS and C plots and sulphate and protons were released to the soil solution when the runoff of soil water exceeded about 600 mm.

The pH and the base saturation were low in the mineral soil and the soil was in a stage of aluminium buffering. The TPL was almost totally buffered by dissolution of solid aluminium compounds in the soil (Figure 7) and at 50 cm depth the aluminium compound was aluminium hydroxide, gibbsite, in both C and NS plots (Paper II).

The amount of total aluminium in Figure 7 was calculated as Al^{3+}. The analysis of inorganic aluminium in November 1997 indicated that the main fraction of total aluminium in the soil solution was in the form of Al^{3+} both at 20 and 50 cm depth and both in C and NS plots. This was expected because of the relatively low pH values and the low concentration of dissolved organic compounds (DOC) in the soil solution, which otherwise might have reacted with aluminium. The Al^{3+} comprised up to about 70% of the total aluminium. The other 30% was bound to organic complexes in the C plots and to sulphate in NS plots. It was also demonstrated that the aluminium in the soil solution at 50 cm depth was in equilibrium with gibbsite (Paper II), while at 20 cm depth this was the case for only a few of the samples. At 20 cm depth, the solubility of aluminium was regulated by equilibrium complexation with soil organic matter, a common reaction at pH <4.2 (Berggren and Mulder, 1995).

The BC/Al ratio, the relationship between the molar sum of potassium, magnesium and calcium and the molar concentration of aluminium in the soil solution, has been used as a measure of a toxic environment for the fine roots (Sverdrup and Warfinger, 1995). If BC/Al<1 there could be a risk for decreasing tree production. The BC/Al ratio was <1 and decreasing in the soil solution at 20 cm depth in C plots during the period 1988-1998 (Figure 8). However, tree production was high and there was no sign of a decrease in growth. The BC/Al ratio was >1 during the period 1988-1989 in NS plots, decreased sharply in the following year to low values and continued at that level (about 0.3) for the rest of the period. The production in NS was higher than in C plots until 1995 (Nilsson, pers. comm.) indicating that the BC/Al ratio is not a good indicator for risk of forest decline, which also was postulated by de Wit (2000).

Rhizosphere soil (Paper IV)

The thin soil layer (0-2 mm) on the fine roots, the rhizosphere soil, may be affected by the nutrient flux to the fine root surface, the presence of mycorrhizal hyphae and exudates from the roots. Nutrients are transferred from the soil solution to the root surface either by diffusion, *e.g.* phosphorus and potassium, or by mass transport, *e.g.* ammonium, magnesium and calcium. In the case of diffusion, nutrients are transported along a concentration gradient. When a nutrient is taken up by the root, the concentration outside the root surface decreases, and more nutrients are transferred to the surface. In the case of mass transport, the nutrients follow the water transport into the root as a result of plant transpiration.

The pH was significantly lower in NS plots compared to C plots (Paper IV). Majdi and Rosengren-Brinck (1994) showed that the rhizosphere soil gradually became more acid and the concentrations of sulphate, magnesium and calcium gradually increased in NS compared to C plots. This was in agreement with the changes in nutrient concentration in soil solution in NS plots (Paper II). The concentration of potassium in the rhizosphere in NS varied from year to year in

relation to C. The variations between years were more pronounced in C than in NS plots. The reason for the variations in concentration of potassium was probably the mobility of potassium in the soil and the environmental conditions prior to the sampling occasions.
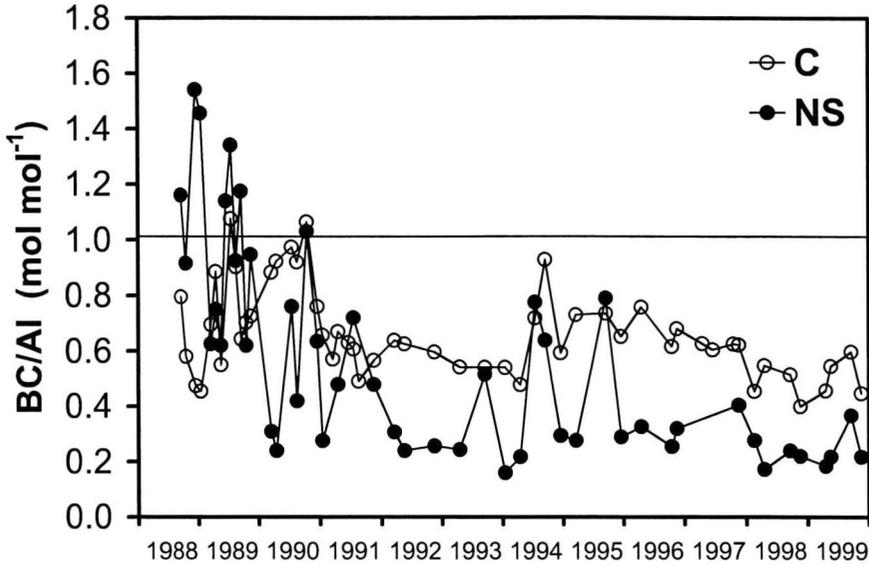

Figuer 8. BC/Al ratio (mol mol^{-1}) in soil solution at 20 cm depth during 1988-1998 in C and NS plots. C=control plots and NS= ammonium sulphate treated plots.

