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Time trends & mechanisms of soil acidification

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Time trends & mechanisms of soil acidification

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STELLINGEN

1. De huidige afname aan basische componenten in atmosferische depositie is zuur.

2. De waargenomen langzaam met de tijd afnemende concentraties van basische kationen in catchment beekwater zijn het gevolg van afnemende voorraden omwisselbare kationen in de bodems van het catchment (Kirchner, 1992); het laatste wordt veroorzaakt door bodemverzuring én afnemende atmosferische depositie van basische kationen.
Kirchner, J.W. 1992. Geochim. Cosmochim. Acta, 56: 2311-2327.
Driscoll et al. 1989. Environ. Sci. Technol., 23: 137-143.
Dit proefschrift.

3. Models represent what the system can do instead of what it will do.
Uit: Hierarchical concepts of ecosystems. O'Neill et al., 1986. Princeton University Press.

4. Het toetsen van modelscenario's met betrekking tot toekomstige bodemverzuring, door middel van veldmetingen, is een lange termijn zaak.

5. Bodemkundig onderzoek in Duitsland is vanzelfsprekend grondig.

6. De oplosbaarheid van aluminium in zure bosgronden is sterk afhankelijk van de verhouding van organisch gebonden aluminium en organisch koolstof in de bodem.
Dit proefschrift.

7. Voorraden organisch gebonden aluminium in bovengronden van zure bosbodems in Duitsland en Nederland dalen meetbaar met de tijd onder invloed van langdurige zure atmosferische depositie. De snelheid waarmee deze afname plaatsvindt is afhankelijk van de mate waarin voorraden organisch gebonden aluminium worden aangevuld uit andere processen zoals het verweren van secundaire hydroxiden en primaire mineralen.
Dit proefschrift.

8. We look to lower levels for mechanisms and to higher levels for significance.
Uit: Hierarchical concepts of ecosystems. O'Neill et al., 1986. Princeton University Press.

9. De aanleg van een kunstijsbaan op de Wageningse berg zal de historische band tussen stuwwal en ijs in ere herstellen.
"Onderzoek naar een kunstijsbaan in Wageningen, stadion de Wageningse berg ideale locatie". De Gelderlander, 9 februari 1994.

10. Promovendi in het zure regen onderzoek verdienen een pH.D.

Stellingen behorende bij het proefschrift "Time trends & mechanisms of soil acidification".
L.G. Wesselink, Wageningen, 6 september 1994.

Aan mijn ouders
Voor Annet, Tim en Koen

VOORWOORD

Graag wil ik een aantal mensen bedanken voor hun bijdrage aan dit proefschrift. Besonders danken möchte ich Dr. Jürgen Prenzel und Prof. Dr. Bernhard Ulrich für die Überlassung des Themas und für die Möglichkeit meine Doktorarbeit auch in Göttingen zu bearbeiten. Ein großer Teil dieser Arbeit baut auf Daten die über einer langen Zeitraum von vielen Personen gesammelt wurden. Großen Dank bin ich dem Institut für Bodenkunde und Waldernährung und dem Forschungszentrum Waldökosysteme in Göttingen für die Überlassung dieser Daten schuldig.

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Bart Wesselink, juli 1994

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Chapter 1

GENERAL INTRODUCTION

Soil Acidification

Soil acidification is defined as a loss of acid neutralization capacity from the soil (van Breemen et al., 1983; 1984). It is a natural process when carbonic and organic acids are neutralized by mineral dissolution or cation exchange, and reaction products are leached from the soil profile or immobilized in living biomass. In the 1970s studies of Ulrich et al. (1979) and Likens et al. (1979) first pointed to atmospheric deposition as an important source of acidity to soils. Soon after, it became evident that the acidity in atmospheric deposition resulted from long-range transport of SO_x, NO_x and NH_3 gasses from fossil fuel combustion, traffic, industry, and animal husbandry. These gasses dissolve in atmospheric water to form H_2SO_4, HNO_3 and $(NH_4)_2SO_4$ which are deposited with rain water on terrestrial and aquatic ecosystems ('wet deposition'). Forest vegetations may strongly enhance deposition through interception of gases and aerosols ('dry deposition'). In Western Europe, the contribution of antrophogenic acid deposition is estimated to be more than 10 times higher than natural 'internal' production of acids in forested ecosystems (Bredemeier, 1987). Note that acidification from deposited $(NH_4)_2SO_4$ results from uptake of NH_4^+ in biomass, or nitrification of NH_4^+ and subsequent leaching of HNO_3 and H_2SO_4 (Mulder, 1988).

