IMPACT OF ACID ATMOSPHERIC DEPOSITION ON SOILS:

FIELD MONITORING AND ALUMINUM CHEMISTRY

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Proefschrift
ter verkrijging van de graad van
doctor in de landbouwwetenschappen,
op gezag van de rector magnificus,
dr. H.C. van der Plas,
in het openbaar te verdedigen
op vrijdag 16 september 1988
des namiddags te kwart voor drie in de aula
van de Landbouwuniversiteit te Wageningen

Stellingen

1. Hoge bomen vangen niet alleen veel wind.
   dit proefschrift.

2. Het definiëren van bodemverzuring als een verlaging van pH en basenverzadiging leidt tot de onjuiste conclusie dat veel zandgronden ongevoelig zijn voor 'zure regen'.
   L. Wiklander. 1974. Grundförbättring 26:155-164.
   B.W. Bache. 1980. In T.C. Hutchinson & M. Havas. Effects of acid precipitation on terrestrial ecosystems. Plenum, New York, p. 569-572.

3. Een verlaging van de pH in de Nederlandse zandgronden wordt bij ongewijzigde zuurdepositie slechts gedurende enkele decennia afgeremd door het oplossen van de beperkte voorraad secundair aluminium.
   dit proefschrift.

4. 'Zure regen' leidt tot een ingrijpende verandering van de bodemvorming in de Nederlandse zandgronden.
   dit proefschrift.

5. In tegenstelling tot de goed onderzochte en gedocumenteerde aluminium toxiciteit bij landbouwgewassen is het effect van aluminium op bosecosystemen slechts in beperkte mate bestudeerd en vertoont de literatuur veel tegenstrijdigheden.
   F. Andersson & J.M. Kelly (eds). 1984. Aluminum toxicity to trees. Dept. Ecology Env. Res., Swedish Univ. Agric. Sci., Uppsala

6. In verband met de versterkte uitspoeling van organische en anorganische verontreinigingen naar het grondwater is een regelmatige controle van de waterkwaliteit van ondiep gewonnen drinkwater, met name uit privé putten, gewenst.

7. Een groter deel van ons zuur verdiende nationaal inkomen zou moeten worden aangewend voor een effectieve bescherming van het leefmilieu.

8. Dat de mens het meer dan honderd jaar na het verschijnen van de eerste publicaties over 'zure regen' niet veel verder heeft kunnen brengen dan het verhogen van de schoorstenen stemt tot scepsis t.a.v. een snelle realisatie van een afdoend milieubeleid.

9. Stabiliteitsdiagrammen met afhankelijke assen resulteren in een bepaalde ordening van de gegevens, zelfs als die gegevens random zijn. Gebruik van dergelijke diagrammen kan aanleiding geven tot misleidende conclusies omtrent de regulering van de aluminium activiteit.

   C. Neil et al. 1987. Earth and Planetary Science Letters 86:105-112.

10. De vorming van jurbaniet ($AlOHSO_4.5H_2O$) in aan 'zure regen' blootgestelde bosbodems is hypothetisch, en is nooit via mineralogische analyse aangetoond.

    J. Prenzel. 1983. Göttinger Bodenk. Ber. 72:1-113.
    G.T. Weaver et al. 1985. Soil Sci. Soc. Am. J. 49:746-750.
    P.K. Khanna et al. 1987. Soil Sci. Soc. Am. J. 51:446-452.

11. De silicium flux in de bodem, als maat voor de silicaat verwering, moet worden gecorrigeerd voor het aandeel van de biocyclus.

    F. Bartoli. 1986. Sci. Géol. Bull. 39:195-209.

12. De stelling van het Kabinet Lubbers II dat het verhogen van de maximum snelheid op de Nederlandse autosnelwegen naar 120 km/uur positief uitwerkt op het milieu is niet te verdedigen.

13. Gezamenlijke koffie- en theepauzes hebben een positief effect op de sociale contacten binnen een afdeling en moeten worden gestimuleerd.

14. De voorgenomen verdere integratie van Europa in 1992 geeft op dit moment nog slechts een grenzeloze verwarring.

Proefschrift van J. Mulder

Impact of acid atmospheric deposition on soils: Field monitoring and aluminum chemistry.

Aan mijn ouders
Aan Annemiek, Paulien & Anne

ABSTRACT

Mulder, J., 1988. Impact of acid atmospheric deposition on soils: Field monitoring and aluminum chemistry. Doctoral thesis. Agricultural University, Wageningen, The Netherlands.

The effect of acid atmospheric deposition on concentrations and transfer of major solutes in acid, sandy soils was studied. Emphasis was given to mobilization and transport of potentially toxic aluminum. Data on solute concentrations and fluxes in meteoric water as well as soil solutions were obtained from intensive monitoring programmes conducted at a number of sites in northwestern Europe and North-America. Specific hypotheses were tested in laboratory experiments.

Atmospheric acid inputs dominated total acid loads in nearly all soils studied. This was particularly true for forest soils in the Netherlands, due to an extreme dry deposition of $(NH_4)_2SO_4$ in the forest canopy. Input of $(NH_4)_2SO_4$ may acidify the soil, due to NH_4 assimilation, or nitrification of NH_4 and subsequent leaching of NO_3.

In soils rich in weatherable minerals, mobilization of base cations dominated acid neutralization, so that percolation water was buffered at relatively high pH values and the mobility of aluminum was low. In these soils the mobilization and transport of aluminum was mainly driven by organic acids, which is consistent with the podzolization theory. However, in soils depleted in weatherable minerals (e.g. most of the acid, sandy soils in the Netherlands), mobilization rates of base cations were too low for a substantial neutralization of atmospheric acidity, so that pH values of the percolation water were often low enough to cause a significant mobilization of aluminum. In these soils the atmospherically derived strong acid load was almost fully neutralized by aluminum dissolution. Much of this dissolved inorganic aluminum is currently lost to the groundwater.

Although aluminum is abundant in soils only a minor fraction, largely consisting of non-silicate organically bound aluminum, formed in the course of soil development (podzolization), was readily dissolved. The current rapid and irreversible depletion of this fraction in many acid, sandy soils of the Netherlands constitutes a drastic change in soil genesis. Depletion may eventually also result in reduced acid neutralization, due to decreased dissolution of aluminum.

The aluminum solubility control varied with soil depth. Surface soil solutions were highly undersaturated with respect to gibbsite solubility, whereas saturation was approached in the subsoil. Possibly, the low aluminum solubility in the surface soil was controlled by an exchange type equilibrium with organic soil aluminum. Insight in the aluminum solubility control in soils is not only relevant for improving our understanding of the aluminum chemistry in soils per se, but it may also help explaining the aluminum chemistry of surface water in mountainous catchments, where soil solutions may reach the stream via different flowpaths through the soil, depending on hydrological conditions.

Additional index words: biogeochemistry, $(NH_4)_2SO_4$ deposition, Nitrogen transformations, nitrification, chemical budget, free aluminum, pedogenesis, podzol, podzolization, flowpath, catchment.

WOORD VOORAF

Dit proefschrift is grotendeels de neerslag van 6 jaar onderzoek, dat onder de paraplu van het 'Zure Regen' project plaatsvond. Onnoemelijk veel meetgegevens zijn in de loop der jaren op diverse locaties in binnen- en buitenland verzameld. Een zeer groot aantal mensen hebben bijgedragen aan de uitvoering van het onderzoek en aan de verslaglegging.

Als eerste wil ik mijn ouders bedanken voor de vrijheid die ze mij hebben gegeven mijn interesse te volgen en deze studie te voltooien, waarbij ze mijn geringe aanwezigheid voor lief hebben genomen.

Grote dank ben ik verschuldigd aan mijn promotor Nico van Breemen. Beste Nico, je enthousiaste belangstelling en stimulerende kritiek zijn een grote steun geweest voor het welslagen van dit onderzoek.

Harry Booltink dank ik voor zijn grote inzet en vindingrijkheid om de monitoring programma's zo goed mogelijk te laten verlopen, en tevens voor het berekenen van de fluxen van water en opgeloste stoffen op de diverse Nederlandse locaties.

Eef Velthorst, Neel Nakken, Hans Sliepenbeek, Antoon van Osch, Astrid Vallent, Ellen Burger, Leo Begheijn en Frans Lettink worden bedankt voor het nauwgezet uitvoeren van grote hoeveelheden water en grond analyses. Eef wil ik ook graag dank zeggen voor het geregeld invallen bij het veldwerk.

Tom Pape slaagde er in om een schier onontwarbare kluwen aan meetgegevens om te toveren in gemakkelijk hanteerbare data bestanden. Tom, ook bedankt voor de assistentie bij het veldwerk.

Han van Dobben (RIN, Leersum), Hans Reijnders (RIVM, Bilthoven) en Jacques Slanina (ECN, Petten) dank ik voor het meten van hoeveelheden en samenstelling van het bovengronds water op enkele van de proeflocaties.

Enkele studenten hebben aan dit onderzoek meegewerkt: René Koppers, Ineke Schipper, Marco Wopereis, Emile Marnette en Helma Eijck bedankt! Ook Chris Zevenbergen wil ik bedanken voor het 'vrijwillig' puzzelen aan de aluminium speciatie met Morin.

Staatsbosbeheer ben ik erkentelijk voor het beschikbaar stellen van de onderzoekslocaties Gerritsfles en Hasselsven. Daarnaast heeft Dr. W.A.M. Rijken (Oisterwijk) mij de gelegenheid gegeven een onderzoekslocatie bij het Tongbersven in te richten. I am also indebted to Mr. J.E. Handberg for making the Klosterhede sites available for this research.

Veel tijd en energie is besteed aan het maken van de veldopstellingen. Piet Looyen wil ik graag bedanken voor het snel gereed maken van de houten kisten, waarin de monitoring-apparatuur kon worden geplaatst. De TFDL is een grote

steun geweest bij het ontwikkelen van de vacuumpompjes en het snel afwerken van 'kleine' klusjes.

G. Buurman en P.G.M. Versteeg ben ik dank verschuldigd voor het maken van een deel van de tekeningen. De fotografie afdeling van het Biotechnion heeft zorg gedragen voor het verkleinen van de figuren.

Naast bovengenoemde mensen zijn er nog velen, met name op de Vakgroep Bodemkunde en Geologie, die in meerdere of mindere mate aan dit onderzoek hebben bijgedragen. Zonder ze persoonlijk te noemen wil ik ieder graag hartelijk bedanken.

Een aparte vermelding verdienen Fré Schelbergen en de administratie voor het afhandelen van veel financiële en administratieve noodzakelijkheden.

Special thanks are due to Charley Driscoll for his interest and support throughout this study, for the many discussions and for his valuable criticism on earlier versions of several of the papers.

I would like to thank Lennart Rasmussen and Preben Jorgensen for the good cooperation we had at the Klosterhede sites.

Nils Christophersen, Hans-Martin Seip, Michael Hauhs, Rolf Vogt, Sjör Andersen and Dag-Olav Andersen are greatfully acknowledged for their hospitality and cooperation during our work at Birkenes.

Dit onderzoek werd gedeeltelijk gefinancierd door de EEG (contract ENV-650-NL) en door de Stichting Technische Wetenschappen (STW). I would like to thank the NTNF (Oslo) for granting me a 3-month fellowship.

'Last', maar zeker niet 'least' wil ik Annemiek, Paulien, en Anne bedanken voor het geduld dat ze met me hebben gehad om weer wat socialer te worden.

CONTENTS

PUBLICATIONS

Several colleagues, who contributed to the collection and evaluation of the vast amount of monitoring data, served as an author in one or more of the chapters. The chapters 2 through 8 were or will be published as seperate papers, with some modifications. References are given below (numbers refer to the chapters).

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Chapter 1
GENERAL INTRODUCTION

1.1 Background

'Acid rain' has been a major environmental concern in Europe and North-America for over a decade and has received considerable attention also from the public (e.g., Time, 1982: 'Acid Rain - The silent plague'; Der Spiegel, 1981: 'Saurer Regen über Deutschland - Der Wald stirbt'). The term 'acid rain' originally referred to precipitation water with pH 5.6. The reference pH 5.6 is obtained, when equilibrating distilled water with atmospheric CO_2. A decrease below the reference pH is caused by the dissolution and oxidation of atmospheric acidic compounds (e.g., SO_2, NO_x) in meteoric water (Likens et al., 1979).

Atmospheric acidic compounds originate from natural and from anthropogenic sources. Natural sources include volcanic emenations as well as volatilization of marine and terrestrial biogenic S and N. The burning of fossil fuels is the major anthropogenic source. Particularly, in the industrialized parts of Europe and North-America anthropogenic sources dominate the emission of NO_x and SO_2 (OECD, 1977).

Besides the acidity dissolved in precipitation water ('wet deposition'), the deposition of atmospheric acidic compounds also proceeds in a 'dry' (gasseous or particulate) form (Ulrich et al., 1979). So, total acid atmospheric deposition is more than that in wet precipitation alone. Therefore, the expression 'acid rain', although formally restricted to wet deposition, is generally used for wet plus dry deposition of acidifying substances. Particularly forests appear to be effective scavengers of dry deposition (Ulrich et al., 1979).

In areas with intensive animal husbandry, dry deposition of NH_3, may also increase the soil's acid load, as was shown by van Breemen et al., (1982). Ammonia, although a neutralizing compound in itself, may cause strong soil acidification after nitrification and subsequent leaching of NO_3 (van Breemen et al., 1987).

Current atmospheric acid loads show strong regional differences. Rates vary from 1.5 - 2 kmol ha^{-1} yr^{-1} in northeastern North-America and Scandinavia, to 3 - 6 kmol ha^{-1} yr^{-1} in Germany and the Netherlands (van Breemen et al., 1984).

The impact of anthropogenically derived strong acid on the acidification of soils and water has been a major topic in recent years. Rosenqvist (1977) as well as Krug and Frink (1983) argued that soil acidification in temperate regions is primarily caused by natural processes of soil development. These authors attributed the currently observed environmental acidification to a changing land-use (a large scale regrowth of temperate forests on former agricultural land) resulting in increasingly acidic and thicker forest floors. Because the atmospherically derived acidity is small relative to the vast amounts of acids already present in the soil, these authors assumed that 'acid rain' could not be a major contribution to the acidification of soils and water. However, this assumption is based on a misconception, because the influx of mobile strong acids are compared with the stores of exchangeable and immobile weak acids, which primarily reside in the forest floor. Van Breemen et al. (1984) showed that only little of the large pools of this 'natural' organic acidity is released to the infiltration water (i.e. by solubilization of organic acids, or by exchange of H^+ for base cations originating from the atmosphere), and are irrelevant to the proton loading of soils and waters under ambient conditions. In contrast, anthropogenically derived acidity was shown to dominate the acidification of most mineral soils and waters of nortwestern Europe and northeastern North-America (van Breemen et al. 1984).

Cronan and Schofield (1979), Johnson (1979), and Ulrich et al. (1979) were among the first to suggest the importance of aluminum mobilization as a mechanism of strong acid neutralization in mineral soils depleted in base cations. Van Breemen et al. (1984), after evaluating a large number of input-output studies, concluded that aluminum mobilization increases with increasing load of strong mineral acids. However, this was disputed by Krug and Frink (1983), who hypothesized that the mobility of aluminum in soil solutions and surface waters is primarily governed by the 'natural' (weak organic plus exchangeable) acidity of the soil and is not affected by the relatively minor influx of atmospheric strong acids.

It is well established that aluminum is toxic to aquatic organisms (Cronan and Schofield, 1979; Baker and Schofield, 1980; Hall et al., 1984). Elevated levels of Al in soil solutions may also cause toxicity to crop roots (Wright et al., 1987), and has been associated with forest die-back (Ulrich et al., 1980; Vogelman, 1982). Aluminum has also been related to the occurrence of Alzheimer's disease, because abnormally high levels of aluminum were found in the diseased regions of the patients' brains (New Scientist, 27 February 1986). One major pathway of aluminum intake by human beings is the consumption of acidified groundwater, enriched in aluminum. So, the suggested increased mobility of aluminum in soils and water, due to 'acid rain' may have significant negative consequences for the functioning of many organisms including humans.

1.2 Aim of the research

In this research emphasis was given to the aluminum chemistry of acid, sandy soils (i) because insight in the dissolution and transfer of aluminum is probably crucial for our understanding of the impact of acid rain on the acidification of soil and water, and (ii) because aluminum may play a key role in the various toxicity problems associated with 'acid rain'.

Therefore, the intent of this study was to evaluate the impact of acidic atmospheric deposition on the in situ chemistry and transport of aluminum in a number of soil types, occurring in northwestern Europe and northeastern North-America. As a part of this study we evaluated the aluminum chemistry of similar sandy soils, which differed strongly in total acid load. Particular attention was given to induced changes in pedogenesis, and how these changes could affect the long term aluminum chemistry of the investigated soils.

This thesis is one of two with the common title: 'Impact of acid atmospheric deposition on soils'. The second thesis ('Quantification of chemical and hydrologic processes'), written by Hans van Grinsven, deals with unsaturated hydrology, kinetics of mineral weathering, and computer simulation of processes involved in soil acidification. The studies underlying both theses were conducted within the framework of the research project on the effects of acid atmospheric deposition on soils and water, under the guidance of Prof. Dr. N. van Breemen, Department of Soil Science and Geology, Agricultural University, Wageningen, the Netherlands.

1.3 Outline of this thesis

In chapter 2 we evaluate the chemistry and transport of aluminum in spodosols, developed in glacial tills at the Hubbard Brook Experimental Forest (New Hampshire, USA). Hubbard Brook soils (i) are relatively rich in weatherable minerals, (ii) have modest atmospheric acid loads, and (iii) have a relatively high pH of infiltration water (pH 4), due to the modest acid load and to the small evaporative concentration. Earlier studies on Hubbard Brook streamwater suggested that mobilization and transport of aluminum is dominated by organic acids, and that atmospherically derived acidity is largely neutralized by the mobilization of base cations.

In contrast to the Hubbard Brook site the atmospheric acid loads in the Netherlands are extremely high. In chapter 3 we discuss the impact of the atmospheric acidity on the aluminum chemistry of three sandy to loamy soils, developed in alluvial deposits at the Hackfort Estate in the Netherlands. Major attention is given to the transfer and the solubility control of aluminum in various soil horizons.

In chapter 4 we evaluate the role of a forest cover in increasing the total atmospheric acid load via dry deposition of NH_3. The study was conducted in the Netherlands at a forested and an adjacent bare driftsand more than 5 km from the nearest intensively managed farmland. In addition we discuss the major chemical processes in both soils, including nitrogen transformation and mobilization of aluminum. In the forest soil we also studied the importance of anthropogenically derived acidity relative to natural acid sources.

In chapter 5 mobilization and transport of aluminum in spodosols, developed in coversands depleted in base cations, in the Netherlands are compared with the chemistry of aluminum in spodosols, developed in richer glacial tills, in New Hampshire. Apart from the difference in parent materials in the Netherlands and New Hampshire, acid loads are also different, and significantly higher in the Netherlands. Particular attention is given to the effect of strong acids on current soil development.

The importance of atmospherically derived strong mineral acids in increasing the mobility of Al in representative sandy forest soils in the Netherlands (podzols on coversands, and driftsands) is evaluated in chapter 6. The study was conducted at six sites differing in acid load, but with similar sandy soils (developed in coversands, driftsands, and fluvio-glacial sands). One site (in Denmark) was considered to be a 'reference' plot with a relatively small acid input. Sites were selected such that a range of atmospheric acid loads was created.

In chapter 7 we evaluate a laboratory experiment where we studied the sources of dissolved aluminum. This research was conducted to get more insight in pool sizes of the most soluble forms of solid phase aluminum, and to relate the pool size to current mobilization rates. In addition we investigated possible relationships between dissolved aluminum concentrations and the contents of various forms of solid phase aluminum.

In chapter 8 we evaluate the relationship between the aluminum solubility controls in soils and streamwater in the Birkenes catchment (Norway). Earlier studies suggested that the variability of the aluminum solubility control with discharge in Birkenes streamwater may be related to variable water flowpaths in the soil. We hypothesized that different water flowpaths are characterized by different aluminum solubility controls. This research should improve our understanding of the streamwater aluminum chemistry, particularly during high flow conditions.

1.4 References

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Chapter 2

ALUMINUM CHEMISTRY IN A FORESTED SPODOSOL, NEW HAMPSHIRE, USA

ABSTRACT

The Al chemistry of seeps, soil solutions and soils was evaluated at the Hubbard Brook Experimental Forest in New Hampshire. Alumino-organic substances predominated in solutions and in the free Al fraction of soils. Concentrations of both organic and inorganic forms of Al were highest at the higher elevations. The extent of spodosol development was consistent with these observations, suggesting the rate of spodosolization is greatest at high elevations in the watershed. We also observed high levels of organic Al entering the mineral soil from the forest floor. Moreover, the historical rate of Al deposition within the mineral soil far exceeds the current rate of organic Al precipitation from soil solutions. Processes such as vegetation turnover and windthrow may be important to the Al cycle at Hubbard Brook. Removal of modest amounts of dissolved inorganic Al from the Bhs1 horizon, and subsequent export from the soil, occurs during winter and early spring. This process may be due to atmospheric inputs of acidic substances.

2.1 INTRODUCTION

There has been considerable interest in the chemistry and transport of Al in spodosols (Mokma and Buurman, 1982). Formation of spodosols is generally thought to involve the mobilization of Al (and Fe) from the upper (E) to lower (B) mineral soil horizons by organic acids leached from foliage as well as from decomposing forest floor (Bloomfield, 1957; Coulson et al., 1960). Transported Al is largely precipitated within the lower soil horizons, so there is generally little mobilization of Al from the terrestrial to the aquatic environment (Ugolini et al., 1977; David and Driscoll, 1984).

In recent years, it has been hypothesized that mineral acids from atmospheric deposition remobilize Al previously precipitated within the soil during spodosolization or held on soil exchange sites, with this Al being transported through the soil to adjacent surface waters (Cronan and Schofield, 1979).

In acidic surface waters of upper New York State and New Hampshire, organically-complexed Al was generally the predominant form of aqueous Al while F-complexed Al was generally the predominant form of inorganic monomeric Al (Driscoll et al., 1984; Johnson et al., 1981). Inorganic Al was observed to increase exponentially with decreases in solution pH, while organic monomeric Al was strongly correlated with soluble Al concentrations but not with pH.

It is well established that Al is toxic to aquatic organisms (Cronan and Schofield, 1979; Baker and Schofield, 1980; Hall et al., 1984), and elevated levels of Al may also cause toxicity to forest vegetation (Ulrich et al., 1980; Vogelman, 1982).

The intent of our study was to evaluate the chemistry and transport of Al within the terrestrial environment of the Hubbard Brook Experimental Forest (HBEF), New Hampshire.

2.2 METHODS

2.2.1 Experimental setting

The HBEF is located in central New Hampshire, USA (43^{o} 56'N, 71^{o} 45'W). The region is primarily a deciduous forest (*Fagus grandifolia, Acer saccharum, Betula aleghaniensis*), with red spruce (*Picea rubens*) and balsam fir (*Abies balsamea*) prominent on north-facing slopes and ridgetops.

Underlying the Hubbard Brook watershed is a pelitic schist of sillimanite grade (Littleton formation), which is extensively intruded by quartz monzonite (Kinsman formation). The material is medium to coarse grained, consisting of quartz, plagioclase and biotite. The region is largely covered by locally derived glacial till.

The soils are well drained spodosols (Typic Fragiorthods) with a sandy loam to loamy sand texture and a thick (3-15 cm) organic layer at the surface. They are highly permeable and overland flow is essentially absent. A fragipan in the sub-soil greatly restricts water flow to the lower soil. The rough pit and mound topography was derived mostly from windthrown trees.

The flux of precipitation inputs and stream outflow have been continuously monitored since 1956. Precipitation and stream chemistry have been monitored weekly since 1963. Such data have provided detailed information on the chemistry and cycling of substances in the experimental forest (Likens et al., 1977; Bormann and Likens, 1979).

2.2.2 Sampling program

In our study, seeps, soil solutions and soils just west of the HBEF reference watershed (WS6) were sampled (Fig. 1). Seeps were sampled approximately at weekly intervals, along an elevational gradient (725 to 400 m) from May through September 1979. Soil pits were dug at three elevations (760 m, 640 m, 520 m) and lysimeters were inserted below the O2, E, Bhs1 and above the Cx horizons in each pit. A tension of about 0.1 bar was maintained by a hanging column. Soil solutions were collected in polypropylene containers at approximately weekly intervals from March through July 1982.

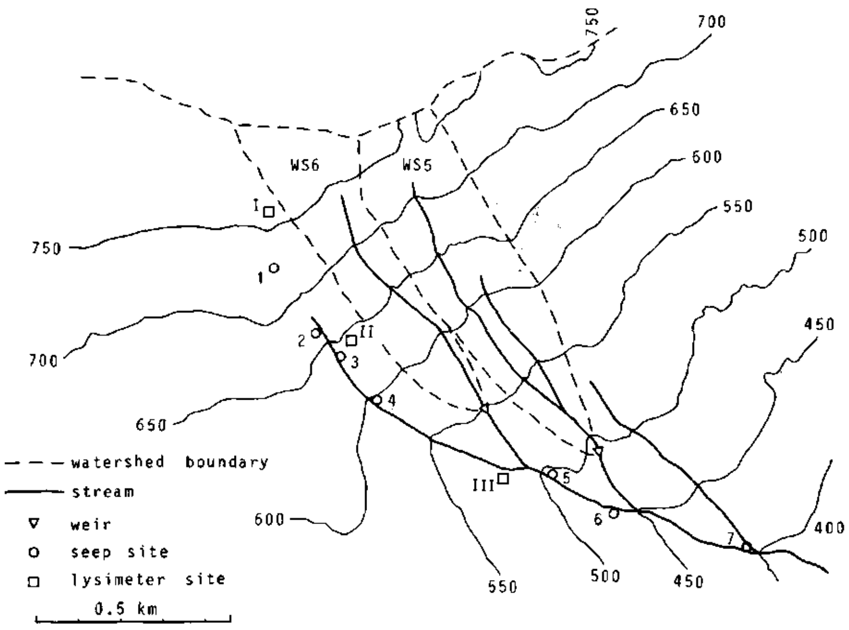

Fig. 1. Seep and soil study sites at the HBEF.

Conventional porous cups or plates of ceramic material may leach Al under acidic conditions or sorb Al from solutions of more neutral pH. To minimize these problems, we designed and constructed a lysimeter for this study (Fig. 2). A circular filter (0.2 μm, acrylic copolymer; Fig. 2b) with internal nylon support was used to hold the applied suction and filter particulates. This membrane was

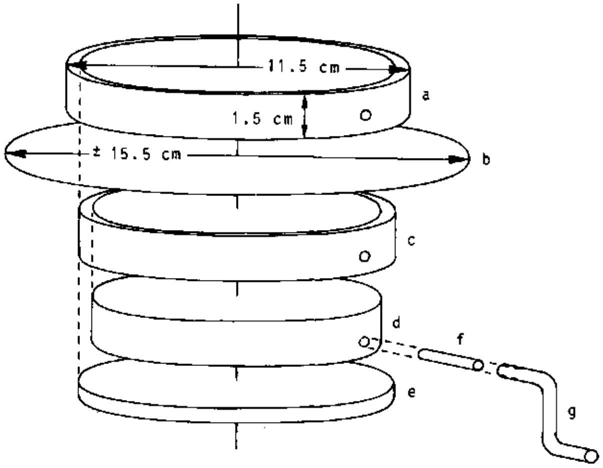

Fig. 2. Diagram of the suction lysimeter used to collect soil solutions.

supported by porous (40 μm) polypropylene material (Fig. 2d), which kept the filter moist. The filter and porous polypropylene supports were placed in a machined circular PVC frame (Fig. 2a, c) and on a circular PVC plate (Fig. 2e). A hole was drilled into the lysimeter (Fig. 2d) to accomodate a polyethylene tube (Fig. 2f) and flexible tubing (Fig. 2g) to transport water to a polypropylene collection vessel.

We passed 0.1 M HNO_3 through the lysimeters and detected no Al (<0.5 mmol m^{-3}) in the leachate. In addition, synthetic and natural solutions which were undersaturated with respect to gibbsite solubility did not loose Al upon passage through the lysimeter, though solutions that were highly oversaturated showed Al retention on the lysimeter.

Samples were collected from all soil horizons on September 1982 within each of the soil pits. Descriptions of soil profiles and horizon designations were made according to the Food and Agriculture Organization (1977). Soils were air dried, sieved and stored for analysis.

2.2.3 Analytical techniques

Immediately after collection, soil and seep solutions were measured for pH and specific conductance. Seep samples were then filtered through 0.45 μm Millipore filters. Samples were processed for Al and dissolved organic carbon (DOC) within 24 h.

Free F was determined with an ion-selective electrode and total F was determined similarly but using a total ionic strength adjustor and buffer (TISAB II; Orion, 1976). DOC was measured using persulfate oxidation (Menzel and Vaccaro, 1964) followed by syringe stripping of CO_2 (Stainton, 1973) and gas chromatography.

Calcium, Mg, Na, and K were determined by atomic absorption spectophotometry (AAS). For seep solutions, SO_4 and Cl were determined by ion chromatography. For soil solutions, SO_4 was determined colorimetrically and dissolved Si was determined by the molybdosilicate method (APHA, 1976) using an autoanalyzer.

For seep solutions, monomeric Al was determined by the ferron-orthophenantroline method (Smith and Hem, 1972). Monomeric Al was fractionated using a cation exchange column on which labile forms of mononuclear Al (inorganic monomeric Al: aquo Al and OH, F and SO_4 monomeric complexes) are thought to be retained, while non-labile forms of monomeric Al (organic complexes) pass on through (Driscoll, 1984).

For soil solutions, monomeric Al was determined using a more sensitive method, where mononuclear Al is complexed by 8 hydroxyquinoline, followed by rapid extraction in methyl isobutyl ketone (Barnes, 1976). Limited sample volumes of soil solutions generally precluded the use of the exchange column to fractionate Al. Therefore we used free and total F measurements, together with thermochemical data, to calculate the distribution of inorganic Al. It was assumed that the difference between total and free F was Al-bound F because Ca, Mg, Fe, and Si complexes of F are insignificant (Johnson et al., 1981). Aquo Al (Al^{3+}) levels were calculated by applying free and Al-bound F concentrations to thermodynamic alumino-F complexation relationships. Individual Al forms were, in turn, calculated with measured values of ligand concentration or activity (e.g. pH, F, SO_4), and alumino-ligand stability constants. Organic Al was calculated as the difference between measured monomeric Al and computed inorganic Al (Driscoll, 1984).

Although Driscoll (1984) found both methods to give similar results for natural water samples, the F technique generally gives somewhat lower values for inorganic (labile) monomeric Al than the cation exchange column method.

Soil pH was measured in a 1:2.5 (mass to volume ratio) distilled water extract. Soil organic C was measured using the method of Begheijn (1976). To estimate various fractions of free (non silicate bound) Al, samples were extracted sequentially with: 1) 1.0 M KCl (exchangeable), 2) 0.1 M $Na_4P_2O_7$ (organic), 3) 0.2 M $(NH_4)_2C_2O_4$ adjusted to pH 2 (amorphous), and 4) citrate-dithionite -bicarbonate (crystalline-free) (USDA, 1972).

This fractionation scheme was actually developed for Fe, so extractions are not entirely specific and may include some overlap (McKeague et al., 1971). The $(NH_4)_2C_2O_4$ and citrate-dithionite-bicarbonate extracts were oxidized with heat and aqua regia before analysis. Aluminum in the pyrophosphate extracts was determined by AAS with a nitrous oxide acetylene flame, while the other extracts were analysed colorimetrically using the pyrocatechol violet method (Wilson and Sargeant, 1963). Organic C was measured in the pyrophosphate extracts by combustion followed by infrared detection. Total Al was measured by x-ray fluorescence spectrometry after fusion of the soil sample with $Li_2B_4O_7$ at $1000^{\circ}C$ for 5 min in a platinum-gold crucible.

2.2.4 Computational procedures

For thermodynamic calculations we used a modified version of the chemical equilibrium model MINEQL (Westall et al., 1976). Thermochemical data are summarized elsewhere (Johnson et al., 1981; Driscoll, 1984). Thermodynamic calculations were corrected for temperature, and ionic strength corrections were made using the Davies equation (Stumm and Morgan, 1981).

To evaluate the potential for equilibrium with mineral phases we computed mineral saturation indices (SI) for soil and seep solutions:

$$\mathbf{SI = \log IAP/K}$$

where: SI is the saturation index for a mineral phase of interest, IAP is the ion activity product of the solution, and K is the thermodynamic equilibrium constant for the selected mineral phase. Positive SI values suggest that the solution is oversaturated with respect to the mineral phase of interest, whereas negative values indicate undersaturation, and values near zero suggest equilibrium.

Soil Al pools were computed for each site and horizon (down to the fragipan), based on soil chemical properties, depth and bulk density. Aluminum fluxes were calculated from estimated water flux through HBEF soil (Wood, 1980), assuming that all water entering during the biologically dormant period (15 October through 15 May) percolates through the soil and is exported as streamflow, while percolation is reduced by transpiration during the growing season (15 May through 15 October). Total transpiration (48.9 ± 1.0 cm annually; Likens et al., 1977) was partitioned proportionally to each soil horizon from the distribution of fine root biomass in each horizon. Average water fluxes observed for the HBEF (Likens et al., 1977) were multiplied by the average Al concentrations observed in the dormant (March - 15 May) and growing (15 May - July) periods, respectively.

On the average, 63% of the annual discharge at the HBEF occurs from March through July (Likens et al., 1977). Although we did not observe any significant temporal trends in soil solution concentrations during our monitoring period, the assumption that soil solution levels of Al for our observational period are representative of the annual cycle should be viewed with caution. Moreover, some water is probably short-circuited through surface horizons and into the stream, particularly during periods of high flow (e.g. snowmelt). This would result in a lower flux of Al from the deeper soil horizons than indicated by our calculations.

2.3 RESULTS

2.3.1 Soil solutions

Soil solutions were characteristically acidic and low in dissolved salts (Table 1). Organic horizon leachates generally had very low pH and elevated DOC levels. Soil solution pH generally increased and DOC decreased with depth in the mineral soil. There were no significant trends in SO_4 concentration with soil depth or site elevation.

The distribution of monomeric Al was calculated for a subset of the samples (Fig. 3). Because of limited sample volume, we were often unable to accomplish the complete chemical analysis required for thermodynamic calculations.

Elevated levels of Al were observed in all horizons. Levels were highest in the more acidic solutions of the highest site and generally decreased with decreasing elevation. Organic monomeric Al was predominant, with inorganic monomeric Al generally decreasing with decreasing elevation.

Table 1. Mean and standard deviation of solute concentrations in all analyzed soil solutions collected from March through July 1982 just beneath the horizons indicated.

Site	Horizon	pH	Specific conductance	Monomeric Al	SO_4	DOC	SiO_2
			$mS\ m^{-1}$	$mmol\ m^{-3}$			
I	O2	3.62 ± 0.45	11.5 ± 14.0	37.4 ± 17.4	85 ± 15	3800	112 ± 52
	E	4.36 ± 0.95	8.7 ± 3.9	21.4 ± 20.7	72 ± 9	1200	70 ± 50
	Bhs1	4.67 ± 0.16	3.2 ± 0.6	31.5 ± 9.3	50 ± 10	840 ± 410	103 ± 50
	Bhs3	4.77 ± 0.79	3.4 ± 0.6	24.1 ± 9.3	52 ± 6	1033	80 ± 15
II	O2	4.95 ± 0.50	4.2 ± 3.4	15.2 ± 7.0	48 ± 11	450 ± 450	133 ± 72
	E	4.63 ± 0.20	3.6 ± 1.3	18.5 ± 13.7	49 ± 5	330 ± 130	107 ± 27
	Bhs1	5.05 ± 0.09	2.2 ± 0.4	11.8 ± 5.2	52 ± 4	190 ± 120	105 ± 14
	Bhs2	5.12 ± 0.20	2.2 ± 0.4	9.3 ± 3.0	52 ± 14	220 ± 70	123 ± 20
III	O2	4.49 ± 0.56	4.2 ± 1.7	7.0 ± 4.1	71 ± 35	2400 ± 1100	50 ± 37
	E	4.93 ± 0.43	3.0 ± 0.6	12.6 ± 9.3	56 ± 24	1000 ± 670	55 ± 48
	Bhs1	5.19 ± 0.16	2.1 ± 0.4	10.4 ± 3.3	47 ± 16	500 ± 120	77 ± 27
	Bhs3	5.22 ± 0.26	2.2 ± 0.5	10.0 ± 3.7	48 ± 9	520 ± 180	112 ± 18

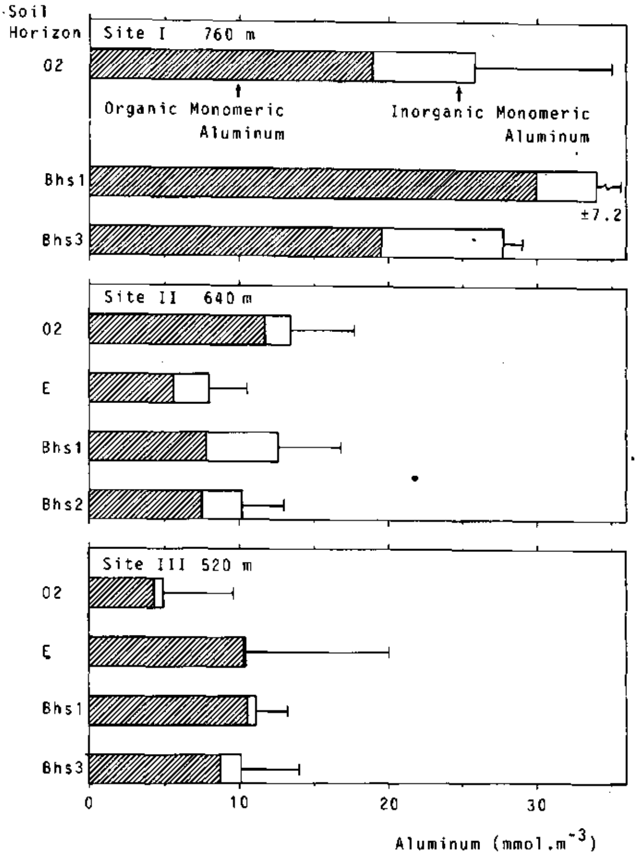

Fig. 3.Concentrations of inorganic, organic and monomeric Al, in those soil solutions for which sufficient data were available to calculate the speciation of Al. Error bars represent one half of a standard deviation of measured monomeric Al values.

Our calculations for the relative distribution of inorganic forms (Fig. 4) suggest that Al^{3+} was the predominant form of Al at the very acidic, high elevation site. At the lower sites, Al-F complexes became predominant. Hydroxy-Al was also present in significant quantities. Aluminum-SO$_4$ forms were generally insignificant.

At the highest site, F was almost entirely Al-bound (Fig. 5). Molar concentrations of Al at this site greatly exceeded molar concentrations of F. At intermediate elevation (site II), molar levels of inorganic Al were comparable to molar F levels. Hence, while Al-F still predominated, there were significant levels of free F in solution. At the low elevation site (site III), molar concentrations of F

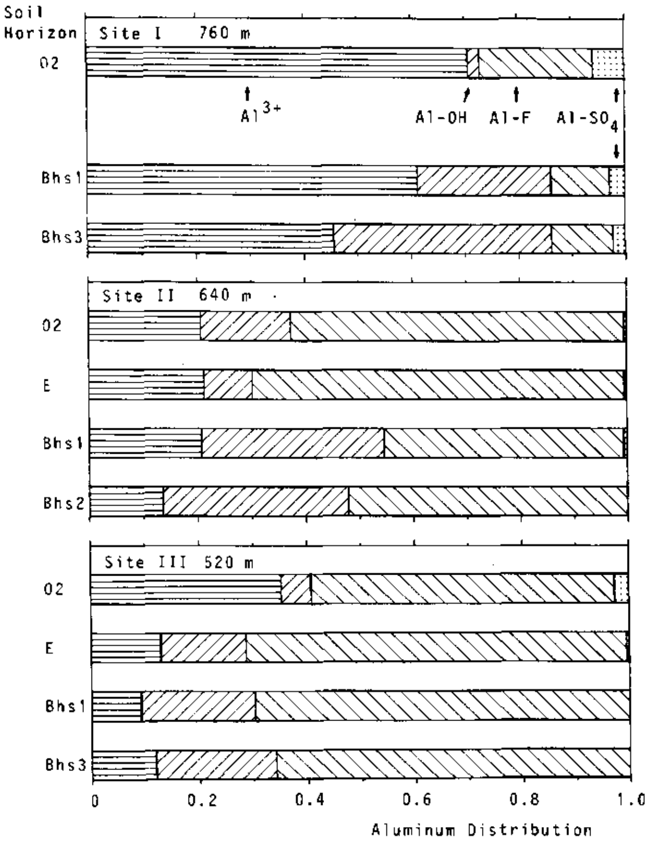

Fig. 4. Relative distribution of inorganic Al in HBEF soil solutions.

generally exceeded inorganic Al levels. Therefore, free F was a large fraction of total F.