The concentrations of ammonium, aluminium (Figure 9) and sulphate (not shown) were similar in bulk and rhizosphere soil. The concentrations of potassium, magnesium (Figure 9) and calcium (not shown) were higher in rhizosphere soil than in bulk soil. The higher concentration of potassium in the rhizosphere soil (2.5 times) was in contrast to the diffusion model (Marschner, 1995). However, Dieffenbach and Matzner (2000) demonstrated that the soil solution concentration of potassium increased towards the root surface of long root tips while the ammonium concentration decreased. For the mycorrhizal roots, the opposite was demonstrated. The increasing concentration of potassium from bulk to rhizosphere soil in Skogaby agrees with rhizosphere soil being attached to long roots. Majdi et al. (2001) reported on the other hand that more than 85% of fine roots in Skogaby were mycorrhizal roots. The data show that rhizosphere soil chemistry follows a similar pattern to the soil solution.
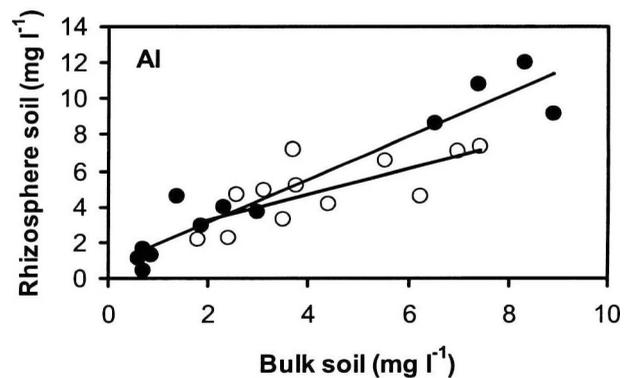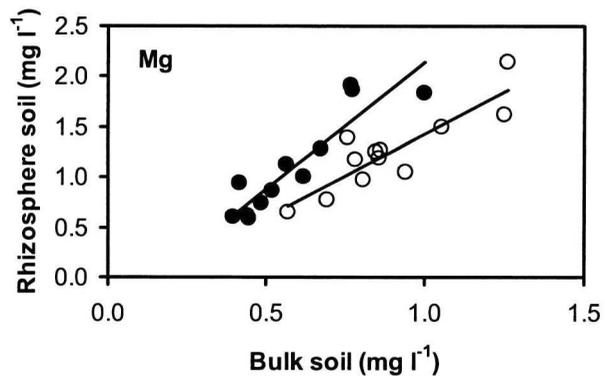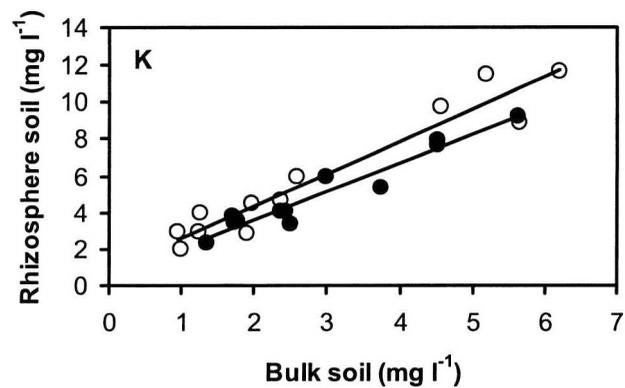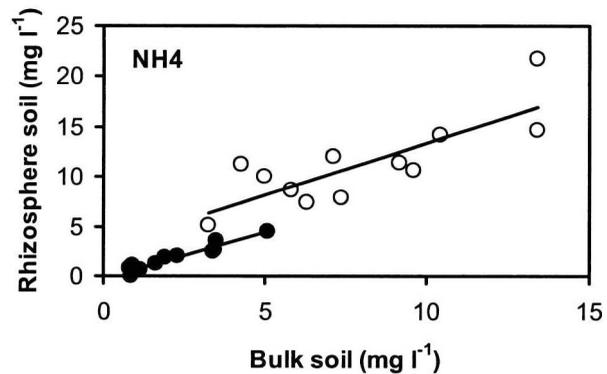
Figure 9. The concentration (mg l^{-1}) of NH$_4$, K, Mg and Al in water extract from bulk and rhizosphere soil from mineral soil in 1992. Data from three depths (0-10, 10-20 and 20-30 cm) were plotted. Filled dot=control plots and open dots= ammonium sulphate treated plots.
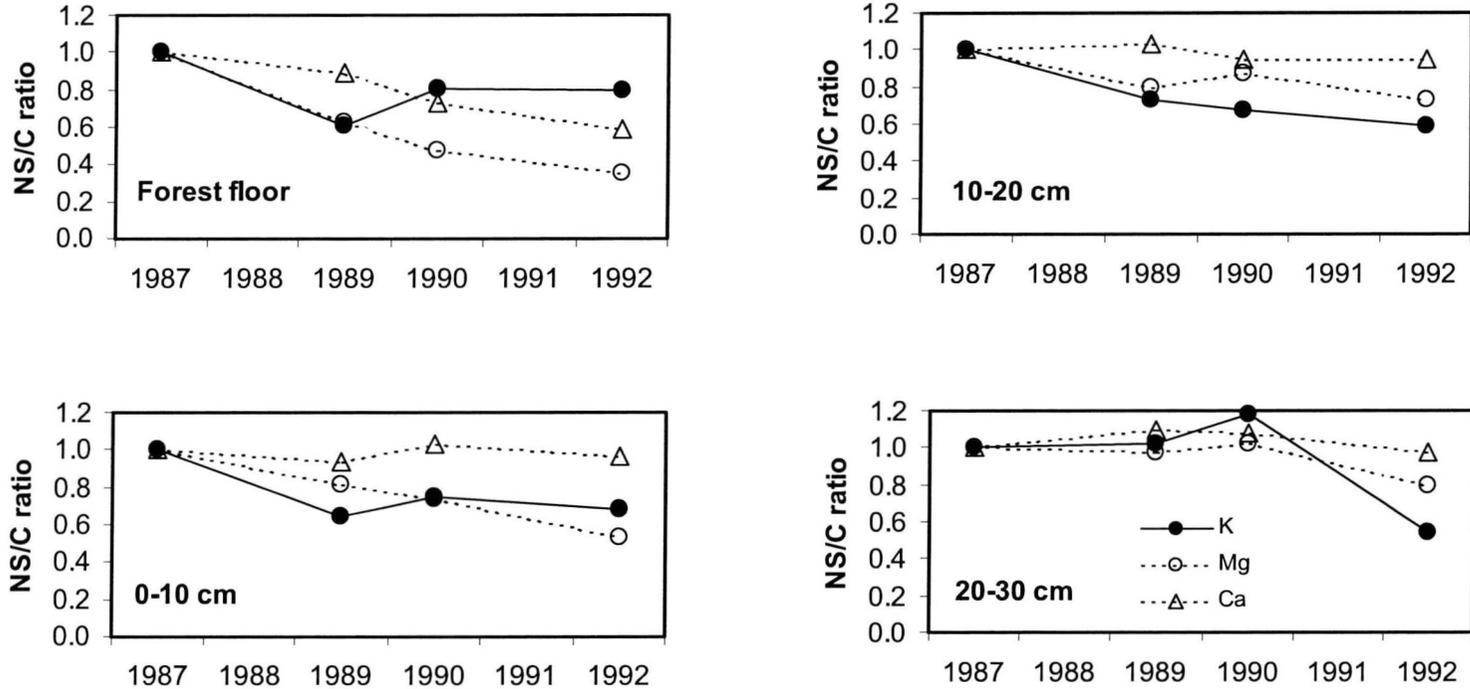
Figure 10. Relative (NS/C) concentrations of K, Mg and Ca in fine roots in four soil layers in C and NS plots. C=control plots, NS= ammonium sulphate treated plots.

