Responses of boreal forest soils to changes in acidifying deposition

Ari Nissinen

Academic dissertation

To be presented, with the permission of the Faculty of Agriculture and Forestry of the University of Helsinki, for public criticism in Auditorium XII of the University Main Building, Fabianinkatu 33, on 24 September 1999, at 12 o'clock noon

Responses of boreal forest soils to changes in acidifying deposition

Ari Nissinen

Helsingin yliopiston metsäekologian laitoksen julkaisuja 20
University of Helsinki Department of Forest Ecology Publications 20

Julkaisija/ *Publisher*: Helsingin yliopiston metsäekologian laitos
Toimittaja/ *Editor*: Ahti Kotisaari

Kansien suunnittelu ja typografia / *Cover design and typography*: Ahti Kotisaari
Tekstin taitto/ *Text layout*: Ari Nissinen
Kansikuva/ *Cover drawing*: Ari Nissinen
Kielentarkastus/ *Revision of English*: Nancy Seidel

Työn ohjaajat/ *Supervisors:* *Prof. Pertti Hari and Dr. Hannu Ilvesniemi, University of Helsinki, Department of Forest Ecology, Helsinki, Finland*
Esitarkastajat/ *Reviewers:* *Prof. Helinä Hartikainen, University of Helsinki, Department of Applied Chemistry and Microbiology, Helsinki, Finland, and Docent Juha Kämäri, Finnish Environment Institute, Helsinki, Finland*
Vastaväittäjä/ *Opponent:* *Prof. Jan Mulder, Agricultural University of Norway, Department of Soil and Water Sciences, Ås, Norway*

ISBN 951-45-8687-5 (PDF version)

Helsingin yliopiston verkkojulkaisut
Helsinki 1999

Contents

Abstract

Nissinen, Ari 1999. Responses of boreal forest soils to changes in acidifying deposition. University of Helsinki Department of Forest Ecology Publications 20. ISBN 951-45-8878-9, ISSN 1235-4449.

The aim of the study is to analyse long-term responses of boreal forest soils to changes in acidifying deposition, by 1) determining chemical reactions that affect ion leaching in soils, 2) developing mathematical models to describe the chemical reactions and biological and microbiological processes that affect soil responses to ion deposition, and 3) analysing long-term soil responses to changes in acidifying deposition using the models and the knowledge that is based on theories and experiments.

The release of salt-exchangeable H^+ and Al from mineral horizons of soils was studied with two sequential extractions with unbuffered 0.1 M $BaCl_2$. Salt-exchangeable H^+ was found to be in equilibrium with weak acid groups, and the modified Henderson–Hasselbach equation was used to explain pH of the extract: $pK_{HH} = pH - n \log(\alpha / (1-\alpha))$. The degree of dissociation (α) was determined as a ratio between effective and potential cation exchange capacity. The value of n was found to be near unity. For Al, two equilibrium models were evaluated, describing 1) complexation reactions of Al with soil organic matter, and 2) equilibrium with $Al(OH)_3$. Apparent equilibrium constants were written as 1) $pK_o = x pH - pAl$, and 2) $\log K_{gibbs} = \log Al^{3+} - 3 \log H^+$. The results suggest that an equilibrium with organic Al complexes can be used to express dissolved Al, reaction stoichiometry x being 2.0.

The relation between the cations in solution and the cations on exchange sites was expressed by using the Gaines–Thomas selectivity coefficient, K. The selectivity coefficient of binary cation-exchange seemed to be applicable to *in situ* soil solutions, which were collected using a centrifuging method. The variation in the apparent cation-exchange coefficients $K_{H\text{-}Ca}$, $K_{Al\text{-}Ca}$, and $K_{K\text{-}Ca}$ was larger in a suction lysimeter method than in the centrifuging method, and the values were different. The differences between the centrifugates and the lysimeter solutions in the total charge of ions and cation-exchange equilibria imply that there cannot be cation-exchange equilibria between the solution in large pores (i.e. the mobile solution) and the bulk exchangeable cations, although there seems to be cation-exchange equilibria in small pores. This means that the assumption of apparent cation-exchange equilibria in mobile solution does not apply well to an analysis of acidic deposition effects on soil.

Aggregation of soil properties in modelling of soil acidification led to an underestimation of Ca and Mg leaching and overestimation of H^+ and Al concentrations in the runoff water.

Model ‘Forest Element Fluxes’ (FEF) was developed and used to analyse the responses of soils to changes in deposition. The analyses utilise information gained in the studies of soil chemistry. The analyses suggest that an increase in hydrogen ion deposition has led to a markedly increased leaching loss of H^+ from soil as well as decreased production of H^+ in dissociation of dissolved organic acids. Base cation leaching from soil has also increased. Consequently this has led and will further lead to a decrease in base saturation and an increase in the ratio Al/Ca in soil solution. Hydrogen ion deposition affects soil acidification, whereas the deposition of NH_4 and NO_3 affects the leaching of nitrogen to surface waters.

If the deposition of hydrogen ions and ammonium and nitrate remains at the level of 1990 or grows, the long-term changes in nutrient availability, leaching of ammonium and nitrate, and tree growth will be large.

Key words: forest soil**,** acidification, cation-exchange, aluminium, solubility, leaching, exchangeable acidity, modelling, tree growth.

Author's address: Department of Forest Ecology, P.O. Box 24, FIN-00014 University of Helsinki, Finland. Visiting address Unioninkatu 40 B. Email ari.nissinen@helsinki.fi.

List of original articles

This thesis is based on the following articles, which are referred to in the text by the word ‘Study’ and their Roman numerals I-V. In addition, some unpublished results are presented.

Study I. Nissinen, A., Ilvesniemi, H. and Tanskanen, N. Equilibria of weak acids and organic Al complexes explain activity of H^+ and Al^{3+} in a salt extract of exchangeable cations. European Journal of Soil Science (accepted).

Study II. Nissinen, A., Ilvesniemi, H. and Tanskanen, N. 1998. Apparent cation-exchange equilibria in podzolic forest soils. European Journal of Soil Science 49, 121-132.

Study III. Nissinen, A., Kareinen, T., Tanskanen, N. & Ilvesniemi, H. Apparent cation–exchange equilibria and aluminium solubility in solutions obtained from two acidic forest soils by centrifuge drainage method and suction lysimeters. Water, Air and Soil Pollution (in print).

Study IV. Nissinen, A. 1995. Simulated effects of acid deposition on podzolic soils: Consequences of process and parameter aggregation. Water, Air, and Soil Pollution, 85, 1107-1112.

Study V. Nissinen, A. & Hari, P. 1998. Effects of nitrogen deposition on tree growth and soil nutrients in boreal Scots pine stands. Environmental Pollution 102 S1: 61-68.

List of commonly used abbreviations

BS = Base saturation
CEC$_e$ = Effective cation-exchange capacity
EA = Exchangeable acidity
SOM = Soil organic matter
FEF = A dynamic model, ‘Forest Element Fluxes’

1 Introduction

1.1 Acidic and acidifying deposition

Combustion of fossil fuels, which is a main source of the sulphur and nitrogen oxides emitted into the atmosphere (Rodhe *et al.* 1995), has increased exponentially during the 19th and 20th centuries. Given as relative values, global emissions of carbon from the combustion have increased from 1 in 1860 to 5 in 1900, 13 in 1940, and 53 in 1980 (Boden *et al.* 1990). Similarly, it has been estimated that the emissions of sulphur dioxide, SO_2, and nitrous oxides, NO_x, began to increase in the late 1800s and early 1900s, primarily in North America and Europe (Galloway 1995). In Finland the emissions of both SO_2 and NO_x were about fivefold in 1990 compared with the emissions in 1950 (Savolainen and Tähtinen 1990). After 1990, the mandated and planned emission should have decreased the total SO_2 and NO_x emissions in Finland considerably (Savolainen and Tähtinen 1990).

The atmospheric reactions of NO_x and SO_2 lead to nitrous and sulphuric acid formation and to an increased inflow of anions and protons into soils, which can increase ion leaching from soils. Consequently, ‘acidic deposition’ can be defined as the inflow of hydrogen ions from the atmosphere to forests. In addition, the reactions of sulphates and nitrates in soil are considered in studies that analyse the effects of acidic deposition on forests. ‘Soil acidification’ is a general term that is used to cover harmful chemical changes in soils due to acidic deposition, but as a phenomenon soil acidification can also occur as a result of internal proton production in soil.

Ammonium, NH_4, is also accounted for in ‘acidifying deposition’, because ammonium can have an acidifying effect on soil. When it is nitrified, protons are produced and the nitrate can be leached from soil with base cations. Ammonium can also replace base cations on cation-exchange sites, and in this way increase base cation leaching. Emissions of its precursor ammonia, NH_3, started to increase only after 1950, but the global emissions of nitrogen in ammonia, NH_3-N, are now slightly larger than the emissions of NO_x–N (Galloway 1995). The increase is caused by the growing use of nitrogen fertilisers, NH_3 being emitted from soils and domestic animals (Graedel *et al.* 1995).

The present bulk deposition in southern Finland is about 500 mg m^{-2} a^{-1} for SO_4-S, 250 mg m^{-2} a^{-1} for NO_3-N and 250 mg m^{-2} a^{-1} for NH_4-N (Appendix 1), with higher values close to the southern coast of Finland (e.g. Leinonen and Juntto 1992, Lövblad *et al.* 1992). The average pH of the bulk deposition is around 4.4 in southern Finland (to be exact, pH has been measured from the collected solution).

Deposition in remote areas is low, and it gives an estimate of ‘natural’ deposition, although this deposition includes the effect of long-range transport of anthropogenic sulphates, nitrates and the oxides (Rodhe *et al.* 1995). In Finland, the deposition of ions is much smaller in Lapland than in the southern part of the country (see Appendix 1). The present bulk deposition in Kevo in northern Lapland is about 150 mg m^{-2} a^{-1} for SO_4-S, 45 mg m^{-2} a^{-1} for NO_3-N and 25 mg m^{-2} a^{-1} for NH_4-N, and the pH of the bulk deposition is about 4.8. The deposition in Kevo may well represent deposition in remote areas: Rodhe *et al.* (1995) refer to studies, in which the bulk deposition of SO_4 in remote areas of northern America has been less than 200 mg S m^{-2} a^{-1}. Globally the deposition range of 100-250 mg S m^{-2} a^{-1} covers large remote areas of the world, far from industrialised regions. Correspondingly, nitrate deposition is between 10 and 50 mg N m^{-2} a^{-1} in large remote areas, and the deposition of NH_4 is 20-50 mg N m^{-2} a^{-1}. Much smaller deposition values can also be found, but because the extremely low deposition values are mainly in the Antarctic and in the middle of oceans, these values may not be representative of the ‘natural deposition’ on forested continents.

The bulk deposition in an open area is an underestimate of the deposition in a forest, because the device collecting bulk deposition does not retain gaseous compounds and particles (or ‘dry deposition’) from the atmosphere as effectively as vegetation does (Mayer and Ulrich 1977). In coniferous forests the dry deposition of sulphur can be 30% to 260% greater than the bulk deposition (Ulrich 1983b, Ivens *et al.* 1989, Hyvärinen 1990).

The dry deposition of nitrogen is difficult to estimate because plants take nitrogen through the leaf surface and there is often less nitrogen in the throughfall than in the bulk deposition (Ulrich 1983b, Hyvärinen 1990, Hanson and Lindberg 1991, Sutton *et al.* 1983, Hallgren Larsson *et al.* 1995). Tuovinen *et al.* (1990) estimated that the average dry deposition of NO_3-N and NH_4-N is slightly more than 50% of the average wet deposition in Finland.

The deposition of base cations decreases the acidifying effect of hydrogen ion deposition in forest soil, because the larger the ratio between base cation concentration and hydrogen ion concentration in the solution percolating through the soil, the less hydrogen ions are retained on cation-exchange sites (Nissinen and Ilvesniemi 1990, de Vries *et al.* 1995). Hedin *et al.* (1994) suggest that base cation deposition is decreasing in Europe and North America, which can slow down the beneficial effects of emission reductions of sulphur and nitric oxides.

1.2 Soil acidification

Historical perspective of soil chemistry

Acid soils occupy approximately 30% of the world’s ice-free land area, and forests growing on acid soils provide the bulk of the world’s timber (von Uexküll and Mutert 1995). Soil acidification is not a recently recognised problem: More than 150 years ago Edmund Ruffin limed his fields to get better crop yield, believing that this procedure could decrease soil acidity caused by organic acids (Ruffin 1832, as cited by Thomas 1977). The true cause of the low fertility of acid soils, namely soluble aluminium, was found by Vietch as early as 1904 (Vietch 1904). He also found that the amount of lime needed to remedy the harmful Al in mineral soil could be determined by neutral salt. This method does not give the total acidity of soil, but it gives the 'active' acidity useful in e.g. soil acidification studies and analyses of cation-exchange equilibria (Nye *et al.* 1961, Thomas 1982). The importance of these findings was understood only 50 years later, when the role of aluminium in soil acidity gained more attention (as reviewed by Thomas 1977 and Thomas 1988).

Von Uexküll and Mutert (1995) defined acid soils as soils with $pH(H_2O)<5.5$ in their surface zones. Soil pH is commonly used as an indicator of soil acidity, because hydrogen ion activity affects many reactions in soil solution: dissolution and precipitation of e.g. aluminium, cation exchange, anion adsorption, reduction and oxidation, and complexation reactions (McBride 1994, p. 169). Actually the term 'soil pH' denotes the activity of hydrogen ions in a suspension soil:water, $pH(H_2O)$, or soil:0.01 M $CaCl_2$, $pH(CaCl_2)$.

Pierre and Scarseth (1931) showed that soil pH is closely connected to the base saturation of the soil (or the relation between the exchangeable base cations and the cation exchange capacity), but the relationship differs greatly from soil to soil, indicating the type of soil material that is responsible for the exchange capacity (Pierre and Scarseth 1931, Thomas and Hargrove 1984). The connection between soil pH, base saturation and dissolution of Al in soils was a central idea in the early development of soil acidification theory (Ulrich 1983c) and some dynamic models of soil acidification (Kauppi *et al.* 1986, Posch *et al.* 1989).

The terms 'base cations' and 'base saturation' are used throughout in this thesis, although they can be regarded as misleading: The word 'base' does not here refer to base as the opposite of an acid. The reason for the use of this word is that when cation-exchange sites are saturated with 'base cations', soil pH is neutral or alkaline. Other terms could be more informative, for example 'alkali and earth alkaline saturation degree related to the effective cation exchange capacity' (Hartikainen 1996). However, base saturation is still commonly used in the literature of soil acidification (see for example Kämäri et al. 1998) as well as in the textbooks of soil chemistry (for example McBride 1994).

Cation-exchange equilibria is a key concept in many analyses of soil acidification. The first quantitative study on cation-exchange was done 150 years ago by H.S. Thompson, a Yorkshire farmer. He discovered that the addition of $(NH_4)_2SO_4$ to a column of soil resulted in the appearance of $CaSO_4$ solution in the bottom of the column (Thompson 1850, as cited by Thomas 1977). Widely used equations that describe the equilibrium state of cation-exchange reactions were developed by Kerr (1928), Vanselow (1932), Gapon (1933) and Gaines and Thomas (1953). The equations were used to describe the reactions between base cations, owing to problems caused by e.g. salinity, irrigation and radioactive isotopes from nuclear experiments and wastes. The first applications of the models to the exchange between Al and base cations were made much later (e.g. Nye *et al.* 1961).

Observations of surface water and soil acidification

Concern over acidic deposition was raised decades ago (Barret and Brodin 1955, Gorham 1955, Oden 1968). Large-scale ecosystem experiments were started in the 60s and 70s, and the results suggested a connection between ion deposition and ionic composition of surface waters (Likens and Bormann 1977, Overrein *et al.* 1981). It was also suggested that a decrease in base cation amounts in soil had a negative effect on plant nutrition (Mayer and Ulrich 1977). Later it has been shown that sulphate concentrations in lakewaters correspond to the pattern of sulphur deposition in Finland (Forsius *et al.* 1990) and that concentration of inorganic aluminium in soil solution is positively correlated with non-marine sulphur deposition and nitrate concentration in soil solution is positively correlated with throughfall nitrogen in Sweden (Hallgren Larsson *et al.* 1995).

Experimental acidification of soils by leaching soil with an acid solution has been used to analyse soil responses to acidic deposition. In many experiments leaching of base cations from soils increased (e.g. Abrahamsen 1983, Bergkvist 1986, Freiesleben and Rasmussen 1986, Skeffington and Brown 1986, Wright *et al*. 1988, Nissinen and Ilvesniemi 1990, David *et al.* 1991) and the amounts of exchangeable base cations decreased (e.g. Abrahamsen 1983, Skeffington and Brown 1986, Kelly and Strickland 1987, Nissinen and Ilvesniemi 1990) due to an increase in acidic input. Dissolution of aluminium was an important mechanism for removing hydrogen ions from solution (Brown 1987, Nissinen and Ilvesniemi 1990). This agrees with Mayer and Ulrich's (1977) observations of soil solution in an acid soil. Experiments suggested that the most important reactions in the consumption of hydrogen ions in podzolic soils were: cation-exchange with base cations in the O horizon, cation-exchange with Al and base cations in the E horizon, and dissolution of Al in the B horizon (Derome 1989, Nissinen and Ilvesniemi 1990, Starr *et al.* 1996).

Time-series of soil chemical characteristics have been measured to determine the long-term effects of acid deposition, but determining any change has been problematic due to the large heterogeneity in forest soils: Ilvesniemi (1991a) studied pine sites on podzolic soils and found that in order to observe a 10 % change in exchangeable Ca between two sampling dates, 376 and 198 samples of E and Bs1 horizon, respectively, should have been analysed. Despite this problem, some studies have found a decrease in soil pH or a decrease in the amount of exchangeable base cations (Hallbäcken and Tamm 1986, Falkengren-Grerup *et al.* 1987, Tamm and Hallbäcken 1988).

1.3 The aim of the study

The aim of the study is to analyse long-term responses of boreal forest soils to changes in acidifying deposition, by 1) determining chemical reactions that affect ion leaching in soils, 2) developing mathematical models to describe the chemical reactions and biological and microbiological processes that affect soil responses to deposition, and 3) analysing long-term soil responses to changes in acidifying deposition using the models and the knowledge that is based on theories and experiments.

To achieve these objectives, the following studies were performed: Chemical reactions were studied experimentally in Studies I, II and III. Study I focuses on effective exchangeable acidity, while Studies II and III focus on chemical equilibria in soil solutions. Studies IV and V deal with developing models for analysing soil responses to acidifying deposition. Study IV is concerned with the effects of model structure (or more precisely, aggregation of soil properties) on the simulated soil response to the deposition. The results of Studies I – IV have an important role in Study V, in which a model is described and used to analyse soil responses to acidifying deposition.

2 Theoretical background

2.1 Theory and modelling of soil acidification

Concepts of soil acidification

Soil acidification could be defined generally as a harmful chemical response of forest soil to acidifying deposition or other proton sources in soil. However, more specific definitions are needed in this work. The base saturation of the effective cation-exchange capacity, BS, can be regarded as a key soil characteristic in such a definition, so that 'soil acidification' is defined as a decrease in the BS of the soil. Low BS is assumed to indicate a low concentration of base cations in soil solution and a low amount of plant-available base cations in soil, which can lead to a deficiency of Mg, K or Ca in plants (Ulrich 1983a, 1983c) or an increased need to allocate carbohydrates to the below-ground parts in plants (Arovaara and Ilvesniemi 1990). Low BS is also assumed to indicate a high concentration of Al in soil solution, which can be harmful to plant roots (Ulrich 1983a, 1983c, Marschner 1986). Although coniferous trees are known to be aluminium tolerant (Arovaara and Ilvesniemi 1990), the toxic effects of Al are seen when the availability of nutrients is low (Ilvesniemi 1991b). High concentration of Al in runoff can also have toxic effects on the biota of surface waters (Overrein *et al.* 1981, Havas and Rosseland 1995).

Soil acidification can also be defined in many ways other than those above. De Vries and Breeuwsma (1987) define actual soil acidification and potential soil acidification. Actual soil acidification is a decrease in the acid-neutralising capacity of soil (ANC), ANC being the total amount of cations in soil. Potential soil acidification is defined as an increase in the base-neutralising capacity of the soil (BNC). BNC is the total amount of the acidic components in soil, including sulphur and nitrogen in organic matter, adsorbed sulphate, and carbon in organic matter. Sulphur and nitrogen can be transformed into sulphate and nitrate respectively, which can be leached out of soil with cations, thus decreasing ANC. Similarly, carbon can be transformed into organic acids or bicarbonate, which can be leached with cations.

In addition to base saturation, the following soil characteristics that indicate soil acidification are considered in this thesis (Chapter 7.5). The amount of base cations in soil (BC) is important for the long-term susceptibility of a soil to acidic deposition, because the release of base cations from minerals (in weathering), from soil organic matter (in decomposition) and from cation exchange sites (in an exchange reaction with protons) to solution consumes hydrogen ions. Here BC is regarded instead of ANC, because the release of e.g. aluminium into soil solution can have harmful effects on soil biota. The thesis focuses also on hydrogen ion activity in solution because it is crucial for many chemical reactions in soils. The ratio between the concentrations of Al and base cations in soil solution is considered because it can indicate the effect of soil acidification on the growth of plants (Sverdrup and Warfvinge 1993, see also critique by Falkengren-Grerup *et al.* 1995). It has also been used as a soil acidification criterion in other modelling studies (de Vries *et al.* 1989, 1994).

Models of solution chemistry in soils

Abundant research on the effects of acidic deposition on soil nutrient leaching and aluminium solubility has been done by using mathematical models which rely mostly on the theoretical and experimental knowledge of solution chemistry. Reuss (1977) and Johnson and Cole (1980) showed that the mobility of anions in soil solution is important for the leaching of cations. The principle presented by Johnson and Cole (1980) was adopted in several models of soil and surface water acidification: “Thus, while cation exchange models could describe the proportions of various cations being leached, anion exchange models could describe the total amount of cations or anions being leached.” (To be exact, unspecific anion exchange does not affect the total amount of ions in solution, while the specific adsorption of, for example, sulphate does).

In order to predict acid rain effects, Reuss (1983) presented a method in which Al^{3+} concentration in soil solution is controlled i) by dissolution of $Al(OH)_3$ as a function of hydrogen ion activity in soil solution, and ii) by cation-exchange equilibria between Ca and Al. Reuss and Johnson (1985) also considered bicarbonate equilibria. Cosby *et al.* (1985a) extended the approach to include all important cations, and Cosby *et al.* (1985b, 1986) also included sulphate adsorption in the analysis. The soil processes were described in a single soil compartment with uniform characteristics (Cosby *et al.* 1985a). In long-term simulations, net uptake (or release) of ions within the catchment were taken into account, including weathering, mineralisation of soil organic matter and biological uptake (Cosby *et al.* 1985b). Mass balance for H+ was not considered necessary (Cosby *et al.* 1985b). The result was a dynamic model, MAGIC, which has been used widely for the analysis of soil and surface water acidification (e.g. Cosby *et al.* 1989, Ferrier *et al.* 1995, Rasmussen *et al.* 1995). Many other models rely heavily on the same assumptions of geochemical processes as MAGIC (see review by Tiktak and Grinsven 1995), and thus there has been a significant convergence concerning key processes in the acidification (Reuss 1986, Kämäri 1989).

A large number of soil acidification analyses have been made using the models (for example Kauppi *et al.* 1986, de Vries and Kros 1989, Holmberg *et al.* 1989, Warfvinge *et al.* 1992, Jönsson *et al.* 1993, Warfvinge *et al.* 1993, de Vries *et al.* 1994), but model development and testing the models or their key assumptions against observations can still be considered important tasks. The assumptions of the cation-exchange equilibria were selected as the area of focus in this thesis. Although solution chemistry has been described in a detailed way in many models, the theory is mainly based on laboratory experiments, not field observations. This was the reason for Studies II and III in this thesis.

From the point of view of soil chemistry, the exchangeable acidity of soil should be a key concept in soil acidification models. However, the chemistry of exchangeable acidity is usually ignored in the models, although exchangeable Al has an important role in the simulated cation-exchange equilibria. Thus, exchangeable acidity became the focus of Study I.

The models usually deal with effectively exchangeable acidity or total acidity, but not with the chemical equibrium between the two. Although it is evident that CEC_e decreases with decreasing pH in variable charge soils (Thomas and Hargrove 1984, Duquette and Hendershot 1987), constancy of effective cation exchange capacity (CEC_e) seems to be implicitly assumed in theoretical analyses of the chemistry of soil acidification (Reuss 1983, Reuss *et al.* 1986, Reuss *et al.* 1987) as well as in many models (Tiktak and Van Grinsven 1995). It would be important to consider both CEC_e and potential cation exchange capacity (CEC_p) in the modelling, because CEC_p represents the number of sites potentially available for H^+ binding, whereas CEC_e represents the amounts of “active” acidity (Thomas 1982) and exchangeable base cations. This was actually recognized in an earlier work by Reuss (1977), in which he states that “as soils become more acid their cation-exchange capacity decreases due to neutralization of negative charge by monomeric Al^{3+} and positively charged hydroxy Al complexes and polymers.”

Aggregation of soil properties in soil modelling

The modelling approach is largely determined by the objectives of the study in which the model is used as a tool (de Vries 1994, p. 17). For example, de Vries (1994) suggests that predicting the chemical composition of surface waters may not require precise knowledge of the spatial variation in the soil properties in a catchment, whereas the prediction of the ion composition in soil solution in the same catchment requires this knowledge. In addition, the lack of the necessary input data restricts the applicability of complex mechanistics models. This is true especially in studies which focus on changes in surface waters and soils on regional scales (de Vries 1994).

Many model analyses of acidic deposition effects on soil and surface waters have considered soil to be a homogenous block with aggregated chemical soil properties (e.g. Cosby *et al.* 1985, Holmberg et al. 1989, De Vries *et al.* 1989). Jenkins and Cosby (1989), Warfvinge et al. (1992), and Van Oene and De Vries (1994) reported differences in ion leaching between model applications in which aggregated one-layer soil or multi-layer soil were described. In podzolic soils, in which the exchangeable aluminium and base cation concentrations have great depth-gradients (Tamminen and Starr 1990), models dealing with consecutive soil layers are required to account for the variable chemical characteristics of soil horizons (Holmberg *et al.* 1989, Nissinen and Ilvesniemi 1990). Study IV of this thesis is concerned with the effects of aggregation on simulated soil responses to acidic deposition.

Relations between soil acidification and element cycling in forests

Although chemical reactions can be the major determinants of the ionic composition in soil leachate over a short period, the acidification phenomena of soils must be seen in a much wider context if realistic descriptions of the hydrogen transfer reactions in soil are to be made. A large number of biogeochemical reactions associated with carbon, nitrogen, sulphur and base cation cycles must be included in the analyses (Reuss 1977, Nilsson *et al.* 1982, Ulrich 1983a, van Breemen *et al.* 1983, 1984, de Vries and Breeuwsma 1987). Biological processes - plant growth, nutrient uptake, litter production and decomposition of soil organic matter - play major roles in these cycles. Water flow is an important process, transporting ions into and out of the soil.

The internal hydrogen ion production of a forest is often larger than the hydrogen ion deposition into the forest (Nilsson *et al.* 1982), even in forests where the deposition is large (van Breemen *et al.* 1984). Accumulation of organic matter is an important internal source of hydrogen ions (Nilsson 1982, Ulrich 1983a, Matzner and Ulrich 1983). Organic matter accumulates due to the rapid growth of trees, for instance in young stands, or the slow decomposition rate of soil organic matter (SOM), for instance in old spruce stands. Another internal process is the nitrification of NH_4, which is released in mineralisation (ammonification) of SOM. This process is important especially after removal of vegetation in clear-cutting (Likens *et al.* 1969, Vitousek *et al.* 1979, Nilsson 1982, Ulrich 1983a).

Empirical studies of the total elemental turnover in each compartment of the soil-plant system have been important in assessing the importance of the different processes in the hydrogen ion budget of ecosystems (Likens and Bormann 1977, Matzner and Ulrich 1983, van Breemen *et al.* 1983, 1984, Horn *et al.* 1989, Likens and Bormann 1995). These compartments (and turnover-processes of cations and anions, shown in parentheses) include soil minerals (weathering), soil organic matter (mineralisation), soil solution (dissociation of organic acids), surfaces of soil particles and colloids (adsorption of cations and anions), soil microbes (uptake), and plants (uptake). Insects and other soil animals are often ignored (in practise insects are often included in SOM), and the inputs and outputs of larger animals are assumed to balance each other because animals often move randomly into and out of the studied ecosystems (Likens and Bormann 1977).

It is evident that the interaction between vegetation and soil is often poorly described and needs much more attention in the models which describe in detail the chemical processes in soil (Tiktak and Grinsven 1995, Mohren and Ilvesniemi 1995). The same holds for the biological control of nitrogen availability in the soil. Study V of this thesis focuses on these linkages.

Van Breemen *et al.* (1983, 1984) and de Vries and Breeuwsma (1987) outlined the hydrogen budget of forest ecosystems. The model in Study V has been developed along these lines. Mälkönen (1974) and Helmisaari (1995) have conducted nutrient budget studies of forests in Finland. These studies provided important information and data for Study V.

2.2 Exchangeable acidity in soils

Exchangeable acidity (EA) determined as H^+ and Al^{3+} replaced with a neutral unbuffered salt (Thomas 1982, Thomas and Hargrove 1984) is large in Podzols, which are the dominant soils in boreal forests (FAO-Unesco 1990). Although it is operationally defined, exchangeable acidity seems to be an indicator of the acidic cations reactive in soil. Exchangeable acidity reacts to an acid load in soil (McLean *et al.* 1964, Nissinen and Ilvesniemi 1990, Hartikainen 1996) and has an equilibrium relationship with base cations in solution (Nissinen and Ilvesniemi 1990).

In the organic (O) horizon, the functional groups of the organic decomposition products, mainly carboxylic and fenolic groups, are responsible for the retention of exchangeable cations. A large share of the potential exchange sites are occupied by H^+ ions, which, because of the weak acid behaviour of the organic groups, are only partly dissociated in the determination of the CEC_e (Wells and Davey 1966, Kalisz and Stone 1980). Al is retained strongly due to complexation by the organic functional groups, and it may block potential exchange sites (Bloom *et al.* 1979a, Hargrove and Thomas 1981, Hargrove and Thomas 1984, Skyllberg 1995).

The accumulated organic material is often responsible for a great deal of the CEC_e in mineral horizons of forest soils (Stephens 1969, Kalisz and Stone 1980, Tamminen and Starr 1990, Ilvesniemi 1991). The size distribution of mineral particles and the minerals present in the soil are other major factors contributing to the reactive surface area and charge density and, thus, CEC_e of mineral horizons. Further, a great vertical variation in the soil's chemical properties is caused by the podzolization process: the leaching of ions produced from easily weatherable minerals in the topmost mineral soil and the accumulation of organic material and poorly ordered polymeric forms of Al and Fe in the illuvial horizon. In the illuvial horizon the soil particles are coated with organic compounds and hydroxy-Al and hydroxy-Fe, this organo-metallic material actually forming the exchange surface (De Coninck 1980). Imogolite-type materials are also present (Gustafsson *et al.*

1995), and interlayers of vermiculitic mixed-clay minerals may be filled with hydroxy-Al polycations (Räisänen 1996). The positively charged Al-polymers are included in the total acidity of the soil but they are mostly non-exchangeable. A separate pool of exchangeable monomeric Al^{3+} has been detected in many studies (Lin and Coleman 1960, Rich 1960, Thomas 1960, Shen and Rich 1962, Frink and Peech 1963, Jackson 1963, Kissel *et al.* 1971, Brown and Newman 1973, Veith 1977, Hodges and Zelagny 1983, Thomas and Hargrove 1984). However, evidence also exists for the exchange of hydrolyzed Al (Hsu 1968, Brown and Newman 1973, Veith 1977, Hodges and Zelagny 1983) and polymerized Al (Bache and Sharp 1976b). It is obvious that no clear demarcation exists between exchangeable Al^{3+} and the non-exchangeable Al-forms (Barnhisel and Bertsch 1982).

Exchangeable H^+ (or the amount of H+ released to the neutral salt extract of effective exchangeable cations) has been ignored in many studies of exchangeable cations because the exchangeable acidity is often composed almost entirely of Al (Thomas and Hargrove 1984). Another reason for its neglect is that ‘exchangeable H^+’ is not a clear concept, because most of the protons measured in the salt extract may come from hydrolysis of exchanged Al^{3+} and nonexchangeable Al (Martin and Reeve 1958, Schnitzer and Skinner 1963, Coleman and Thomas 1967, Kissel *et al.* 1971, Veith 1977, Hargrove and Thomas 1981, Thomas and Hargrove 1984, Rasmussen *et al.* 1991). On the other hand, H^+ may form a large part of the effective exchangeable acidity, especially in the O horizon (Ross *et al.* 1991). Such ‘exchangeable’ H^+ can be important in cation exchange reactions: Nissinen and Ilvesniemi (1990) found that 90% of hydrogen ion consumption in the humus layer could be explained by cation-exchange with Ca, Mg and K. Studies II and III of this thesis focus on the cation-exchange equilibria of H^+ with Ca^{2+}.

Soil acidity has been explained by weak acid equilibrium. The weak acid behaviour of soils was shown in the titration of soil samples (Martin and Reeve 1958, Thomas and Hargrove 1984), and Skyllberg (1995) applied this model successfully to explain the effect of the solution:soil ratio on the pH of 0.01 M $CaCl_2$ in O and E horizons. In Study I of this thesis the assumption of weak acid behaviour is extended to describe reactions of exchangeable H^+.

Exchangeable Al is one of the most important soil properties when soil reaction to environmental changes and agricultural and forestry practises, such as liming, are analysed. The lime requirement equivalent to exchangeable Al has been used as a criterion for liming mineral soils (Kamprath 1970, Thomas and Hargrove 1984). Cation-exchange equilibrium between Al^{3+} and Ca^{2+} has been assumed in most of the soil acidification models (Tiktak and Van Grinsven 1995). The equilibrium has been successfully described in laboratory conditions by using the Gaines–Thomas selectivity coefficient (Nye *et al.* 1961, Coulter and Talibudeen 1968). Study II analyses the applicability to cation pair Al^{3+}–Ca^{2+} in *in situ* solutions of acidic forest soils.

Exchangeable Al is not a well-defined pool in soil (Barnhisel and Bertsch 1982). Rather, it can be considered operationally defined, as it depends on the exchanging cation and its concentration (Bloom *et al.* 1979b). Exchangeable Al is often measured by a single extraction with an unbuffered salt solution (Thomas 1982, Barnhisel and Bertsch 1982, Hendershot and Duquette 1986). In successive extractions a gradually decreasing release of Al is observed (Bache and Sharp 1976a). However, if the solution is acidified to a certain pH value, a constant release of Al is found after the large release in the first few extractions, and this constant release has been used to separate nonexchangeable Al from exchangeable Al (Skeen and Sumner 1965). However, the exchangeable Al may be related to the pH of the extract in the same way as the nonexchangeable Al is related to the adjusted pH. Ponette *et al*. (1996) have shown most clearly the importance of pH for exchangeable Al: An inverse relation between the dissolved Al and pH of the final extract was found to be the same for exchanging cations Cu^{2+}, NH_4^+ and K^+, although the equilibrium pH differed for the exchanging cations.

It has long been recognized that Al may occupy a large share of the potential exchange sites in soil organic matter, the Al being only partly exchangeable (Martin and Reeve 1958, McLean *et al*. 1965, Pionke and Corey 1967). On the other hand, Dahlgren and Walker (1994) found that concentration of Al extracted with 1 M KCl was determined by the solubility of a precipitated $Al(OH)_3$ phase in variable charge soils, some of which contained mostly organically complexed Al. Complexation of Al with soil organic matter has also been used to explain the activity of Al^{3+} in soil solutions and dilute salt solutions (Bloom *et al*. 1979a, Mulder and Stein 1994, Wesselink *et al*. 1996), and dissolution of $Al(OH)_3$ has been used for this purpose in almost all soil solution studies since the study of Marion *et al*. (1976). Although the reactions with organic matter seem to be important for aluminium chemistry in soils, they have not been used to explain the amount of exchangeable Al in soils. Study I of this thesis analyses a possible equilibrium relationship between exchangeable Al and organic Al complexes, and also considers the solubility of $Al(OH)_3$.

2.3 Solution chemistry in soils

Knowledge of soil solution ion concentrations is important for evaluations of soil fertility, soil acidity, and leaching of nutrients from soil. However, characterizations of soil properties seldom include the ionic composition of soil solution. In addition to the problems connected to soil solution sampling, solution ion concentrations have a great deal of temporal variation (e.g. Nilsson and Bergkvist 1983, Bergkvist 1987, Zabowski and Ugolini 1990, Lundström 1993, Johnson 1995) and the total amounts of cations in soil solution are usually minor compared with the amounts on exchange sites.

Numerous chemical reactions between solid particles, particle surfaces, solution and the soil gaseous phase affect ion concentrations in soil solution (see e.g. Lindsay 1979). Dissociation of H_2CO_3 and organic acids are generally important sources of hydrogen ions and anions for soil solution, especially if deposition of acid ions is low and/or soil pH is high (Johnson and Cole 1980).

Additionally, cation-exchange processes are important in affecting the concentration of each cation in solution, because cation retention due to the negative charge of soil constituents is a common property of soils, and cation-exchange reactions are rapid. Equilibrium has been observed in many experiments (Vanselow 1932, Nye *et al.* 1961, Clark and Turner 1965, Turner 1965, Coulter and Talibudeen 1968), but studies dealing with apparent cation-exchange equilibrium in "*in situ*" soil solutions are rare, although a related study by Upchurch *et al.* (1973) is already 25 years old. Hendershot and Courchesne (1991), Sogn (1993) and Johnson (1995) collected soil solutions with lysimeters, and compared the observed solution cation concentrations with simulated concentrations using cation-exchange equilibrium models. There were major differences between the simulated and the observed cation concentrations, implying that the assumption of cation-exchange equilibria did not apply well to the solutions.

Experimental studies with soils have implied the control of gibbsite or amorphous $Al(OH)_3$ over solution Al^{3+} activity, together with silicate minerals having apparent control over the solubility of Al^{3+} and Si (e.g. Marion *et al.* 1976, Dahlgren *et al.* 1989, Johnson and McBride 1991). It has also been suggested that solubility of sulphate minerals control sulphate concentration and activities of Al^{3+} and H^+ in experimental soil leachates (van Breemen 1973, Adams and Rawajfih 1977, Prenzel 1983, Freiesleben 1988). Experiments have shown departure from the solubility of $Al(OH)_3$ to be most evident in the topmost soil horizons, such as E horizons of podzolic soils (Johnson and McBride 1991, Nissinen and Ilvesniemi 1990, Prietzel and Feger 1992). In agreement, Bloom *et al.* (1979a) suggested that the exchange of Al ions from organic matter exchange sites controls the relationship between pH and Al^{3+} activity in acid soils, which have a low amount of permanent cation-exchange sites relative to the amount of organic matter. Cronan *et al.* (1986) proposed an equilibrium model for predicting Al^{3+} activities in organic soil horizons as a function of solution pH and the degree of Al saturation of the organic exchange sites, and Wesselink *et al.* (1996) showed that a similar model can be applied to mineral soils as well.