We also evaluated the IAP for a number of Al mineral phases. Our results for B horizon soil solutions were similar to those reported by Johnson et al. (1981) for HBEF streams. Briefly, B horizon solutions were generally undersaturated with respect to jurbanite ($Al(OH)SO_4.5H_2O$; p*Kso = 17.8; Nordstrom, 1982) and kaolinite ($Al_2Si_2O_5(OH)_4$; p*Kso = -3.3; Stumm and Morgan, 1981), and oversaturated with respect to halloysite ($Al_2Si_2O_5(OH)_4$; p*Kso = -5.66; Hem et al., 1972). To illustrate soil depth trends in SI values we used natural gibbsite (May et al., 1979) as an index mineral. Johnson et al. (1981) reported that HBEF streams were close to saturation with this mineral. Soil solutions were highly

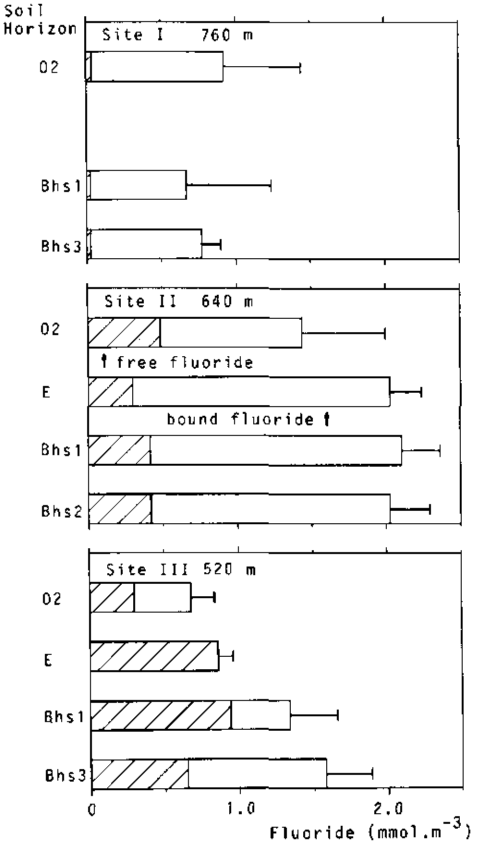

Fig. 5.Concentrations of free and total F in HBEF soil solutions. Error bars represent one half of a standard deviation of measured total F values.

undersaturated with respect to natural gibbsite in the surface horizons (O2, E) but approached saturation, particularly at the higher sites (I, II; Table 2) and in the deeper horizons.

2.3.2 Soil properties

The soils sampled in our study were generally acidic, with the high elevation site exhibiting the lowest pH values (Table 3). Free Al was a relatively small (20%) fraction of total soil Al. The distribution of free Al was similar at all sites but the

Table 2. Mean saturation indices (SI) and standard deviations with respect to natural gibbsite solubility ($p^{*}K_{so}$=-8.77, May et al., 1979) for HBEF solutions.

Horizon	Site I-760 m	Site II-640 m	Site III-520 m
		Soil solutions (SI = log IAP/K)	
O2	-5.33 ± 3.18	-1.50 ± 1.45	-2.57 ± 1.21
E	-	-1.64 ± 0.20	-3.11 ± 1.73
Bhs1	-0.54 ± 0.50	-0.03 ± 0.25	-1.48 ± 1.45
Bhs2	-0.03 ± 0.21	-0.38 ± 0.49+	-0.87 ± 0.64
		Seep solutions	
			SI = 0.04 ± 0.20
		Stream solutions $	
			SI = -0.11 ± 0.36

+ Site II lower horizon is Bhs2

$ Johnson et al., 1981

Table 3. Some properties of HBEF soils.

Site	Horizon	Bulk density+	pH (H_2O)	Total Al	TOC	Organic C in 0.1 M $Na_4P_2O_7$
		kg m^{-3}		--------	mol kg^{-1}	-------
I-760 m	O2	270	3.58	0.233	31.76	3.12
	E	1060	3.77	0.832	1.51	0.64
	Bhs1	750	4.00	0.896	3.99	2.19
	Bhs2	880	4.14	1.029	3.68	2.72
	Bhs3	880	4.39	1.214	2.30	1.89
	Cx	1500	4.18	1.002	0.64	0.68
II-650 m	O2/A1	770	4.31	0.754	11.73	1.45
	E	1060	4.21	0.773	1.12	0.50
	Bhs1	750	4.20	0.909	3.66	2.36
	Bhs2	880	4.39	1.006	2.55	2.07
	Cx	1500	5.25	1.089	1.12	0.77
III-520 m	O2	270	4.21	0.288	31.42	3.40
	E	1060	3.90	0.957	1.07	0.40
	Bhs1	750	4.05	1.032	2.03	2.28
	Bhs2	880	4.24	1.193	1.92	1.92
	Bhs3	880	4.29	1.180	1.62	1.35
	Cx	1500	4.56	1.314	0.51	0.37

+ Wood, 1980

concentration varied from site to site (Fig. 6). Organic Al (pyrophosphate extractable) was generally the dominant form of free Al. The free Al content was

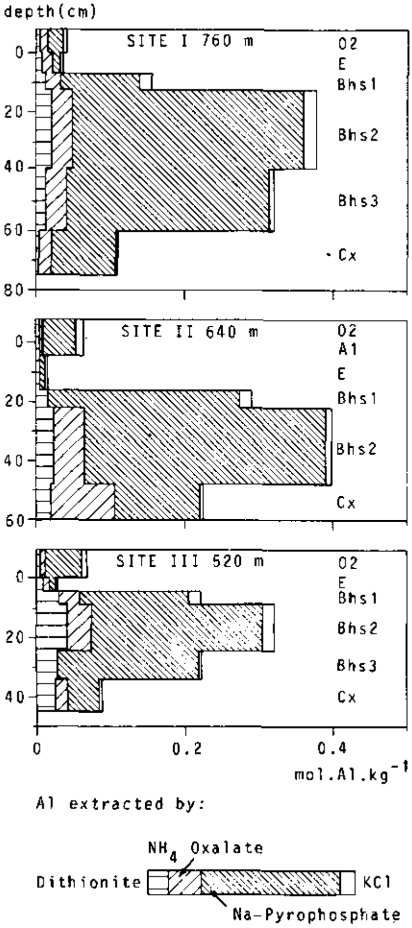

Fig. 6.The vertical distribution of free Al at HBEF soil study sites. The soils were extracted sequentially with potassium chloride, sodium pyrophosphate, ammonium oxalate and citrate-dithionite-bicarbonate solutions.

depleted in the E horizons and enriched in the B horizons. At all sites the free Al content was greater in the O2 than in the E horizon.

Total organic C and pyrophosphate extractable C were highest in the O2 horizon, exhibited a minimum in the E horizon, peaked in the Bhs1 horizon, and declined with further depth in the soil (Table 3). In the surface horizon, the ratio of pyrophosphate extractable C to TOC was low (0.1). This ratio approached one (0.55 - 1.12) in the B horizons, suggesting that the bulk of the organic C in the lower soil (B and upper Cx horizons) was associated with Al and Fe.

2.3.3 Seep solutions

The composition of seep solutions was generally similar to that of soil solutions (Table 4). The headwater seeps (725 m, 665 m) were acidic and contained relatively low concentrations of basic cations (Ca, Mg, Na, K). The lower elevation seeps (635 - 400 m) were less acidic and more enriched with respect to basic cations. The headwater seeps contained the highest concentrations of monomeric Al, and in particular inorganic Al (Fig. 7). In the lower elevation seeps, organic forms of Al predominated. Seep solutions were essentially in equilibrium with natural gibbsite (Table 2), similar to HBEF stream waters (Johnson et al., 1981).

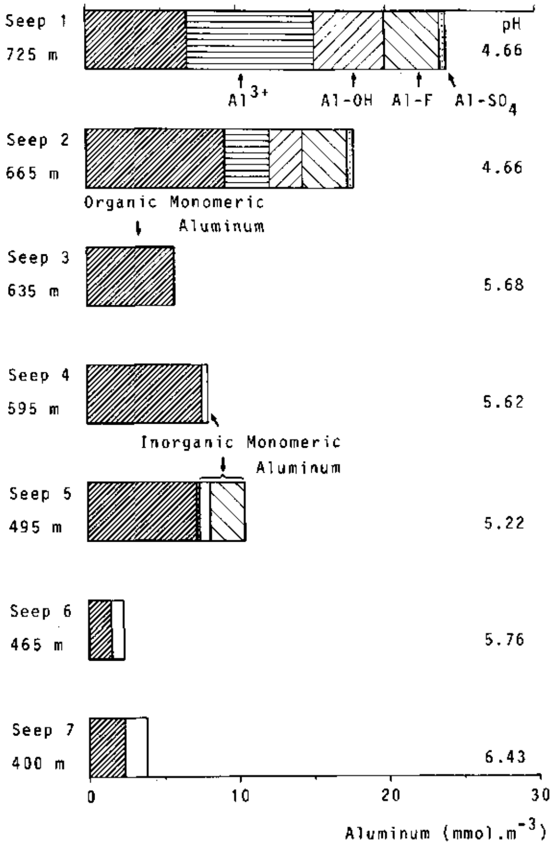

Fig. 7. The concentrations of Al species in HBEF seeps.

Table 4. Mean and standard deviation of solute concentrations in seep solutions collected from May through September 1979.

Seep	Elevation	pH	SC	Monomeric Al	Ca	Mg	Na	K	SO_4	Cl	DOC
	m		mS m^{-1}	mmol m^{-3}							
1	725	4.73 ± 0.08	1.9 ± 0.3	17.3 ± 7.3	16 ± 3	5 ± 1	22 ± 5	3 ± 1	54	16	240
2	665	4.77 ± 0.07	2.1 ± 0.2	17.9 ± 2.5	23 ± 3	7 ± 1	24 ± 6	3 ± 4	55	32	400
3	635	5.69 ± 0.15	2.1 ± 0.1	3.5 ± 3.0	39 ± 4	17 ± 2	76 ± 5	3 ± 0	45	31	1600
4	595	5.60 ± 0.25	2.4 ± 0.3	8.4 ± 4.8	46 ± 11	25 ± 5	59 ± 9	7 ± 2	72	25	1500
5	495	5.22 ± 0.07	1.8 ± 0.2	8.6 ± 2.1	28 ± 2	11 ± 1	49 ± 11	4 ± 2	55	15	340
6	465	5.67 ± 0.22	1.8 ± 0.1	2.2 ± 1.8	34 ± 0.8	14 ± 1	47 ± 9	8 ± 1	38	15	60
7	400	6.32 ± 0.12	2.7 ± 0.4	3.7 ± 1.9	66 ± 7	19 ± 3	67 ± 15	11 ± 2	60	23	540

To examine the nature of seeps more closely, we exposed the soil of a seep (635 m) area. This seep was characterized by an AC horizon covered with organic matter. It appeared that the water flowed laterally over the Cx horizon and then exited the soil through the O2 and AC horizons when the fragipan came to the surface of the mineral soil. Hence, seep water was in intimate contact with both mineral and organic soil just prior to leaving the soil.

2.3.4 Pools and fluxes

Free Al and pyrophosphate extractable organic C were primarily associated with the Bhs2 and Bhs3 horizons. Pools of TOC were generally elevated in the O2 horizon and to a lesser extent in the Bhs2 and Bhs3 horizons. Although pools of Al in the forest floor were low relative to other soil horizons, a comparison with previous HBEF studies (Gosz et al., 1976; Likens et al., 1977) suggests that Al is still the most abundant cation in the forest floor, on a molar basis. Pools of nearly every Al and organic C fraction declined with decreasing elevation.

Most of the Al migrating through the soil profile appeared to be associated with organic solutes. On an annual basis 8.5 mmol m^{-2} yr^{-1} of monomeric Al entered the mineral soil from the forest floor, an additional 2.6 mmol m^{-2} yr^{-1} was solubilized from the Bhs1 horizon and an equal amount was deposited in the Bhs2/Bhs3 horizons, resulting in an annual loss of 8.5 mmol m^{-2} yr^{-1} (Table 5). However, the mineral soil served as a net sink for organic Al (1.1 mmol m^{-2} yr^{-1}) and a net source of inorganic Al (1.1 mmol m^{-2} yr^{-1}). Fluxes of Al were also considerably different during the dormant and growing seasons. During the dormant period there was a slight net loss of organic Al (0.4 mmol m^{-2} yr^{-1}) and a pronounced net loss of inorganic Al (1.1 mmol m^{-2} yr^{-1}) from the mineral soil. During the growing season the mineral soil served as a net sink for both inorganic (0.1 mmol m^{-2} yr^{-1}) and organic (1.5 mmol m^{-2} yr^{-1}) Al.

2.4 DISCUSSION

2.4.1 Spodosolization at the HBEF

Our observations indicate that Al transport and spodosolization was most intense at the high elevation site. This is in accordance with the research of Legros and Barthes (1975), who found that spodosol morphology became more

Table 5. Water^{+} and monomeric aluminum fluxes for the dormant (15 October-15 May) and growing (15 May-15 October) periods at the HBEF.

	Dormant season				Growing season				Annual			
		Monomeric Al				Monomeric Al				Monomeric Al		
Horizon	Water	Total	Organic	Inorganic	Water	Total	Organic	Inorganic	Water	Total	Organic	Inorganic
	m yr^{-1}	----- mmol m^{-2} yr^{-1} -----			m yr^{-1}	----- mmol m^{-2} yr^{-1} -----			m yr^{-1}	----- mmol m^{-2} yr^{-1} -----		
O2	0.600	5.2	4.8	0.4	0.361	3.3	2.9	0.4	0.961	8.5	7.8	0.7
E	0.600	4.4	3.7	0.7	0.323	4.1	3.7	0.4	0.923	8.5	7.4	1.1
Bhs1	0.600	7.8	6.3	1.5	0.297	3.3	2.2	1.1	0.897	11.1	8.5	2.6
Bhs2/Bhs3	0.600	6.7	5.2	1.5	0.181	1.7	1.4	0.3	0.781	8.5	6.7	1.8

+ 1.32 m of water enter HBEF annually; Likens et al., 1977 distinct with increasing elevation in the Central Massif of France. Because the soils at the HBEF are so heterogeneous, we are reluctant to extrapolate these trends to the ecosystem as a whole. Indeed, the soil depth of our sites increased with elevation, which may be atypical for HBEF soils (Johnson et al., 1981).

Our results were generally consistent with spodosolization theory (Ugolini et al., 1977). Organic C to organic Al ratios generally decreased with increasing soil depth (Table 6). It is well established that the solubility of alumino-organic substances decreases as the molar ratio of organic C to Al (and Fe) decreases (Schnitzer and Skinner, 1963a, b). If alumino-organic substances are precipitated within HBEF soils, due to a decrease in the organic C to Al ratio of organic solutes, we would anticipate that the soil solution would have a greater organic C to organic Al ratio than the soil. Indeed, within the B horizon, organic C to organic Al ratios were almost always higher in the soil solution than in the soil (Table 6).

Table 6. Molar ratios of organic C to organic Al in soil (0.1 M $Na_4P_2O_7$ extract) and soil solutions collected beneath the horizon indicated.

Site	Horizon	Soil	Soil solution
I	02	228	198
	E	109	-
	Bhs1	37	28
	Bhs2	17	-
	Bhs3	14	53
	Cx	16	-
II	02/A1	55	38
	E	185	59
	Bhs1	18	24
	Bhs2	13	29
	Cx	13	-
III	02	124	548
	E	82	100
	Bhs1	29	48
	Bhs2	16	-
	Bhs3	14	60
	Cx	17	-

In soils, a reduction in the organic C to Al ratio may be accomplished by: (i) Al complexation by organic acids as these solutes are transported through the mineral soil and/or (ii) microbial oxidation of organic C within the soil profile. It would appear that the former mechanism was operating to some extent at our sites. Over the annual cycle organic Al was solubilized from the Bhs1 horizon and deposited in the lower B horizons, indicating a deepening of the spodosol profile. However, the most prominent feature of our flux calculations is the high levels of organic Al exported from the O2 horizon. Although high concentrations of Al in organic horizon leachates and relatively large pools of Al in the forest floor have been reported previously (Cronan and Schofield, 1979; David and Driscoll, 1984), such phenomena have not been incorporated adequately into the theory of spodosol development. While the source of this forest floor Al is unknown, it is most likely transported from the mineral soil by biocycling (e.g. via leaf or root litter) or by windthrown trees.

If we divide the pool of organic (pyrophosphate extractable) Al in the mineral soil by the age of the soil (time elapsed since the time of the last glaciation, 14,500 yr), an estimate for the historical rate of Al deposition can be made. This gives 8.9, 6.1, and 3.6 mmol m^{-2} yr^{-1} for the 760, 640, and 520 m sites respectively. The historical rate of organic Al deposition is thus considerably greater than the current rate of organic Al precipitation from the soil solution (1.1 mmol m^{-2} yr^{-1}). This suggests either that the rate of spodosol development has decreased or that additional, more significant, mechanisms of organic Al accumulation in the Bhs horizon, e.g. by root turnover, are operating in HBEF soils.

2.4.2 The role of acidic deposition in Al transport at the HBEF

Johnson and co-workers (Johnson, 1979; Johnson et al., 1981) have hypothesized that acidic deposition entering the HBEF was initially neutralized by the dissolution of reactive alumina, resulting in a solution that consisted of a mixture of hydrogen ions and aluminum acidity. This acidity was subsequently neutralized by the relatively slow dissolution of basic cations. Cronan and Schofield (1979) reported elevated levels of Al in the O and E horizons of a New Hampshire forest soil, and attributed the leaching and seepage of this Al to acidic deposition.

Our results also suggest that Al cycling within the terrestrial environment is much more complicated than previously thought. Biota within the forest ecosystem appear to have a profound effect on Al chemistry and transport. Much of the free Al in soils appears to be associated with organic matter, and much of the Al in soil solutions and seeps, appears complexed to organic solutes. Nevertheless, we report the removal of significant quantities of dissolved inorganic Al, largely from the Bhs1 horizon, which are not retained in the lower B horizons but rather are exported to streams. Like Johnson (1979), we observed the highest levels of inorganic monomeric Al at high elevation sites, where inputs of acidic deposition may be much greater than at lower sites (Lovett et al., 1982), and where contact time of the solution phase with the soil may be relatively short.

If solutions tend to approach equilibrium with an $Al(OH)_3$ mineral phase, as our SI data suggest, then increases in mineral acid loadings to the system should increase the dissolution of inorganic Al (Driscoll and Likens, 1982). During the biologically dormant period in particular, inorganic forms of dissolved Al were removed from the Bhs1 horizon and transported through the soil profile. This process is similar to that reported by Cronan and Schofield (1979). During snowmelt, which coincides with the biologically dormant period at the HBEF, large quantities of mineral acids that have accumulated in the snowpack are also released to the soil and may facilitate the removal of dissolved inorganic Al. High rates of dissolved inorganic Al export from soil during the dormant season and limited inorganic Al flux during the growing season are consistent with the findings of Johnson et al. (1981) for HBEF streams. In view of the significance of Al as a potential toxicant, further research to evaluate the natural cycling of Al and the effects of atmospheric inputs of mineral acids on this cycling appear to be warranted.

ACKNOWLEDGMENTS

We are indebted to F.H. Bormann, J.S. Eaton, C.R. Frink, N.M. Johnson, G.E. Likens, W. Martin and R.S. Pierce for their support and encouragement in our study. We would particularly like to thank M. van de Pol for sampling and analysis of soil solutions, M.T.M.H. Lubbers and A.J. Kuijper for analyzing the soil samples, P.G.M. Versteeg for preparing the figures, and the Department of Textprocessing, Agricultural University, for doing the typing. Financial support was provided by the National Science Foundation. The Hubbard Brook Experimental Forest is operated by the USDA Forest Service, Broomall, Pennssylvania.

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Chapter 3

IMPACTS OF ACID ATMOSPHERIC DEPOSITION ON WOODLAND SOILS IN THE NETHERLANDS: III. ALUMINUM CHEMISTRY

ABSTRACT

Annual element budgets for three acidic oak-birch (Quercus robur L.-Betula pendula L.) woodland soils in the Netherlands indicate high inputs of atmospheric $(NH_4)_2SO_4$ *(2.35 to 3.45 kmol* NH_4 *ha*$^{-1}$ *yr*$^{-1}$*). Nitrogen transformations lead to strong acid inputs of 3.0 to 7.5 kmol*$_c$ *ha*$^{-1}$ *yr*$^{-1}$ *in these soils, which were neutralized primarily by solubilization of Al in the surface 20-cm mineral layers (3 to 7 kmol*$_c$ *ha*$^{-1}$ *yr*$^{-1}$*). We hypothesize that Al was relatively important in neutralizing strong acid inputs, due to the high acid loading and the low content of base cations. At the low pH (pH 3.27 - 4.26) dissolved Al in the mineral soil was mainly in aquo-*Al^{3+} *form. Highest Al concentrations (up to 4 mol*$_c$ *m*$^{-3}$*) were reached in summer and coincided with high* NO_3 *concentrations. In winter and spring, the export of Al with drainage water peaked and solute concentrations decreased. All Al mobilized in the surface layers of soil A was retained below the 40-cm depth, probably due to cation exchange, since below this depth base saturation increased. In the deeper horizons of soils B and C, immobilization of Al was less, probably because base saturation was low. All subsoil solutions were undersaturated with respect to gibbsite, and near equilibrium with jurbanite. Formation of jurbanite is unlikely, however, because mass balance calculations do not indicate net* SO_4 *retention.*

3.1 INTRODUCTION

An increased mobilization of Al from acidic forest soils in central and northwestern Europe (Ulrich et al., 1979; Nilsson and Bergkvist, 1983) and northeastern North America (Cronan and Schofield, 1979; Johnson et al., 1981; David and Driscoll, 1984; Driscoll et al., 1985) has been suggested recently. Three lines of evidence indicate that Al mobilization is associated with atmospherically derived H_2SO_4 and HNO_3. Compared with relatively unpolluted regions (Ugolini et al., 1977), soil solutions in areas with high atmospheric acid input (i) have increased total Al concentrations, (ii) contain significant amounts of inorganic monomeric Al forms (David and Driscoll, 1984; Driscoll et al., 1985;

Mulder and van Breemen, 1987), and (iii) have increased concentrations of SO_4^{2-} and sometimes NO_3^- (Johnson et al., 1981; Ulrich et al., 1979).

Chemical budgets for a variety of catchments (van Breemen et al., 1984) show that in northeastern North America and central and northwestern Europe, the input of strong acid enhances soil acidification in acidic soils and is associated with leaching of inorganic Al and/or partial retention of SO_4^{2-}.

Increased concentrations and fluxes of dissolved Al in acidic soils not only indicate a change in pedogenetic processes, but may also have adverse effects on terresrial and aquatic biota (Andersson and Kelly, 1984; Baker and Schofield, 1980). Therefore, detailed information on mechanisms of strong acid neutralization and Al chemistry in acidic soils impacted by acid deposition is highly relevant.

The objective of this research was to study the effect of high loading of atmospherically derived strong acids on the Al chemistry and transfer in acidic sandy soils, poor in easily weatherable minerals. Soil solution chemistry and hydrochemical budgets for 3 yr were evaluated for three acidic woodland soils in the Netherlands and for individual layers between the 0 and 90-cm depth. Calculation of hydrochemical budgets as well as the associated uncertainties and the importance of N transformations in soil acidification are discussed in two companion papers (van Grinsven et al., 1987; van Breemen et al., 1987). A calcareous site, which also occurs in the same woodland, is not discussed in this paper, because no Al mobilization was observed there (van Breemen et al., 1988).

3.2 MATERIALS AND METHODS

3.2.1 Experimental setting and monitoring program

The research was conducted in three different soils, located in a 3.2 ha oak-birch (*Quercus robur L.-Betula pendula L.*) woodland in the Netherlands. Briefly, these soils include (A) an acidic, loamy sand, with a calcareous subsoil starting at the 75-cm depth (Haplaquept); (B) an acidic sandy soil (Dystrochrept); and (C) a moderately acidic sandy soil (Udipsamment). For details on the research sites see van Breemen et al. (1988) and van Grinsven et al. (1987). Selected chemical data of the three soils are given in Table 1.

The monitoring procedure for meteoric water and soil solutions are given by van Breemen et al. (1987, 1988). Soil solutions were sampled monthly from type

Table 1. Selected chemical properties for the three soils studied.

Site	Soil depth	pH(H_2O)	CEC	Base sat.	Exch. Al	CEC*	Al pools*	
							Exch.	Free
	cm		$mmol_c\ kg^{-1}$	----- %	------	----	$kmol_c\ ha^{-1}$	----
A	0-10	3.8	67	11	31	72	22	395
	10-20	3.7	64	3	33	80	26	612
	20-30	3.9	41	2	44	57	25	680
	30-40	3.8	50	-	-	70	-	634
	40-50	3.9	39	4	38	59	23	634
	50-60	4.1	36	36	25	54	13	510
	60-70	5.8	43	100	0	65	0	415
B	0- 4	3.8	98	20	28	28	8	80
	4- 8	3.7	62	8	39	25	10	92
	8-20	4.0	31	3	48	39	19	473
	20-30	4.1	20	2	45	22	10	496
	30-40	4.2	15	3	40	17	7	525
	40-48	4.2	16	1	38	16	6	430
	48-60	4.3	11	2	27	21	6	344
	60-90	4.5	7	5	43	33	14	337
C	0-10	4.0	41	27	22	42	93	403
	10-15	4.1	28	16	32	17	6	149
	15-25	4.2	27	10	44	38	17	735
	25-40	4.1	17	5	53	37	20	1137
	40-50	4.2	14	7	43	21	9	581
	50-57	4.2	13	8	46	14	6	345
	57-70	4.2	9	8	33	18	6	629
	70-80	4.4	7	4	43	10	4	225
	80-90	4.4	3	6	0	5	0	276

* Bulk densities were taken from van Breemen et al., 1987b

1910 ceramic cups (Soil Moisture Corp., Santa Barbara, CA), using a vacuum of 50 to 80 kPa. We anticipated a release of significant amounts of Al from the ceramic cups in our acidic soils. However, when flushed slowly with dilute H_2SO_4 (pH 3 - 4), the cups released Al to concentrations of 0.01 to 0.15 $mol_c\ m^{-3}$, which were low in comparison to values observed in soil solutions over the same pH range (0.3 to 3 $mol_c\ m^{-3}$).

3.2.2 Analytical techniques

Within 1 d of collection, all solution samples were analyzed for pH, specific conductance, and total and inorganic dissolved C. Within 14 d after collection all samples, stored at room temperature, were analyzed for Ca, Mg (atomic absorption), Na, K (atomic emission), H_4SiO_4 (colorimetrically as the blue silica-molibdic acid complex), F, Cl, NO_3, SO_4 (ion chromatography), NH_4 (van Breemen et al., 1988) and total Al (colorimetrically with pyrocatechol violet, Wilson and Sergeant, 1963). All colorimetric analyses were conducted with an autoanalyzer.

Total dissolved Al (monomeric plus polymeric forms) was determined after acidifying solutions to pH 2, at least 24 h before analysis. In four monthly series of soil solutions from all three sites, monomeric Al was measured in nonacidified samples, 6 min after addition of pyrocatechol violet. An upper limit of organic monomeric Al was estimated by assuming all organic anions, calculated from charge balance discrepancies, were associated with Al. Organic monomeric Al concentrations could not be estimated reliably from measured Al in the effluent of an Amberlite 120 IR cation exchange column (Driscoll, 1984); due to its high concentration only 90 to 95% of the dissolved inorganic Al was removed by the Amberlite.

Soil pH was measured in a 1:2.5 (mass to volume ratio) distilled water extract. Cation Exchange Capacity (CEC) and exchangeable cations (base cations, H and Al) were both determined using Bascomb's (1964) $BaCl_2$-$MgSO_4$ procedure (unbuffered). In all acidic soil layers, exchangeable acidity was higher than exchangeable base cations (Table 1). A considerable fraction of the exchangeable acidity was H^+. Extraction with 1 M KCl gave essentially the same results. Free Al in soil was estimated by oxalate-dithionite extraction (Begheijn, 1980).

3.2.3 Computational procedures

Fluxes of solutes in meteoric water were calculated by multiplying monthly determined concentrations and measured amounts of rain and throughfall. Solute fluxes in the soil at various depths were calculated as described by van Grinsven et al. (1987).

We calculated the annual strong acid load of the soil as the sum of acid production caused by H, N, S, and Cl transformations:

$$\begin{aligned} H^+_{prod} &= (H^+)_{in} - (H^+)_{out} + (NH_4^+)_{in} - (NH_4^+)_{out} \\ &+ (NO_3^-)_{out} - (NO_3^-)_{in} + (SO_4^{2-})_{out} - (SO_4^{2-})_{in} \\ &+ (Cl^-)_{out} - (Cl^-)_{in} \qquad [1], \end{aligned}$$

where parentheses denote fluxes and the subscripts 'in' and 'out' indicate input and output, respectively. Because dry deposition was an important contribution to the total input of NH_4, NO_3, SO_4, and Cl in the system, throughfall fluxes were used to estimate the total inputs of these components. The input of H^+ was taken as free H^+ in precipitation plus the acidity in dry deposition. Dry deposited acidity was estimated as (see van Breemen et al., 1988):

$$H^+_{dry} = (SO_4^{2-})_{th} - (SO_4^{2-})_{pr} + (NO_3^-)_{th} - (NO_3^-)_{pr} + (NH_4^+)_{pr} - (NH_4^+)_{th} \quad [2],$$

where the subscripts 'pr' and 'th' denote bulk precipitation and throughfall fluxes, respectively.

Mobilization of Al (Al_{mob}), base cations (cat_{mob}), and SiO_2 ($(SiO_2)_{mob}$) were calculated as:

$$Al_{mob} = (Al)_{out} - (Al)_{in} \quad [3],$$

$$cat_{mob} = (Na)_{out} - (Na)_{in} + (K)_{out} - (K)_{in} + (Ca)_{out} - (Ca)_{in} + (Mg)_{out} - (Mg)_{in} \quad [4],$$

$$(SiO_2)_{mob} = (SiO_2)_{out} - (SiO_2)_{in} \quad [5],$$

where parentheses denote fluxes. Because dry deposition of Al, K, Ca, Mg and SiO_2 was negligible (van Breemen et al., 1988), bulk precipitation fluxes of these compounds were used as input to the ecosystem. Total deposition of Na was partly due to dry deposition (van Breemen et al., 1988), so for this cation, throughfall fluxes were taken as input.

Annual solute fluxes (mol m^{-2} yr^{-1}) were divided by corresponding water fluxes (m yr^{-1}) to give flux-weighted soil solution concentrations (mol m^{-3}).

Variability for fluxes and budgets of Al (i.e., inputs from above minus drainage outputs) were mainly due to spatial variability and coefficients of variation (CV) ranged from 10 to 30% for all three profiles. The CV values for budgets of individual soil layers, which do not include the soil surface (10-40 and 40-90 cm depth) amount to 40 to 200% (van Grinsven et al., 1987). These large CV values refer to small budget values, obtained by subtracting two large fluxes, and are therefore of little importance.

Mineral equilibria in soil solutions were calculated for all soil solution samples from April 1981 to March 1983, using the chemical equilibrium model MINEQL (Westall et al., 1976). Thermodynamic calculations were corrected for temperature, and ionic strength corrections were made using the Davies equation. Soluble Al-Si complexes (Farmer et al., 1980; Childs et al., 1983) could not be included in the MINEQL calculations, because of lack of accurate thermodynamic data. However, dissolved Al-Si complexes presumably occur in polymeric forms (Wada and Wada, 1980) and can probably be disregarded in equilibrium calculations involving monomeric Al. Aluminum activities were calculated assuming that all monomeric Al was in an inorganic form. This leads to an overestimation of the Al activity only for soil solutions from the top 20-cm (see Results).

Mineral saturation indices (SI) of soil solutions with respect to some secondary minerals were calculated according to:

$$\mathbf{SI = \log Q_p/K_p} \qquad \mathbf{[6],}$$

where Q_p = ionic activity product for the solid phase p, and K_p = solubility product for the solid phase p, and where $SI = 0$ indicates equilibrium, $SI > 0$ oversaturation and $SI < 0$ undersaturation with respect to the solubility of the mineral considered. The K_p values were taken from Johnson et al. (1981); basaluminite values were from Singh and Brydon (1969). The K_p values for synthetic and natural gibbsite were corrected for temperature using the reaction enthalpy of microcrystalline gibbsite (Ball et al., 1980).

3.3 RESULTS AND DISCUSSION

3.3.1 Soil solution composition

In solutions draining from the rooting zone in all three soils Al was the major cation, and NO_3 and SO_4 were the major anions. This is illustrated in Table 2 for soil B. High Al, NO_3 and SO_4 concentrations were characteristic for all solutions from depths below 20 cm.

Table 2. *Soil solution composition in soil B at the 60-cm depth.* Concentrations are flux-weighted annual means and (temporal) standard deviations, from April 1981 to March 1984 (n=3). Mean pH was calculated from flux-weighted mean H^+ activities.

Uncharged		Cations		Anions	
$mol\ m^{-3}$		$mol_c\ m^{-3}$		$mol_c\ m^{-3}$	
SiO_2	0.29 ± 0.01	K^+	0.19 ± 0.01	F^-	0.01 ± 0.01
DOC	2.31 ± 0.26	Na^+	0.24 ± 0.07	Cl^-	0.43 ± 0.05
		Ca^{2+}	0.44 ± 0.02	NO_3^-	1.45 ± 0.21
		Mg^{2+}	0.24 ± 0.04	SO_4^{2-}	1.13 ± 0.14
		Al^{3+}	1.86 ± 0.12	A^- *	0.19 ± 0.11
		H^+	0.10 ± 0.01		

* A^- is the mean annual charge balance discrepancy, which is mainly due to deprotonation of organic acids

Concentrations of total dissolved Al (ranging from 0.3 to 4 $mol_c\ m^{-3}$) were high compared to maximum values reported for spodosol solutions in the USA and Scandinavia (0.15 $mol_c\ m^{-3}$; Ugolini et al., 1977; David and Driscoll, 1984; Driscoll et al., 1985; Nilsson and Bergkvist, 1983). Sulfate and NO_3 were also higher in our soil solutions than in those from the USA and Scandinavia, due to higher loadings of S and N compounds (van Breemen et al., 1987, 1988) and a strong evaporative concentration of soil solutions (ranging from 2.9 - 3.7; van Grinsven et al., 1987). Only Typic Dystrochrepts in the Solling area (FRG) have similar solute concentrations (Ulrich et al., 1979).

3.3.2 Aluminum chemistry

Dissolved Al concentrations increased with depth (except for site A > 60-cm depth) and were highest in soils A and B, and lowest in soil C (Table 3).

Table 3. Total Al concentrations and pH in solutions from soils A, B, and C. Values are flux-weighted annual means and (temporal) standard deviations from April 1981 to March 1984 (n=3).

Site	Soil depth	pH	Al
	cm		$mol_c\ m^{-3}$
A	10	3.40 ± 0.08	0.69 ± 0.23
	20	3.51 ± 0.08	1.05 ± 0.20
	40	3.73 ± 0.08	2.33 ± 0.48
	60	4.49 ± 0.18	0.50 ± 0.13
	90	6.74 ± 0.42	0.08 ± 0.11
B	10	3.27 ± 0.12	0.54 ± 0.43
	20	3.33 ± 0.10	0.98 ± 0.15
	40	3.82 ± 0.09	1.73 ± 0.45
	60	3.98 ± 0.01	1.85 ± 0.14
	90	4.03 ± 0.13	1.86 ± 0.34
C	10	3.74 ± 0.04	0.60 ± 0.18
	20	3.69 ± 0.04	0.51 ± 0.14
	40	4.04 ± 0.03	0.81 ± 0.11
	60	4.04 ± 0.18	0.74 ± 0.13
	90	4.26 ± 0.23	1.06 ± 0.16

Concentrations of Al varied seasonally, with highest values at the end of summer (Fig. 1). Chloride concentrations increased much less over the summer period, suggesting that the observed increase in Al concentration was only partly due to evaporative concentration. The main cause for the seasonal increase in dissolved Al was the increase in NO_3 concentration (Fig. 1), due to nitrification of NH_4 and organic N. The importance of nitrification in Al mobilization has been noted by van Breemen and Jordens (1983), who found good correlations ($0.51 < r < 0.89$ and $p < 0.01$) between concentrations of Al and NO_3 in these acidic soils, whereas SO_4 and Al were correlated only weakly. Unlike soils A and B, soil C showed only a slight net NO_3 production (van Breemen et al., 1987) through summer, hence NO_3 and Al concentrations increased mainly by evaporative concentration. Although Al concentrations were highest in summer,

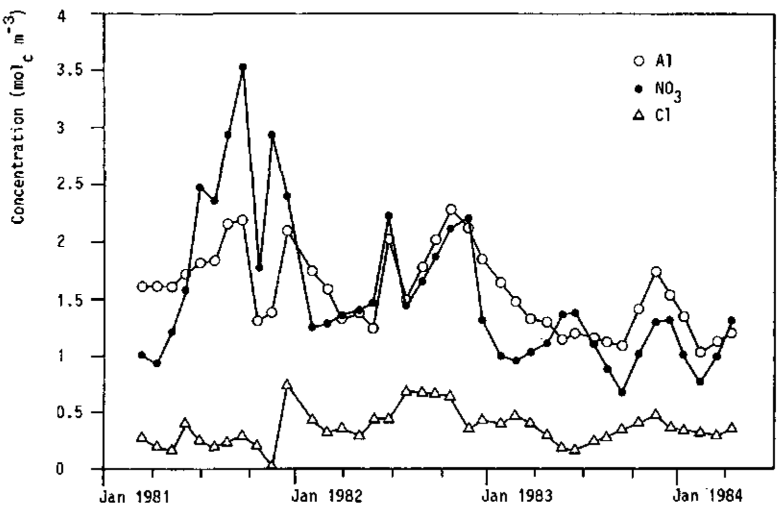

Fig. 1.Variations with time in concentrations of total dissolved Al, NO_3, and Cl in soil B at the 60-cm depth, from April 1981 to April 1984.

Al transport was most significant during the dormant season, when water fluxes were highest (Fig. 2).

The importance of strong acids in mobilizing Al in our acidic soils is supported by the inorganic rather than organic character of dissolved Al. At all depths polymeric (total minus monomeric) Al was negligible. From annual mean charge balance discrepancies we estimated that organically complexed monomeric Al contributed at most, 30 to 50% to total monomeric Al at the 10-cm depth and < 20% in the deeper soil layers (Fig. 3). In contrast, organic acids play a more prominent role in mobilizing and transporting Al in spodosols in New York and New Hampshire (USA) (David and Driscoll, 1984; Driscoll et al., 1985).

Inorganic monomeric Al was mainly (> 80%) aquo-Al^{3+}, whereas approximately 10% was $AlSO_4^{+}$, and 5 to 10% was present as AlF^{2+} + $Al(OH)^{2+}$ (Fig. 3). Inorganic monomeric Al in spodosol solutions from New York consisted primarily of F complexes (David and Driscoll, 1984). These soil solutions had similar F, but far lower concentrations of inorganic Al than ours.

Throughout soils B and C and in the upper 40 cm of soil A, both dissolved Al concentrations and pH increased with depth (Table 3). In most soils and waters, dissolved Al decreased with increasing pH, due to the strongly pH-dependent solubility of Al-containing minerals. We hypothesized that the simultaneous

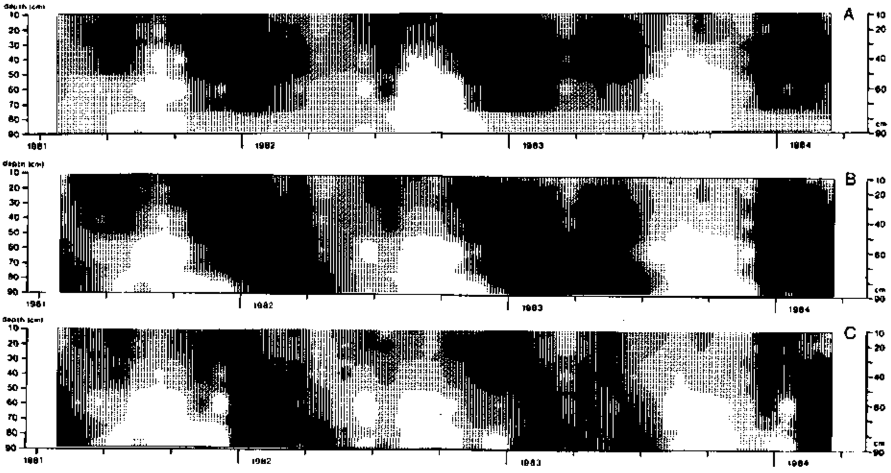

Fig. 2. Variations in Al fluxes with time and depth in each of the three soils studied. Darker shading indicates increasing downward Al fluxes from -2.5 to -1.0 kmol$_c$ ha^{-1} 30 d^{-1} (white), -1.0 to -0.1, -0.1 to 0, 0 to 0.1, 0.1 to 0.2, 0.2 to 0.3, 0.3 to 0.4, 0.4 to 0.5, 0.5 to 1.0, 1.0 to 1.5, 1.5 to 2.5, and 2.5 to 5.0 kmol$_c$ ha^{-1} 30 d^{-1} (black). Plots were generated by interpolating between actual observations.

increase in Al concentration and pH with depth was due to the extreme rate of acid addition to our soils and to the relatively slow dissolution of Al-minerals, resulting in an incomplete acid neutralization in the surface layers. This hypothesis is supported by mineral equilibria calculations.