A number of processes are involved in proton buffering in soils (van Breemen et al., 1983), e.g. uptake of nitrate by the forest:

$$NO_3^- + H^+ +]R{\cdot}OH \text{ <----> }]R{\cdot}NH_2 + 2O_2 \qquad [1]$$

where]R indicates a potential binding site for amino groups in the plant,

and adsorption of SO_4 in the soil:

$$]S\text{-}OH_2 + SO_4^{2-} + 2H^+ \text{ <----> }]S\text{-}SO_4 + 2H_2O \qquad [2]$$

where]S indicate soil adsorption sites.

Ulrich (1981) ranked the soil processes involved in acid neutralization in so called buffer ranges. At low rates of acid production (internal or atmospheric), acidity is largely neutralized by silicate weathering. At near neutral pH this may for example be illustrated by the incongruent weathering of microcline feldspar:

$$KAlSi_3O_8(s) + H^+ + 7H_2O \text{ ---> } K^+ + Al(OH)_3(s) + 3H_4SiO_4 \qquad [3]$$

Subsequently, at increasing acid inputs, Al is released from secondary (hydr)oxides and replaces exchangeable base cations:

$Al(OH)_3(s) + 3H^+ + 3K_a <--> Al_a + 3K^+ + 3H_2O$ [4]

where the subscript *a* stands for adsorbed cations. Exchanged base cations, here represented by potassium (K), are transported from the soil and irreversibly lost. Gradually, base cations will be depleted from adsorption sites, and Al is no longer stored on exchange sites (Eqn. [4]) but released to solution:

$AlOH_3(s) + 3H^+ <---> Al^{3+} + 3H_2O$ [5]

In the long run, pools of reactive Al may become depleted and dissolution of Fe may neutralize acidity when the soil pH is sufficiently low (pH<3):

$Fe(OH)_3(s) + 3H^+ <---> Fe^{3+} + 3H_2O$ [6]

This sequence of events leads to increasingly lower soil pH, depletion of exchangeable base cation pools, elevated concentrations of dissolved Al, and decreased Ca/Al rations in soil solutions, which, in various complex ways, are all unfavourable for forest growth (Ulrich, 1989).

The processes outlined in Eqn. 1-6 form the conceptual basis of most soil acidification models, which reflects the general consensus on the relevance of these processes in acid neutralization.

Study sites

Central in this thesis are chemistry data from the Solling experimental forest. This monitoring site is located on a plateau of the Solling mountain range in central northern Germany, 500 m above see level. In two adjacent forested plots, covered by, in 1993, a 109 years old spruce forest (F1) and a 138 year old beech forest (B1), the hydrology and chemistry of rainfall, throughfall water, and soil water have been measured since the late 1960s. Today, measurements are still going on. The length and intensity of monitoring at Solling is almost unique in the world. The geographical position of the Solling sites is indicated in Fig. 1. Though located in a remote area, the Solling area receives high loads of acid atmospheric deposition from the Ruhr industrial region in the West and industrial areas of eastern Germany and the Czech Republic to the Southeast (Bredemeier et al., 1994). Figure

1 also includes the geographical position of study sites at Hackfort and Gerritsfles the Netherlands, from which data are used in this thesis.