Studies with *in situ* solutions have verified that several minerals may control solution ion activities, depending on soil type, soil horizon, and retention time of the soil solution. Manley *et al.* (1987) found that solutions from Bf, BC and C horizons of three podzolic soils were supersaturated with respect to gibbsite and undersaturated with respect to amorphous $Al(OH)_3$. Similar findings were made by Lundström (1993). Norflect *et al.* (1993) found that the solution residence time was an important factor for mineral formation: gibbsite was formed in a steep slope, while kaolinite was formed in a less steep slope, the residence time being long enough to allow for considerable Al-Si interactions and kaolinite precipitation. As experiments have shown, departure from the solubility of $Al(OH)_3$ has been most evident in the organic horizon (Mulder and van Breemen 1987, Lundström 1993) and in the topmost mineral soil (Manley *et al.* 1987, Mulder and van Breemen 1987, Grieve 1990, Lundström 1993). In many studies the relationship between Al^{3+} and pH has shown a marked departure from $Al(OH)_3$ solubility, also in B horizons and subsoils, ion activities indicating an apparent equilibrium with jurbanite (van Breemen 1973, Nilsson and Bergkvist 1983, Prenzel 1983, Mulder and van Breemen 1987) or another sulphate mineral, such as alunite (Courchesne and Hendershot 1990). However, jurbanite has never been found in soils (pers.comm. van Breemen 1997). Neal *et al.* (1989), Joslin and Wolfe (1992) and Hughes *et al.* (1994) concluded that dissolution and precipitation of gibbsite could not be responsible for the short-term or episodic fluctuations in Al concentrations in the soil solutions which they studied, and suggested that cation-exchange processes would have been the proximal mechanism controlling the rapid changes.

Generally the aim in soil solution studies is to analyse unaltered *in situ* solution samples. Indeed, some experiments have shown that similar solutions are collected by centrifugation with different speeds (Gillman 1976); vacuum displacement and centrifugation (Wolt and Graveel 1986); and centrifugation, immisciple displacement with centrifugation, and column-displacement (Adams *et al.* 1980). Studies of in situ solutions collected in field experiments have shown large differences between different methods. Haines *et al.* (1982) and Barbee *et al.* (1986) proposed that zero-tension samplers provide more representative samples of chemical movement through unsaturated soils at high soil moisture potentials than suction cup samplers. Hendershot and Courchesne (1991) and Magid and Christensen (1993) also concluded that zero-tension samples represented the flux concentrations, whereas the tension samples were approximations of resident concentrations. Zabowski and Ugolini (1990) and Giesler *et al.* (1996) found that many ion concentrations were over twofold in centrifugates compared with the leachates from zero-tension lysimeters.

In Studies II and III of this thesis the cation-exchange equilibria are analysed in *in situ* solutions. Apparent solubility of Al-minerals in the same solution samples is also studied. Two methods are used for the extraction of the solutions: centrifuge drainage technique and suction lysimeters.

2.4 Relations between tree growth and nutrient availability in soil

The various parts of plants have a functional value for the plant, and thus functional balance has been proposed as a cause of the structure of trees. This approach has been used in some mathematical models of tree growth, so that the balance determines the allocation of the carbohydrates (produced in the photosynthesis in leaves) to various parts of the tree (Hari *et al.* 1985, Mäkelä 1986, Nikinmaa 1992). Leaves produce carbohydrates, branches spread the leaves apart so that they gain abundant energy from light, and the stem lifts the foliage above other plants which could shade the leaves. The roots maintain firm contact between the tree and the soil, keeping it in a vertical position. They spread fine roots to harvest water and plant-available nutrients from a large volume of soil. Transport of water to the leaves is an important task of the woody system, which covers roots, stem and branches.

Nutrients are needed for the structure formation and the proper functioning of the various tissues in plants. Ingestad (1979) showed in a solution culture experiment that seedlings of pine and spruce have certain mineral nutrient requirements, and that maximum growth can be reached when nutrients are given in certain proportions and at an increasing rate. In field conditions, fertilisation which is planned to satisfy the requirements of trees can result in a manyfold production of stemwood, as compared with an unfertilised stand (Linder and Bergh 1996).

It is also evident that site fertility is connected to the availability of soil nutrients. This can be implied from the studies of Urvas and Erviö (1974) and Tamminen (1991), in which the site type has been compared with the amount of plant-available nutrients in soil. However, because site properties other than nutrients are also important for the plants at each site, the amount of plant-available nutrients does not directly indicate site fertility, and the connection between fertility and nutrients can only be seen in data covering a large number of sites.

In soil, the mobility of many nutrients is low, and the ability of roots to take nutrients from soil is different from solution culture. Root amount and growth are critical for nutrient uptake, because new roots can harvest soil which is not in the vicinity of other living roots. Every piece of soil has evidently been in the vicinity of a root at sometime, but after root death the harvested nutrients are replenished by ions transported with flowing water, mineralisation of soil organic matter and weathering.

If the nutrient uptake is not large enough to ensure the proper functioning of the new tissues in a plant, plants have several ways to acclimate: i) allocate more carbohydrates to the root system so that a larger proportion of the plant-available nutrients can be taken up by fine roots (Nikinmaa 1992), ii) allocate more carbohydrates to mycorrhiza, which enhance the decomposition rate of soil organic matter, increasing release of nutrients to plant-available forms in soil (Zhu and Ehrenfeld 1996), and iii) decrease the growth of tissues by limiting carbohydrate production in photosynthesis. Sometimes, however, this acclimation fails, and plants suffer from nutrient deficiency, which can be apparent in the poor habitus of the plant, indicating malfunctioning of the physiological system (Marchner 1986, Mengel and Kirkby 1987). In leaves the deficiency of nitrogen may not be visible, but the photosynthetic rate decreases due to decreasing nitrogen content in many plant species (Evans 1989), because nitrogen-containing compounds play a crucial role in photosynthesis. However, in Scots pine the relationship is not so clear as in broadleaved tree species (Vapaavuori *et al.* 1995).

3 Experimental materials and methods

3.1 Sites

Samples were taken from the soil of six sites, representing a large range of fertility and cation-exchange capacity of boreal forest soils (Appendix 2, Table 1 in Study I). Three sites, S1, S2 and S3, were in Siuntio, in the catchment of the Rudbäck River, near the Baltic coast in southern Finland, 60°08 ' N, 24°18 ' E. The three other sites, J1, J2 and J3, were in Juupajoki, 61°48 ' N, 24°19 ' E. More details about the sites are found in Study II.

The soil texture (Table 1 in Study I) and the dominant vegetation show great variation in the fertility of the sites. The clay-fraction of the mineral soil is by far the highest at site S1. The soil of site S2 also has a large clay-fraction, 16% in the ground soil. The clay-fraction on the other sites varies between 0.4% and 5.5%. On the most infertile site, J3, the sand-fraction (0.06 - 2 mm) of the ground soil is 98%.

Soil S1 is a Cambisol, S2 is a weakly developed Podzol, and the other four soils are Haplic Podzols (FAO-Unesco 1990). All the soils have a fibric organic layer between 4 and 9 cm thick, consisting mainly of the fermentation layer O_f.

The age of the tree stand is about 70 years at site J3 and 90-100 years on the other sites. According to the site classification system for forest types in Finland, ground vegetation has been used as an indicator of potential stand productivity and site fertility (Cajander 1925). Plant species diversity is highest at site S1, and the presence of *Oxalis acetocella* suggests that it is more fertile (OMT-site) than the other sites. Vegetation at sites S1, S2, S3 and J1 is quite similar in other respects, with *Vaccinium myrtillus* dominating the field layer (sites S2, S3 and J1 are MT-sites). However, in the sampling area of site S3 there is hardly any vegetation in either the field or bottom layer. The reason for this is a dense cover of Norway spruce understorey. At site J2 *Vaccinium vitis-idaea* dominates *V. myrtillus*, and *Calluna vulgaris* is also present, suggesting a less fertile site than the previous ones (VT-site). On J3 the vegetation is dominated by *Calluna vulgaris* and *V. vitis-idaea*; *Cladonia arbuscula* and *C. rangiferina* are also abundant, suggesting low fertility (CT-site).

3.2 Sampling of soil and soil solution

3.2.1 Soil sampling

The soil sampling was begun by digging three pits at each site in order to examine the soil profile and to take the first soil samples for the measurements of soil pH, particle size distribution and organic matter content. The samples that were used for the extraction of soil solution by the centrifuge drainage method and the determination of soil chemical properties (exchangeable cations, extractable aluminium and iron, and total acidity) were composite soil samples, each consisting of ten subsamples. A rectangular sampling area was divided off at each site, the sizes being 24 m ∗ 2 m in S1, 17 m ∗ 2 m in S2 and 12 m ∗ 2 m in S3. At the Juupajoki sites the sizes were 15 m ∗ 1 m. Five (in Siuntio) or three (in Juupajoki) sampling lines were marked with strings, 0.5 m from each other. Potential sampling points were situated 0.25 cm from each other along the lines. Each area was divided into five subplots. Two sampling points were randomly selected from each subplot, so that the composite sample of each horizon included ten subsamples.

The sample of the organic horizon (O) included all dead organic material above the mineral soil, representing L, F and H horizons. The sample of the A horizon (including E and Ah horizons) was sampled to a depth of 6 cm or the total depth was sampled if it was thinner. The samples from the Bs1 and Bw1 horizons are also 6 cm thick. The samples from the O, A and Bs1 and Bw1 horizons were taken with steel cylinders (Ø 5.8 cm) from the same point. Samples representing the Bs2, Bw2 and C horizons were taken with a steel auger (Ø 2.5 cm), also from the same point. The sample of the C horizon was taken from a depth of about 0.50 m, which was below the most distinct Bs2 horizon. However, for the physical and pH measurements, the sample of the C horizon was taken from a deeper level, the depth being determined as 1.5(the summed thicknesses of the A and Bs horizons); see Table 1.

Sampling intensity varied: site S2 was sampled eight times, S1 five times, S3 five times, J2 four times, J3 three times and J1 twice. The first sampling date was 21 May 1991 and the last 26 October 1992. The composite samples were stored at 3^{o} C in polyethene bags. Soil solution was extracted by centrifuging and air-drying of the soil sample was begun within 48 hours.

3.2.2 Solution sampling by a centrifuge drainage method

Method description

A modification of a centrifuge technique developed by Reynolds (1984) was used to collect soil solutions. The unit for extracting soil solution consisted of a sample holder, a solution collection cup, and a plastic lid. A Whatman 5 disk cut to the diameter 10 mm was placed in the sample holder and fixed in place by moistening it with 10 µl of MQ water. Prior to fixing, the filter disk was washed with MQ water and allowed to dry. For each set of 30 soil centrifugings two units were centrifuged with 5 ml distilled water and two with 5 ml test solution containing all the major cations and anions. No ion contamination or retention was observed. The samples were centrifuged for 60 minutes, the acceleration being between 940 *G* and 2100 *G* in the sample of soil. Prior to centrifuging, the composite samples were homogenized in the closed bags by squeezing and by turning the bags over at least ten times. Duplicates were centrifuged from each bulked soil sample. The samples of soil solution obtained from these duplicates were analysed separately, except for a few minor solution samples, which were combined. For more details of the method, see Studies II and III.

Calculation of the emptied pore size

The force *F* acting on a water unit on distance *r* from the axis of rotation in a centrifuge is

$$F_x = m\omega^2 r = \rho h A \omega^2 r \tag{1}$$

where *m* is the mass of the water unit, ω is the angular velocity, ρ is the density of water, *h* is the length of the water unit in the same direction as the centrifugal force F_x, and *A* is the area of the water unit, being in a straight angle to the force F_x. The centrifugal pressure P_x is

$$P_x = \frac{F_x}{A} = \rho h \omega^2 r \tag{2}$$

However, the centrifugal force acts differently on each water unit whose distance *r* to the axis of rotation is different. If we assume that water capillaries are continuous between distances r_1 and r_2 from the axis of rotation, and the height *h* of the capillaries ($h = r_2 - r_1$) is so great that *r* changes markedly between them, the pressure must be integrated over indefinitely short distances d*h* (d*r*) in order to obtain the pressure in the distance r_2 (Batley and Giles 1979, Giesler 1996)

$$P_x = \int_{r_1}^{r_2} \rho \omega^2 r \; dr = \frac{\rho \omega^2}{2}(r_2^2 - r_1^2) \tag{3}$$

The size of the pores which are emptied in the centrifugation can be calculated by assuming that P_x equals capillary pressure P_c

$$P_x = P_c = \frac{4s \cos q}{d} \tag{4}$$

where *s* is surface tension, *q* is contact angle, and *d* is pore diameter. Note that *d* is the diameter of the pore on the level of the uppermost water surface in the capillary.

In our work, ω was 335 s^{-1}, r_2 was 0.182 m, r_1 was 0.082 m, *s* was assumed to be 0.0728 N m^{-1} , *r* 998 kg m^{-3}, and cos*q* 1. The calculated pressure in the bottom of the soil and tube was 1480 kPa, which is quite near the wilting point 1555 kPa, or pF 4.2. However, this was the pressure when centrifuging was begun. As the water leaves the tube and enters the collection cup, the water capillaries shorten, and P_x decreases. When the cohesion force does not allow the water capillary to break down despite the greater pressure in the bottom of the soil than in the top of the soil, the top part of the soil will be drier than the bottom part. For example in the beginning, when the capillaries can be assumed to be 100 mm long, the pressure is capable of removing water from pores larger than 0.2 µm. However, only pores larger than 0.33 µm can shorten half of their length, to 50 mm. Batley & Giles (1979) suggested that compaction of the soil in the bottom of the sample caused restrictions to free movement of water, resulting in more dry top part than bottom part of the soil. It seems that the decrease in the amount of the emptied pores with decreasing capillary length could be another reason to their results.

If it is assumed that there are no continuous capillaries through the sample, the centrifugal pressure is much smaller. In a separate pore, which has the same length and diameter of 30 µm, the pressure would have been 0.61 kPa and 0.28 kPa in the bottom and top of the tube respectively. This is much less than the capillary pressure of 9.73 kPa in the pore, or the pressure in the field capacity, 9.81 kPa, or pF 2. Evidently some continuity must be assumed to explain the relatively high water yield in the centrifugation.

Testing the method

In principle, centrifuging could cause dissolution of inorganic or organic soil constituents in the soil sample. Gillman (1976) studied the effects of centrifuging time and speed on soil solution properties, using experimentally moistened surface soil samples. Electrical conductivity and solution concentrations of Ca, Mg, K, Na and Cl were reasonably constant in the obtained solutions, which implies that the centrifugation method does not cause any major dissolution. Zabowski (1989) and Grieve (1996) showed that cell contents from roots or microbes were not introduced into soil solutions during centrifugation. Bulking of soil samples may affect ion composition of soil solutions (Giesler and Lundström 1993). However, this was not considered a problem, as it also evidently affects contents of exchangeable cations, and the destruction of soil structure was a part of both solution sampling and determination of CEC_e.

3.2.3 Solution sampling by a suction lysimeter method

The suction lysimeters, length 9.5 cm and diameter 2.1 cm, were of teflon (PTFE), with pore size of 3 µm. They were installed on the sites at three different depths. A steel auger was used to make a horizontal hole in the soil, so that the lysimeters could be installed more than 20 cm away from the wall of a pit. At site S1 the lysimeters were installed at depths of 3 cm, 12 cm and 20 cm, corresponding to horizons Ah, Bw1 and Bw2. Similarly, at site S2 the lysimeter depths were 3 cm, 13 cm and 25 cm (horizons E, Bs1 and Bs2). The soil sample removed from the hole made for each lysimeter was used to determine the chemical properties of the soil.

Several litres of soil solution were collected from the soil to precondition each lysimeter, and the lysimeters were allowed to settle for more than 2 weeks before the first solution samples were taken on 13 May 1991. The solution samples were collected more often than once a month. The samples of May and June 1991 were collected in glass bottles during 24 hours of suction. After June 1991 the samples were collected in polystyrene tubes (volume 10 ml) which were installed inside a glass erlenmeyer, the collection period being a few hours. Small samples and short collection periods were used so that the sample would represent the soil surrounding the lysimeter (Grossmann and Udluft 1991). The pressure difference was 76 kPa, implying that the minimum pore size that could be emptied was 4 µm.

3.3 Chemical and physical methods for studying soil properties

After taking subsamples of each soil sample to the centrifuging, the rest of each bulked soil sample was air-dried at 25^{o} C, and the water content of the air-dry sample was determined. The exchangeable cations were determined by a batch method from the sieved fraction < 2 mm, the duplicates being analysed from each bulked soil sample. The Hendershot and Duquette (1986) method to determine effectively exchangeable cations was slightly modified, in that instead of filter papers, a membrane-equipped filter system with vacuum was used. Two grams of organic horizon or 10 g mineral soil were shaken in a bottle containing 100 cm^3 of 0.1 M $BaCl_2$ for 1 h. For each set of 14 samples, a blank was shaken and filtered. After filtering, a 50 cm^3 subsample was taken for immediate pH-analysis and manual titration of exchangeable acidity with 0.01 M NaOH to pH 7. Ca and Mg were determined in a solution which contained 1% La by atomic absorption spectrophotometry (AAS). Al was determined by AAS, and potassium was measured by flame emission spectroscopy. For more details see Study II.

The exchangeable H^+ was calculated from the pH of the $BaCl_2$-extract by dividing the activity by the activity coefficient calculated using the extended Debye-Hückel expression (Lindsay 1979, p. 14). The expression was also used to estimate the activity of Al^{3+} in the $BaCl_2$-extract. The Davies equation was used to calculate the activity coefficients of the hydrolyzed forms of aluminium (Lindsay 1979). The measured H^+ activity in the solution and the equilibrium constants of the hydrolysis reactions (Lindsay 1979) were used to determine the proportions of the hydrolyzed forms in the monomeric aluminium.

Because the titrated exchangeable acidity (EA_T) was close to the sum of exchangeable Al^{3+} and H^+ in each case, the sum of exchangeable H^+ and Al^{3+} was referred to as the exchangeable acidity (EA). The sum of exchangeable cations H^+, Al^{3+}, Ca^{2+}, Mg^{2+} and K^+ was referred to as the effective cation-exchange capacity (CEC_e).

Total acidity (TA) and oxalate-extractable Al and Fe of the mineral soil samples were measured from the sieved fraction < 0.2 mm, but expressed as the content in the fraction < 2 mm. The total acidity was determined by the $BaCl_2$-TEA-method (Thomas 1982), but using the membrane filter system instead of Whatman 42 filter paper. The sum of total acidity and exchangeable base cations Ca^{2+}, Mg^{2+} and K^+ was referred to as the potential cation-exchange capacity (CEC_p). For the extraction of aluminium and iron with acid 0.2 M ammonium oxalate, the Wang (1981) method was slightly modified, so that the extract was filtered with Whatman 5, the first 4-5 ml being discarded to avoid anomalies due to possible retention of Al and Fe in the filter paper. The calculation of the ‘extractable’ Al and Fe was based on the total amount of extract and on the Al and Fe concentrations in the collected extract. For pH($CaCl_2$) 10 cm^3 of air-dry soil and 25 cm^3 0.01 M $CaCl_2$ were mixed in a polypropylene cup. After standing overnight, the suspension was stirred again and the pH was measured.

3.4 Chemical methods for studying exchangeable acidity

Two sequential extractions with unbuffered 0.1 M $BaCl_2$ were done to study the release of H^+ and Al from each soil sample. The first extraction was done as described above (3.3). After the filtered extract was collected, another $BaCl_2$-portion of 100 ml was added to each bottle and treated similarly to the first one. The amount of solution that remained in the bottle after the first extraction was below 10 ml. Subscripts e1 and e2 (e.g. H_{e1} and H_{e2}) indicate amounts of cations released from soils in extractions 1 and 2 respectively (expressed as mmol kg^{-1}).

3.5 Chemical methods for studying solution chemistry

Samples of solution were in contact only with plastic apparatus. New disposable apparatus was rinsed at least twice with distilled water and once with MQ (Milli-Q Plus) water. All other plastic apparatus, as well as glassware, were washed before use, soaked in 0.1 M HCl, and rinsed several times with distilled and MQ water. The rinsing water was collected and its conductivity was monitored. Immediately after centrifuging, the solution pH was measured from a subsample. The pH of the lysimeter solutions was measured within 24 hours after sampling. In order to avoid anomalies in cation concentrations (Jardine *et al.* 1986; Bartlett *et al.* 1987) the lysimeter solutions were filtered only for the measurement of anions, which was done by ion chromatography. The centrifugates occasionally contained particles, and they were filtered using Millex-HV13 with a pore size of 0.45 µm (Jardine *et al.* 1986). Reactive Al was measured with a spectrophotometer within 24 hours after reaction with pyrocatechol violet (Bartlett *et al.* 1987). The concentration measured after a reaction time of one minute is referred to as monomeric aluminium Al_{mon}. Values lower than 6 µmol l^{-1} were not used in the calculations of chemical equilibrium but they were recorded. Potassium was measured by flame emission spectrophotometry. Ca and Mg were determined by AAS in acidified solution which contained 1% La. Anions SO_4^{2-}, NO_3^- and Cl^- were measured by ion chromatography from the samples of a few selected sampling dates. For more details see Studies II and III.

Ion activities in solution were calculated using the molar ion concentrations and activity coefficients estimated by the extended Debye-Hückel expression (Lindsay 1979, p. 14). However, the Davies equation was used to calculate the activity coefficients of the hydrolyzed forms of aluminium (Lindsay 1979). In Study II Al_{mon} was assumed to be Al^{3+} because the pH was generally low in the centrifugates. In Study III lysimeter solutions were also studied, and because many of the solutions had relatively high pH, the measured H^+ activity in the solution and the equilibrium constants of the hydrolysis reactions (Lindsay 1979) were used to determine the proportions of the hydrolyzed forms in the monomeric aluminium. However, the calculated activity of Al^{3+} can be an overestimation in some solution samples, because the measured monomeric aluminium can include organic-Al complexes (Jardine and Zelazny 1987, Bartlett *et al.* 1987) and some exchangeable Al on suspended colloidal solids, which can even pass 0.1 µm filters (Bartlett *et al.* 1987).

In connection with the solution pH measurement, the samples of a few sampling dates were bubbled with the ambient outdoor air in order to examine the bicarbonate equilibrium in the solutions. See Study III for more details and calculations.

3.6 Data analyses

The Cambisol (S1) and the five Podzols had many similar features in their soil chemistry, e.g. similar depth gradients for pH, CEC_e and base saturation (Appendix 2, Table 1 in Study I). Thus in many analyses the samples from the Cambisol and the Podzols were treated as belonging to the same sample groups, based on five horizons in the soils. Abbreviations O, A and C stand for the O horizons, the E and Ah horizons, and the C horizons, respectively. Because it is often important to also refer to the horizons Bs1 and Bw1 separately, a specific abbreviation is used for the combined data of the Bs1 and Bw1 horizons: (Bs1&Bw1). The combined data of the Bs2 and Bw2 horizons is abbreviated similarly: (Bs2&Bw2).

In many instances there was too little solution to measure all of the ions from the soil solution samples. If the results of Mg^{2+} or K^+ were missing, the horizon-specific mean value was given to the missing ion in the estimation of the ionic strength of the solution. If anions were not measured, they were assumed to be SO_4^{2-} and Cl^- in mole charge ratio 1:1, which corresponded to the ratio between SO_4^{2-} and other anions in each horizon. The replicate samples of the centrifugates were treated as separate samples in the data analysis, because a fresh soil sample cannot be perfectly homogenized and thus subsamples of the sample are different (Study II).

Statistical analyses were calculated using SPSS/PC+ V3.0 programs (SPSS Inc., Chigaco, USA). For more details, see Study II.

4 Exchangeable acidity

4.1 Exchangeable H^+

Two sequential extractions with unbuffered 0.1 M $BaCl_2$ were done to study the release of ‘salt-exchangeable’ H^+ and Al from soils (Study I). It is assumed that the activity of H^+ in the 0.1 M $BaCl_2$ extract is in equilibrium with a single weak acid, despite the likely presence of several kinds of weak organic and inorganic acids in the soils. The dissociation reaction of a weak acid is

$$\mathrm{HA} \leftrightarrow \mathrm{H}^{+} + \mathrm{A}^{-} \tag{5}$$

and the equilibrium constant K_{wa} for the dissociation of a weak acid in solution is

$$K_{\mathrm{wa}} = \frac{\langle \mathrm{H}^{+} \rangle \langle \mathrm{A}^{-} \rangle}{[\mathrm{HA}]}, \tag{6}$$

where $\langle\rangle$ and $[\ ]$ denote activities and molar concentrations in solution respectively. Now the constant can be written as

$$\mathrm{p}K_{\mathrm{wa}} = \mathrm{pH} - \log \left\{ \frac{\langle \mathrm{A}^{-} \rangle}{[\mathrm{HA}]} \right\} \tag{7}$$

However, in the case of exchange sites, the anion (A^-) and the acid (HA) are not dissolved in solution. Thus it is assumed that the ratio between anion activity and acid concentration can in this case be estimated by the ratio of anion content and acid content in soil. This ratio is often expressed using a term, ‘degree of dissociation of the acidic functional groups’ (α), which is

$$\alpha = \frac{\mathrm{A}^{-}}{\mathrm{A}^{-} + \mathrm{HA}} \tag{8}$$

Martin and Reeve (1958) showed that in the case of a weak acid like soil, Equations 7 and 8 can be applied to describe the acid behavior after introducing an empirical constant *n*. The result is the modified Henderson-Hasselbach equation (Martin and Reeve 1958, Thomas and Hargrove 1984, McBride 1994). When it is applied to the first extraction, the equation is

$$\mathrm{p}K_{\mathrm{HH1}} = \mathrm{pH}_{\mathrm{Ba1}} - n \log \left\{ \frac{\alpha_1}{1 - \alpha_1} \right\}, \tag{9}$$

where $\mathrm{p}K_{\mathrm{HH1}}$ is the soil acid dissociation constant and $\mathrm{pH}_{\mathrm{Ba1}}$ is the pH of the extract. Following McBride (1994), α_1 can be determined as:

$$\alpha_1 = \frac{\mathrm{CECe}}{\mathrm{CEC_p}}, \tag{10}$$

where CEC_e is the sum of effectively exchangeable acidity (EA_1) and base cations (determined using the 0.1 M $BaCl_2$ extract) and CECp is the sum of total acidity (TA, determined at pH 8.2) and exchangeable base cations. In the second extraction the dissociated sites are increased by the released amount of acidity (EA_2), and α is larger than in the first extraction.

In a titration of the soil extract, the value of constant n in Equation (9) can be estimated by plotting pH as a function of log $\{ \alpha_1 / (1-\alpha_1)\}$, n being equal to the slope of the regression line in a range where the relation is approximately linear (Thomas and Hargrove 1984). Here we applied the same principle to the pH-change in sequential extractions. Assuming that pK_{HH2} equals pK_{HH1}, n can be estimated from Equation (9) as

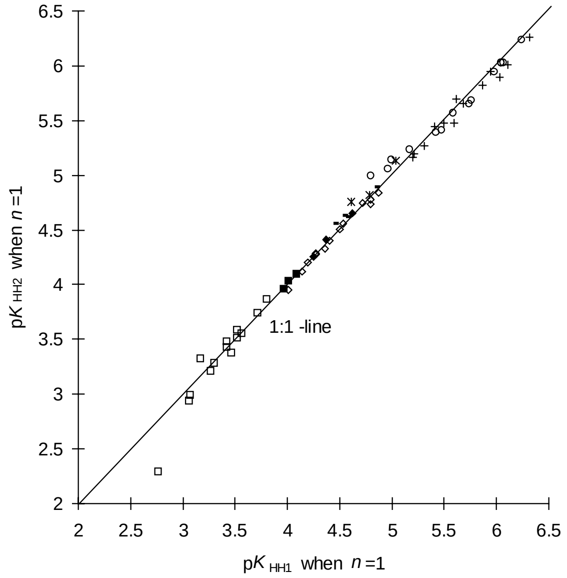
$$n = \frac{\mathrm{pH}_{\mathrm{Ba1}} - \mathrm{pH}_{\mathrm{Ba2}}}{\log\left\{\dfrac{\alpha_1}{1-\alpha_1}\right\} - \log\left\{\dfrac{\alpha_2}{1-\alpha_2}\right\}} \; . \tag{11}$$

In our study the estimated n was close to unity in the samples in which the change in α between the extractions had been large (Tables 2 and 3 in Study 1). It seemed reasonable to use value 1.0 for all horizons, thus assuming that all horizons reacted similarly to monoprotic acids. As a result, the average difference between pK_{HH2} and pK_{HH1} was close to zero in all other horizons except the C horizon of the Cambisol (Table 3 in Study 1). It was the only horizon in which the model could not explain the activity of H^+ in the extracts, as the average change in pK_{HH} between the extractions was about the same as the average change in pH_{Ba}.

It seems reasonable to suggest that the pH of the extract of effectively exchangeable cations can be generally explained by the modified Henderson–Hasselbach equation (pK_{HH}) in Podzols and Cambisols. The differences between the two extractions were small with regard to the equilibrium constant of the modified Henderson–Hasselbach equation (pK_{HH}, Fig. 1), although pH was higher in the second than in the first extraction. This behaviour of soil agrees with soil titration studies of e.g. Martin and Reeve (1958) and Thomas and Hargrove (1984). In the model the degree of dissociation (α) was determined as the ratio between effective and potential cation exchange capacity, thus assuming that the exchange sites of effectively exchangeable cations act as dissociated acidic functional groups in the extraction. The estimated value 1.0 of n is in accordance with the behaviour of organic acids with a large Al content (Thomas and Hargrove 1984). This evidently corresponds to the state of organic acids in the studied horizons, which had large contents of oxalate-extractable Al (Table 1 in Study I).

The values of pK_{HH1} increased in the horizon order E<Bs1<Bs2 in each Podzol and in the Cambisol the Ah horizon had a smaller value than the horizons below it (Table 3 in Study 1), indicating decreasing acid strength of the soil with increasing depth.

Figure 1. Horizon-specific relations between pK_{HH2} and pK_{HH1}, or the values of pK_{HH} in the second and first extraction. The value of n was assumed to be 1.0, see Equation (9). The line shows the 1:1 -relation between the two pK_{HH} values. Redrawn from Study I, European Journal of Soil Science (accepted).



4.2 Exchangeable Al

Model of organic Al complexes

When it is assumed that organic complexes determine the activity of Al in the BaCl$_2$-extracts, the bonding reaction of Al with exchange sites in organic matter is written analogously to the reaction in solution, giving

$$\mathrm{Al}^{3+}_{\mathrm{Ba1}} + \mathrm{RH}_x \Leftrightarrow \mathrm{R\text{-}Al}^{(3\text{-}x)+} + x\mathrm{H}^{+}_{\mathrm{Ba1}} \tag{12}$$

where subscript Ba1 indicates activities of Al^{3+} and H^{+} in the BaCl$_2$-solution of the first extraction, RH and R-Al represent protonated sites and Al bound by organic matter (McBride 1994, Wesselink *et al.* 1996), and x is the reaction stoichiometry (Study I). The complexation constant p$K_{\mathrm{R\text{-}Al}}$ of the reaction is defined by the equation

$$\mathrm{p}K_{\mathrm{R\text{-}Al}} = -\log\frac{\left\langle \mathrm{R}-\mathrm{Al}^{(3\text{-}x)+}\right\rangle}{\left[\mathrm{RH}_x\right]} + x\mathrm{pH}_{\mathrm{Ba1}} - \mathrm{pAl}^{3+}_{\mathrm{Ba1}} \tag{13}$$

where $\langle\ \rangle$ and [ ] represent activities and concentrations, respectively. Because the released amounts of H^+ and Al^{3+} in the extractions are small compared with TA and extractable Al of the soils, it can be assumed that the ratio between R-Al and RH is about the same in the two extractions. Now we get in the first extraction (McBride 1994)

$$\mathrm{p}K_{\mathrm{o1}} = \mathrm{p}K_{\mathrm{R\text{-}Al}} + \log\frac{\langle \mathrm{R-Al}^{(3\text{-}x)+}\rangle}{[\mathrm{RH}_x]} = x\mathrm{pH}_{\mathrm{Ba1}} - \mathrm{pAl}^{3+}_{\mathrm{Ba1}}\,. \tag{14}$$

There are two alternatives to studying the reaction stoichiometry *x*. Firstly, it can be estimated by plotting $\mathrm{pAl}_{\mathrm{Ba}}$ as a function of $\mathrm{pH}_{\mathrm{Ba}}$, if we assume that $\mathrm{p}K_{\mathrm{o}}$ and the ratio between R-Al and RH are constant for a horizon. This assumption is not generally valid (Wesselink *et al.* 1996), but plots of pAl and pH have been widely used to study Al equilibria in soils. The results clearly showed (Study I) that the plot between $\mathrm{pAl}_{\mathrm{Ba}}$ and $\mathrm{pH}_{\mathrm{Ba}}$ cannot be used to determine the reaction stoichiometry *x* in the E and Bs1 horizons, which was an expected result regarding the generally large variation in the ratio between R-Al and RH in topmost mineral soils (Wesselink *et al.* 1996).

Secondly, if it is assumed that pK_{o} is the same in both extractions ($\mathrm{p}K_{\mathrm{o1}} = \mathrm{p}K_{\mathrm{o2}}$), Equation (14) gives us

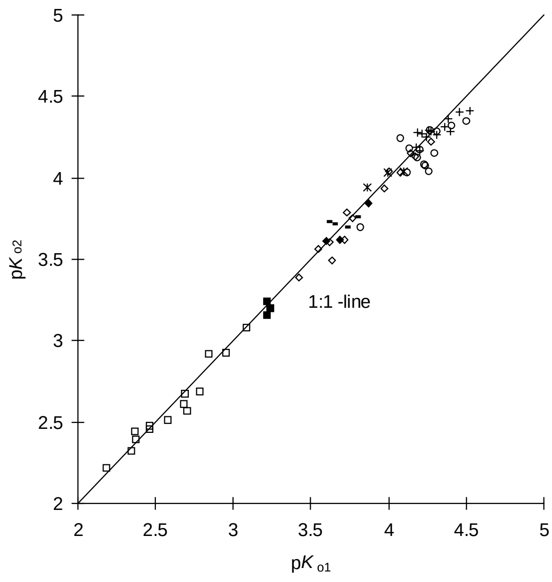
$$x = \frac{\mathrm{pAl}^{3+}_{\mathrm{Ba1}} - \mathrm{pAl}^{3+}_{\mathrm{Ba2}}}{\mathrm{pH}_{\mathrm{Ba1}} - \mathrm{pH}_{\mathrm{Ba2}}} \tag{15}$$

and *x* can be determined for individual soil samples.

In our study the average values of *x* were 2.10, 2.18, 2.15 and 2.46 in the E, Bs1, Bs2 and C horizons of the Podzols respectively (Table 5 in Study I). Because the method gave values close to 2.0 for all horizons, it was assumed that Al had been mainly bound as a bidentate complex in organic matter. When *x* was given the value 2.0 in Equation (14), the values of $\mathrm{p}K_{\mathrm{o}}$ were close to each other in the two extractions (Fig. 2), and the average difference between the equilibrium constants of the two extractions (or $\mathrm{p}K_{\mathrm{o2}}$-$\mathrm{p}K_{\mathrm{o1}}$) did not differ from zero in any of the horizons (Table 5 in Study I).

When the pH of the solution is high the bonding reaction of the hydrolysed forms, for example $AlOH^{2+}$, should also be accounted for (Tipping *et al.* 1991). However, because similar equations such as (12)-(15) can also be written for $AlOH^{2+}$ and $Al(OH)_2^+$, it was assumed that total Al behaves like Al^{3+} in the reaction, as far as Al^{3+} is the major form of Al in the solution. In our study speciation of total Al showed that Al^{3+} was the major form of Al in the extracts, contributing 99%, 97%, 84% and 76% in the horizons A, (Bs1+Bw1), (Bs2+Bw2) and C respectively.

Figure 2. Horizon-specific relations between pK_{o2} and pK_{o1}, or the values of pK_o in the second and first extraction. The value of x was assumed to be 2.00, see Equation (14). The line shows the 1:1 - relation between the two pK_o values. Redrawn from Study I, European Journal of Soil Science (accepted).



The value of the complexation constant pK_o did not change much between the extractions, when bidentate binding of Al^{3+} was assumed. Thus the model of organic complexes could explain Al^{3+} dissolved in the extracts of effectively exchangeable cations. The recent study by Skyllberg (1999), in which organically adsorbed H+ and Al were also determined, gives full support to the conclusion that aluminium activity in a salt extract is determined by reactions of H^+ and Al with organic functional groups.

The differences in the pK_o of the horizons were much larger in the Podzols than in the Cambisol, but the estimated binding stoichiometry was about 2 in both soils. This suggests that the same model can be used to explain the dissolved Al^{3+} in the soils. However, it seems that the result can also be interpreted so that $Al(OH)^{2+}$ is the form of Al that is preferably complexed, instead of assuming that bidentate sites are the regulating factor. Bidentate binding has also been proposed by Tipping *et al.* (1991) and McBride (1994), and Bloom *et al.* (1979a) found values between 1.4 and 2.4 for the binding stoichiometry x by using 0.02 N salt solutions.

Model of $Al(OH)_3$ solubility

Solubility of a precipitated $Al(OH)_3$ phase has been used to explain the activity of Al^{3+} in a neutral salt solution for determining exchangeable acidity (Dahlgren and Walker 1994). Applied to the extractions, the reaction would be

$$\mathrm{Al(OH)_3} + 3\mathrm{H}^{+}_{\mathrm{Ba}} \Leftrightarrow \mathrm{Al}^{3+}_{\mathrm{Ba}} + 3\mathrm{H_2O}\,. \tag{16}$$

The equilibrium constant of the reaction was named according to the $Al(OH)_3$-mineral gibbsite, as log Q_{gibbs1} and log Q_{gibbs2} in extractions 1 and 2 respectively:

$$\log Q_{\mathrm{gibbs1}} = \log \mathrm{Al}^{3+}_{\mathrm{Ba1}} - 3\log \mathrm{H}^{+}_{\mathrm{Ba1}}\,. \tag{17}$$

The values of log Q_{gibbs1} and log Q_{gibbs2} are compared with the solubility of gibbsite (log K_{gibbs} = 8.04) and the solubility of amorphous $Al(OH)_3$ (log $K_{\mathrm{Al(OH)3}}$ = 9.66) (Lindsay 1979).