Fine root biomass and nutrients (Paper V)

Root sampling and preparation of fine roots is tedious work, which may explain why there are only a few investigations concerning fine root biomass and fine root nutrient determinations. The fine root studies at Skogaby cover the period 1987-1992.

The mean fine root biomass in forest floor and mineral soil was 5.0±0.3 ton in C and 4.9±0.3 ton ha^{-1} in NS plots. The FF alone contained 2.3±0.4 and 2.1±0.5 ton ha^{-1} in C and NS plots, respectively. The mineral soil (0-30 cm) contained more fine root biomass than FF in both C and NS plots. The total amount of nitrogen in the fine roots decreased in FF and increased in mineral soil in both NS and C plots during the period 1988-1992, although the change was not statistically significant (p<0.05). During the same period, the concentrations of total potassium, magnesium and calcium in fine roots in NS plots decreased in relation to C plots both in forest floor and mineral soil (Figure 10). The decrease in potassium was not as pronounced in FF as in the upper mineral soil layers. The total concentration of calcium decreased only in the FF, while the concentration of magnesium was affected in all soil layers.

The decreasing concentration of calcium and magnesium in fine roots in NS plots (Figure 10) could not be an effect of decreasing concentrations in the soil solution. The concentration in the soil solution was rather higher in NS than in C plots (Figure 11). Enhanced concentrations of ammonium and aluminium reduce the uptake of base cations (Gloser and Gloser, 2000). Aluminium would not be a problem in FF as the concentration of free aluminium was low and below the concentrations that may have effects on seedling roots (2.7-5.4 mg l^{-1}, Göransson and Eldhuset, 1991). The decreasing concentration of magnesium and calcium in fine roots in FF in NS plots was probably caused by the high concentrations of ammonium added to the soil. The decreasing concentrations of magnesium in fine roots in the upper two mineral soil layers may have been an effect of both high ammonium and high aluminium concentrations in the soil solution. The aluminium concentration at 20 cm depth followed a similar pattern as at 50 cm (Paper II) and was about 14 mg l^{-1} in 1992. The decreased concentration of potassium in the fine roots in the mineral soil could reflect the low concentration in the soil and soil solution. The demand for potassium was higher in NS than in C plots due to increased uptake by the litter biomass (Paper V).