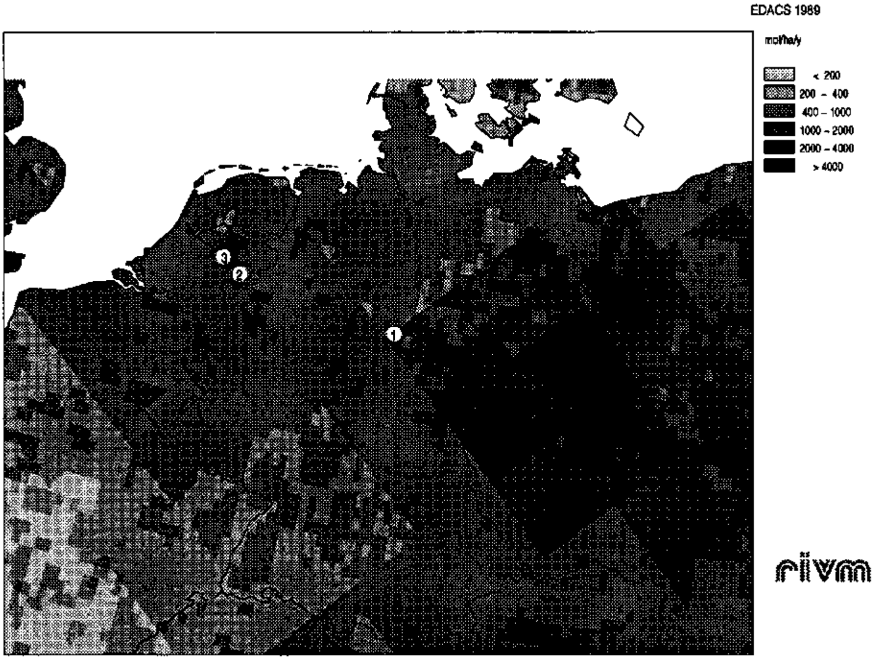

Figure 1. *Total atmospheric deposition of SO_x in Western Europe in 1989. Location of the study sites at Solling (1), Hackfort (2) and Gerritsfles (3) is indicated (Erisman et al., 1994).*

Aim of this thesis

The aim of this thesis is to investigate chemical processes in soils under high loads of acid atmospheric deposition. Although a vast body of literature exists on this topic, key processes, as outlined in the introduction, are either still poorly understood, have been derived from laboratory experiments, or have been tested on field data sets of a few years only. The long data sets from Solling, extending over two decades, provide the unique opportunity to test and derive model concepts. This thesis presents a step by step evaluation of time trends and mechanisms of soil acidification in acid forest soils, involving long-term changes in atmospheric deposition and its effects on base cation chemistry of the soil, and mechanisms of silicate weathering, anion mobility, and aluminum release.

Outline of this thesis

In chapter 2, changes in deposition and soil water chemistry at Solling over a period of nearly two decades are analyzed. Attention focuses on how concentrations of dissolved and exchangeable base cations in the soil are affected by deposition of acid anions and base cations through the process of cation exchange.

In chapter 3, base cation supply from mineral weathering at Solling is quantified. Field weathering rates are estimated from input-output flux budgets as well as elemental analysis of the soil profile. Laboratory experiments are carried out to investigate release mechanisms of K and Mg from illite which is the dominant mineral source of base cations at Solling.

In chapter 4, processes that control observed seasonal and long-term changes in soil water chemistry of Cl, SO_4 and NO_3 at Solling are discussed. For this purpose a simulation model that describes hydrological and biogeochemical soil processes is introduced.

Chapters 5 an 6 focus on the mechanism of Al release in acid forest soils. Despite the long established significance of Al mobilization as an acid neutralizing process, its mechanism is still poorly understood. In chapter 5, different mechanisms of Al release that have been suggested in literature are put to test on the Solling data, and a semi-empirical model of Al-proton (H) exchange on soil organic matter is introduced.

In chapter 6, the proposed model for Al-proton exchange on soil organic matter is further developed and generalized by including data from a number of European research sites. Furthermore, the hypothesis that organically bound soil Al is being depleted at present, as a result of prolonged atmospheric acid deposition, is tested by comparing pools of organically bound soil Al in old and recent soil samples from a number of research sites.