In our study the model did not explain the dissolved Al in the E, Ah and Bw1 horizons, where the values of log Q_{gibbs1} were clearly below 8.04 (Fig. 5 and Table 5 in Study I). In the Bs1 horizon, the range of log Q_{gibbs1} values was 7.1 – 8.4; in the Bs2 and C horizons of Podzols it was 8.0 – 9.0; and in the Bw2 and C horizons of S1 it was 7.9-8.3. Thus the values of log Q_{gibbs1} and log Q_{gibbs2} imply oversaturation with respect to gibbsite in many extracts of the Bs1, Bs2, Bw2 and C horizons.

There are two reasons why we suggest that equilibrium with $Al(OH)_3$ did not control the activity of Al^{3+} in any horizon other than the C horizon of Podzols. Firstly, the value of reaction stoichiometry x was close to two (instead of three) in all horizons except C of Podzols. Secondly, the apparent solubility was larger in the second than in the first extraction in all other horizons except the C horizons, and we do not see any reason why the solubility would increase between the extractions (see also Bloom et al., 1979b, for use of the same argument in the case of liming).

4.3 The amount and reactions of exchangeable acidity in soils

Fractioning of the total Al using an equilibrium model showed that Al^{3+} was the major form of Al in the extracts of exchangeable acidity. The charge of Al was also analysed by comparing the titrated exchangeable acidity TEA and the sum of exchangeable acids (H_e + $z$$Al_e$), which were determined by measuring pH and Al concentration in the extract. When the charge z was assumed to be 3, the relationship was close to 1:1 in all horizons and in both extractions, implying that the exchangeable acidity (EA) can be estimated by the sum (H_e + $3Al_e$).

The exchangeable acidity is only a small proportion of the total acidity of the soils, TA, and the proportion varies greatly. Consequently, the effective cation exchange capacity does not reflect well the ability of each soil and horizon to retain exchangeable cations. The site-specific average value of the ratio H_e/TA is 1.4-16.8% in the A horizon and 0.2-2.0% in the other mineral horizons (average values of TA and exchangeable cations are given in Table 1 in Study I and Appendix 2). The corresponding proportions $3Al_e$/TA are 16-45%, 15-24%, 1-9% and 0.6-7% in the A, (Bs1&Bw1), (Bs2&Bw2) and C horizons, respectively. The proportions

H_e/TA and 3Al_e/TA decrease with increasing depth down to the (Bs2&Bw2) horizon at each site.

Kaila (1971a) examined soil acidity in 298 Finnish soil samples representing both surface horizons and deeper horizons of agricultural and virgin soils. The proportion of exchangeable Al in the total acidity was on a level between the Bs1 and Bs2 horizons in our study: averages in clay, silt and loam, and sandy soils were 12.5%, 11.4%, and 12.4% respectively. Soil acidity is closely coupled to organic matter. Kaila (1971a) found that the organic carbon content explained 60%, 75% and 78% of the variation in non-exchangeable total acidity (or TA-EA) in clay soils, silt and loam soils, and sandy soils, respectively. Another major group of acidic compounds are the positively charged Al compounds, related to the amount of aluminium compounds which can be extracted with acid oxalate-extractable Al. Oxalate-extractable Al explained 78% and 60% of the non-exchangeable acidity in clay soils and silt and loam soils respectively, but only 6.5% of that in sandy soils (Kaila 1971a).

Exchangeable Al is only a small proportion of the extractable Al in the Bs1, Bs2 and C horizons: site-specific average values vary in the range 3.1-7.1% in the Bs1 horizon, 0.2-1.9% in the Bs2 horizon and 0.4-1.4% in the C horizon of the four well developed podzols S3, J1, J2, J3 (compare Appendix 2 and Table 1 in Study I). At site S2 the exchangeable Al forms a larger proportion of the extractable pool: 23.4%, 2.9% and 3.8% in the Bs1, Bs2 and C horizons respectively. The proportions are also high in the Bw1 (17.6%) and Bw2 (8.4%) horizons of site S1. However, the proportion is largest, 22-80%, in the A horizon of each profile. The exchangeable Al does not correlate with the extractable Al in any horizon. In Kaila's study (1971a) the average proportions of exchangeable Al in the extractable Al corresponded to our Bs1 horizons, being 4.0%, 3.6%, and 3.1%.

The exchangeable H^+ seems to form a large part of the exchangeable acidity in the O horizon. Ross *et al.* (1991) also found high values for exchangeable H^+ (90 $mmol_c\ kg^{-1}$) in low pH Oa horizons. Despite the low exchangeable H^+ content in the mineral horizons, it seems to have a crucial role in surface reactions (Study II). However, Thomas and Hargrove (1984) treat it only as a hydrolysis product, and it has also been neglected in some methods for estimating CEC_e (e.g. Hendershot and Duquette 1986, Rasmussen *et al.* 1991). One reason for this might be that when filter papers have been used, erroneous results of exchangeable H^+ have been obtained. In this study membrane filters were used, as it was found in the preliminary studies that filter paper may, depending on the paper, determine the pH of the solution to be e.g. 4.4, when the actual pH of the solution might be 5.5. Jardine *et al.* (1986) have documented some effects of various filter papers and membrane filters on different solutions. It is evident that the pH of extracts filtered with such papers is of no use for the studies of illuvial horizon and ground soil, and that it may also introduce major errors into the studies of the O and A horizons, even if the pH of the zero-experiment were taken into account. If the membrane filters and filter systems are considered too time-consuming or expensive, the pH should be determined before filtering. In this case the adsorption of metal cations, especially Al, from the extract to the filter paper should be checked. The titrated EA is quite meaningless in this case, so there will be no check on the charge of the exchangeable Al.

Although exchangeable Al could be explained by the model of organic complexes, the active Al in soil includes many other kinds of noncrystalline Al material, namely sorbed Al hydroxides and amorphous polymeric Al hydroxides, as well as imogolite type materials which may be abundant in the Bs horizon (Gustafsson *et al.* 1995). Polymeric Al hydroxides can be associated with organic matter (De Coninck 1980). It is evident that these materials are in an equilibrium with each other and with exchangeable Al (Pionke and Corey 1967, Barnhisel and Bertsch 1982, Duquette and Hendershot 1987, Soon 1993, Soon 1995). Thus in the soil acidification process the exchangeable Al can increase even if Al is extensively leached out of the soil, because exchangeable Al is replenished from the other active Al material (McLean *et al.* 1964, Nissinen and Ilvesniemi 1990, Hartikainen 1996).

In conclusion, exchangeable acidity is not a well defined pool in soil, but seems to have an equilibrium relationship with total acidity and organic complexes of Al. To our knowledge, this was a novel approach to exchangeable acidity.

5 Chemical equilibria in soil solutions

5.1 Analysis of apparent cation-exchange equilibria

Consider the cation-exchange reaction between cations on negatively charged exchange sites (CaX and AlX) and cations in soil solution (Ca^{2+} and Al^{3+}):

$$3\,\mathrm{Ca\,X} + 2\,\mathrm{Al}^{3+} \leftrightarrow 2\,\mathrm{Al\,X} + 3\,\mathrm{Ca}^{2+}\,. \tag{18}$$

The equilibrium constant for the reaction would be

$$K = \frac{\langle \mathrm{AlX} \rangle^2 \langle \mathrm{Ca}^{2+} \rangle^3}{\langle \mathrm{CaX} \rangle^3 \langle \mathrm{Al}^{3+} \rangle^2} \tag{19}$$

where $\langle\rangle$ denote activities. However, the activity of cations on negatively charged exchange sites cannot be determined. Several approaches have been used to approximate the activities (see review by Thomas 1977), but the most profound analysis was done by Gaines and Thomas (1953). For the cation-exchange reaction the Gaines-Thomas selectivity coefficient $K_{\mathrm{Al\text{-}Ca}}$ is defined by the equation (Gaines and Thomas 1953, McBride 1994)

$$K_{\mathrm{Al-Ca}} = \frac{E_{\mathrm{Al}}^{2} \langle \mathrm{Ca}^{2+} \rangle^{3}}{E_{\mathrm{Ca}}^{3} \langle \mathrm{Al}^{3+} \rangle^{2}} \tag{20}$$

where $\langle \rangle$ represents the activity in solution, and E_{Al} represents the charge fraction of exchangeable cations. In a binary exchange process the charge fraction of exchangeable cations is defined as

$$E_{\mathrm{Al(bin)}} = \frac{\mathrm{AlX}}{\mathrm{AlX+CaX}} \quad . \tag{21}$$

The unit for exchangeable cations is $\mathrm{mol_c\ kg^{-1}}$. However, in a natural situation exchangeable cations other than AlX and CaX are present, and the charge fraction of all exchangeable cations might be relevant in the coefficient equation. Thus a charge fraction of an exchangeable cation from all exchangeable cations is defined by

$$E_{\mathrm{Al(CEC)}} = \frac{\mathrm{AlX}}{\mathrm{CEC_e}} \quad , \tag{22}$$

where $\mathrm{CEC_e}$ is the effective cation-exchange capacity, or the sum of exchangeable cations HX, AlX, CaX, MgX and KX (Study II).

In Study II, two types of selectivity coefficients, $K_{\mathrm{Al\text{-}Ca(bin)}}$ and $K_{\mathrm{Al\text{-}Ca(CEC)}}$, were calculated using $E_{\mathrm{Al(bin)}}$ and $E_{\mathrm{Al(CEC)}}$ respectively. Because $K_{\mathrm{Al\text{-}Ca(CEC)}}$ was less variable, it is considered here as well as in Study III. Corresponding coefficients were calculated for exchange reactions $\mathrm{Mg^{2+}\text{-}Ca^{2+}}$, $\mathrm{K^{+}\text{-}Ca^{2+}}$ and $\mathrm{H^{+}\text{-}Ca^{2+}}$. The calcium ion was selected for the reference cation because it was the main cation in all soil solutions.

The selectivity coefficient can be used to define the preference of soil for a pair of cations. When $K = 1$ neither of the cations is preferred by the exchange sites, as

$$\frac{\langle \mathrm{Ca}^{2+} \rangle^{3}}{\langle \mathrm{Al}^{3+} \rangle^{2}} = \frac{E_{\mathrm{Ca}}^{3}}{E_{\mathrm{Al}}^{2}} \quad . \tag{23}$$

A value of K less than 1 indicates that $\mathrm{Ca^{2+}}$ is preferred over $\mathrm{Al^{3+}}$, see Equation (20).

The right side of the Equation (2) can be divided into two parts: ions in solution (S) and ions on exchange sites (Q)

$$S_{\mathrm{Al-Ca}} = \frac{\left\langle \mathrm{Ca}^{2+} \right\rangle^3}{\left\langle \mathrm{Al}^{3+} \right\rangle^2} \quad , \tag{24}$$

and

$$Q_{\mathrm{Al-Ca}} = \frac{E_{\mathrm{Ca}}^3}{E_{\mathrm{Al}}^2} \quad . \tag{25}$$

Now *K* and the logarithm of *K* to base 10 (log *K*) can be written

$$K_{\mathrm{Al-Ca}} = \frac{S_{\mathrm{Al-Ca}}}{Q_{\mathrm{Al-Ca}}} \tag{26}$$

and

$$\log K_{\mathrm{Al-Ca}} = \log S_{\mathrm{Al-Ca}} - \log Q_{\mathrm{Al-Ca}} \quad . \tag{27}$$

A linear regression model, based on Equation (27), was used to study log *K*:

$$\log S_{\mathrm{Al-Ca}} = a + b \log Q_{\mathrm{Al-Ca}} \quad . \tag{28}$$

The regression model and Equation (27) can be used to express log *K* as a function of log *Q* (Studies II and III):

$$\log K_{\mathrm{Al-Ca}} = a + b \log Q_{\mathrm{Al-Ca}} - \log Q_{\mathrm{Al-Ca}} \, . \tag{29}$$

The selectivity coefficient can vary with log *Q*, as it is not a true thermodynamic equilibrium constant. If the regression coefficient (*b*) exceeds 1, log *K* increases with increasing log *Q*. However, if *b* equals 1, then log *K* does not depend on log *Q*, and the intercept (*a*) shows the value of log *K* (Vanselow 1932, Coulter and Talibudeen 1968). Two criteria were used to judge each log *K*, namely 1) the proportion of explained variance (R^2) should be high, so that much of the variation in log *S* is explained by the variation in log *Q*, and 2) the regression coefficient *b* should be near unity, so that the selectivity coefficient does not depend on the exchangeable cations.

Chemical equilibrium can only be studied in controlled experiments. In addition, $\mathrm{CEC_e}$ was measured from the whole surface area of the soil, whereas only the fraction of solution which could be obtained by centrifuging was analysed. The terms ‘apparent equilibrium’ and ‘apparent selectivity coefficient’ are used here since the components of true equilibrium have not been measured.

Exchangeable cations of each sampling date were used to calculate cation–exchange coefficients of the centrifuge drainage method. In the lysimeter method it was assumed that the exchangeable cations have a constant value, determined from the soil sample which was taken when the hole was made for each lysimeter.

5.2 Apparent cation-exchange equilibria in the centrifugates of the experimental sites

Apparent cation-exchange equilibria were analysed in the three uppermost horizons (Study II), in which the effects of CO_2 degassing on H^+ activity were small (Study III). The amount of water obtained by centrifuging was only a part of the water content of each sample of soil, the average yield being between 16% and 21% in the three horizons.

The large proportions of explained variance (R^2) for the linear regression models of each log K suggest that the Gaines–Thomas selectivity coefficient satisfactorily represents the relation between cations Ca^{2+}, Mg^{2+}, K^+, Al^{3+} and H^+ in the centrifugates and on exchange sites in the soils.

In Mg^{2+}–Ca^{2+} exchange the value of R^2 (70%) was high for the linear regression model (Fig. 3, Table 1), although the range in exchangeable cation fraction CaX:(CaX+MgX) was small in each horizon (Study II). The regression coefficient (b) of the model was much lower than 1, indicating that log $K_{\text{Mg-Ca}}$ decreased with increasing log Q. The three horizons O, A and (Bs1&Bw1) were similar in respect to the average log K. In K^+–Ca^{2+} exchange in the A and B horizons the regression coefficient b of the model log $K_{\text{K-Ca(CEC)}}$ was near unity, but in the O horizon log $K_{\text{K-Ca}}$ decreased with increasing log Q.

In Al^{3+}–Ca^{2+} exchange the value of R^2 was high and b was near unity. In H^+-Ca^{2+} exchange the value of R^2 was high, the value of b was close to unity and the three horizons O, A and (Bs1&Bw1) were similar with respect to the average log $K_{\text{H-Ca(CEC)}}$.

For log $K_{\text{K-Ca}}$ and log $K_{\text{Al-Ca}}$ the values increased considerably with increasing depth, indicating a decreasing preference for Ca^{2+} over Al^{3+} and K^+ with increasing depth. A great part of the large variation in $K_{\text{K-Ca}}$ and $K_{\text{Al-Ca}}$ was explained by the horizons. Thus the chemical properties which affected the soil preference for Ca^{2+} relative to K^+ and Al^{3+} were related to the horizons, although the chemical properties of each horizon varied greatly within the six sites.

However, the horizons did not seem to differ in selectivity for the cation pair Mg^{2+}–Ca^{2+}. Obviously these bivalent cations have such a similar behaviour in the cation-exchange reaction that even large differences in the properties of the adsorbing material do not cause any major differences in selectivity. The similarity of the horizons in the selectivity for H^+ and Ca^{2+} is more surprising. One reason might be that soil organic matter is responsible for the majority of cation exchange sites in each horizon.

Regarding soil acidification models, an important result was that in the Al^{3+}–Ca^{2+} and H^+–Ca^{2+} exchange reactions the apparent selectivity coefficients did not depend on fractions of the exchangeable cations. Similarly, Clark and Turner (1965), Turner (1965), Coulter and Talibudeen (1968), and Foscolos (1968) found that the selectivity coefficient in Al^{3+}–Ca^{2+} exchange did not vary with Al saturation of exchangeable cations. This suggests that an invariant selectivity coefficient can be applied to analyses of soil acidification in which the cation-exchange reaction between Ca^{2+} and Al^{3+} is simulated, even if the simulated exchangeable cation composition changes in the simulation. However, some studies have shown that the preference for Al^{3+} relative to Ca^{2+} decreased with increasing Al saturation of CEC_e (Pleysier *et al.* 1979, Chung *et al.* 1994).

Some statistically significant differences between the sites were found (Table 4 in Study II), but they had no clear pattern, such as some sites would differ in respect to all horizons. Generally, the variation was large at each site. For example, standard deviations of some coefficients were similar in size for the intensively sampled site, S2, and for all six sites (Study II).

The large variation in the values of the coefficients is partly explained by the heterogeneity of the soil material studied. However, two other reasons are also important if we wish to compare this study with other experimental cation-exchange studies. First, cation-exchange has often been studied in binary systems that differ from field conditions. Our study, and those by Pleysier *et al.* (1979), Rhue and Mansell (1988) and Chung *et al.* (1994), suggest that other ions present in natural situations may considerably affect the equilibrium between two ions. Second, in the field the contact surface between soil solution and exchangeable cations is not as invariant as it is in experiments.

HX and AlX were measured with unbuffered salt extraction, and they represent only a small fraction of total adsorbed H^+ and Al (Thomas 1982; compare also TA and CEC_e, found in Table 1 in Study I and Appendix 2). However, the fit of the Gaines–Thomas selectivity coefficient to the data was better in Al^{3+}–Ca^{2+} and H^+–Ca^{2+} exchange reactions than in the exchange reactions between the base cations. This suggests that the use of effectively exchangeable HX and AlX in a simulation of a cation-exchange equilibrium is reasonable.

5.3 Ionic composition and apparent chemical equilibria in centrifugates and suction lysimeter solutions of two experimental sites

Ionic composition in centrifugates and suction lysimeter solutions

Centrifuge method and suction lysimeters were used to extract soil solution at two sites. Although the centrifugates represent composite samples that were taken randomly from the whole site and the lysimeter solutions represent only the point of installation at the site, the results imply that the differences observed cannot be explained only by the differences in sampling. Large differences were found when

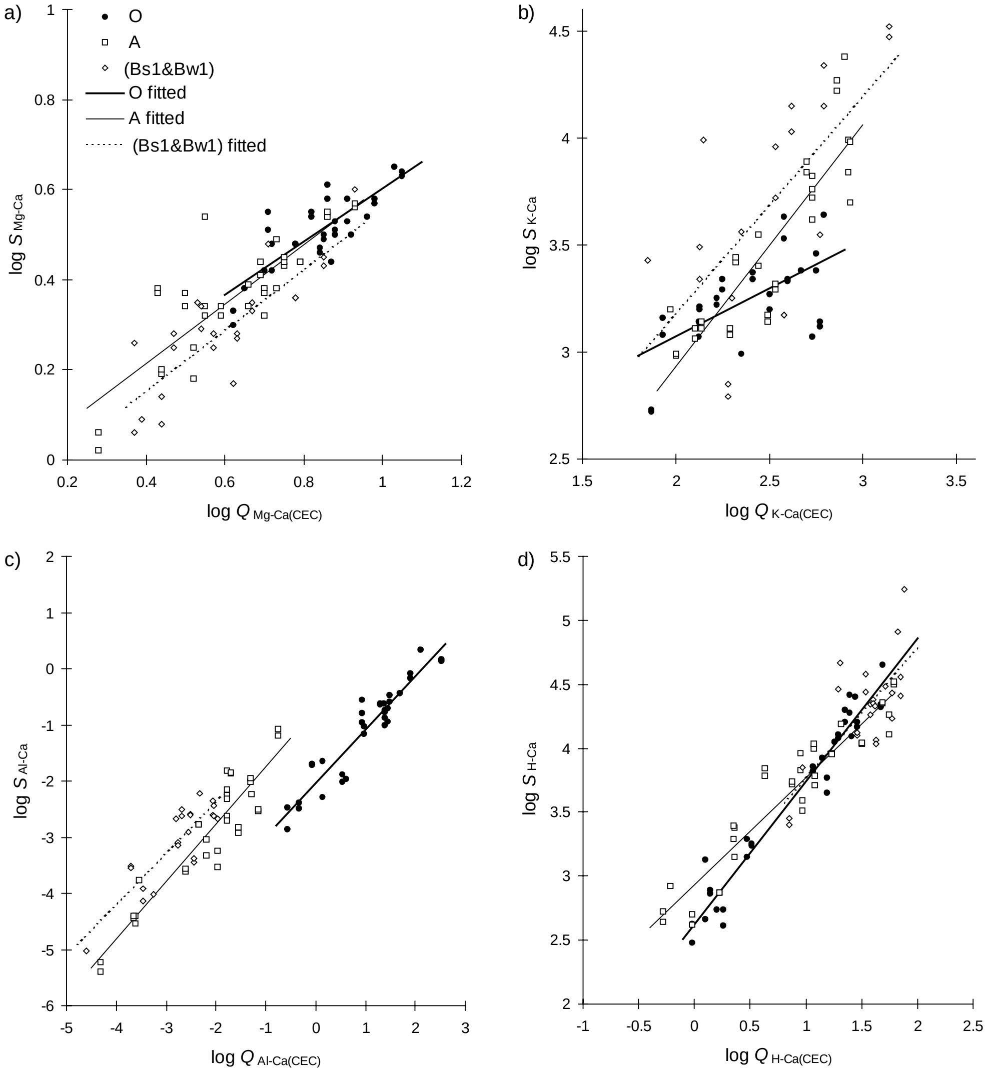


Figure 3. Horizon-specific relations between log *S* and log *Q*. (a) Mg^{2+} –Ca^{2+}, (b) K^{+} –Ca^{2+}, (c) Al^{3+} –Ca^{2+}, (d) H^{+} –Ca^{2+}. The fitted regression lines correspond to the linear regressions presented for log $K_{(CEC)}$ in Table 1. Redrawn from Study II, European Journal of Soil Science 49: 121-132.

Table 1. Fit of the Gaines–Thomas model to the data. Models, their coefficients of determination (R^2) and number of observations (n) for the linear regression of log S on log Q are presented, based on the equations of log $K_{(\mathrm{CEC})}$. The mean values of log $K_{(\mathrm{CEC})}$ are also shown. Redrawn from Study II, European Journal of Soil Science 49: 121-132.

Horizon	Parameters of the regression model log S = b log $Q_{(\mathrm{CEC})}$ + a				Mean of log $K_{(\mathrm{CEC})}$	n
	b [e]	SE of b [f]	a	R^2		
			Exchange Mg-Ca			
O	0.59	0.07	0.01	0.70	-0.33	34
A	0.66	0.08	-0.05	0.70	-0.26	33
(Bs1&Bw1)	0.68	0.10	-0.12	0.70	-0.31	23
			Exchange K-Ca			
O	0.45	0.11	2.17	0.38	0.85	28
A	1.13	0.12	0.67	0.77	1.01	30
(Bs1&Bw1)	1.01**	0.28	1.16	0.43	1.18	19
			Exchange Al-Ca			
O	0.95	0.06	-2.03	0.90	-2.08	33
A	1.02	0.07	-0.74	0.86	-0.78	32
(Bs1&Bw1)	0.90	0.12	-0.59	0.74	-0.32	22
			Exchange H-Ca			
O	1.12	0.04	2.62	0.95	2.73	34
A	0.84	0.05	2.93	0.90	2.79	34
(Bs1&Bw1)	1.01	0.20	2.76	0.56	2.78	23

[e] The regression coefficients (b) differed from zero at the p <0.001 level, except that marked with ** (p <0.01).

[f] Standard error of the regression coefficient.

the centrifugates and the lysimeter solutions were compared in regard to ion concentrations and the apparent cation-exchange equilibria (Study III).

Cation concentrations were much larger in the soil centrifugates than in the lysimeter solutions (Table 2). The greatest differences between the methods were seen for H^+ and K concentration in all horizons, and Al concentration in (Bs1&Bw1) and (Bs2&Bw2) horizons, many of the concentrations being over ten times larger in the centrifugates than in the lysimeter solutions. The relative difference between the two methods in most horizons was smaller for Ca and Mg than for H^+, Al and K.

H^+ concentration decreased with increasing depth in both methods. A similar trend of decreasing concentration with increasing depth could be seen for Ca in both methods. However, the two methods differed in regard to the depth patterns of the other cations. Al concentration in the centrifugates was high in the A and (Bs1&Bw1) horizons, while in the lysimeter solutions the Al concentration was clearly highest in the A horizon. Concentrations of Mg and K decreased with increasing depth in the centrifugates of both sites, but in lysimeter solutions the decrease holds only for concentration of K at site S1.

The total positive charge of the measured cations decreased with increasing depth in both methods (Table 2). It was 2.4-3.7 -times larger in the centrifugates than in the corresponding lysimeter solutions (except for horizon Bw2).

The temporal variation in cation concentrations was large for both methods. For example, the coefficient of variation (CV) for Al concentration varied between 19% and 81 % in the centrifugates and between 26% and 114% in the lysimeter solutions. CV for Ca concentration was between 5% and 49% in the centrifugates and between 8% and 24% in the lysimeter solutions.

Apparent cation-exchange equilibria in centrifugates and suction lysimeter solutions

The values of apparent log $K_{\mathrm{H\text{-}Ca}}$ were clearly different in the two methods. The variation in log $K_{\mathrm{H\text{-}Ca}}$ was smaller in the centrifuge drainage method than in the lysimeter method. A linear relationship well described the relation between log S and log Q in the centrifugates of the A and (Bs1&Bw1) horizons, and the regression coefficient was close to unity (Fig. 4a). In the lysimeter solutions log S did not depend on log Q (Fig. 4b). The variation in log S shows the variation in the apparent log $K_{\mathrm{H\text{-}Ca}}$ of each lysimeter soil, because a constant value of log Q was assumed for each lysimeter, i.e. the content of exchangeable cations was assumed to be constant in the soil surrounding each lysimeter during the experiment.

A maximum effect of degassing on solution H^+ activity was estimated to see if degassing of CO_2 could be a reason for the difference between the centrifugates and the lysimeter solutions. The calculated H^+ activity resulted in much lower values of log S than the measured H^+ activity, but the values were still larger than those of the centrifugates (Fig. 4b). Because the calculated H^+ activity is an over-

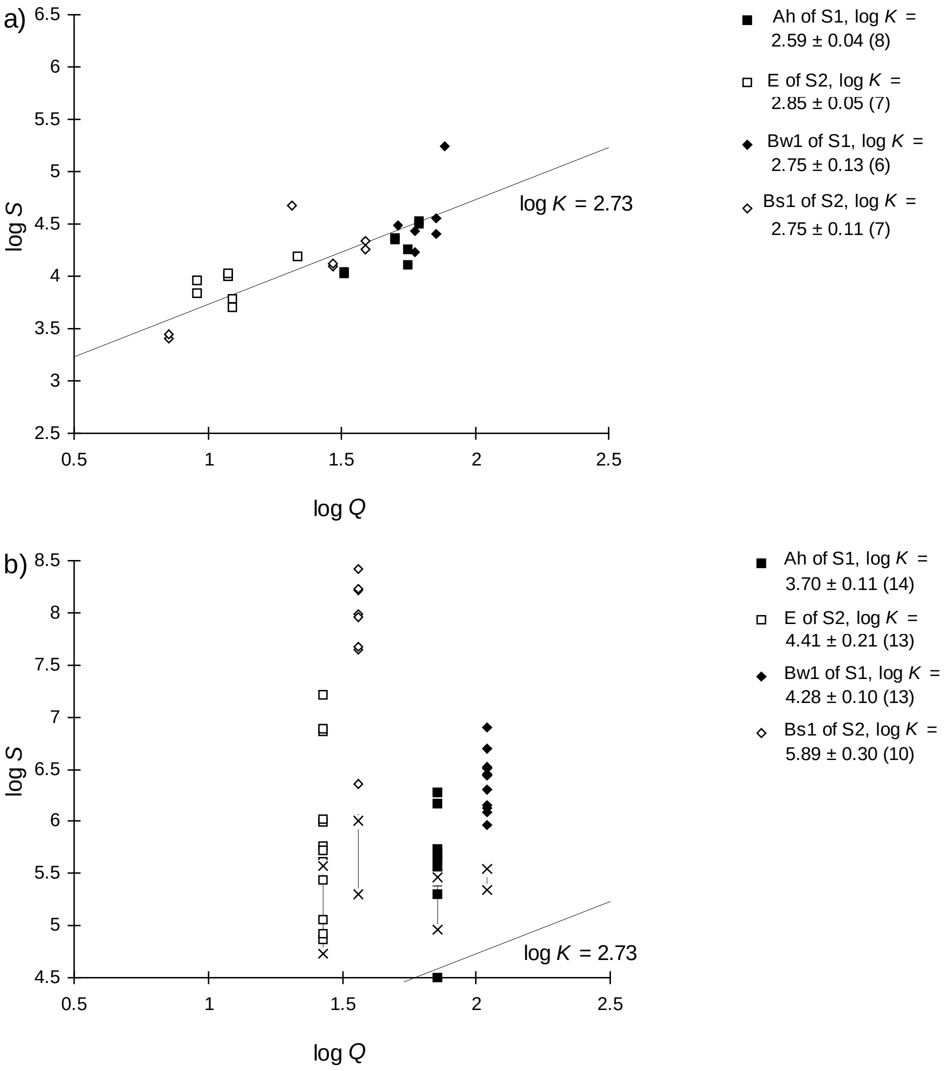


Figure 4. Relation between log $S_{\text{H-Ca}}$ and log $Q_{\text{H-Ca}}$ in (a) the centrifugates and in (b) the lysimeter solutions. The mean value of log $K_{\text{H-Ca}}$ in each site and horizon is given in the legend, as well as the standard error of the mean and the number of observations (the latter in parentheses). The average value of the centrifugates is indicated with a line. In Fig. 4a the regression equation between log S and log Q was: log S = 0.88(log Q) + 2.91, coefficient of determination = 0.63, and n = 28. In Fig. 4b the effect of an assumed CO_2 degassing on log $S_{\text{H-Ca}}$ is also presented, the range of values being shown with a line and marker x. Redrawn from Study III, Water, Air and Soil Pollution (in print).

Table 2. Ion concentrations and hydrogen ion activity in soil solutions acquired by centrifuging and by suction lysimeters. Significance of the difference between the methods is shown for both sites. Horizon-specific average values which differ from each other are marked with differing letters. Redrawn from Study III, Water, Air and Soil Pollution (in print).

	Horizon	Site S1										
		Centrifuging					Suction lysimeter					Significance of method difference ^{h}
		Mean	±	SE	(*n*)	^{e}	Mean	±	SE	(*n*)		
H$^+$ activity, µmol l^{-1}	O	154	±	16	(8)	a ^{f}						
	A	121	±	12	(8)	ab	12.8	±	1.0	(13)	a ^{f}	*** (k)
	Bw1	74	±	14	(8)	b	5.4	±	0.6	(15)	b	*** (k)
	Bw2	12	±	2	(5)	c	1.1	±	0.6 k	(8)	c	** (k)
Al$_{mon}$, µmol l^{-1}	O	37	±	4	(8)	a ^{g}						
	A	97	±	14	(8)	b	29.5	±	2.3	(11)	a ^{g}	*** (k)
	Bw1	101	±	31	(6)	ab	9.0	±	1.2	(13)	b	*** (k)
	Bw2	13	±	6	(3)	a	3.1	±	1.2 k	(9)	b	NS (k)
Ca, µmol l^{-1}	O	619.7	±	35	(6)	a ^{f}						
	A	350.4	±	51	(8)	b	89.9	±	6.0	(13)	a ^{g}	*** (k)
	Bw1	267.6	±	54	(6)	b	83.3	±	1.7	(14)	a	*** (k)
	Bw2	90	±	3	(2)	b	70.5	±	4.5	(12)	a	NS (o)
Mg, µmol l^{-1}	O	197.1	±	11	(6)	a ^{f}						
	A	164.6	±	21	(7)	a	69.6	±	4.2	(13)	a ^{f}	*** (k)
	Bw1	151.3	±	24	(6)	a	81.4	±	5.4	(14)	a	*** (k)
	Bw2	97	±	12	(2)	a	105.8	±	7.2	(12)	b	NS (o)
K, µmol l^{-1}	O	469	±	29	(8)	a ^{f}						
	A	197	±	24	(8)	b	11.8	±	1.6	(13)	a ^{f}	*** (k)
	Bw1	128	±	7	(8)	bc	11.5	±	1.1	(13)	a	*** (k)
	Bw2	56	±	5	(5)	c	5.8	±	1.0	(11)	b	** (k)
Total positive charge of the measured cations, µmol$_c$ l^{-1} ^{j}	O	2412	±	122	(6)	a ^{f}						
	A	1636	±	231	(7)	ab	438	±	23	(11)	a ^{g}	*** (k)
	Bw1	1356	±	268	(6)	b	368	±	8	(10)	b	** (k)
	Bw2	414			(1)	b	353	±	16 k	(5)	b	NS (k)

Table 2 continues.

	Horizon	Site S2										
		Centrifuging					Suction lysimeter					Significance of method difference [h]
		Mean	±	SE	(*n*)		Mean	±	SE	(*n*)		
H$^+$ activity, µmol l^{-1}	O	168	±	14	(10)	a [f]						
	A	138	±	9	(11)	a	18.4	±	5.6	(15)	a [g]	*** (o)
	Bs1	86	±	12	(10)	b	2.8	±	0.8	(14)	b	*** (k)
	Bs2	22	±	3	(14)	c	6.1	±	1.0	(18)	b	*** (k)
Al$_{mon}$, µmol l^{-1}	O	24	±	3	(9)	a [f]						
	A	76	±	4	(10)	b	26.7	±	4.1	(15)	a [g]	*** (o)
	Bs1	68	±	4	(8)	b	6.4	±	1.0	(12)	b	*** (k)
	Bs2	27	±	7	(8)	a	4.6	±	0.6	(18)	b	** (k)
Ca, µmol l^{-1}	O	412	±	37	(9)	a [g]						
	A	186	±	17	(8)	ab	86.32	±	5.4	(14)	a [f]	*** (k)
	Bs1	119	±	14	(7)	b	89.82	±	5.3	(14)	a	* (o)
	Bs2	123	±	14	(10)	b	65.82	±	3.1	(17)	b	** (k)
Mg, µmol l^{-1}	O	129	±	14	(9)	a [g]						
	A	74	±	4	(8)	ab	35.29	±	2.4	(14)	a [f]	*** (o)
	Bs1	61	±	4	(7)	b	46.11	±	1.9	(14)	b	** (o)
	Bs2	54	±	4	(10)	b	29.79	±	1.5	(17)	a	*** (k)
K, µmol l^{-1}	O	475	±	87	(6)	a [g]						
	A	155	±	12	(8)	a	10.0	±	1.2	(12)	a [f]	*** (k)
	Bs1	132	±	22	(7)	ab	11.9	±	1.6	(12)	a	*** (k)
	Bs2	59	±	5	(8)	b	26.1	±	1.2	(15)	b	*** (k)
Total positive charge of the measured cations, µmol$_c$ l^{-1} [j]	O	1747	±	271	(5)	a [g]						
	A	1071	±	38	(5)	ab	323	±	22	(10)	a [f]	*** (o)
	Bs1	813	±	49	(3)	b	307	±	23	(8)	a	*** (o)
	Bs2	553	±	89	(3)	b	230	±	11	(13)	b	** (k)

[e] SE = standard error of mean, *n* = number of observations.

[f] Oneway analysis of variance and Tukey's test were performed to compare horizons, $p<0.05$ level is shown.

[g] As variances were different, Kruskall-Wallis test was performed. Differences at the $p<0.05$ level are shown.

[h] Methods are different at the probability level: $p<0.001$ ***, $p<0.01$ **, $p<0.05$ *. NS = no significant difference. Test is shown in parentheses: o = oneway analysis of variance, k = Kruskal Wallis test.

[j] Al$_{mon}$ was assumed to be Al^{3+} in the calculation of the total positive charge of the measured cations.

estimate for almost all lysimeter solutions (Study III), degassing can explain only a part of the difference between the methods in log $K_{H\text{-}Ca}$.

The apparent exchange equilibria Al^{3+}- Ca^{2+} and K^{+}- Ca^{2+} were different in the two methods, the average log $K_{Al\text{-}Ca}$ and log $K_{K\text{-}Ca}$ being larger in the lysimeter method than in the centrifuging method at both sites (Study III). The variations of log $K_{Al\text{-}Ca}$ and log $K_{K\text{-}Ca}$ were larger in the lysimeter method than in the centrifuging method. There seems to be no consistent difference between the methods in the apparent exchange equilibria Mg^{2+}- Ca^{2+}, although differences are statistically significant.

Solubility of Al^{3+} in centrifugates and suction lysimeter solutions

The activities of H^{+} and Al^{3+} together with the solubility lines of gibbsite (p*K* = 33.96 at 25 °C, Lindsay 1979) and amorphous $Al(OH)_3$ (p*K* = 31.20, Stumm and Morgan 1981) were plotted in the diagrams shown in Fig. 5. Activity of Al^{3+} was between gibbsite and amorphous $Al(OH)_3$ in the centrifugates with a low H^{+} activity (less than 60 µmol l^{-1}). The centrifugates with a H^{+} activity larger than 60 µmol l^{-1} were undersaturated with respect to the gibbsite. Aluminium solubility was also compared to linear regression lines fitted for pAl and pH by Cronan *et al.* (1986). They presented Al solubility as a function of a 'bound aluminium ratio' (BAR), which means the ratio between bound aluminium (extracted with 0.5 M $CuCl_2$) and total acidity (determined with $BaCl_2$-TEA-method, Thomas 1982). Regressions for BAR 0.60-0.70 and 0.90-1.00 are shown in Fig. 5. A corresponding regression was fitted for pAl and pH in the centrifugates of the (Bs1&Bw1) and (Bs2&Bw2) horizons, giving the equation pAl = 1.31(pH) - 1.11 (coefficient of determination = 0.89, *n* = 21, standard error of estimate = 0.14). The regression line was close to that of BAR 0.90-1.00. In the A horizon, only a weak correlation was found between Al^{3+} activity and H^{+} activity, but the solubility of Al was close to the regression for BAR 0.60-0.70. A straightforward comparison is not possible as we did not measure the BAR, but the ratio of the oxalate-extractable Al to the total acidity was much larger in the (Bs1&Bw1) horizon than in the A horizon (Table 1 in Study II).

The centrifugates were undersaturated with respect to jurbanite, the horizon-specific average values of apparent p*K* being between 18.0 and 18.6 in the centrifugates (compare with p*K* 17.8, Nordstrom 1982). Al^{3+} activity generally exceeded that suggested by the solubility of alunite (p*K* = 85.40, Adams and Rawajfih 1977). However, the solutions were undersaturated with respect to alunite in the O horizon, and a few centrifugates of the A horizon showed solubility corresponding to a p*K* of 85.40.

In lysimeter solutions, Al^{3+} activity was between the solubility of gibbsite and amorphous $Al(OH)_3$, and the average p*K* was close to 32.0 in all three horizons. The lysimeter solutions were undersaturated with respect to jurbanite, the horizon-specific average values of apparent p*K* being between 18.3 and 19.7. Activity of Al^{3+} generally exceeded that suggested by the solubility of alunite.