Effects on nutrient uptake (Paper III and V)

The annual accumulation of nitrogen in the total biomass in NS plots (58 kg ha^{-1}) was nine times more than was accumulated in the biomass in C plots during the period 1988-1993. Most of the nitrogen was incorporated into the needle biomass (60%). The needle biomass increased as well as the concentration of nitrogen, which gradually increased from about 14 mg g^{-1} to about 20 mg g^{-1} in current needles. The nitrogen pool in C needles was not affected during the same period. The accumulation of phosphorus, potassium, calcium, magnesium and sulphur

was slightly higher in NS than in C plots. The trees in NS plots utilised the additional nitrogen to increase the above ground biomass by 47% more than the trees in C plots during the period 1988-1993, despite a low input of other macronutrients.
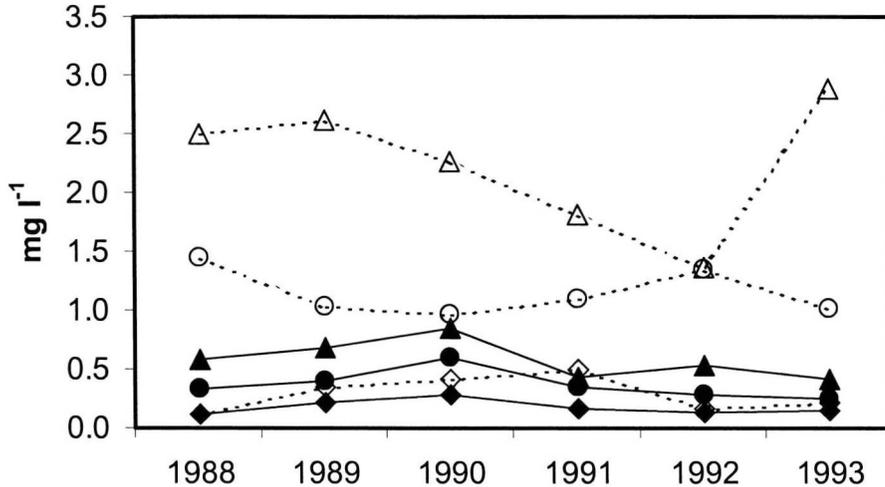

Figure 11. Annual mean concentrations of K (diamond), Mg (triangle) and Ca (circle) in soil solution at 20 cm depth in NS (open symbols) and C plots (filld symbols). C=control and NS= ammonium sulphate treated plots.

The retention of nitrogen in NS plots was 93% and the leaching was 7% of the total addition. Of the amount retained, 48% was accumulated in the trees and 43% in the soil. Of the amount accumulated in the soil, 10% came from fine root and needle litter and 31% from deposition and fertilisation.

The addition of nitrogen to NS plots increased the amounts of nitrogen and potassium circulating in the ecosystem. Compared to C plots, the uptake of nitrogen by needles increased by a factor of 2.6 and the flux in litterfall and net mineralisation increased by a factor of 1.5. The fluxes of potassium increased in an almost identical way. The annual accumulation of nitrogen in the soil was 52 kg ha^{-1}, of which 8 kg ha^{-1} was in the form of ammonium. During a 6-year period, the NS plots became nitrogen saturated, whichwas indicated by increased nitrogen concentration in the needles and nitrate in the soil solution. However, the total fine root biomass had not decreased, which could be expected as this is also a sign of nitrogen saturation (Aber et al., 1989).