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Chapter 2

Time trends in atmospheric deposition at Solling, Germany, and responses of soil base cation chemistry

Bart Wesselink, Karl-Joseph Meiwes, Egbert Matzner & Alfred Stein

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ABSTRACT

With declining sulfur emissions in western Europe, the degree and time scales of reversibility of soil and freshwater acidification are of major interest. We analyzed long-term changes (1969-1991) in the chemistry of bulk precipitation, throughfall water, soil water and exchangeable base cations in a beech and a spruce forest in Solling, Germany. Time trends in dissolved and exchangeable pools of base cation in the soils were compared with simulations from a simple mechanistic soil chemistry model to identify the processes controlling long-term changes in soil chemistry. In the early 1970s, profound acidification occurred in the spruce and beech soils due to increasing concentrations of dissolved SO_4. After 1976, atmospheric deposition of SO_4, Ca and Mg decreased significantly as a result of reduced industrial emissions. Nevertheless, acidification continued in the spruce soil due to declining atmospheric inputs (Ca) and continuously high dissolved SO_4 in the soil. In the beech soil, with lower deposition levels, smaller declines of base cation deposition and a more diluted soil solution, reduced atmospheric inputs of SO_4 in the 1980s started a recovery of the soil's base saturation.

INTRODUCTION

Acid atmospheric deposition may strongly affect the chemistry of soil and drainage waters in forested ecosystems (1-4). Increased rates of acidification of soils and waters have been demonstrated by continuously monitoring soil and water chemistry (1-4), and are in accordance with results from process-based models describing the hydrochemistry of forested ecosystems (5). Since the mid-1970s, acid sulfur deposition in western Europe and the United States has been declining (6-8). Of major interest now are the degree and time scales of reversibility of soil and freshwater acidification (9). For this purpose, a proper understanding of the processes regulating a soil's base cation chemistry (Ca+Mg+Na+K) is crucial.

Recently, the catchment studies at Hubbard Brook, New Hampshire, USA (7) and Birkeness in southern Norway (8) have revealed continuous long-term decreases in stream water concentrations of base cations since the mid-1970s. In these studies, several processes were proposed to control these declines: (a) declining deposition of base cations (7), (b) reduced leaching of acid anions from the catchment (7, 15), which, through charge balance constraints, results in a concurrent decrease in base cation leaching, and (c) continued depletion of exchangeable base cations, while leaching of acid anions remained constant (8). The relative importance of these processes, which may occur simultaneously, was, however, strongly debated (8, 10-18). Unfortunately, these studies did not include repeated measurements of exchangeable soil base cation pools. How these pools responded to the offsetting processes of (b), which increases the soil's base saturation, versus (a) and (c), which decrease base saturation, remained unknown.

In Solling, a forested area in Germany which is strongly impacted by acid deposition, measurements of bulk precipitation chemistry, throughfall and soil solution chemistry have been going on since 1969 (1, 2, 3). At Solling, field observations include repeated measurements of pools of exchangeable cations (2, 4), which makes it a unique data set, worldwide. In this paper, we will report on the analysis of the long-term changes in the chemistry of bulk precipitation, throughfall and soil water, and exchangeable base cations in the adjacent spruce and beech forests in Solling. The aim was to identify process controls of long-term changes of the soils' base cation chemistry. We have introduced model simulations to demonstrate how individual as well as combined processes (a-c) may contribute to these long-term changes.

THEORY

Soils may, in a simplified way, be considered as cation exchange systems responding to fluxes to and from the system (8). Our interest focuses on the response of base cations in the soil to changing deposition of acid anions and base cations. To evaluate this, model simulations were introduced. A soil system with the chemical species SO_4^{2-}, C_b^{2+} (sum of base cations), H^+, and Al^{3+} was considered, where soil solution chemistry was influenced by atmospheric deposition, evapotranspiration (constant) and chemical equilibria involving ion exchange between Al and C_b (Gaines-Thomas) and gibbsite ($Al(OH)_3$). Other processes like weathering and bio-element cycling of base cations were not modeled, as these were assumed constant factors. Previously, an extended version of this model was used to study the dynamics of anions (19) and Al and H (chapter 5), at Solling. Here, we used the model to evaluate the response of soil chemistry in two deposition scenarios, calculated for a total period of 22 years. The first deposition scenario was characterized by increasing, followed by decreasing, H_2SO_4 deposition, while atmospheric input of C_b remained constant. In the second scenario, deposition of H_2SO_4 and C_b decreased simultaneously. This scenario is of particular interest as concurrent long-term declines in atmospheric SO_4 and base cations have recently been reported for regions of Europe and North America (20).