3.3.3 Mineral equilibria

Soil solutions in the surface 20 cm of the mineral soils were highly undersaturated with respect to all secondary Al-minerals considered. Only at greater depth (> 20 cm), soil solutions tended to approach equilibrium with Al-containing minerals (Table 4). Below the 20-cm depth, soil solutions continued to be undersaturated with respect to gibbsite and basaluminite, but were slightly undersaturated with respect to amorphous ("reversible non-ideal") alumino-silicate, and oversaturated with respect to kaolinite and halloysite. Subsoil solutions were close to equilibrium with jurbanite ($AlSO_4OH.5H_2O$). Nilsson and Bergkvist (1983) and Ulrich and Matzner (1983) also reported that their soil solutions reached saturation with jurbanite at greater depth. Soil solutions in

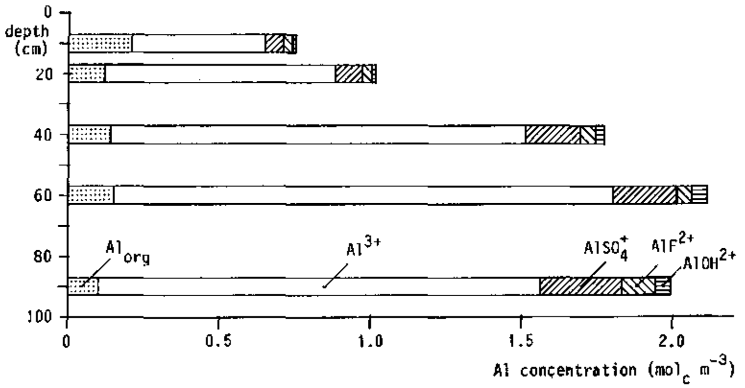

Fig. 3.Speciation of monomeric Al in the soil solution at site B (mean composition from April 1981 to January 1983).

Adirondack spodosols were close to saturation with gibbsite and undersaturated with jurbanite (David and Driscoll, 1984). Theoretically, jurbanite could regulate the Al activity in acidic soils affected by acid deposition (Nordstrom, 1982), but to our knowledge, this mineral has only been found in post-mine stalactitic material from Cu mining (Anthony and McLean, 1977), and never in acidic forest soils with high SO_2 inputs.

3.3.4 Chemical budgets

The mean annual load of strong acids (Table 5), mainly from nitrification, was highest in soil A (8.1 kmol$_c$ ha^{-1}) and lower in soils B and C (3.7 and 3.0 kmol$_c$ ha^{-1}, respectively). The strong acid load in soils B and C (0-90 cm) and soil A (0-40 cm) essentially equalled the sum of mobilized Al and base cations (Table 5), indicating that weak acids (organic acids and CO_2) were relatively unimportant in soil acidification. In the calcareous subsoil of A, all dissolved Al entering from above was immobilized, and replaced by Ca and Mg. Due to additional Ca and Mg dissolution by carbonic acid in the near-neutral subsoil, total cation mobilization at A exceeded strong acid inputs from the atmosphere.

Table 4. Saturation indices (SI) in soil solutions for some secondary minerals from April 1981 to March 1983. Values are means and (temporal) standard deviations (n=15-20).

	Saturation Indices[+] (SI)				
	Depth, cm				
Minerals	10	20	40	60	90[*]
			Site A		
synth. gibbs.	-2.5 ± 0.8	-2.1 ± 0.6	-1.1 ± 0.6	-0.7 ± 0.9	- -
nat. gibbsite	-3.2 ± 0.8	-2.8 ± 0.6	-1.8 ± 0.6	-1.4 ± 0.9	- -
kaolinite	0.8 ± 1.6	1.7 ± 1.0	3.5 ± 1.2	4.7 ± 1.8	- -
halloysite	-1.6 ± 1.6	-0.7 ± 1.0	1.2 ± 1.2	2.4 ± 1.8	- -
basaluminite	-7.0 ± 3.0	-5.7 ± 2.0	-2.2 ± 2.1	-1.8 ± 3.3	- -
jurbanite	-0.8 ± 0.3	-0.6 ± 0.2	0.1 ± 0.2	-0.9 ± 0.6	- -
amorphous-Al-silicate	-0.7 ± 0.2	-0.6 ± 0.1	-0.3 ± 0.1	-0.2 ± 0.3	- -
			Site B		
synth. gibbs.	-2.7 ± 0.7	-2.4 ± 0.7	-0.8 ± 0.6	-0.7 ± 0.6	-0.9 ± 0.8
nat. gibbsite	-3.4 ± 0.7	-3.1 ± 0.7	-1.5 ± 0.6	-1.4 ± 0.6	-1.6 ± 0.8
kaolinite	0.1 ± 1.4	0.6 ± 1.4	3.8 ± 1.2	4.0 ± 1.3	3.8 ± 1.6
halloysite	-2.2 ± 1.4	-1.7 ± 1.4	1.4 ± 1.2	1.6 ± 1.3	1.5 ± 1.6
basaluminite	-7.9 ± 2.5	-6.9 ± 2.4	-1.3 ± 2.0	-0.9 ± 2.3	-1.4 ± 2.8
jurbanite	-0.9 ± 0.4	-0.7 ± 0.3	-0.0 ± 0.3	0.1 ± 0.3	0.1 ± 0.3
amorphous-Al-silicate	-0.8 ± 0.2	-0.8 ± 0.2	-0.5 ± 0.2	-0.4 ± 0.2	-0.4 ± 0.2
			Site C		
synth. gibbs.	-1.4 ± 0.8	-1.6 ± 0.7	-0.9 ± 0.6	-0.7 ± 0.7	-0.7 ± 0.7
nat. gibbsite	-2.1 ± 0.8	-2.3 ± 0.7	-1.6 ± 0.6	-1.4 ± 0.7	-1.4 ± 0.7
kaolinite	2.9 ± 1.6	2.3 ± 1.5	3.9 ± 1.2	4.2 ± 1.4	4.3 ± 1.3
halloysite	0.5 ± 1.6	-0.0 ± 1.5	1.5 ± 1.2	1.8 ± 1.4	2.0 ± 1.3
basaluminite	-3.5 ± 2.7	-4.5 ± 2.3	-2.0 ± 2.0	-1.2 ± 2.4	-0.9 ± 2.4
jurbanite	-0.5 ± 2.7	-0.7 ± 0.2	-0.3 ± 0.2	-0.2 ± 0.3	0.0 ± 0.3
amorphous-Al-silicate	-0.5 ± 0.3	-0.6 ± 0.3	-0.4 ± 0.2	-0.4 ± 0.2	-0.3 ± 0.2

[+] The equilibrium relationships at 298°K are, $pAl-3pH=-8.11$ (synth. gibbs.); $pAl-3pH=-8.77$ (nat. gibbs.); $pAl+pH_4SiO_4-3pH=-3.30$ (kaolinite); $pAl+pH_4SiO_4-3pH=-5.64$ (halloysite); $4pAl+pSO_4-10pH=-22.70$ (basaluminite); $pAl+pSO_4-pH=3.23$ (jurbanite); $xp_4SiO_4+(1-x)pAl-(3-3x)pH=5.7-1.68pH$, where $x=1.24-0.135pH$ (amorphous Al-silicate; Paces, 1978)

[*] No values at site A, because only total Al was determined at this depth. Total Al presumably was largely in a polymeric form.

Release of Al in soils A (0-40 cm), B, and C was 6.6, 3.8 and 2.6 $kmol_c\ ha^{-1}\ yr^{-1}$, respectively, neutralizing 70 to 100% of the total acid load. Aluminum dissolution was most prominent in the surface layers of all soils. In the calcareous substratum of soil A, 100% of the dissolved Al entering from the layers above was removed from the percolating soil solution, however, little or no Al immobilization took place in the subsoils of B and C (Table 5).

Our values for acid inputs and rates of Al mobilization are extremely high compared to those reported elsewhere. For example, for New Hampshire spodosols with atmospheric acid inputs of 1.4 $kmol_c\ ha^{-1}\ yr^{-1}$, Driscoll et al.

Table 5. Annual strong acid production (H^{+}_{prod})$^{+}$ and mobilized Al (Al_{mob}), base cations (cat_{mob})*, SO_4 [$(SO_4)_{mob}$] and SiO_2 [$(SiO_2)_{mob}$] in soil A, B, and C per soil layer and complete profile from April 1981 to March 1984. Values$^{\$}$ are annual means and (temporal) standard deviations (n=3).

Site	Layer	H_{prod}	Al_{mob}	Cat_{mob}	$(SO_4)_{mob}$	$(SiO_2)_{mob}$
	cm	$kmol_c$ ha^{-1} yr^{-1}				
A	input-10	8.7 ± 1.6	3.2 ± 0.8	5.7 ± 1.1	1.1 ± 0.8	2.2 ± 0.3
	10-40	0.9 ± 1.5	3.4 ± 1.0	-2.9 ± 1.3	-0.2 ± 1.3	-0.5 ± 0.5
	40-90	-1.5 ± 0.5	-6.7 ± 0.7	9.0 ± 2.4	-1.0 ± 0.2	-1.0 ± 0.2
	total	8.1 ± 0.9	-0.1 ± 0.2	11.8 ± 2.1	-0.1 ± 0.7	0.7 ± 0.3
B	input-10	5.0 ± 1.1	2.5 ± 1.9	3.7 ± 1.3	0.2 ± 0.7	1.5 ± 0.6
	10-40	1.2 ± 0.3	2.6 ± 1.4	-1.6 ± 0.8	-0.4 ± 0.6	-0.6 ± 0.6
	40-90	-2.5 ± 2.6	-1.3 ± 1.6	-1.9 ± 0.4	0.2 ± 0.9	-0.3 ± 0.2
	total	3.7 ± 1.3	3.8 ± 1.1	0.2 ± 0.3	0.0 ± 0.3	0.6 ± 0.2
C	input-10	5.1 ± 1.0	2.9 ± 0.8	2.8 ± 0.6	1.4 ± 0.7	2.2 ± 0.4
	10-40	-1.0 ± 1.1	-0.3 ± 0.7	-1.0 ± 0.1	-1.4 ± 0.8	-0.8 ± 0.4
	40-90	-1.1 ± 0.7	0.0 ± 0.3	-0.9 ± 0.4	0.2 ± 0.1	-0.4 ± 0.2
	total	3.0 ± 0.7	2.6 ± 0.6	0.9 ± 0.2	0.2 ± 0.0	1.0 ± 0.2

+ In H, N, S, and Cl transformations

* Na, K, Ca, Mg

$ Negative numbers indicate immobilization

(1985) reported an inorganic Al mobilization of 0.05 $kmol_c$ ha^{-1} yr^{-1}. The role of Al in buffering acidity in our soils may be so prominent, because of (i) the relatively high acid intensity of the infiltration water and (ii) the soils' relatively low amount of base cations. Elemental analyses indicate a sum of CaO, MgO and K_2O ranging from 0.9 - 2.7% for the Hackfort soils (van Breemen et al., 1988), relative to 3.3 - 5.3% (Mulder, 1980) mass fraction for the New Hampshire soils.

3.3.5 Aluminum chemistry and the soil solid phase

The amount of Al leached annually from the surface 10 cm of soils A, B, and C was large compared with the pools of exchangeable Al (15, 12, and 32%, respectively), but small compared with the free Al present in the soils, viz., at most, 1% (Table 1). Therefore, *free Al is more likely to be an important source* of dissolved Al than exchangeable Al. However, since Al mobilization coincided with a considerable SiO_2 solubilization in the surface mineral soil of *all* three sites

(2.2, 1.5 and 2.2 kmol ha^{-1} yr^{-1} in soils A, B and C, respectively; Table 5), dissolution of Al-silicate minerals may contribute to Al mobilization as well. The clay fraction in the mineral surface layers, amounting to 11% (A), 8% (B), and 2% (C) mass fraction, primarily consists of vermiculites, chlorites and smectites (van Breemen et al., 1988). Congruent dissolution of vermiculites and smectites would result in molar Al/Si ratios ranging from 0.1 to 0.9, and to values from 0.9 to 2.1 for chlorites (Weaver and Pollard, 1973). Mean annual molar Al/Si ratios in solutions from the 10-cm soil depth were 0.48, 0.56, and 0.44 for soil A, B, and C, respectively; indicating that congruent dissolution of vermiculites and smectites in the acidic surface soil may occur.

Aluminum fluxes in soil A decreased most strongly between the 40- and 60-cm soil depth (not shown), where soil solutions were clearly undersaturated with respect to gibbsite solubility (Table 4) and where the soil's base saturation increased sharply (Table 1). Therefore, immobilization of Al below the 40-cm depth in soil A was more likely due to cation exchange than to $Al(OH)_3$ formation. We assumed that the 40% contribution of (Bascomb extractable) Al to the exchangeable cations, between the 30- and 50-cm soil depth, represents the maximum Al occupation of the CEC in our soils, at the ambient soil solution conditions, because no Al immobilization was observed at this depth. If this is true, the maximum exchangeable Al between the 50- and 70-cm soil depth would be approximately 24 $kmol_c$ ha^{-1} per 10-cm soil depth. If cation exchange was solely responsible for the Al immobilization (6.6 $kmol_c$ ha^{-1} yr^{-1}) in the subsoil of A, this would mean that the Al front moved down into the soil at a rate of about 3 cm yr^{-1}. However, preliminary data from continued monitoring from 1984 to 1987 indicate that during certain periods with high groundwater tables in winter and early spring, upwelling of calcium-bicarbonate containing groundwater took place at approximately the 40-cm depth for A. This will have resulted in a recharge of the pool of exchangeable bases and could therefore stop the downward movement of the Al front. Probably due to lower CEC values, soils B, and C had already reached the apparent maximum exchangeable Al (40% of the CEC) between the 20- and 90-cm depth, at the start of the monitoring program (Table 1), so that cation exchange was not expected to strongly modify dissolved Al concentrations in these soils.

Although mineral equilibrium calculations indicate that precipitation of jurbanite may have occurred in the subsoils of A, B, and C, the relative rates of removal of SO_4 and Al from the percolation water at these depths were not in agreement with the stoichiometry of jurbanite precipitation (Table 5). Moreover, van Breemen et al. (1988) demonstrated that SO_4 budgets reflect biocycling (mineralization at the surface followed by assimilation at greater depth) and give little evidence for net sorption of SO_4. Assuming (i) a H_2SO_4 input at concentrations of 250 mmol m^{-3}, fully neutralized by Al solubilization, (ii) evaporative concentration of solution by a factor of three, and (iii) equilibrium soil solution pH 3.8, the resulting solution concentrations come very close to that in equilibrium with jurbanite (SI = 0.1). Thus the observed near-equilibrium with jurbanite may be fortuitous and entirely unrelated to solubility control by this mineral.

ACKNOWLEDGMENTS

Thanks are due to E.J. Velthorst, N. Nakken, and H. Sliepenbeek for help during sampling and chemical analysis; to Th. Pape and W.J.F. Visser for help with data management; and to C.T. Driscoll for reviewing the paper. Drawings were made by G. Buurman and P.G.M. Versteeg. Figure 2 was made using a computer program by G. Oerlemans. This research was supported in part by the EEC (contract ENV-650-NL), by the Netherlands Directorate General for Science and by the Netherlands Technology Foundation (STW).

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Chapter 4

EFFECT OF VEGETATION COVER (PINE FOREST VS. NO VEGETATION) ON ATMOSPHERIC DEPOSITION AND SOIL ACIDIFICATION

ABSTRACT

We evaluated the effect of the presence or absence of a forest cover on (i) the total atmospheric acid load, (ii) soil acidification, and (iii) overall acid neutralization processes, in a driftsand in the Netherlands. The study was conducted at a forested (Pinus sylvestris) and an adjacent bare plot. Soils were acidic, and low in exchangeable as well as total base cations. Input-output budgets were calculated for four hydrological years from measured chemical fluxes in meteoric water, simulated soil water fluxes, measured soil solution concentrations, and from estimated tree growth. The atmospheric deposition was dominated by NH_4 *and* SO_4*. The mean atmospheric input in the forest had a slight positive alkalinity (0.1 kmol* ha^{-1} yr^{-1}*), due to the surplus of* NH_3 *deposition over* HNO_3 *and* H_2SO_4*. In contrast, the bare soil had a slight net input of free* H^+ *(0.4 kmol* ha^{-1} yr^{-1}*). Mean annual* NH_4 *deposition was higher in the forest canopy than at the surface of the bare sand (3.0 vs. 1.4 kmol* ha^{-1} yr^{-1}*). Notwithstanding, the low influx of free* H^+ *from the atmosphere, total acid loads were high (5.3 and 2.2 kmol* ha^{-1} yr^{-1} *in the forest and bare soil, respectively), and mainly due to* NH_4 *transformations (uptake and nitrification). The contribution of organic acids and nutrient assimilation to forest soil acidification was relatively small. Acid loads were largely neutralized by dissolution of Al, whereas the mobilization of base cations was small and independent of acid load.*

4.1 INTRODUCTION

In areas with high concentrations of intensive animal husbandry enhanced soil acidification, due to $(NH_4)_2SO_4$ deposition, is a major environmental problem (van Breemen et al., 1982). Acidification by $(NH_4)_2SO_4$ occurs when NH_4^+ is assimilated by the vegetation or nitrified and leached as NO_3^-. Note that even in acid soils nitrification has been reported (van Breemen et al., 1987). In the Netherlands the acid loads of deciduous forest soils are extremely high, ranging from 3 to 7 kmol ha^{-1} yr^{-1}, and are largely due to elevated rates of $(NH_4)_2SO_4$ deposition (van Breemen et al., 1987). In contrast, Scandinavian and North

American forest soils often have acid loads less than 2 $kmol_c$ ha^{-1} yr^{-1} (van Breemen et al., 1984).

Generally, atmospheric acidity in acid, sandy soils is only partly neutralized by mobilization of base cations (Mulder et al., 1987; Matzner, 1983). As a consequence the soil solution pH will decrease and the mobility of Al increase. Particularly in acid soils, low in base cations, mobilization of Al has become the major acid neutralizing process (Mulder et al., 1987; Ulrich et al., 1979). Elevated dissolved Al concentrations in forest soils have been associated with the occurrence of forest die-back (Ulrich et al., 1980; Andersson and Kelly, 1984). In addition, a large scale Al mobilization from forest soils may cause a significant pollution of drinking water supplies in the near future.

To date the most complete data set on acid loads and soil acidification in the Netherlands was obtained for the Hackfort sites (van Breemen et al., 1988). However, (i) these sites are in the close vicinity of dairy and chicken farms (i.e., 500 m; van Grinsven et al., 1987), where atmospheric NH_3 concentrations are probably elevated, and (ii) the soils at these sites have developed in pleistocene river deposits, and are atypical for Dutch forest soils.

To evaluate the current acid loads, soil acidification, and Al mobilization of more representative Dutch forest soils we set up an input-output study in an area with aeolian sands in the central part of the Netherlands. In order to measure 'background' $(NH_4)_2SO_4$ deposition levels we selected our study site so that it had the maximum possible distance to the nearest area with intensively managed farmland. In this study we also aimed at evaluating the overall neutralization processes in sandy soils as a function of acid load. Therefore we included an adjacent, bare driftsand soil in our study. At this bare site we anticipated a significant reduction in acid load relative to that in the forest, due to a decreased efficiency of $(NH_4)_2SO_4$ entrappment.

A detailed discussion on the impact of acidic deposition on the Al chemistry in acid, sandy soils, including the sites presented here, will be given in a second paper (Mulder et al., 1988a).

4.2 MATERIALS AND METHODS

The study sites are located in the driftsand area 'Gerritsfles' in the central part of the Netherlands, at ca. 7 km distance from the nearest intensively managed farmland. We selected a forested (GF) and a bare plot (GB), which are about 40 m apart. The forested GF plot carries an undisturbed, uneven-aged *Pinus* *sylvestris* stand (maximum age 65 years) and a ground cover of *Deschampsia flexuosa*. The bare GB plot is an active driftsand with some scattered algae and mosses. Except for a 10 cm thick forest floor at GF, consisting of partly decomposed Pinus litter, the forested and the bare soil are fairly similar. Both soils have developed in the same parent material, and are young, somewhat excessively drained Typic Udipsamments, without distinct characteristics of soil formation (Soil Survey Staff, 1975). Circa 75% of the soils' fine earth fraction consists of very fine and fine sand and 20% of medium sand, whereas the clay content is only about 1%. Textural changes with depth are not observed. X-ray diffraction indicates that the clay fraction mainly consists of amorphous material, with only traces of illite, kaolinite and soil chlorites (Wopereis, 1985). The sand fraction contains mainly quartz (92%) and about 7% alkali-feldspars.

The soils are acidic, with lowest pH values in the surface layers (Table 1).

Table 1. Some relevant soil chemical characteristics for the forested (GF) and bare (GB) driftsand at 'Gerritsfles', the Netherlands. Analytical techniques are described elsewhere (Appendix).

	GF			GB		
depth (cm)	0-25	25-75	75-150	0-25	25-75	75-150
pH(0.01M $CaCl_2$)	3.52	3.95	4.00	4.10	4.38	4.33
C (%)	0.45	0.24	0.33	0.24	0.22	0.08
N (%)	0.03	0.02	0.01	0.02	0.01	<0.01
'free' Al_2O_3 (%)	0.26	0.40	0.29	0.25	0.30	0.39
CEC ($mmol_c\ kg^{-1}$)	11.6	9	4	3	2	2
exch. Ca ($mmol_c\ kg^{-1}$)	0.3	0	0	0	0	0
exch. Mg (,,)	0.1	0	0	0	0	0
exch. Na (,,)	0	0	0	0	0	0
exch. K (,,)	0	0	0	0	0	0
exch. Al (,,)	6	2	1.5	0	0	0
exch H (,,)	5.2	7	2.5	3	2	2

Values for pH are somewhat lower in the forest soil than in the bare soil. Total contents of organic carbon and nitrogen are low, as can be expected for young soils, but slightly higher in the forest soil. In accordance with the minor amounts of clay and organic carbon, the Cation Exchange Capacity (CEC) is also low, with highest values in the surface layer of the forest soil. In both soils the exchange sites are almost exclusively occupied by H and Al, at all depths. The contents of 'free' (dithionite-oxalate extractable) Al are similar in GF and GB soils. Soil characteristics are discussed in more detail in the appendix of this thesis.

For the input-output study we sampled bulk precipitation, throughfall and soil solutions bi-weekly from November 1982 to April 1987. All solutions were pooled to monthly samples before analysis. Analytical techniques were as described by van Breemen et al. (1988) and were summarized by Mulder et al. (1988a). Bulk deposition was collected ca. 120 cm above the soil surface in an open funnel, mounted on a 5 liter polyethylene bottle. Polyethylene bottles were permanently kept in the dark. Throughfall water at GF was collected in four 1800 cm^2 PVC gutters, which drained in 50 l polyethylene containers, stored below the soil surface. Soil solutions at GF were sampled at the surface of the soil (below the forest floor), as well as the 10-cm, 40-cm and 100-cm soil depth. At GB solutions were sampled at the 2-cm, 40-cm and 100-cm soil depth. Soil solutions were collected using (acrylic copolymer) filterplates (Driscoll et al., 1985), and applying a constant vacuum of 100 to 150 mbar. During the two-week sampling period the polypropylene 500 ml bottles were kept below the soil surface in the dark. All equipment and sampling techniques are discussed in van Dobben and Mulder (in preparation).

Above and below ground solute fluxes were calculated for four hydrological years (from April 1983 to April 1987), by multiplying monthly measured concentrations and waterfluxes. Soil water fluxes were estimated, using the deterministic water transport model SWATRE (Belmans et al., 1983; van Grinsven et al., 1987). Tree nutrient uptake was estimated by de Visser (1986) from the mean annual incremental growth and the nutrient composition of roots and stemwood (Ovington and Madgwick, 1959). Collected flux data were interpreted using the H^+-budget approach as outlined by van Breemen et al. (1983).

4.3 RESULTS AND DISCUSSION

4.3.1 Atmospheric deposition

The total atmospheric input of K, Na, Ca, Mg, Cl and SO_4 was assumed to be equal to fluxes in bulk deposition plus estimated amounts of dry deposition (Table 2). Dry deposition of Cl was estimated by subtracting bulk deposition from throughfall fluxes (GF), or from fluxes at the 2-cm soil depth (GB). Dry deposition of the other seasalt components was calculated assuming K/Cl, Na/Cl, Ca/Cl, Mg/Cl and SO_4/Cl ratios in dry deposition similar to those in seawater (Weast, 1976). Our assumption of the additional dry deposition of seasalt components

Table 2. Mean annual solute fluxes for four hydrological years (April 1983-April 1987) in bulk deposition, in total atmospheric deposition, and in the soil at the 100-cm depth in a forest (GF) and a bare plot (GB), respectively.

type	H^+	K	Na	Ca	Mg	Al	NH_4	Cl	NO_3	SO_4	water
	$kmol_c\ ha^{-1}\ yr^{-1}$										mm
					FOREST (GF)						
bulk	0.18	0.04	0.70	0.23	0.16	--	0.89	0.77	0.42	0.93	839
total	-0.07	0.06	1.47	0.26	0.34	--	3.02	1.66	0.80	2.61	
soil	0.20	0.13	1.37	0.24	0.39	4.65	0.04	1.98	1.93	3.16	283
					BARE (GB)						
bulk	0.18	0.04	0.70	0.23	0.16	--	0.89	0.77	0.42	0.93	839
total	0.43	0.05	0.83	0.23	0.19	--	1.41	0.92	0.69	1.48	
soil	0.22	0.05	1.44	0.21	0.18	1.44	0.03	0.75	0.99	1.96	677

+ Negative numbers net input of alkalinity (HCO_3^-)

in the tree canopy was supported by the close agreement between Cl fluxes in throughfall and at the 100-cm soil depth (Table 2). The dry deposition of Cl in the forest canopy was of the same order of magnitude as the Cl flux in bulk deposition. In contrast, the dry deposition of Cl at the bare sand was only small (Table 2).

Throughfall fluxes (or solute fluxes in the soil at the 2-cm depth in the case of GB) suggest that the dry deposition of SO_4 was more than from seasalt aerosols alone. Therefore, we took throughfall deposition as a measure for the total atmospheric SO_4 input, where the non-seasalt fraction was assumed to originate from atmospheric SO_2 (van Breemen et al., 1986). In the forest plot the total deposition of NH_4 and NO_3 were, like SO_4, estimated from throughfall inputs (van Breemen et al., 1986). However, dry deposition of N compounds at the surface of the bare sand could not be estimated from direct measurements, because the N flux at the 2-cm soil depth was lower than that in bulk deposition (Table 3), probably due to N assimilation at the soil surface. The dry deposition of NH_4 and NO_3 at GB was estimated assuming that the ratios of NH_4 and NO_3 to SO_2-derived SO_4 in dry deposition were the same as the ratios in bulk deposition. If this assumption is true the N accumulation at the GB soil surface amounted to 15 kg ha-1 yr-1 and must be largely attributed to N uptake by mosses and algae (Table 3).

Ammonium and SO_4 were the dominant solutes in atmospheric deposition. The total atmospheric input of NH_4 and SO_4 in the forest soil was considerably

Table 3: Mean annual NH_4, NO_3, and Al fluxes for four hydrological years (April 1983 to April 1987) and standard deviations in the forested (GF) and bare (GB) soil.

Depth	Site											
	GF						GB					
	NH_4		NO_3		Al		NH_4		NO_3		Al	
	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd
cm	$kmol_c\ ha^{-1}\ yr^{-1}$											
bulk[+]	0.9	0.1	0.4	0.0	--	--	0.9	0.1	0.4	0.0	--	--
total[$]	3.0	0.3	0.8	0.0	--	--	1.4	0.3	0.7	0.2	--	--
0[*]	4.9	1.5	2.4	1.6	0.2	0.1	0.5	0.4	0.6	0.2	1.0	0.2
10	3.1	2.5	2.1	1.3	2.1	1.7	--	--	--	--	--	--
40	0.2	0.2	2.8	1.1	5.6	1.4	0.0	0.0	0.8	0.2	1.7	0.4
100	0.0	0.1	1.9	0.7	4.7	1.9	0.0	0.0	1.0	0.1	1.4	0.4

+ bulk deposition flux

$ estimated atmospheric input flux

* flux at the interface of forest floor and mineral soil (GF); or at the 2-cm soil depth (GB)

higher than in the bare soil (for NH_4: 3.0 vs. 1.4 kmol ha^{-1} yr^{-1}, and for SO_4: 3.2 vs. 2.0 kmol ha^{-1} yr^{-1}; Table 2). These total deposition rates for NH_4 and SO_4 in the pine forest were similar to those reported for deciduous and coniferous forests in the close vicinity of intensively managed farmland (van Breemen et al., 1982). Note that the annual variation in the atmospheric NH_4 input was small in both plots, with standard deviations between 10 and 20% of the mean.

A significant portion of the total NH_4 input was due to dry deposition, particularly in the forest soil. This is illustrated by the ratios of the NH_4 flux in total atmospheric deposition and in bulk deposition, which were 3.4 in the forest and 1.6 in the bare plot (Table 3). Apparently, even the bare soil is more effective in collecting dry deposition of NH_3 than bulk precipitation collectors.

The mean annual dry deposition of NH_4 in the forest canopy was slightly higher than that of NO_3 plus non-seasalt derived SO_4 (Table 2). We assumed that this NH_4 surplus was deposited as NH_4HCO_3. At the bare plot the reverse was true, i.e., part of the dry deposited H_2SO_4 and HNO_3 was not neutralized by NH_3. Notwithstanding the small content of free H^+, atmospheric deposition may cause a significant soil acidification, due to assimilation or nitrification of NH_4, as will be demonstrated below.

4.3.2 Nitrogen transformations and acid loads

In the bare sand, the flux of atmospheric NH_4 already decreased in the surface cm's. In contrast, the NH_4 load of the percolation water in the GF forest floor increased, probably due to mineralization of organic N. However, in both soils the NH_4 flux at the 100-cm soil depth was negligible (Table 3). The loss of NH_4 from percolation water was probably due to adsorption or conversion into other N forms (e.g., organic N, NO_3). Although, adsorption of NH_4 may have occurred it is unlikely to account for a significant fraction of the NH_4 retention in our low CEC soils (Table 1). Nitrification of NH_4 and the subsequent leaching as NO_3 accounted for 38% (GF) and 22% (GB) of the total NH_4 deposition. We assume that the remainder of the NH_4 lost during percolation (1.9 and 1.1 kmol ha^{-1} yr^{-1} at GF and GB, respectively) was largely transformed into organic N.

Recent changes in organic N pools of the forest site are available from earlier studies. De Visser (1986) estimated a net N accumulation in the woody biomass at GF of 0.3 kmol ha^{-1} yr^{-1}. From the age of the oldest trees, Nieuwenhuyse (1986) assumed that 70 years ago the open driftsand landscape gradually changed into a Pine forest, and that a forest floor started to develop. The mean annual organic N accumulation in this forest floor was estimated to be 2.6 kmol ha^{-1} yr^{-1}. No data are available on recent changes in the organic N pool of the mineral soil. So, the mean annual accumulation of organic N during the last 70 years must have been at least 2.9 kmol ha^{-1} yr^{-1}. This minimum estimate is lower than the current input of atmospheric N (3.8 kmol ha^{-1} yr^{-1}).

Comparison of the annual N accumulation in the period 1983-1987 (1.9 kmol ha^{-1} yr^{-1}), obtained from budget studies, and the annual mean for the last seven decades indicates a current decrease in N retention. Similar observations were made in an oak-birch woodland in the Netherlands and were attributed to the approach of N saturation (van Breemen et al., 1987).

Total acid loads were 5.3 (GF) and 2.2 kmol ha^{-1} yr^{-1} (GB) (Table 4). Particularly the acid load of the forest soil was extreme relative to values reported elsewhere (van Breemen et al., 1984). In both soils, N transformations accounted for 77% of the acid load. Mobilization of SO_4, which was particularly high in the first year, also contributed to the total acid load in both soils (Table 2). The contribution of other acid sources, including organic acids and base cation uptake by the vegetation was small even in the forest soil.

Table 4. Annual mean H^+-budget for the forested (GF) and bare (GB) driftsand at 'Gerritsfles' for four hydrological years (April 1983 to April 1987). The 100-cm soil depth was taken as the lower boundary. Biomass assimilation data were taken from de Visser (1986).

Site	H+ sources*						H+ sinks$			
	free H^+	N transf.	Org. acids	Biom. assim	Anion mob.	SUM+	SUM-	mobilization Al	mobilization Base cat	free H^+
	kmol$_c$ ha^{-1} yr^{-1}						kmol$_c$ ha^{-1} yr^{-1}			
GF	-0.1	4.1	0.0	0.4	0.9	5.3	5.3	4.7	0.4	0.2
GB	0.4	1.7	-0.2	0.0	0.3	2.2	2.2	1.4	0.6	0.2

* Sources are atmospheric input of free H^+ (free H^+), Nitrogen transformations (N transf.), dissociation of organic acids, estimated from charge balance discrepancies (Org. acids), Accumulation of base cations in the standing biomass (Biom. assim), and net mobilization of the anions of strong acids (Anion mob.)

$ Sinks include mobilization of Al and base cations (Base cat), and drainage of free H^+

4.3.3 Acid neutralization

Aluminum mobilization was the most important acid sink, and accounted for the neutralization of 89% (GF) and 64% (GB) of the total acid input (Table 4). Mobilization of base cations was small in both soils, but slightly higher at the bare site. In the unvegetated soil, Na accounted for much of the base cation *mobilization* (0.6 kmol$_c$ ha^{-1} yr^{-1}; *Table 2*). *Note that the mobilization of* Na *at* GB was not accompanied by the release of Cl. The relatively high Na mobilization was observed in all four years and mainly occurred between the 40- and 100-cm soil depth, probably due to weathering of Na containing feldspars. At GF the depletion of base cations was small and mainly due to uptake by the vegetation. In view of the similarity in mineralogy and chemistry of both soils, the elevated Na mobilization at GB is surprising.

Dissolution of Al mainly took place in the upper 40-cm of the mineral soil, where most of the N transformations and associated acid production occurred (Table 3). Mineral weathering was probably the dominant source of dissolved Al, because the pools of exchangeable Al were rather small in both soils, as is suggested in Table 1. However, the weathering of Al-silicates was relatively slow at GF and GB, as is suggested by the low mobilization rate of base cations. Therefore we hypothesize that 'free' Al was the major source of dissolved Al in both soils. This hypothesis will be further discussed in two following papers (Mulder et al., 1988a,b).

The standard deviations of the Al fluxes were high relative to the mean in the upper 10-cm of the forest soil, where the annual variation in NO_3 flux was also highest. A strong positive correlation between fluxes of Al and NO_3 is not surprising, because N transformations were the most important acid source, whereas Al mobilization was the most important acid sink.

4.4 CONCLUSIONS

The atmospheric input in a *Pinus sylvestris* stand in the central part of the Netherlands, situated ca. 7 km from the nearest area with intensively managed farmland, was dominated by NH_4 and SO_4. Ammonium and non-seasalt derived SO_4 plus NO_3 in throughfall water were deposited in nearly equivalent amounts, so that the free acidity in infiltration water was small. The deposition rate of NH_4, as $(NH_4)_2SO_4$ and NH_4NO_3, was 3.0 kmol ha^{-1} yr^{-1}, which is similar to values estimated by van Breemen et al. (1982) for deciduous and coniferous forests, directly surrounded by agricultural land.

The mean annual acid load in the pine forest was high (5.3 kmol ha^{-1} yr^{-1}) and mainly due to N transformation processes, including nitrification. Currently, nearly 40% of the deposited NH_4 is nitrified and leached as NO_3. However, this fraction of nitrified and leached N may further increase, if the decrease in the current N accumulation rate continues. Such a scenario would also result in increased acid loads. A decrease in the N accumulation rate is suggested by changes in the ecosystem's N pools. The atmospherically derived acidity was largely neutralized by mobilization of Al, probably due to dissolution of non-silicate bound solid phase forms. Mobilization of base cations was small.

The acid load in an adjacent, similar, but unvegetated soil was significantly lower than in the forest soil, due to a strong reduction in dry deposition of NH_3, SO_2, and NO_x. However, annual mobilization rates of base cations were similar to those in the forest soil. Therefore, the reduced acid inputs in the bare plot, mainly resulted in a reduction of the Al dissolution rate. These results suggest that additional strong acid loads in aeolian sands, commonly found in the Netherlands, are largely neutralized by dissolution of solid phase Al. Because dissolved Al is probably involved in forest die-back and may also cause large scale groundwater pollution, further study of the impact of 'acid rain' on the Al chemistry is warranted.

ACKNOWLEDGMENTS

Thanks are due to E.J. Velthorst and N. Nakken for chemical analyses and to Th. Pape for help with data management. Staatsbosbeheer is greatfully acknowledged for making 'Gerritsfles' available for our research. This research was supported in part by the EEC (contract ENV-650-NL) and by the Netherlands Technology Foundation (STW).

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Chapter 5

DIFFERENCES IN ALUMINUM MOBILIZATION IN SPODOSOLS IN NEW HAMPSHIRE (USA) AND IN THE NETHERLANDS, AS A RESULT OF ACID DEPOSITION

ABSTRACT

We studied Al mobilization in two spodosols from the Netherlands (one under coniferous forest, and one under heather), and compared the results with Al mobilization data for North-American spodosols in a deciduous forest in New Hampshire. The Dutch spodosols, developed in coversands, were extremely low in weatherable base cations, whereas the glacial till, in which the US spodosols developed were considerably richer. Annual solute fluxes in the soil were calculated by multiplying measured solute concentrations and estimated water fluxes. Drainage fluxes of SO_4 *plus* NO_3*, which were both largely anthropogenically derived, were lower in the North American than in the Dutch spodosols. Therefore, acid loads, which are directly related to* SO_4 *plus* NO_3 *fluxes in the soil, were lowest in the North American soils. In contrast, the weathering rates of base cations were considerably higher in the base-rich American soils than in the Dutch spodosols. So, whereas in the New Hampshire spodosols most of the strong acid deposition was neutralized by base cation dissolution, Al dissolution dominated the acid neutralization in the Dutch soils. Mobilization of Al by mineral acids was most pronounced in the soil horizons where 'free' non-silicate bound Al had accumulated previously as organic precipitates. The importance of non-silicate bound Al as a major source of dissolved Al was supported by the small release of Si in the Dutch soils. In the North American spodic horizons (organic) Al precipitation and (inorganic) Al removal were about equal, indicating that there was no net break down of this horizon. In contrast, the current breakdown of the spodic horizon of the Dutch spodosols, proceeds at rates upto 10 times the accumulation rate of organic Al in these soils.*

5.1 INTRODUCTION

In areas where precipitation exceeds evapotranspiration, soil acidification is a natural phenomenon, due to leaching of dissolved metal cations (van Breemen et al., 1983). Dissolution of metal cations consumes acidity, which in natural background situations mainly originates from organic acids and CO_2. In many soils mobilization of base cations alone is enough to fully neutralize the naturally derived acidity. However, in the course of soil formation the pools of easily weatherable base cations gradually decrease, and so will their weathering rates. As a result acid neutralization rates tend to decrease, so that soil solution pH values will drop. Organic acids may lower the soil solution pH to values well below 4.0. At these low pH values organic acids effectively chelate Al and Fe, resulting in increased solubility of these elements (Martin and Reeve, 1958). Aluminum chelates migrate downward with percolation water, until the organic acids become saturated with Fe and/or Al and precipitate (Petersen, 1976; Mokma and Buurman, 1982; Buurman, 1984). This theory of transport and subsequent precipitation of Al and Fe in spodosols is primarily based on chemical studies of soil samples and on laboratory studies of the interaction between dissolved Al and Fe, organic acids and the soil solid phase (Schnitzer and Skinner, 1963; Petersen, 1976). The podzolization theory is supported by data from a Washington spodosol, where dissolved Al peaked in the E (eluvial) and decreased in the B (accumulation) horizon (Ugolini et al., 1977). The export of Al from acid soils with drainage water is small (Ugolini et al., 1977; David and Driscoll, 1984). Using a newly developed Al fractionation technique (Driscoll, 1984), David and Driscoll (1984) and Driscoll et al. (1985) demonstrated the importance of Al-chelates in the transport of Al from the E to the B horizon in New York and New Hampshire spodosols.

Currently, the Al chemistry of acid soils (spodosols, acid brown forest soils), in large parts of northeastern North-America and northwestern and central Europe is significantly affected by the atmospheric input of strong acids. Various researchers indicate that in 'acid rain' affected soils strong mineral acids become increasingly important in the mobilization and transport of Al (Cronan and Schofield, 1979; Ulrich et al., 1979; Johnson et al., 1981; Ulrich and Matzner, 1983; Nilsson and Bergkvist, 1983; David and Driscoll, 1984; Driscoll et al., 1985; Mulder et al., 1987). Changes in Al mobilization rates, dissolved Al concentrations, as well as the chemical form of dissolved Al are of great importance from a pedological and ecological viewpoint.