Production (measured as annual basal area increment) started to decrease in NS plots in 1992 and from 1996 onwards it was lower than in C plots (Nilsson, pers. comm.) indicating nutrient imbalances.
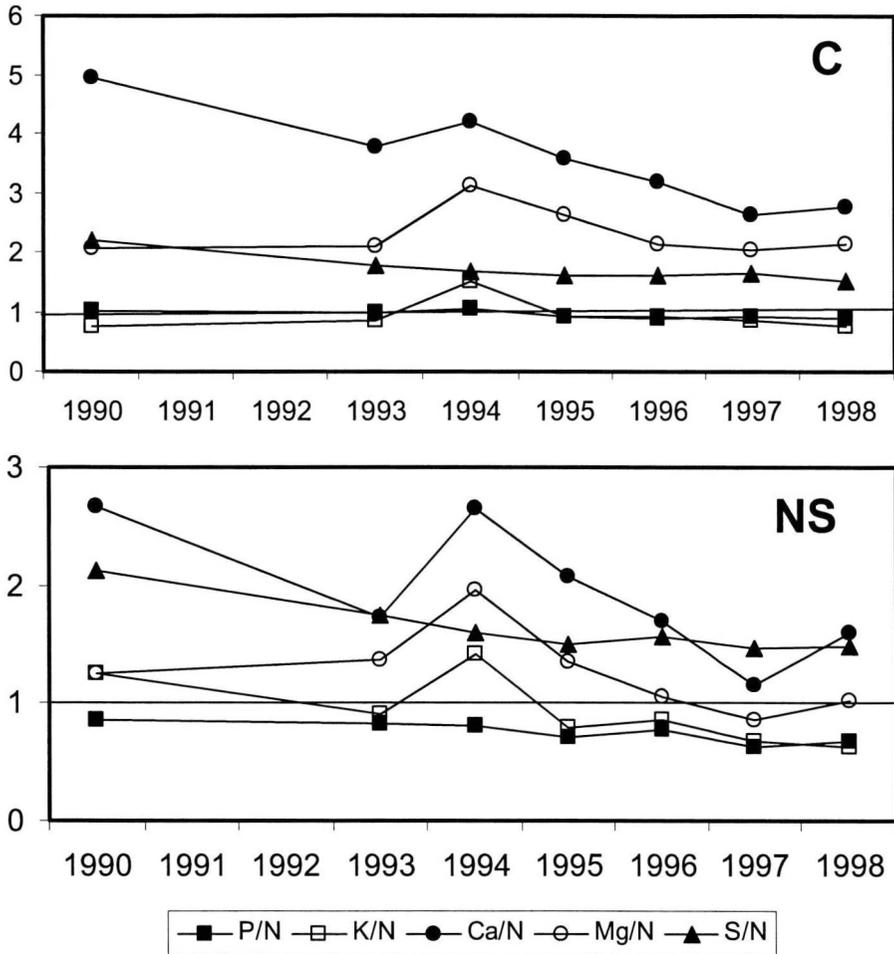
Figure 12. Nutrient/nitrogen ratio in current needles in relation to the nutrient/nitrogen values proposed by Braekke (1998). C=control plots and NS= ammonium sulphate treated plots.

Nutrient:nitrogen ratios in needles are often used as indicators of nutrient imbalances (Braekke, 1998). Ratios lower than the limit values: P/N=0.1, K/N=0.3, Ca/N=Mg/N=S/N=0.04, indicate nutrient imbalances. Figure 12 indicates that there was already a deficiency of potassium in C plots in 1990 and that phosphorus was just at the border of deficiency. The Ca/N ratio decreased gradually and there was also a tendency for a decreasing S/N ratio. During the winter 1993/1994, a 25% thinning of the stand was performed and during the growing season 1994 the ratios for potassium, calcium and magnesium increased. A rough estimate indicates that the increased concentration of potassium in current needles in 1994 corresponded to an uptake of about 6-7 kg ha⁻¹. The concentration in the needles increased by 2.3 mg g⁻¹ compared to 1993. The production of current needles was about 4 ton ha⁻¹ 1990 (Nilsson and Wiklund,

1992). Presuming that production was similar in 1994, the current needle biomass was 3 ton ha^{-1} on the remaining trees. The fine root biomass could deliver at most 0.5 kg ha^{-1} by decomposition of the remaining fine roots from cut trees. This indicates that potassium was released by processes in the soil other than decomposition of fine root litter, *e.g.* by increased decomposition rate of needle litter and soil organic matter due to changed climate in the stand after the thinning. In addition to this, the leaching of potassium increased by about 4 kg ha^{-1} in 1994 (Paper II).

The relevance of the NS treatment

It can be argued that the 'deposition rate' of 100 kg nitrogen and 114 kg sulphate was unrealistically high and that the addition of nitrogen was only in the form of ammonium. The 'natural' deposition usually contains equal amounts of ammonium and nitrate (Lövblad, 2000). However, the addition rate of ammonium and sulphate in Skogaby was not far from what has been measured in certain regions of Europe. van Breemen et al (1984) reported deposition rates of above 60 kg ha^{-1} yr^{-1} in throughfall and stemflow in a Scots pine and a mixed broad-leaved tree stand. The deposition contained mainly ammonium. de Schrijver et al. (2000) found 95 kg ha^{-1} yr^{-1} of nitrogen in throughfall under Corsican pine in Belgium in an area with intensive livestock production. About 80% was in the form of ammonium. In Sollingen, Germany, the throughfall under Norway spruce contained over 100 kg ha^{-1} yr^{-1} of sulphur during the mid 1970s. The deposition of nitrogen was increasing during this period by about 40 kg ha^{-1} yr^{-1} during the late 1980s (Matzner and Meiwes, 1994). This indicates that the 'deposition' rate in Skogaby was not totally unrealistic when compared with other countries.

It is not easy to convert the results obtained from Skogaby directly into future effects on Swedish forests. It is quite different for an ecosystem to receive a heavy load of nitrogen and sulphur during a 10-year period than to receive the same amount during a 50 year period. Nevertheless, the Skogaby experiment, with its corresponding studies on the different compartments of the ecosystem, has provided a considerable amount of information on reactions of the ecosystem under nutrient and water stress.