Note that the aim of the simulations was to provide a qualitative illustration and not a quantitative operation. Still, we chose model parameters representative for the Solling spruce site to conceptualize soil chemical responses to changes in atmospheric deposition, and the time scales of these responses for the Solling case study. Trends and concentration levels of SO_4 and base cations in the deposition scenarios were comparable to those in throughfall of the Solling spruce site (in the case of base cations comparable to the sum of Ca+Mg). We considered a single soil compartment of 50 cm with a constant water input flux of 70 cm/yr and a drainage flux of 35 cm/yr (19), a CEC of 250 keq/ha (2), an initial base saturation of 5%, and a gibbsite solubility constant ($pK_{Al(OH)3}$) of -8.7 (chapter 5). The Gaines-Thomas selectivity coefficient of Ca displacement by Al was set at 7 mol/L to meet steady-state conditions at the start of simulations. All these parameters were held constant throughout the sample simulations.

The simulated responses of base cations in the soil to the different deposition scenarios are discussed briefly for each of the three stages distinguished (see Figure 1).

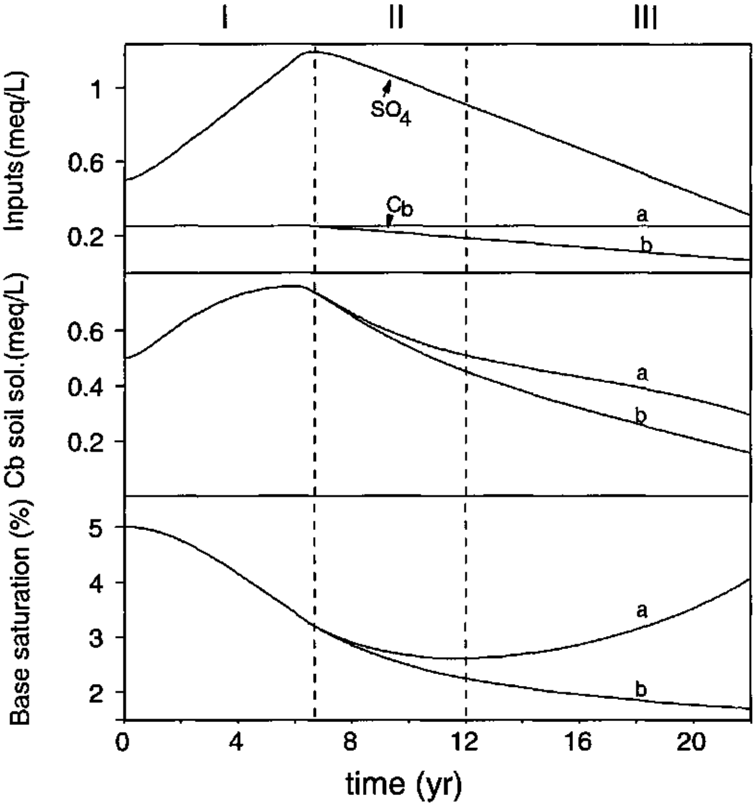

Figure 1. Simulated response stages (I, IIa/b, IIIa/b) of soil chemistry to different input conditions (upper panel). Middle panel shows dissolved base cations in the soil and lower panel exchangeable base cations in the soil.

Stage I: increased deposition of SO_4 and constant deposition of C_b. Increased H_2SO_4 deposition was reflected by increases in dissolved SO_4 and Al in the soil solution (not shown). Subsequently, displacement of base cations by Al caused an increase of base cation concentrations in soil water and a decrease in base saturation (Figure 1).

Stage IIa:reduced deposition of SO_4 and constant deposition of C_b. Sulfate concentrations in deposition and the soil solution were reduced from the previous high level of stage I. In response, C_b concentrations also decreased, forced by charge balance constraints. Yet base saturation continued to decrease by displacement by Al. This illustrates that depletion of base cations from exchange sites may occur despite reduced SO_4 levels (16).