In this paper we evaluate the current Al chemistry of two 'acid rain' impacted spodosols in the coversand area of the Netherlands. In addition, we will compare the recent Al transport with that over the course of soil formation. Dutch spodosols probably present an extreme example of the effect of atmospheric acidity on the soil Al chemistry, because of their intrazonal character. In intrazonal spodosols not climatic factors (as in most North-American and Scandinavian spodosols), but the extremely poor soil material (further impoverished by centuries of biomass export by man) is the primary factor predisposing the soil for spodosolization. To illustrate the importance of parent material as well as the regime of acid atmospheric deposition on the Al chemistry in spodosols, our results will be compared with the current and historic Al transport in zonal spodosols in North-America, developed in richer parent material (Mulder, 1980; Driscoll et al., 1985).

5.2 MATERIALS AND METHODS

Input-output studies were set up at the Hasselsven (HH) and Tongbersven (TF) sites in the eastern part of Brabant, the Netherlands. Both soils, developed in coversands, are well drained and classified as Typic Haplorthods (Soil Survey Staff, 1975). The Hasselsven site has a 50% coverage with heather (*Calluna vulgaris*), whereas the other 50% of the soil surface is bare with some scattered mosses and algae. Tongbersven has a pine (*Pinus sylvestris*) vegetation. The North-American spodosols, used for comparison, are situated in the Hubbard Brook Experimental Forest (HBEF), New Hampshire, USA. HBEF spodosols have developed in glacial till, are well drained and classified as Typic Fragiorthods. The vegetation is a deciduous forest (*Fagus grandifolia, Acer saccharum and Betula alleghaniensis*), with red spruce (*Picea rubens*) and balsam fir (*Abies balsamea*) near ridgetops.

All solution data presented here were collected between October 1982 and April 1984. Bulk deposition of water and solutes at TF was estimated from open bucket precipitation data, a few km from the site. At HH bulk deposition was estimated from precipitation volumes at the nearby Maarheze meteorological station and the solute concentrations measured at TF. Throughfall deposition at TF was measured from four 1800 cm^2 PVC gutters. For the HH site no throughfall data were available. However, throughfall measurements in a later stage of this study indicate only small increases in solute fluxes due to dry deposition. Meteoric water samples were stored at 4^oC and analyzed within 1 wk of collection. Analytical techniques are discussed in detail by van Dobben and Mulder (in preparation). Atmospheric deposition fluxes at the HBEF were taken from Likens et al. (1977).

Soil solution samples were analyzed monthly at TF and HH from October 1982 - April 1984, whereas at HBEF soil solutions were analyzed weekly from May 1979 - September 1979 and from March 1982 - July 1982. Soil solutions were sampled from acrylic copolymer tension lysimeters as described in detail by Driscoll et al. (1985). Only the 1979 HBEF soil solutions were sampled from zero tension perspex plates installed underneath the various soil horizons (Mulder, 1980). The different soil solution collection technique in 1979 did not result in significant differences in concentrations of the major solutes, as compared to values found in the 1982 tension lysimeter samples.

Procedures for the analyses of the HBEF soil solutions were given by Driscoll et al. (1985). HH and TF soil solutions were analyzed as described by van Dobben and Mulder (in preparation) and Mulder et al. (1987). Fractionation of dissolved monomeric Al into an organic and an inorganic fraction was done by cation exchange according to Driscoll (1984). Analytical procedures for soil samples, which were collected from all horizons, are given by Driscoll et al. (1985), and Mulder et al. (1987).

Chemical fluxes in the HH and TF soils between April 1983 - April 1984 were calculated by multiplying measured monthly solute concentrations and estimated monthly soil water fluxes. Soil water fluxes were estimated using the deterministic water transport model SWATRE (van Grinsven et al., 1987; van Dobben and Mulder, (in preparation)). At HBEF chemical fluxes were estimated using mean concentrations and water fluxes for the dormant and for the growing season (Driscoll et al., 1985). Because detailed soil physical data for the HBEF sites, necessary for a deterministic soil water transport model, were lacking, water fluxes were estimated after Wood (1980), by partitioning total transpiration (Likens et al., 1977) to each horizon on the basis of the distribution of fine root biomass (Driscoll et al., 1985). Estimated drainage water fluxes from the Bs horizons were 59, 42 and 27% of precipitation input for HBEF, HH and TF, respectively.

Thermodynamic calculations were carried out using a modified version of the chemical equilibrium program MINEQL (Westall et al., 1976). Thermochemical data are summarized elsewhere (Johnson et al., 1981; Driscoll, 1984). Thermodynamic calculations were corrected for temperature, and ionic strength corrections were made using the Davies equation (Stumm and Morgan, 1981). Saturation indices (SI), indicating the degree of saturation of a solution with mineral phases of interest were calculated according to:

$$\mathbf{SI = \log (Q_p/K_p),}$$

where Q_p is the ionic activity product for solid phase p, and Kp is the solubility product for this solid phase. $SI = 0$ indicates equilibrium with the phase considered, $SI > 0$ indicates oversaturation and $SI < 0$ undersaturation.

5.3 RESULTS AND DISCUSSION

Selected soil characteristics for the HBEF, HH, and TF soils are presented in Table 1. Soils are acidic and pH profiles are similar for all sites, except that the eluvial E horizon is slightly more acidic at HH and TF than at HBEF. Organic C and organically bound ($Na_4P_2O_7$-extractable) Al in the mineral soils are characteristically high in the spodic B horizons. However, the lower levels of organic C and Al in the HH and TF spodic horizons indicate that spodosolization has been less pronounced here than at HBEF. The concentrations of Al, Fe, and

Table 1. Selected soil chemical characteristics for three sites from the Hubbard Brook Experimental Forest (HBEF I, HBEF II, HBEF III), as well as for the Hasselsven (HH) and Tongbersven (TF) sites.

Site	Horizon	depth	$pH(H_2O)$	C	Sequentially extracted Al_2O_3*				
					KCl	$Na_4P_2O_7$	Am.ox.	D.ox	total
		cm		%$					
HBEF I	O	+10- 0	3.58	38	0	0.1	0.1	0	0.2
	E	0- 7	4.00	5	0.1	0.5	0.1	0.1	0.8
	Bhs1	7-13	4.14	4	0.1	1.6	0.1	0.1	1.9
	Bhs2	13-40	4.39	3	0	1.4	0.1	0.1	1.6
	Bhs3	40-60	4.18	1	0	0.4	0.1	0	0.5
HBEF II	O+Al	+8- 3	4.31	14	0.1	0.2	0	0	0.3
	E	3-16	4.21	1	0	0	0	0	0
	Bhs1	16-22	4.20	4	0.1	1.3	0	0.1	1.5
	Bhs2	22-48	4.39	3	0	1.6	0.2	0.1	1.9
HBEF III	O	+8- 0	4.21	38	0	0.3	0	0	0.3
	E	0- 4	3.90	1	0	0	0	0.1	0.1
	Bhs1	4- 9	4.05	2	0.1	0.7	0.1	0.2	1.1
	Bhs2	9-24	4.24	2	0.1	1.2	0.2	0.2	1.7
	Bhs3	24-33	4.29	2	0	1.0	0	0.1	1.1
HH	O	+3- 0	-	-	-	-	-	-	-
	E	0- 9	3.90	2	0	0.1	0	0	0.1
	Bhs	9-15	4.17	2	0	0.3	0.1	0	0.4
	Bs1	15-33	4.29	1	0	0.5	0.1	0	0.6
	Bs2	33-70	4.56	0	0	0.3	0.2	0.1	0.6
TF	O	+5- 0	-	-	-	-	-	-	-
	E	0-20	3.82	2	0	0	0	0	0
	Bhs	20-40	3.93	5	0	1.0	0.1	0	1.1
	Bs	40-60	4.20	1	0	0.6	0.2	0.1	0.9

* According to Driscoll et al. (1985). The successive extractants are: 1 M KCl, 0.1 M $Na_4P_2O_7$, 0.2 M $(NH_4)_2C_2O_4$ adjusted to pH 3.0 (Am.ox.), and $Na_2S_2O_4$ plus 0.2 M $(NH_4)_2C_2O_4$ adjusted to pH 3.0 (D.ox.).

$ Percentage of the fine earth fraction.

Table 1. (Continued).

Site	Horizon	Elemental concentration+					
		SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O
		%$					
HBEF I	O	19	2.4	0.6	0.1	0.4	0.6
	E	77	7.7	0.7	0.1	0.4	2.6
	Bhs1	72	9.0	2.4	0.2	0.6	2.6
	Bhs2	73	11.0	3.1	0.3	0.8	2.7
	Bhs3	78	12.0	2.2	0.4	0.9	3.0
HBEF II	O+A1	72	2.9	1.5	0.1	0.7	0.6
	E	87	7.9	0.9	0.1	0.5	2.5
	Bhs1	71	9.9	2.8	0.3	0.7	2.3
	Bhs2	74	9.6	3.6	0.2	0.6	2.3
HBEF III	O	22	2.9	0.6	0.1	0.7	0.6
	E	87	10.3	1.4	0.1	0.7	0.6
	Bhs1	69	10.5	5.1	0.5	0.6	2.3
	Bhs2	67	12.2	4.8	0.8	0.6	2.3
	Bhs3	73	12.0	2.9	0.8	0.6	2.6
Hasselsven	O	-	-	-	-	-	
	E	94	1.2	0.3	0.1	0.1	0.4
	Bhs	93	1.4	0.0	0.0	0.0	0.5
	Bs1	95	1.8	0.4	0.0	0.1	0.5
	Bs2	94	2.4	0.5	0.1	0.1	0.8
Tongbersven	O	-	-	-	-	-	
	E	98	0.5	0.1	0.0	0.0	0.3
	Bhs	87	2.3	0.5	0.0	0.1	0.6
	Bs	96	2.4	0.4	0.1	0.1	0.7

+ Elemental concentrations were determined using x-ray fluorescence spectroscopy of a Li-tetraborate melt of the soil material. Only FeO, Fe_2O_3 and MgO were analyzed colorimetrically with orthophenantroline before (Fe(II)) and after reduction (Fe(II) + Fe(III)) with hydroquinone, or by atomic absorption spectrophotometry (MgO) after a 10 s $HF-H_2SO_4$ destruction at 60°C.

$ Percentage of the fine earth fraction.

base cations in the soil's fine earth fraction at HBEF (ca 15%), are high relative to those in the HH and TF soils (ca 3%). This suggests that the HBEF soils are relatively rich in Al-silicate minerals, whereas the Dutch soils mainly consist of quartz sand.

Climatic conditions are favorable for spodosol formation at HBEF, where mean annual precipitation (1.32 m), and runoff (0.84 m) are high (Likens et al., 1977), and where the mean monthly temperature at the 50-cm soil depth is 7°C (Federer, 1973). At HH and TF, where annual precipitation (ca 0.80 m) and drainage fluxes (ca 0.3 m) are significantly lower, spodosolization could take place mainly because the parent material is rich in quartz and has a low content of base cations.

Input-output budgets show that SO_4 plus NO_3 fluxes in drainage water from the B horizons increased in the order HBEF, HH, TF (Table 2). Because soil solution SO_4 and NO_3 were largely derived from from H_2SO_4 and HNO_3, these drainage fluxes suggest a significant variation in acid load for the study sites. Acid neutralization processes also differed strongly between the sites (Table 2). In the HBEF soils a considerable mobilization of base cations (0.59 $kmol_c\ ha^{-1}\ yr^{-1}$) was observed, whereas these values were significantly lower in the HH (0.25 $kmol_c\ ha^{-1}\ yr^{-1}$) and TF soils (-0.26 $kmol_c\ ha^{-1}\ yr^{-1}$). The negative number for the TF site was due to assimilation of atmospherically derived base cations (i.e., base cation weathering rates at this site were too low to satisfy the need for nutrients). Continued monitoring (Mulder et al., 1988) confirmed the extremely low base cation weathering rates in both HH and TF soils. Mobilization and transport of Al by mineral acids was low at HBEF, and considerably higher in the Dutch spodosols. The relatively low mobilization rates of Al at HBEF were due to (i) the quantitatively important acid neutralization by base cation dissolution, (ii) the relatively low acid loads, and (iii) the low acid intensity of the percolation water, which was partly due to the high water fluxes.

Table 2. Fluxes of SO_4 plus NO_3 below the spodic horizons, as well as mobilization rates of base cations (K, Na, Ca, Mg) and inorganic Al in the soil profiles. Soil solution data for HBEF were taken from Mulder (1980), whereas annual waterflux data were obtained from Driscoll et al. (1985). Data for the Dutch sites refer to the hydrological year April 1983-April 1984.

Site	Bhs drainage	net mobilization for complete profile	
	(NO_3 + SO_4)	base cations	inorganic Al
	$kmol_c\ ha^{-1}\ yr^{-1}$		
HBEF	0.92	0.59	0.10
HH	2.03	0.25	1.16
TF	4.94	-0.26	4.50

In line with the lower acid loads and the higher base cation weathering rates at HBEF the pH values in the B horizon soil solutions were high (4.6 - 5.2), relative to those in the HH and TF B horizons (4.1 - 4.4) (Table 3). At all sites soil solution pH was lowest in the eluvial E horizons (4.4 - 4.9 at HBEF and 3.3 - 3.5 at HH and TF). Soil solution pH values differ by + 1.1 to - 0.5 units from the pH of an aqueous soil extract (pH(H_2O)). The difference may be due to (i) a higher degree of acid neutralization in air-dried, stored soil samples, (ii) soil N transformations

Table 3. Arithmatic means and standard deviations of pH and concentrations of monomeric Al, and SiO_2 in bulk deposition and soil solutions, collected March-July, 1982 (HBEF profiles) and October 1982-October 1983 (HH and TF).

Site	Horizon	pH	Al(monomeric)	SiO_2
			--------- mmol m^{-3}	---------
HBEF	bulk[a]	4.13 (0.02)	-	-
HBEF I	O	3.62 (0.45)	37 (17)	112 (52)
	E	4.36 (0.95)	24 (21)	70 (50)
	Bhs1	4.67 (0.16)	32 (9)	103 (50)
	Bhs3	4.77 (0.79)	24 (9)	80 (15)
HBEF II	O	4.95 (0.50)	15 (7)	133 (72)
	E	4.63 (0.20)	19 (14)	107 (27)
	Bhs1	5.05 (0.09)	12 (5)	105 (14)
	Bhs2	5.12 (0.20)	9 (3)	123 (20)
HBEF III	O	4.49 (0.56)	7 (4)	50 (37)
	E	4.93 (0.43)	13 (9)	55 (48)
	Bhs1	5.19 (0.16)	10 (3)	77 (27)
	Bhs3	5.22 (0.26)	10 (4)	112 (18)
HH	bulk[b]	4.44	-	-
HH	O	3.81 (0.13)	22 (19)	150 (146)
	E	3.52 (0.14)	108 (87)	98 (54)
	Bhs	4.37 (0.05)	170 (28)	62 (26)
	Bs2	4.33 (0.22)	92 (29)	76 (7)
TF	bulk[b]	4.70	-	-
TF	O	4.33 (0.49)	13 (8)	33 (29)
	E	3.34 (0.14)	54 (29)	137 (47)
	Bhs	4.07 (0.08)	580 (120)	204 (67)
	Bs	4.12 (0.18)	552 (101)	167 (34)

a From Likens et al, 1977.
b Flux weighted mean.

during air drying and storage, and (iii) dilution and ion exchange effects during extraction with H_2O. We believe that soil solution pH values are most relevant for in-situ ecological conditions.

Monomeric Al concentrations in the O-horizon leachates were similar at all sites (7 to 37 mmol m^{-3}). In the HBEF E and upper B horizons no significant change in the percolation water's monomeric Al concentration was found. In the HH and TF soils, however, dissolved Al increased considerably in the E (108 and 54 mmol m^{-3}, respectively) and upper B horizons (170 and 580 mmol m^{-3}, respectively). In all soils monomeric Al concentrations decreased below the upper B horizon. So, whereas the forest floor was the major contributor of dissolved Al in HBEF soil solutions, the mineral soil, particularly the spodic horizon, was far more important at HH and TF. The relevance of the forest floor as a source of dissolved Al in spodosols from New York and New Hampshire was noted earlier by David and Driscoll (1984) and Cronan and Schofield (1979).

In the forest floor leachates of all soils monomeric Al was primarily (60 to 100%) organically complexed. Dissolved Al was also mainly organically complexed in the HBEF mineral soil. In the TF and HH soils, however, the major portion of dissolved Al in the mineral soil was in an inorganic form. Dissolved inorganic Al at HH and TF was mainly aquo-aluminum (Al^{3+}), with the positive charge primarily balanced by dissolved SO_4 (mean concentrations of 307 and 672 mmol m^{-3}, respectively.).

Estimated soil water fluxes and fluxes of dissolved organic and inorganic monomeric Al, SO_4 and Si are presented in Table 4. Inorganic monomeric Al fluxes increased most strongly in the E (HH) and Bhs horizon (HBEF, TF). Maximum inorganic monomeric Al fluxes were reached in the spodosol B. In the Dutch spodosols the inorganic Al fluxes were relatively high, which illustrates the current importance of strong mineral acids in mobilizing and transporting Al. In contrast, the Al chemistry at HBEF was less affected by strong acid inputs and

Table 4. Estimated fluxes of water, inorganic as well as organic monomeric Al, and total dissolved Si. In addition molar Al/Si budget ratios per soil horizon are given. Data for the Dutch sites refer to the hydrological year April 1983-April 1984.

Site	Horizon	Water	Al(inorg)	Al(org)	Si*	Al/Si
		cm yr^{-1}	--------	$kmol_c$ ha^{-1} yr^{-1}	--------	
HBEF	precip.	132.0	--	--	--	--
	O	96.1	0.021	0.234	1.06	0.08
	E	92.3	0.033	0.222	0.98	--
	Bhs1	89.7	0.078	0.255	0.97	--
	Bhs2/3	78.1	0.054	0.201	0.96	--
HH	precip.	78.5	--	--	--	--
	O	50.2	0.06	0.20	0.45	0.2
	E	45.3	1.69	0.37	0.58	4.6
	Bhs	35.4	1.85	--	0.19	--
	Bs	33.2	1.16	--	0.21	--
TF	precip.	77.5	--	--	--	
	O	39.0	0.05	0.09	0.09	0.5
	E	28.2	0.34	0.07	0.39	0.3
	Bhs	21.5	3.58	--	0.45	18
	Bs	21.3	4.50	--	0.37	--

* Si in kmol ha^{-1} yr^{-1}

the major portion of the dissolved Al was mobilized and transported by organic acids.

Fluxes of inorganic Al (Table 4) decreased markedly in the subsoil (Bhs2/3 or Bs) of HBEF and HH. However, only at HBEF this was associated with a pronounced increase in the fluxes of base cations (Mulder, 1980), whereas the decreased inorganic Al flux at HH was merely due to storage changes (as suggested by a simultaneous decrease in anion fluxes). Dissolution of base cations will result in an increase in soil solution pH, and in a decreased mobility of Al. Continuation of the mobilization of base cations in the subsoils at HBEF is supported by the higher concentrations of base cations in water, that had a longer residence time in the soil (Johnson et al., 1981; Driscoll et al., 1985). For the HBEF catchment as a whole Johnson et al. (1981) estimated a base cation mobilization rate (mean runoff times mean base cation concentration) of 1 kmol ha^{-1} yr^{-1}. The considerably lower base cation mobilization rates in the Dutch soils found in our study are supported by earlier observations in groundwater of the pleistocene sands of the Netherlands (Appelo, 1985).

Although, Si concentrations were highest in the TF subsoils, Si fluxes were significantly higher in the HBEF soils, due to the elevated water fluxes (Table 4). In the HBEF and the HH soil a significant portion of dissolved Si was mobilized in the O horizon and was probably related to mineralization. At TF most Si mobilization occurred in the E horizon. The fluxes of Si did not change considerably with depth in the HBEF soils. However, sorption or assimilation (Bartoli, 1983) of Si took place in the B horizons of the Dutch spodosols. Molar ratios of mobilized Al and Si per soil horizon (Al/Si) were 0.1 - 0.5 in the O horizons. However, in the HH and TF mineral soil horizons Al/Si ratios increased to values well above 1. In case of congruent dissolution of Al-silicate minerals we would expect molar Al/Si flux ratios of 0.33 (albite, microcline) or 1 (anorthite, muscovite). So, the higher Al/Si ratios at HH and TF suggest that solubilized Al originated primarily from 'free' (non-silicate bound) Al forms, which occur in high concentrations in the Bhs horizon.

Additional information on the interaction between solutions and mineral phases were obtained from saturation indices (SI; Table 5). At all sites the trend in solution saturation with natural gibbsite was similar: highly undersaturated in the surface horizons (O and E) and approaching saturation in the B horizon. At many sites the gibbsite solubility model was successfully applied to subsurface horizons (e.g. Cronan et al., 1986). The O horizon leachates were also undersaturated with kaolinite, whereas at greater depth oversaturation with this mineral occurred. The difference in SI values for the HBEF and the Dutch sites were most pronounced for the basic Al-SO_4 containing minerals: jurbanite

Table 5. Mean saturation indices (SI) and standard deviations in soil solutions with respect to natural gibbsite ($pAl - 3pH = -8.77$; May et al., 1979), kaolinite ($pAl - 3pH + pH_4SiO_4 = -3.30$; Stumm and Morgan, 1981) and jurbanite ($pAl + pSO_4 - pH = 3.23$; van Breemen, 1973). HBEF soil solutions were from March 1982 through July 1982; HH and TF equilibrium calculations were only conducted for the November 1982 and May 1983 samples.

Site	Horizon	Nat. Gibbsite		Kaolinite		Jurbanite	
HBEF I	O	-5.33	(3.18)	-3.07	(0.43)	-2.83	(0.49)
	E	-	-	-	-	-	-
	Bhs1	-0.54	(0.50)	3.21	(1.28)	-1.88	(0.43)
	Bhs3	-0.03	(0.21)	3.93	(1.15)	-1.72	(0.36)
HBEF II	O+A1	-1.50	(1.45)	1.50	(3.24)	-3.19	(1.49)
	E	-1.64	(0.20)	1.56	(0.34)	-2.76	(0.16)
	Bhs1	-0.03	(0.25)	3.95	(1.93)	-2.29	(0.93)
	Bhs2	-0.38	(0.49)	4.01	(0.93)	-2.50	(0.28)
HBEF III	O	-2.57	(1.21)	-2.47	(1.79)	-3.38	(0.85)
	E	-3.11	(1.73)	-3.03	(4.59)	-4.92	(1.98)
	Bhs1	-1.48	(1.45)	1.23	(2.89)	-3.82	(1.53)
	Bhs3	-0.87	(0.64)	2.86	(3.58)	-2.98	(0.72)
Hasselsven	O	-3.27	-	-1.47	-	-2.61	-
	E	-3.47	-	-1.51	-	-1.10	-
	Bhs	-0.49	-	3.78	-	-0.10	-
	Bs	-0.56	-	4.16	-	-0.58	-
Tongbersven	O	-4.27	-	-3.11	-	-1.95	-
	E	-3.88	-	-2.11	-	-1.35	-
	Bhs	-0.95	-	3.86	-	0.37	-
	Bs	-0.12	-	4.93	-	0.64	-

($Al(SO_4)(OH).5H_2O$) and basaluminite ($Al_4(SO_4)(OH)_{10}.5H_2O$) (Nordstrom, 1982). Whereas HBEF solutions were undersaturated with jurbanite and basaluminite, HH and TF B horizon solutions approached saturation (HH) or were even oversaturated with respect to jurbanite. TF and HH soil solutions were highly undersaturated with respect to basaluminite in the surface horizons, and highly oversaturated in the subsoil. The possible role of basic Al-SO_4 minerals in regulating soil solution Al at HH and TF will be further discussed by Mulder et al. (1988).

The current elevated Al leaching rates from the spodic horizons of the HH and TF soils were compared with historic accumulation rates of organic Al in the B horizons. Historic rates were estimated by dividing the organic Al pool by the age of the soil (time elapsed since the last glaciation, 10,000 yr), and amounted to 0.20 and 0.29 $kmol_c$ Al ha^{-1} yr^{-1} at HH and TF, respectively. Particularly in the TF forest soil the current Al mobilization rate is 10 times higher than the historic rate of accumulation. This suggests a rapid breakdown of the spodic horizon due to strong mineral acid inputs. In the HBEF soils the present day rate of organic Al precipitation from the soil solution (0.033 $kmol_c$ ha^{-1} yr^{-1}) is considerably lower than the mean rates over the past 14,500 years (0.11 - 0.27 $kmol_c$ ha^{-1} yr^{-1}). From these data Driscoll et al. (1985) concluded, that either the spodosol development had decreased in recent times, or that other processes (e.g. root turnover) contributed to the formation of pyrophosphate extractable aluminum. At present, the organic Al accumulation in the HBEF soils balances the inorganic Al mobilization.

5.4 CONCLUSIONS

Mobilization of Al in acid soils, due to atmospheric strong acid inputs depends on (i) the mobilization rates of base cations, (ii) the total acid load, and (iii) the acid intensity (concentration of dissolved acidity) of the percolation water. All three factors differ significantly for the Dutch and the North-American spodosols. In the Netherlands the rates of base cation mobilization are low, acid loads are high and therefore the acid intensity of the percolation water is also high. For the HBEF site the reverse is true. Note that the acid intensity is also affected by the waterflux, which determines the dilution of the atmospheric acid load. The waterflux is relatively low at HH and TF and relatively high at HBEF.

Particularly in the Netherlands anthropogenically derived strong mineral acids have drastically changed the mobilization and transport of Al in spodosols. Currently, the previously deposited, organically complexed Al forms are probably remobilized and transported by H_2SO_4 at rates upto 10 times the historic rate of accumulation. Because base cation weathering rates are low in the Dutch coversands significant portions of the dissolved inorganic Al are transported to the groundwater.

In the HBEF soils Driscoll et al. (1985) found no evidence for a breakdown of the spodosol B horizon: net organic aluminum transport to the B horizon equalled net export of inorganic Al from this horizon.

ACKNOWLEDGMENTS

Thanks are due to E.J. Velthorst, N. Nakken, H. Sliepenbeek and A.J. Kuyper for help during sampling and chemical analyses, and to Th. Pape for help with data management. RIN-Leersum and RIVM-Bilthoven collected and analyzed bulk deposition and throughfall at Tongbersven. Staatsbosbeheer and W.A.M. Rijken are greatfully acknowledged for making the Hasselsven and Tongbersven sites available for our research. We thank Dr. P. Buurman for his comments on the first draft of this paper.

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Chapter 6

ALUMINUM CHEMISTRY OF ACID SANDY SOILS WITH VARIOUS INPUTS OF ACIDIC DEPOSITION IN THE NETHERLANDS AND IN DENMARK

ABSTRACT

The Al chemistry of a number of acid sandy soils, extremely depleted in weatherable base cations, was studied. Mean annual atmospheric acid inputs varied from 0.5 to 4.0 kmol$_c$ *ha*$^{-1}$ *yr*$^{-1}$*. Acidic deposition was neutralized mainly by solubilization of Al. Aquo-Al*$^{3+}$ *was the dominant form of Al in soil solutions, with polymeric Al being quantitatively insignificant. Organically complexed Al contributed ca. 5% of total dissolved Al, except in the surface horizons and in the soils with the lowest acid load, where more than 25% of total dissolved Al was complexed by organic ligands. Aluminum was generally the dominant cation in the soil solutions, with* NO_3 *and* SO_4 *as accompanying anions. With increasing depth below the soil surface, both pH and dissolved Al tended to increase. This trend of coincident increases in pH and dissolved Al runs counter to the inverse pH-Al relationship expected from chemical equilibrium between the solution and one single Al-bearing soil mineral. Continued acid neutralization and evaporative concentration of the soil solution by plant roots was responsible for the higher Al concentrations at depth. In most soils, the soil solution reached equilibrium with gibbsite at some depth below the surface. Chemical budgets for our soils and soil horizons show that (i) atmospheric acid inputs did not increase the rate of base cation weathering, (ii) Al dissolution occurred primarily in surface soils (driftsands) and spodic horizons (spodosols), (iii) part of the mobilized Al was sorbed at greater depth, and (iv) significant amounts of Al are now lost to the groundwater. A comparison of soils receiving low and high acid loads shows that high rates of acid atmospheric deposition have dramatically influenced the mobilization and transport of Al in acidic soils.*

6.1 INTRODUCTION

In acidic, sandy soils in areas with a precipitation surplus, dissolution, downward transport and the subsequent precipitation of Al is a natural process. This process of podzolization is generally believed to be the result of mineral dissolution and complexation of Al by natural organic acids, originating from the forest floor and from canopy throughfall (Duchaufour, 1982). At greater depth organic solutes are retained, due to reduced solubility with increasing saturation by Al and Fe, resulting in the formation of a so-called spodic B horizon. Recently, the podzolization hypothesis has been challenged by a number of researchers, who suggest that Al and Fe may be mobilized by labile organic acids and subsequently transported as Al-Fe-SiO_2 sols (Farmer et al., 1980; Childs et al., 1983). Soil solution data from North-American spodosols suggest that both organically complexed Al, and polymeric forms (which may include Al-Fe-SiO_2 sols), contribute to total dissolved Al (David and Driscoll, 1984; Driscoll et al., 1985), and that in background situations, with low atmospheric acid inputs, the solubility of Al is low (Ugolini et al., 1977; Manley et al., 1987).

Recently, increased inorganic monomeric Al concentrations have been observed in drainage water from acidic, sandy soils, in parts of North-America and northwestern Europe, indicating that the Al chemistry of these soils has changed. These changes have been attributed to both acidic deposition as well as changes in land-use resulting in accumulation of soil organic acids (Rosenqvist, 1977; Krug and Frink, 1987). By using the proton budget approach, however, van Breemen et al. (1984) (i) demonstrated that atmospheric acidic deposition rather than internal sources of soil acidity is the dominant constituent of the total acid load of many North-American and northwestern European soils, and (ii) found support for the hypothesis that acid deposition is the main cause for the observed increase in Al mobilization. Monitoring studies (Mulder et al., 1987) and manipulation experiments on soil columns (Brown, 1987; Rasmussen et al., 1988) also supported this hypothesis. However, to date the hypothesis was never tested in situ on similar soil vegetation systems, with prolongued inputs of various amounts of acidic deposition.

In this paper we evaluate the impact of atmospheric acidity on the Al chemistry in six acid, sandy soils. The soils were chemically nearly identical (i.e. similar low contents of base cations and high contents of Si), but received progressive amounts of atmospherically derived acidity. Data were used from 2 to 4 year of hydrochemical monitoring at sites in the Netherlands and in Denmark.

6.2 STUDY APPROACH AND PROCEDURES

6.2.1 Experimental setting

Monitoring was conducted at three paired sites, of which two were situated in the Netherlands and one in Denmark. All sites had similar acid, sandy soils, but the two members of each pair differed in vegetation (one with and one without forest cover). We anticipated significant variations in acid inputs (i) between the paired sites, due to the generally higher acid loads in the Netherlands than in Scandinavia (van Breemen et al., 1984), and (ii) between the two members of one pair, due to a more effective entrappment of acidic dry deposition in forest canopies, relative to non-forest vegetation (van Breemen et al., 1982). Earlier, the dry deposition of $(NH_4)_2SO_4$ in Dutch forest soils was demonstrated to be extremely high and a major cause of soil acidification after assimilation of NH_4 or nitrification of NH_4 to a mixture of H_2SO_4 and HNO_3 (van Breemen et al., 1982). Selected sites were located (i) in the driftsand area Gerritsfles (central part of the Netherlands) and were bare (Gerritsfles bare; GB) or had a pine vegetation (Gerritsfles forest; GF), (ii) in the southern coversand landscape of the Netherlands and were covered with heather (Hasselsven, HH) or with pine (Tongbersven, TF), and (iii) in the fluvioglacial sand area of western Jutland in Denmark, and were covered with heather (Klosterhede heather, KH) or with spruce (Klosterhede forest, KF). Background information on the parent material, soil, vegetation and annual precipitation at the selected sites is given in Table 1.

Table 1. Selected characteristics of the six research sites. Soil classification according to Soil Survey Staff (1975); annual precipitation is from 1 April 1983 to 1 April 1987 (the Netherlands, NL) and 1 June 1985 to 31 May 1986 (Denmark, DK).

Site	code	country	vegetation	parent material	soil class.	precip
						mm
Klosterhede	KH	DK	Calluna vulgaris	poorly sorted fluvioglacial sands	Typic Haplorthod	992
Klosterhede	KF	DK	Picea abies	poorly sorted fluvioglacial sands	Typic Haplorthod	992
Gerritsfles	GB	NL	bare sand	well sorted driftsands	Typic Udipsamment	839
Gerritsfles	GF	NL	Pinus sylvestris	well sorted driftsands	Typic Udipsamment	839
Hasselsven	HH	NL	Calluna vulgaris	well sorted coversands	Typic Haplorthod	785
Tongbersven	TF	NL	Pinus sylvestris	well sorted coversands	Typic Haplorthod	800

6.2.2 Soil analysis

Total contents of the major oxide components in the parent material are given in Table 2. Elemental analysis, except for MgO and Na_2O, was conducted by x-ray fluorescence spectroscopy of a Li-tetraborate melt of the soil material. MgO and Na_2O were analyzed by atomic absorption after a 10 s HF-H_2SO_4 destruction at 60°C (Begheijn, 1980). The chemical composition of all parent materials is characterized by high concentrations of Si and low concentrations of Al and base cations (Na, K, Ca, Mg). Concentrations of Al and base cations in the Dutch soils are slightly lower than in the Danish soils.

Table 2. Total elemental contents of the parent material (fraction < 2 mm) at the six sites.

Site	SiO_2	Al_2O_3	MgO	CaO	Na_2O	K_2O
	mass fraction % of fine earth					
KH	89.2	5.0	0.2	0.4	0.8	1.6
KF	92.6	4.3	0.2	0.3	0.8	1.1
GB	97.2	2.3	0.0	0.1	0.4	0.9
GF	96.8	2.4	0.1	0.1	0.5	0.9
HH	95.2	2.5	0.1	0.1	0.4	0.9
TF	98.3	1.8	0.1	0.1	0.3	0.7

Soil pH was measured in a 1:2.5 (mass to volume) extract in 0.01M $CaCl_2$; organic carbon was determined potentiometrically, after wet combustion in a phosphoric-chromic acid mixture (Begheijn, 1980); and free Al_2O_3 refers to the dithionite-oxalate extractable fraction, essayed colorimetrically with pyrocatechol violet (Begheijn, 1980). The Cation Exchange Capacity (CEC) and percent Base Saturation (BS) were measured using Bascomb's $BaCl_2$-$MgSO_4$ method (Bascomb, 1964) for the Dutch soil samples and Li-EDTA (Begheijn, 1980) for the Danish KH and KF soils. In general, similar results are obtained with the two methods. Only for soils low in CEC and BS the Li-EDTA method gives somewhat lower values for exchangeable base cations.

Soil chemical characteristics of the six sites are given in Table 3. All six soils are acidic and low in CEC and exchangeable bases. A considerable fraction of the exchangeable acidity is Al. Base saturation is low in all soils, but highest in the two Danish spodosols (KH and KF) and in the heathland soil in the Netherlands (HH). Variation in free Al concentrations with depth (Table 3), which

Table 3: Selected soil chemical characteristics of the six research sites.

Site	depth	horizon	pH($CaCl_2$)	C	free Al_2O_3	CEC	BS
	(cm)			% mass fraction		$mmol_c$ kg^{-1}	%
KH	0- 8	A1	3.1	4.22	0.11	46	37
	8-19	E	3.4	0.66	0.07	19	26
	19-43	Bhs	4.0	3.16	1.23	65	5
	43-60	Bs	4.4	1.02	0.75	10	0
	+60	C	4.5	0.20	0.53	11	27
KF	0-13	E	3.0	2.54	0.07	27	19
	13-29	Bhs	3.9	4.68	1.23	77	1
	29-66	Bs	4.5	0.54	0.56	12	25
GB	0-25	C	4.1	0.24	0.25	3	0
	25-75	C	4.4	0.22	0.30	2	0
	+75	C	4.3	0.08	0.39	2	0
GF	0-25	C	3.5	0.45	0.26	22	5
	25-75	C	4.0	0.24	0.40	9	0
	+75	C	4.0	0.33	0.29	5	0
HH	0- 9	E	3.0	2.48	0.12	64	6
	9-15	Bhs	3.5	2.27	0.31	77	4
	15-33	Bs1	4.0	1.17	0.54	33	6
	33-73	Bs2	4.3	0.00	0.42	9	22
	+73	C	4.3	0.00	0.44	12	50
TF	0-20	E	3.0	1.60	0.06	27	4
	20-40	Bhs	3.6	4.54	1.17	127	0
	40-58	Bs	4.2	0.62	0.70	14	0
	58-88	BC1	4.3	0.02	0.31	4	0
	+88	BC2	4.3	0.05	0.33	5	0

is evident in the four spodosols, shows depletion in the E horizon and enrichment in the Bhs horizon. This pattern differs markedly from the nearly constant free Al concentrations with depth in the udipsamments (GB and GF).

Both members of each soil-pair (KH and KF, GB and GF, HH and TF) are chemically similar (Tables 2 and 3). However, in comparison to the Dutch soils the two Danish soils (KH and KF) are somewhat richer in bases. This characteristic could result in a somewhat higher contribution of base cation mobilization to acid neutralization at the Danish sites.

6.2.3 Monitoring program

To establish input-output budgets, which was one of the major goals of this project, the monitoring program included (i) the determination of the quantity and chemical composition of precipitation and throughfall water, (ii) chemical analysis of soil solutions, (iii) estimation of waterfluxes in the soil using a water transport model, and (iv) estimation of the net annual nutrient uptake by the vegetation. The monitoring programmes were conducted from November 1982 to April 1987 for GB, GF, TF, and HH, and from June 1985 to May 1987 for KH and KF.

Bulk precipitation was collected in open funnels mounted on 5 or 10 liter polyethylene bottles. Collection bottles were kept permanently in the dark. Throughfall was collected in 2 to 4 PVC gutters (1800 cm^2) (van Dobben and Mulder, in prep.) in the Dutch forests (GF, TF), whereas in the Danish forest (KF) 3 plexiglass gutters (ca. 600 cm^2) (Rasmussen, 1987) were used. At the Dutch heathland (HH) site, throughfall was collected by means of 4 rectangular open-top PVC boxes (6 cm high, 5x20 cm surface area). At the Danish heathland (KH) throughfall was not collected. Meteoric water was sampled bi-weekly and pooled to monthly samples before analysis. A discussion of the characteristics of meteoric water inputs for the Dutch sites is available in van Dobben and Mulder (in prep.) and for the Danish sites in Rasmussen (1987). Note that we corrected the mean bulk deposition and throughfall Cl concentrations at the Danish sites, because (i) comparison of the analytical results showed that Cl concentrations reported by the Danish laboratory were consistently too low, and (ii) even in bulk deposition samples relatively high anionic charge deficits (10% of cationic charge) were reported. Corrected values for Cl concentrations, obtained by multiplying Na concentrations by the Cl/Na ratio in seawater, resulted in an acceptable anionic charge surplus in bulk deposition of 1%.

Soil solutions were sampled continuously, using acrylic copolymer filterplates and a permanent vacuum of ca. 150 mbar (Driscoll et al., 1985; van Dobben and Mulder, in prep.). Solutions were collected bi-weekly and pooled to monthly samples prior to analysis. Lysimeters were installed in holes excavated laterally from a soil pit, by pressing the filterplates tightly to the undisturbed soil above. In order to prevent contamination of the forest floor leachates with water from the mineral soil, a segment of the forest floor was cut out and placed in a plate lysimeters with an extended PVC rim. Note that the use of a rim also prevents nutrient uptake by the vegetation. Single (KF) or duplicate lysimeters (all other sites) were installed at specific depths (GB and GF) or below specific soil horizons (HH, TF, KH, KF). Duplicate lysimeters were placed at a 2 to 3 m distance. Only at the KH site duplicate soil solutions were pooled before analysis. At all other sites, individual lysimeter collections were analyzed. For additional details on lysimeter design, installation and collection of the soil solution, see van Dobben and Mulder (in prep).

Soil moisture in the field, necessary for calibrating the water transport model SWATRE, was measured monthly with a neutron probe. The neutron probe was calibrated gravimetrically.

Estimates of the annual nutrient uptake by the vegetation were taken from de Visser (1986) (TF and GF), Nieuwenhuyse (1986) (HH) and Rasmussen (1987) (KF). Nutrient uptake in the Danish heathland (KH) was assumed to equal that in the Dutch heathland (HH).

6.2.4 Analytical procedures

Within 1 d of collection, all samples from the Dutch sites were analysed for pH, specific conductance (EC), as well as total and inorganic dissolved C. Within 14 d of collection all soil solution samples were analysed for Ca, Mg (atomic absorption), Na, K (atomic emission), H_4SiO_4 (colorimetrically as the blue silica-molibdic acid complex), F, Cl, NO_3, SO_4 (ion chromatography), NH_4 (colorimetrically using Na-salicylate) and total Al (colorimetrically, using pyrocatechol violet). Soil solution samples from the two Danish sites were ca. 8 days in the mail before analyses. However, analytical results for the first year did not indicate significant changes in the major solute concentrations during transport. For dissolved cations in meteoric water at the Dutch sites the same analytical techniques were used as discussed for soil solutions. In contrast, different techniques were used for the analysis of SO_4 (colorimetrically, using Ba-perchlorate and thorin), Cl (potentiometric titration with $AgNO_3$), NO_3 (colorimetrically), and F (ion selective electrode).