Recovery

Encouraging reports are emerging concerning recovery from acidification in Sweden, Europe and North America (Warfinge and Bertills, 1999; Stoddard et al., 1999; Alewell et al., 2000). The emissions of sulphur dioxide have decreased in Europe since the mid 1970s, resulting in decreasing sulphur and proton deposition. The deposition in a spruce stand in Southeast Sweden decreased from 20 to 8 kg S ha^{-1} yr^{-1} during the period 1988-1998 (Westling and Lövblad, 1999), resulting in an increased pH in precipitation. This was similar to the findings at Skogaby. Effects of decreasing sulphuric acid concentrations in throughfall could be seen as decreasing sulphur, calcium and magnesium concentrations in soil

solution at 20 and 90 cm depth (Alewell et al., 2000). The pH did not increase, indicating strong buffering capacity in the soil. However, there was a significant decrease in aluminium at 90 cm depth. Only weak responses in soil solution to decreasing acid deposition were seen in C plots at Skogaby.

The chemical status of lakes in southern Sweden has improved. Measurements in a lake in Scania since 1984 showed decreasing sulphate and base cation concentrations and increasing alkalinity and same tendencies have been found in many other lakes in southern Sweden (Wilander and Lundin, 1999). This shows that ecosystems are starting to recover from decades of acid deposition. However, complete rehabilitation will take a long time as there are buffering systems involved, *e.g.* the desorption of adsorbed sulphate in the soil profile will result in release of protons to the soil solution.

There is now a golden opportunity in Skogaby to study the recovery from a strong acid situation with small base cation reserves and high aluminium concentrations in the soil and soil solution. This may throw light on the question of how long it will take to improve tree production and soil chemical status after the heavy 'deposition' of nitrogen and sulphur ceases.

Conclusions

The spruce forest in the study region has the potential for high biomass production. Addition of nitrogen in addition to current nitrogen deposition increased forest production, at least in a short-term perspective. There seems to be no long-term risk of nutrient imbalances of calcium and magnesium with the current nitrogen deposition in south-western Swedish forests as deposition of sea salts and weathering compensate for the amounts of these nutrients leaching from the soil. In the case of potassium, there seems to be a risk of deficiency, since potassium accumulation and leaching often exceed the input by deposition and weathering.

Enhanced ammonium addition initially increased the biomass production until the forest became nitrogen saturated. Thereafter, tree production decreased, most probably due to high ammonium and aluminium concentrations in the soil and soil solution constraining the uptake of base cations and causing nutrient imbalances.
Adsorption and desorption of sulphate in the mineral soil regulated the total proton load in the soil, which fluctuated considerably between years. The fluctuation depended partly on the water runoff during the year, resulting in variable annual leaching patterns of aluminium and base cations.

The nitrogen addition increased nitrogen accumulation in the biomass without a corresponding increase in accumulation of other nutrients, while the turnover rate of nitrogen and potassium in the soil increased.

The input of nutrients by decomposition of fine root litter was higher than the input by decomposition of litterfall.

Most soils in the region are acidified by sulphuric acid deposition. The contribution from nitrogen deposition is of minor importance as ammonium and nitrate are taken up in almost similar proportions and there is no leaching of inorganic nitrogen.

References

Aber, J., Nadelhoffer, K.J., Steudler, P. and Melillo, J.M. 1989. Nitrogen saturation in northern forest ecosystems. *Bioscience 39 (6),* 378-386.

Ågren, G.I. and Bosatta, E. 1988. Nitrogen saturation of terrestrial ecosystems. *Environmental Pollution 54,* 185-197.

Alavi, G. 1996. Radial stem growth of *Picea abies* in relation to spatial variation in soil moisture conditions. *Scandinavian Journal of Forest Research 11,* 209-219.

Alewell, C., Manderscheid, B., Gerstberger, P. and Matzner. E. 2000. Effects of reduced atmospheric deposition on soil solution chemistry and elemental contents of spruce needles in NE-Bavaria, Germany. *Journal of Plant Nutr. Soil Sci. 163,* 509-516.

Anon. 1986. Luftföroreningar – trädvitalitet – skogsskador, ramprogram för pågående och planerade insatser. *Skogsvetenskapliga fakulteten,* Rapport 1 (in Swedish)

Braekke, F., Salih, N. and Ingerslev, M. 1998. Nutrient status of stands – needle analyses. In F. Andersson, F. Braekke and L. Hallbäcken (Eds).Nutrion and growth of Norway spruce forests in a Nordic clmatic and deposition gradient. *Nordic Council of Ministers, Forestry, Tema Nord,* 566.

Beier, C. and Rasmussen, L. 1993. The EXMAN Project. Experimental Manipulation of Forest Ecosystems in Europe. *Commission of the European Communities, Ecosystem research,* Report 7.

Berggren, D. and Mulder, J. 1995. The role of organic matter in controlling aluminium solubility in acidic mineral soil horizons. *Geochimica et Cosmochimica 59 (20),* 4167-4180.

van Breemen, N., Burrough, P.A., Velthorst, E.J., van Dobben, H.F., de Wit, T. Ridder, E.J. and Reijnders, H.F.R. 1984. Soil acidification from atmospheric ammonium sulphate in forest canopy throughfall. *Nature* 299, 548-550.