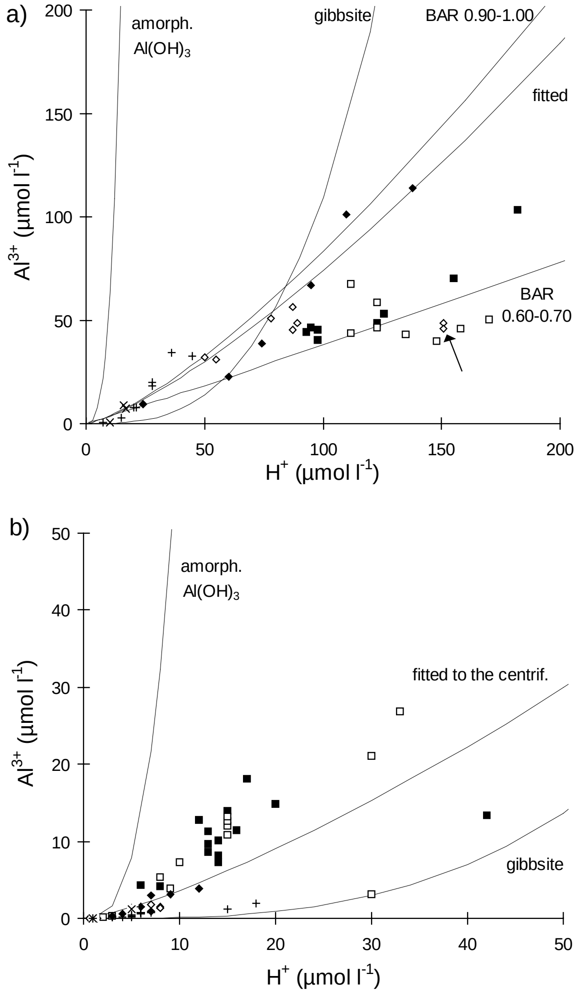


Figure 5. Activity of Al^{3+} as a function of H^+ activity in (a) the centrifugates and in (b) the lysimeter solutions. Solubilities of gibbsite and amorphous $Al(OH)_3$ are shown with lines, as well as a linear regression fitted to pAl and pH in the horizons (Bs1&Bw1) and (Bs2&Bw2) (two observations shown with an arrow were excluded as outliers). In Fig. 5a the solubility presented by Cronan et al. (1986) for two 'bound aluminium ratios' (BAR) is also shown. Redrawn from Study III, Water, Air and Soil Pollution (in print).

5.4 Ionic composition and chemical equilibria in soil solutions

Even if there exists a theoretical limit for the pore size which the centrifuge drainage method can empty, the centrifugates do not represent a well defined fraction of the soil solution. Quite the opposite; Zabowski and Ugolini (1990) found that solutions extracted with different centrifuge speeds had a similar ion composition, and concluded that the 18 to 30 h period between soil sampling and centrifuging of the bulked soil sample allowed an equilibration between the waters of different pore sizes. Giesler and Lundström (1993) found great differences in ion composition of centrifugates from bulked and unbulked soil samples, and proposed that mixing of samples created new compositions of pore water and pore surfaces. The suction lysimeters also collect water from all pores, but the flow velocity depends on the pore size (Grossmann and Udluft 1991). However, because the centrifuge drainage method should be able to extract more water from small pores than the suction lysimeter method, it seems that the total charge of ions in soil solution is greater in small pores than in large pores, especially in the topmost mineral soil. The findings are supported by the results of Zabowski and Ugolini (1990) and Giesler *et al.* (1996). In particular H^+ was concentrated in some of the centrifugates they collected, the ratio centrifugate:lysimeter solution being over 10. It is also known that ion concentrations increase in lysimeter solution when the suction is increased (Grossmann *et al*. 1987).

The differences between solutions from zero-tension lysimeters and suction lysimeters (Hendershot and Courchesne 1991, Magid and Christensen 1993) have been quite small compared to the differences between centrifugates and suction lysimeter solutions. It seems that studies on the properties of stagnant water and plant-soil interactions in a soil horizon should focus on centrifugates instead of suction lysimeter solutions.

The decrease in ion concentrations and the total positive charge with depth has been found in many studies of in situ solutions collected with suction lysimeters (Haines *et al*. 1982, Yarie *et al.* 1993) and centrifugation (Manley *et al.* 1987, Norflect *et al.* 1993, Giesler *et al.* 1996). Retention of organic acids and sulphate in the B horizon is the most probable reason for the decrease in our lysimeter solutions, which we assume to represent the mobile water in soil. In the centrifugates, the decrease may also result from depth gradients in the water and nutrient uptake rates of plants.

In our study, there are two evident reasons for the larger variation in the cation–exchange coefficients $K_{\mathrm{H\text{-}Ca}}$, $K_{\mathrm{Al\text{-}Ca}}$, and $K_{\mathrm{K\text{-}Ca}}$ with the suction lysimeter method as compared with the centrifuge drainage method. First, the extent of the soil volume from which the sample is obtained varies in the suction lysimeter method (Starr 1985, Grossmann and Udluft 1991), and thus the assumption of constant CEC_e is not valid. It is more valid in the centrifuging method, in which subsamples of a composite sample are used for the determination of the CEC_e and the extraction of water. Second, the suction lysimeter method extracts less solution from small pores than the centrifuge drainage method, and thus it is evident that the centrifugates have been in closer contact than the lysimeter solutions with soil surfaces and the measured exchangeable cations.

Similarly to the findings of Manley *et al.* (1987) and Lundström (1993) for podzolic soils, the lysimeter solutions in our study were supersaturated with respect to gibbsite and undersaturated with respect to amorphous $Al(OH)_3$. In the centrifugates, the slope of regression between pAl and pH was close to 1 in the (Bs1&Bw1) and (Bs2&Bw2) horizons and below 1 in the A horizon, which may imply that complexation reactions rather than $Al(OH)_3$ solubility have determined Al activity in the centrifugates (Cronan *et al.* 1986, Wesselink *et al.* 1996). The apparent cation-exchange equilibrium also explained a large part of the variation in Al activity in the centrifugates. The solution samples did not seem to be in equilibrium with sulphate minerals.

5.5 Implications for modelling of soil solution chemistry

The apparent non-equilibria in the lysimeter solutions apparently does not support the assumption of cation-exchange equilibria in the mobile soil solution, assuming that the suction lysimeter solutions better represent the loosely bound runoff solution than the centrifugates. However, because the suction lysimeter –method has the specific problems mentioned above (and in Study III), the assumption of equilibria in the mobile soil solution cannot be directly rejected due to the apparent non-equilibria in the lysimeters.

Some reasons for the apparent non-equilibria in soil solution samples and in runoff can be analysed following the idealized soil system of Neal (1992) and Neal and Robson (1994, 1997) (Study III). There is chemical variability in the pores of the soil system, including total charge of ions in solution and relative proportions of soil exchangeable cations. Assuming that each solution sample collected from the soil represents a random proportion of the pores, the samples display non-equilibria of cation-exchange reactions, even though the solution in each pore is in equilibrium with the exchangeable cations of the pore. Thus it is not possible to determine the short-term (e.g. daily or weekly) variation in the ionic composition of the bulk solution using cation-exchange coefficients. However, when the ionic compositions of a large number of solution samples are averaged in such a soil system, the relationships between cations are similar to the theoretical ones, and the apparent selectivity coefficients do not depend on the total charge of the ions in solution (Neal and Robson 1994). Thus Neal and Robson (1994, 1997) suggest that apparent cation-exchange equilibria could be assumed in long-term analyses in which yearly properties of runoff are focused on, such as analyses with the model MAGIC by Cosby *et al*. (1985).

For the soils used in our study, the difference between the centrifugates and the lysimeter solutions in the total charge of ions implies that the lysimeter solution does not represent a random proportion of the soil pores, but instead represents a random proportion of the large pores (Study III). The transfer of ions between the small and large pores cannot be a rapid process because ion concentrations are so different in the pores. When the solution in small pores has cation-exchange equilibria with the bulk exchangeable cations of soil, there cannot be cation-exchange equilibria between the solution in large pores (i.e. the mobile solution) and the bulk exchangeable cations.

However, some results imply that transfer of ions from small pores to large pores affects the ionic composition of the solution in large pores (Study III). First, the depth gradients in the ion concentrations in the lysimeter solutions suggest that chemical reactions have affected the lysimeter solutions. Second, similar values of the coefficient of homovalent exchange ($K_{\text{Mg-Ca}}$) in lysimeter solutions and centrifugates indicate that some relationship exists between the lysimeter solution and the bulk exchangeable cations.

In conclusion, the apparent selectivity coefficients used to determine ionic composition of mobile soil solution in soil acidification models seem to aggregate cation-exchange processes in small pores and diffusion of ions and water fluxes between small and large pores (Study III). In order to see the justification of this aggregation in long-term simulations, analyses performed by Neal and Robson (1994, 1997) could be extended to include immobile water in small pores and diffusion and water fluxes between large and small pores. Cation-exchange equilibria in small pores could be calculated using the coefficient values of the centrifuging method.

It is evident that the dependence of each cation concentration on the total charge is different in solution which has cation-exchange equilibria with exchangeable cations (i.e. the higher the valence of a cation, the more its concentration in solution increases with increasing total charge) when compared with the mobile soil solution (Study III). Thus the assumption of cation-exchange equilibria in the mobile soil solution should not be applied if the total charge in the mobile solution changes (e.g. due to change in acidic deposition). This means that the assumption of apparent cation-exchange equilibria in mobile solution does not apply well to an analysis of acid deposition effects.

6 Consequences of process and parameter aggregation in modelling of soil acidification

6.1 Soil acidification model ACIDIC

The dynamic soil model ACIDIC was used to analyse how the simulated soil response to acidic deposition differs between detailed and aggregated soil descriptions (Study IV). The model ACIDIC includes features and processes common to dynamic soil acidification models (de Vries *et al.* 1989, Warfvinge *et al.* 1992). The model describes 1) a soil that is divided into several interacting layers and 2) a tree stand that takes up water and nutrients from the soil layers. The fluxes of ions to and from the soil are assumed to be controlled by atmospheric inputs, inputs from the weathering of soil minerals, net uptake in trees, and losses in runoff. Input data includes daily values of precipitation, ion deposition, and minimum and maximum air temperature. Here a general description of the model is given, and more details can be found in Kareinen *et al.* (1998).

The soil layers described can differ in respect to physical and chemical properties, but each layer is homogenous. The driving force for the water flow between the layers is the difference in the water potential, while the hydraulic conductivity and the relationship between water potential and water content are the horizon-specific soil properties that determine the flow. Chemical equilibrium reactions are assumed to determine ion concentrations in the soil solution of each layer. Dissolved ions are transported between the layers by the water flow. Daily values of soil water contents and ion composition in soil solution in each layer are usually produced as model outputs. The timestep varies between one minute and one hour, depending on the water fluxes between the soil layers.

Cation-exchange equilibria between H^+, Al^{3+}, Ca^{2+}, Mg^{2+}, and K^+ in solution and on exchange sites are assumed in each layer, using the Gaines–Thomas cation-exchange coefficients (Studies II and III, Gaines and Thomas 1953). Other chemical reactions that are assumed to be in equilibrium are dissolution of $Al(OH)_3$ and reactions of Al hydroxides in solution (Lindsay 1979), the formation of carbonic acid and its dissociation products (Lindsay 1979), and sulphate adsorption, which is described using the Langmuir isotherm. Near-equilibrium of each reaction is confirmed at each hydrological time step, so that reactions are simulated until each chemical equilibrium constant, which is based on simulated concentrations, is within ±5% of the preset value. Release of cations Ca^{2+}, Mg^{2+}, and K^+ in the weathering of soil minerals is assumed to be constant with time in the model.

Net uptake of ions by trees is calculated as the amount of ions needed for stem growth, which is assumed to be regulated by the air temperature. The uptake for the growth of needles, branches, and roots is assumed to equal the release in the decomposition of soil organic matter. The distribution of nutrient uptake between the layers is based on the amounts of roots and solution nutrient concentrations in each layer. The uptake of cations produces equivalent amounts of H^+ in the solution, and uptake of NO_3^- produces OH^-. Release of cations from mineral lattices in weathering consumes an equivalent amount of H^+ from the solution.

6.2 Application of the model ACIDIC

In order to study what effects the aggregation of soil properties has on the simulated soil response to acidic deposition, three simulated cases were evaluated. In the most detailed model structure (the reference case), soil was divided into five layers with horizon-specific chemical properties (abbreviation dhdc or dc, meaning "different horizons, different coefficient values"). In the second case all five layers were assumed to have the same cation-exchange coefficient values (dhsc or sc, "same coefficient values"). In the third case a homogenous soil block was described (one-layer). The total amount of each exchangeable cation was the same in the one-layer soil and in the five-layer soil.

The simulations were done for two ‘hypothetical’ sites, J2 and S2. However, each soil horizon on the sites was given site-specific values of exchangeable cations, measured at the J2 and S2 sites in Studies I and II (see Table 1 in Study IV). Ion deposition was measured close to each of the two sites (Study IV). Other stand and soil properties were the same in the simulations of the J2 and S2 sites. Cation-exchange coefficients of the mineral horizons were based on ion concentrations in suction lysimeter solutions at site S2, and they were calculated as in Study III but assuming that all inorganic Al in solution behaves like Al^{3+} in the cation-exchange reactions. The horizon-specific median value of each coefficient was used in the multi-layer simulations. In one-layer simulations the mean or median of the horizon-specific values was used (see Table 2 in Study IV for the values of the cation-exchange coefficients). No aluminium dissolution from $Al(OH)_3$ was assumed.

Tree growth was calibrated to 5 m^3 ha^{-1} a^{-1}. A low weathering rate of 16 $mmol_c$ m^{-2} a^{-1} was assumed for the base cations (on mole charge basis, the proportions were: Ca^{2+} 42.3%, Mg^{2+} 22.5%, K^+ 11.3% and Na^+ 23.9%, Sverdrup and Warfvinge 1993a). A water retention curve and hydraulic conductivities of a sandy podzolic soil were assumed for the multi-layer soil. The hydrological properties were calibrated for the one-layer simulations, so that the same run-off was reached as with the multi-layer structure.

The throughfall was assumed to be 75% of the daily precipitation (Hyvärinen 1990). The precipitation was 799 l m^{-2} in 1991 in Siuntio (Kämäri *et al.* 1992). Simulated throughfall was 599 l m^{-2}, simulated water uptake by trees was 249 l m^{-2} from the 55 cm deep topmost soil and 82 l m^{-2} from the deeper layers. The total evapotranspiration was 531 l m^{-2} (66%) of the precipitation. The percolation at depth 55 cm was 350 l m^{-2}. One year was simulated.

6.3 Results of simulations with different model structures

Cation leaching in the multi-layer cases was clearly different from the one-layer cases (Table 3). The H^+ and Al concentrations were much lower and Mg concentration 15-40% higher in the multi-layer case dhdc than in the one-layer case, making the decrease in the soil exchangeable Mg much larger with the multi-layer structure. This also holds for Ca in soil J, but not in soil S.

The difference between soils J2 and S2 in Ca leaching clearly demonstrates the importance of the lowest soil layer to the simulated base cation leaching downwards. In soil J2 the C layer had much higher base saturation than the average soil, and the base cations were leached much more in the multi-layer structure than in the one-layer structure. In soil S2 the difference between the C layer and the average soil was smaller, and mainly caused by Mg, which explains the small difference between the structures in Ca leaching from soil S. The importance of the lowest layer to the base cation leaching downwards is also supported by Van Oene and De Vries's (1994) modelling study. Their multi-layer structure produced greater leaching of base cations than the one-layer structure for sites 6 and 9, in which the base saturation of the lowest layer was higher than the average in the upper soil.

Solution cation concentrations and cation leaching were quite similar in all multi-layer simulations compared to the one-layer simulations. Thus, the multi-layer simulation with the horizon-specific cation exchange coefficient values (dhdc) and the same coefficient values for all layers (dhsc) showed only minor differences in the Al / (Ca + Mg) ratio (Fig. 6) and H^+ and Al leaching (Table 3). Although some large differences were seen in Ca and Mg leaching, the differences in the

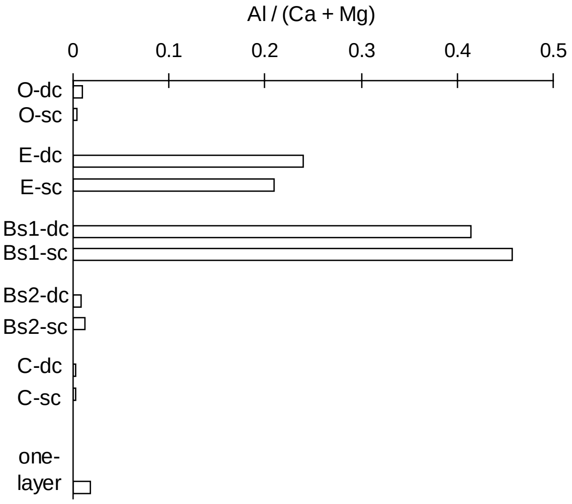


Figure 6. Simulated molar ratio Al / (Ca + Mg) in solution in the multi-layer simulations dc (dhdc) and sc (dhsc) and the one-layer simulation (one-layer). Results of 11th July are shown.

Table 3. Cation concentrations in the runoff and averaged soil exchangeable Ca and Mg contents and base saturation (BS) at the end of the simulation period. Redrawn from Study IV, Water, Air, and Soil Pollution, 85, 1107-1112.

Case	Runoff concentrations					Exchangeable cations		
	H+	Al	Ca	Mg	K	Ca	Mg	BS
	------------------- $\mu mol\ l^{-1}$ ----------------					-- $mmol_c\ kg^{-1}$ --		
				Soil J				
dhdc	1.1	0.10	29.9	12.9	9.3	1.743	0.411	0.2897
dhsc	1.2	0.12	28.1	13.6	10.4	1.745	0.409	0.2896
one-layer	16.7	0.48	19.3	7.9	7.6	1.755	0.416	0.2918
				Soil S				
dhdc	1.3	0.19	43.4	32.8	3.3	9.572	3.776	0.5204
dhsc	1.0	0.21	40.3	37.9	3.8	9.575	3.770	0.5203
one-layer	4.4	0.56	40.5	27.7	4.8	9.576	3.783	0.5208

exchangeable cation amounts between soil horizons obviously affect the simulated concentrations more than differences in the cation exchange coefficients. It is then useful to account for the vertical variation in the soil chemical properties even if horizon-specific information of e.g. cation-exchange coefficients is unavailable.

The largest decrease in exchangeable Ca and Mg concentrations occurred in the O layer, while the other layers showed either decrease or increase. In the A layer the Ca concentration increased considerably, 6.1% for soil J, which was assumed to relate to root distribution. In Study IV it was shown that when the root distribution assumed more roots in the A layer (case four), Ca increase was only 44 % of that in the reference case. Note, however, that the cases did not differ in respect to cation leaching from the whole soil.

The need for detailed information on processes and parameters is an evident disadvantage in multi-horizon simulations (see also Van Oene and De Vries 1994). It seems reasonable to assume that any large cation amount changes in the opposite direction (decrease - increase) in the subsequent layers usually suggest that either the distribution of processes which consume and produce base cations is wrong, or that the cation exchange equilibrium is not adequately described.

As expected, important horizon-specific information on the ionic composition in soil solution is lost with aggregated modelling. As the Al/(Ca+Mg) ratio was below 0.02 in the one-layer simulation, as compared with 0.15-0.35 in the A and Bs1 horizons of soil J, the one-layer model greatly underestimated the Al / (base cations) ratio (commonly used as critical parameters for vegetation damage, Sverdrup and Warfvinge 1993b) in the 10 cm deep top-layer of the mineral soil, in which over 50 % of the fine root biomass of trees may be found (Persson 1980). Kros and Warfvinge (1995) concluded that multi-layer models are useful for determining changes in the topsoil, which is important when the Al concentration and Al/Ca ratio are used for the quantification of the damage of fine roots.

This study focused on modelling of cation-exchange equilibria. In the field, other chemical processes, e.g. sulphate adsorption, also affect the vertical gradients in ionic composition of soil solution. In addition, a large proportion of forests in Finland do not have a flat topography, but are located on slopes of varying steepness. On such slopes a large share of water fluxes occur as subsurface flow (Lepistö 1996), which does not react chemically with lower horizons. When modelling leaching of ions from a soil volume, it is important to identify the soil layer that controls the ion composition in the leachate.

In conclusion, in order to get precise quantitative estimates of leaching losses of base cations from podzolic forest soils, detailed dynamic models of soil hydrology and chemistry, such as the present version of ACIDIC (Kareinen *et al.* 1998), should be developed and applied. However, detailed soil models can be difficult to connect with a detailed model of tree growth before more is known about the interaction between vegetation and soil.

7 Simulated effects of hydrogen ion and nitrogen deposition on soil acidification, nitrogen leaching and tree growth in boreal Scots pine stands

7.1 Theory and model of element fluxes in boreal Scots pine stands - model ‘FEF’

7.1.1 General

In order to analyse the effects of deposition on boreal forest soils, a dynamic model was developed (FEF, ‘Forest Element Fluxes’, Study V). The model describes the annual nutrient fluxes of a Scots pine stand, and is based on theories of carbon and nutrient metabolism of trees, decomposition of soil organic matter (SOM), and solution chemistry in forest soil. The main functional components of the stand described are trees and soil, but ground and field vegetation are also accounted for (Fig. 7).

Compared with the model ACIDIC (Study IV), FEF has a more detailed description of primary production, litter production, decomposition of soil organic matter, and cycling of nutrients N, Mg, K and Ca at the stand. The soil chemistry submodel of FEF includes most of the processes that are included in ACIDIC (except sulphate adsorption), but FEF describes only one aggregated soil layer whereas ACIDIC takes into account the different chemical properties of soil horizons. FEF simulates exchangeable acidity and total acidity while ACIDIC only accounts for exchangeable H^+ and Al^{3+}. As in ACIDIC, equilibrium is assumed in FEF for chemical reactions other than weathering. In FEF, runoff is based on soil water holding capacity, precipitation and evapotranspiration, whereas ACIDIC includes a detailed hydrology model (Kareinen *et al.* 1998). FEF can be used to analyse the responses of tree growth, soil organic matter content, soil nutrient content, and the ion composition of runoff to changes in acidifying deposition, climate and silvicultural practises.

An overview of interactions between soil and trees is presented below. For more details see Study V, Appendix 3 and Hari (in print). The nutrient and carbon balances are the core of the tree model. The carbon balance in trees is determined as follows: carbohydrates produced in photosynthesis are consumed in maintenance and growth respiration and in the growth of tree organelles. The nutrient balance is

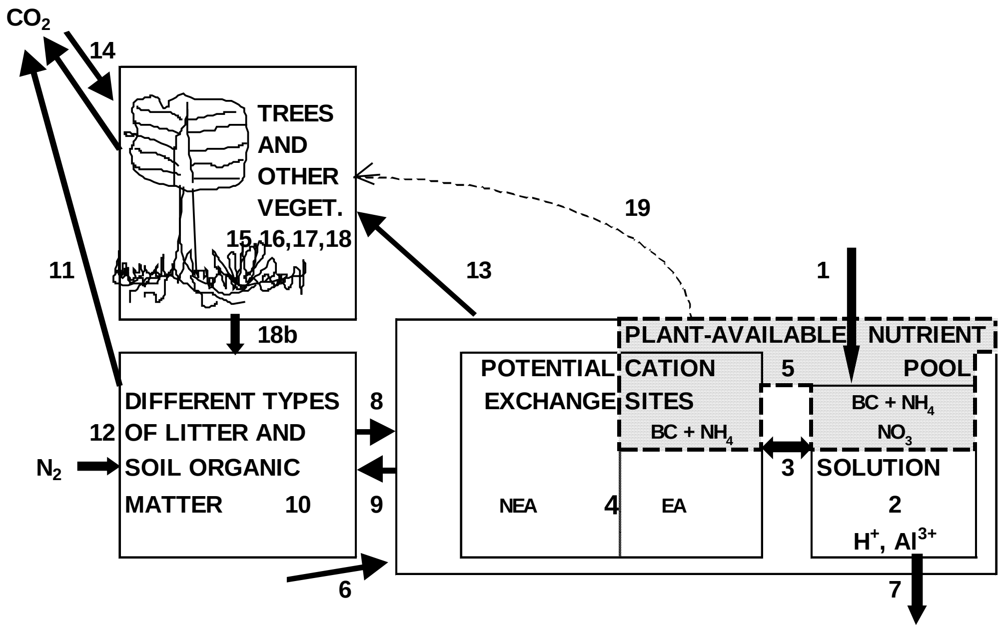


Figure 7. A schematic diagram of element storages and fluxes in a forest in the model FEF. The boxes denote storages and arrows fluxes of elements. The numbers refer to processes and model features that are given below:

1. Deposition into a forest.
2. Chemical equilibrium reactions in solution: CO_2 dissolution and dissociation of H_2CO_3, dissociation of dissolved organic acids.
3. Cation-exchange reactions between H^+, Al^{3+}, Ca^{2+}, Mg^{2+}, K^+ and NH_4^+ in solution and on exchange sites.
4. Equilibria of weak acid dissociation and complexation of Al^{3+} by organic matter determine the ratio between non-exchangeable acidity (NEA) and exchangeable acidity (EA). The potential cation exchange sites are reserved by exchangeable base cations and NH_4 (BC + NH_4), EA and NEA.
5. Nitrification of plant-available NH_4.
6. Release of base cations in weathering of soil minerals.
7. Leaching of ions in runoff.
8. Release of base cations and NH_4 in mineralisation of soil organic matter (SOM).
9. Microbiological and chemical immobilisation of NH_4 to SOM.
10. Change of the quality of litter and SOM in the decay process:fluxes of organic matter from litter to rapidly and slowly decomposing fractions of SOM, and from rapidly to slowly decomposing fraction and further to humus fraction of SOM.
11. Release of CO_2 into the atmosphere in mineralisation of SOM.
12. Nitrogen (N_2) fixation by microbes.
13. Nutrient uptake by trees and ground and field vegetation.
14. Photosynthesis and respiration in trees and in ground and field vegetation.

15. Processes at a whorl-level of trees: photosynthesis and respiration; allocation of carbohydrates; growth of needles, branches, stem, large roots, fine roots; nutrient uptake; dying of needles, branches, fine roots.
16. Processes at a tree-level: growth of the new, topmost whorl.
17. Processes at a stand-level: shading, dying of trees, thinnings.
18. Growth and litter production (18b) of ground and field vegetation.
19. A specific feature of the FEF model is that the amount of plant-available ammonium, magnesium and potassium control the allocation of carbohydrates in trees.

determined as follows: the growth of tree components determine the need for nutrients (N, Mg and K), and the need is satisfied with retranslocation of nutrients from dying needles and uptake of nutrients from soil. For nitrogen we get

$$\begin{aligned} &N(t)c_{\mathrm{NH2,N}} + FR(t)c_{\mathrm{NH2,FR}} + \Delta\,(\mathrm{B+S+LR})c_{\mathrm{NH2,S}} = \\ &FR(t)e_{\mathrm{NH4}}E_{\mathrm{NH4}} + (c_{\mathrm{NH2,N}} - c_{\mathrm{NH2,N(t\text{-}3)}})\,N(t\text{-}3) \end{aligned} \tag{30}$$

where $N(t)$ and $FR(t)$ denote the amounts of new needles and fine roots grown during the year t, $N(t\text{-}3)$ denotes the amount of dying needles, and B, S, LR denote the amounts of branches, stem, and large roots and branches in each whorl of a tree (see Appendix 3). The symbol Δ refers to annual change, $c_{\mathrm{NH4,i}}$ is a component-specific nitrogen content, and $c_{\mathrm{NH4,N(t\text{-}3)}}$ is the nitrogen content of dead needles. E_{NH4} denotes the amount of exchangeable NH_4, and e_{NH4} denotes the efficiency of fine roots in the uptake of NH_4 (Nikinmaa 1992). The assumptions lead to a dynamic behaviour of fine root amount, and to a tree growth that depends on soil nutrient content, similarly as in the model by Nikinmaa (1992).

7.1.2 Soil processes

General

Yearly fluxes of H^+, NH_4, NO_3, Ca, Mg and K change ion contents in a pool of plant-available nutrients, which includes ions on exchange sites (E_{Mg}) and ions in solution (AQ_{Mg}). For Mg we get

$$\begin{aligned} &E_{\mathrm{Mg}}(\mathrm{t}) + AQ_{\mathrm{Mg}}(\mathrm{t}) = E_{\mathrm{Mg}}(\mathrm{t\text{-}1}) + AQ_{\mathrm{Mg}}(\mathrm{t\text{-}1}) + \\ &D_{\mathrm{Mg}} - Q_{\mathrm{Mg}} + M_{\mathrm{Mg}} + W_{\mathrm{Mg}} - UT_{\mathrm{Mg}} - UGF_{\mathrm{Mg}} \end{aligned} \tag{31}$$

where D_{Mg} denotes deposition of Mg, Q_{Mg} leaching of Mg from soil in run-off , M_{Mg} release of Mg in mineralisation of SOM, W_{Mg} release of Mg in weathering of soil minerals, UT_{Mg} uptake of Mg to trees, and UGF_{Mg} uptake of Mg to ground and field vegetation. The yearly budget is analogous for K and Ca.

The budget of NH_4 also includes immobilisation of NH_4 by microbes (IM_{NH4}) and nitrification of NH_4 to NO_3 (NI_{NO3}) (see Fig. 1 in Study V):

$$E_{NH4}(t) + AQ_{NH4}(t) = E_{NH4}(t\text{-}1) + AQ_{NH4}(t\text{-}1) + D_{NH4} - Q_{NH4} + M_{NH4} - UT_{NH4} - UGF_{NH4} - IM_{NH4} - NI_{NO3} \quad (32)$$

De Vries and Breeuwsma (1987) were followed in determining the hydrogen budget of the processes included in FEF. Processes that consume H^+ are: release of K, Ca and Mg in mineralisation of SOM and in weathering; uptake and immobilisation of NO_3; and leaching of H^+. Processes that produce H^+ are: uptake of NH_4, Ca, Mg and K; immobilisation and nitrification of NH_4; dissociation of dissolved organic matter (DOM) and dissolved CO_2; and deposition of H^+.

Organic acids that are included in the potential cation exchange capacity are the most important storage of hydrogen ions in the soil. Cation exchange determines the distribution of H^+ between exchange sites and solution. An approximate distribution of cations between exchange sites and solution is done using ion concentrations of the previous year. The final solution chemistry is determined by cation exchange equilibria and the dissociation equilibria of DOM and CO_2.

The amount of nutrient leaching is determined as a product of water transport and the concentration of each nutrient in soil water. Runoff equals the difference between precipitation and evapotranspiration (ET).

Decomposition of soil organic matter

Climate and substrate quality affect decomposition of litter and soil organic matter SOM. However, only the quality aspect is considered in this study, and the decomposition parameters that are used have been measured in a climate similar to that of southern Finland.

The mass-loss rate of litter depends on its nutrient and lignin contents. However, the lignin content seems to be the major factor after the first few years (Berg 1984, Berg *et al.* 1987). In the model the litter is divided into a slowly decomposing fraction (f_S) corresponding to lignin and other aromatic material (Berg *et al.* 1982, Berg 1986), and a rapidly decomposing fraction (f_R) which consists of other components. These fractions of litter form a slowly decomposing component (O_S) and a rapidly decomposing component (O_R) of SOM (Fig. 8). Fraction m_R of O_R is mineralised annually, and fraction o_R is released as dissolved organic matter (DOM). Also, more resistant compounds, which belong to O_S, are synthesised with rate $z_{R\text{->}S}$ from O_R, including, e.g. cell walls of dead microbes and lignified cellulose (Berg 1986). However, a major part of SOM belongs to the humus fraction of SOM (O_H), which has a very low mass loss rate. It is synthesised mainly from lignin (Melillo *et al.* 1982), and in the model from O_S.

The woody litters decompose slowly due to their structure. Thus it is assumed that each type of woody litter is released at a specific rate k to O_R and O_S (see structural litter in Parton *et al.* 1987).

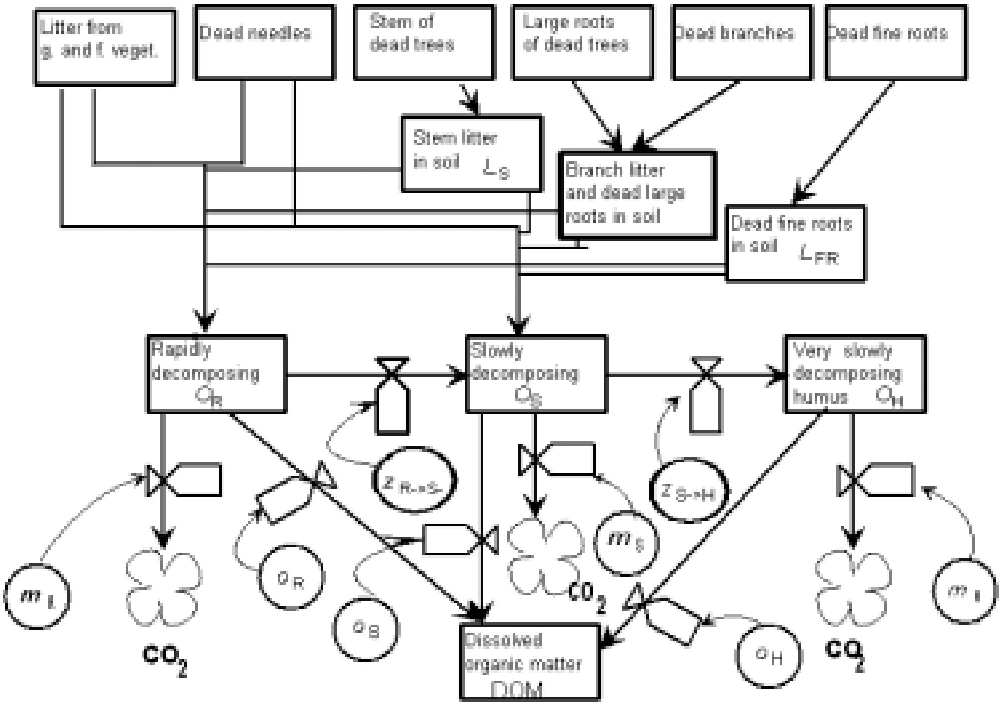


Figure 8. A schematic presentation of organic matter cycle and decomposition of soil organic matter in a forest. ‘g. and f. veget.’ denotes ground and field vegetation.

The coefficients of mineralisation, release of DOM, and net synthesis were calibrated by comparing observed and simulated mass losses of needle and root litters. Total mass loss of needle litter was 67% and 68% in two four-year experiments (Berg *et al.* 1982, Berg *et al.* 1987), whereas the simulated mass-loss was 68%. Mass loss of lignin was 42% in the latter experiment. In simulation it was smaller, 36%. On the other hand, mass loss of lignin in roots was greater in simulation (18%) than in an experiment in which the lignin amount increased by 9% in three years (Berg 1984). The total mass loss of roots was the same, 41%, in both the experiment and simulation.

The synthesis rate of O_H from O_S and the mineralisation rate of O_H were calibrated by simulating accumulation of SOM on a Scots pine site, assuming an annual litter fall of 700 g m^{-2} (Viro 1955, Koivisto 1959, Mälkönen 1974, Persson 1980, Helmisaari 1992), and a final amount of SOM of 15 kg m^{-2} (Tamminen 1991). The simulated SOM is close to its final level after 2000 years, which was proposed by Liski *et al.* (1998) to be the time for SOM to reach an equilibrium.

Nutrients are released to solution from the mineralised SOM. However, the element content of the synthesised compounds can be different from the source material. Nitrogen content of leaves and needles increases as the litter decays (Berg *et al.* 1987, Melillo *et al.* 1982), and nitrogen content is much greater in humus than in tree components (Mälkönen 1974). It is assumed here that the increase of nitrogen content in the decaying litter is partly a microbial process and partly a chemical reaction (Johnson 1992).

It is assumed in the model, that when the O_R fraction is decomposed by microbes, some part of the synthesised compounds belonging to O_S always have a larger nitrogen content than O_R due to their chemical structure, and that the humified material, O_H, always has a larger nitrogen content than its precursor, O_S. Chemical reactions are especially important in the formation of stable nitrogenous compounds (humus) from lignin by-products (Smith 1982 p.127, Johnson 1992), and only a minor part of nitrogen is tied up in microbial biomass (Berg 1986). This enrichment of nitrogen is treated separately from nitrogen immobilisation, because it is assumed that enrichment does not depend on nitrogen availability, but reflects the basic differences in the chemical composition of the different fractions of organic matter. On the contrary, microbial and chemical immobilisation is assumed to depend on nitrogen availability, and to produce compounds with a larger nitrogen content than this 'baseline' content produced in the enrichment process.

In the model, coefficients (b) are introduced to describe nutrient flux between mineralised and synthesised SOM; thus the mineralised amount of NH_4 from SOM is

$$M_{\mathrm{NH4}} = c_{\mathrm{NH2,OR}}\,(1\text{-}b_{\mathrm{NH4,R\text{->}S}})m_R O_R + c_{\mathrm{NH2,OS}}\,(1\text{-}b_{\mathrm{NH4,S\text{->}H}})m_S O_S + c_{\mathrm{NH2,OH}}\,m_H O_H \tag{33}$$

where $c_{\mathrm{NH2,OR}}$, $c_{\mathrm{NH2,OS}}$ and $c_{\mathrm{NH2,OH}}$ denote nitrogen contents in the O_R, O_R and O_H fractions of SOM. Nitrogen contents in the vegetation and SOM at infertile forest sites (CT sites), where availability of nitrogen is low, are used to determine the values of the coefficients.

It is assumed that the content of each nutrient in DOM equals the content in the original fraction of SOM. Thus the released amount of organic nitrogen that is lost from SOM in the dissolution of DOM is equal to the product of released DOM and the nitrogen content:

$$\mathrm{DOM}_{\mathrm{NH2}} = c_{\mathrm{NH2,OR}}\,o_R O_R + c_{\mathrm{NH2,OS}}\,o_S O_S + c_{\mathrm{NH2,OH}}\,o_H O_H \tag{34}$$

Competition between fine roots, heterotrophs and cation-exchange sites for NH_4^+ and NO_3^-

Competition for N among heterotrophs (decomposers), plants and nitrifiers is thought to play a major role in determining the N fluxes within forests (Riha *et al.* 1986, Johnson 1992). It seems reasonable to include cation-exchange sites in the competition, because they retain nitrogen in a plant-available form. Although large pools of NH_4^+ seldom occur in undisturbed forest soils (Johnson 1992), exchangeable NH_4^+ may be elevated for brief periods following fertilisation (Nômmik and Möller 1981, Johnson 1992) and clear-cut (Covington 1981). Thus a fraction of large NH_4^+ pulses seems to be retained on cation exchange sites of soil.