Aluminum, determined after acidifying solutions to pH 2, at least 24 hours before analysis, was assumed to represent total dissolved Al (monomeric plus polymeric forms). In four monthly series of soil solutions from the sites in the Netherlands, monomeric Al, measured in non-acidified samples 6 min after addition of pyrocatechol violet, was not significantly different from total dissolved Al, indicating that polymeric Al was negligible in our low pH soil solutions. In the Danish soil solutions only total Al concentrations were determined, because we anticipated a shift in the distribution of the various Al fractions during transport.

Organic monomeric Al concentrations, estimated from experimentally determined binding capacity values of dissolved organic acids, were quantitatively important only in forest floor and E horizon leachates (ranging from 25 to 100% of total Al). In soil solutions from the deeper horizons monomeric Al is almost exclusively (ca. 95%) in inorganic forms. The binding capacity of dissolved organic acids for Al (11 mmol Al/mol DOC at pH 4.0), determined from a Langmuir regression model, were of the same order of magnitude as those reported for organic acids in natural waters of the southeastern USA (Pott et al., 1985) and for organic acids in soil leachates of the Solling area, FRG (Dietze, 1986). Driscoll's cation exchange method (Driscoll, 1984) for the direct analytical estimation of organic monomeric Al could only be used for forest floor and E horizon leachates. In the lower mineral soil (e.g. B horizons) at the most 90 to 95% of the inorganic monomeric Al forms could be removed with the exchange column, due to extremely elevated concentrations.

6.2.5 Computational procedures

Fluxes of solutes in meteoric water were calculated by multiplying monthly determined solute concentrations and measured amounts of rain and throughfall. Total atmospheric input of the major seasalt components (K, Na, Ca, Mg, Cl and SO_4) was assumed to be equal to fluxes in bulk precipitation plus estimated amounts of additional dry deposition. Additional dry deposition of Cl was calculated by subtracting bulk deposition from throughfall fluxes (or from soil solution fluxes at the 2-cm depth in the case of the bare driftsand GB). Dry deposition of the other seasalt components was calculated from dry deposition of Cl, using K/Cl, Na/Cl, Ca/Cl, Mg/Cl and SO_4/Cl ratios in seawater.

Total atmospheric input of SO_4 was assumed to equal fluxes in throughfall (or in the case of GB to fluxes in soil solution at the 2-cm depth). Non-seasalt derived SO_4 in the atmospheric input was assumed to originate from atmospheric H_2SO_4.

Only in the Dutch forests, where N deposition is highest, total atmospheric inputs of NO_3 and NH_4 were assumed to equal throughfall fluxes. At all other sites throughfall input may underestimate total N deposition, due to foliar uptake. Therefore, the dry deposition of NO_3 and NH_4 at the non-forested sites was estimated by multiplying dry deposition fluxes of H_2SO_4 with the (NO_3/non-seasalt SO_4) and (NH_4/non-seasalt SO_4) ratios in bulk deposition.

At the Danish heathland (KH), where we did not measure throughfall deposition, we assumed the total atmospheric input of all major solutes to be equal to bulk deposition fluxes, because (i) additional dry deposition of NH_3, SO_2 and NO_x was probably small, like at the forested KF site and (ii) additional dry deposition of seasalts at the other non-forested sites (GB, HH) was small relative to bulk deposition fluxes.

Atmospheric acid loads (H_{dep}) were calculated according to van Breemen et al. (1983):

$$H_{dep} = (H)_{bu} + (H)_{dry} + (NH_4)_{in} - (NH_4)_{out} + (NO_3)_{out} - (NO_3)_{in} \quad (1),$$

where brackets denote fluxes, 'bu' bulk precipitation, 'dry' dry deposition, 'in' atmospheric input and 'out' output with drainage water. $(H)_{dry}$ is calculated according to van Breemen et al. (1986) as:

$$(H)_{dry} = (SO_4)_{in,nss} - (SO_4)_{bu,nss} + (NO_3)_{in} - (NO_3)_{bu} + (NH_4)_{bu} - (NH_4)_{in} \quad (2),$$

where 'nss' indicates the non-seasalt component of SO_4. Solute fluxes at various depths in the GB, GF, HH and TF soils were calculated by multiplying simulated monthly water fluxes and measured monthly soil solution concentrations. Waterfluxes were simulated using SWATRE, a one-dimensional model for unsaturated water transport (van Grinsven et al., 1987; van Dobben and Mulder, in prep.). For the two Danish sites (KH and KF) annual soil water fluxes were estimated assuming Cl input equalled Cl output. Solute fluxes in the Danish soils were estimated by multiplying annual water fluxes with mean annual solute concentrations. Solute fluxes and budgets were calculated for one hydrological year in the Danish soils (1 June 1985 - 31 May 1986), and for four hydrological years in the Dutch soils (1 April 1983 - 1 April 1987).

Although no error analysis has been conducted on our flux estimates, we feel that uncertainties in the major solute fluxes in the Dutch soils must have been similar to the ones reported for the Hackfort loamy sands in the Netherlands. Errors in the major solute fluxes (Al, SO_4) below the rooting zone in these loamy sands were less than 50% (van Grinsven et al., 1987), while flux errors at shallower depth were generally even lower. For the Danish sites, the uncertainty in the annual solute fluxes was probably larger, because water fluxes, and associated with that solute fluxes, could only be estimated on an annual basis, rather than at monthly intervals. Errors in budget values (output minus input fluxes) can be larger (100%) than errors in fluxes, especially when budget values are small (subtraction of two large numbers). For instance, large budget errors may have occurred for Na, Mg and Cl at KF, because both input and drainage water were dominated by seasalt components (see results).

Mineral equilibria in soil solutions were calculated for all solution samples from the mineral soil using the chemical equilibrium model ALCHEMI (Schecher and Driscoll, 1987). ALCHEMI includes temperature and activity correction

(Debye-Hückel). Aluminum activities were calculated assuming all monomeric Al was in an inorganic form. Only for soil solutions from the surface 15 cm and for the KH site also for solutions at greater depth, this assumption leads to an overestimation of inorganic Al activities. Saturation Indices (SI) with various secondary minerals were calculated according to:

$$\mathbf{SI = Log\ (Q_p/K_p)} \qquad \mathbf{(3),}$$

where Q_p = ionic activity product and K_p = solubility product for the solid phase p. SI = 0 indicates saturation, SI > 0 oversaturation and SI < 0 undersaturation with respect to the solubility of the mineral considered.

6.3 RESULTS AND DISCUSSION

6.3.1 Atmospheric acid loads

Atmospheric inputs differed markedly among the six sites studied (Table 4). The input of most solutes was considerably higher at forested than at

Table 4: Estimated atmospheric deposition fluxes (input), output fluxes (at various depths below the rooting zone) and atmospheric acid loads (calculated according to equation 1) from April 1983 to April 1987 (NL) and from June 1985 to May 1986 (DK).

Site	depth	water	$H^{\$}$	NH_4	$BC^{\#}$	Al	Cl	NO_3	SO_4	Si	atm. acid load
	cm	mm	kmol$_c$/ha.yr*							kmol/ha.yr	
KH	input	992	0.39	0.99	3.96	0.10	3.45	0.84	1.25	-	0.5
	49	693	0.22	0.01	4.26	0.46	3.45	0.01	1.36	0.55	
KF	input	992	0.60	1.28	9.82	0.10	8.72	1.08	2.06	-	0.8
	31	650	0.30	0.01	8.57	3.21	8.72	0.01	2.99	0.39	
GB	input	839	0.43	1.41	1.30	-	0.92	0.69	1.48	-	2.1
	100	677	0.22	0.03	1.87	1.44	0.75	0.99	1.96	0.48	
GF	input	839	-0.07	3.02	2.13	-	1.66	0.80	2.61	-	4.0
	100	283	0.20	0.04	2.12	4.65	1.98	1.93	3.16	0.43	
HH	input	785	0.22	0.94	1.07	-	0.65	0.44	1.06	-	1.3
	70	366	0.21	0.01	1.12	2.05	0.59	0.54	2.20	0.26	
TF	input	800	-0.45	3.68	1.67	-	1.20	0.55	3.21	-	4.0
	57	238	0.22	0.69	1.33	5.32	1.18	2.05	4.35	0.46	

sum of base cations (K, Na, Ca, Mg)

* kmol$_c$/ha.yr refers to kmoles of unit charge per ha and year

$ negative numbers indicate net alkalinity (HCO_3^-) input non-forested sites. The Dutch sites differed from their counterparts in Denmark, because of lower input of seasalt components and considerably higher $(NH_4)_2SO_4$ load. Seasalt inputs were high at the Danish sites, because of the short distance (16 km) from the North Sea. At the Dutch forested sites inputs of $(NH_4)_2SO_4$ were particularly elevated and mainly due to a large contribution of dry deposition. Total deposition of NO_3 was similar at all sites and less than that of non-seasalt derived SO_4. Atmospheric inputs of free H^+ were small at all sites and ranged from 0 to 0.6 kmol ha^{-1} yr^{-1} (Table 4). The negative values for free H^+ deposition at TF and GF were due to net alkalinity in input water, resulting from surplus NH_3 deposition over SO_2 plus NO_x.

Atmospheric acid loads, calculated from equation 1, strongly depend on the fate of N in the ecosystem considered (van Breemen et al., 1983; van Breemen et al., 1984). They were highest in the Netherlands and considerably lower in Denmark (Table 4). In the Netherlands the atmospheric acid load was primarily due to transformation of atmospherically derived N (assimilation, nitrification), while in Denmark this load was predominantly caused by the input of free H^+ from the atmosphere. The contribution of N transformations to the acid load at the Danish sites was small, because removal of NH_4 (acid production) and NO_3 (acid consumption) from the percolating soil solutions nearly balanced. Due to increased dry deposition of (potentially) acidic compounds, atmospheric acid loads at forested sites were invariably higher than at their non-forested counterparts.

6.3.2 Aluminum concentrations in soil solutions

Aluminum was the major dissolved cation (on an equivalent basis) in all sub-soil solutions of the Dutch sites (Table 5a). In the Danish soils, Na concentrations, included in BC (base cations), were higher than the concentrations of Al, due to elevated inputs of seaspray. The higher deposition of seasalt at the Danish sites was also reflected by the relatively high dissolved Cl concentrations.

Coefficients of variation were small for all major solute concentrations (Table 5b) and mainly due to temporal variations. The contribution of spatial variability to CV values at our 3x3 m^2 plots was small, as is illustrated by the Al concentrations in duplicate lysimeters in Fig 1. Inorganic monomeric Al was primarily (80%) free aquo-Al (Al^{3+}) in solutions from all mineral soils. Other dissolved Al species (e.g. $AlSO4^+$, $AlOH^{2+}$) were only of minor significance.

Total dissolved Al concentrations corresponded to the sum of NO_3 and SO_4 concentrations (Table 5a), suggesting that these anions rather than Cl, were

Table 5a. Mean solute concentrations in soil solutions below the rooting zones^x. Data are from duplicate lysimeters for the complete monitoring period.

Site	depth	pH*	BC$^{\#}$	Al	F	Cl	NO$_3$	SO$_4$	Si
	cm		mmol$_c$ m$^{-3\$}$						mmol m^{-3}
KH	49	4.50	615	67	0	498	1	196	80
KF	31	4.34	1319	494	0	1341	2	460	60
GB	100	4.51	301	188	3	114	128	298	79
GF	100	4.15	905	1751	11	771	799	1173	171
HH	70	4.25	339	488	6	149	103	583	75
TF	57	4.03	563	2065	6	469	698	1757	187

x to facilitate comparison between sites, soil solutions below the rooting zone were used, so that effects of biocycling on solute concentrations (which will be significantly different for the various vegetations) will be small

* calculated from mean H$^+$ concentrations

\# sum of base cations (K, Na, Ca, Mg)

\$ mmol$_c$/m^3 refers to mmol of unit ionic charge per m^3

Table 5b. Coefficients of variation (100% * standard deviation/mean) of major solute concentrations in soil solutions below the rooting zones. Data are from duplicate lysimeters for the complete monitoring period.

Site	depth	H	BC	Al	Cl	NO$_3$	SO$_4$	Si
	cm							
KH	49	60	25	52	40	283	22	33
KF	31	39	36	66	56	214	23	28
GB	100	27	54	42	45	67	29	60
GF	100	28	52	51	61	68	41	39
HH	70	40	48	65	40	246	24	23
TF	57	40	40	22	31	65	17	25

associated with solubilization of Al. Nitrate concentrations were distinctly higher in forested than in non- forested soils, but virtually nill in both Danish soils.

Lowest Al concentrations, observed in the Danish heathland soil (KH), were similar to those reported for spodosol solutions in the USA and Scandinavia (Ugolini et al., 1977; Nilsson and Bergkvist, 1983; David and Driscoll, 1984; Driscoll et al., 1985). Dissolved Al concentrations were extremely high in the forested GF and TF soils. Similar high values are known to us only from other

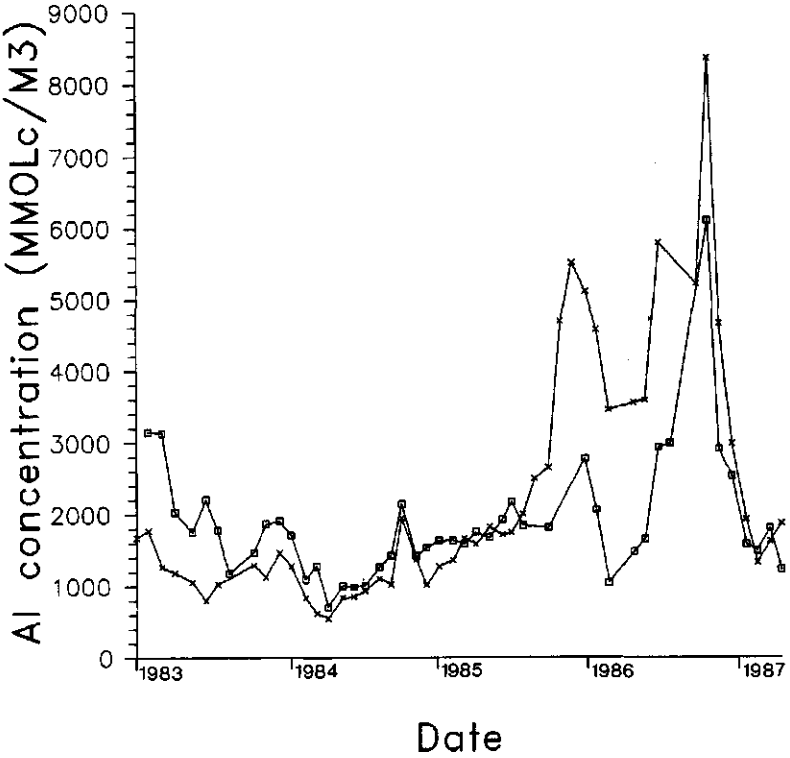

Fig. 1.Total dissolved Al concentrations (mmol$_c$ m^{-3}) in duplicate lysimeters at GF at the 40-cm depth.

sandy to loamy soils with high atmospheric acid inputs (> 2.5 kmol ha^{-1} yr^{-1}) in the Netherlands (Mulder et al., 1987) and in the FRG (Ulrich and Matzner, 1983).

Increased mean dissolved Al concentrations and decreased mean pH in our sub-soils were associated with increased atmospheric acid loads (Fig. 2). This trend was also true for the Danish soils, even though they have a slightly higher base content than the Dutch soils. Our data support the hypothesis that strong acid inputs play a prominent role in the current increase in soil acidification rate and Al solubility in acidic sandy soils.

6.3.3 Al chemistry

Dissolved Al correlated positively with both NO_3 and SO_4 concentrations in almost all Dutch soil horizons (Table 6). The prominent covariation of dissolved Al and NO_3 is also illustrated for the GF and TF sites in Fig 3. Our findings suggest

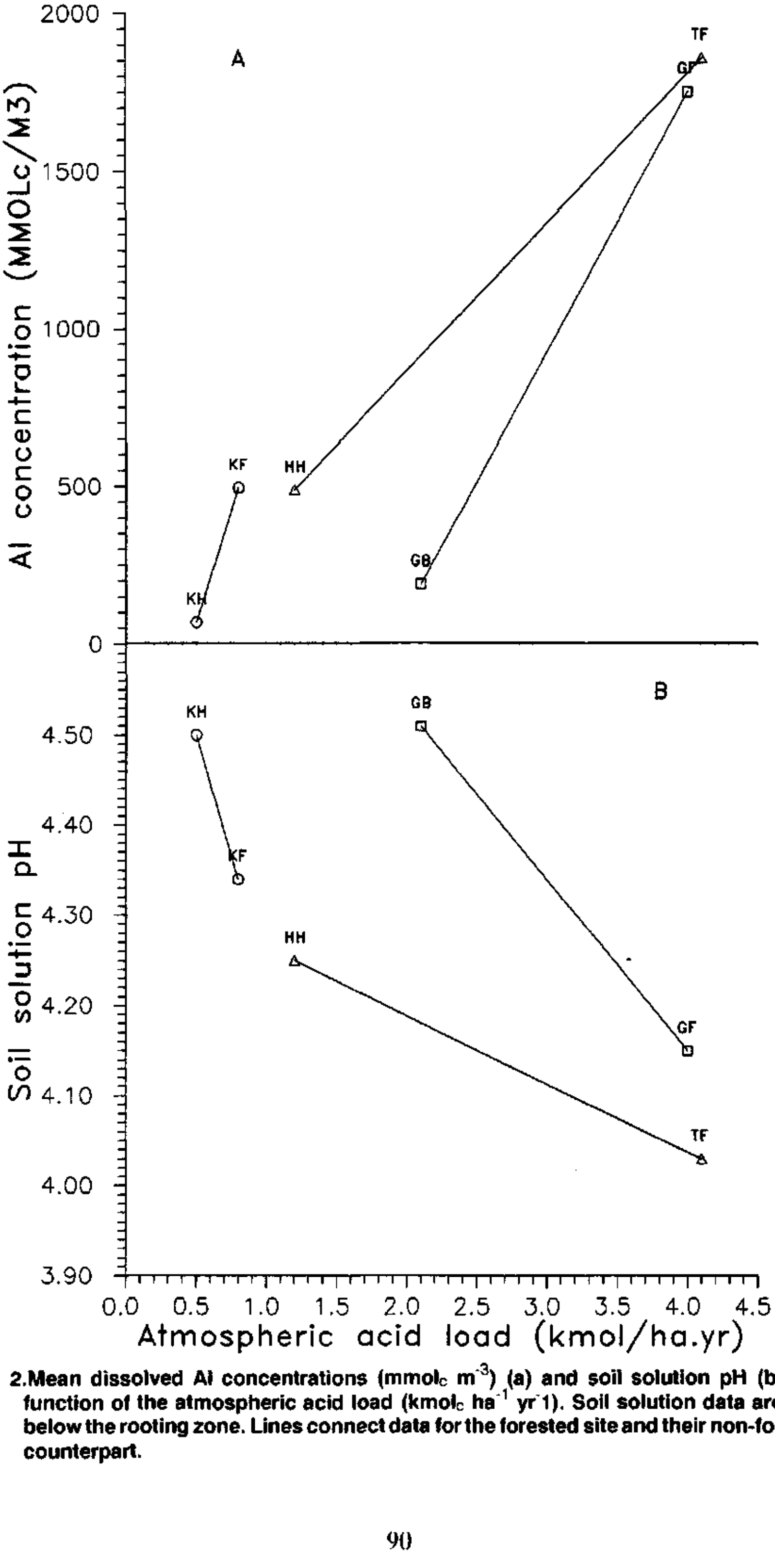

Fig. 2. Mean dissolved Al concentrations (mmol$_c$ m^{-3}) (a) and soil solution pH (b) as a function of the atmospheric acid load (kmol$_c$ ha^{-1} yr^{-1}). Soil solution data are from below the rooting zone. Lines connect data for the forested site and their non-forested counterpart.

Table 6. Correlation coefficients for Al and pH and for Al and various anions in soil solutions over the complete monitoring period.

Site	depth	Al/pH	Al/NO3	Al/SO4	Al/Cl
	cm				
KH	0	-0.77*	0.45	0.96**	0.89
	13	-0.46	-0.37	-0.41	0.03
	49	-0.65*	0.04	-0.77*	0.80*
KF	0	0.08	-0.23	0.36	0.40
	12	-0.41	0.13	0.13	0.77*
	31	-0.71*	-0.17	-0.05	0.96*
	80	-0.58	0.62*	0.35	0.92*
GB	0	-0.54***	0.59***	0.55***	0.31**
	40	-0.41**	0.76***	-0.29*	-0.05
	100	-0.53***	0.46***	-0.58***	-0.17
GF	0	-0.12	-0.01	0.19*	0.09
	10	-0.46*	0.94***	0.56**	0.70**
	40	-0.46***	0.95***	0.65***	0.58***
	100	-0.51***	0.88***	0.81***	0.88***
HH	0	-0.33**	0.30**	0.05	-0.04
	7	-0.55***	-0.30*	0.85***	0.32*
	22	-0.34**	0.50***	0.80***	0.60***
	70	-0.55***	0.62***	0.02	0.09
	110	0.34	0.70**	-0.17	-0.52**
TF	0	-0.10	0.01	0.14	0.07
	12	-0.60***	0.02	0.69***	0.54***
	35	-0.40***	0.40***	0.40***	0.52***
	57	-0.43**	0.75***	0.41**	0.45**
	100	-0.80**	0.36	-0.16	0.50*

* $P<0.05$
** $P<0.01$
*** $P<0.001$

the importance of H_2SO_4 and HNO_3 for Al mobilization in the Dutch soils. In contrast, no significant correlations between dissolved Al and NO_3 or SO_4 were observed in the Danish soils, indicating that other processes may also have been relevant in Al mobilization there. Dissolved Al also correlated positively with Cl concentrations in almost all soil horizons (Table 6). However, because atmospheric HCl input was negligible, this correlation must have been due to evaporative concentration effects or to cation exchange, where Al was exchanged for Mg and Na.

Soil solutions from most individual mineral soil layers of all sites showed significant negative pH-Al correlations (Table 6 and Fig. 4), as is expected on the basis of chemical equilibrium between solutions and Al-bearing minerals. In

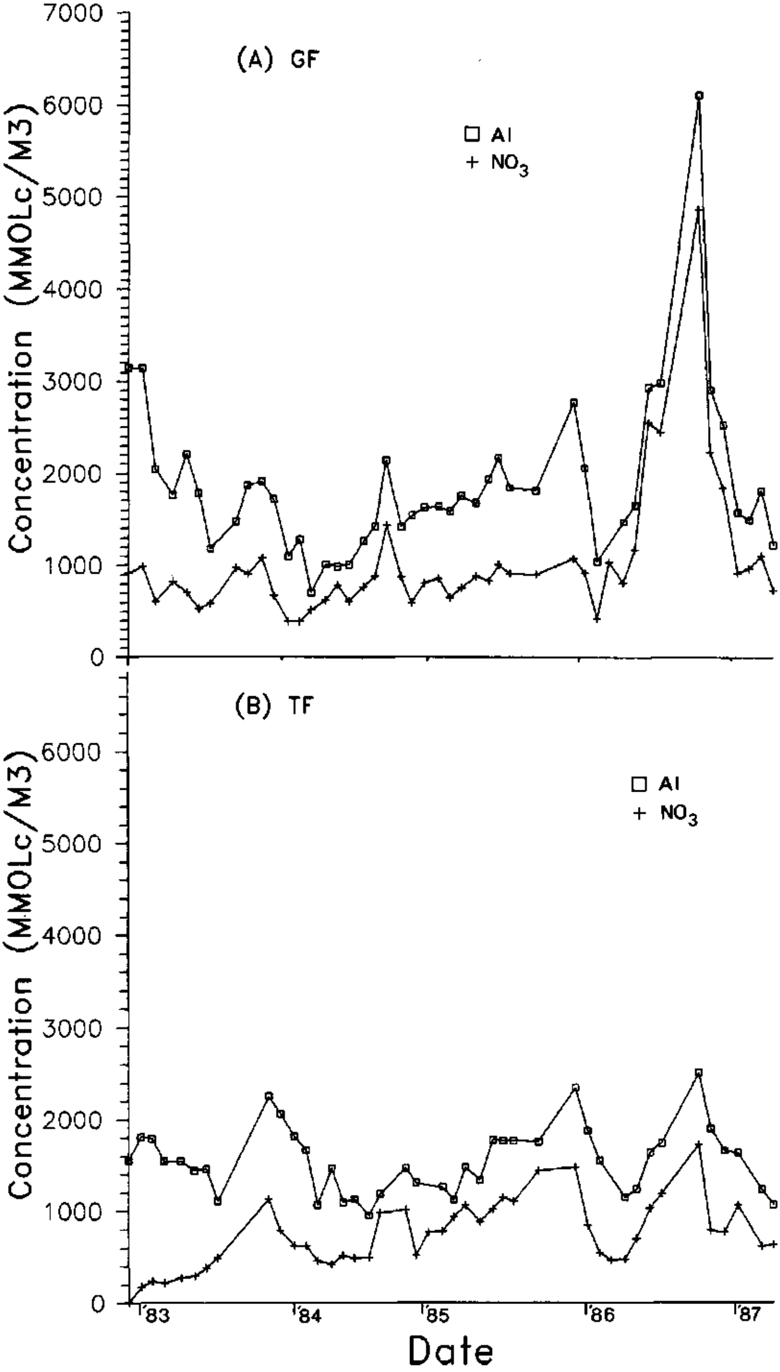

Fig. 3.Concentrations of Al and NO_3 in GF, 40-cm (a) and TF, 35-cm (b) soil solutions as a function of time. Concentrations are in $mmol_c$ m^{-3}.

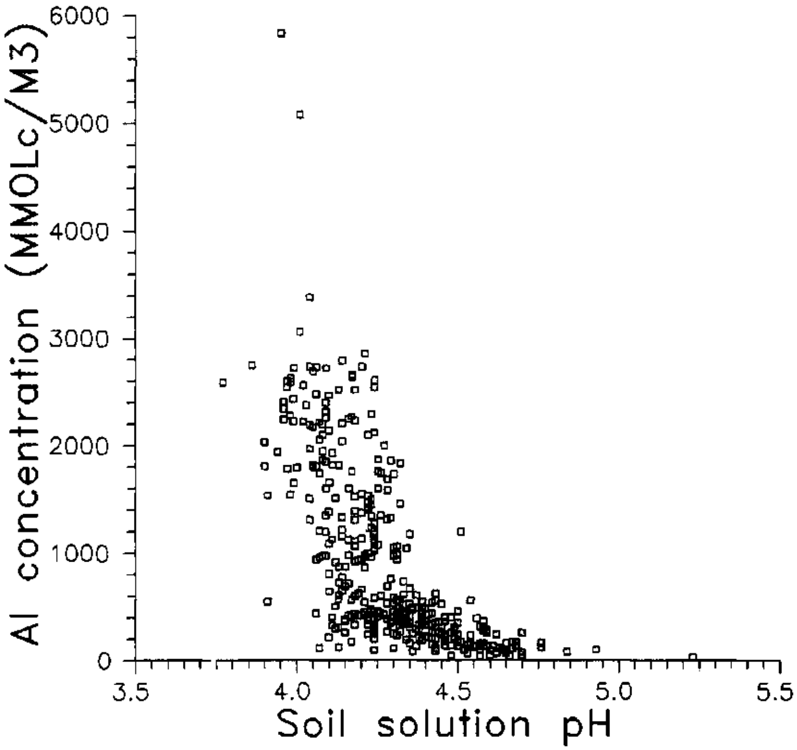

Fig. 4.Total dissolved Al as a function of soil solution pH in all sub-soil solutions (below the 50-cm depth) of the six study sites. Concentrations are in mmol$_c$ m^{-3} (all Al was assumed to be trivalent).

contrast, the pH-Al relationship with depth was positive: concentrations of dissolved Al and pH values increased simultaneously in the upper 40-cm of nearly all soils (Table 7). Similar trends with depth were reported for acidic loamy sands in the Netherlands, which also receive high atmospheric acid inputs (Mulder et al., 1987).

Chemical equilibrium calculations confirmed that surface soil horizons were highly undersaturated with respect to secondary Al-bearing minerals and that saturation increased with depth (Table 8). Subsoil solutions at all sites reached saturation with gibbsite solubility, indicating that this mineral may serve as an Al solubility control. Other researchers also found (sub)soil solutions close to saturation with respect to the solubility of gibbsite (Nilsson and Bergkvist, 1983; David and Driscoll, 1984; Driscoll et al., 1985).

Table 7. Mean soil solution pH values and total dissolved Al at various depths for the complete monitoring period.

Site	depth	pH	Al(tot)
	cm		$\text{mmol}_c\ \text{m}^{-3\$}$
KH	0	4.04	20
	13	4.11	65
	49	4.50	67
KF	0	3.60	32
	12	3.62	194
	31	4.34	494
	80	4.57	312
GB	0	4.41	178
	40	4.40	239
	100	4.51	188
GF	0	4.08	43
	10	3.91	839
	40	3.97	2073
	100	4.15	1751
HH	0	3.83	43
	7	3.53	372
	22	4.21	551
	70	4.25	488
	110	4.13	364
TF	0	3.95	33
	12	3.38	107
	35	4.02	1515
	57	4.03	2065
	100	4.03	1821

$\$$ mmol of unit ionic charge per m^3

In the KH, KF and HH soils, with relatively low acid loads, Bhs horizon leachates attained equilibrium with gibbsite solubility, whereas in the TF soil, with a higher acid load, saturation with gibbsite did not occur until the soil solution reached the Bs horizon. In driftsands with relatively low acid loads (GB) all soil solutions were close to saturation with respect to gibbsite solubility, whereas at GF, with the high acid load, saturation was not evident until the soil solution reached a depth between the 40 and 100-cm.

In an earlier paper (Mulder et al., 1987) we hypothesized that in the surface layers of the mineral soils Al dissolution could not keep pace with the addition of strong acids, so that chemical equilibrium was not reached until in the subsoil. In this hypothesis kinetic constraints were the major cause of the strong undersaturation with respect to most Al-bearing minerals in the surface soil

Table 8. Saturation index (SI) with respect to gibbsite ($pAl - 3pH = -9.00$ at 10°C+) and jurbanite ($pAl+pSO_4-pH=3.80$; Nordstrom, 1982). Values are means, standard deviations and number of observations for the complete monitoring period.

Site	depth	horizon	Gibbsite		Jurbanite		
	(cm)		mean	sd	mean	sd	n
KH	13	E*	-1.36	0.64	-1.09	0.26	8
	49	Bhs*	-0.26	0.46	-0.64	0.16	9
KF	12	E*	-2.43	0.88	-0.83	0.27	10
	31	Bhs	-0.02	0.44	0.23	0.23	10
	80	C	0.36	0.32	0.34	0.08	7
GB	0	C	-0.26	0.48	-0.37	0.51	95
	40	C	0.03	0.36	-0.12	0.20	54
	100	C	0.05	0.26	-0.08	0.31	55
GF	10	C*	-1.12	0.66	0.16	0.31	27
	40	C	-0.64	0.30	0.67	0.22	86
	100	C	-0.15	0.27	0.84	0.21	69
HH	7	E*	-2.48	0.78	-0.35	0.28	57
	22	Bhs	-0.38	0.34	0.39	0.25	69
	70	Bs	-0.15	0.30	0.36	0.18	41
	110	C	-0.10	0.27	0.42	0.12	13
TF	12	E*	-3.52	0.41	-1.06	0.26	54
	35	Bhs	-0.60	0.34	0.78	0.20	83
	57	Bs	-0.39	0.28	1.00	0.10	45
	100	BC	-0.04	0.44	1.00	0.13	8

* values are overestimated, because organic monomeric Al was assumed to be negligible

\+ mean annual soil temperature is close to 10°C

solutions. However, preliminary results from batch studies, where we added strong acid to mineral soil samples, showed that chemical equilibrium was rapidly reached, even in surface soils. Surface soil equilibrium in these experiments was characterized by solutions that were highly undersaturated with respect to $Al(OH)_3$ solubility. Therefore the observed in situ undersaturation with $Al(OH)_3$ in surface soil horizons did not necessarily have to be related to kinetic constraints in Al dissolution, but alternatively may have been caused by chemical equilibrium with low solubility soil Al. Possibly, a H-Al exchange equilibrium with a humic phase adsorbent, as recently proposed by Cronan et al. (1986), could explain the in situ dissolved Al concentrations in our organic-rich surface horizons. In a recent paper Mulder et al. (submitted) already showed the importance of organically complexed soil Al as a source of aqueous Al in our surface soils.

Although chemical equilibrium calculations indicate gibbsite may be present in the sub-soils, this mineral was not detected by x-ray or optical mineralogical analysis. Gibbsite may form more readily from soil solutions with elevated concentrations of dissolved inorganic Al than from solutions with relatively high amounts of organic acids, where dissolved Al is primarily in an organic form. This latter condition is true in natural podzolic soils, where acidification is mainly driven by production and transport of organic acids. So, gibbsite formation, if it takes place at all, will most likely be a recent phenomenon, associated with elevated acid inputs. The 'gibbsite-like' Al solubility control may also have been caused by Al-containing secondary minerals, which have solubility characteristics similar to gibbsite, but which are mineralogically different, e.g. Al interlayers in clay minerals, or 'free' Al.

Jurbanite, a basic Al-hydroxy-sulfate (Nordstrom, 1982), has also been proposed to control Al solubility in mineral soils receiving high inputs of H_2SO_4 (Ulrich and Matzner, 1983). However, only GB subsoil solutions were in equilibrium with respect to jurbanite solubility; at the other sites solutions ranged from undersaturated ($SI = -0.64$; KH) to oversaturated ($0.34 < SI < 1.00$; KF, HH, GF, TF). Because in most soils conditions of oversaturation with respect to the solubility of jurbanite and net SO_4 release (Table 4) occurred simultaneously, the formation and occurrence of jurbanite seems unlikely.

6.3.4 Al budgets

Proton budgets (van Breemen et al., 1983) indicate that atmospheric acid inputs were by far the major source of the total acid load in the Dutch soils (Table 9). In the Danish soils, atmospheric acid inputs were relatively low and about equal to internally produced acidity (base cation assimilation by the biomass, deprotonation of dissolved organic acids). Dissolution of Al was the major acid sink in all soils, neutralizing 30 to 95% of the total acid load. In the KF soil Al mobilization even exceeded the total acid load, which may have been due to exchange of Al for Mg and Na, as is also suggested by the negative value for base cation mobilization (Table 9). Possibly, major seasalt inputs, which commonly occur at KF, mobilized exchangeable Al and caused a (short term) increase in base saturation. It should be stressed that neutral seasalts can not dissolve Al from the soil minerals, but can only mobilize previously dissolved Al, stored in an exchangeable form. Strong or weak acids are necessary for the

Table 9. Proton budgets for all sites for 4 (GB, GF, HH and TF) and 1 (KH, KF) hydrological years. The respective categories of acid sources and sinks are: free H^+ input, N transformations*, deprotonation of organic acids, *biomass assimilation, anion mobilization, sum of acid sources, sum of* acid sinks, base cation mobilization, Al mobilization, H^+ in drainage water. Values are in $kmol_c$ ha^{-1} yr^{-1}.

	Acid Sources						Acid Sinks			
Site	$H^{\$}$ inp	N tr.	Org Ac.	Biom assi	Anion mob.	SUM	SUM	Base mob.	Al mob.	H out
KH	0.4	0.2	0.2	0.3	0.1	1.4	1.4	0.6	0.4	0.2
KF	0.6	0.2	0.4	0.7	0.9	2.8	2.8	-0.6	3.1	0.3
GB	0.4	1.7	-0.2	0.0	0.3	2.2	2.2	0.6	1.4	0.2
GF	-0.1	4.1	0.0	0.4	0.9	5.3	5.3	0.4	4.7	0.2
HH	0.2	1.0	0.0	0.3	1.1	2.6	2.6	0.3	2.1	0.2
TF	-0.4	4.5	0.0	0.5	1.1	5.7	5.6	0.1	5.3	0.2

* acid production due to N transformation is essentially caused by net removal of atmospherically derived NH_4 in the percolating soil solution and its partial transformation to NO_3. Therefore H^+ input plus N- transformations represent atmospheric acid input

$ negative number indicates net alkalinity (HCO_3^-) deposition

actual dissolution of Al from soil minerals. So, continued acidification after the event will reduce base saturation and restore exchangeable acidity.

Rates of base cation mobilization (weathering plus cation exchange), which were low relative to total acid loads, were similar in all soils (-0.6 to 0.6 $kmol_c$ ha^{-1} yr^{-1}; Table 9) and hence did not seem to vary much with acid input. Although cation exchange probably modified the mobilization rates of base cations, our data indicate that the rates of base cation weathering were not greatly increased (i) by elevated acid loads or (ii) in soils with a somewhat higher base cation content (KH and KF). The suggestion that weathering rates in Dutch spodosols do not strongly depend on acid loads is supported by similar rates, estimated for the whole period of soil formation (ca. 10,000 yr) (Breeuwsma and de Vries, 1984). Also, the rates of mobilization of Si, which were similar in all soils, do not seem to depend on acid load (Table 5).

The apparent minor effect of acid load on the weathering rates of primary minerals implies that any additional acid input will be neutralized almost exclusively by Al solubilization in these soil types. Relative to the 'natural' rate of Al mobilization (i.e. the mean Al weathering rate from 10,000 yr BP until now, estimated for similar soils; Breeuwsma and de Vries, 1984) current rates have increased from only slightly (KH) to ca. 10 times at GF and TF.

Chemical budgets for individual soil horizons (Table 10) indicate that Al mobilization was limited in the forest floor (0.14 to 0.23 $kmol_c$ ha^{-1} yr^{-1}), and increased markedly in the surface mineral soil. Solubilization of Al in the spodosol E horizons ranged from 0.34 to 1.50 $kmol_c$ ha^{-1} yr^{-1}. In the two forested spodosols, Al mobilization continued in the Bhs horizon (1.95 and 3.44 $kmol_c$ ha^{-1} yr^{-1} at KF and TF, respectively). Some Al retention was observed in four of the subsoils, but most of the mobilized Al is currently leached and lost to the groundwater at all sites.

Table 10. Annual mean Al and Si budgets and molar ratios of mobilized Al and Si per soil layer for 1 (KH, KF) to 4 hydrological years (other sites). Negative values denote immobilization.

Site	Depth	Horizon	Al	Si	Al/Si
	cm		$kmol_c$ ha^{-1} yr^{-1}	kmol ha^{-1} yr^{-1}	
KH	surf- 0	O	0.16	0.16	0.3
	0- 13	E	0.34	0.39	0.2
	13- 49	Bhs	-0.04	0.00	-
KF	surf- 0	O	0.20	0.29	0.2
	0- 12	E	1.06	0.62	0.5
	12- 31	Bhs	1.95	-0.52	-
GB	0- 2	C	1.00	0.20	1.7
	2- 40	C	0.70	0.15	1.6
	40-100	C	-0.26	0.13	-
GF	surf- 0	O	0.18	0.17	0.4
	0- 10	C	1.91	0.29	2.8
	10- 40	C	3.55	0.19	6.2
	40-100	C	-0.99	-0.23	-
HH	surf- 0	O	0.23	0.46	0.2
	0- 7	E	1.50	0.07	7.1
	7- 22	Bhs	0.45	-0.29	-
	22- 70	Bs	-0.13	0.02	-
TF	surf- 0	O	0.14	0.12	0.4
	0- 12	E	0.16	0.20	0.3
	12- 35	Bhs	3.44	0.10	11.5
	35- 57	Bs	1.58	0.04	13.2

6.3.5 Implications for pedogenesis

The amounts of Si mobilized or immobilized in the various soil horizons were small compared to those of Al (Table 10). Only at KH mobilization rates of Al and Si were similar. Like Al, Si was mostly mobilized in the surface soil and partly retained in the subsoil. The ratio of Al/Si mobilized provides information on the source of mobilized Al. Congruent dissolution of Al-silicates would result in molar Al/Si ratios between 0.3 and 1.0. Because the observed ratios generally exceeded 1.0 in the horizons where most of the mobilization of Al took place (Table 10), non-silicate bound, free Al, rather than Al-silicates, was probably the predominant source of mobilized Al. The importance of free Al as a major source of dissolved Al in soil solutions is supported by laboratory experiments on the same soils (Mulder et al., submitted). Free Al is present in all soils and peaks in the spodosol Bhs horizons.

Relative to the current Al mobilization rate, the soils' free Al pools are small, so that they may be exhausted in a short period of time, even in spodosols. From the free Al content, bulk density, and the thickness of the Bhs, it can be calculated that at the present mobilization rate all free Al can be removed from this horizon in a few hundreds of years. In forested driftsands, with low free Al contents, the free Al depleted soil layer currently even deepens at a rate of ca 0.5 cm yr^{-1}.

Once free Al has been depleted, acid buffering of the soil will be limited, so that, upon continuation of the present deposition rates, soil solutions low in pH and dissolved Al will occur at increasing depth in the future. Currently, this condition is only evident in the spodosol E horizons.