Clarke, N., Danielsson L-G. and Sparén A. 1992. The determination of quickly reacting aluminium in natural waters by kinetic discrimination in a flow system. *Intern. J. Environ. Anal. Chem.* 48, 77-100.

Cowling, E.B. 1982. Acid precipitation in historical perspective. *Environmental Sci. and Technol.* 16 (2), 110-122.

Dieffenbach, A. and Matzner, E. 2000. *In situ* soil solution chemistry in the rhizosphere of mature Norway spruce (*Picea abies* (L.) Karst.) trees. *Plant and soil 222,* 149-161.

Ek, A.S., Löfgren, S., Bergholm, J. and Qvarfort, U. 2001. Environmental effects of one thousand years of copper production at Falun, Central Sweden. *Ambio* 30 (2), 96-103.

Falkengren-Grerup, U. 1987. Long-term changes in pH of forest soils in southern Sweden. *Environmental Pollution 43,* 79-90.

FAO-Unesco. 1990. Soil Map of the World

Gloser, V. and Gloser, J. 2000. Nitrogen and base cation uptake in seedlings of *Acer pseudoplatanus* and *Calamagrostis villosa* exposed to an acidified environment. *Plant and Soil 226,* 71-77.

Göransson, A. and Eldhuset, T.D. 1991. Effects of aluminium on growth and nutrient uptake of small *Picea abies* and *Pinus sylvestris* plants. *Trees 5,* 136-142.

Hallbäcken, L. 1992. Long term changes of base cation pools in soil and biomass in a beech and spruce forest of southern Sweden. *Zeitschrift für Planzenernährung und Bodenkunde 155,* 51-60.

Hallbäcken, L. and Tamm, C.O. 1986. Changes in soil acidity from 1927 to 1982-1984 in a forest area of South-west Sweden. *Scandinavian Journal of Forest Research 1,* 219-232.

Hultberg, H., Moldan, F. Andersson, B.I. and Skeffington, R. 1998. Experimental Reversal of Acid Rain Effects. *The Gårdsjö Roof Project.* John Wiley and Sons Ltd.

Hüttl, R.F. 1990. Forest decline, nutrient supply and diagnostic fertilisation in southwest Germany and in South Carolina. *Forest Ecology and Management 30,* 341-350.

Jansson, P-E. 1990. Air Pollution – Tree Vitality – Forest Damage and Production. The Skogaby Project. *Swedish University of Agricultural Sciences, Department of Agricultural Hydrology,* Report 90:2. ISSN 0282-6569, ISBN 91-576-4180-3.

Jansson, P.-E. 1998. Simulation Model and Heat Conditions. Description of the SOIL-model. *Swedish University of Agricultural Sciences, Dept. of Soil Science, Uppsala,* 81 pp.

Karltun, E. 1995. Acidification of Forest Soils on Glacial Till in Sweden. *Swedish Environmental Protection Agency, Report 4427.*

von Linné, C. 1889. The Early Works of Carl von Linné. *P.A. Norstedt & söners förlag,* Stockholm, Sweden. (In Swedish).

Lövblad, G. 2000. Nitrogen deposition. Now and in the future. In U. Bertills and T. Näsholm (Eds) Effects of Nitrogen Deposition on Forest Ecosystems. *Swedish Environmental Protection Agenc Report 5067,* 21-28.

Majdi, H. and Persson, H. 1993. Spatial distribution of fine roots. rhizosphere and bulk-soil chemistry in an acidified *Picea abies* stand. *Scandinavian Journal of Forest Research 8,* 147-155.

Majdi, H. and Persson, H. 1995. Effects of ammonium sulphate application on the chemistry of bulk soil, rhizosphere, fine roots and fine-root distribution in a *Picea abies* (L.) Kast. stand. *Plant and Soil 168-169,* 151-160.

Majdi, H. and Rosengren-Brinck, U. 1994. Effects of ammonium sulphate application on the rhizosphere, fine root and needle chemistry in a *Picea abies* (L.) Karst. stand. *Plant and Soil 162,* 71-80.

Majdi, H., Damm, E. and Nylund, J-E. 2001. Longevity of mycorrhizal root depends on branching order and nutrient availability. *New Phytologist 150,* 195-202.

McLaughlin, S.B. 1985. Effects of air pollution on forest: a creatical review. *Journal of air pollution control 35,* 512-534.

Marschner, H. 1995. *Mineral Nutrients of Higher Plants.* Academic Press.

Matzner, E. and Meiwes, K.J. 1994. Long-term development of element fluxes with bulk precipitation and throughfall in two German forests. Journal of *Environmental Quality 23,* 162-166.

Mulder, J., van Grinsven, J. J. M. and van Breemen, N. 1987. Impact of acid atmospheric deposition on woodland soils in the Netherlands: III Aluminium chemistry. *Soil Science Society American J. 51,* 1640-1645.

Näsholm, T. and Persson, J. 2001. Plant acquisition of organic nitrogen in boreal forests. *Phyiologia Plantarum 111,* 419-426.

Nihlgård, B. 1985. The ammonium hypothesis – An additional explanation to the forest dieback in Europe. *Ambio 14 (1),* 2-8.