Johnson (1992) suggested that trees can be better competitors for N than heterotrophs on N-deficient sites, as they take the N necessary to supply structure increment. It is assumed in Study V that this effectiveness is related to the amount of carbohydrates which the trees can allocate to roots, realised as the amount of fine roots. Further it is assumed that fine roots of Scots pine have a certain efficiency, e_{NH4}, for the uptake of NH_4^+ (see Equation (30)). The larger the allocation to roots, the more nitrogen the trees can take. However, increased nutrient uptake tends to decrease exchangeable NH_4^+, which leads to decreased nitrogen uptake per root unit.

The nitrogen uptake of conifers prefers ammonium to nitrate (Ingestad 1979). In the simulation the uptake first consumes the annual inputs of NH_4 to soil in deposition and mineralisation of SOM. The rest of the need is satisfied by nitrate and exchangeable NH_4.

If all nitrate in soil is not taken up by plants, a fraction (im_{NO3}) of it is assumed to be immobilised by microbes. Because nitrate concentration is very low in surface waters, it is assumed that immobilisation is complete in stands which do not receive fertilisation during the simulated stand rotation period. However, after fertilisation a large fraction of added nitrate can be leached: When nitrogen was added with a dose of 150 kg ha^{-1} in the form NH_4NO_3, so that the added amount of NO_3-N was 75 kg ha^{-1} , the leaching of NO_3-N increased by 20 kg ha^{-1} (Westling and Hultberg 1990/91) or even 50 kg ha^{-1} (Melin 1986).

The concept 'immobilisation of NH_4' in this study includes both heterotrophic uptake and non-biological chemical reactions (see also Johnson 1992), but immobilisation is described here using mainly concepts of microbial immobilisation. The main assumption is that both microbial and chemical retention depend on i) the availability of NH_4 in soil, and ii) the nitrogen content in the labile organic matter.

Immobilisation of NH_4 is introduced in the model using three ideas. 1) The larger the ratio between the nitrogen content in microbes ($c_{\mathrm{NH2,Oim}}$) and the nitrogen content in O_{S} ($c_{\mathrm{NH2,OS}}$), the larger the amount of immobilised nitrogen. Heterotrophic demand for nitrogen depends on the supply of labile organic carbon-substrates (Riha *et al.* 1986, Johnson 1992), and it is assumed here that the larger the C:N ratio in the organic matter, the larger the amount of 'fresh food' for microbes (Parnas 1975). Because immobilisation of nitrogen depends on the lignin content of litter (Aber and Melillo 1982, Melillo *et al.* 1982, Berg 1986), it is assumed that the immobilised nitrogen accumulates mainly in O_{S}. 2) The larger the exchangeable NH_4, the larger the immobilised fraction of plant-available NH_4. The availability of NH_4 is approximated by E_{NH4}. Analogously to the use of nitrogen content $c_{\mathrm{NH2,Oim}}$, we use the critical exchangeable NH_4 level, $E_{\mathrm{NH4,im}}$. However, the ratio between exchangeable cations is raised to a power which was calibrated to the value 2 to meet the small range of E_{NH4} in Scots pine stands (Mälkönen 1974, Helmisaari 1995). 3) When the nitrogen content of O_S increases to the same level as in microbes, $c_{NH2,Oim}$, microbial immobilisation should end, even though nitrogen availability is high. This effect is introduced with the ratio $c_{NH2,OS}$ / $c_{NH2,Oim}$ raised to the power of 10. Thus we get

$$im_{NH4} = \mathrm{Max}\left[0, \frac{c_{NH2,Oim}}{c_{NH2,OS}}\left(\frac{E_{NH4}}{E_{NH4,im}}\right)^2 - \left(\frac{c_{NH2,OS}}{c_{NH2,Oim}}\right)^{10}\right] \tag{35}$$

Immobilisation of NH_4 is determined as a product of im_{NH4} and plant-available NH_4:

$$\begin{aligned} IM_{NH4} = im_{NH4}(E_{NH4}(t-1) + AQ_{NH4}(t-1) + \\ D_{NH4} - Q_{NH4} + M_{NH4} - UT_{NH4} - UGF_{NH4}) \end{aligned} \tag{36}$$

Similarly to immobilisation of NH_4, nitrification is also determined as a product of a coefficient (ni_{NO3}) and the plant-available NH_4, however accounting for IM_{NH4}:

$$\begin{aligned} NI_{NO3} = ni_{NO3}(1- im_{NH4})(E_{NH4}(t-1) + AQ_{NH4}(t-1) + \\ D_{NH4} - Q_{NH4} + M_{NH4} - UT_{NH4} - UGF_{NH4}) \end{aligned} \tag{37}$$

The nitrification coefficient is assumed to have a small value in boreal podzolic soils. Autotrophic nitrifiers are known to be inhibited by low pH and naturally produced nitrification inhibitors (Johnson 1992). In boreal podzolic soils the nitrification activity can be very low, as indicated by measurements of net nitrification and enumeration of autotrophic nitrifiers (Martikainen 1986). It is also low after fertilisation with ammonium salts, but fertilisation with urea stimulates nitrification, probably due to the simultaneous increase in soil pH and ammonium availability after decomposition of the urea (Martikainen 1986).

Fixed N_2 from air (F_{N2}) is assumed to increase nitrogen content in the same fraction of SOM as immobilisation, namely O_S.

Loss of NH_4 as volatilised NH_3 can be notable after urea fertilisation (Nômmik and Möller 1981, Melin and Nômmik 1988) but it was not considered significant in unfertilised stands. Denitrification is thought to be important in forest soils which have elevated inputs of nitrate and experience anaerobic conditions (Johnson 1992). However, Martikainen (1986) found denitrification in well aerated, nitrifying Finnish soils. The processes are not accounted for in this thesis, because the amount of nitrogen involved is not important for the nitrogen balance of unfertilised boreal soils.

Chemical soil processes

The description of the soil processes, especially cation-exchange reactions and reactions of soil acids, relies greatly on Studies I, II and III of this thesis. Cation exchange equilibria is assumed between H^+, Al^{3+}, Ca^{2+}, Mg^{2+} and K^+ using the Gaines-Thomas equation (Equation (20)), but replacing activities with molar concentrations in solution. The technical modelling and mathematical solution of cation-exchange equilibria is based on iterative calculations, developed in Oksanen *et al.* (1983), Heikkilä *et al.* (1983), Holmberg (1984), and Kareinen *et al.* (1998). Dissolution and dissociation of CO_2 are determined in the partial pressure pCO_2 of soil (Lindsay 1979). DOM is assumed to have a certain total acidity and equilibrium coefficient of dissociation (pk_{DOM}) (Kortelainen 1993). Ion concentrations are determined numerically, so each equilibrium coefficient (k) of simulated solution chemistry is within a given range (k ±5%).

Effectively exchangeable hydrogen and aluminium are used in the cation exchange calculations. As found in Study I, the exchangeable hydrogen is assumed to be a result of weak acid equilibrium, described with the Henderson-Hasselbach equilibrium coefficient pk_{HH} (McBride 1994, p. 109; Study I)

$$\mathrm{pH} = \mathrm{p}k_{\mathrm{HH}} + n\log\left\{\frac{\mathrm{CEC_e}/\mathrm{CEC_p}}{1-\left(\mathrm{CEC_e}/\mathrm{CEC_p}\right)}\right\} \tag{38}$$

where CEC_e and CEC_p denote effective and potential cation exchange capacity, respectively. The estimated value of n was 1.0. The pH denotes the activity of hydrogen ions in the salt extract of exchangeable cations, and it is transformed to exchangeable H^+ as in Study I.

It is assumed that CEC_p can be explained by the contents of SOM and clay in soil. The relationship was determined by a multiple regression analysis for the mineral horizons of the six sites in Siuntio and Hyytiälä, and it explained 78% of the variance in CEC_p:

$$\mathrm{CEC_p} = 2430\ \mathrm{SOM} + 366\ \mathrm{clay}, \tag{39}$$

where the units are $mmol_c$ for CECp, $mmol_c\ kg^{-1}$ for the coefficients 2430 and 366, and kg for SOM and clay. Regarding the heterogeneity of SOM in soils, the charge of SOM is not far from 3000 $mmol_c\ kg^{-1}$, a general estimate given by McBride (1994) for organic matter near neutral pH.

As found in Study I, it is assumed that exchangeable Al can be explained by a release from organic complexes, so that pAl in the extract of exchangeable cations is:

$$\mathrm{pAl} = 2\mathrm{pH} - \mathrm{p}k_{\mathrm{o}}. \tag{40}$$

The yearly release of nutrients K, Ca and Mg in the weathering of soil minerals is assumed to have a stand-specific constant value.

7.2 Applications of the model FEF

Simulated cases

The main model applications were the simulations of soil responses to acidifying deposition at Scots pine stands. In addition, responses of Scots pine stands to changes in initial soil characteristics and responses of nitrogen leaching to clear-cut were simulated to consider the model behaviour qualitatively. The simulated stands were given soil properties that represent average measured values or otherwise reasonable literature-based values for each site type. The stands are ‘hypothetical’, so we did not try to simulate the responses of existing sites, but instead ‘typical’ sites of each site type.

In all cases, 90 years of stand development was simulated, starting from a clear-cut at year 1, and assuming planting of three-year-old Scots pine seedlings at year 4. Thinning of the stand was simulated at years 29, 45 and 65. The parameters of the tree submodel had the same values in all cases (Table 1 in Study V).

In the study of model behaviour, the simulated response of tree growth to soil nutrient contents was studied by introducing average soil properties of three different forest site types as initial conditions for the simulations. The Finnish classification system of forest sites is based on the composition of ground vegetation. Three common site types in southern Finland are *Calluna* type (CT), *Vaccinium* type (VT), and *Myrtillus* type (MT). In the 50s the cumulative stemwood production at typical CT sites was 290 m^3 ha^{-1} at a stand age of 90 years (including bark, Koivisto 1959), whereas the production was 535 m^3 ha^{-1} at VT sites and 660 m^3 ha^{-1} at MT sites. Average soil properties at CT, VT and MT sites have been measured by Tamminen (1991, see also Table 2 in Study V). For comparing the simulated growth to values reported by Koivisto (1959), the simulations were done assuming low ion deposition, thus starting from the year 1851. The cases were named on the basis of the site type and the first year of the simulated stand development: CT-1851, VT-1851 and MT-1851.

Nitrogen fixation (Nohrstedt 1985), weathering and the production of ground and field vegetation after clear-cut were assumed to increase with increasing site fertility (Table 2 in Study V). The first approximation of the weathering rate at VT site was based on an average of five sites in Sweden and Norway (Sverdrup and Warfvinge 1993a); thus the most and least fertile sites of the seven sites in the study were excluded. The value was further multiplied by 1.5 in the calibration of the model (see below).

The responses of soils and trees to acidifying deposition were studied for the VT site. The soil properties, which were measured in the 90s (Tamminen 1991), were used as an initial state in all simulations, but they obviously represent a proper initial state only for the simulated case H^+&N –1991. As representatives of soils in

1801, 1851 and 1901 the exchangeable base cations evidently have too small a value and soil nitrogen contents have too large a value at the beginning of the simulations. Thus the simulations do not actually represent typical VT sites at different times, but the changes over time in similar soils under different deposition regimes. The year can be denoted as ‘deposition-year’.

Effects of clear-cut on nutrient leaching have been studied in eastern Finland since 1978 (Ahtiainen 1991, Ahtiainen and Huttunen 1995). Before clear-cut, water quality was measured in brooks of four undisturbed catchments in 1978-1982. Clear-cut was done in 1983 in two of the catchments, the proportion of the clear-cut areas being 56% and 58% of the total catchment areas. The simulations of the VT site were used to analyse the patterns of nitrogen leaching after clear-cut.

Deposition scenarios

In the 19th century the deposition of nitrogen and hydrogen ions was assumed to be the same as the present deposition in remote areas. The annual deposition of H^+, NH_4–N and NO_3-N were 7 mg m^{-2}, 28 mg m^{-2} and 44 mg m^{-2} respectively in northernmost Finland in 1989-1992, assuming no dry deposition of sulphate (Leinonen and Juntto 1992, Appendix 1).

The deposition in Jokioinen in southern Finland in 1989-1992 was used as the deposition in 1990 (Leinonen and Juntto 1992), however increasing hydrogen ion deposition by assumed dry deposition of sulphate (60% of measured sulphate deposition, Ivens *et al.* 1989, Appendix 1). Thus the annual deposition of H^+, NH_4-N and NO_3-N was 44 mg m^{-2}, 270 mg m^{-2} and 255 mg m^{-2} respectively (Appendix 1). ‘Total anthropogenic deposition’ was calculated as the difference between the deposition in Jokioinen and northernmost Finland.

The ratio between anthropogenic nitrogen deposition in 1950 and 1990 was assumed to be equal to the ratio between the emissions of NO_x in 1950 and 1990 in Finland. The same approach was used for the deposition of SO_4 and emissions of SO_2. The ratios were about 0.20 for both NO_x and SO_2 (Savolainen and Tähtinen 1990), and a linear increase to 20% of the total anthropogenic depositions of H^+, NH_4^+ and NO_3^- was assumed between 1900 and 1950.

Between 1950 and 1990, linear increase from 20% to 100% of the total anthropogenic depositions of NH_4^+ and NO_3^- was assumed. For SO_2, the emissions were highest between 1970 and 1980, being about 190% of the level in 1990 (Savolainen and Tähtinen 1990). In the estimation of anthropogenic deposition of H^+, it was assumed that 75% of protons were accompanied by anthropogenic deposition of sulphate and 25% by anthropogenic deposition of nitrate. The ratio 75:25 between sulphate and nitrate approximates the molar charge ratio between sulphate and nitrate deposition in a forest in southern Finland (Appendix 1). The protons accompanied by nitrate were assumed to increase similarly to the deposition of nitrate between 1950 and 1990. Two scenarios were produced for sulphate and its accompanying protons. In scenario A, a linear increase to 190% of the level in 1990 was assumed between 1950 and 1970. Between 1970 and 1980, a constant deposition was assumed, and between 1980 and 1990 a linear decrease from 190% to 100% of the level in 1990 was assumed for sulphate and its accompanying protons. Scenario A, however, overestimates the difference in H^+ deposition between 1990 and 1970 (see for example Kämäri *et al.* 1998), because the deposition is also affected by the emissions in other countries besides Finland. Another scenario (B) was done by assuming that the increase in the deposition of H^+ (associated with sulphate) increases between 1950 and 1970, and is constant between 1970 and 1990. Scenario B underestimates H^+ deposition between 1970 and 1990. See Fig. 9.

The annual deposition of K, Ca and Mg in a forest was assumed to be 92 mg m^{-2}, 172 mg m^{-2} and 43 mg m^{-2} respectively, or 1.6 times greater than deposition in Jokioinen (Leinonen and Juntto 1992, Appendix 1).

Simulations of VT-sites under different scenarios of acidic deposition

The responses of soil and trees to acidifying deposition at the VT site were studied by simulating different time periods. For low deposition, simulation starts from the year 1801, and the case is named H^+,N-1801. For high deposition, simulation starts from year 1991, and the case is named H^+,N-1991. In addition, simulations starting from 1851, 1881, and 1901 were produced. The scenario that overestimates H^+ deposition between 1970 and 1990 was denoted with A (H^+,N-1881A, H^+,N-1901A) while the other scenario was denoted with B.

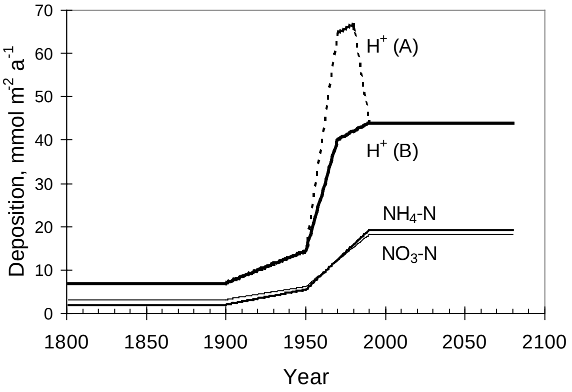
Two additional simulations were done in order to separate the effects of hydrogen ion deposition from the effects of NH_4^+ and NO_3^-. Firstly, it was assumed that the deposition of hydrogen ions is high at the same time as the deposition of NH_4^+ and NO_3^- is low (Case H^+-1991, N-1801). Secondly, low deposition of hydrogen ions and high deposition of NH_4^+ and NO_3^- were assumed (Case H^+-1801, N-1991).

Calibration of parameters

Qualitative features in the model behaviour were used to calibrate the efficiency of fine roots in the uptake of NH_4 (e_{NH4}), weathering, and some parameters that control the release of nitrogen to plant-available form. Nutrient uptake efficiency was calibrated so that the observed cumulative stemwood production at the VT site is produced at a stand age of 90 years, and the amount of fine roots is comparable to observed one (Helmisaari 1995, Persson 1980, Vanninen et al. 1996). The weathering rate was calibrated assuming that at the end of the simulation the values of exchangeable Ca, Mg and K could be somewhat larger than the initial value at the VT site, when a small acidic deposition was assumed (Case H^+,N-1801). Response of nitrogen leaching to clear-cut in forested catchments was used to calibrate parameters that control the release of nitrogen to plant-available form in soil (mainly im_{NH4}, Equations (35) and (36)).

The acceptable range of each cation-exchange coefficient was selected as the range in the suction lysimeter solutions of horizons E and Bs1 at sites S2 and S3 (S2 in Study III). The values were further calibrated so that the simulated ion

Figure 9. Scenarios for deposition of H^+, NH_4-N and NO_3-N that were used in the simulations.



concentrations were close to the average ion concentrations in brooks of the clear-cut study (Ahtiainen 1991). Finally, the values were slightly changed so that the change in the amount of each exchangeable base cation was similar in size (in the case VT-1801).

7.3 Model behaviour

Simulated stemwood production increases at sites in the order CT<VT<MT, and the differences between the sites are considerable (Fig. 4 in Study V). Thus the simulated wood production clearly responds to site fertility, which was determined by the soil properties at the beginning of the simulations. The simulated cumulative stemwood production is close to that observed at all sites at a stand age of 90 years.

In experiments, clear-cutting increased the leached amounts of organic nitrogen, NH_4 and NO_3, until they were between 2-fold and 4-fold compared with the undisturbed catchments (Ahtiainen 1991, Ahtiainen and Huttunen 1995). However, leaching decreased after the first few years, being close to the level of undisturbed catchments after ten years. After calibration, the model can produce the relative difference between clear-cut and mature forest during the first years after clear-cut (Fig. 10). However, the small decrease in the simulated leaching of NH_4 and NO_3 implies that nitrogen is bound to humus at a higher rate than in the simulations.

After a stand age of 20 years the simulated leaching of inorganic nitrogen remains for a long period close to average leaching from forested catchments in southern Finland: NH_4-N 31 mg m^{-2} a^{-1} and NO_3-N 32 mg m^{-2} a^{-1} (Saukkonen and Kortelainen 1995). However, at a stand age of 90 years, which corresponds to the simulated deposition-year 1990, the simulated leaching is high, and even more so when considering that the site is a relatively poor one (VT). Thus the parameters that regulate the leaching of NH_4 and NO_3 could have been better calibrated. At old stand the simulated leaching of organic nitrogen is lower than the observed value of 150 mg m^{-2} a^{-1}.

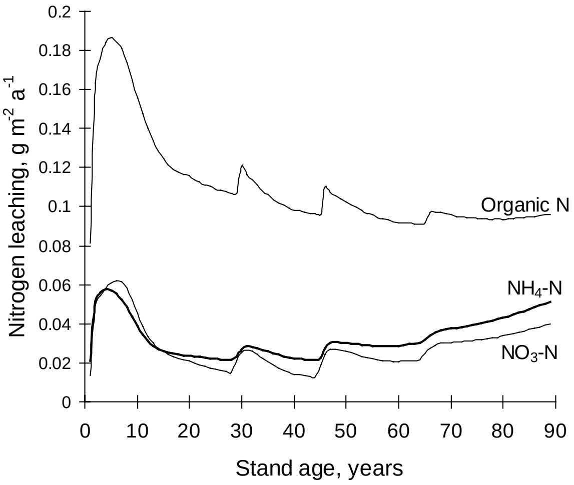


Figure 10. Simulated nitrogen leaching during a stand rotation period of 90 years. The simulated period starts from a mature forest, and a clear-cut is assumed at year 1. A low deposition of nitrogen is assumed at the beginning of the simulation, corresponding to the year 1901 (Case H$^+$,N-1901). Thus the deposition of 1990 in southern Finland is assumed at a stand age of 90 years. The fluctuations after stand ages of 25, 45 and 65 years are caused by simulated thinnings of the stand.

By studying groundwaters after a clear-cut, Kubin (1995) found a similar behaviour of nitrate leaching as above: nitrate concentrations were highest at the 3rd, 4th and 5th year after clear-cut, and started to decrease at the 6th year. Ammonium concentration in groundwater did not change due to clear-cut, an evident reason being retention by cation-exchange in the mineral soil above the groundwater.

Simulations show that the large losses of ammonium and nitrate from stands to surface waters after a clear-cut can be explained by decreased nutrient uptake by vegetation, large release of ammonium in the mineralisation of logging residues, and increased nitrification (Study V, see also Kämäri *et al.* 1998).

Simulated exchangeable NH_4 is low after the first 15 years of stand development, being below 2.5 g m^{-2} at VT and CT sites (Fig. 2 in Study V). Thus it is only slightly higher than proposed by the studies of Mälkönen (1974) and Helmisaari (1995), the values being generally in the range between 0.5 g m^{-2} and 2 g m^{-2}. Fluctuations after a stand age of 25 years at VT and MT sites reflect the increased litter amount due to thinnings of the stand. Fluctuation is large at CT sites, where low E_{NH4} causes decrease of needlemass and increased mortality of trees, resulting in increased litter amount and release of nitrogen.

7.4 Hydrogen ion budgets under low and high deposition of H$^+$ and nitrogen

A detailed analysis is made of hydrogen ion transfers in the various processes for the cases with low deposition and high deposition of hydrogen ions and nitrogen, i.e. cases H$^+$,N-1801 and H$^+$,N-1991. In both cases, the production of H$^+$ in the soil is largest in the uptake of NH_4 and uptake of base cations to plants (Fig. 11).

Immobilisation of NH_4 produces an abundance of H^+ ions during the first 20 years. In case H^+,N-1801, the dissociation of DOC produces more H^+ ions after this.

The largest consistent difference between the cases, except for the deposition, is found for the dissociation of DOC: dissociation produces more H^+ in case H^+,N -1801 than in case H^+,N -1991. Regarding the H^+ budgets, dissociation of CO_2 is neglible in both cases.

Despite the larger stemwood production in Case H^+,N-1991, the uptake produces even more hydrogen ions in Case VT-1801 during some periods. Due to the low availability of nitrogen in soil, trees have to produce great amounts of fine roots with large nutrient contents. The difference in H^+ leaching is small compared to the difference in H+ deposition between the two cases. Mineralisation of NH_4 is larger in Case H^+,N-1991 than in Case H^+,N-1801, but at the same time immobilisation of NH_4 is also larger in Case H^+,N-1991, with the result that the net release of NH_4 in mineralisation and immobilisation is only slightly larger in Case H^+,N-1991.

The soil budget of H^+ can be calculated in two ways. If a total budget is required, it should include the H^+ producing and consuming processes shown in Chapter 7.1.2 and Fig. 11, also taking into account the change in the total acidity of SOM. This is defined here as soil H^+-balance. The budget can also be calculated so that only processes directly affecting H^+ amount in solution are accounted for (solution H^+-balance), thus neglecting changes in total acidity of SOM.

The net H+ production to solution (solution H^+-balance) is negative in the beginning of the stand development because mineralisation of base cations from soil organic matter is large at the same time as the uptake to plants is small (Figs. 11 and 12). The net production of H^+ starts at a stand age of about 15 years. The balance shows that there are differences between the cases: at a stand age of 5 years, H^+ consumption is larger in the case with low deposition; at a stand age of 50 years, H^+ production is larger in the case with high deposition; and at a stand age of 90 years the balance is negative in the case of low deposition and positive in the case of high deposition. Soil H^+-balance is mostly affected by the changes in soil organic matter content, and after the first 15 years it fluctuates above and below zero (Fig. 12). At a stand age of 5, 50 and 90 years it is negative in both cases (Fig. 11).

7.5 Soil acidification under low and high deposition of hydrogen ions and nitrogen

Looking at the change between the initial condition and at a stand age of 90 years, the base saturation BS increases slightly, Al/Ca ratio in solution decreases slightly, and pH of soil solution increases from 4.30 to 4.40 in case H^+,N-1801 (Figs. 13a and 14a). On the contrary, in case H^+,N-1991 the result is marked soil acidification (Fig. 13b and 14b). This holds for all the indicators, but it is seen most profoundly for the ratio Al/Ca and pH in solution, Al/Ca being 0.82 in case H^+,N-1991 at stand age of 90 years, whereas it is only 0.18 in case H^+&N-1801.

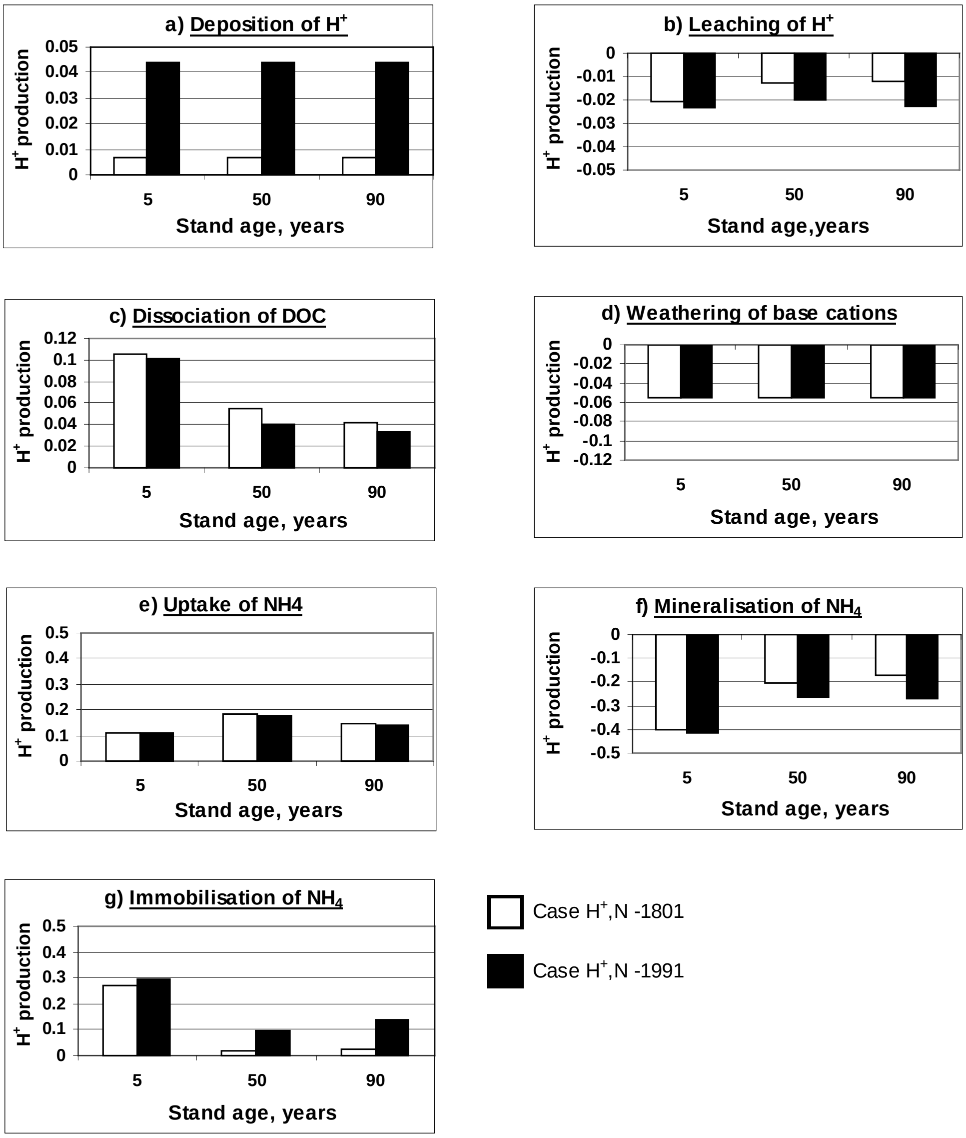


Figure 11. Production of H^+ (mol$_c$ m^{-2} a^{-1}) in different processes under low (Case H^+,N-1801) and high (Case H^+,N-1991) deposition of H^+ and nitrogen, at stand ages of 5, 50 and 90 years.

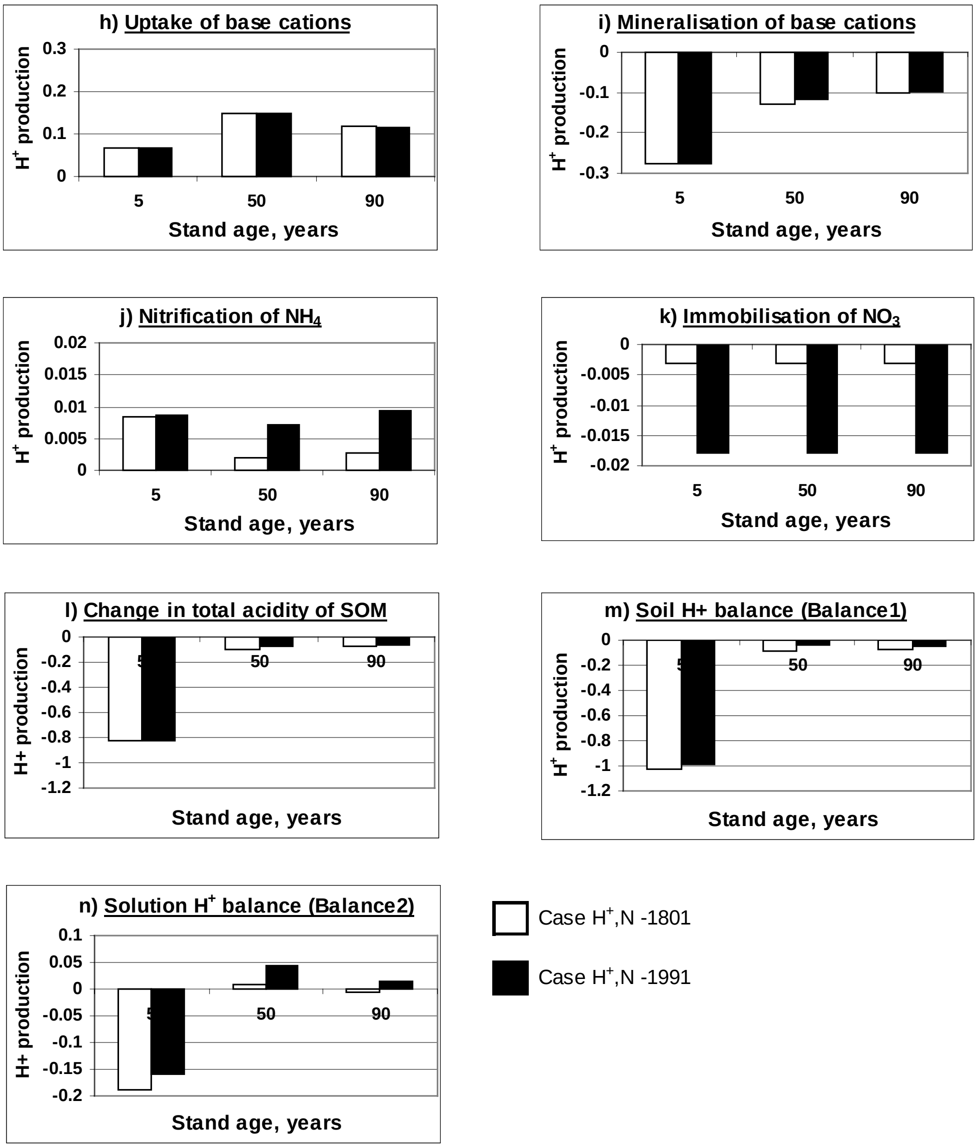
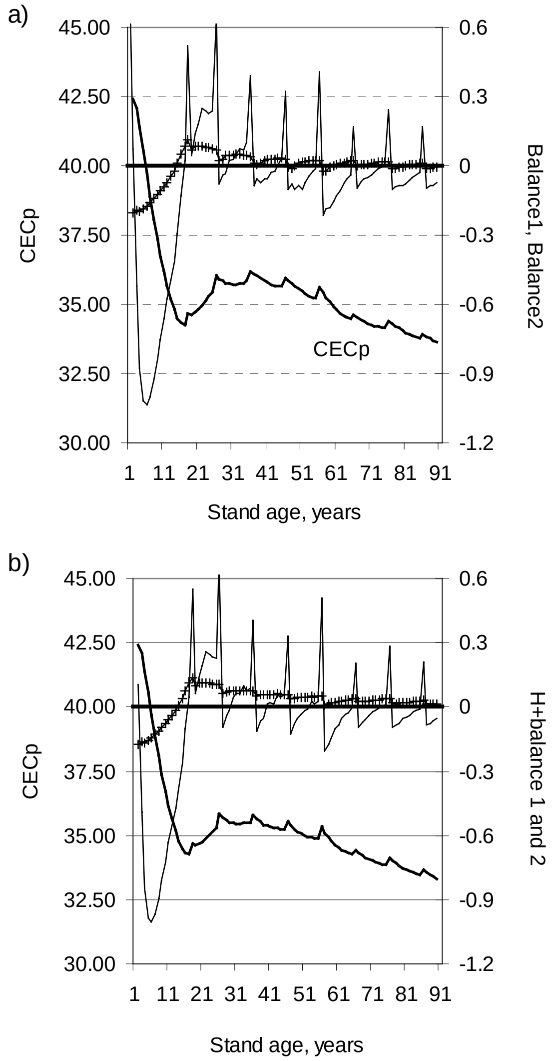


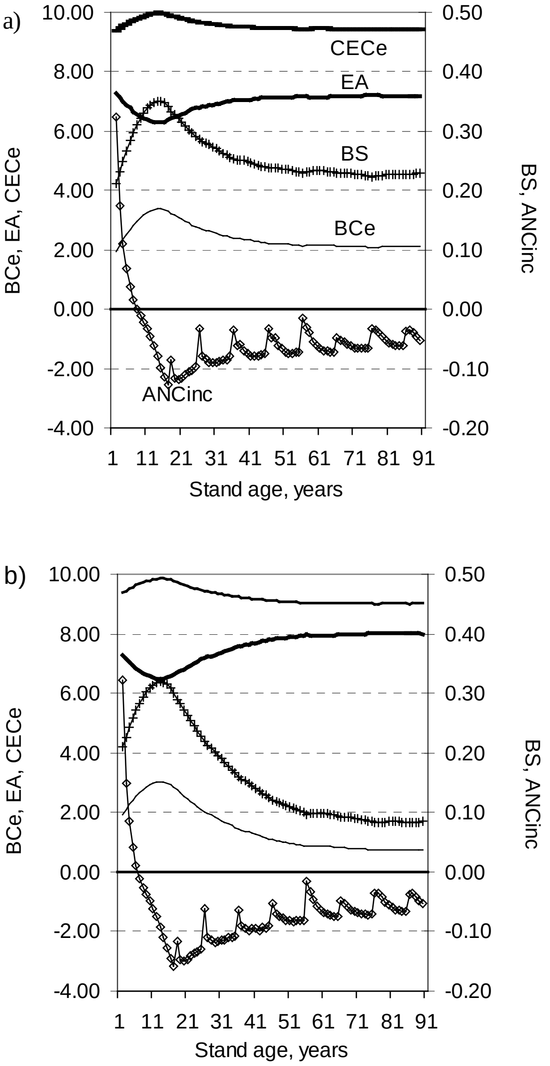
Figure 11 continues.

Figure 12. Potential cation exchange capacity (CEC$_p$, mol$_c$ m^{-2}), solution H$^+$ balance (Balance2, mol$_c$ m^{-2} a^{-1}), and soil H$^+$-balance (Balance1, mol$_c$ m^{-2} a^{-1}, which includes the change in the total acidity of SOM) as a function of stand age in a) Case H$^+$,N-1801, and b) Case H$^+$,N-1991.



High deposition of hydrogen ions results in highly acidified soil even if the deposition of NH_4 and NO_3 are low (Table 4, Case H$^+$-1991, N-1801). In agreement with this, high deposition of NH_4 and NO_3 does not alone increase soil acidification from the present state, as E_{Mg} and BS are higher in case H$^+$-1801, N-1991 than in Case H$^+$,N-1901. These cases H$^+$-1991, N-1801 and H$^+$-1801, N-1991 are hypothetical, but they show that soil acidification in southern Finland is at present mainly caused by high hydrogen ion deposition, which results in increased leaching of base cations in runoff. Effects of increased tree growth due to increased nitrogen deposition are much smaller, although the effect is considerable.

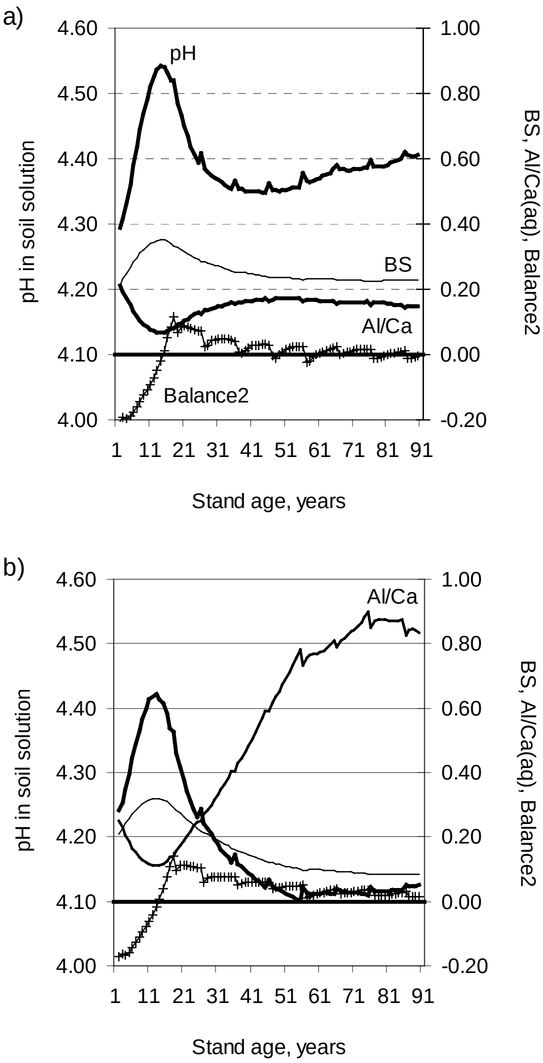
Figure 13. Soil acidification as a function of stand age in a) Case H^+,N-1801, and b) Case H^+,N-1991. Following soil properties and indicators of soil acidification are considered: Amounts (mol_c m^{-2}) of exchangeable base cations (BC_e), exchangeable acidity (EA), and effective cation exchange capacity (CEC_e) in soil; increase in acid neutralizing-capacity of soil (ANCinc, mol_c m^{-2} a^{-1}); and base saturation of effective cation exchange capacity (BS).