6.4 CONCLUSIONS

Atmospheric acid inputs have a strong impact on the Al chemistry of acidic, sandy soils, with low concentrations of base cations. Such soils, which cover large areas of Belgium, the Netherlands, northwestern Germany and Denmark, are highly vulnerable to acidic deposition. Their base saturation is low and the rate of base cation weathering does not increase with the rate of acid input. Therefore, any additional strong acid deposition in these soils is almost exclusively neutralized by Al solubilization. Aluminum concentrations in the surface soil layers are relatively small and may be in equilibrium with organically bound soil Al. Soil bound Al is probably least soluble in the surface horizons, where most of the Al leaching has occurred. Upon percolation, the soil solution probably attains equilibrium with more soluble Al compounds. Due to continued Al mobilization at greater depth sub-soil solutions reach equilibrium with respect to gibbsite solubility.

The source of mobilized Al is probably mostly free, non-silicate bound Al. Pools of free Al will be exhausted rapidly at the present high rate of Al leaching. Our data indicate that the strong impact of atmospheric acid input on the Al chemistry of the soil may not only result in negative effects on nutrient solutions in the rooting environment, and on ground- and surface water quality, but may also dramatically change pedogenic processes.

ACKNOWLEDGMENTS

Thanks are due to E.J. Velthorst, N. Nakken, H. Sliepenbeek, A. Van Osch, A. Vallent and H.W.G. Booltink for help during sampling and chemical analysis. Calculation of the waterfluxes was carried out by H.W.G. Booltink and P.H.B. de Visser. We greatfully acknowledge Staatsbosbeheer (Gerritsfles, Hasselsven), Mr. W.A.M. Rijken (Tongbersven) and Mr. J.E. Handberg (Klosterhede) for making the sites available for our research. This research was supported in part by the EEC (contract ENV-650-NL), the Netherlands Technology Foundation (STW), the (Danish) Agency of Environmental Protection and the (Danish) Ministry of Energy.

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Chapter 7

ACID RAIN ON ACID SOIL: IRREVERSIBLE CHANGES IN SOLID PHASE ALUMINUM AND IMPLICATIONS FOR ACID NEUTRALIZATION

ABSTRACT

In acid soils acid rain is often largely neutralized by dissolution of aluminum, which is potentially phyto-toxic. Here we show that only a minor fraction of soil aluminum is readily dissolved. This most soluble fraction consists largely of non-silicate, organically bound aluminum, which has been formed in the course of soil development. The current rapid and irreversible depletion of this fraction constitutes a drastic change in soil genesis. Depletion may eventually result in reduced acid neutralization, due to decreased dissolution of aluminum, and should be accounted for in soil acidification models.

7.1 INTRODUCTION

Dissolution of aluminum in acid soils is one of the most pronounced soil chemical effects of acidic deposition (van Breemen et al., 1984; Khanna et al., 1987; Mulder et al., 1987). Aqueous aluminum is toxic to crop roots (Pavan and Bingham, 1982; Andersson and Kelly, 1984; Wright et al., 1987) and has also been associated with forest die-back (Ulrich et al., 1980). Because of its toxicity the soil chemical behaviour of aluminum has been a major topic in agronomic (Richburg and Adams, 1970; Bloom et al., 1979) and ecological (David and Driscoll, 1984) studies. Most of these studies deal with short-term phenomena like speciation, exchange characteristics and solubility control. Long-term effects on aqueous aluminum in soils, e.g. due to changes in the soil solid phase, are generally ignored. In many acid, sandy soils, however, the current annual aluminum leaching makes up a sizable portion of the pools of various solid phase aluminum fractions. Table 1 suggests that leaching could lead to a significant depletion of certain fractions within several decades. Decreasing contents of various fractions of solid phase aluminum could affect the aqueous aluminum concentrations. Insight in these aspects is essential for evaluating long-term effects of acidic deposition.

Table 1: Pools and annual mobilization rates of aluminium in 3 acid, sandy soils from the Netherlands, and 1 in New Hampshire (USA).

Site	Soil	Depth	Horizon	Extractable aluminum KCl	 $Na_4P_2O_7$	 $(NH_4)_2C_2O_4$	Total aluminum++	Annual removal of aluminum$
		cm		mmol kg^{-1}				
Gerritsfles	driftsand	0-10	C	2.2	33.3	3.7	450	0.5
		10-40	C	0.7	35.7	6.3	427	0.3
Tongbersven	podzol	0-12	E	1.3	5.0	1.5	101	0.1
		12-35	B	13.7	196	3.3	446	0.4
Hasselsven@	podzol	0- 7	E	11.1	21.2	7.7	221	0.5
		7-22	B	16.3	55.8	13.5	273	0.1
Hubbard Brook	podzol	0- 5	E	1.2	7.8	3.0	1660	0.005
		15-30	B	5.8	322	51.1	2185	-0.004

+ Solid phase aluminum was extracted using selective dissolution. One-gram soil samples were sequentially extracted with 50 ml 1M KCl (0.5 hour), 50 ml 0.1 M $Na_4P_2O_7$ (16 hours), and 50 ml 0.2 M $(NH_4)_2C_2O_4$ adjusted to pH 3.0 (4 hours in the dark), (Driscoll et al., 1985). Extracted amounts represent exchangeable aluminum (KCl), organic aluminum and minor amounts of non-crystalline hydrous oxydes ($Na_4P_2O_7$) and most amorphous aluminum hydroxides ($(NH_4)_2C_2O_4$) (USDA, 1972). This fractionation scheme was originally developed for iron, so extractions may not be entirely specific and may include some overlap (McKeague et al., 1971). Extracted aluminum was measured using colorimetry with pyrocatechol violet (KCl), ICP ($Na_4P_2O_7$), and atomic absorption with a nitrous oxide acetylene flame ($(NH_4)_2C_2O_4$)

++Elemental aluminum was determined by X-ray fluorescence spectroscopy of a Li-tetraborate melt of the soil material

$ Calculated from bulk density (kg m^{-3}) (van Dobben and Mulder, in prep.), and estimated aluminum fluxes (kmol ha^{-1} yr^{-1}) (Mulder et al., submitted). Aluminum fluxes were estimated per month by multiplying the simulated soil water flux and the measured monthly dissolved aluminum concentration in the soil solutions collected from suction plates in the field. Inorganic aluminum in the Hubbard Brook soils were taken from Driscoll et al. (1985). Negative numbers indicate immobilization

@ Not included in the leaching study

7.2 MATERIALS AND METHODS

Data on the sources of dissolved aluminum were obtained from a laboratory leaching experiment. Air-dried, < 2 mm fractions of soil samples from the Netherlands and New Hampshire (USA) were taken from the surface and sub-surface soil of 2 podzols (Haplorthods) and of a recent driftsand (Udipsamment) (Table 1). In a batch study the soil samples were repeatedly leached for 24 hours with hydrochloric acid of pH 3.0, which is close to the current pH of the water infiltrating many surface soils of forests and heathlands in northwestern Europe (Mulder et al., submitted). Acid addition rates were high relative to those in the field and amounted to 20 mmol H^+ kg^{-1} d^{-1}. This is considerably higher than the actual acid loads in the field (4 mmol H^+ kg^{-1} yr^{-1}). After 10, 25 and 50 leaching cycles (i) pooled leachates were analysed for all major solutes, (ii) residual solid aluminum fractions were estimated by selective dissolution, and (iii) equilibrium aluminum concentrations were measured. Details on the methods are given in Table 1 and in Fig. 1.

7.3 RESULTS AND DISCUSSION

The cumulative amount of aluminum leached by HCl is invariably close to the amount of non-silicate bound ('free') solid aluminum removed (Fig. 1). This shows that the dissolution rate of 'free' aluminum is high relative to that of the more abundant alumino-silicates (Table 1). Organically complexed ($Na_4P_2O_4$-extractable) aluminum is the fraction that dissolves most, whereas the net contribution of the exchangeable fraction (KCl-extractable) is small (Fig. 1). So, aluminum transfer mainly occurs from organically complexed solid phase aluminum to solution, even when the pool of organic aluminum is small.

In the HCl leachates stable aluminum concentrations, which suggest chemical equilibrium, are reached within 24 hours. Equilibrium aluminum concentrations show a significant positive correlation with the organic ($Na_4P_2O_7$-extractable) aluminum content of the soil sample (Fig. 2). This further supports the importance of alumino-organics as a major source of dissolved aluminum. A similar positive correlation in forest floor samples (Cronan et al., 1986) was attributed to exchange equilibrium between dissolved and adsorbed aluminum. Probably, a similar exchange equilibrium with solid phase alumino-organics holds true in the mineral soil, as our equilibrium extracts were highly undersaturated with respect to gibbsite solubility.

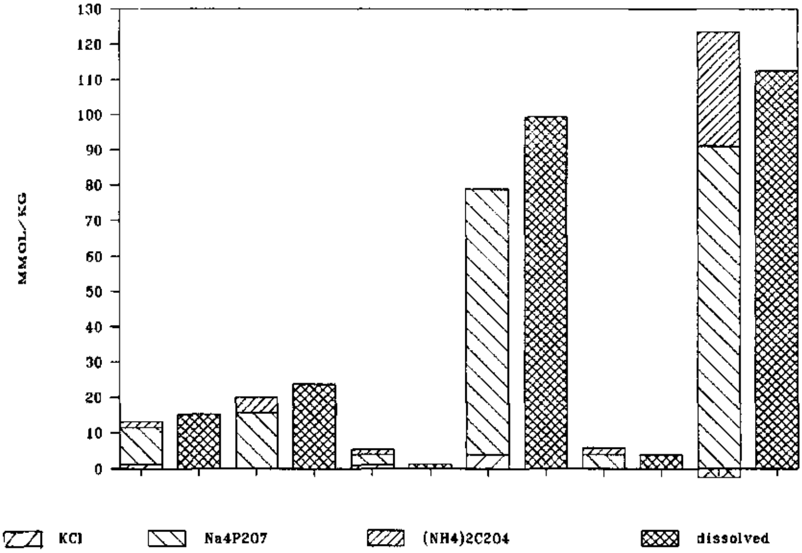

Fig. 1.The decrease in solid phase aluminum (left bar) as well as the dissolved amount of aluminium for 6 soil horizons (right bar) after leaching 25 times with HCl. Values are means of two replicates. Replicate values of dissolved aluminum were within 37% (E horizons) or 6% (all other horizons) of the mean, whereas the these values for the depletion of the $Na_4P_2O_7$-extractable fraction were within 38% (E horizons) or 22% (other horizons) of the mean. Five gram of soil was leached with 100 ml HCl (pH 3.0) for 24 hours in tightly capped centrifuge tubes at 20 ± 2°C. Suspensions were shaken manually 3 times per 24 hours. After 24 hours the suspensions were centrifuged at 2,000 rpm for 15 minutes. Of the clear supernatants 80 ml was decanted and replaced by 80 ml of fresh HCl solution. Sub-samples of each supernatant were pooled to give one extract (in duplicate) after 25 HCl batches. At the end of the experiment the soil samples were freeze dried and analysed for various fractions of solid phase aluminum, using selective dissolution (Table 1). Dissolved aluminum concentrations were analysed colorimetrically, using pyrocatechol violet.

Generally, the KCl extractable aluminium fraction is assumed to represent exchangeable aluminum (Kamprath, 1970). However, our data show that $Na_4P_2O_7$-extractable aluminum is also readily mobilized and may be a better estimate of the exchangeable fraction.

In the field 1 to 2% of the alumino-organics are removed from the surface soil annually (Table 1). Note that the current aluminum mobilization rate from surface horizons is lowest where the content of organic aluminum is also lowest. Based on the content of soil organic aluminum the mobilization rates of aluminum are potentially high in the spodic B horizons. However, the elevated aluminum dissolution rates cause a rapid acid consumption and consequently an increase in solution pH, which restricts further aluminum mobilization. B horizon solutions

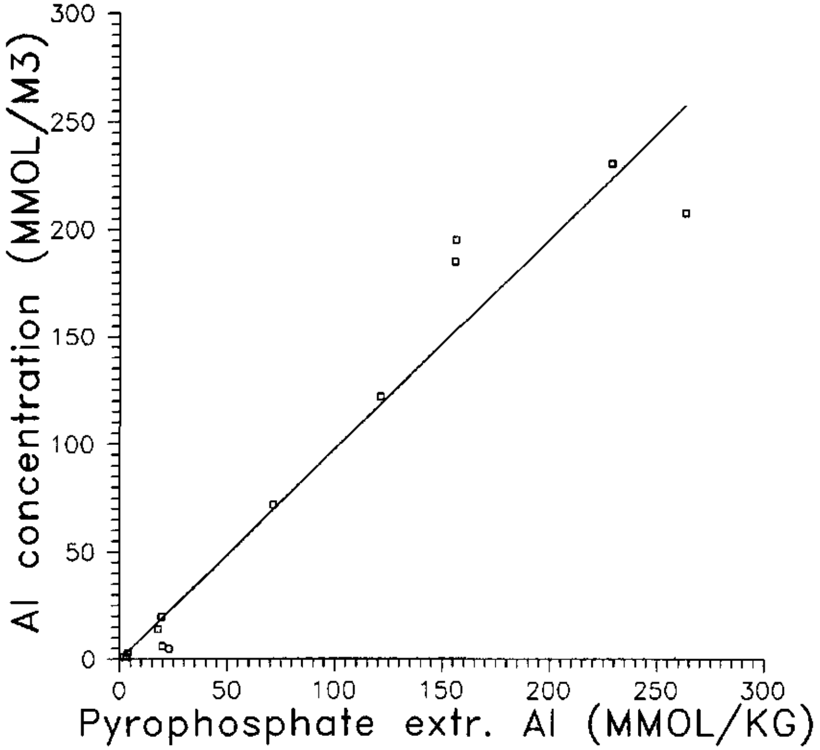

Fig. 2.Equilibrium aluminum concentrations in individual HCl leachates, after 10, 25 and 50 acid additions, as a function of $Na_4P_2O_7$-extractable aluminum. Data refer to all 6 soil horizons. Equilibrium concentrations of aluminum ([Al]) are significantly correlated ($R^2 = 0.9466$) with $Na_4P_2O_7$-extractable soil aluminum (Al_{pyro}): $[Al] = -0.60 + 0.98 \times Al_{pyro}$, where [Al] is in mmol m^{-3} and Al_{pyro} is in mmol kg^{-1}. Data were obtained by leaching 3 duplicate sets of soil samples with HCl, 10, 25 and 50 times, respectively. At the end of the experiment pooled HCl extracts and residual soil samples of each of the 3 sets were processed as described in Fig. 1. Charge balance calculations of the extracts indicate that aluminum is mainly present as Al^{3+}.

generally follow a gibbsite type equilibrium (pAl - 3pH = -8.11). In podzols the current depletion of alumino-organics in absolute terms is most pronounced in the upper centimeters of the B horizon, which has formed due to the precipitation of organic aluminum in the course of soil development. In such soils the introduction of acid rain marks a drastic change in the naturally occurring podzolization process.

7.4 CONCLUSIONS

The current high leaching rate of aluminum causes a rapid depletion of alumino-organics in the rooting zone of many acid, sandy soils, which is irreversible on a time scale of decades or centuries. Because aqueous aluminum concentrations are in equilibrium with solid phase alumino-organics, depletion upon continued acid deposition will inevitably lead to a reduction in dissolved aluminum concentrations. At the same time, soil solution pH values, which are now buffered in the range of pH 3.5 to 4.2 by dissolution of aluminum (Mulder et al., submitted) will drop to values well below 3.0. Such dramatic changes in the soil solution chemistry of the rooting zone may have significant ecological consequences. Therefore, depletion of solid phase organic aluminum and the associated changes in the chemical composition of soil solutions should be incorporated in current soil acidification models.

ACKNOWLEDGMENTS

We thank Staatsbosbeheer and W.A.M. Rijken for making the research sites available. This study was supported in part by the EEC and by the Netherlands Technology Foundation (STW).

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Chapter 8

WATER FLOW PATHS AND ALUMINUM SOLUBILITY CONTROL AT BIRKENES AND IMPLICATIONS FOR HYDROCHEMICAL MODELLING

ABSTRACT

At Birkenes, a small forested catchment with acidic soils in southernmost Norway, streamwater has high concentrations of SO_4*, H and Al, due to acidic deposition. Simulation of short term variations in dissolved Al, using a previously developed model, were not successful, possibly because a universal equilibrium with* $Al(OH)_3$ *was assumed. Recent studies have shown that such a universal equilibrium does not apply in Birkenes streamwater, because increased undersaturation with* $Al(OH)_3$ *was observed with increasing discharge. We hypothesized that streamwater chemistry is largely determined by variations in water flowpaths, which differ in Al solubility control. In the autumn of 1987 we tested this hypothesis during and after an exceptional event with an extremely high seasalt loading. Monitoring the Cl pulse showed that precipitation inputs rapidly flowed laterally through the O horizons to the stream, over nearly water-saturated soils. Vertical percolation of Cl-rich water was slow, even when groundwater tables dropped and new rainstorms occurred. In between rainstorms the contribution of O horizon leachates to streamwater discharge decreased considerably. Solutions from the B and C horizons were close to equilibrium with* $Al(OH)_3$ *(*$pK_S = -9.0$ *at* 10^oC*). O horizon leachates, however, had a considerably lower Al solubility, probably regulated by cation exchange. Reduced Al concentrations in streamwater at peak discharge, often observed when soils are almost or wholly water saturated, was mainly caused by the increased contribution of laterally flowing water through the O horizons. Therefore, model improvement should include different Al solubility controls for surface- and subsoils.*

8.1 INTRODUCTION

Elevated levels of dissolved inorganic Al, often observed in areas with acid deposition on acidic soils, are of major environmental concern due to the adverse effects of aqueous Al on terrestrial and aquatic organisms. In spite of much progress in acid rain research during the last decade, hydrological and chemical processes affecting the Al chemistry at a catchment scale are still far from understood. This severely limits our ability to predict changes in streamwater chemistry, particularly during snowmelt and rainstorm events.

Most hydrochemical models assume general equilibrium with a single $Al(OH)_3$ *mineral phase. However, several workers (e.g. Hooper and Shoemaker, 1985;* Sullivan et al., 1986; Neal et al., 1986) found that during peak flow, streamwater becomes highly undersaturated with respect to $Al(OH)_3$ solubility. From streamwater Al chemistry at peak discharge in the Birkenes catchment, southernmost Norway, Sullivan et al. (1986) hypothesized that (i) hydrological flowpaths, and (ii) different mechanisms for Al activity regulation in the various soil horizons are the major controlling variables for streamwater Al. Support for various Al solubility controls within the soil was given by Cronan et al., (1986), who showed that much of the variation in soil solution Al concentrations could be accounted for by a two-component equilibrium model, involving both a solid phase humic adsorbent and an $Al(OH)_3$ mineral phase.

To test the flowpath hypothesis in the Birkenes catchment we conducted an intensive hydrochemical monitoring study in the Birkenes soils and stream in the autumn of 1987. The study period happened to include a storm event with an exceptionally high NaCl loading, superimposed on representative hydrological conditions in the catchment. Tracing the sea salt pulse through the catchment and into the stream considerably increased our insight in water pathways. Also, the elevated level of dissolved solutes enabled testing of ion exchange equilibrium in the Birkenes soils, as a control for the activity of major cations, including Al.

8.2 SITE DESCRIPTION AND METHODS

8.2.1 Experimental setting

Birkenes is a small (0.41 km^2) forested catchment, dominated by Norway spruce, with shallow soils on granitic bedrock. The catchment is situated ca. 30 km north of Kristiansand in southernmost Norway, in an area with relatively high atmospheric acidic deposition, amounting to nearly 7 g SO_4 m^{-2} yr^{-1} (Christophersen and Wright, 1981). The catchment is drained by three small second-order streams which converge 150 m above a V-notch weir (Fig. 1). Measurements of precipitation amount and quality, as well as streamwater chemistry and discharge were conducted since 1971/72. The routine monitoring program currently includes (i) daily precipitation amount and quality (Norwegian

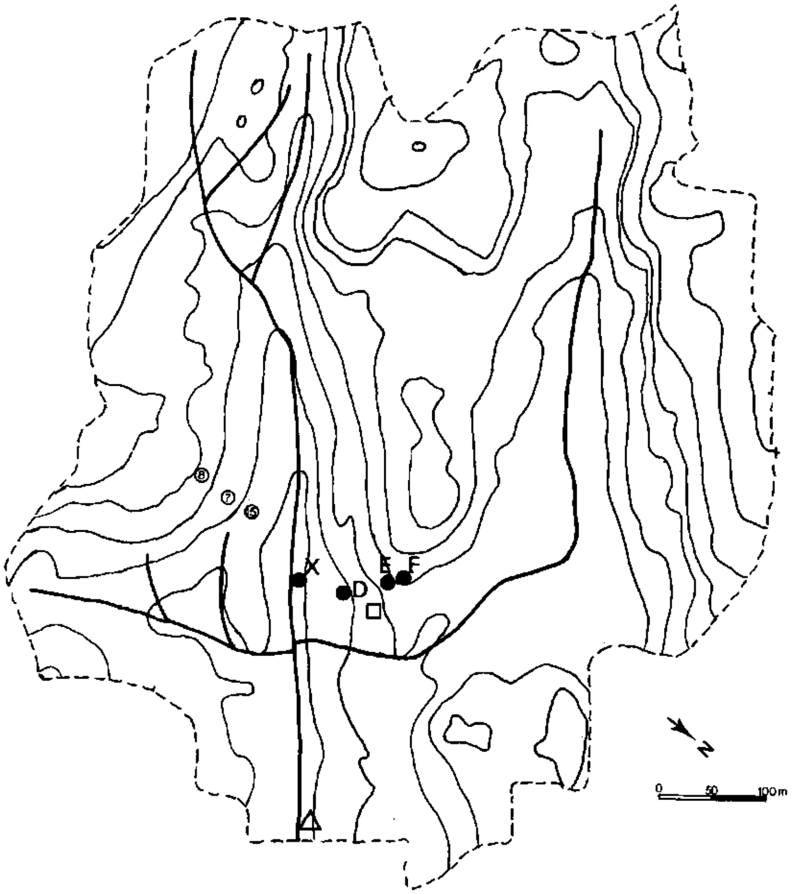

Fig. 1.The Birkenes catchment showing lysimeter plots (dots), piezometers (circels), the weir in the main brook (triangle), and the pits, where soil samples were taken (square).

Air Research Institute, NILU), (ii) continuous stream gaging (Norwegian Water Resources and Energy Board, NVE), and (iii) weekly sampling for streamwater chemistry (Norwegian Institute for Water Research, NIVA). Streamwater is acidic, with SO_4 as the major anion and has an annual volume-weighted pH of 4.5.

Mineral soils have developed in a layer of glacial till, which in most cases is less than 1 m thick. Soil depth generally decreases with increasing elevation. Mineral soils range from true podzols to acid brown earths. Where the soils are poorly drained, e.g. along the main brook and in pockets on the slopes, peat layers have formed, varying in thickness from a few dm to a few m. The spatial distribution of parent materials and soils is given in more detail by Dale et al. (1974).

Selected chemical characteristics of the major soil type (podzolized brown earth) are given in Table 1. Soil samples were collected from three horizons in duplicate from three plots. Only one bog sample was taken. Analytical techniques were according to Begheijn (1980, 1987). Briefly, soil pH was measured in 1:2.5 (mass to volume) extracts in distilled water. Exchangeable base cations were determined in Li-EDTA at pH 7.0, and exchangeable H and Al in 1N KCl extracts. The Cation Exchange Capacity (CEC) was calculated as the sum of the exchangeable base cations and exchangeable acidity (Al, H).

Table 1: Selected chemical characteristics[+] of various horizons of the 2 major soil types in the Birkenes catchment.

		podzolized brown earth			bog		
		E	Bhs	Bs	top[@]	sub[$]	bot[&]
$pH(H_2O)$		4.2	4.7	4.8	3.7	4.2	5.1
Ca(ex)	%CEC	4.1	3.7	2.8	1.2	5.2	33.4
Mg(ex)	"	2.1	1.5	1.2	0.4	0.5	6.1
Na(ex)	"	<2.2	<1.8	<1.8	<0.4	<0.5	<8.4
K(ex)	"	<2.2	<1.8	<1.8	<0.4	<0.5	<8.4
Al(ex)	"	49.0	63.4	63.2	78.8	70.6	8.8
H(ex)	"	43.9	29.9	32.1	19.6	23.7	49.4
CEC	$mmol_c/kg$	47	59	61	245	194	15

+ values are means of 6 samples (podzolized brown earth), 3 samples (mineral soil below bog), or 1 sample (top- and subsoil bog). Standard deviations are low for pH (2-6% of the mean), CEC of the podzolized brown earths (16-27% of the mean), and exchangeable H and Al of the brown earths (11-29% of the mean). Standard deviations are higher for exchangeable base cations in the brown earths (20->100% of the mean). In the mineral soil below the bog standard deviations are relatively low for exchangeable H, Ca, and Mg, only

@ between the 25 and 35-cm below the surface of the bog near the brook

$ organic mud (ca 70 cm below the surface) in the bog near the brook

& mineral soil below the bog near the brook (N.B. particle size distribution is highly variable, probably reflecting variations in deposition environment in the former valley bottom.

The mineral soils are acidic (pH 4.8), with lowest pH values in the E horizons. Bogs are somewhat more acidic than the acid brown forest soils. In contrast, the mineral soil layer below the bog is least acidic in terms of pH (5.1) and base saturation (40%). In all other soil horizons base saturation is low (ca 5%). Exchangeable acidity (H + Al) in the mineral soils is increasingly dominated by Al when going from the E to the B horizons. Only in the mineral soil layer below the bog the exchangeable acidity consists primarily of H. Conversely, the overlying bog is extremely high in exchangeable Al, whereas exchangeable H is reduced. The CEC values are low in all mineral soil horizons, and considerably higher in the organic soil, due to the dominance of organic exchange sites.

8.2.2 Field study

Soil solution samples were collected about every three weeks, starting August 1987. The main episode study was conducted from 15 to 25 October and included high resolution sampling of precipitation, soil solutions, and streamwater, as well as recording the groundwater levels. Additional data were provided by the routine monitoring programme. Methods are given below.

Four soil solution monitoring plots were set up at one of the southeast facing slopes of the Birkenes catchment. The four plots were situated along a transect perpendicular to the main brook (Fig. 1), and included the major soil types. Plot F is a shallow (22 cm deep) acid brown forest soil with a 10 cm thick humic surface layer, and plot E is a more than 40 cm deep podzolized acid brown forest soil, with a 1 cm thick humic layer and a 13 cm deep E horizon. Plot D consists of both a podzolized acid brown earth similar to the one at plot E, and an adjacent ca. 50 cm deep peat bog. Plot X is a deep (1-2 m) peat bog near the stream.

Soil solutions were sampled in various horizons at all plots from type 655X1-B1M3 ceramic cups (Soil Moisture Corp., Santa Barbara, CA), using a vacuum of ca. 50 kPa. In addition, we sampled percolation water below a surface layer of living mosses at plot X, using an acrylic copolymer filterplate, with 20 kPa suction (Driscoll et al., 1985). Neither one of the lysimeter types showed significant interaction with the major solutes, including Al (e.g. Driscoll et al., 1985).

Groundwater tables were recorded manually throughout October, at 3 piezometer plots (Fig. 1).

Streamwater samples were collected from the main brook at the weir. The sampling intensity of streamwater and soil solutions during the episode study varied according to hydrological conditions, with most frequent sampling (hourly) on the rising limb of the hydrograph and at peak discharge. Additional details on the field work may be found in Sullivan et al. (1986, 1987a, 1987b).

8.2.3 Analytical

Soil solution samples from the cup and plate lysimeters were collected in pre-evacuated glass bottles with a septum in the PVC screw cap. After collection, all solutions were transferred into clean polyethylene bottles. Glass bottles were continuously used for sampling the same lysimeter. In laboratory experiments no significant change of solute concentrations in the glass containers, under monitoring conditions, was observed.

After collection, all samples were transported to an on-site mobile field laboratory for direct processing to minimize changes during storage. Direct measurements on unfiltered samples included the determination of temperature, pH, specific conductivity, UV absorbance at 254 nm (for TOC determination), and fractionation of monomeric Al. For Al fractionation we followed the procedure outlined by Driscoll (1984), and which is described in detail elsewhere (Sullivan et al., 1987b). The speciation of inorganic Al was calculated using the chemical equilibrium program ALCHEMI (Schecher and Driscoll, 1987). Sub-samples of streamwater were filtered (45 μm millipore filters) before further analyses. Soil solutions did not need additional filtration, as the collector itself acted as a filter. Selected streamwater and soil solution samples were analysed for all major anions (SO_4, NO_3, Cl) and cations (Ca, Mg, Na, K) by ion chromatography and atomic absorption spectroscopy, respectively. Si was determined colorimetrically, using the molibdosilicate method (Begheijn, 1980). Total fluoride was determined by an Orion ion selective electrode after addition of TISAB buffer. Total Organic Carbon (TOC) concentrations were determined in selected samples at the Norwegian Institute for Water Research (NIVA), using persulphate oxidation and an Astro Model 1850 carbon analyzer, and calibrated against UV absorbance in the field ($R^2 = 0.94$).

8.3 RESULTS AND DISCUSSION

Long-term streamwater chemistry data at Birkenes show that Cl is the second-most abundant anion after SO_4 (volume-weighted concentrations 120 vs 150 mmol$_c$ m^{-3}; Christophersen and Wright, 1981). In the monitoring period from 1 August to 15 October 1987 streamwater Cl and SO_4 concentrations were significantly lower than the long-term mean (ca 80 and 100 mmol$_c$ m^{-3}, respectively), probably due to the relatively high amounts of rainfall (NILU, unpublished data). However, on 16 and 17 October streamwater Cl concentrations suddenly increased to 180 mmol$_c$ m^{-3}, whereas SO_4 concentrations stayed relatively constant. Later on in October, streamwater Cl concentrations even increased to values well over 200 mmol$_c$ m^{-3}.

The significant increase in streamwater Cl on 16 October was due to a Cl-rich, 22 mm precipitation event (bulk concentration 862 mmol$_c$ m^{-3}). This concentration of Cl was extremely high relative to bulk deposition Cl levels observed in the 2 preceeding weeks (9 to 134 mmol$_c$ m^{-3}; Fig. 2). More frequent

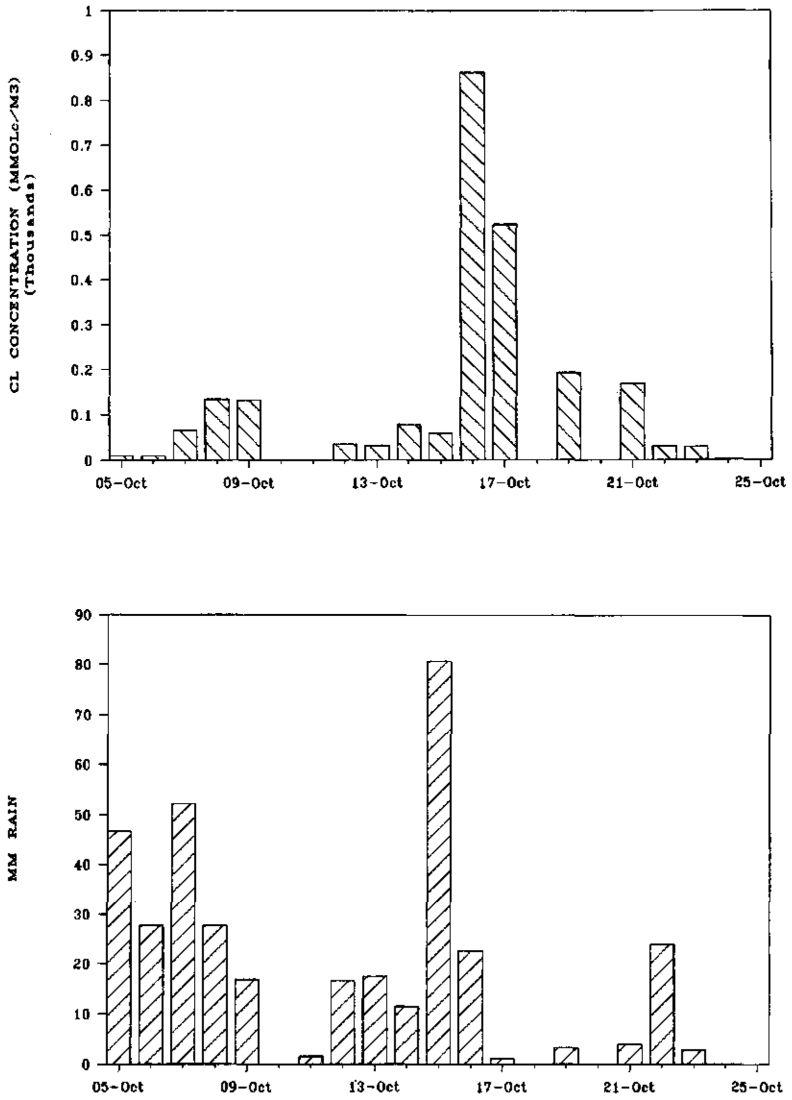

Fig. 2.Precipitation amount (lower panel) and Cl concentration (upper panel) at Birkenes in October 1987. We estimated the Cl concentration on 17 October from Na, assuming a Na/Cl ratio similar to that on 16 October.

sampling of bulk deposition suggested that most of the Cl was present in the last few mm of the 16 October rain storm, where the specific conductivity (EC) even went up to 649 $_{\mu}$S cm^{-1} (as compared to a mean bulk deposition EC of 120.5 $_{\mu}$S cm^{-1}).

Generally, the variation in autumn streamwater Cl is small, as is illustrated by the data from 1984 and 1985, where the variation in concentrations was less than 20% of the mean (c.f. Sullivan et al., 1987b). Therefore, the extreme event in the autumn of 1987 was a unique opportunity to study water pathways, using Cl as a tracer. We here present data on the movement of Cl through the Birkenes soils and the stream till 10 days after the episode.

With the Cl pulse the deposition of Na was high, too. The resulting wide variation in soil solution Na levels with time also enabled us to test the role of cation exchange as a mechanism for the control of dissolved cation concentrations.

8.3.1 Water pathways

Chloride concentrations in soil solutions showed a pronounced response to the high inputs on 16 October (Fig. 3). Due to small volumes, Cl concentrations could no be determined in all soil solutions. Therefore we also included specific conductivity (EC) in Fig. 3. The EC was determined in nearly all solutions from the soil. Note that per lysimeter both variables were well correlated.

The EC, as well as dissolved Cl concentrations of the O horizon leachates increased instantaneously on 16 October and reached a maximum between 17 and 18 October (plots D and X) or between 19 and 20 October (plot F). Maximum Cl concentrations in the O horizon leachates at plot F were ca 75% of the bulk Cl concentration in the major storm event. Maximum EC values at plot F were even slightly higher than those in bulk deposition on 16 October, but this was probably due to additional dissolution of solutes (e.g. organic acids) in the forest floor. At plots D and F, maximum EC values of the O horizon leachates (250 and 470 $_{\mu}$S cm^{-1}, respectively) were well above the EC in bulk deposition during the major storm event (120.5 $_{\mu}$S cm^{-1}), but significantly lower than the 649 $_{\mu}$S cm^{-1}, reported for the last few mm of the storm. Our data suggest that the temporal variation in salt content within the rainstorm was best preserved in the O horizon of plot X, less in the O horizon of plot D, and least in plot F's O horizon. Probably, vertical mixing of soil solution during percolation is most pronounced at plot F and least at plot X. This is consistent with the decreasing soil water content above the depth of sampling in the order plot F > plot D > plot X, because plot F is sampled from the O2, 3 cm below the surface; plot D is sampled from the O2,

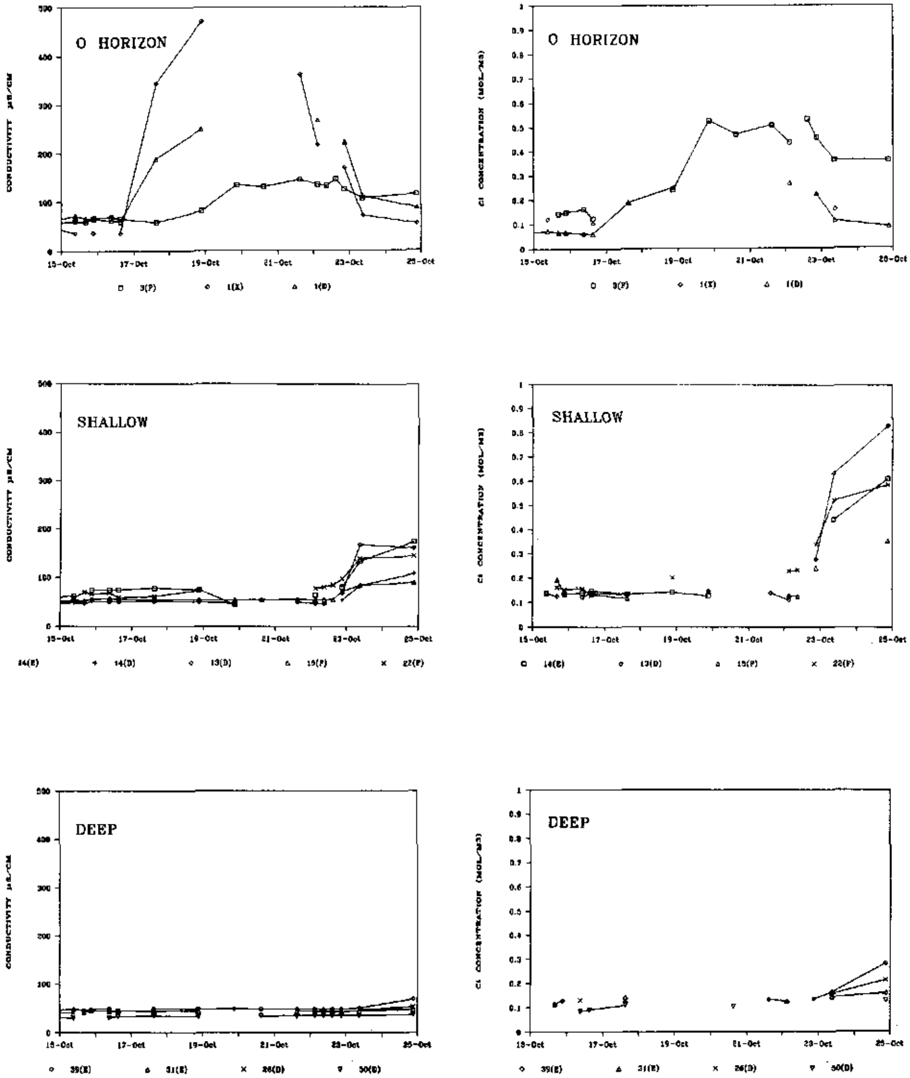

Fig. 3.Chloride concentration (right) and specific conductivity (left) in soil solutions from the O horizons (upper), shallow mineral soil (middle) and deep mineral soil (lower panels) in Birkenes cup lysimeters. Numbers refer to depth (cm) below the soil surface; lysimeter plot is indicated in brackets.

1 cm below the surface; and plot X is sampled 1 cm below a highly permeable layer of living mosses.

The fast response to changes in the external loading of solutes at plot X is also illustrated by the decrease in EC between 19 and 21 October, which was probably caused by the minor storm on 19 October (Fig. 2). In contrast, at plots D and F the O horizon's specific conductivity did not decrease appreciably until the major 22 October event. On 25 October total solute concentrations in the O horizon leachates at plots D and X had returned to their pre-event levels, while those at F were still somewhat elevated.

In the mineral soil, Cl did not increase significantly until a second major storm on 22 October, i.e. when the concentrations in the overlying O horizons decreased most strongly. Although the seasalt pulse did not reach the mineral soil horizons until 7 days after its deposition, Cl concentrations in the shallow lysimeters (< 25 cm below the surface) increased to values between 350 and 850 mmol$_c$ m^{-3} (Fig. 3). These concentrations are similar to those observed in the deepest O horizon lysimeter at plot F. In the deeper soil layers (> 25 cm below the surface) the increase in Cl levels after 22 October was small and no peak levels were reached before the end of the monitoring period.

In contrast to the soils, stream water showed three peaks in Cl concentration (Fig. 4). The first peak (180 mmol$_c$ m^{-3}), on 17 October, was directly associated with the seasalt event. A second, but minor increase in Cl (150 mmol$_c$ m^{-3}) occurred on 20 October and a third and highest peak (230 mmol$_c$ m^{-3}) on 23 October. The two latter peaks in streamwater Cl occurred several hours after the onset of rain storms.

Chloride retention in the catchment between 15 and 25 October, estimated from bulk deposition and streamwater output, was 4 mmol$_c$ m^{-2}, or 15% of the input (Fig. 5). This number was less than the estimated increase in Cl storage in the soils (9 mmol$_c$ m^{-2}). We estimated Cl storage in Birkenes soils from soil solution concentration data assuming (i) that a net increase in Cl levels only occurred in the surface 20 cm of the mineral soil (Fig. 3), (ii) that the average increase in Cl concentration was 450 mmol$_c$ m^{-3}, and (iii) that on 15 and 25 October the mineral soil was at field capacity, having a moisture content of 10%.

The difference in the estimates for Cl retention may be due to an underestimation of the atmospheric Cl input, caused by additional dry deposition of seasalt. If this is true, the total Cl deposition in this period must have been ca. 30 mmol$_c$ m^{-2}, of which 30% was still present in the soils on 25 October. Dry deposition of Cl was likely to occur, because the episode was accompanied by violent winds, which may have contained large amounts of seasalt aerosols.