Stage IIIa:reduced deposition of SO_4 and constant deposition of C_b. Forced by charge balance constraints, C_b concentrations in soil water continued to decrease. In contrast to stage IIa, however, this also resulted in reduced leaching from exchange sites. As a result, base saturation recovered at the expense of exchangeable Al, which was transferred to the gibbsite pool.

Stage IIIb:reduced deposition of SO_4 and C_b. In addition to the charge balance effect (stage IIIa), reduced C_b inputs further decreased C_b concentrations in the soil solution. The recovery of base saturation modeled in stage IIIa was overridden by the reduction in C_b inputs.

The simulations illustrate that soils with small pools of base cations are very sensitive to changes in atmospheric deposition of both acid anions and base cations on a time scale of two decades. Moreover, they illustrate that declining concentrations of dissolved base cations in the soil solution (stages II, III) can be concerted by increasing as well as decreasing base saturation, depending on the dominating processes. Therefore knowledge of temporal changes in exchangeable base cation pools will be of great help in identifying these processes.

SITE DESCRIPTION FIELD STUDY

The study area was located in northern Germany (9°30' east, 51°40' north) on the plateau of the Solling mountains 500 m above sea level. Two adjacent sites of about 1 ha each were investigated for more than 20 years: a 140-year old beech stand (*Fagus silvatica*) and a 110-year old spruce stand (*Picea abies*). Acid atmospheric deposition loads on the stands are high (Table 1), and pools of exchangeable base cations are low (Table 2). The sites have developed on the same parent material and soils are classified as Typic Dystrochrepts (1) consisting of 60-80 cm loess on soliflucted material from weathered Triassic sandstone. The clay content of the soils is around 17% in the loess layer and 23% in the weathered sandstone, and consists of mainly illite and vermiculite.

Bulk precipitation and throughfall water have been monitored at Solling since 1969. Rainfall and throughfall were collected at 15 locations evenly spread in the 1-ha sites and pooled monthly to three samples for chemical analysis. Monitoring of soil water chemistry at the 90-cm depth started in the beech soil in 1969 and in the spruce soil in 1973. Soil solutions were sampled by ceramic plates; seven (spruce) and three (beech) replicate lysimeters were installed inside a 15-m^2 area within each of the 1-ha sites. Solutions from individual lysimeters were collected by continuous low suction and pooled monthly to generally three samples for chemical analysis. Lysimeter plates in the spruce soil were renewed in December 1976.

To measure exchangeable cations, the spruce and beech site were sampled in 1966, 1968, 1973, 1979, 1983, 1986 (beech) and 1991 (spruce) (2, 4, 32). The top 50 cm of the mineral soil was sampled in 4 to 6 depth intervals, and at each depth interval 12 (1966), 15 (1973, 1979), or 20 (1968, 1983, 1986, 1990) probes evenly distributed over the sites were sampled with sampling cores of 8 cm diameter. We considered the number of samples taken sufficiently high to represent the 1-ha sites. At each depth interval, each five (six in 1966) probes were mixed for chemical analysis. Thus, 2 (1966), 3 (1973, 1979), or 4 (other years) depth profiles of exchangeable cations were obtained. Table 2 shows the average sum of exchangeable cations (0-50 cm) from these profiles and their standard deviations.

Table 1. *Average Deposition[a] and Weathering Rates[b] at Solling (keq/ha/yr).*

	deposition beech	deposition spruce	weathering
Na	0.58	0.71	0.05
K	0.16	0.19	0.06
Ca	0.74	0.87	0.06
Mg	0.19	0.24	0.33
SO_4	2.71	4.32	-

[a] Average bulk plus interception deposition in the 1981-1985 period (2)

[b] Estimated for the upper 90 cm of the spruce soil (21)

ANALYTICAL METHODS

Methods for the analysis of solutions, given by König et al. (22) and Meiwes et al.