Comparing of cases H^+,N-1801 and H^+-1801, N-1991 shows that E_{Mg} decreases from 5.0 to 3.8 g m^{-2} and BS decreases from 0.23 to 0.18 due to large deposition of NH_4 and NO_3.

Deposition of NH_4 and NO_3 crucially affects the simulated leaching of NH_4 and NO_3. In case H^+,N-1991 the leaching of inorganic nitrogen would be 4-fold compared with case H^+,N-1801, and 56% larger than it was in 1990 (in case H^+,N-1901). The difference between the leaching of inorganic nitrogen at 90-year old stands in 1970 and 1990 is 46% (of the leaching in 1970).

Figure 14. Soil acidification as a function of stand age in a) Case H$^+$,N-1801, and b) Case H$^+$,N-1991. Following indicators of soil acidification are considered: pH in soil solution (pH(aq)), base saturation, the molar ratio between Al and Ca in soil solution (Al/Ca(aq)), and solution H$^+$-balance (Balance2, mol$_c$ m^{-2} a^{-1}).



7.6 Effects of hydrogen ion and nitrogen deposition on tree growth

The simulations suggest that the increase of nitrogen deposition has had a large impact on stemwood production. Compared with the case of the lowest nitrogen deposition (H$^+$,N-1801), the cumulative stemwood production at a stand age of 90 years is 3% greater when the stand rotation period starts from the year 1851 and 12% greater when it starts from the year 1901 (see cumulated stemwood production *P* in Table 4). The present level of nitrogen deposition would result in 30% greater production (H^+,N-1991). The difference between cumulated stemwood production at 90-year old stands in 1970 and 1990 is 4.5%.

Table 4. Simulated effects of nitrogen deposition on cumulated stemwood production (P), exchangeable Mg (E_{Mg}), base saturation (BS) and annual leaching of inorganic nitrogen ($Q_{NH4+NO3}$) at stand age of 90 years. Initial E_{Mg} and BS were 3.5 g m^{-2} and 0.21 in all cases. Values in parentheses show the results of simulations H^+,N-1881B and H^+,N-1901B. Redrawn from Study V, Environmental Pollution 102 S1: 61-68.

Case	Considered year	P m^3 ha^{-1}	E_{Mg} g m^{-2}	BS	$Q_{NH4+NO3}$ mg m^{-2} a^{-1}
H^+,N-1801	1890	505	5.0	0.23	41
H^+,N-1851	1940	510	4.7	0.22	49
H^+,N-1881A (B)	1970	528 (528)	3.1 (3.6)	0.17 (0.19)	83 (76)
H^+,N-1901A (B)	1990	549 (551)	2.0 (2.6)	0.12 (0.14)	112 (108)
H^+,N-1991	2080	626	1.6	0.08	155
H^+-1991, N-1801	-	494	2.1	0.11	57
H^+-1801, N-1991	-	638	3.8	0.18	127

7.7 Effects of model structure on the simulated results

Exchangeable acidity

The effective cation-exchange capacity shows fluctuation, which is connected to changes in the amounts of exchangeable base cations, as only a small part of the H^+ and Al that replace base cations on exchange sites is effectively exchangeable. As a result, changes in base saturation BS are smaller than if an invariant CEC_e was assumed. Thus the reactions that regulate exchangeable H^+ and Al also buffer the changes in BS, and at the same time they buffer the changes in the concentrations of base cations, hydrogen ions and Al in soil solution.

Cation-exchange equilibria

In FEF and many other soil acidification models the leaching of cations is determined assuming cation-exchange equilibria in the mobile soil solution. In

Study III it is suggested that the mobile solution does not have cation-exchange equilibria with the bulk exchangeable cations of the soils, and the assumption of cation-exchange equilibria in the mobile soil solution should not be applied if the total charge in the mobile solution changes (e.g. due to change in acidic deposition). This means that the assumption of apparent cation-exchange equilibria in mobile solution does not apply well to an analysis of acid deposition effects, and the analysis with the model FEF could not produce accurate estimates of ion leaching under various deposition scenarios. This conclusion would also hold true for other models used to analyse soil acidification (see model descriptions in Tiktak and Grinsven 1995). However, the subject needs to be studied further.

Aggregation of soil properties

In podsolized soils in which the base saturation BS increases with increasing depth below the eluvial horizon, it is clear that an aggregated model underestimates leaching of base cations if all water percolates downwards and there is no sulphate adsorption. However, the topography of forests is somewhat hilly in most parts of Finland, and a large fraction of runoff can be subsurface flow (Lepistö 1996). In such a situation, it is not certain that an aggregated soil description would give a less accurate estimate of leaching than the multi-layer soil description.

Nitrogen immobilisation

Several approaches have been used in the model descriptions of nitrogen immobilisation. Assumption of a constant carbon/nitrogen (C/N) ratio in the humified organic matter has often been adopted. Either mineralisation or immobilisation of nitrogen can result in the decay process, depending on the initial C/N ratio of material, the C/N ratio of pools receiving the C, and the fraction of C lost in respiration (Parnas 1975). In the forest floor model and Fortnite forest growth model of Aber *et al.* (1978, 1982) the decaying litter enters the humified organic matter (or forest floor layer) when it has lost 50% of its original mass. It is assumed to have a nitrogen content of 2.2% at this stage, which determines release or immobilisation of nitrogen. In the Century-model, which simulates primary productivity, soil nutrient dynamics and soil water, several different compartments of organic matter are assumed to have compartment-specific C/N ratios (Parton *et al.* 1987). In the SoilN model, which describes water and nitrogen dynamics in soil, it is assumed that the humified material has the same C/N ratio as microbial biomass and metabolites (Johnsson and Jansson 1993).

However, the nitrogen content of the humified organic matter is hardly constant in boreal forest soils. The nitrogen content of soil organic matter increases with increasing site fertility (Tamminen 1991), and it seems logical to assume that the nitrogen content of the humified organic matter increases with increasing nitrogen availability in soil. The models above do not analyse such a change in soil.

Ågren and Bosatta (1987) and Bosatta and Ågren (1995) introduced ‘quality of soil organic matter’ in their model. The quality is highest in the litter, which contains a large fraction of readily decomposable material, and the quality decreases during the decay process when only the more resistant parts of the material and newly formed resistant compounds remain. This drift in quality (humification) is followed by retention of nitrogen in the more recalcitrant parts of the decaying substrate. The approach avoids the somewhat artificial fractioning of organic matter. In addition, it is possible that measurable quantities can be developed for the quality of organic matter (pers. comm. Ågren 1998), whereas the different fractions of SOM (e.g. in model FEF) are not measurable.

In the Merlin model, which is a catchment-scale mass-balance model of linked carbon and nitrogen cycling, immobilisation of N is directly proportional to: the solution concentration of inorganic N; carbon fluxes through the organic compartments in soil; and the assumed maximum amount of nitrogen in the assimilated microbial biomass (Cosby *et al.* 1997). It is inversely proportional to the nitrogen content in the organic compartments. Adsorption of inorganic nitrogen is also described, and thus Merlin has a direct dynamic competition between biotic and abiotic processes, which according to Cosby *et al.* (1997) is a unique feature of the Merlin model. The FEF and Merlin models have two common features in their nitrogen dynamics: 1) competition between biotic and abiotic processes, and 2) responses to nitrogen availability in soil of plant nitrogen uptake, microbial uptake and the nitrogen content in soil organic compartments.

Sulphate adsorption

Studies suggest that sulphate adsorption capacity is large in Podzols of boreal forests (Karltun and Gustafsson 1993, Gustafsson 1995), but the capacity and the reaction of Finnish forest soils are poorly known. On the basis of model analysis, Kareinen *et al*. (1998) propose that the process would have great effects on solution chemistry at site S2. The adsorption slows down the actual soil acidification, e.g. decrease in BS, because OH^- ions are released in the specific adsorption of SO_4 (David *et al.* 1991). On the other hand, sulphate adsorption is included in potential soil acidification, and the adsorbed sulphate slows down the recovery of soil when sulphate deposition decreases, because the adsorbed sulphate is desorbed from soil to solution together with H^+.

Weathering and decomposition

It was assumed that trees do not directly or indirectly affect the decomposition rate of soil organic matter or the weathering rate of soil minerals. However, in reality trees may somehow enhance the decomposition rate, as indicated by the strong positive relationship between tree height and decomposition rate of cellulose in a study by Kurka and Starr (1997). The results of Zhu and Ehrenfeld (1996) agree with this, as they suggest that the presence of mycorrhiza enhances the decomposition rate of soil organic matter. A recent study by Jongmans *et al.* (1996) shows that roots can penetrate mineral particles, and Lundström and Öhman (1990), Heyes and Moore (1992) and Lundström *et al.* (1995) have shown that dissolution rates of minerals increase in the presence of organic acids. Ochs *et al.* (1993) stress that ectomycorrhizal exudates enhance the weathering of an aluminium oxide whereas humic material and non-mycorrhizal root exudates have an opposite effect. Considering all the evidence above, it seems logical to assume that decomposition and weathering are increased by the function of roots and mycorrhiza. However, the inclusion of these effects in the acidification analysis requires that the relationships between e.g. organic acid release and increases in the rates are quantified.

8 Discussion

8.1 Modelling of soil acidification

Constancy of effective cation exchange capacity has been assumed in many models (Tiktak and Van Grinsven 1995), although it is evident that the effective cation exchange capacity decreases with decreasing pH in variable charge soils (Thomas and Hargrove 1984, Duquette and Hendershot 1987). Reuss *et al.* (1990) suggest that pH-dependency of CEC_e is not important in modelling of mineral horizons, but our studies suggest the opposite. It would be important to consider both CEC_e and CEC_p in the modelling, because CEC_p represents the number of sites potentially available for H^+ binding, whereas CEC_e represents the amounts of "active" acidity (Thomas 1982) and exchangeable base cations. However, it has been difficult to explain the relations between the effective and potential cation exchange capacity, or as Reuss and Walthall (1990) state: "... we are often unable to predict the amount of pH-dependent charge that will be deactivated as base depletion proceeds."

In dynamic soil acidification models the reaction of H^+ with hydroxy-Al is usually described as the dissolution of $Al(OH)_3$, the dissolution having an effect on the exchangeable cation phase only through stoichiometric cation exchange of Al^{3+} with Ca^{2+} (e.g. Cosby *et al.* 1985, De Vries and Kros 1989) and in the model of De Vries *et al.* (1989) also through the exchange reactions H^+-Ca^{2+} and H^+-Al^{3+}. However, this description does not take into account the change in CEC_e following the exchange reactions of H^+ and Al^{3+}. It is proposed in Study I and here that the model of weak acid dissociation (pK_{HH}) together with the model of organic aluminium complexes (pK_o) can be used to simulate exchangeable H^+ and Al in soil acidification models. Both models are needed, because dissolution of Al depends on the pH of the extract, and the degree of dissociation α depends on the release of Al from the complexing sites. However, if the acid deposition is high and leaching of Al leads to a marked depletion of organically bound Al, pK_o probably decreases gradually (Mulder and Stein 1994), and the general model including protonated and Al bound sites in organic matter should be applied (Equation (13)).

The use of lysimeter solution chemistry to determine cation–exchange coefficients of a soil can be a first estimate in simulations of solute leaching and soil acidification, when the description is based only on the chemistry of mobile solution in soil. We assume that the suction lysimeter solutions represent the loosely bound runoff water better than the centrifugates. If cation-exchange coefficients that are based on centrifugates were used to simulate runoff chemistry, concentrations of H^+, Al and K would be overestimated and that of Ca would be underestimated. However, it is questionable whether cation-exchange equilibria can be assumed in the most mobile soil solution, and thus models describing solution chemistry in pores of different sizes should be developed.

Soil heterogeneity causes a great deal of problems to soil chemistry studies at scales of centimeters and meters (Ilvesniemi 1991). In addition, it seems that we still have to deal with another level of spatial variation if we want to analyse chemical equilibrium in soil solutions. Thus several solution samples should be collected from each soil sample, because the various solution samples differ so much from each other (see also Nissinen 1997). In other words, soil solution should be extracted from pores of different sizes in order to estimate parameters for models describing solution chemistry in pores of different sizes.

Solution cation concentrations and cation leaching were quite similar in all multi-layer simulations compared to the one-layer simulations. It was then useful to account for the vertical variation in the soil chemical properties even if some details of the chemical processes and parameters were unavailable. However, comparisons of the multi-layer cases showed that the need for detailed information on processes and parameters is an evident disadvantage in multi-horizon simulations (see also Van Oene and De Vries 1994). In general, any great opposite changes (decrease - increase) in the amounts of exchangeable cations of the subsequent layers suggest that either the distribution of processes which consume and produce base cations is wrong, or the cation exchange equilibrium is not adequately described.

The model FEF does not give the correct speed of soil acidification because it ignores sulphate adsorption and vertical variation in soil properties. However, the analysis can be seen useful. The models describing both vegetation and soil in a detailed way can only be developed when the interactions between trees and soil are better understood. Models like FEF can increase this understanding. Only detailed, well balanced models can produce accurate quantitative estimates of soil acidification, especially when long-term predictions are needed (Tiktak and van Grinsven 1995).

8.2 Soil acidification due to increases in acidifying deposition

The evidence for acidic deposition as a cause of soil acidification can be divided into several classes. Theoretical evidence, time series of ionic composition in soil solution, time series of exchangeable base cation contents in soil, large-scale experiments with acid inputs, and experiments with lysimeters are considered below, together with the results of model applications in this study.

Theoretical evidence

Theoretical evidence can be based on the knowledge about A) the reactions of hydrogen ions in soil, and B) the relations between element cycling and soil acidification. Regarding A, it is known that hydrogen ions are retained on weakly acidic groups in organic matter and Al hydroxides, and that these hydrogen ions affect the cation-exchange equilibria, base cation concentrations in soil solution, and pH of soil solution (Studies I, II and III). Hydrogen ions are also consumed in dissolution of aluminium hydroxides, and the dissolved Al takes part in cation-exchange reactions, affecting base cation concentrations. Although cation-exchange equilibria cannot be assumed in the mobile solution, the ionic composition of the mobile solution is affected by the ionic composition of the solution in small pores, which has cation-exchange equilibria with the bulk exchangeable cations of the soil (Study III). Thus chemical reactions of hydrogen ion with weak acidic groups and other potential cation-exchange sites in soil lead to base cation leaching and soil acidification (e.g. decrease of base saturation BS) when the hydrogen ion deposition is increased.

Regarding evidence B, an attempt to estimate H^+ production and consumption in relation to element cycling in a Scots pine stand was made with model FEF. The analysis suggests that the increase in hydrogen ion deposition lead to i) a marked increase in leaching loss of H^+ from soil as well as ii) a decrease in production of H^+ in dissociation of dissolved organic acids. However, in the hydrogen ion budget, these changes (i and ii) can not counteract the increase in H^+ deposition. As a result, H^+ is retained on cation-exchange sites, and base cation leaching from soil increases. Consequently this lead to a decrease in base saturation BS and an increase in ratio Al/Ca in soil solution.

The increase in deposition of NH_4 and NO_3 does not seem to affect soil acidification as much as the increase in H^+ deposition, but the higher deposition of NH_4 and NO_3 increases the leaching of NH_4 and NO_3 to surface waters. However, it must be noted that the simulated case of high nitrogen deposition is only hypothetical, as in reality nitrate deposition is accompanied by hydrogen ion deposition. The result is also based on the assumed low rate of nitrification in soil. The amount of available NH_4-nitrogen in soil would be large in such a case, and the ability of the soil microbial communities to nitrify NH_4 could be increased with increasing availability (Johnson 1992).

The results are generally consistent with the results of other modelling studies: the soil response to changes in ion deposition is slow, and soil acidification continues with the present deposition of acidic compounds (Cosby et al. 1989, Warfvinge *et al.* 1992, de Vries *et al.* 1994). In agreement with this, Johansson and Savolainen (1990) calculated with their model, assuming a reduction of about 40% for sulphur emissons in Finland after 1990, that base saturation would decrease in 50 years from 0.15 (rich mineral soils) or 0.10 (poor mineral soils) to less than 0.05 in large areas in southern Finland.

Time series of ionic composition in soil solution

The ionic composition of soil solution, leaching losses of base cations and soil content of exchangeable cations can be monitored during a time-period when the deposition of hydrogen ions is high or changes markedly. At a Norway spruce site in Solling, Germany, exchangeable Ca has decreased in a 50 cm thick soil layer, and sulphate and Al concentrations in solution increased manyfold at depth 90 cm between 1968 and 1991 (Tiktak *et al*. 1995a).

The effect of stand development on the solution chemistry, while difficult to estimate, can have a great effect, as indicated by the simulated solution chemistry as a function of stand age (Fig. 14). In addition, year-to-year variations in weather and ion deposition can produce short-term temporal variation in the soil solution, and thus long-term trends must be focused.

Time series of soil pH and exchangeable base cation contents in soil

Exchangeable base cation contents and acidity can be determined from the soil at sites which have been sampled long ago. Tamm and Hallbäcken (1988) showed that pH(H_2O) had decreased 0.5-0.7 units after 1920 in ground soil at a soil depth below 0.5 m. Decrease in soil pH or decrease in the amount of exchangeable base cations were shown by Hallbäcken and Tamm 1986, Falkengren-Grerup *et al.* 1987, and Billett *et al.* 1990. At a pine-spruce forest in southern Finland, between 1970 and 1989 pH($CaCl_2$) decreased in the humus layer and in 10 cm thick mineral soil layers to a depth of 60 cm (Westman and Jauhiainen 1998). The decrease in pH of humus was large, from 3.6 to 3.2, while pH decreased about 0.2 units from pH 4.9 in a depth of 40-60 cm. In the simulations, the difference in the solution pH of 90 year-old stands in 1970 and in 1990 was smaller, being about 0.1 units.

Large-scale experiments with acid inputs

Acidic deposition can be increased experimentally in a stand or a catchment, which allows observations of stand- and catchment-scale response to the additional hydrogen ions. In Norway, in an area with low acidic deposition, half of the added sulphate was realised as increased sulphate leaching from a catchment (Wright *et al.* 1988), and leaching of Ca and Mg increased markedly.

Acidic deposition can also be eliminated by a roof, which allows the study of recovery after deposition-caused soil acidification. When acidic deposition was excluded in an area with high deposition, leaching of sulphate, nitrate and base cations was decreased (Wright *et al.* 1988). However, increase in pH in the runoff can be small due to the buffering of organic acids (Rasmussen *et al.* 1995). This is consistent with the effect of dissolved organic acids in the simulations with FEF.

Lysimeter experiments with acid inputs

Different amounts of acid can be added to a restricted soil volume, e.g. lysimeter. Leached amounts of Ca and Mg have usually increased with increasing acidity of the added solution (Freiesleben and Rasmussen 1986, Skeffington and Brown 1986, Bergkvist 1986, Nissinen and Ilvesniemi 1990), while the amounts of exchangeable Ca and Mg have decreased (Abrahamsen and Stuanes 1986, Skeffington and Brown 1986, Brown 1987, Kelly and Strickland 1987, Nissinen and Ilvesniemi 1990). Nissinen and Ilvesniemi (1990) found that an increase in exchangeable H^+ was small compared with the amount of H^+ retained in the soil, and that exchangeable Al increased at the same time. This behaviour of soil agrees with the results of Study I and the simulated behavior of soils with the FEF model.

Conclusions from the evidence

In conclusion, there is convincing evidence that acidic deposition causes soil acidification, but any estimates of the rate of soil acidification are highly uncertain. Soil heterogeneity makes it difficult to study the acidification experimentally. Internal processes can cause large fluctuation in base saturation, the variation being connected to stand development and yearly weather conditions. In addition, the large size of a reasonable study object (a tree stand or a catchment) as well as the long time periods (several years or even decades) that are needed to see any long-term changes pose extra challenges to the research (Rasmussen et al. 1995). At the same time, modelling faces the problems of insufficient knowledge of the processes. The assumption of cation-exchange equilibria in mobile soil solution seems to not be adequate to estimate soil response to changing ion deposition, and a more detailed presentation of the soil pore system will be a future task. The division of soil into the major horizons would increase the accuracy of the soil acidification rate if chemical equilibria reactions alone were considered, but the functioning of roots and mycorrhiza at different soil depths as well as the response of roots and mycorrhiza to soil acidification are not well known (Mohren and Ilvesniemi 1995).

The problems should not obscure the main result from the analysis. Soil acidification is a slow process, and soils can be far from a steady-state with the present ion deposition. Thus it is obvious that the base saturation of forest soils will continue to decrease with the present acidic deposition, leading to a lower pH, higher Al concentration, and higher Al/Ca ratio in soil solution.

8.3 Changes in nitrogen leaching due to increases in acidifying deposition

The simulated leaching of inorganic nitrogen increases by 173% in Scenario A and 163% in Scenario B between 1890 and 1990. It increases almost 300% between 1890 and 2080. Although these changes are large, the time periods are also long. The simulated increase between 1970 and 1990, 35% in Scenario A, can be compared with observations in two catchments in southernmost Finland, the increases being 200% and 40% (Lepistö 1996). Although the bulk deposition of NH_4 and NO_3 in southernmost Finland is higher than the estimate for southern Finland used in simulations, and although the dry deposition to forest was not included in the study with FEF, it is not evident that the model would overestimate the effects of nitrogen deposition on nitrogen leaching. This suggests that nitrogen leaching to surface waters can be very problematic for water quality in future, as the increase in concentration of inorganic nitrogen can increase the occurrence of blue algae in surface waters (Autio *et al.* 1996).

NITREX experiments have shown that leaching of nitrogen from forests can respond rather quickly to increased year-to-year experimental additions of nitrogen

(Moldan and Wright 1998) or excluded nitrogen deposition (Tietema *et al.* 1998). This change in nitrogen leaching was not expected on the basis of many fertilisation experiments: although the leaching increased for a year or two after a high dose of nitrogen (Melin 1986, Westling and Hultberg 1990/91, Nohrstedt 1992) it decreased to a low level after this (Nohrstedt 1992, 1998). It seems evident that the chemical and microbiological reactions are different in cases of one high dose and a moderate but continuous input (Johnson 1992).

8.4 Changes in tree growth due to increases in acidifying deposition

Schulze *et al.* (1989) and Matzner and Murach (1995) have presented a hypothesis stating that as base saturation and exchangeable Mg decrease to a low level and Al/Ca in soil solution increases, fine root amounts in trees decrease, because fine roots avoid the severely acidified soil. In FEF, trees increase the allocation of carbohydrates to fine roots when exchangeable Mg is low. However, this also results in a decrease in fine root amount after some years, because the production of carbohydrates in foliage decreases when the allocation to fine roots increases. Thus the simulated fine root dynamics does not contradict the hypothesis presented by Matzner, although the mechanism is different.

The increase in simulated stemwood production between the 18th to the 19th centuries and further to the 20th century is large, the increase being more than 20% of the initial level in the 18th century. However, it is much less than the observed trend between the early 1970s and late 1980s in Finland, France and Sweden. Kauppi *et al.* (1992) suggest that the growth increase, 30% in 20 years, can be largely explained by increase in nitrogen deposition, while other potential causes are silvicultural development, favorable climatic conditions, and the fertilisation effect of additional carbon dioxide in the air. With FEF, the simulated increase in growth between 1970 and 1990 was around 4.5% for both scenarios A and B. Thus it seems that the model underestimates rather than overestimates the effects of nitrogen deposition on tree growth. Exchangeable Mg decreased 35% and base saturation from 0.17 to 0.12 in Scenario A, but this harmful change had a neglible effect compared with the growth enhancing effect of increased nitrogen availability in the simulations.

However, it may be that the predicted tree growth increase in the 20th century is an overestimate, and that in reality growth would respond more to a decrease in base cation status and increase in aluminium solubility in soil. In the simulations, the exchangeable Mg in 2080 will be about 50% of the level in 1970, and base saturation will have decreased from 0.17 to 0.08. At the same time, the ratio Al/Ca in solution will have increased to a level which is considered critical for ecosystem function, or close to 1.0 (Fig. 14b). The simulated growth response takes into account the base cation amounts in soil, but it does not include the harmful effects of aluminium.

The model seems to be rather conservative in its predictions, as the simulated decrease in soil pH, increase in the leaching of ammonium and nitrate nitrogen, as well as the increase in tree growth between 1970 and 1990 were smaller than the observed changes. This suggests that the changes in nutrient availability, leaching of ammonium and nitrate, and tree growth will be large if the deposition of hydrogen ions and ammonium and nitrate are at the present level or higher. Although tree growth can increase for decades due to large deposition of NH_4 and NO_3, the high H^+ deposition will lead to highly acidified soils within a time period of 50-100 years. It is evident that tree growth will also suffer from soil acidification.

8.5 Critical loads of sulphur and nitrogen for forest soils

Concepts of critical load and target load have been developed to build bridges between environmental policy and science. For forest soils the critical load can be defined as “the highest deposition of acidifying compounds that will not cause chemical changes in soil leading to long-term harmful effects on ecosystem structure and function” (Nilsson and Grennfelt 1988). The target load is a political instrument to define the level of deposition that can be accepted (Warfvinge *et al.* 1992, Kämäri *et al.* 1993).

This study does not show how much the emissions and deposition of acidifying compounds should be decreased in order to prevent harmful changes in the soils of a certain area, but it focuses on the soil acidification process, describing one ‘typical’ soil profile at a Scots pine stand in southern Finland. Analyses of critical and target loads require data of regional soil properties, just as regional estimates of lake chemistry were used to determine critical loads of lakes in Finland (Kämäri *et al.* 1993). In addition to uncertainty connected with the model structure which was considered in this study, great emphasis is put on the uncertainty in the parameter values (Kämäri *et al.* 1993).

In producing regional estimates of soil acidification and critical loads, the models need to have a low data requirement and complexity (Johansson and Savolainen 1990). In Finland, model HAKOMA has been used to analyse the regional acidification of soils under different emission scenarios for sulphur, nitrous oxides and ammonia (Johansson and Savolainen 1990, Johansson *et al.* 1990). Regarding such aggregated models, the important results of this study concern 1) the reactions of exchangeable acids, 2) the importance of dissolved organic acids in buffering solution pH, 3) the non-equilibria of cation-exchange in the mobile soil solution, and 4) the effects of aggregation of soil horizons on the simulated ion leaching. The submodel of exchangeable acids can be introduced to models as such, but the theory and submodel of ion transfers between large and small soil pores (Kareinen *et al.* 1998) need more development.

9 Conclusions

An equilibrium with weak monoprotic acids can be used to explain the activity of H^+ in the extract of effectively exchangeable cations, and an equilibrium with organic Al complexes can be used to explain the dissolved Al^{3+} in the extract. The degree of dissociation of the acidic functional groups can be determined as the ratio between effective and potential cation exchange capacity. The reaction stoichiometry of the binding reaction of Al to soil was close to 2.0 in all horizons of Podzols and a Cambisol. Solubility of $Al(OH)_3$ phases does not seem to be a general explanation for salt-exchangeable Al in acidic soils. It is proposed that the model pK_{HH} together with the model pK_o can be used to simulate exchangeable H^+ and Al in soil acidification models.

The differences between the centrifugates and the lysimeter solutions in the total charge of ions and cation-exchange equilibria suggest that there cannot be cation-exchange equilibria between the solution in large pores (i.e. the mobile solution) and the bulk exchangeable cations, although there seems to be cation-exchange equilibria in small pores. This means that the assumption of apparent cation-exchange equilibria in mobile solution is not well applicable to an analysis of acidic deposition effects, and the analysis with the model FEF, or any other model describing the mobile soil solution alone, cannot produce accurate estimates of ion leaching under various deposition scenarios.

Simulations of multi-layered soil and one layer with aggregated properties showed that it is useful to account for the vertical variation in the soil chemical properties even if the vertical patterns in the cation-exchange coefficients were not known, because an aggregated one-layer model can simulate biased base cation leaching in podzolized soils. However, it is evident that the need for detailed information of processes and parameters is a disadvantage in multi-horizon simulations.

The dynamic model FEF is based on material balances and relates tree structure and functions to soil properties. Although the model is based on rather few processes and few initial stand properties, it was able to generate the generally known stand growth and could also produce the patterns of nitrogen leaching after clear-cut.

Analyses with model FEF suggest that an increase in hydrogen ion deposition has led to a decrease in base saturation BS and an increase in ratio Al/Ca in soil solution. The changes in nutrient availability, leaching of ammonium and nitrate, and tree growth will be sizeable if the deposition of hydrogen ions and ammonium and nitrate are at the level of 1990. Hydrogen ion deposition affects soil acidification, whereas the deposition of NH_4 and NO_3 affects the leaching of nitrogen to surface waters. In order to slow down or stop further soil acidification, emissions of sulphur oxides should be decreased from the level of 1990. In order to decrease leaching of NH_4 and NO_3 to surface waters, emissions of nitrous oxides and ammonia NH_3 should be decreased.

Acknowledgements

This study was mainly financed by the Academy of Finland (through ‘The Research Program on Climate Change’ (SILMU) and ‘The APFE’s Proposal for Research Training’). The University of Helsinki and the Foundation for Research of Natural

Resources in Finland provided scholarships, and the European Union financed the modelling work in the project ‘Long-Term Effects of Climate Change on European Forests: Impact Assessment and Consequences for Carbon Budgets’ (LTEEF-II, ENV4-CT97-0577).

Professor Pertti ‘Pepe’ Hari and Dr. Hannu Ilvesniemi have been my supervisors. Pepe has always encouraged me in my work, and guided me in making links between the clear and beautiful world of theory, the messy world of observations, and the world in between, i.e. the reality. Hannu was of great help in all experimental matters. Thank you Hannu and Pepe for your unfailing support during this long process.

I wish to express my thanks to the heads of the Department of Forest Ecology: Professor Matti Leikola and Professor Juhani Päivänen. The Department has supported my work by providing excellent working facilities in both the laboratory and office. Anne Koponen, Iris Heikkilä and Sirkka Bergström have helped and advised me in practical and bureaucratic matters. I wish to thank them and everyone in the Department for all the support I have received.

Professor Helinä Hartikainen and Docent Juha Kämäri reviewed the thesis. I am grateful to them for their encouragement, constructive criticism and valuable suggestions. I wish to thank Pekka Kauppi, Professor of Environmental Protection, for guidance during the last months of my doctoral studies.

My interest in soil acidification and element cycling in forests began in the late 80s, when I as a young student had the pleasure to be involved in a reserch group concerned with these issues. In addition to Pepe and Hannu I., the group consisted of Hannu Arovaara, Maria Holmberg, Eero Nikinmaa and Anneli Ylimartimo. It was an inspiring team, and the feeling of co-operation and curiosity that we had that time has sustained me through the years. The same feeling made me come back after working for the Espoo Environmental Office as well as the Ministry of Environment, and go on with soil research.

We had a fine ‘field and laboratory’ group in the SILMU-project. In addition to Hannu I., I had the pleasure to work with Mikko Jauhiainen, Timo Kareinen and Niina Tanskanen. Professor C.J. Westman offered us his support and pleasant company during the establishment of the experiments at Rudbäcken, Siuntio. Silja Aho offered us her friendly and valuable help in the laboratory, ensuring the functioning of the chemical measuring devices. Later, Hannu, Niina, Timo and Mikko worked with me in analysing the data and writing scientific papers - thanks to you, my closest colleagues in soil science, for all the time and effort you have shared with me in this work.

I have always felt that it is important to connect my detailed studies to a larger framework. The existence of the research group, APFE (‘Atmosphere Physics and Forest Ecology’), has given added motivation to my work. My warmest thanks to Eija Juurola, Sari Palmroth, Annikki Mäkelä, Nuria Altimir, Jaana Bäck, Kaisa Särkkä, Jukka Pumpanen, Frank Berninger, Martti Perämäki, Roope Kivekäs and Tapio Linkosalo in our department, and Markku Kulmala, Jyrki Mäkelä, Timo

Vesala, Petri Keronen and all the other group members in the Department of Physics.

I wish to thank the many people who have been important in this long process. It has been a pleasure to work at the Forestry Field Station in Hyytiälä, where Tuula Ruusunen, Antti Uotila, Jussi Rasinmäki, Reino Saarinen and all the staff ensured excellent working and living conditions. Antti Uusi-Rauva provided me with good working facilities in the isotope laboratory during the development of the centrifuging method. Dr. Kari Leinonen and Dr. Jukka Lippu offered me valuable help in the midst of the various tasks related to the finalisation of this doctoral thesis. Nancy Seidel revised the English, and Ahti Kotisaari designed the cover of this book.

Our interest in the water and element cycles of the forests at Rudbäcken was shared by a research group at the Finnish Environment Institute. I want to thank Jaana Roos, Yrjö Kivinen, Ahti Lepistö, Sirkka Tattari and all the others who participated in this pleasant collaboration.

Since June 1998 I have had the pleasure to be involved in the research project LTEEF-II. My special thanks to Frits Mohren, Koen Kramer, Hank Bartelink and all my newly found colleagues. This project has been a source of ideas and insights for my future work.

Hannu Arovaara and Marja Mecke deserve special thanks. Hannu has tolerated my absent-minded table tennis on those (numerous) Mondays when my thoughts have focused on chemistry equations instead of the ball. Marja’s uncompromising attitude towards science has been an example to me, and helped me to be patient with the slowness of the scientific writing process.

My parents have always encouraged me to study further. Kiitokset vanhemmilleni, Raisalle ja Martille, kannustuksesta opin tielle.

My sister’s husband, Toni Sulameri, gave me one of the two kicks that made me begin the writing of this thesis. I am thankful to him for his practical, goal-oriented viewpoint.

The other kick was given by my wife, Virpi Ruohomäki, who has always encouraged me to go on with my research. It has been of crucial importance to me to have a partner who understands the value and the problems of scientific work. Our 3-year old son, Pyry, has been the best teacher I have ever had – he opens up a new (or: forgotten) world for me every day after working hours.

References

Aber, J.D. & Melillo, J.M. 1982. Nitrogen immobilization in decaying hardwood leaf litter as a function of initial nitrogen and lignin content. Canadian Journal of Botany 60: 2263-2269.

Aber, J.D., Botkin, D.B. & Melillo, J.M. 1978. Predicting the effects of different harvesting regimes on forest floor dynamics in northern hardwoods. Canadian Journal of Forest Research 8: 306-315.

Aber, J.D., Melillo, J.M. & Federer, C.A. 1982. Predicting the effects of rotation length, harvest intensity, and fertilization on fiber yield from northern hardwood forests in New England. Forest Science 28: 31-45.

Abrahamsen, G. 1983. Sulphur pollution: Ca, Mg and Al in soil and soil water and possible effects on forest trees. In: Ulrich, B. & Pankrath, J. (Eds.) Effects of Accumulation of Air Pollutants in Forest Ecosystems, pp. 207-218. Reidel Publishing Company, Dordrecht.

Abrahamsen, G. & Stuanes, A.O. 1986. Lysimeter study of effects of acid deposition on properties and leaching of gleyed dystric brunisolic soil in Norway. Water, Air and Soil Pollution 31: 865-878.

Adams, F. & Rawajfih, Z. 1977. Basalaluminite and alunite: a possible cause of sulfate retention by acid soils. Soil Science Society of America Journal 41: 686-692.

Adams, F., Burmester, C., Hue, N.V. & Long, F.L. 1980. A comparison of column-displacement and centrifuge methods for obtaining soil solutions. Soil Science Society of America Journal 44: 733-735.

Ågren, G.I. & Bosatta, E. 1987. Theoretical analysis of the long-term dynamics of carbon and nitrogen in soils. Ecology 68: 1181-1189.

Ahtiainen, M. 1991. The Effects of Clear-cutting and Forestry Drainage on Water Quality of Forest Brooks. Publications of the Water and Environment Administration, Series A 45. The National Board of Waters and the Environment, Finland. (In Finnish, abstract in English). 122 pp.

Ahtiainen, M. & Huttunen, P. 1995. Metsätaloustoimenpiteiden pitkäaikaisvaikutukset purovesien laatuun ja kuormaan. In: Saukkonen, S. & Kenttämies, K. (Eds.) Metsätalouden vesistövaikutukset ja niiden torjunta, pp. 33-50. Suomen ympäristö 2, Suomen ympäristökeskus, Helsinki. (In Finnish).

Andersen, H.V. & Hovmand, M.F. 1995. Ammonia and nitric acid deposition and throughfall. Water, Air and Soil Pollution 85: 2211-2216.

Arovaara, H., & Ilvesniemi, H. 1990. The effects of soluble inorganic aluminium and nutrient imbalances on *Pinus sylvestris* and *Picea abies* seedlings. In: Kauppi, P., Anttila, P. & Kenttämies, K. (Eds.) Acidification in Finland, pp. 715-733. Springer-Verlag, Berlin, Heidelberg.

Autio, R., Kuosa, H., Kuuppo, P., Setälä, O. & Tanskanen, S. 1996. Potential effects of climate change on coastal pelagial ecosystems in the Gulf of Finland. In: Roos, J. (Ed.) The Finnish Research Programme on Climate Change, Final Report, pp. 202-207. Publications of the Academy of Finland, 4/96. Helsinki.

Bache, B.W. & Sharp, G.S. 1976a. Characterization of mobile aluminium in acid soils. Geoderma 15: 91-101.

Bache, B.W. & Sharp, G.S. 1976b. Soluble polymeric hydroxy-aluminum ions in acid soils. Journal of Soil Science 27: 167-174.

Barbee, G.C. & Brown, K.W. 1986. Comparison between suction and free-drainage soil solution samplers. Soil Science 141: 149-154.

Barnhisel, R. & Bertsch, P.M. 1982. Aluminum. In: Page, A.L., Miller, A.H. & Keeney, D.R. (Eds.) Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties, 2nd edition, pp. 275-300. American Society of Agronomy, Madison, WI.

Barret, E. & Brodin, G. 1955. The acidity of Scandinavian precipitation. Tellus 7: 251-257.

Bartlett, R. J., Ross, D. S. & Magdoff, F. R. 1987. Simple kinetic fractionation of reactive aluminum in soil “solutions”. Soil Science Society of America Journal 51: 1479-1482.

Batley, G.E. & Giles, M.S. 1979. Solvent displacement of sediment interstitial waters before trace metal analysis. Water Research 13: 879-886.

Berg, B. 1984. Decomposition of root litter and some factors regulating the process: Long-term root litter decomposition in a Scots pine forest. Soil Biology and Biochemistry 16: 609-617.

Berg, B. 1986. Nutrient release from litter and humus in coniferous forest soils - a mini review. Scandinavian Journal of Forest Research 1: 359-369.