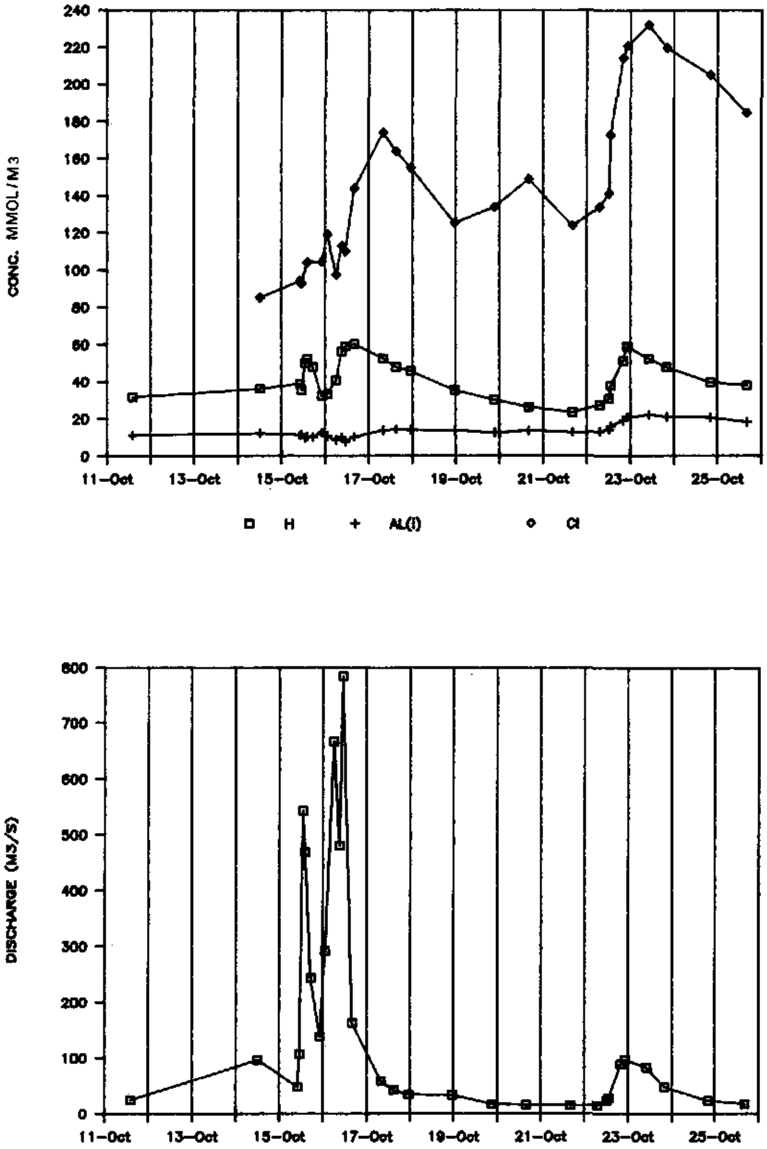

Fig. 4.Hydrograph (lower panel) as well as streamwater H, Cl and inorganic monomeric aluminum (Al(i)) concentrations (upper panel) at the weir in the main brook at Birkenes in October 1987.

Standard bulk precipitation collectors are generally less effective scavengers of dry deposition than tree canopies.

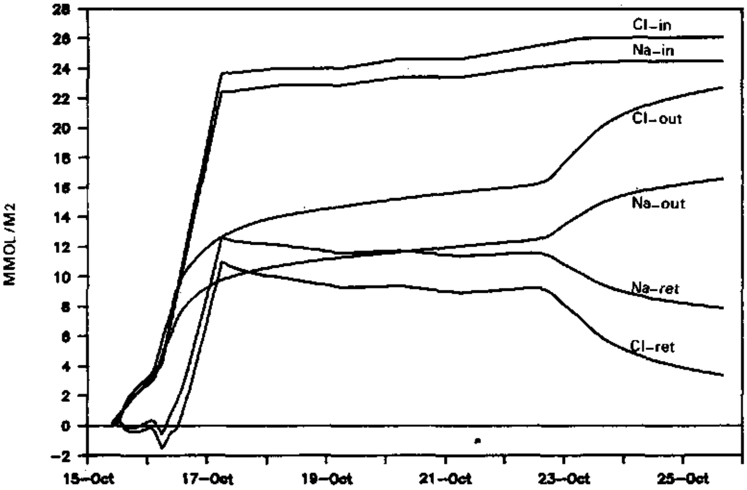

Fig. 5.Input, output and retention of Cl and Na in the Birkenes catchment between 15 and 25 October 1987, after a major atmospheric seasalt input.

Budget calculations indicate that the Cl pulse on 16 October had largely left the catchment within 10 days, with only minor percolation into the mineral soil. So, most of this Cl was routed laterally to the stream via the O horizon.

The nearly water-saturated condition of the catchment at the onset of the seasalt event was probably a key factor in the observed Cl response. Near-saturation on 16 October is evidenced by the high groundwater table, intercepting the organic surface soil at all piezometer plots (Fig. 6). This high groundwater table was caused by the 80 mm precipitation event on 15 October (Fig. 2), which also resulted in a major hydrograph response. In autumn and spring similar high groundwater tables are fairly common in the Birkenes soils (e.g. Sullivan et al., 1987a).

The superposition of the 16 October (22 mm) rain storm on the saturated soils must have caused the high-velocity lateral movement of water through the O horizons into the stream. At the same time, vertical percolation was relatively small. If we assume that the solutions at plot D were representative for the Cl-rich water in the O horizon, peak Cl concentrations in the stream, one day after the event, suggest that ca. 10% of the stream discharge consisted of these leachates. However, the total contribution of O horizon leachates to stream discharge probably exceeded the flux of Cl-rich water, because the Cl pulse had not yet reached the bottom of the O horizon (e.g. plot F; Fig. 3). Although

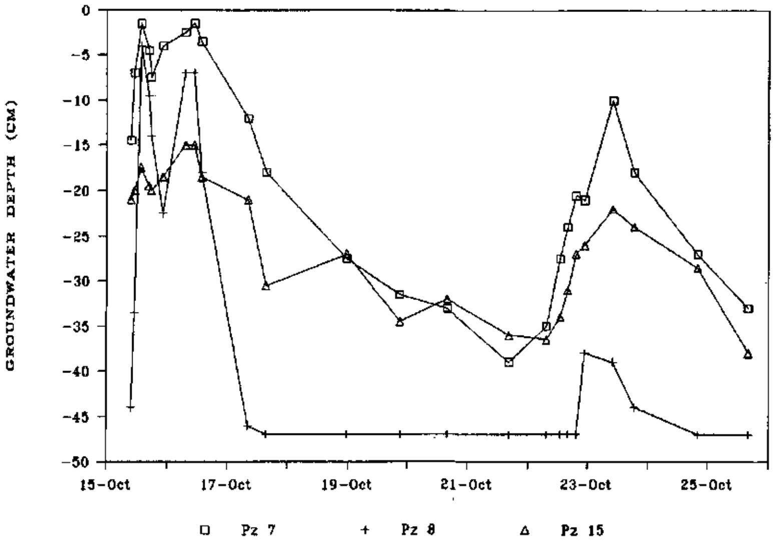

Fig. 6.Groundwater depth below the soil surface (cm) at three piezometer plots in the Birkenes catchment in October 1987.

groundwater tables gradually declined after the 16 October event (Fig. 6), water percolation from the O horizon into the mineral soil was probably small, because the Cl-rich water did not appear in the E horizons (Fig. 3). Apparently, water contents in the O horizons were reduced little during the decline of the groundwater table. This is in line with the common observation that water contents in humic horizons change little with changes in soil water suction.

The minor (3.2 mm) rainstorm on 19 October did not result in a significant hydrograph response, but did cause a considerable increase in the stream's Cl concentration. So, even a small precipitation input in nearly water-saturated O horizons may trigger lateral flow into the stream. Assuming average O horizon Cl concentrations of 600 $mmol_c\ m^{-3}$ (Fig. 3) we estimated that at peak discharge ca. 10% of the stream water originated from the O horizons, even at this minor event.

During the major 22 October rainstorm (24 mm), when groundwater tables were low, part of the Cl-rich water from the O horizons percolated into the mineral soils (Fig. 3), whereas the remainder was laterally transported to the stream. The well preserved Cl concentrations in the upper mineral soil suggest that Cl-rich water was forced out of the O horizon by piston flow. The occurrence of piston flow is also indicated by the return of the Cl concentrations to pre-seasalt event values in two out of three O horizons. During the last event at least 30% of the stream water originated from the O horizons.

In conclusion, our data show that in wet conditions, when the organic surface layer is water-saturated, the O horizons may constitute a major water pathway to the stream. After the seasalt episode the contribution of O horizon leachates to streamwater discharge was relatively small. However, this must have been due to the low precipitation intensities, which did not exceed 24 mm day^{-1}. In between rainstorms the contribution of O horizon leachates to stream discharge decreased rapidly.

8.3.2 Al chemistry in soils and stream

At the 15 and 16 October peakflows, stream water inorganic monomeric aluminum (Al(i)) and H^+ showed an opposite trend, as H^+ increased and Al(i) decreased with discharge (Fig. 4). This indicates that a universal chemical equilibrium with one single $Al(OH)_3$ phase or an Al-H exchange reaction, which both would lead to:

$$\frac{(Al^{3+})}{(H^+)} = \text{constant},$$

did not apply in Birkenes stream water. Indeed, chemical equilibrium calculations showed a strong decrease in stream water saturation with respect to $Al(OH)_3$ solubility ($pK_S = -9.0$) at peak discharge and a gradual return to saturation at low flow (Fig. 7). Similar observations led Sullivan et al. (1986) to formulate the flowpath hypothesis.

Before the seasalt pulse, the soil exhibited a distinct vertical stratification of H^+ and inorganic monomeric Al (Al(i)): H^+ levels were generally highest in the O horizons and decreased with depth, while the reverse was true for Al(i) (Fig. 8). This shows that each soil horizon, which is a potential lateral flowpath to the stream, has its own, characteristic and relatively stable H^+ and Al(i) concentration. The observed stratification suggests that H^+ neutralization and Al solubilization occurred simultaneously during vertical percolation. The, albeit limited, observations indicate that the variation in solute concentrations within horizons was relatively small, particularly in the O and B horizon (Fig. 8). This shows that chemical changes in soil solutions during lateral transport were small. Note that the solution composition in plot F's B horizon was somewhat

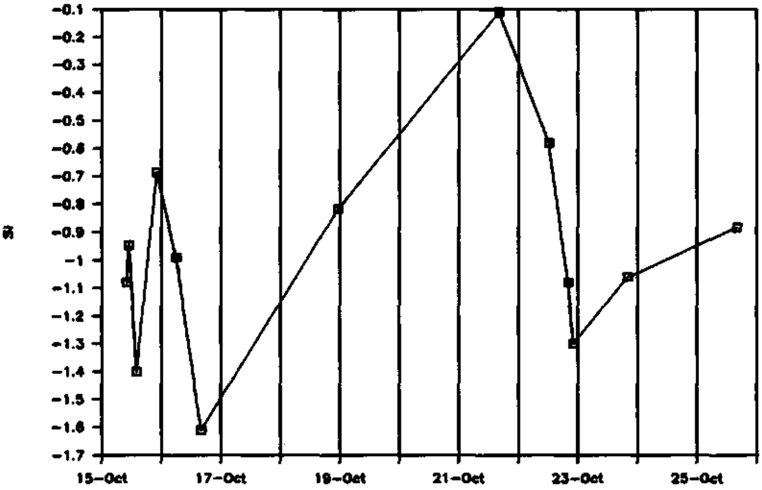

Fig. 7.Streamwater saturation index (SI) with respect to $Al(OH)_3$ solubility (pK_s=-9.0, at 10°C).

exceptional. However, the position of the B horizon at plot F is not representative, as it is directly overlain by the O horizon.

Chemical equilibrium calculations indicate that O horizon solutions were strongly undersaturated with respect to $Al(OH)_3$ solubility (Fig. 9). Nevertheless, the relationship between H^+ and Al^{3+} was not far from cubic, which indicates that cation exchange may have acted as Al solubility control. The data points of Fig. 9 indicate that the exchange reaction can be described by:

$$\mathbf{pAl - 3pH = -7}$$

Further support of cation exchange, controlling solute activities in the Birkenes O horizons, follows from the linear relationships between Ca and Mg, and Na and H concentrations and by the squared relationship between Na and Ca concentrations (Fig. 10). Cation exchange is also suggested by the net retention of Na over Cl in the catchment (Fig. 5).

Solutions from the shallow lysimeters were also strongly undersaturated with respect to $Al(OH)_3$ solubility. However, a pronounced relationship between H^+ and Al^{3+} was lacking (Fig. 9). In addition, no clear relationships between other pairs of cations, indicative for cation exchange equilibrium, were observed in the E horizons. Solutions sampled from greater depth (primarily B and C horizons)

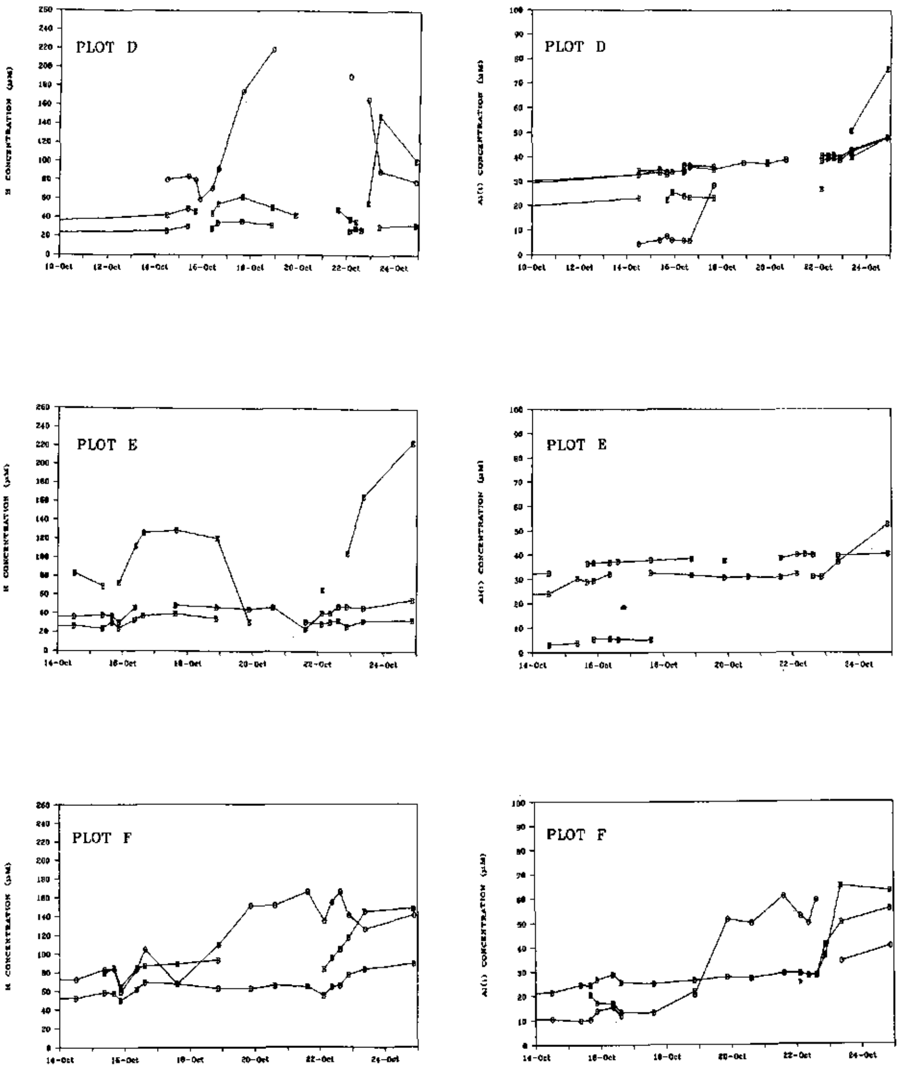

Fig. 8. Soil solution H^+ (left) and Al(i) (right) concentrations at lysimeter plot D (upper), E (middle), and F (lower panels) of the Birkenes catchment in October 1987. Letters in the plots refer to O, E, and B horizons.

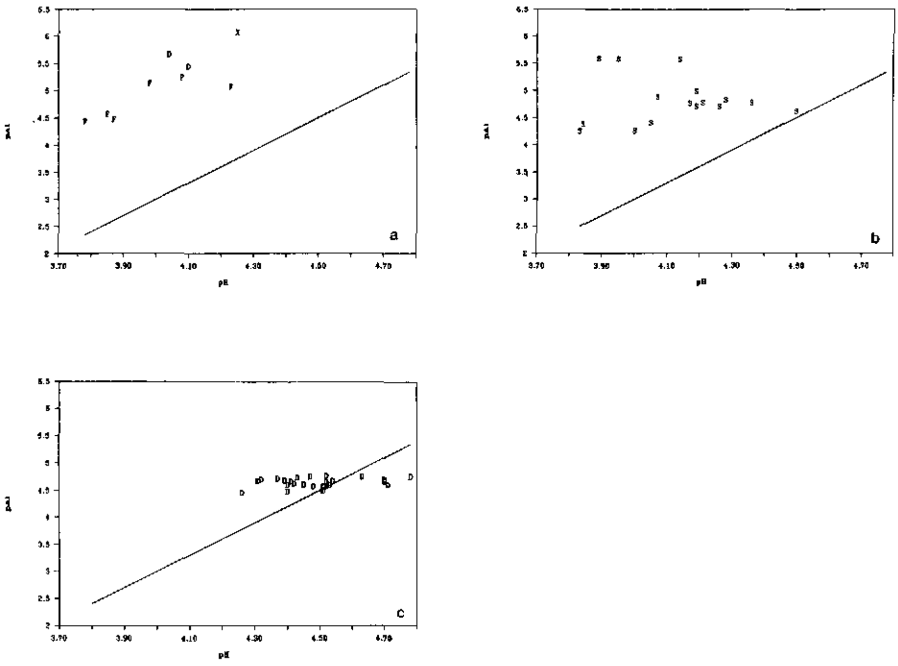

Fig. 9.Soil solution pAl (=-log(Al^{3+})) as a function of pH in the O horizon (a), shallow mineral soil (b), as well as deeper mineral soil (c). The solid line represents the gibbsite solubility line (pK_S=-9.0, at 10°C). Letters in graph a refer to the research plots.

showed only minor variations in solute concentrations, and most solutions were close to saturation with respect to Al(OH)$_3$ solubilty (Fig. 9).

8.4 CONCLUSIONS

A unique storm event with high seasalt input in the Birkenes catchment enabled us to test model assumptions on water flowpaths and Al solubility control. When close to water-saturation the organic surface horizon constituted a major water pathway to the stream. Nearly water-saturated organic surface soils are a fairly common phenomenon in the Birkenes catchment in spring and autumn. The O horizon's contribution to stream discharge decreased strongly after the end of a storm. Vertical water transport into the soil profile was

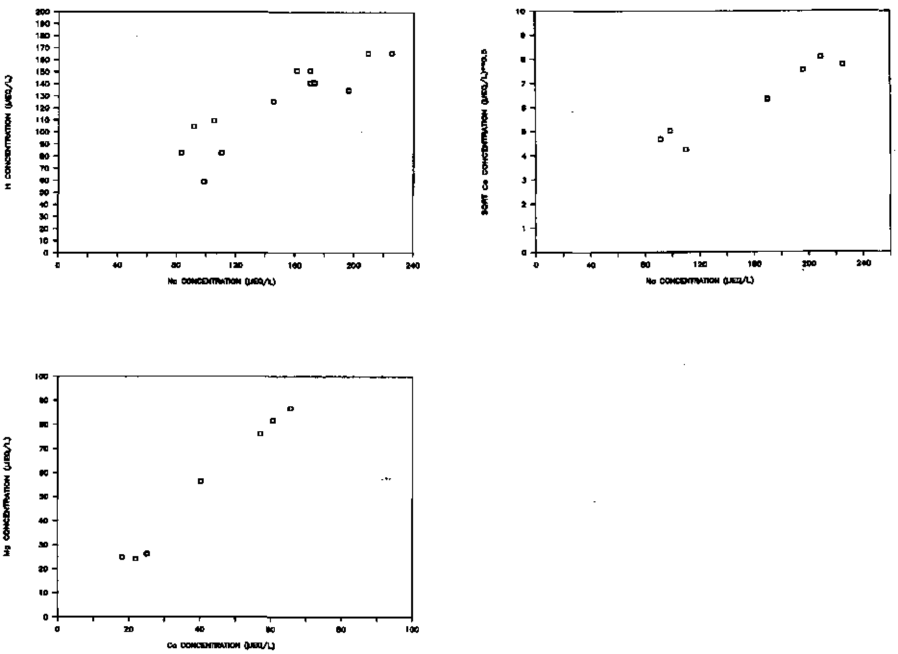

Fig.10.Relationship between the concentrations of various cations in plot F's O horizon.

significantly slower than lateral transport of water through and over the saturated O horizon. Our data demonstrate that the contribution of O horizon solutions to stream discharge changed as a function of precipitation input, and therefore give strong support for the flowpath hypothesis.

The Birkenes soils showed a pronounced vertical stratification of H^+ and Al(i) concentrations, giving each soil horizon its own, characteristic and relatively stable solute levels. In general, pH and Al(i) are lowest in the O horizon leachates and increase with depth. Sub-soil solutions were close to equilibrium with respect to $Al(OH)_3$ solubility, while O horizon solutions were highly undersaturated with respect to this mineral, but in equilibrium with the cation exchange complex. In contrast to the pronounced vertical variation in H^+ and Al(i) concentrations, the horizontal variation per soil horizon was small. This indicates that most chemical changes in percolation water occurred during vertical, rather than horizontal solution transport.

Qualitatively our data on soil hydrology and chemistry can explain the increased H^+ and decreased Al(i) concentrations at peak discharge from wet soils. At low flow most of the discharge water originates from the deeper mineral soil, which is close to equilibrium with $Al(OH)_3$ solubility. However, during subsequent storm events increasing amounts of streamflow are generated in the O horizons, in which the Al solubility is relatively low.

The importance of soil hydrology and chemistry in determining the chemistry of streamwater indicates that incorporation of a realistic description of the variable water flowpaths in hydrochemical modelling is urgently needed.

ACKNOWLEDGMENTS

This work was supported by the Surface Water Acidification Programme (SWAP) and by the Netherlands Technology Foundation (STW). J.M. held a postdoctoral scholarship from the Norwegian Council for Scientific and Industrial Research (NTNF). E.J. Velthorst and N. Nakken are greatfully acknowledged for carrying out laboratory analyses. We thank H.M. Seip, C. Neal and N. van Breemen for valuable criticism.

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Chapter 9

GENERAL CONCLUSIONS

Anthropogenically derived atmospheric acidity is a general phenomenon over large parts of northwestern Europe and northeastern North-America. Extreme acid loads occur in areas with intensive animal husbandry (e.g. the Netherlands), where NH_3, from agricultural sources, may combine with SO_x, largely from industrial origin, to form $(NH_4)_2SO_4$. Particularly in forests the entrappment of NH_3 and SO_x is high relative to that in heathland or bare sand. Atmospheric inputs, high in $(NH_4)_2SO_4$, often have a pH between 5 and 7, due to the neutralization of atmospheric H_2SO_4 by NH_3. Nevertheless, a strong soil acidification may result after assimilation of NH_4, or nitrification of NH_4 and subsequent leaching of HNO_3 and H_2SO_4. Note that not all the acidity generated in the transformation of NH_4 originates from NH_3. The H^+ attached to NH_3 to form NH_4^+ originates from atmospheric acidity like NO_x or SO_x. Currently, in most of the Dutch forest soils between 20 and 100% of the deposited NH_3 acidifies the soil. However, the role of NH_3 in acidification may be more important than these values suggest, because NH_3 probably enhances the dry deposition of NO_x and SO_x. In the near future a larger fraction of the deposited NH_3 may nitrify and acidify many of the forest soils, due to a gradual saturation of the ecosystem with N.

Our results show that in the industrialized parts of the northern hemisphere atmospheric acid inputs are the major cause of the currently observed acidification of soils and water. The quantitative importance of the natural causes of soil acidification (e.g. CO_2, solubilization and transport of organic acids, nutrient uptake by the vegetation) is generally small. Only in coastal areas short-term acidification of soil drainage water (and alkalinization of the soil) may occur, due to H^+-base cation exchange, where base cations originate from seaspray. However, such a short-term water acidification pulse is usually followed by a period where soil percolation water decreases in acidity, due to re-exchange of base cations for H^+. Generally, seasalts are not involved in a quantitative important long-term acidification of soil and water.

In soils, depleted in base cations (coversands, driftsands), acid neutralization is dominated by dissolution of aluminum, whereas the annual mobilization rates of base cations are low. Sandy soil types, poor in easily weatherable minerals, are fairly common in large parts of Belgium, the Netherlands, northern Germany and Denmark. Additional atmospheric acid inputs in such soils are almost fully neutralized by dissolution of aluminum, whereas the dissolution rate of base cations does not strongly depend on the acid load.

In contrast, acidic soils with modest amounts of weatherable minerals, and a modest acid load (e.g. the soils developed in glacial tills at the Hubbard Brook Experimental Forest, USA) largely neutralize the input of mineral acidity by mobilization of base cations. Leaching of inorganic aluminum from the rooting zone of the mineral soil is generally small and believed to be dissolved and transported by strong mineral acids. In the Hubbard Brook spodosols most of the aluminum dissolution and transport is accomplished by organic acids.

Laboratory studies suggest that 'acid rain' dissolves most of the potentially toxic aluminum from non-silicate (mainly organically) bound aluminum ('free' Al). Concentrations of 'free' Al are highest in the surface soil horizons; in the case of spodosols 'free' Al is highest in the spodic horizon. The minor importance of Al-silicates as a source of dissolved aluminum is also suggested by the relatively small leaching rates of silica. Only in the Hackfort soils silica mobilization is elevated in the surface horizons. Although we originally suggested these high leaching rates of silica from the surface soil were possibly due to break-down of clay minerals, they may also have been caused by the elevated biocycling of silica in the deciduous Hackfort forest.

Currently, pools of organically bound soil aluminum deplete rapidly, particularly in many of the Dutch forests. Rates of depletion of 'free' Al may be ten times higher than the historic accumulation rates in the spodic horizons, as derived from pools of organic Al divided by the age of the soil. So, 'acid rain' constitutes a major change in pedogenesis. The strong depletion of 'free' Al in the surface soil may also result in a reduced dissolution of aluminum and therefore in reduced acid neutralization within the next decades.

Generally, the retention of dissolved aluminum in the sub-soils is small, so that most aluminum is lost to the groundwater. Only where a calcareous sub-soil occurs (Hackfort A) aluminum is fully retained.

Dissolved aluminum in soils is not in equilibrium with one single aluminum solubility control at all depths. Surface soil solutions are highly undersaturated with respect to gibbsite solubility, but aqueous aluminum may be regulated by an exchange-type equilibrium with a humic adsorbent. In contrast, sub-soil solutions are generally near equilibrium with gibbsite solubility, with the exception of the Hackfort sub-soils, which are somewhat undersaturated. Possibly, cation exchange regulates the aluminum activity in the Hackfort sub-soils. Sub-soil solutions are generally not in equilibrium with jurbanite.

The variation in the aluminum solubility control with depth in the soil is of major importance in explaining the chemistry of aluminum in Birkenes streamwater.

Our data show that the decreased saturation of streamwater with respect to gibbsite solubility at high flow (e.g. snowmelt) is due to the increased contribution of O horizon leachates to stream discharge. During low flow, when discharge water largely originates from the sub-soil, streamwater aluminum is in equilibrium with gibbsite solubility. The relevant information on water flowpaths was obtained by tracing Cl from a unique seasalt pulse in the Birkenes catchment.

SUMMARY

In the last decade a large number of publications have documented a strong acidification of soils and natural waters. Many authors have attributed this acidification of the environment to anthropogenically derived atmospheric acidity. However, others have hypothesized that the increase in acidification in temperate regions is largely due to extensive regrowth of forests. On acidic soils, regrowth of forests is generally associated with the production of significant amounts of organic acidity, stored in the litter layer.

Here we show that in many acidic (non-agricultural) soils of northwestern Europe anthropogenically derived acidity dominates the total acid load and is the major cause of the current acidification. In contrast, the huge store of organic acids in the surface soil does not contribute significantly to the acidification of (mineral) soils and water.

Anthropogenically derived atmospheric acidity largely originates from SO_x and NO_x, both produced when burning fossil fuels. In areas with intensive animal husbandry atmospheric NH_3 adds to the total acid load of soils and water, too, after nitrification and subsequent leaching of NO_3.

Acidification of acidic soils is often associated with an increase in the mobility of aluminum in soil solutions and drainage water. Therefore 'acid rain' may significantly change the natural pedogenesis in these soils (e.g. podzolization). Increased concentrations of inorganic aluminum have earlier been shown to have adverse effects on many aquatic and terrestrial organisms, including humans.

The intent of this research was to evaluate the quantitative importance of 'acid rain' on acidification rates of acidic, sandy soils and also to study its impact on the dissolution and transfer of aluminum. A large number of study sites were selected in order to have a wide variation in deposition rates and soil types. Although emphasis is given to chemical processes in the soil, we also tried to relate the chemistry of aluminum in soils to that in streamwater at one of the research sites.

The chemistry and transport of aluminum in spodosols, developed in glacial till at the Hubbard Brook Experimental Forest (New Hampshire, USA), is evaluated in chapter 2. These soils have significant amounts of easily weatherable minerals and the atmospheric acid loads are modest. Most of the atmospheric acidity is neutralized by mobilization of base cations, so that soil solution pH values are generally well above 4. At these pH values dissolution of inorganic aluminum, which occurs primarily in the spodic horizon, is modest.

Aqueous aluminum in these soils is largely organically complexed. At the high elevation sites, where the contact time of the solution phase with the mineral soil is probably short before the drainage water enters the stream, most of the inorganic aluminum appears in seeps and streamwater. At the lower elevation sites, however, where the residence of the percolation water in the soil is believed to be significantly longer, much of the inorganic aluminum is retained in the sub-soils, probably due to neutralization by base cation weathering, or cation exchange.

In chapter 3 we discuss the aluminum chemistry in three oak-birch woodland soils in the eastern part of the Netherlands. In contrast to the North-American sites in chapter 2 the acid loads are extremely high, whereas the soils are lower in weatherable base cations. In the Hackfort soils mobilization of aluminum is by far the major acid neutralizing process. Dissolution of aluminum occurs primarily in the surface soil layers, whereas some immobilization may occur in the sub-soil. Only where sub-soils are calcareous all aluminum is retained.

The effect of a forest cover on the total atmospheric acid load, as well as on soil acidification plus acid neutralization processes is evaluated in chapter 4. The research was conducted in two adjacent driftsand soils in the Netherlands, one having a (pine) forest cover, the other being bare. The sites have a more than 5 km distance to the nearest area with intensively managed farmland. Results indicate that the forest canopy collects considerably more dry deposition of $(NH_4)_2SO_4$ than the bare soil. The total $(NH_4)_2SO_4$ deposition in the forested plot is similar to values observed in forests at smaller distance from farmland. Acidification rates are considerably higher in the forest soil than in the bare plot. The contribution of natural processes to forest soil acidification is only small. Most of the strong acid inputs are neutralized by mobilization of aluminum. Concentrations of aluminum are significantly higher in the forest soil, due to (i) higher acid loads, and (ii) a significantly higher evapotranspirative concentration of the percolating water.

In chapter 5 we compare the aluminum mobilization and transport in spodosols, developed in North-American glacial tills, with that in spodosols, developed in Dutch coversands. The difference between the sites is tremendous, partly because the till sites have (i) higher contents of easily weatherable minerals, and (ii) lower acid loads. Whereas in the glacial till most of the aluminum is mobilized and transported by organic acids, anthropogenically derived strong mineral acids dominate the dissolution and transport of aluminum in the spodosols developed in coversands. In addition, the absolute concentrations and fluxes of dissolved aluminum are significantly higher in the Dutch soils. Currently, the spodic horizons of Dutch spodosols are rapidly dissolved. In the

North-American spodosols the accumulation of organic aluminum in the spodic horizon equals the mobilization of inorganic aluminum.

A comparitive study of strong acid neutralization in similar, acidic, sandy soils, which are depleted in base cations, is presented in chapter 6. The soils selected in this study (developed in driftsands and coversands) are representative for many of the Dutch forest and heathland soils. The results suggest that an increase in the acid load does not significantly increase the weathering rate of base cations and Si, but is largely neutralized by aluminum solubilization. Our results indicate that most of the dissolved aluminum orginates from non-silicate bound, solid phase aluminum. Particularly at the forested sites a considerable transport of inorganic aluminum to the groundwater occurred. This study provides direct evidence of the pronounced effect of strong mineral acidity on the current mobilization and transport of aluminum in acidic soils.

Our monitoring studies indicate that most of the aqueous aluminum is mobilized from non-silicate bound soil Al in the surface horizons. We tested this in a laboratory experiment. Results, evaluated in chapter 7, .indicate that organically complexed non-silicate aluminum from the soil solid phase, is the dominant source of aqueous aluminum, indeed. This finding has important consequences for acid rain modelling, as not all, but only a minor fraction of total soil aluminum is readily dissolved.

The aluminum activity in soil solutions is not regulated by one single aluminum solubility control. In most sub-soils aqueous aluminum is in equilibrium with gibbsite solubility. However, in the surface soil horizons soil solutions are generally undersaturated with respect to this secondary mineral and dissolved aluminum may be controlled by an exchange type equilibrium. Because in mountainous catchments soil solutions are rapidly converted into streamflow, the aluminum solubility control in soils are also important for understanding the chemistry of aluminum in streamwater. Insight in the aluminum chemistry of streamwater is highly relevant, because aluminum is potentially toxic to fish. In chapter 8 we evaluate the aluminum chemistry in the soils and a stream of a small forested catchment in southernmost Norway. During low flow the stream is close to equilibrium with respect to gibbsite solubility. However, at high flow streamwater gets increasingly undersaturated. In this study we demonstrate that water flowpaths in this forested catchment vary, depending on the prevailing hydrological conditions. During low flow the stream is primarily fed by gibbsite-saturated sub-soil drainage water, whereas at high flow gibbsite-undersaturated surface soil solutions contribute increasingly to discharge.

SAMENVATTING

In de afgelopen tien jaar is in een toenemend aantal publicaties gewezen op de sterke verzuring van bodem, grond- en oppervlaktewater. Veel onderzoekers hebben deze verzuring van het milieu toegeschreven aan depositie van sterke, minerale zuren vanuit de atmosfeer ('zure regen'). Het hierbij veronderstelde verband tussen 'zure regen' en verzuring wordt echter door andere onderzoekers aangevochten. Volgens de laatsten wordt de algemeen waargenomen verzuring in de gematigde streken vooral veroorzaakt door grootschalige herbebossing. Hierbij moet worden bedacht dat in zure bodems herbebossing samengaat met een sterke toename van de strooisellaag, die grote hoeveelheden organische zuren bevat.

In dit onderzoek wordt aangetoond dat de verzuring van zure, niet door de landbouw gebruikte bodems in noordwest Europa in de meeste gevallen wordt gedomineerd door 'zure regen'. De grote hoeveelheid organische zuren in de strooisellaag draagt niet of nauwelijks bij aan de huidige sterke verzuring van (minerale) bodem en water.

'Zure regen' is voornamelijk van antropogene oorsprong en ontstaat o.a. uit SO_X en NO_X, die beide vrijkomen bij de verbranding van fossiele brandstoffen. In gebieden met intensieve veehouderij draagt bovendien NH_3 bij aan de verzuring. Verzuring door NH_3 treedt op door nitrificatie gevolgd door uitspoeling van NO_3.

Bodemverzuring wordt hier gedefinieerd als het uitspoelen van zuur-neutraliserende stoffen uit de bodem, en is vaak gekoppeld aan een verlaging van de pH en een verhoging van de mobiliteit van aluminium in bodemoplossingen en drainage water. Dit betekent dat 'zure regen' de natuurlijke bodemvorming in relatief arme zandgronden ingrijpend zou kunnen veranderen (denk bij voorbeeld aan het podzolisatie proces). Van minstens zo groot belang is het dat de toegenomen aluminium concentraties toxisch kunnen zijn voor verscheidene aquatische en terrestrische organismen; de mens inbegrepen (nierdialyse patienten, optreden van seniele dementie).

Het doel van dit onderzoek was om de bijdrage van 'zure regen' aan de huidige verzuring van zandige bodems te kwantificeren. Vanwege de belangrijke rol die anorganisch aluminium speelt bij de bodemverzuring en vanwege het toxische karakter van dit anorganisch aluminium heeft het oplossen en het transport van dit element de nadruk gekregen in dit onderzoek. Het onderzoek is vooral uitgevoerd op zure zandgronden, omdat juist daar de sterkste effecten op de aluminium chemie te verwachten zijn. Om een grote variatie in zuuraanvoer alsmede in bodemtypes te verkrijgen zijn veel verschillende locaties voor dit onderzoek geselecteerd. Hoewel de nadruk in dit proefschrift ligt op de bodem, hebben we daarnaast geprobeerd een koppeling te leggen met de aluminium chemie van het oppervlaktewater op één van de onderzoekslocaties.

De chemie en het transport van aluminium in podzolen, ontwikkeld in morene materiaal in het Hubbard Brook Experimental Forest, New Hampshire, Verenigde Staten, wordt besproken in hoofdstuk 2. Deze bodems zijn relatief rijk aan gemakkelijk verweerbare mineralen en de zuuraanvoer is bescheiden. 'Zure regen' wordt voornamelijk geneutraliseerd door het oplossen van basische cationen. Hierdoor blijft de pH van de percolerened oplossing in het algemeen gemakkelijk boven 4. Bij deze pH waarden lost slechts een geringe hoeveelheid anorganisch aluminium op. Opgelost aluminium in deze bodems is dan ook voornamelijk in een organisch gecomplexeerde vorm (N.B. organisch gecomplexeerd aluminium is van nature in podzolen aanwezig en is in het algemeen niet toxisch voor biota). Op grote hoogte in het stroomgebied wordt het opgeloste, anorganische aluminium grotendeels naar de beek afgevoerd. Lager op de helling verschijnt echter maar weinig anorganisch aluminium in de beek en wordt het merendeel in de ondergrond vastgelegd door omwisseling en/of verwering van basische cationen. De contacttijd van het water met de ondergrond, is waarschijnlijk de oorzaak van de verschillen in drainagewater samenstelling; deze contacttijd is korter naarmate we ons hoger op de helling bevinden.

Hoofdstuk 3 handelt over de aluminium chemie in drie zandige tot lemige bodems op het landgoed Hackfort, nabij Vorden (Achterhoek). In tegenstelling tot de Noord-Amerikaanse locatie uit hoofdstuk 2 hebben de Hackfort locaties een extreem hoge zuurlast, gedeeltelijk als gevolg van nitrificatie van het atmosferisch aangevoerde NH_4. Daarnaast is de hoeveelheid gemakkelijk verweerbare mineralen in de Hackfort bodems geringer dan in de Hubbard Brook bodems. In Hackfort is de mobilisatie van (anorganisch) aluminium veruit het belagrijkste zuurneutralisatie proces. Het oplossen van aluminium gebeurt voornamelijk in de bovengrond, terwijl op grotere diepte enige aluminium vastlegging kan optreden. Alleen daar waar de ondergronden kalkrijk zijn treedt een volledige vastlegging van aluminium op.

Het effect van een bosvegetatie op de totale zuurlast is geëvalueerd in hoofdstuk 4. Daarnaast zijn ook de bodemverzuring en de zuurneutralisatie processen bekeken. Het onderzoek werd uitgevoerd op twee naast elkaar liggende stuifzand locaties op de Veluwe, één met grove den en één onbegroeid. De afstand tot het dichtst bijzijnde landbouwgebied bedraagt meer dan 5 km. Het bos vangt aanzienlijk meer droge depositie van $(NH_4)_2SO_4$ in dan het kale stuifzand. De totale $(NH_4)_2SO_4$ depositie in het bos is van dezelfde orde van grootte als in bossen, die dichterbij de intensieve veehouderij zijn gelegen (b.v. Hackfort). De verzuring van de bodem is aanmerkelijk groter onder bos, dan in het kale stuifzand. De bijdrage van natuurlijke bodemverzuring aan de totale verzuring van de bosbodem is zeer gering. In beide bodems levert aluminium de belangrijkste bijdrage aan de zuurneutralisatie. De opgeloste aluminium concentraties zijn echter aanmerkelijk hoger in de bosbodem als gevolg van (i) de hogere zuurlast, en (ii) een grotere indikking van het percolerende water als gevolg van evapotranspiratie.