Nilsson, J. 1986. Critical Loads for Nitrogen and Sulphur. *The Nordic Council of Ministers. Environmental Report,* 1986:11.

Nilsson, L.O. 1991. Investigation of impact of air pollution on tree vitality, forest damage and forest production. The Skogaby project. Biomass performance after 3 years treatment. *Proceedings of the IUFRO and ICP-forest workshop on Monitoring Air Pollution Impact on Permanent Sample Plots, Data Processing and Results Interpretation,* Prachatice, CSFR, September 2-6, 1991 pp 69-77.

Nilsson, L-O. and Wiklund, K. 1992. Influence of nutrient and water stress on Norway spruce production in south Sweden – the role of air pollutants. *Plant and Soil 147,* 251-265.

Nilsson, L-O. and Wiklund, K. 1994. Nitrogen uptake in a Norway spruce stand following ammonium sulphate application, fertigation, irrigation, drought and nitrogen-free-fertilisation. *Plant and Soil 164,* 221-229.

Nilsson, L-O. and Wiklund, K. 1995. Nutrient balance and P, K, Ca, Mg, S and B accumulation in a Norway spruce stand following ammonium sulphate application, fertigation, irrigation, drought and N-free-fertilisation. *Plant and Soil 168-169,* 437-446.

Odén, S. 1967. Nederbördens försurning. *Dagens Nyheter, October 24*. (in Swedish)

Odén, S. 1968. Nederbördens och luftens försurning – dess orsaker, förlopp och verkan i olika miljöer. *Ekologikommittén, Bulletin no 1*, 86 pp (summary in English).

Persson, H., von Frick, Y., Majdi, H. and Nilsson, L-O. 1995. Root distribution in a Norway spruce (*Picea abies* (L.) Karst.) stand subjected to drought and ammonium-sulphate application. *Plant and Soil 168-169*, 161-165.

SAS Institute Inc. 1996. The SAS System for Windows vers. 6.12.

Schecher, W.D. and Driscoll, C.T. 1987. An evaluation of uncertainty associated with aluminium equilibrium calculations. *Water Resources Research. 23,* 525-534.

de Schrijver, A., van Hoydonck, G., Nachtergal, L., de Keersmaeker, L., Mussche, S. and Lust, N. 2000. Comparison of nitrate leaching under Silver birch (*Betula pendula*) and Corsican pine (*Pinus nigra ssp. laricio*) in Flanders (Belgium). *Water, Air, and Soil Pollution 122,* 77-91.

Ragsdale, S.E., Lindberg, S.E., Lovett, G.M. and Schaefer, D.A. 1992. Atmospheric Deposition and troughfall fluxes of base cations. In: Johnson, D.W. and Lindberg, S.E. (Eds.), Atmospheric deposition and forest nutrient cycling. *Ecological Studies 91*, 235-253.

Schulze, E-D. 1989. Air pollution and forest decline in a spruce (Picea abies) forest. *Science 244,* 776-783.

Stoddard, J.L., Jeffries, D.S., Lükewiile, A., Clair, T.A., Dillon, P.J., Driscoll, C.T., Forsius, M., Johannesen, M., Kahl, J.S., Kellogg, J.H., Kemp, A., Mannio, J., Monteith, D.T., Murdoch, P.S., Patrick, S., Rebsdorf, A., Skjelkvåle, B.L., Stainton, M.P., Traaen, T., van Damm, H., Webster, K.E., Wieting, J. and Wilander, A. 1999. Regional trends in aquatic recovery from acidification in North America and Europe. *Nature 401,* 575-578.

Sverdrup, H. and Warfinge, P. 1995. Critical loads of acidity for Swedish forest ecosystems. *Ecological Bulletins 44*, 75-89.

Troedsson, T. and Nilsson, Å. 1984. pH in Swedish Forest Soils. *National Swedish Environment Protection Board, Report 1853.*

UN-ECE. 2000. Convention on Long-range Transboundary Air Pollution.

Viro, P.J.: 1952. On the determination of stoniness. *Communicationes instituti forestalis fenniae 40 3,* 1-23. (in Finnish with English summary).

Warfinge, P. and Bertills, U. 1999. Recovery from acidification in natural environment. *Swedish Environmental Protection Agency, Report 5034.*

Westling, O. and Lövblad, G. 1999. Deposition trends in Sweden. In P. Warfinge and U. Bertills (Eds). Recovery from Acidification in the Natural Environment. *Swedish Environmental Protection Agenc,. Report 5034.*

Wilander, A. and Lundin, L. 1999. Recovery of surface waters and forest soils in Sweden. In P. Warfinge and U. Bertills (Eds). Recovery from Acidification in the Natural Environment. *Swedish Environmental Protection Agency, Report 5034.*

de Wit, H.A. 2000. Solubility Controls and Phyto-toxicity of Aluminium in a Mature Norway Spruce Forest. *Agricultural University of Norway.* Doctor Scientiarum Theses 2000:14.

Wright, R.E. and Rasmussen, L. 1998. Introduction to the NITREX and EXMAN projects. *Forest Ecology and Management 101*, 1-7.

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