Berg, B., Hannus, K., Popoff, T. & Theander, O. 1982. Changes in organic chemical components of needle litter during decomposition. Long-term decomposition in a Scots pine forest. I. Canadian Journal of Botany 60: 1310-1319.

Berg, B., Staaf, H. & Wessén, B. 1987. Decomposition and nutrient release in needle litter from nitrogen-fertilized Scots pine (*Pinus sylvestris*) stands. Scandinavian Journal of Forest Research 2: 399-415.

Bergkvist, B. 1986. Leaching of metals from a spruce forest soil as influenced by experimental acidification. Water, Air and Soil Pollution 31: 901-916.

Bergkvist, B. 1987. Soil solution chemistry and metal budgets of spruce forest ecosystems in S. Sweden. Water, Air and Soil Pollution 33: 131-154.

Billett, M.F., Parker-Jervis, F., Fitzpatrick, E.A. & Cresser, M.S. 1990. Forest soil chemical changes between 1949/50 and 1987. Journal of Soil Science 41: 133-145.

Bloom, P.R., McBride, M.B. & Weaver, R.M. 1979a. Aluminum organic matter in acid soils: Buffering and solution aluminum activity. Soil Science Society of America Journal 43: 488-493.

Bloom, P.R., McBride, M.B. & Weaver, R.M. 1979b. Aluminum organic matter in acid soils: Salt-extractable aluminum. Soil Science Society of America Journal 43: 813-815.

Boden, T.A., Kanciruk, P. & Farrell, M.P. 1990. Trends ‘90: A compendium of data on global change. ORNL/CDIAC-36. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee. 286 pp.

Bohn, H.L., McNeal, B.L. & O'Connor, G.A. 1985. Soil Chemistry. John Wiley & Sons, New York.

Bosatta, E. & Ågren, G.I. 1995. Theoretical analyses of interactions between inorganic nitrogen and soil organic matter. European Journal of Soil Science 46: 109-114.

Brown, K. 1987. Chemical effects of pH 3 sulphuric acid on a soil profile. Water, Air and Soil Pollution 32: 201-218.

Brown, G. & Newman, A.C.D. 1973. The reactions of soluble aluminum with montmorillonite. Journal of Soil Science 24: 339-354.

Cajander, A.K. 1925. The theory of forest types. Acta Forestalia Fennica 29: 1-108.

Chung, J.–B., Zasoski, R. J. & Burau, R. G. 1994. Aluminum-potassium and aluminum-calcium exchange equilibria in bulk and rhizosphere soil. Soil Science Society of America Journal 58: 1376-1382.

Clark, J. S. & Turner, R. C. 1965. Extraction of exchangeable cations and distribution constants for ion exchange. Soil Science Society of America Proceedings 29: 271-274.

Coleman, N.T. & Thomas, G.W. 1967. The basic chemistry of soil acidity. In: Pearson, R.W. & Adams, F. (Eds.) Soil acidity and liming, pp. 1-41. Agronomy 12, American Society of Agronomy, Madison, WI.

Cosby, B.J., Hornberger, G.M., Galloway, J.N. & Wright, R.F. 1985a. Modeling the effects of acid deposition: Assessment of a lumped parameter model of soil water and streamwater chemistry. Water Resources Research 21: 51-63.

Cosby, B.J., Wright, R.F., Hornberger, G.M., & Galloway, J.N. 1985b. Modeling the effects of acid deposition: Estimation of long-term water quality responses in a small forested catchment. Water Resources Research 21: 1591-1601.

Cosby, B.J., Hornberger, G.M., Wright, R.F. & Galloway, J.N 1986. Modeling the effects of acid deposition: Control of long-term sulfate dynamics by soil sulfate adsorption. Water Resources Research 22: 1283-1291.

Cosby, B.J., Hornberger, G.M., Wright, R.F 1989. Estimating time delays and extent of regional de-acidification in southern Norway in response to several deposition scanarios. In: Kämäri, J., Brakke, D.F., Jenkins, A., Norton, S.A. & Wright, R.F. (Eds.) Regional acidification models, pp. 151-166. Springer-Verlag, Berlin, Heidelberg.

Cosby, B.J., Ferrier, R.C., Jenkins, A., Emmett, B.A., Wright, R. & Tietema, A. 1997. Modelling the ecosystem effects of nitrogen deposition: Model of ecosystem retention and loss of inorganic nitrogen (MERLIN). Hydrology and Earth System Sciences 1: 137-158.

Coulter, B. S. & Talibudeen, O. 1968. Calcium:aluminium exchange equilibria in clay minerals and acid soils. Journal of Soil Science 19: 237-250.

Courchesne, F. & Hendershot, W.H. 1990. The role of basic aluminum sulfate minerals in controlling sulfate retention in the mineral horizons of two spodosols. Soil Science 150: 571-578.

Covington, W.W. 1981. Changes in forest floor organic matter and nutrient content following clear cutting in northern hardwoods. Ecology 62: 41-48.

Cronan, C.S., Walker, W.J. & Bloom, P.R. 1986. Predicting aqueous aluminum concentrations in natural waters. Nature 324: 140-143.

Dahlgren, R.A. & Walker, W.J. 1994. Solubility control of KCl extractable aluminum in soils with variable charge. Communications in Soil Science and Plant Analysis 25: 2201-2214.

Dahlgren, R.A., Driscoll, C.T. & McAvoy, D.C. 1989. Aluminum precipitation and dissolution rates in spodosol Bs horizons in the northeastern USA. Soil Science Society of America Journal 53: 1045-1052.

David, M.B., Vance, G.F. and Fasth, W.J. 1991. Forest soil response to acid and salt additions of sulfate: II. Aluminum and base cations. Soil Science 151: 208-219.

de Coninck., F. 1980. Major mechanisms in formation of spodic horizons. Geoderma 24: 101-128.

de Vries, W. 1994. Soil acidification on a regional scale: Critical loads and long-term impacts of acidic deposition. Doctoral thesis, Agricultural University, Wageningen, the Netherlands.

de Vries, W. & Breeuwsma, A. 1987. The relation between soil acidification and element cycling. Water, Air and Soil Pollution 35: 293-310.

de Vries, W. & Kros, H. 1989. The long-term impact of acid deposition on the aluminium chemistry of an acid forest soil. In: Kämäri, J., Brakke, D.F., Jenkins, A., Norton, S.A. & Wright, R.F. (Eds.) Regional acidification models, pp. 113-128. Springer-Verlag, Berlin, Heidelberg.

de Vries, W., Posch, M. & Kämäri, J. 1989. Simulation of the long-term soil response to acid deposition in various buffer ranges. Water, Air and Soil Pollution 48: 349-390.

de Vries, W., Reinds, G.J., Posch, M. & Kämäri, J. 1994. Simulation of soil response to acidic deposition scenarios in Europe. Water, Air and Soil Pollution 78: 215-246.

de Vries, W., Posch, M., Oja, T., van Oene, H., Kros, H., Warfvinge, P. & Arp, P.A. 1995. Modelling critical loads for the Solling spruce site. Ecological Modelling 83: 283-293.

Derome, J. 1989. Acid-induced aluminum mobility in Finnish mineral soils. In: Kämäri, J., Brakke, D.F., Jenkins, A., Norton, S.A. & Wright, R.F. (Eds.) Regional acidification models, pp. 23-30. Springer-Verlag, Berlin, Heidelberg.

Duquette, M. & Hendershot, W.H. 1987. Contribution of exchangeable aluminum to cation exchange capacity at low pH. Canadian Journal of Soil Science 67: 175-185.

Elonen, P. 1971. Particle-size analysis of soil. Acta Agriculturae Fennica 122: 1-122.

Evans, J.R. 1989. Photosynthesis and nitrogen relationship in leaves of C_3 plants. Oecologia 78: 9-19.

Falkengren-Grerup, U., Linnermark, R. & Tyler, G. 1987. Changes in acidity and cation pools of south Swedish soils between 1949 and 1985. Chemosphere 16: 2239-2248.

Falkengren-Grerup, U., Brunet, J., Quist, M.E. & Tyler, G. 1995. Is the Ca:Al ratio superior to pH, Ca or Al concentrations of soils in accounting for the distribution of plants in deciduous forest? Plant and Soil 177: 21-31.

FAO - Unesco 1990. Soil Map of the World. Revised legend. World Soil Resources Report No 60, FAO, Rome.

Ferrier, R.C., Jenkins, A., Cosby, B.J., Helliwell, R.C., Wright, R.F. & Bulger, A.J. 1995. Effects of future N deposition scenarios on the Galloway region of SW Scotland using a coupled sulphur and nitrogen model (MAGIC-WAND). Water, Air and Soil Pollution 85: 707-712.

Forsius, Kämäri, J., Kortelainen, P., Mannio, J., Verta, M. & Kinnunen, K. 1990. Satistical lake survey in Finland: Regional estimates of lake acidification. In: Kauppi, P., Anttila, P. & Kenttämies, K. (Eds.) Acidification in Finland, pp. 759-780. Springer-Verlag, Berlin, Heidelberg.

Foscolos, A.E. 1968. Cation-exchange equilibrium constants of aluminum-saturated montmorillonite and vermiculite clays. Soil Science Society of America Proceedings 32: 350-354.

Freiesleben, N.E.v. 1988. Sulfate mobility in an acid Danish soil. Journal of Environmental Quality 17: 278-284.

Freiesleben, N.E.v. & Rasmussen, L. 1986. Effects of acid rain on ion leaching in a danish forest soil. Water, Air and Soil Pollution 31: 965-968.

Frink, C.R. & Peech, M. 1963. Hydrolysis and exchange reactions of the aluminum ion in hectorite and montmorillonite suspensions. Soil Science Society of America Proceedings 27: 527-530.

Gaines, G.L. & Thomas, H.C. 1953. Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption. The Journal of Chemical Physics 21: 714-718.

Galloway, J.N. 1995. Acid deposition: Perspectives in time and space. Water, Air and Soil Pollution 85: 15-24.

Gapon, E.N. 1933. Theory of exchange adsorption in soils. Journal of General Chemistry of the USSR 3: 144-152.

Giesler, R. 1996. Chemistry of soil solution extracted by centrifugation - Methodology and field applications. Dissertation, Umeå, Sweden. ISBN 91-576-5079-9.

Giesler, R. & Lundström, U. 1993. Soil solution chemistry: Effects of bulking soil samples. Soil Science Society of America Journal 57: 1283-1288.

Giesler, R., Lundström, U. & Grip, H. 1996. Comparison of soil solution chemistry assessment using zero-tension lysimeters or centrifugation. European Journal of Soil Science 47: 395-405.

Gillman, G. P. 1976. A Centrifuge Method for Obtaining Soil Solution. Division of Soils, Divisional Report 16, CSIRO, Melbourne, Australia.

Gorham, E. 1955. On the acidity and salinity of rain. Geochimica et Cosmochimica Acta 7: 231-239.

Graedel, T.E., Benkovitz, C.M., Keene, W.C., Lee, D.S., & Marland, G. 1995. Global emissions inventories of acid-related compounds. Water, Air and Soil Pollution 85: 25-36.

Grieve, I.C. 1990. Soil and solution chemical composition at three sites within the Loch Dee catchment, SW Scotland. Journal of Soil Science 41:269-277.

Grieve, I.C. 1996. Effects of the centrifuge drainage method on total organic carbon concentrations in soil solutions from peaty soils. Geoderma 74: 115-123.

Grossmann, J. & Udluft, P. 1991. The extraction of soil water by the suction-cup method: a review. Journal of Soil Science 42: 83-93.

Grossmann, J., Quentin, K.-E. & Udluft, P. 1987. Sickerwassergewinnung mittels Saugkerzen - eine Literaturstudie. Zeitschrift fur Pflanzenernahrung und Bodenkunde 150: 258-261.

Gustafsson, J.P. 1995. Modelling pH-dependent sulfate adsorption in the Bs horizons of podzolized soils. Journal of Environmental Quality 24: 882-888.

Gustafsson, J.P., Bhattacharya, P., Bain, D.C., Fraser, A.R. & McHardy, W.J. 1995. Podzolisation mechanisms and the synthesis of imogolite in northern Scandinavia. Geoderma 66: 167-184.

Haines, B.L., Waide, J.B. & Todd, R.L. 1982. Soil solution nutrient concentrations sampled with tension and zero tension lysimeters: report of discrepancies. Soil Science Society of America Journal 46: 658-661.

Hallbäcken, L. & 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.

Hallgren Larsson, E., Knulst, J., Malm, G. & Westling, O. 1995. Deposition of acidifying compounds in Sweden. Water, Air and Soil Pollution 85: 2271-2276.

Hanson, P.J. & Lindberg, S.E. 1991. Dry deposition of reactive nitrogen compounds: a review of leaf, canopy and non-foliar measurements. Atmospheric Environment 25A: 1615-1634.

Hargrove, W.L. & Thomas, G.W. 1981. Extraction of aluminum from aluminum-organic matter complexes. Soil Science Society of America Journal 45: 151-153.

Hargrove, W.L. & Thomas, G.W. 1984. Extraction of aluminum from aluminum-organic matter in relation to titratable acidity. Soil Science Society of America Journal 48: 1458-1460.

Hari, P. 1998. Towards a quantitative theory in the research of plant production. Agro's Annual Review of Plant Physiology (Basic and Applied), Fourth issue 1998 (in print).

Hari, P., Kaipiainen, L., Korpilahti, E., Mäkelä, A., Nilson, T., Oker-Blom, P., Ross, J. & Salminen, R. 1985. Structure, Radiation and Photosynthetic Production in Coniferous Stands. Research notes 54, Department of Silviculture, University of Helsinki. Helsinki.

Hartikainen, H. 1996. Soil response to acid percolation: Acid-base buffering and cation leaching. Journal of Environmental Quality 25: 638-645.

Havas, M. & Rosseland, B.O. 1995. Response of zooplankton, benthos and fish to acidification: An overview. Water, Air and Soil Pollution 85: 51-62.

Hedin, L.O., Granat, L., Likens, G.E., Buishand, T.A., Galloway, J.N., Butler, T.J. & Rodhe, H. 1994. Steep declines in atmospheric base cations in regions of Europe and North America. Nature 367: 351-354.

Heikkilä, E., Katainen, H. S., Hari, P., Raunemaa, T., & Kellomäki, S. 1983. Ravinteiden saatavuuden muutokset maaperässä. In: Hari, P. (Ed.) Energiatuotannosta peräisin olevien ilman epäpuhtauksien vaikutus metsän tuotokseen, III 2 (26 pp.) Research notes 44. University of Helsinki, Department of Silviculture, Helsinki. (In Finnish).

Helmisaari, H.-S. 1992. Nutrient retranslocation in three *Pinus sylvestris* stands. Forest Ecology and Management 51: 347-367.

Helmisaari, H.-S. 1995. Nutrient cycling in *Pinus sylvestris* stands in eastern Finland. Plant and Soil 168-169: 327-336.

Hendershot, W.H. & Courchesne, F. 1991. Simulation of solution chemistry in an acidic forest soil. Water, Air and Soil Pollution 60: 11-25.

Hendershot, W.H. & Duquette, M. 1986. A simple barium chloride method for determining cation exchange capacity and exchangeable cations. Soil Science Society of America Journal 50: 605-608.

Heyes, A. & Moore, T.R. 1992. The influence of dissolved organic carbon and anaerobic conditions on mineral weathering. Soil Science 154: 226-236.

Hodges, S.C. & Zelagny, L.W. 1983. Interactions of dilute, hydrolyzed aluminum solutions with clays, peat and resin. Soil Science Society of America Journal 47: 206-212.

Holmberg, M. 1984. Modell av jondynamiken i skogsmark under surt regn. Utveckling och utvärdering. Diplomarbete. Tekniska högskolan, Elektrotekniska avdelningen, Esbo.

Holmberg, M., Hari, P. & Nissinen, A. 1989. Model of ion dynamics and acidification of soil: Application to historical soil chemistry data from Sweden. In: Kämäri, J., Brakke, D.F., Jenkins, A., Norton, S.A. and Wright, R.F. (Eds.), Regional acidification models, pp. 229-240. Springer-Verlag, Berlin, Heidelberg,.

Horn, R., Schulze, E.-D. & Hantschel, R. 1989. Nutrient balance and element cycling in healthy and declining Norway spruce stands. In: Schulze, E.-D., Lange, O.L. & Oren

R. (Eds.) Forest Decline and Air Pollution: A Study of Spruce (*Picea abies*) on acid soils, pp. 444-455. Springer-Verlag, Berlin.

Hsu, Pa Ho 1968. Heterogeneity of montmorillonite surface and its affect on the nature of hydroxy-aluminum interlayers. Clays and clay minerals 16: 303-311.

Hughes, S., Norris, D.A., Stevens, P.A., Reynolds, B., Williams, T.G. & Woods, C. 1994. Effects of forest age on surface drainage water and soil solution aluminium chemistry in stagnopodzols in Wales. Water, Air and Soil Pollution 77: 115-139.

Hyvärinen, A. 1990. Deposition on forest soils- effect of tree canopy on throughfall. In: Kauppi, P., Anttila, P. & Kenttämies, K. (Eds.) Acidification in Finland, pp. 199-213. Springer-Verlag, Berlin, Heidelberg.

Ilvesniemi, H. 1991. Spatial and temporal variation of soil chemical characteristics in pine sites in southern Finland. Silva Fennica 25: 99-108.

Ilvesniemi, H. 1992. The combined effect of mineral nutrients and soluble aluminium on *Pinus sylvestris* and *Picea abies* seedlings. Forest Ecology and Management 51: 227-238.

Ingestad, T. 1979. Mineral nutrient requirements of *Pinus sylvestris* and *Picea abies* seedlings. Physiologia Plantarum 45: 373-380.

Ivens, W., Tank, A.K., Kauppi, P. & Alcamo, J. 1989. Atmospheric deposition of sulfur, nitrogen and basic cations onto European forests: observations and model calculations. In: Kämäri, J., Brakke, D.F., Jenkins, A., Norton, S.A. & Wright, R.F. (Eds.) Regional acidification models, pp. 103-111. Springer-Verlag, Berlin, Heidelberg.

Jackson, M.L. 1963. Aluminium bonding in soils: A unifying principle in soil science. Soil Science Society of America Journal 27: 1-10.

Jardine, P.M. & Zelazny, L.W. 1987. Influence of organic anions on the speciation of mononuclear and polynuclear aluminum by ferron. Soil Science Society of America Journal 51: 885-889.

Jardine, P.M., Zelazny, L.W. & Evans, Jr., A. 1986. Solution aluminum anomalies resulting from various filtering materials. Soil Science Society of America Journal 50: 891-894.

Jenkins, A. & Cosby B.J. 1989. Modelling surface water acidification using one and two soil layers and simple flow routing. In: Kämäri, J., Brakke, D.F., Jenkins, A., Norton, S.A. & Wright, R.F. (eds.) Regional acidification models, pp. 253-266. Springer-Verlag, Berlin Heidelberg.

Johansson, M. & Savolainen, I. 1990. Regional acidification model for forest soils. In: Kauppi, P., Anttila, P. and Kenttämies, K. (eds.) Acidification in Finland, pp. 253-269. Springer-Verlag, Berlin, Heidelberg.

Johansson, M., Kämäri, J., Pipatti, R., Savolainen, I., Tuovinen, J.-P., & Tähtinen, M. 1990. Development of an integrated model for the assessment of acidification in Finland. In: Kauppi, P., Anttila, P. and Kenttämies, K. (eds.) Acidification in Finland, pp. 1171-1193. Springer-Verlag, Berlin, Heidelberg.

Johnson, D.W. 1992. Nitrogen retention in forest soils. Journal of Environmental Quality 21: 1-12.

Johnson, D.W. 1995. Temporal patterns in beech forest soil solutions: Field and model results compared. Soil Science Society of America Journal 59: 1732-1740.

Johnson, D.W. & Cole, D.W. 1980. Anion mobility in soils: relevance to nutrient transport from forest ecosystems. Environment International 3: 79-90.

Johnson, M.G. & McBride, M.B. 1991. Solubility of aluminium and silicon in acidified spodosols: Evidence for soluble aluminosilicate. In: Wright, R.J., Baligar, V.C. & Murrmann, R.P. (Eds.) Plant-soil interactions at low pH: Proceedings of the 2nd international symposium on plant-soil interactions at low pH, pp. 15-24. Developments in Plant and Soil Sciences 45. Kluwer Academic Publishers, Dordrecht.

Johnsson, H. & Jansson, P.-E. 1993. SOILN model. Technical description of soil processes and the simple plant N uptake function. Department of Soil Science, Swedish University of Agricultural Sciences, Uppsala.

Jongmans, A.G., van Breemen, N., Lundström, U., van Hees, P.A.W., Finlay, R., Srinivasan, M., Unestam, T., Giesler, R., Melkerud, P.A. & Olsson, M. 1996. Rock-eating fungi. Nature 389: 682-683.

Jönsson, C., Schöpp, W., Warfvinge, P. & Sverdrup, H. 1993. Modelling long-term impact on soil acidification for three sites in Northern Europe. Report 1:1993, Department of Chemical Engineering II, Lund University. Lund, Sweden. 29 pp.

Joslin, J.D. & Wolfe, M.H. 1992. Red spruce soil solution chemistry and root distribution across a cloud water deposition gradient. Canadian Journal of Forest Research 22: 893-904.

Kaila, A. 1971. Aluminium and acidity in finnish soils. Journal of Scientific Agricultural Society of Finland 43: 11-19.

Kalisz, P.J. & Stone, E.L. 1980. Cation exchange capacity of acid forest humus layers. Soil Science Society of America Journal 44: 407-413.

Kämäri, J. 1990. Introduction. In: Kämäri, J. (Ed.) Impact Models to Assess Regional Acidification, pp. vii-xiv. Kluwer Academic Publishers, Dordrecht, Boston, London.

Kämäri, J., Seuna, P., Ahlberg, T., Holmberg, M., Kivinen, Y. Lepistö, A., Roos, J. and Soveri, J. 1992. The effect of climate change on the hydrology and material fluxes of forested catchments. In: Kanninen, M. & Anttila P. (Eds.) The Finnish Research Programme on Climate Change, Progress report. Publications of the Academy of Finland 3/1992, pp. 101-108.

Kämäri, J., Forsius, M., & Posch, M. 1993. Critical loads of sulfur and nitrogen for lakes II: Regional extent and variability in Finland. Water, Air and Soil Pollution 66: 77-96.

Kämäri, J., Rankinen, K., Finér, L., Piirainen, S. & Posch, M. 1998. Modelling the response of soil and runoff chemistry to forest harvesting in a low deposition area (Kangasvaara, Eastern Finland).

Kamprath, E.J. 1970. Exchangeable aluminum as a criterion for liming leached mineral soils. Soil Science Society of America Proceedings 34: 252-254.

Kareinen, T., Nissinen, A. & Ilvesniemi, H. 1998. Analysis of forest soil chemistry and hydrology with a dynamic model ACIDIC. Acta Forestalia Fennica, 262. 42 pp.

Karltun, E. & Gustafsson, J.P. 1993. Interference by organic complexation of Fe and Al on the SO_4^{2-} adsorption in Spodic B horizons in Sweden. Journal of Soil Science 44: 625-632.

Kauppi, P., Kämäri, J., Posch, M., Kauppi, L. & Matzner, E. 1986. Acidification of forest soils: Model development and application for analyzing impacts of acidic deposition in Europe. Ecological Modelling 33: 231-253.

Kauppi, P.E., Mielikäinen, K. & Kuusela, K. 1992. Biomass and carbon budget of European forests, 1971 to 1990. Science 256: 70-74.

Kelly, J.M. & Strickland, R.C. 1987. Soil nutrient leaching in response to simulated acid rain treatment. Water, Air and Soil Pollution 34: 167-181.

Kerr, H.W. 1928. The nature of base exchange and soil acidity. Journal of the American Society of Agronomy 20: 309-335.

Kissel, D.E., Gentsch, E.P. & Thomas, G.W. 1971. Hydrolysis of non-exchangeable acidity in soils during salt extractions of exchangeable acidity. Soil Science 111: 293-297.

Koivisto, P. 1959. Growth and yield tables. Communicationes Instituti Forestalis Fenniae 51.8.

Kortelainen, P. 1993. Contribution of organic acids to the acidity of Finnish lakes. Publications of the Water and Environment Research Institute, No 13. National Board of Waters and the Environment, Finland. 48 pp.

Kros, H. & Warfvinge, P. 1995. Evaluation of model behaviour with respect to the biogeochemistry at the Solling spruce site. Ecological Modelling 83: 255-262.

Kubin, E. 1995. The effect of clear-cutting, waste wood collecting and site preparation on the nutrient leaching to groundwater. In: Nilsson, L.O., Hüttl, R.F. & Johansson, U.T (Eds.) Nutrient Uptake and Cycling in Forest Ecosystems, pp. 661-670. Kluwer Academic Publishers, Dordrecht.

Kurka, A.-M. & Starr, M. 1997. Relationship between decomposition of cellulose in the soil and tree stand characteristics in natural boreal forests. Plant and Soil 197: 167-175.

Leinonen, L. & Juntto, S. 1992 (eds.) Air quality measurements 1991. Finnish Meteorological Institute, Helsinki.

Lepistö, A. 1996. Hydrological processes contributing to nitrogen leaching from forested catchments in Nordic conditions. Monographs of the Boreal Environment Research, No 1. Finnish Environment Institute, Helsinki. 72 pp.

Likens, G.E. & Bormann, F.H. 1977. Biogeochemistry of a Forested Ecosystem. Springer-Verlag, New York, Berlin.

Likens, G.E. & Bormann, F.H. 1995. Biogeochemistry of a Forested Ecosystem. Second Edition. Springer-Verlag, New York, Berlin.

Likens, G.E., Bormann, F.H. & Johnson, N.M. 1969. Nitrification: Importance to nutrient losses from a cutover forested ecosystem. Science 163: 1205-1206.

Lin, C. & Coleman, N.T. 1960. The measurement of exchangeable aluminum in soils and clays. Soil Science Society of America Proceedings 24: 444-446.

Linder, S. & Bergh, J. 1996. Näringsoptimering- granen växer ur produktionstabellerna. Fakta Skog 4. Sveriges Lantbruksuniversitet, Uppsala.

Lindsay, W.L. 1979. Chemical Equilibria in Soils. Wiley-Interscience, New York.

Liski, J., Ilvesniemi, H., Mäkelä, A. & Starr, M. 1998. Effect of soil age, forest fires and harvesting on the storage of organic carbon in podzolizing boreal forest soil. European Journal of Soil Science 49: 407-416.

Lövblad, G., Amann, M., Andersen, B., Hovmand, M., Joffre, S. & Pedersen, U. 1992. Deposition of sulfur and nitrogen in the Nordic countries: present and future. Ambio 21: 339-347.

Lundström, U. 1993. The role of organic acids in the soil solution chemistry of a podzolized soil. Journal of Soil Science 44: 121-135.

Lundström, U. & Öhman, L.-O. 1990. Dissolution of feldspars in the presence of natural organic solutes. Journal of Soil Science 41: 359-369.

Lundström, U., van Breemen, N. & Jongmans, A.G. 1995. Evidence for microbial decomposition of organic acids during podzolization. European Journal of Soil Science 46: 489-496.

Magid, J. & Christensen N. 1993. Soil solution sampled with and without tension in arable and heathland soils. Soil Science Society of America Journal 57: 1463-1469.

Magnusson, T. 1992. Temporal and Spatial Variation of the Soil Atmosphere in Forest Soils of Northern Sweden. Stencil No. 22, Department of Forest Site Research, Swedish University of Agricultural Sciences. ISSN 0280-9168.

Mäkelä, A. 1986. Implications of the pipe model theory on dry matter partitioning and height growth of trees. Journal of Theoretical Biology 123: 103-120.

Mälkönen, E. 1974. Annual primary production in some Scots pine stands. Communicationes Instituti Forestalis Fenniae, 84.5.

Mälkönen, E. & Kukkola, M. 1991. Effect of long-term fertilization on the biomass production and nutrient status of Scots pine stands. Fertilizer Research 27: 113-127.

Manley, E.P., Chesworth, W. & Evans, L.J. 1987. The solution chemistry of podzolic soils from the eastern Canadian shield; a thermodynamic interpretation of the mineral phases controlling soluble Al^{3+} and H_4SiO_4. Journal of Soil Science 38:39-51.

Marschner, H. 1986. Mineral nutrition of higher plants. Academic Press, London.

Marion, G.M., Hendricks, D.M., Dutt, G.R. & Fuller, W.H. 1976. Aluminum and silica solubility in soils. Soil Science 121: 76-82.

Martikainen, P. 1986. Nitrification in two fertilized pine forest soils. Academic dissertation. Department of General Microbiology, University of Helsinki. Helsinki.

Martin, A.E. & Reeve, R. 1958. Chemical studies of podzolic illuvial horizons. III. Titration curves of organic-matter suspensions. Journal of Soil Science 9: 89-100.

Matzner, E. & Ulrich, B. 1983. The turnover of protons by mineralization and ion uptake in a beech (*Fagus silvatica*) and a Norway spruce ecosystem. In: Ulrich, B. & Pankrath, J. (Eds.) Effects of Accumulation of Air Pollutants in Forest Ecosystems, pp. 93-103. D. Reidel Publishing Company, Dordrecht.

Matzner, E. & Murach, D. 1995. Soil changes induced by air pollutant deposition and their implication for forests in central Europe. Water, Air and Soil Pollution 85: 63-76.

Mayer, R. & Ulrich, B. 1977. Acidity of precipitation as influenced by the filtering of atmospheric sulphur and nitrogen compounds - its role in the element balance and effect on soil. Water, Air and Soil Pollution 7: 409-416.

McBride, M. B. 1994. Environmental Chemistry of Soils. Oxford University Press, New York.

McLean, E.O., Hourigan, W.R., Shoemaker, H.E. & Bhumbla, D.R. 1964. Aluminum in soils: V. Form of aluminum as a cause of soil acidity and a complication in its measurement. Soil Science 97: 119-126.

McLean, E.O., Reicosky, D.C. & Lakshmanan, C. 1965. Aluminum in soils: VII. Interrelationships of organic matter, liming, and extractable aluminum with “permanent charge” (KCl) and pH-dependent cation-exchange capacity of surface soils. Soil Science Society of America Proceedings 29: 374-378.

Melillo, J.M., Aber, J.D. & Muratore, J.F. 1982. Nitrogen and lignin control of hardwood leaf litter decomposition dynamics. Ecology 63: 621-626.

Melin, J. 1986. Turnover and distribution of fertilizer nitrogen in three coniferous ecosystems in central Sweden. Rapport nr 55, Department of Forest Soils, Swedish University of Agricultural Sciences. Uppsala.

Melin, J. & Nômmik, H. 1988. Fertilizer nitrogen distribution in a *Pinus sylvestris*/*Picea abies* ecosystem, Central Sweden. Scandinavian Journal of Forest Research 3: 3-15.

Mengel, K. & Kirkby, E.A. 1987. Principles of plant nutrition. 4th ed. International Potash Institute, Bern.

Mohren, G.M.J. & Ilvesniemi, H. 1995. Modelling effects of soil acidification on tree growth and nutrient status. Ecological Modelling 83: 263-272.

Moldan, F. & Wright, R.F. 1998. Episodic behaviour of nitrate in runoff during six years of nitrogen addition to the NITREX catchment at Gårdsjön, Sweden. Proceedings of the first international nitrogen conference, pp. 439-444. Elsevier, Amsterdam.

Mulder, J. & van Breemen, N. 1987. Differences in aluminum mobilization in spodosols in New Hampshire (USA) and in the Netherlands as a result of acid deposition. In: Hutchinson, T.C. and Meema, K.M. (Eds.) Effects of atmospheric pollutants on forests, wetlands and agricultural ecosystems, pp. 361-375. NATO ASI Series, Vol. G 16. Springer-Verlag, Berlin.

Mulder, J. & Stein, A. 1994. The solubility of aluminum in acidic forest soils: Long-term changes due to acid deposition. Geochimica et Cosmochimica Acta 58: 85-94.

Neal, C. 1992. Describing anthropogenic impacts on stream water quality: the problem of integrating soil water chemistry variability. Science of Total Environment 115: 207-218.

Neal, C. & Robson, A.J. 1994. Integrating soil water chemistry variations at the catchment level within a cation exchange model. Science of Total Environment 144: 93-102.

Neal, C. & Robson, A.J. 1997. Integrating variations of soil-adsorbed cations into a cation exchange model. Science of Total Environment 199: 277-292.

Neal, C., Reynolds, B. Stevens, P.A. & Hornung, M. 1989. Hydrogeochemical controls for inorganic aluminium in acidic stream and soil waters at two upland catchments in Wales. Journal of Hydrology 106: 155-175.

Nikinmaa, E. 1992. Analyses of the growth of Scots pine: Matching structure with function. Acta Forestalia Fennica, 235.

Nilsson, J. & Grennfelt, P. 1988. Critical Loads for Sulphur and Nitrogen. Miljørapport 15/1988. Nordic Council of Ministers, Copenhagen.

Nilsson, S.I. & Bergkvist, B 1983. Aluminium chemistry and acidification processes in a shallow podzol on the Swedish westcoast. Water, Air and Soil Pollution 20: 311-329.

Nilsson, S.I., Miller, H.G. & Miller, J.D. 1982. Forest growth as a possible cause of soil and water acidification: an examination of the concepts. Oikos 39: 40-49.

Nissinen, A. 1997. Relation between pore size and chemical composition of solution in the pore - a new challenge in forest soil chemistry. In: Kulmala, M. & Hämeri, K. (Eds.) Seminar on Environmental Analysis, pp. 29-35. Report Series in Aerosol Science 34. Finnish Association for Aerosol Research, Helsinki.

Nissinen, A. & Ilvesniemi, H. 1990. Effects of acid deposition on exchangeable cations, acidity and aluminium solubility in forest soils and soil solution. In: Kauppi, P., Anttila, P. & Kenttämies, K. (Eds.) Acidification in Finland, pp. 287-304. Springer-Verlag, Berlin, Heidelberg.

Nohrstedt, H.-Ö. 1985. Nonsymbiotic nitrogen fixation in the topsoil of some forest stands in central Sweden. Canadian Journal of Forest Research 15: 715-722.

Nohrstedt, H.-Ö. 1992. Soil water chemistry as affected by liming and N fertilisation at two Swedish coniferous forest sites. Scandinavian Journal of Forest Research 7: 143-153.

Nohrstedt, H.-Ö. 1998. Residual effects of N fertilization on soil-water chemistry and ground vegetation in a Swedish Scots pine forest. Environmental Pollution 102 S1: 77-83.

Nômmik, H. & Möller, G. 1981. Nitrogen recovery in soil and needle biomass after fertilization of a Scots pine stand, and growth responses obtained. Studia Forestalia Suecica, Nr 159. Swedish University of Agricultural Sciences, Uppsala.

Nordstrom, D.K. 1982. The effect of sulfate on aluminum concentrations in natural waters: Some stability relations in the system Al_2O_3-SO_3-H_2O at 298 K. Geochimica Cosmochica Acta 46: 681-692.

Norfleet, M.L., Karathanasis, A.D. & Smith, B.R. 1993. Soil solution composition relative to mineral distribution in Blue Ridge Mountain soil. Soil Science Society of America Journal 57: 1375-1380.

Nye, P., Craig, D., Coleman, N.T. & Ragland, J.L. 1961. Ion exchange equilibria involving aluminum. Soil Science Society of America Proceedings 25: 14-17.

Ochs, M., Brunner, I., Stumm, W. & Cosovic, B. 1993. Effects of root exudates and humic substances on weathering kinetics. Water, Air and Soil Pollution 68: 213-229.

Oden, S. 1968. The acidification and precipitation and its consequences in the natural environment. Ecology Committee Bulletin No 1. Swedish National Scientific Research Council, Stockholm. 87 pp.

Oksanen, T., Mäkelä, A. & Hari, P. 1983. Happaman sateen aiheuttama ravinteiden huuhtoutuminen metsämaasta - simulointimalli. In: Hari, P. (Ed.) Energiatuotannosta peräisin olevien ilman epäpuhtauksien vaikutus metsän tuotokseen, III 1 (49 pp.) Research notes 44, Department of Silviculture, University of Helsinki, Helsinki. (In Finnish).

Overrein, L.N., Seip, H.M. & Tollan, A. 1981. Acid precitation - effects on forest and fish. Final Report of the SNSF-project 1972-1980. Research Report, Fagrapport FR 1980. 2nd edition. Oslo, Ås. 175 pp.

Parnas, H. 1975. Model for decomposition of organic material by microorganisms. Soil Biology and Biochemistry 7: 161-169.

Parton, W.J., Schimel, D.S., Cole, C.V. & Ojima, D.S. 1987. Analysis of factors controlling soil organic matter levels in Great Plains grasslands. Soil Science Society of America Journal 51: 1173-1179.

Persson, H. 1980. Spatial distribution of fine-root growth, mortality and decomposition in a young Scots pine stand in Central Sweden. Oikos 34: 77-87.

Pierre, W.H. & Scarseth, G.D. 1931. Determination of the percentage base saturation of soils and its value in different soils at definite pH values. Soil Science 31: 99-114.

Pionke, H.B. & Corey, R.B. 1967. Relations between acidic aluminum and soil pH, clay and organic matter. Soil Science Society of America Proceedings 31: 749-752.

Pleysier, J. L., Juo, A. S. R. & Herbillon, A. J. 1979. Ion exchange equilibria involving aluminum in a kaolinitic Ultisol. Soil Science Society of America Journal 43: 875-880.

Ponette, Q., Andre, D. & Dufey, J.E. 1996. Chemical significance of aluminium extracted from three horizons of an acid forest soil, using chloride salt solutions. European Journal of Soil Science 47: 89-95.

Posch, M., Falkengren-Grerup, U. & Kauppi, P. 1989. Application of two soil acidification models to historical soil chemistry data from Sweden. In: Kämäri, J., Brakke, D.F., Jenkins, A., Norton, S.A. & Wright, R.F. (Eds.) Regional acidification models, pp. 241-251. Springer-Verlag, Berlin, Heidelberg.

Prenzel, J. 1983. A mechanism for storage and retrieval of acid in acid soils. In: Ulrich, B. & Pankrath, J. (Eds.) Effects of Accumulation of Air Pollutants in Forest Ecosystems, pp. 157-170. Reidel Publishing Company, Dordrecht.

Prietzel, J. & Feger, K.H. 1992. Dynamics of aqueous aluminum species in a podzol affected by experimental $MgSO_4$ and $(NH_4)_2SO_4$ treatments. Water, Air and Soil Pollution 65: 153-173.

Räisänen, M.-L. 1996. Geochemistry of podzolized tills and implications for Al mobility near industrial sites: a study in Kuopio Eastern Finland. Bulletin 387, Geological Survey of Finland, Espoo.

Rasmussen, P.E., Schiff, S.L. & Nesbitt, H.W. 1991. The determination of exchangeable cations in acid soils: Errors caused by weathering reactions during neutral salt extraction. Canadian Journal of Soil Science 71: 155-163.