In hoofdstuk 5 vergelijken we de mobilisatie en het transport van aluminium in podzolen, ontwikkeld in grondmorene in de V.S., met die in podzolen ontwikkeld in dekzanden in Nederland. Het verschil tussen de locaties is groot, gedeeltelijk omdat de morene bodem (i) rijker is aan gemakkelijk verweerbare mineralen, en (ii) een lagere zuurlast heeft. In de grondmorene vindt het oplossen en het transport van aluminium voornamelijk plaats door organische zuren, terwijl in de dekzanden sterke minerale zuren, afkomstig van 'zure regen', een veel belangrijker rol spelen. Bovendien zijn de absolute concentraties en fluxen van aluminium aanmerkelijk hoger in de Nederlandse dan in de Amerikaanse podzolen. Momenteel vindt er een snelle afbraak plaats van de Nederlandse podzol B horizonten, terwijl in de Amerikaanse podzolen accumulatie en uitspoeling elkaar in evenwicht houden.

Een vergelijkend onderzoek naar de neutralisatie van 'zure regen' in vergelijkbare, zure zandgronden, arm aan verweerbare mineralen wordt besproken in hoofdstuk 6. De geselecteerde bodems (ontwikkeld in stuifzanden en dekzanden) zijn representatief voor veel van de Nederlandse bos- en heidebodems. De resultaten laten zien dat een verhoging van de zuurlast geen beduidend effect heeft op de verweringssnelheid van basische cationen en silica. Extra mineraal zuur wordt bijna volledig geneutraliseerd door het oplossen van aluminium. Opgelost aluminium lijkt voornamelijk afkomstig te zijn van niet-silicaat gebonden, vaste fase aluminium. Dit meest oplosbare aluminium komt vooral voor in de podzol B horizonten en geeft aanleiding tot een snelle afbraak van deze horizont. Met name in bosbodems vindt een sterke uitspoeling van aluminium naar het grondwater plaats.

Het hierboven gesuggereerde belang van niet-silicaat gebonden aluminium als belangrijkste bron voor het opgelost aluminium is getest in een laboratorium experiment (hoofdstuk 7). Deze studie laat zien dat niet-silicaat gebonden aluminium (en met name de organisch gecomplexeerde fractie) inderdaad het meest oplosbaar is. Dit heeft belangrijke consequenties voor o.a. het modelleren van het effect van 'zure regen' op de bodem, omdat niet alle, maar slechts een beperkte fractie van het totaal aanwezige aluminium betrekkelijk snel oplost. Uitputting van de meest oplosbare vormen van vaste fase aluminium zal uiteindelijk leiden tot een verminderde zuurneutralisatie alsmede tot een lagere pH en aluminium concentratie van de percolerende bodemoplossing.

De activiteit van opgelost aluminium in de bodem wordt niet gecontroleerd door één enkele vaste fase. De meeste ondergronden in dit onderzoek zijn in evenwicht met gibbsiet. De bovengronden zijn echter in het algemeen onderverzadigd met betrekking tot dit mineraal, en mogelijk wordt de aluminium activiteit hier gereguleerd door een adsorptie evenwicht met organische stof. Omdat in heuvelachtig terrein de bodemoplossing snel kan worden afgevoerd naar de beek is inzicht in de regulering van de aluminium activiteit in de bodem waarschijnlijk eveneens van belang voor een beter begrip van de aluminium chemie van beekwater. Dit laatste is weer belangrijk vanwege de grote gevoeligheid van vis voor verhoogde anorganische aluminium concentraties. In hoofdstuk 8 evalueren we de aluminium chemie in bodems en beek van een klein bebost stroomgebied in het zuiden van Noorwegen. Bij geringe waterafvoer is het beekwater in evenwicht met gibbsiet. Bij piekafvoer, echter, raakt het beekwater in toenemende mate onderverzadigd met gibbsiet. In dit onderzoek laten we zien dat de stroombanen, waarlangs het watertransport door de bodems van het stroomgebied naar de beek plaatsvindt, kunnen variëren afhankelijk van de hydrologische omstandigheden: Bij een geringe waterafvoer wordt de beek voornamelijk gevoed door gibbsiet-verzadigd water uit de ondergrond, terwijl gibbsiet-onderverzadigd water uit de bovengrond (met name de strooisellaag) een toenemende bijdrage levert aan het beekwater tijdens piekafvoer.

APPENDIX. CHARACTERISTICS OF SOME DUTCH RESEARCH SITES

In this appendix we present background information on four of the Dutch research sites (Gerritsfles-forest, Gerritsfles-bare, Tongbersven and Hasselsven). For details on the Hackfort sites reference is made to van Breemen et al. (1988).

General

Two of the research sites are located in the nature reserve Gerritsfles, which is situated 4.5 km southeast of Kootwijk (Veluwe), the Netherlands (52° 10'N, 5° 49'E). The soil parent material consists of aeolian sand (coversand), which was deposited in periglacial conditions, during the Weichselien glaciation. During the Holocene this coversand was locally blown and resedimentated (drift sands), giving the landscape a more pronounced relief. To date a part of the driftsand landscape is still active and is only partly covered with some algae and mosses. One of the research sites (Gerritsfles Bare; GB) is situated in this active driftsand, whereas the other site (Gerritsfles Forest; GF) is situated in an adjacent, uneven aged *Pinus sylvestris* stand, with a ground cover of *Deschampsia flexuosa*. The maximum age of the trees in the Pinus stand is 65 yr (de Visser, 1986).

The Tongbersven site is located 4 km east of Oisterwijk (Brabant), the Netherlands (51° 34'N, 5° 14'E). Soils were developed in Pleistocene coversands. The forest at the research site (Tongbersven Forest; TF) consists largely of *Pinus sylvestris* and some *Picea abies*. The Pinus trees in the stand are even aged, and ca. 35 yr (de Visser, 1986). A groundcover vegetation is absent.

The Hasselsven site is located 3 km southwest of Leende (Brabant), the Netherlands (51° 20'N, 5° 30'E). Hasselsven soils were also developed in Pleistocene coversands. The research site (Hasselsven Heather; HH) is covered by *Calluna vulgaris*, as well as some mosses and lichens. Approximately 50% of the soil surface is bare.

Soils

Description and classification

All soils were described using the 'Guidelines for soil description' (FAO 1977). Soils were classified according to de Bakker and Schelling (1966) and Soil Survey Staff (1975).

Gerritsfles Forest (GF)

I) Information on the site sampled

Date of examination: 09-15-1982
Description: J. Mulder and N.van Breemen
Location: ca. 0.5 km southwest of the moorlandpool "Gerritsfles", near Kootwijk, the Netherlands.
Elevation: ca. 40 m above sea level
Land-form: drift sand with a rolling topography (slopes up to 40%, but the range in elevation less than 10 m)
Physiographic position of the site: at the lower part of an east-facing slope of a 4 m high sanddune
Slope: concave, moderately steep (13-25%)
Vegetation: *Pinus sylvestris* (ca. 60 yr); Undergrowth: *Deschampsia flexuosa*
Climate: humid, with a well-distributed rainfall (ca. 800 mm annually)

II) General information on the soil

Soil name (Dutch classification system): Duinvaag
Soil Taxonomy: Typic Udipsamment
Soil moisture regime: udic
Soil temperature regime: mesic
Parent material: driftsand (105-300 μm) of local origin
Drainage class 5: somewhat excessively drained
Moisture condition soil, prevailing at moment of examination: dry throughout
Stoniness class 0: no stones
Rock outcrop class 0: no rocks

III) Description of individual soil horizons

O1 +10/+7- 0 cm slightly, decomposed Pinus litter with abundant very fine and fine roots and common medium roots, having a clear, smooth boundary.

C 0 > 200 cm well sorted fine driftsand (median 157 μm). Throughout the profile 0.5 to 30 mm thick wavy bands occur, that differ in organic matter content. Particularly the top 40-cm has evenly darkened (10YR 5.5/3.5; light yellowish brown to brown), presumably due to transported organic matter from the forest floor. Color > the 40-cm depth: 10YR 6/4 (light yellowish brown). In the upper 0.5-cm of the soil some bleached sandgrains are present. No color mottles. Structure grade 0: Structureless (single grain). Consistency when dry: soft. No cutans. Very few large pores, very few coarse pores and few very fine pores. Many fine roots (up to the 60-cm depth), common coarse roots to below the 120-cm depth; most very coarse roots (4 to 5 cm diameter) grow horizontally between the 40- and 70-cm depth.

Gerritsfles bare (GB)

I) Information on the site sampled

Date of examination: 09-30-1982

Description: J. Mulder

Location: 40 m south of profile GF

Elevation: 40 m above sea level

Land-form: drift sand with a rolling topography (slopes up to 40%, but they range in elevation less than 10 m)

Physiographic position of the site: at the lower part of a southwest facing slope of an 8 m high sanddune

Slope: concave, moderately steep (13-25%)

Vegetation: a few mm thick layer of algae

Climate: humid, with a well distributed rainfall (ca. 800 mm annually)

II) General information on the soil

Soil name (Dutch soil classification system): Duinvaag

Soil Taxonomy: Typic Udipsamment

Soil moisture regime: udic

Soil temperature regime: mesic

Parent material: driftsand (105-300 μm), of local origin

Drainage class 5:somewhat excessively drained

Moisture condition soil, prevailing at moment of examination: dry from 0 to the 20-cm, moist below the 20-cm depth

Stoniness class 0: no stones

Rock outcrop class 0: no rocks

III) Description of individual soil horizons

C 0 > 200 cm well sorted fine driftsand (median 169 μm) with 1 to 2 mm thick layers, which differ in organic matter content. The top 25- to 35-cm has a more even and darker color (10YR 5/4; dull yellowish brown) than the soil below this depth (consisting of a few mm to 10 cm thick bands of lighter (10YR 7/6; bright yellowish brown) and darker (10YR 5/4; dull yellowish brown) material). No color mottles. Structure class 1: very weak, medium subangular blocky from 0 to 3 cm (probably due to the influence of the algae); Structure class 0: structureless, single grain below the 3-cm depth. Consistency when dry: soft between the 0-

and 3-cm and loose at greater depth. No cutans. Very few fine pores. Few very fine roots in the upper 25-cm; no roots at greater depth.

Tongbersven (TF)

I) Information on the site sampled

Date of examination: 10-11-1982

Description: J. Mulder

Location: 10 m southeast of moorlandpool Tongbersven near Oisterwijk, the Netherlands

Elevation: 10 m above sea level

Land-form: coversands with a rolling topography (slopes up to 30%, but the range in elevation less than 10 m)

Physiographic position of the site: summit of a dune with a 30% northwest and a 5% southeast facing slope

Slope: almost flat

Vegetation: *Pinus sylvestris* (ca. 35 years old); no undergrowth

Climate: humid with a well distributed rainfall (ca. 800 mm annually)

II) General information on the soil

Soil name (Dutch soil classification system): Haarpodzol

Soil Taxonomy: Typic Haplorthod

Soil moisture regime: udic

Soil temperature regime: mesic

Parent material: well sorted coversand (75-300 μm)

Drainage class 4: well drained

Moisture condition soil, prevailing at moment of examination: moist throughout

Depth of groundwater table, between October 1982 - April 1985: minimum -354 cm, maximum -479 cm.

Stoniness class 0: no stones

Rock outcrop class 0: no rocks

III) Description of individual soil horizons

O1 +5/+3 - 0 cm partly decomposed Pinus litter; many very fine roots. An abrupt smooth boundary

E 0 -17/23 cm well sorted fine sand (median 147 μm). Color 5YR 4/2 (grayish brown) with prominent coarse patches of 10YR 4/3 (brown). No color mottles present. Structure grade 0: structureless (single grain). Consistency when moist: loose. Few fine pores. Common coarse, medium and fine roots. An abrupt wavy boundary.

Bhs 17/23 -38/40 cm	well sorted fine sand (median 150 µm). Color 5YR 2.5/1 (brownish black) with some very thin, lighter colored fibers. No color mottles present. Structure grade 1: weak; thin platy structure. Consistency when moist is firm. Few fine pores. Very few medium and few fine roots, which are limited to the upper portion of this horizon. A gradual broken boundary.
Bs 38/40 -54/58 cm	well sorted fine sand (median 142 µm). Color 7.5YR 4/4 (brown); a few 5 to 10 mm thick wavy fibers are present. Common coarse, distinct mottles (2.5 Y 7/4; light yellow). Structure grade 0: structureless (single grain). Consistency when moist: loose.Few fine pores; very few fine roots. A clear wavy boundary.
BC1 54/58-87/88 cm	well sorted fine sand (median 158 µm). Color 10 YR 5/6 (yellowish brown). Few coarse distinct sharp mottles (2.5 Y 7/4; light yellow) containing very loosely packed sand. Few fibers (10 YR 4/4; brown). Structure grade 0: structureless (single grain); Consistency when moist: loose. Few fine pores. Very few fine roots. A diffuse boundary.
BC2 > 87/88 cm	well sorted fine sand (median 147 µm). Color 10 YR 6/6 (bright yellowish brown) with irregular shaped patches of 10 YR 6/8 (bright yellowish brown). To a depth of 250 cm still few fibers present. Structure grade 0: structureless (single grain). Consistency when moist: loose. Very few fine pores pores. No roots.

Hasselsven (HH)

I) Information on the site sampled

Date of examination: 10-25-1982

Description: J. Mulder

Location: ca. 75 m. southeast of moorlandpool Groot Hasselsven, near Leende, the Netherlands

Elevation: 28 m above sea level

Land-form: coversand with undulating topography

Physiographic position of the site: lower part of a northwest facing slope

Slope: 100 m long (3%)

Vegetation: *Calluna vulgaris* with some mosses and lichens

Climate: humid with a well distributed rainfall (ca. 800 mm annually)

II) General information on the soil

Soil name (Dutch soil classification system): Haarpodzol

Soil Taxonomy: Typic Haplorthod

Soil moisture regime: udic

Soil temperature regime: mesic

Parent material: coversand (75-300 μm)

Drainage class 4: well drained

Moisture condition soil, prevailing at moment of examination: moist throughout

Depth of groundwater table between October 1982 - April 1985: minimum -128 cm, maximum -282 cm

Stoniness class 0: no stones

Rock outcrop class 0: no rocks

III) Description of individual soil horizons

O1 +3- 0 cm Calluna vulgaris residues. Many very fine roots, common medium and fine roots. An abrupt smooth boundary

E 0 - 10/11 cm fairly well sorted sand (median 146 μm), containing a few gravels (up to 1 cm in diameter). Color 5 YR 3/1, at the lower end changing to 5 YR 2.5/1 (both brownish black). No color mottles. Structure grade 0: structureless (single grain). Consistency when moist: loose. Common very fine pores. Few very fine roots and common fine and medium roots. A clear wavy boundary.

Bhs1	10/11-13/16 cm	fairly well sorted sand (median 147 μm), containing a few gravels (up to 1 cm in diameter). Color 5 YR 3/2 (dark reddish brown). Few faint medium mottles of lighter colored material present. Structure grade 0: structureless (massive). Consistency when moist is very friable. Few very fine pores. Common fine and very fine roots. A clear wavy boundary.
Bhs2	13/16-29/31 cm	fairly well sorted sand (median 149 μm), containing a few gravels (up to 1 cm in diameter). Color 5 YR 3/3 (dark reddish brown) changing with depth to 10 YR 5/8 (yellowish brown) plus fibers (7.5 YR 4/4; brown). No color mottles. Structure grade 0: structureless (massive). Consistency when moist is very friable. Few very fine pores. Few fine and medium roots. A clear wavy boundary
Bs	*29/31- 81/85 cm*	*fairly well sorted sand (median 141 μm), with a few* gravels (up to 1 cm in diameter). Color 10 YR 7/8 (yellow orange) with few coarse, diffuse, faint mottles of darker *(more black) material; no fibers. Structure grade 0:* structureless (single grain). Consistency when moist: loose. Many micropores. No roots. A gradual boundary.
C	> 81/85 cm	fairly well sorted sand (median 125 μm), containing a few gravels (up to 1 cm in diameter). Color: irregularly shaped patches of 10 YR 8/2 (light gray) and 10 YR 6/8 (bright yellowish brown); no fibers. Structure grade 0: structureless (single grain). Consistency when moist is loose (light gray patches) or friable (bright yellowish brown patches). Many micropores and few very fine pores. No roots.

Chemical and mineralogical characteristics (methods)

Soil particle size analysis was done at the 'Laboratorium voor grond- en gewasanalyse Mariendaal' at Oosterbeek, by sieving and gravity sedimentation, after treatment with hydrogenperoxide to remove organic matter. Bulk density measurements were carried out at the Dept. of Tillage Research, Agric. University Wageningen.

Most of the analytical methods are described in detail by Begheijn (1980). All analyses were conducted on the fine earth (< 2 mm) fraction of air-dried soil. Briefly, these methods are as follows:

Soil pH was determined in a 1:2.5 (mass to volume) extract in distilled water and in 0.01 M $CaCl_2$. Organic C was converted into CO_2, after wet combustion in a phosphoric-chromic acid mixture, and measured potentiometrically (Begheijn, 1976). Nitrogen was transferred to ammonia with sulfuric acid and selenium, followed by steam destillation into boric acid and back titration of ammonium borate. 'Free' Al_2O_3 and Fe_2O_3 refer to dithionite-oxalate extractable fractions, essayed colorimetrically with orthophenantroline (Fe) and pyrocatechol violet (Al). 'Amorphous' Fe_2O_3 was extracted by oxalic acid-ammonium oxalate and measured by atomic absorption spectrofotometry (AAS). Various fractions of 'free' Al were extracted sequentially with: 1) 1.0 M KCl (exchangeable), 2) 0.1 M $Na_4P_2O_7$ (organic), 3) 0.2 M $(NH_4)_2C_2O_4$, adjusted to pH 2 (amorphous), and 4) dithionite-oxalate (crystalline, free) (USDA 1972). The $(NH_4)_2C_2O_4$ and dithionite-oxalate extracts were oxidized with heat and aqua regia before colorimetric analysis with pyrocatechol violet. Aluminum in the pyrophosphate extracts was determined by AAS with a nitrous oxide acetylene flame. The Cation Exchange Capacity (CEC) and the exchangeable cations were measured using Bascomb's (1964) $BaCl_2$-$MgSO_4$ method (unbuffered). Soil elemental analysis, except for FeO, Fe_2O_3, Na_2O and MgO, was done by x-ray fluorescence spectroscopy of a Li-tetraborate melt of the soil material. FeO, Fe_2O_3, Na_2O and MgO were analysed colorimetrically with orthophenantroline before (Fe(II)) and after reduction (Fe(II) + Fe(III)) by hydroquinone; or by AAS (Na_2O, MgO) after a 10 second HF-H_2SO_4 destruction at $60^{\circ}C$.

Mineralogical analysis of the sand fraction of GF and GB soils were conducted using Scanning Electron Microscopy (SEM) and staining techniques. Semi quantitative determination of clay minerals was conducted by x-ray diffraction-(Wopereis, 1985).

Chemical and mineralogical characteristics (results)

Results are given in Tables 1-7 and in Fig. 1. Mass fractions refer to oven-dried (105°C) soil. The main characteristics will be discussed for pairs of soils (GF and GB, TF and HH), because in each pair, parent material and profile development are similar.

In both Gerritsfles soils (GF and GB) the parent material is well-sorted and contains 75% very fine and fine sand and 20% medium sand (Table 1). The soils have a characteristic sedimentary layering resulting from slight differences in the organic matter content. The clay fraction is only 1% of the mineral soil. The texture is uniform with depth in both profiles, with medians ranging from 158 to 172 μm (GB) and 154 to 159 μm (GF).

The bulk density at GF ranges from 1.37 kg dm^{-3} near the surface to 1.49 kg dm^{-3} at the 100-cm soil depth, and is distinctly lower than at GB (1.6 kg dm^{-3}). Bulk density is constant over the whole GB soil profile (Table 2).

The most pronounced chemical difference between GF and GB is the soil pH (Table 3). The bare GB soil being slightly less acidic, with a lowest pH(H_2O) of 4.4 between the 25- and 75-cm depth, than the forested site (GF), where pH ranges from 3.6 near the surface to 4.2 in the subsoil. The lower soil pH at GF may be related to (i) soil acidification due to nutrient uptake, (ii) production and leaching of organic acids (chelating agents) in the forest soil and (iii) higher atmospheric acid loadings in the pine stand, due to increased dry deposition of $(NH_4)_2SO_4$ (van Breemen et al. 1982).

Although a marked difference in organic C content of the GF soil relative to that in GB is suggested by the darker color of the forest soil, our data indicate only slightly higher values below 25-cm depth (0.24 and 0.33% at GF vs. 0.22 and 0.08% at GB) (Table 4). The difference in organic C content of the surface mineral soil (5.38 and 0.45% at GF vs. 0.48 and 0.25% at GB) may be largely due to the presence of discrete organic particles (e.g. from dead roots) at the forested site. The slightly elevated organic C level in the GB surface soil is probably due to the presence of algae and mosses.

At GF, the N content is highest in the forest floor and is also high in the surface layer of the mineral soil (Table 4). Below the 0.5-cm depth the N content does not exceed 0.03% (weight basis) in either soil. C/N ratios in the GF forest floor and in the mineral soils of both sites are low and indicate a luxurious N supply (Table 4).

Associated with the low clay and organic matter contents, the Cation Exchange Capacity (CEC) is low in both soils. Only in the surface mineral soil layer of GF the CEC reaches values of 52 mmol$_c$ kg^{-1}. The CEC consists largely of exchangeable Al and H (Table 3).

The content of 'free' Fe (III)-oxides is low (0.19 - 0.21% at GB and 0.20 - 0.27% at GF) and constant with depth. Only a minor portion of this 'free' Fe_2O_3 is in an amorphous form (Table 5). Also the levels of 'free' Al are low (0.25 - 0.39% at GB and 0.17 - 0.40% at GF; Table 5). Sequential extraction of Al (Figure 1) demonstrates two distinct differences between GB and GF: (i) in the upper 0.5-cm the 'free' Al level is lower at GF than at GB, whereas GF and GB do not differ in this respect at greater depth, and (ii) free Al at GB is primarily in an oxalate extractable (amorphous, non organically complexed) form, whereas the forested soil has higher pyrophosphate extractable (organically complexed) Al levels.

Although Al is the second most abundant element in the soil (on an oxide mass basis), total Al_2O_3 contents amount to only 2.0 - 2.3% (GB) and 2.2 - 2.4% (GF) of the soil solid phase. This shows that ca. 10 - 20% of total Al is in a 'free' form (Al hydroxides and organic Al compounds), whereas the remainder is present in aluminum silicates (Table 5). The extremely high contents of SiO_2 ($>$ 95%) and low contents of MgO, CaO, Na_2O and K_2O (ca 0.05, 0.10, 0.45 and 0.90%, respectively) indicate that both GF and GB are poor in weatherable base cations.

Quartz is by far the most important mineral phase present in GF and GB soils. Only 7% of the grains in all sand and silt fractions were identified as feldspars (Table 7). Feldspars are predominantly K and Na feldspars, which is supported by the total chemical analysis (Table 6). Contents of heavy minerals (primarily opaque, tourmaline, granate) are similar for both soils and range from about 6% (volume fraction) in the 2 - 75 μm fraction to 0.5% in the 106 - 212 μm fraction (Wopereis, 1985).

X-ray diffraction analyses of the 0 - 2 μm mineral fractions of GB and the subsoil of GF show the presence of primarily amorphous material with relatively small amounts of illite, kaolinite and soil chlorites. In the upper 10 cm of GF, apart from the amorphous material, only traces of kaolinite were found (Wopereis 1985).

At Tongbersven and Hasselsven the parent material is well-sorted (TF) and fairly well-sorted (HH) coversand, and consists for 75 - 81% (TF) and 65 - 83% (HH) of very fine and fine sand (50 - 210 μm). The clay fraction ($<$ 2 μm) ranges from 0.1 - 1.8% (TF) and 1.3 - 2.1% (HH) and reaches its maximum in the Bhs horizons. In contrast to the GB, GF and TF soils, the HH soil contains considerable amounts (4.7 - 7.4%) of coarse and very coarse sand (420 to 2000 μm) (Table 1). The textures are fairly uniform with depth in both TF and HH profiles and the medians are slightly lower than at GB and GF (142 - 158 μm at TF and 125 - 149 μm at HH).

In both spodosols the bulk densities are lowest in the spodic horizons (1.2 - 1.3 kg dm^{-3}) and increase with depth to ca. 1.5 kg dm^{-3} in the BC2 (TF) and C (HH) horizon (Table 2).

The TF soil is slightly more acidic than the HH soil. In both soils pH(H_2O) increases with depth: at TF from 3.77 (upper E) to 4.38 (BC2) and at HH from 3.90 (E) to 4.49 (C). Compared to the forested GF site these spodosols have a strongly acidic surface soil.

The organic C distribution in the TF mineral soil is characteristic for spodosols, with a maximum in the Bhs (4.54%) and a rapid decrease with depth. In accordance with the faint spodosol characteristics observed in the field the HH's E horizon organic C content (2.48%) is even slightly higher than the organic C content in the Bhs1 horizon (2.27%). Note that the organic C content in the GF and GB subsoils is higher than in the spodosol subsoils.

The N content of the TF and HH surface layers (1.6%) is slightly lower than that in the GF forest floor (2%). In contrast, the N content in the mineral horizons of both spodosols is higher than in the two driftsands (Table 4). The relatively high N content of the mineral soil at the heathland site HH is somewhat unexpected. Although C/N ratios are similar in the organic surface layers at TF, HH and GF (25 - 28), they differ considerably for the mineral soil horizons at the three sites, with highest values at TF (> 43) and lowest at HH and GF (< 33) (Table 4).

The CEC in both spodosols is primarily related to the organic matter content and is highest in the TF Bhs horizon (127 $mmol_c$ kg^{-1}) and the HH E and Bhs1 horizons (64 and 77 $mmol_c$ kg^{-1}, respectively). These values are substantially higher than those reported for the GF and GB soils. Subsoil (Bs, BC and C horizon) CEC values are less than 10 $mmol_c$ kg^{-1} and similar to those in GB and GF soils. The exchangeable cations are almost exclusively Al and H (Table 3).

'Free' Fe_2O_3 is lowest in the E horizon (0.04% at TF and 0.21% at HH), increases to a maximum in the Bhs horizon (0.44% at TF and 0.66% at HH) and drops to 0.20% in the BC2 (TF) and 0.33% in the C (HH). 'Free' Fe_2O_3 in the Bhs horizons is largely in an amorphous (oxalate extractable) form (Table 5).

'Free' Al at TF and HH also exhibits a typic spodosol distribution pattern with lowest values in the E (0.05 and 0.12%, respectively) and highest in the Bhs (1.17 and 0.54%, respectively). In the subsoils 'free' Al levels decrease again to 0.33 (TF) and 0.44% (HH). Sequential extraction of the 'free' Al fraction (Figure 1) shows the importance of pyrophosphate extractable (organically complexed) Al forms in the two spodosols. Only in both subsoils oxalate and dithionite extractable Al become relatively important; at these depths both level and chemical form of free Al are similar for the spodosols and the much younger soils in driftsands at GF.

The elemental analysis of both spodosols shows that Al, although present in small amounts, is the second most abundant element (on an oxide mass basis) in all soil horizons. Assuming that the difference between total elemental and 'free' Al is due to silicate bound Al, a continuous increase of silicate bound Al with depth is found in both spodosols, ranging from 0.4 - 1.7% (TF) and 1.0 - 2.1% (HH) (Table 6). Note that not only the E horizons, but also the Bhs horizons in both spodosols have low contents of silicate bound Al relative to the amounts present in the BC2 (TF) and C (HH) horizon. The levels of silicate bound Al in the HH C horizon are similar to those found in the GF and GB soils (2.0 and 1.9%, respectively). However, in the TF subsoil amounts are lower (1.5%), which may be due to (i) lower contents of silicate minerals of the parent material at TF, or (ii) leaching of Al during (natural) soil development from deeper soil horizons at this site.

The parent material of both spodosols is extremely rich in SiO_2 and depleted in K, Na, Ca and Mg. The relative composition of elements in silica bound form in the spodosols indicates that weatherable base cations are predominantly alkali feldspars (Table 6). Table 6 also shows that the alumino silicate composition is similar for spodosols and driftsands, with K-feldspar as the major Al-silicate.

Table 1. Particle size distribution. Size classes are in µm.

Site	Depth	Horizon	0-2	2-50	50-105	105-210	210-420	420-2000	M
	cm		% of mineral soil						µm
GF	0- 0.5	C	1.1	2.7	9.2	71.0	14.3	1.7	154
	0.5- 25	C	1.1	1.4	9.0	71.3	15.9	1.3	157
	25 - 75	C	0.8	1.1	8.5	66.7	21.0	2.0	159
	75 -150	C	0.6	1.4	10.8	65.5	18.9	2.8	157
GB	0- 0.5	C	0.8	1.1	8.7	70.9	16.5	2.0	158
	0.5- 25	C	0.9	1.2	6.6	62.7	23.3	5.3	172
	25 - 75	C	1.0	0.9	5.8	68.9	22.8	0.6	169
	75 -150	C	1.1	0.6	4.6	72.4	20.5	0.8	167
TF	0 - 10	E	1.2	3.6	18.6	57.0	17.1	2.5	146
	10 - 20	E	0.4	3.9	15.9	59.6	18.9	1.4	147
	20 - 40	Bhs	1.8	3.0	17.0	58.0	18.7	1.7	150
	40 - 58	Bs	1.3	4.8	19.0	58.9	15.2	0.8	142
	58 - 90	BC1	0.1	2.1	14.5	58.7	22.7	1.7	158
	90 -150	BC2	0.2	2.5	18.2	62.3	16.2	0.7	147
HH	0 - 9	E	1.3	6.9	16.2	50.3	18.5	6.9	146
	9 - 15	Bhs1	2.1	7.5	14.3	51.0	19.2	6.1	147
	15 - 33	Bhs2	1.6	7.5	15.8	49.4	19.9	5.8	149
	33 - 73	Bs	2.1	4.4	18.3	53.2	14.8	7.4	141
	73 -120	C	1.7	3.5	28.6	54.7	6.9	4.7	125

Table 2. Bulk densities in kg dm^{-3} (means and standard deviations).

Site	depth	horizon	mean	s.d.
	cm			
GF	0 - 25	C	1.37	0.01
	25 - 75	C	1.47	0.09
	75 -150	C	1.49	0.05
GB	0 - 25	C	1.62	0.04
	25 - 75	C	1.62	0.02
	75 -150	C	1.60	0.02
TF	0 - 10	E	1.31	0.07
	25 - 40	Bhs	1.23	0.02
	40 - 58	Bs	1.32	0.02
	70 - 88	BC1	1.41	0.01
	90 -150	BC2	1.56	0.03
HH	0 - 9	E	1.47	0.00
	9 - 15	Bhs1	1.33	0.01
	15 - 33	Bhs2	1.16	0.09
	33 - 73	Bs	1.45	0.02
	73 -120	C	1.52	0.01

Table 3. Soil pH and exchange characteristics.

Site	depth	horizon	pH(H_2O)	pH($CaCl_2$)	Ca	Mg	Na	K	Al	H	sum
	cm				mmol$_c$ kg^{-1}						
GF	0 -0.5	C	3.63	2.77	3	1	0	0	18	30	52
	0.5- 25	C	4.05	3.52	0	0	0	0	6	5	11
	25 - 75	C	4.08	3.95	0	0	0	0	2	7	9
	75 -150	C	4.16	4.00	0	0	0	0	2	2	4
GB	0 -0.5	C	5.87	4.54	0	0	0	0	0	4	4
	0.5- 25	C	5.43	4.10	0	0	0	0	0	3	3
	25 - 75	C	4.40	4.38	0	0	0	0	0	2	2
	75 -150	C	4.82	4.33	0	0	0	0	0	2	2
TF	0 - 10	E	3.77	2.95	1	0	0	0	11	15	27
	10 - 20	E	3.86	3.07	0	0	0	0	8	14	22
	20 - 40	Bhs	3.93	3.63	0	0	0	0	109	18	127
	40 - 58	Bs	4.20	4.21	0	0	0	0	11	3	14
	58 - 90	BC1	4.35	4.29	0	0	0	0	0	4	4
	90 -150	BC2	4.38	4.25	0	0	0	0	0	5	5
HH	0 - 9	E	3.90	3.00	2	1	0	1	34	26	64
	9 - 15	Bhs1	4.17	3.49	2	1	0	0	49	25	77
	15 - 33	Bhs2	4.29	4.04	1	1	0	0	29	2	33
	33 - 73	Bs	4.56	4.34	1	1	0	0	7	0	9
	73 -120	C	4.49	4.27	1	1	4	0	5	1	12

Table 4. Soil organic carbon and nitrogen contents, as well as C/N ratios.

Site	depth	hor.	%C	%N	C/N
	cm		%		
GF	10 - 0	O1	49.60	2.00	24.8
	0 -0.5	C	5.38	0.23	23.4
	0.5- 25	C	0.45	0.03	15.0
	25 - 75	C	0.24	0.02	12.0
	75 -150	C	0.33	0.01	33.0
GB	0 -0.5	C	0.48	<0.01	-
	0.5- 25	C	0.24	0.02	12.0
	25 - 75	C	0.22	0.01	22.0
	75 -150	C	0.08	<0.01	-
TF	5 - 0	O1	44.40	1.60	27.8
	0 - 10	E	2.13	0.05	42.6
	10 - 20	E	1.06	0.02	53.0
	20 - 40	Bhs	4.54	0.09	50.0
	40 - 58	Bs	0.62	0.01	62.0
	58 - 90	BC1	0.02	<0.01	-
	90 -150	BC2	0.05	<0.01	-
HH	3 - 0	O1	41.80	1.60	26.1
	0 - 9	E	2.48	0.12	20.7
	9 - 15	Bhs1	2.27	0.17	13.4
	15 - 33	Bhs2	1.17	0.08	14.6
	33 - 73	Bs	0.00	0.14	-
	73 -120	C	0.00	0.05	-

Table 5. Amorphous and free Fe_2O_3, as well as free, elemental, and elemental minus free (delta) Al_2O_3.

Site	depth	horizon	Fe_2O_3		Al_2O_3		
			amorph.	free	free	elem.	delta
	cm		% of fine earth				
GF	0- 0.5	C	0.10	0.27	0.17	2.38	2.21
	0.5- 25	C	0.07	0.22	0.26	2.34	2.08
	25 - 75	C	0.10	0.21	0.40	2.22	1.82
	75 -150	C	0.07	0.20	0.29	2.34	2.05
GB	0- 0.5	C	0.08	0.19	0.26	2.31	2.05
	0.5- 25	C	0.06	0.19	0.25	2.02	1.77
	25 - 75	C	0.06	0.21	0.30	2.29	1.99
	75 -150	C	0.07	0.19	0.39	2.33	1.94
TF	0 - 10	E	0.04	0.04	0.07	0.50	0.43
	10 - 20	E	0.02	0.04	0.05	0.55	0.50
	20 - 40	Bhs	0.41	0.44	1.17	2.32	1.15
	40 - 58	Bs	0.14	0.28	0.70	2.39	1.69
	58 - 90	BC1	0.06	0.16	0.31	1.61	1.30
	90 -150	BC2	0.06	0.20	0.33	1.84	1.51
HH	0 - 9	E	0.09	0.21	0.12	1.15	1.03
	9 - 15	Bhs1	0.50	0.66	0.31	1.42	1.11
	15 - 33	Bhs2	0.30	0.44	0.54	1.77	1.23
	33 - 73	Bs	0.11	0.39	0.42	2.37	1.95
	73 -120	C	0.09	0.33	0.44	2.51	2.07

Table 6. Molar elemental composition in silica-bound form, relative to aluminum.

Site	depth	hor.	Si	Al	Mg	Ca	Na	K
GF	0- 0.5	C	33.17	1.00	0.04	0.06	0.34	0.44
	0.5- 25	C	38.65	1.00	0.03	0.05	0.38	0.46
	25 - 75	C	45.26	1.00	0.04	0.06	0.41	0.52
	75 -150	C	40.14	1.00	0.04	0.05	0.43	0.48
GB	0- 0.5	C	40.03	1.00	0.04	0.05	0.39	0.48
	0.5- 25	C	46.34	1.00	0.02	0.05	0.41	0.51
	25 - 75	C	41.35	1.00	0.04	0.04	0.36	0.51
	75 -150	C	42.60	1.00	0.02	0.05	0.36	0.52
TF	0 - 10	E	192.67	1.00	0.00	0.02	0.50	0.71
	10 - 20	E	167.72	1.00	0.00	0.02	0.33	0.74
	20 - 40	Bhs	64.44	1.00	0.00	0.04	0.30	0.54
	40 - 58	Bs	48.27	1.00	0.04	0.04	0.29	0.46
	58 - 90	BC1	64.16	1.00	0.03	0.04	0.34	0.52
	90 -150	BC2	55.33	1.00	0.05	0.04	0.32	0.51
HH	0 - 9	E	77.68	1.00	0.06	0.04	0.29	0.46
	9 - 15	Bhs1	71.05	1.00	0.05	0.03	0.27	0.47
	15 - 33	Bhs2	65.44	1.00	0.04	0.04	0.27	0.44
	33 - 73	Bs	40.97	1.00	0.05	0.04	0.23	0.45
	73 -120	C	39.08	1.00	0.04	0.04	0.29	0.47

Table 7. Mineralogical composition of the 75-106 µm fraction of the Gerritsfles soils.

Site	depth	heavy min.	alkali feldsp.	plagioclase	quartz
	cm	% of the < 2mm fraction			
GF	0- 10	0.38	7.4	0	92.2
	100-130	0.44	7.4	-	-
GF	0- 10	0.39	4.7	2.4	92.5
	100-130	0.52	5.7	0.8	93.0

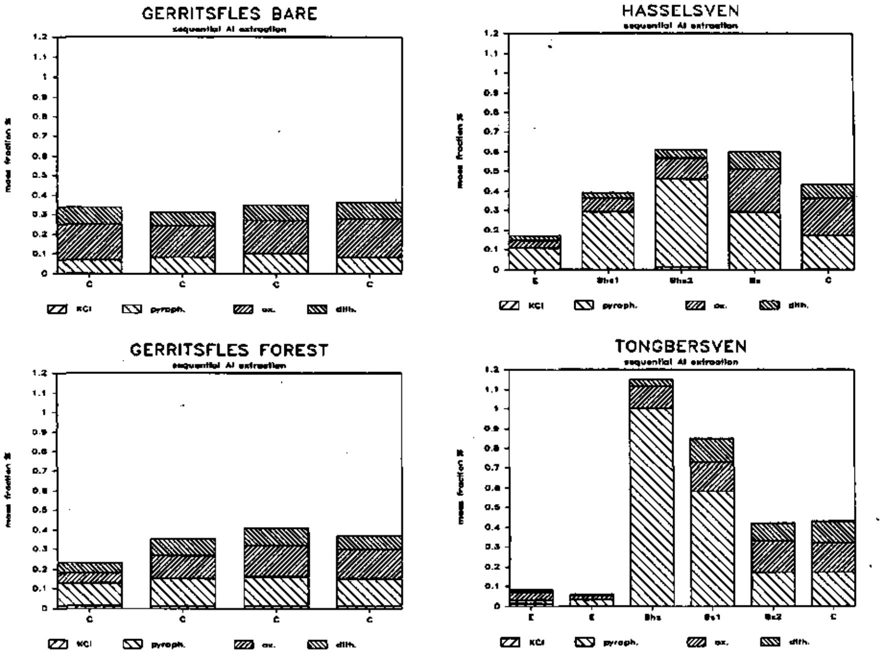

Fig. 1: Sequentially extracted Al_2O_3 in % of the mass fraction.

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CURRICULUM VITAE

Jan Mulder werd geboren op 27 november 1955 te Annen. In 1972 behaalde hij het MAVO diploma aan de openbare school voor MAVO te Zuidlaren, en in 1975 het diploma Atheneum-B aan het Zernike College te Groningen. Hij studeerde vanaf 1975 Bodemkunde en Bemestingsleer aan de Landbouw Hogeschool te Wageningen, waar hij in 1979 het kandidaats examen behaalde. Van April tot October 1979 bracht hij zijn praktijktijd door aan de 'School of Forestry and Environmental Studies', Yale University (New Haven, CT) en het 'Department of Ecology and Systemeatics', Cornell University (Ithaca, NY), beide in de Verenigde Staten van Amerika. De praktijktijd bestond uit een veldonderzoek naar de neutralisatie van zure regen in het Hubbard Brook Experimental Forest (New Hampshire). Van Mei tot Augustus 1981, tijdens een tweede praktijktijd aan de 'Edinburgh School of Agriculture' in Schotland, werkte hij aan de mangaan beschikbaarheid voor gerst. In April 1982 studeerde hij (met lof) af als landbouwkundig ingenieur, met als vakken bodemscheikunde en bodemnatuurkunde (verzwaard hoofdvak), regionale bodemkunde (bijvak), en colloïdchemie (bijvak).

Vanaf September 1982 is hij werkzaam aan de Vakgroep Bodemkunde en Geologie van de Landbouw Universiteit te Wageningen, eerst in het kader van zijn vervangende dienstplicht, later in aansluitende tijdelijke dienstverbanden. Gedurende de afgelopen 6 jaar heeft hij gewerkt binnen het Zure Regen onderzoek van de vakgroep onder leiding van Prof. Dr. Ir. N. van Breemen. Met behulp van een fellowship van de 'Norges Teknisk-Naturvitenskapelige Forskningsrad' (NTNF), werkte hij van Januari tot April 1988 voor het Center for Industrial Research te Oslo aan de regulering van de aluminium activiteit in oppervlaktewater.