Rasmussen, L., Hultberg, H. & Cosby, B.J. 1995. Experimental studies and modelling of enhanced acidification and recovery. Water, Air and Soil Pollution 85: 77-88.

Reuss, J.O. 1977. Chemical and biological relationships relevant to the effect of acid rainfall on the soil-plant system. Water, Air and Soil Pollution 7: 461-478.

Reuss, J.O. 1983. Implications of the calcium–aluminum exchange system for the effect of acid precipitation on soils. Journal of Environmental Quality 12: 591-595.

Reuss, J.O. & Johnson, D.W. 1985. Effect of soil processes on the acidification of water by acid deposition. Journal of Environmental Quality 14: 26-31.

Reuss, J.O. & Walthall, P.M. 1990. Soil reaction and acidic deposition. In: Norton, S.A., Lindberg, S.E. & Page, A.L. (Eds.) Acidic precipitation. Volume 4. Soils, aquatic processes, and lake acidification, pp. 1- 33. Springer-Verlag, New York, Berlin, Heidelberg.

Reuss, J.O., Christophersen, N. & Seip, H.M. 1986. A critique of models for freshwater and soil acidification. Water, Air and Soil Pollution 30: 909-930.

Reuss, J.O., Cosby, B.J. & Wright, R.F. 1987. Chemical processes governing soil and water acidification. Nature 329: 27-32.

Reuss, J.O., Walthall, P.M., Roswall, E.C. & Hopper, R.W.E. 1990. Aluminum solubility, calcium-aluminum exchange, and pH in acid forest soils. Soil Science Society of America Journal 54: 374-380.

Reynolds, B. 1984. A simple method for the extraction of soil solution by high speed centrifugation. Plant and Soil 78: 437-440.

Rich, C.I. 1960. Aluminum in interlayers of vermiculite. Soil Science Society of America Proceedings 24: 26-32.

Riha, S.J., Campbell, G.S. & Wolfe, J. 1986. A model of competition for ammonium among heterotrophs, nitrifiers, and roots. Soil Science Society of America Journal 50: 1463-1466.

Rodhe, H., Langner, J., Gallardo, L. & Kjellström, E. 1995. Global scale transport of acidifying pollutants. Water, Air and Soil Pollution 85: 37-50.

Ross, D.S., Bartlett, R.J. & Magdoff, F.R. 1991. Exchangeable cations and the pH-independent distribution of cation exchange capacities in Spodosols of a forested watershed. In: Wright, R.J., Baligar, V.C. & Murrmann, R.P. (Eds.) Plant-soil interactions at low pH: Proceedings of the 2nd international symposium on plant-soil interactions at low pH, pp. 81-92. Developments in Plant and Soil Sciences 45. Kluwer Academic Publishers, Dordrecht.

Saukkonen, S. & Kortelainen, P. 1995. Metsätaloustoimenpiteiden vaikutus ravinteiden ja orgaanisen hiilen huuhtoutumiseen. In: Saukkonen, S. & Kenttämies, K. (Eds.) Metsätalouden vesistövaikutukset ja niiden torjunta, pp. 15-32. Suomen ympäristö 2. Suomen ympäristökeskus, Helsinki. (In Finnish).

Savolainen, I. & Tähtinen, M. 1990. Sulphur dioxide and nitrogen oxide emission scenarios for Finland. In: Kauppi, P., Anttila, P. & Kenttämies, K. (Eds.) Acidification in Finland, pp. 1-19. Springer-Verlag, Berlin, Heidelberg.

Schnitzer, M. & Skinner, I.M. 1963. Organo-metallic interactions in soils, 2. Reactions between different forms of iron and aluminum and the organic matter of a podzol Bh horizon. Soil Science 96: 181-186.

Schulze, E.-D., Oren, R. & Lange, O.L. 1989. Processes leading to forest decline: A synthesis. In: Schulze, E.-D., Lange, O.L. & Oren R. (eds.) Forest Decline and Air Pollution: A Study of Spruce (*Picea abies*) on acid soils, pp. 459-468. Springer-Verlag, Berlin.

Shen, M.J. & Rich, C.I. 1962. Aluminum fixation in montmorillonite. Soil Science Society of America Proceedings 26: 33-36.

Skeen, J.B. & Sumner, M.E. 1965. Measurement of exchangeable aluminum in acid soils. Nature 208: 712.

Skeffington, R.A. & Brown, K.A. 1986. The effect of five years treatment on leaching, soil chemistry and weathering of a humo-ferric podzol. Water, Air and Soil Pollution 31: 891-900.

Skyllberg, U. 1995. Solution/soil ratio and release of cations and acidity from spodosol horizons. Soil Science Society of America Journal 59: 786-795.

Smith, O.L. 1982. Soil Microbiology: A model of decomposition and nutrient cycling. CRC series in mathematical models in microbiology. Boca Raton CRC Press. ISBN 0-8493-5952-X. 273 pp.

Sogn, T.A. 1993. A test of chemical equilibrium equations and assumptions commonly used in soil-oriented charge balance models for soil and freshwater acidification. Ecological Modelling 70: 221-238.

Soon, Y.K. 1993. Fractionation of extractable aluminum in acid soils: A review and a proposed procedure. Communications in Soil Science and Plant Analysis 24: 1683-1708.

Soon, Y.K. 1995. Forms of extractable aluminium in Canadian acid soils and their relations to plant growth. In: Date, R.A. et al. (Eds.) Plant Soil Interactions at Low pH: Principles and management, pp. 65-70. Developments in Plant and Soil Sciences 64. Kluwer Academic Publishers, Dordrecht.

Starr, M., Westman, C.J. & Ala-Reini, J. 1996. The acid buffer capacity of some Finnish forest soils: Results of acid addition laboratory experiments. Water, Air and Soil Pollution 89: 147-156.

Starr, M.R. 1985. Variation in the quality of tension lysimeter soil water samples from a finnish forest soil. Soil Science 140: 453-461.

Stephens, F.R. 1969. Source of cation exchange capacity and water retention in southeast Alaskan spodosols. Soil Science 108: 429-431.

Stumm, W. & Morgan, J.J. 1981. Aquatic Chemistry. John Wiley and Sons, New York.

Sutton, M.A., Pitcairn, C.E.R. & Fowler, D. 1983. The exchange of ammonia between the atmosphere and plant communities. In: Begon, M. & Fitter, A.H. (Eds.) Advances in Ecological Research, Vol. 24. Academic Press, Harcourt Brace & Company, Publishers, London.

Sverdrup, H. & Warfvinge, P. 1993a. Calculating field weathering rates using a mechanistic geochemical model PROFILE. Applied Geochemistry 8: 273-283.

Sverdrup, H. & Warfvinge P. 1993b. The effect of soil acidification on the growth of trees, grass and herbs as expressed by the (Ca+Mg+K)/Al ratio. Reports in Ecology and Environmental Engineering 1993:2. Lund University, Lund.

Tamm, C.F. & Hallbäcken, L. 1988. Changes in soil acidity in two forest areas with different acid deposition: 1920s to 1980s. Ambio 17: 56-61.

Tamminen, P. 1991. Expression of soil nutrient status and regional variation in soil fertility of forested sites in southern Finland. Folia Forestalia, No 777. 40 pp.

Tamminen, P. & Starr, M. 1989. A survey of forest soil properties related to soil acidification in southern Finland. In: Kauppi, P., Anttila, P. & Kenttämies, K. (Eds.) Acidification in Finland, pp. 237-252. Springer-Verlag, Berlin, Heidelberg.

Thomas, G.W. 1960. Forms of aluminum in cation exchangers. Transactions of 7th International Congress of Soil Science 2: 364-369. Madison, WI.

Thomas, G.W. 1977. Historical developments in soil chemistry: Ion exchange. Soil Science Society of America Journal 41: 230-238.

Thomas, G.W. 1982. Exchangeable cations. In: Page, A.L., Miller, A.H. & Keeney, D.R. (Eds.) Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties, 2nd edition, pp. 159-165. American Society of Agronomy, Madison, WI.

Thomas, G.W. 1988. Beyond exchangeable aluminum: another ride on the merry-go-round. Communications in Soil Science and Plant Analysis 19: 833-856.

Thomas, G.W. & Hargrove, W.L. 1984. The Chemistry of soil acidity. In: Adams, F. (Ed.) Soil acidity and liming, Second edition, pp. 3-56. Agronomy No 12. American Society of Agronomy, Madison, WI.

Thompson, H.S. 1850. On the absorbent power of soils. Journal of the Royal Agricultural Society of England 11: 68-74.

Tietema, A., Boxman, A.W., Bredemeier, M., Emmett, B.A., Moldan, F., Gundersen, P., Schleppi, P. & Wright, R.F. 1998. Nitrogen saturation experiments (NITREX) in coniferous forest ecosystems in Europe: a summary of results. Proceedings of the first international nitrogen conference, pp. 433-437. Elsevier, Amsterdam.

Tiktak, A. & van Grinsven, H.J.M. 1995. Review of sixteen forest-soil-atmosphere models. Ecological Modelling 83: 35-53.

Tiktak, A., Bredemeier, M. & van Heerden, K. 1995a. The Solling dataset. Site characteristics, monitoring data and deposition scenarios. Ecological Modelling 83: 17-34.

Tiktak, A., van Grinsven, J.J.M., Groenenberg, J.E., van Heerden, C., Janssen, P.H.M., Kros, J., Mohren, G.M.J., van der Salm, C., van de Veen, J.R. & de Vries, W.: 1995b, Application of three Forest-Soil-Atmosphere models to the Speuld experimental forest, Report no. 733001003, RIVM, Bilthoven, Netherlands.

Tipping, E., Woof, C. & Hurley, M.A. 1991. Humic substances in acid surface water; modelling aluminium binding, contribution to ionic charge balance, and control of pH. Water Research 25: 425-435.

Tørseth, K. & Semb, A. 1998. Deposition of nitrogen and other major inorganic compounds in Norway, 1992-1996. Proceedings of the first international nitrogen conference, pp. 299-304. Elsevier, Amsterdam.

Tuovinen, J.P., Kangas, L. & Nordlund, G. 1990. Model calculations of sulphur and nitrogen deposition in Finland. In: Kauppi, P., Anttila, P. & Kenttämies, K. (eds.), Acidification in Finland, pp. 167-197. Springer-Verlag, Berlin, Heidelberg.

Turner, R. C. 1965. A study of the lime potential: 5. Significance of the lime potential in aqueous acid clay systems. Soil Science 100: 14-19.

Ulrich, B. 1983a. A concept of forest ecosystem stability and of acid deposition as driving force for destabilization. In: Ulrich, P. & Pankrath, J. (eds.) Effects of Accumulation of Air Pollutants in Forest Ecosystems, pp. 1-29. Reidel, Dordrecht.

Ulrich, B. 1983b. Interaction of forest canopies with atmospheric constituents: SO_2, alkali and earth alkali cations and chloride. In: Ulrich, P. & Pankrath, J. (eds.) Effects of Accumulation of Air Pollutants in Forest Ecosystems, pp. 33-45. Reidel, Dordrecht.

Ulrich, B. 1983c. Soil acidity and its relations to acid deposition. In: Ulrich, P. & Pankrath, J. (eds.) Effects of Accumulation of Air Pollutants in Forest Ecosystems, pp. 127-146. Reidel, Dordrecht.

Upchurch, W.J., Chowdury, M.Y. & Marshall, C.E. 1973. Lysimetric and chemical investigations of pedological changes, Part 1. Lysimeters and their drainage waters. Soil Science 116: 266-281.

Urvas, L. & Erviö, R. 1974. Influence of the soil type and the chemical properties of soil on the determining of the forest type. Journal of the Scientific Agricultural Society of Finland 46: 307-319.

van Breemen, N. 1973. Dissolved aluminum in acid sulfate soils and in acid mine waters. Soil Science Society of America Proceedings 37: 694-697.

van Breemen, N., Mulder, J. & Driscoll, C.T. 1983. Acidification and alkalinization of soils. Plant and Soil 75: 283-308.

van Breemen, N., Driscoll, C.T. & Mulder, J. 1984. Acidic deposition and internal proton sources in acidification of soils and waters. Nature 307:599-604.

van Oene, H. & de Vries, W. 1994. Comparison of measured and simulated changes in base cation amounts using a one-layer and a multi-layer soil acidification model. Water, Air and Soil Pollution 72: 41-65.

Vanninen, P., Ylitalo, H., Sievänen, R. & Mäkelä, A. 1996. Effects of age and site quality on the distribution of biomass in Scots pine (*Pinus sylvestris* L.). Trees 10: 231-238.

Vanselow, A.P.1932. Equilibria of the base-exchange reactions of bentonites, permutites, soil colloids, and zeolites. Soil Science 33: 95-113.

Vapaavuori, E.M., Vuorinen, A.H., Aphalo, P.J. & Smolander, H. 1995. Relationship between net photosynthesis and nitrogen in Scots pine: Seasonal variation in seedlings and shoots. Plant and Soil 168-169: 263-270.

Veith, J.A. 1977. Basicity of exchangeable aluminum, formation of gibbsite, and composition of the exchange acidity in the presence of exchangers. Soil Science Society of America Journal 41: 865-870.

Vietch, F.P. 1904. Comparison of methods for the estimation of soil acidity. Journal of the American Chemical Society 26: 637-662.

Viro, P.J. 1955. Investigations on forest litter. Communicationes Instituti Forestalis Fenniae, 45.6.

Vitousek, P.M., Gosz, J.R., Grier, C.C., Melillo, J.M., Reiners, W.A. & Todd, R.L. 1979. Nitrate losses from disturbed ecosystems. Science 204: 469-474.

von Uexküll, H.R. & Mutert, E. 1995. Global extent, development and economic impact of acid soils. Plant and Soil 171: 1-15.

Wang, C. 1981. Extractable Al, Fe and Mn. In: A. McKeague, J. (Ed.) Manual on Soil Sampling and Methods of Analysis, 2nd Edition reprinted, pp. 98-105. Canadian Society of Soil Science, Ottawa.

Warfvinge, P., Holmberg, M., Posch, M. & Wright, R.F. 1992. The use of dynamic models to set target loads. Ambio 21: 369-376.

Warfvinge, P., Falkengren-Grerup, U., Sverdrup, H. & Andersen, B. 1993. Modelling long-term cation supply in acidified forest stands. Environmental Pollution 80: 209-221.

Wells, C.G. & Davey, C.B. 1966. Cation exchange characteristics of forest floor materials. Soil Science Society of America Proceedings 30: 399-402.

Wesselink, L.G., van Breemen, N., Mulder, J. & Janssen, P.H. 1996. A simple model of soil organic matter complexation to predict the solubility of aluminium in acid forest soils. European Journal of Soil Science 47: 373-384.

Westling, H. & Hultberg, H. 1990/91. Liming and fertilization of acid forest soil: Short-term effects on runoff from small catchments. Water, Air and Soil Pollution 54: 391-407.

Westman, C.J. & Jauhiainen, S. 1998. Soil acidity in 1970 and 1989 in a coniferous forest in southwest Finland. Canadian Journal of Soil Science 78: 477-479.

Westman, C.J., Fritze, H., Helmisaari, H.S., Ilvesniemi, H., Lehto, T., Liski, J., Mecke, M., Pietikäinen, J. & Smolander, A. 1996. Carbon in boreal coniferous forest soil. In: Roos, J. (Ed.) The Finnish Research Programme on Climate Change, pp. 223-231. Publications of the Academy of Finland 4/96. Edita Ltd., Helsinki.

Wolt, J. & Graveel, J.G. 1986. A rapid routine method for obtaining soil solution using vacuum displacement. Soil Science Society of America Journal 50: 602-605.

Wright, R.F., Lotse, E. & Semb, A. 1988. Reversibility of acidification shown by whole-catchment experiments. Nature 334: 670-675.

Wright, R.F., Roelofs, J.G.M., Bredemeier, M., Blanck, K., Boxman, A.W., Emmett, B.A., Gundersen, P., Hultberg, H., Kjønaas, O.J., Moldan, F., Tietema, A., van Breemen, N. & van Dijk, H.F.G. 1995. NITREX: responses of coniferous forest ecosystems to experimentally changed deposition of nitrogen. Forest Ecology and Management 71: 163-169.

Yarie, J., van Cleve, K., Dyrness, C.T., Oliver, L., Levison, J. & Erickson, R. 1993. Soil-solution chemistry in relation to forest succession on the Tanana River floodplain, interior Alaska. Canadian Journal of Forest Research 23: 928-940.

Zabowski, D. 1989. Limited release of soluble organics from roots during the centrifugal extraction of soil solutions. Soil Science Society of America Journal 53: 977-979.

Zabowski, D. & Ugolini, F. C. 1990. Lysimeter and centrifuge soil solutions: seasonal differences between methods. Soil Science Society of America Journal 54: 1130-1135.

Zabowski, D. & Sletten, R.S. 1991. Carbon dioxide degassing effects on the pH of Spodosol soil solutions. Soil Science Society of America Journal 55. 1456-1461.

Zhu, W. & Ehrenfeld, J.G. 1996. The effects of mycorrhizal roots on litter decomposition, soil biota, and nutrients in a spodosolic soil. Plant and Soil 179: 109-118.

Appendix 1. Measured bulk deposition and calculated deposition into a forest in southern Finland (Jokioinen) and in northern Finland (Sodankylä and Kevo)

Station / Measuring program	Year	Rain	H+	Na+	K+	Ca^{2+}	Mg^{2+}	NH_4^+ -N
Equivalent mass, mg $mmol_c^{-1}$:			1.0	23.0	39.1	20.0	12.2	14.0
		mm (l m^{-2})	$mmol_c$ m^{-2}	$mmol_c$ m^{-2}	$mmol_c$ m^{-2}	$mmol_c$ m^{-2}	$mmol_c$ m^{-2}	$mmol_c$ m^{-2}
Jokioinen /	1989	631	28.2	4.6	1.5	6.4	1.9	24.1
BAPMON	1990	669	23.6	9.1	1.9	4.3	2.3	19.5
	1991	681	23.2	9.1	1.6	5.2	2.6	17.0
	1992	574	22.4	7.0	0.9	5.5	2.1	16.4
	average	*638.8*	*24.4*	*7.5*	*1.5*	*5.4*	*2.2*	*19.3*
	mg m^{-2}		24.4	171.8	57.3	107.5	26.8	269.5
	(1+filter factor)		filtered SO_4 [a]	1.6	1.6	1.6	1.6	1.0
Deposition into forest, mg m^{-2}			44.0	274.8	91.6	172.0	42.8	269.5
		mm (l m^{-2})	$mmol_c$ m^{-2}	$mmol_c$ m^{-2}	$mmol_c$ m^{-2}	$mmol_c$ m^{-2}	$mmol_c$ m^{-2}	$mmol_c$ m^{-2}
Sodankylä /	1989	493	10.9	2.1	1.0	1.7	0.7	5.3
BAPMON	1990	437	9.3	2.4	0.7	1.1	0.4	2.9
	1991	449	10.3	4.4	1.3	1.7	0.6	5.3
	1992	788	11.9	4.2	0.9	2.1	0.9	7.6
	average	*541.8*	*10.6*	*3.3*	*1.0*	*1.7*	*0.6*	*5.3*
	mg m^{-2}		10.6	75.8	39.3	33.5	7.8	73.8
	(1+filter factor)		filtered SO_4 [a]	1.6	1.6	1.6	1.6	1.0
Deposition into forest, mg m^{-2}			17.6	121.2	62.8	53.6	12.4	73.8
		mm (l m^{-2})	$mmol_c$ m^{-2}	$mmol_c$ m^{-2}	$mmol_c$ m^{-2}	$mmol_c$ m^{-2}	$mmol_c$ m^{-2}	$mmol_c$ m^{-2}
Kevo /	1989	500	10.2	5.5	1.7	2.6	2.0	4.0
National	1990	287	4.7	9.5	0.7	1.2	2.0	1.1
	1991	429	6.5	7.3	0.8	1.5	1.5	0.7
	1992	545	7.9	12.6	0.8	1.8	2.8	2.1
	average	*440.3*	*7.3*	*8.7*	*1.0*	*1.8*	*2.1*	*2.0*
	mg m^{-2}		7.3	200.8	39.3	36.0	25.0	27.8
	(1+filter factor)		filtered SO_4 [a]	1.6	1.6	1.6	1.6	1.0
Deposition into forest, mg m^{-2}			12.7	321.2	62.8	57.6	40.0	27.8

[a] Filter factor is not assumed for H^+, but the additional (to bulk deposition) H^+ inflow to forest is assumed to be equal to the filtered SO_2 (as $mmol_c$ m^{-2} SO_4).

Appendix 1 continues.

Station / Measuring program	Year	NO_3^- -N	SO_4^{2-} -S	Cl-	pH	Charge of cations	anions	HCO_3^- [b]	H+
Equivalent mass, mg $mmol_c^{-1}$:		14.0	16.0	35.5					
		$mmol_c\ m^{-2}$	$mmol_c\ m^{-2}$	$mmol_c\ m^{-2}$		$mmol_c\ m^{-2}$		$mmol_c\ m^{-2}$	$mmol\ l^{-1}$
Jokioinen / BAPMON	1989	19.1	39.9	7.0	4.3	66.6	66.0	0.00	0.045
	1990	18.6	29.4	9.1	4.5	60.7	57.0	0.00	0.035
	1991	17.4	31.5	9.4	4.5	58.7	58.3	0.00	0.034
	1992	17.8	29.9	6.4	4.4	54.4	54.0	0.00	0.039
	average	*18.2*	*32.7*	*8.0*	*4.4*	*60.1*	*58.9*	*0.0*	*0.038*
	mg m^{-2}	254.8	523.8	283.0					
	(1+filter factor)	1.0	1.6	1.6					
Deposition into forest, mg m^{-2}		254.8	838.0	452.8					
		$mmol_c\ m^{-2}$	$mmol_c\ m^{-2}$	$mmol_c\ m^{-2}$					
Sodankylä / BAPMON	1989	5.9	12.5	3.2	4.7	21.7	21.6	0.00	0.022
	1990	5.1	8.7	2.1	4.7	16.8	15.9	0.00	0.021
	1991	6.5	11.3	4.1	4.6	23.6	21.9	0.00	0.023
	1992	7.9	14.1	3.2	4.8	27.8	25.2	0.00	0.015
	average	*6.3*	*11.7*	*3.1*	*4.7*	*22.5*	*21.1*	*0.0*	*0.020*
	mg m^{-2}	88.8	187.0	111.5					
	(1+filter factor)	1.0	1.6	1.6					
Deposition into forest, mg m^{-2}		88.8	299.2	178.4					
		$mmol_c\ m^{-2}$	$mmol_c\ m^{-2}$	$mmol_c\ m^{-2}$					
Kevo / National	1989	4.0	14.9	6.9	4.7	26.0	25.8	0.00	0.020
	1990	2.9	4.2	9.9	4.8	19.2	17.0	0.00	0.016
	1991	2.1	7.2	6.9	4.8	18.3	16.1	0.00	0.015
	1992	3.7	9.4	13.1	4.8	28.0	26.2	0.00	0.014
	average	*3.2*	*8.9*	*9.2*	*4.8*	*22.9*	*21.3*	*0.0*	*0.017*
	mg m^{-2}	44.3	143.3	326.3					
	(1+filter factor)	1.0	1.6	1.6					
Deposition into forest, mg m^{-2}		44.3	229.2	522.0					

[b] Calculated assuming pCO_2 0.000350 atm.

References:

Leinonen, L. & Juntto, S. 1990 (eds.). Air Quality Measurements 1989. Finnish Meteorological Institute. Helsinki.

Leinonen, L. & Juntto, S. 1991 (eds.). Air Quality Measurements 1990. Finnish Meteorological Institute. Helsinki.

Leinonen, L. & Juntto, S. 1992 (eds.). Air Quality Measurements 1991. Finnish Meteorological Institute. Helsinki.

Leinonen, L. 1993 (ed.). Air Quality Measurements 1992. Finnish Meteorological Institute. Helsinki.

Appendix 2. Soil exchangeable cations and base saturation.

Mean and standard error of mean have been calculated from the values representing different sampling times. The number of observations (*n*) varies because exchangeable cations were measured only from the samples which yielded a solution sample by centrifuging. Sites which differ significantly ($p<0.05$) with respect to CEC_e and BS in each horizon are shown with differing letters.

Site	Horizon	H^+	Al^{3+}	EA	Ca^{2+}
		--------------------------------------	$mmol_c\ kg^{-1}$		--
		a			
S1	O	45.2 ± 1.91	31.8 ± 2.44	87.8 ± 11.4	194.3 ± 16.6
	Ah	4.59 ± 0.22	48.7 ± 1.25	54.0 ± 1.04	14.6 ± 2.45
	Bw1	2.28 ± 0.44	35.6 ± 4.98	37.5 ± 5.45	5.69 ± 0.89
	Bw2	0.82 ± 0.06	11.1 ± 0.11	11.9 ± 0.41	7.60 ± 1.56
	C	0.28 ± 0.03	0.71 ± 0.14	1.90 ± 0.32	55.3 ± 4.10
S2	O	42.2 ± 2.54	25.1 ± 1.69	75.6 ± 4.77	133.3 ± 3.9
	E	5.78 ± 0.53	26.0 ± 0.88	32.4 ± 0.87	7.87 ± 1.00
	Bs1	2.04 ± 0.30	24.0 ± 1.38	26.4 ± 1.32	3.78 ± 0.57
	Bs2	0.43 ± 0.04	8.89 ± 1.40	9.29 ± 1.19	1.98 ± 0.20
	C	0.56 ± 0.04	7.30 ± 0.64	8.14 ± 0.46	14.4 ± 2.25
S3	O	62.2 ± 5.94	17.1 ± 1.36	84.4 ± 7.14	237.6 ± 17.7
	E	8.14 ± 0.93	22.3 ± 2.33	30.3 ± 1.40	12.3 ± 2.06
	Bs1	1.80 ± 0.16	23.5 ± 2.63	24.9 ± 2.19	4.50 ± 0.61
	Bs2	0.46 ± 0.06	9.29 ± 1.46	9.64 ± 1.40	2.26 ± 0.36
	C	0.25 ± 0.02	3.02 ± 0.72	3.76 ± 0.65	1.26 ± 0.29
J1	O	90.4 ± 1.56	27.9 ± 5.66	118.7 ± 3.42	101.9 ± 2.7
	E	7.86 ± 0.72	24.4 ± 2.03	31.4 ± 2.91	4.96 ± 0.87
	Bs1	1.20 ± 0.19	25.2 ± 2.76	25.3 ± 2.35	1.90 ± 0.54
	Bs2	0.12 ± 0.02	0.53 ± 0.13	1.06 ± 0.33	1.78 ± 0.47
	C	0.11 ± 0.01	0.43 ± 0.07	1.08 ± 0.18	0.63 ± 0.13
J2	O	117.3 ± 4.03	32.9 ± 4.67	145.3 ± 5.52	72.0 ± 8.4
	E	5.68 ± 0.48	15.1 ± 1.04	20.1 ± 1.56	0.97 ± 0.06
	Bs1	0.74 ± 0.13	18.1 ± 1.66	18.4 ± 1.73	0.72 ± 0.08
	Bs2	0.12 ± 0.03	1.03 ± 0.27	1.22 ± 0.38	0.53 ± 0.07
	C	0.06 ± 0.02	0.40 ± 0.04	0.39 ± 0.25	0.77 ± 0.06
J3	O	91.8 ± 16.2	42.5 ± 0.93	127.7 ± 14.3	58.6 ± 14.8
	E	5.55 ± 0.96	23.7 ± 2.15	29.3 ± 1.12	1.33 ± 0.22
	Bs1	0.71 ± 0.19	12.3 ± 2.64	13.9 ± 2.36	0.36 ± 0.08
	Bs2	0.22 ± 0.04	3.01 ± 0.65	3.04 ± 0.78	0.19 ± 0.03
	C	0.06 ± 0.03	0.34 ± 0.04	0.41 ± 0.30	0.26 ± 0.04

Appendix 2 continues.

Site	Horizon	Mg^{2+}	K^+	CEC_e	BS	*n*
		-----------------[a]	mmol$_c$ kg^{-1}	-----------------------		
S1	O	24.7 ± 1.52	11.7 ± 0.95	307.7 ± 14.6 a	0.75 ± 0.03 a	4
	Ah	3.40 ± 0.30	1.29 ± 0.16	72.6 ± 3.2 a	0.26 ± 0.03 ab	4
	Bw1	1.82 ± 0.16	0.84 ± 0.07	46.3 ± 6.1 a	0.18 ± 0.02 a	5
	Bw2	7.12 ± 2.24	0.76 ± 0.05	27.4 ± 3.9 a	0.54 ± 0.06 ac	4
	C	62.8 ± 4.43	2.07 ± 0.09	121.2 ± 8.7 a	0.99 ± 0.00 a	5
S2	O	18.2 ± 0.90	11.4 ± 0.89	230.3 ± 4.9 b	0.71 ± 0.01 a	6
	E	1.60 ± 0.14	0.77 ± 0.05	42.1 ± 1.8 bd	0.24 ± 0.02 ab	8
	Bs1	0.79 ± 0.09	0.41 ± 0.05	31.0 ± 1.9 b	0.16 ± 0.02 a	8
	Bs2	0.38 ± 0.05	0.21 ± 0.03	11.9 ± 1.4 b	0.23 ± 0.03 b	7
	C	7.78 ± 1.32	0.68 ± 0.06	30.8 ± 3.4 b	0.72 ± 0.04 b	8
S3	O	23.0 ± 1.00	12.2 ± 0.58	352.2 ± 12.8 a	0.77 ± 0.03 a	4
	E	1.67 ± 0.20	1.35 ± 0.12	45.8 ± 2.7 b	0.33 ± 0.04 a	5
	Bs1	0.65 ± 0.08	0.69 ± 0.09	31.1 ± 3.2 abc	0.19 ± 0.02 a	4
	Bs2	0.29 ± 0.03	0.63 ± 0.31	12.9 ± 1.7 b	0.25 ± 0.03 b	4
	C	0.20 ± 0.02	0.09 ± 0.03	4.8 ± 0.6 c	0.36 ± 0.09 c	5
J1	O	14.8 ± 0.26	12.8 ± 0.91	247.7 ± 3.8 b	0.52 ± 0.02 b	2
	E	1.13 ± 0.03	1.10 ± 0.21	39.4 ± 2.1 bd	0.18 ± 0.03 bc	2
	Bs1	0.53 ± 0.06	0.57 ± 0.06	29.4 ± 3.6 abc	0.10 ± 0.01 ab	2
	Bs2	0.49 ± 0.06	0.30 ± 0.05	3.2 ± 0.7 bc	0.80 ± 0.00 c	2
	C	0.18 ± 0.06	0.24 ± 0.15	1.6 ± 0.4 c	0.65 ± 0.05 b	2
J2	O	14.0 ± 1.82	15.5 ± 1.29	251.7 ± 5.0 b	0.40 ± 0.04 bc	3
	E	0.34 ± 0.02	0.46 ± 0.03	22.5 ± 1.4 c	0.08 ± 0.01 c	4
	Bs1	0.24 ± 0.02	0.25 ± 0.03	20.0 ± 1.9 bc	0.06 ± 0.00 b	4
	Bs2	0.15 ± 0.03	0.04 ± 0.02	1.9 ± 0.4 c	0.38 ± 0.11 ab	4
	C	0.21 ± 0.01	0.13 ± 0.05	1.6 ± 0.2 c	0.71 ± 0.02 b	4
J3	O	13.6 ± 2.97	9.4 ± 2.50	215.8 ± 37.4 b	0.37 ± 0.03 c	2
	E	0.59 ± 0.05	0.56 ± 0.04	31.7 ± 1.6 cd	0.08 ± 0.01 c	3
	Bs1	0.20 ± 0.02	0.24 ± 0.07	13.9 ± 3.0 c	0.06 ± 0.01 b	3
	Bs2	0.12 ± 0.02	0.08 ± 0.03	3.6 ± 0.7 bc	0.12 ± 0.02 b	3
	C	0.12 ± 0.02	0.05 ± 0.02	0.8 ± 0.1 c	0.53 ± 0.01 bc	3

[a] Mean ± standard error of mean

Appendix 3. Tree growth in Scots pine stands

A tree stand is formed by individual trees interacting with each other. The size differences between trees is a characteristic feature of forests, and the bigger trees shade the smaller ones, reducing their photosynthetic production. We assume that the trees in a stand can be divided into a few size classes, and that a description of the stand can be produced by 1) the functions and structure of a representative tree in each size class and 2) the number of trees in each size class (Nikinmaa 1992, Hari 1998).

A pine tree forms a whorl each year. We assume that a whorl is a functional unit of a tree, so that the photosynthetic products of a whorl are apportioned to the growth of 1) new needles, 2) new fine roots and mycorrhiza, and 3) water transport capacity in stem, branches and large roots. However, a proportion of the products are allocated to the top of the tree.

Photosynthesis produces carbohydrates for tree growth. Shading reduces photosynthesis. Consider potential photosynthesis in unshaded conditions, determined over the whole growing season. Assume that the ratio of actual photosynthetic production to potential production depends on the shading needle mass above the whorl. The photosynthetic production in the volume of the whorl (V) during time interval $[t_1,t_2]$ is

$$P(t) = \int_{t_1}^{t_2} p(t, x_0)\mathrm{d}t \int_{\mathrm{V}} g_{\mathrm{N}}(x)\mathrm{f}(N(h))\mathrm{dV} \tag{41}$$

where x is a point in the stand and x_0 is a point in unshaded conditions, p denotes density of photosynthetic rate, g_{N} needlemass distribution, $N(h)$ the total shading mass of needles above height h, and f $(N(h))$ determines the ratio between photosynthetic production at the height h and in unshaded conditions as a function of $N(h)$ (Hari 1998). This equation combines the structure of the stand with its photosynthetic production.

The top of the tree (three uppermost whorls) must get a share of the carbohydrates produced in the lower whorls. Thus we assume that some of the carbohydrates produced in each lower whorl are allocated to the top (T_{w}), approximated with the following semi-empirical function

$$T_{\mathrm{w}}(t) = \frac{0.4}{1 + h(t) / 40} P(t) \tag{42}$$

where $h(t)$ is the height of the tree at the stand age t.

Maintenance respiration $R(t)$ consumes a part of the carbohydrates $P(t)$. Let us assume that the respiration rate r_i is a component-specific constant for each component i of a whorl

$$\begin{aligned} R(t) = r_{\mathrm{N}}(N(t-1) + N(t-2) + N(t-3)) + r_{\mathrm{FR}}FR(t-1) + \\ r_{\mathrm{S}}S(t-1) + r_{LR}LR(t-1) + r_{\mathrm{B}}B(t-1) \end{aligned} \tag{43}$$

where FR, S, LR and B denote the amounts (g whorl^{-1}) of fine roots, stem, large roots and branches in the whorl, and $N(t\text{-}1)$, $N(t\text{-}2)$ and $N(t\text{-}3)$ denote amounts of needles grown during the years t-1, t-2 and t-3.

Growth respiration and the conversion efficiency of carbohydrates to dry matter (s) varies according to the tissue which is produced. However, we assume that it is the same for all components of a whorl. The pool of new dry matter available for growth (DM, g whorl^{-1}) is in the lower whorls

$$DM(t) = s\left(P(t) - T_{\mathrm{w}}(t) - R(t) - K(t)\ \right) \tag{44}$$

and in the three topmost whorls

$$DM(t) = s\left(P(t) + \frac{\sum T_w(t)}{3} - R(t) - K(t)\right) \tag{45}$$

where carbohydrates allocated to the top, $\sum T_w$, is summed over the lower whorls, and K is a loss of carbohydrates due to low availability of soil nutrients, described below.

There is a linear relationship between the sap-wood area of the stem and the needlemass of Scots pine (Hari *et al.* 1985, Nikinmaa 1992). Assume that the ratio between the amount of new needles and the sap-wood area which transports water to the needles is constant in the stem (a_{S}) and branches (a_{B}). Further assume that the proportion a_{r} of the water transport capacity in stem and branches can be reused from the four-year-old dying needles of a whorl (Mäkelä 1986). The remaining need for water transport to the new needles of a whorl is satisfied by the growth of cross sectional area of the stem (ΔA_{S}) and branches (ΔA_{B}). Thus

$$\Delta A_{\mathrm{S}} = a_{\mathrm{S}}\left(N(t) - a_{\mathrm{r}}N(t-3)\right) \tag{46}$$

where the symbol Δ refers to annual change. Branches are treated analogically. The growth of stem cross-sectional area at each height h is obtained by summing up the cross-sectional growths of the whorls at height h and above it.

The ratio between large roots and stem is assumed to be constant, v (estimated from e.g. Vanninen *et al.* 1996).

The carbon balance, i.e. tree growth equals photosynthetic production minus respiratory consumption, is with our notations

$$N(t) + FR(t) + \Delta B + \Delta S + \Delta LR = DM(t) \tag{47}$$

where

$$\Delta B + \Delta S + \Delta LR = (a_B l_B(t\text{-}1)u_B + (1+v)a_S h_w u_S)(N(t) - a_r \mathrm{N}(t\text{-}3)) \tag{48}$$

h_w denotes the height of the whorl w, l_B length of branches, u_B and u_S density of branches and stem.

The uptake of nitrogen depends on the efficiency of fine roots, e_{NH4}, and the amount of exchangeable NH_4, E_{NH4}, in soil. Retranslocation from dying needles is an important source of nutrients. The nutrient balance for nitrogen states that nitrogen uptake corresponds to the need for nutrients, see Equation (30). Now the new needles and fine roots can be solved from the balances. Nutrient retranslocation from dead fine roots can also be assumed, but there is no nutrient retranslocation from the woody components.

If the soil nutrient content is low, the uptake can be too low to satisfy the nutrient need of new components. We define this as a nutrient crisis, and assume that trees respond to low nutrient availability by increasing outflows to mycorrhiza and rhizosphere and/or by decreasing photosynthetic production. The outflow/decrease is assumed to be equal to the maintenance respiration of fine roots at an infertile site, and to increase with decreasing amount of exchangeable base cations and NH_4:

$$K = r_{\mathrm{FR}} FR \frac{E_{\mathrm{X,critK}}}{E_{\mathrm{X}}} \tag{49}$$

where r_{FR} is the respiration rate of fine roots, and $E_{X,critK}$ is the amount of exchangeable cation X at an infertile site. The nutrient X that gives the largest outflow K determines the flux of carbohydrates.

In the early years of stand development the pine seedlings and small pine trees are shaded by other vegetation, e.g. broad-leaved trees. Because this shading is not well known for an average site, we take it into account simply by decreasing maximal photosynthesis p, so that it is multiplied by a factor which accounts for the shading. The coefficient is the ratio between stand age and the year when such effect no longer exists, which we assume to take place between 10 and 20 years of age.

We assume that the new fine roots die during the same year as they are produced (Persson 1980). In the model, the dead trees and tree parts form litter the same year as they die.