(23) will be shortly described. Until 1982, SO_4 was determined by precipitation with Ba and analyzing excess Ba by potentiometric titration with EDTA, using a wolfram electrode (24). From 1982 on, SO_4 was analyzed colorimetrically using methyl thymol blue (25). Ammonium and NO_3 were determined colorimetrically with indophenol green and *K*-perrhenate respectively, until 1981 (26, 27). From 1982 on, NH_4 was analyzed with *Na*-salicylate and *Na*-dichlorcyanurate, while NO_3 was determined with the cadmium reduction method (25). Until 1980, Cl was determined by potentiometric titration with a $AgNO_3$ solution in a system with a glass and a Ag-AgCl electrode. After 1980, Cl was determined by the ferricyanide method (25). Sodium, K, Ca, Mg, and Mn were measured by atomic absorption spectroscopy (26). Aluminum was measured colorimetrically until 1982 (28) and by atomic absorption afterwards (22) and pH was measured with a glass combination electrode. Before a new analytical method was introduced, it was tested against the old method for a large number of samples. The new methods did not significantly differ from the old ones. Exchangeable cations were measured after percolation of the soil with 1 N NH_4Cl (23).

STATISTICAL METHODS

Long-term changes in concentrations with time were analyzed using linear regression models with autocorrelated errors (29).

For precipitation and throughfall data:

$$[X] = A_0 + A_1 t + A_2/V \qquad [1]$$

For soil water data:

$$[X] = A_0 + A_1 t + A_2[Cl] \qquad [2]$$

where :

[ ] indicates monthly volume-weighted solute concentrations (meq/L) calculated from the available, spatially distributed, observations.

X = Na, K, Ca, Mg, NH_4, Al, H, SO_4, NO_3, Cl

t = time (yr)

V = water flux density (cm per month)

A_0, A_1, A_2 are model parameters estimated by linear regression.

The value of A_1 corresponds to the linear concentration change with time, also called time trend. A separate regression analysis was carried out for each of the solutes on the left hand side of Eqs. [1] and [2]. To minimize temporal variations in concentrations caused by variations in meteoric water fluxes, the term A_2/V was introduced in Eq. [1]. To account for concentration changes due to evaporation and dilution in the soil, the term $A_2[Cl]$ was used in Eq. [2]. The correction with Cl is based on the assumed conservative behaviour of Cl in the soil, which was verified from long-term input-output budgets of the Solling soils (30).

Time series of soil solution concentrations show autocorrelation. Ordinary linear regression on such data is likely to yield too narrow confidence intervals for the model parameters; hence their significance is overestimated (31). To take into account the autocorrelation of the monitoring data, the error term $\underline{\varepsilon}$ was described as: $\varepsilon_t = e_t - \alpha_1\varepsilon_{t-1} - \alpha_{12}\varepsilon_{t-12}$, where e_t represents independent normal error terms with zero mean and variance σ^2; ε_{t-1} and ε_{t-12} are the errors 1 month and 12 months before t. The parameters which link those errors with the errors at time t are α_1 and α_{12}. We considered this procedure sufficiently general as it accounts for short time dependencies in the time series (i.e. time lag one month) and for seasonal time dependencies (i.e. time lag 12 months). The model parameters and the autoregressive terms were estimated by an ordinary least-square approach, and were in turn used to re-estimate the parameters, the so-called Yule-Walker estimates (32). All analyses were done with the SAS Autoreg procedure (33).

RESULTS

Concentrations of a number of solutes in the soil solution strongly increased until the mid-1970s and decreased thereafter (e.g. SO_4 in Figure 2). To apply a linear regression model to these data, time series were split into two parts: 1969/73-1978 and 1978-1991. To be able to relate trends in soil solution chemistry to deposition inputs, a similar time split was introduced for precipitation and throughfall data. As their concentrations appeared to peak in about 1976, the time split was introduced somewhat earlier: 1969-1976 and 1976-1991. Average solute concentrations, time trends, significance of trends, and the R squares of the regression models are given in Table 3, and annual concentrations of SO_4 and Ca in Figures 2 and 3.

The spruce and beech sites receive similar bulk deposition, which showed no significant change over time between 1969 and 1976. After 1976, however, concentrations of Ca, Mg, H, Al, SO_4, and Cl decreased significantly. In throughfall before 1976, significant time trends were only found for Ca under beech (decrease) and NO_3 under spruce (increase). After 1976, SO_4, H, and Ca concentrations in throughfall water of the spruce and beech stands decreased significantly.

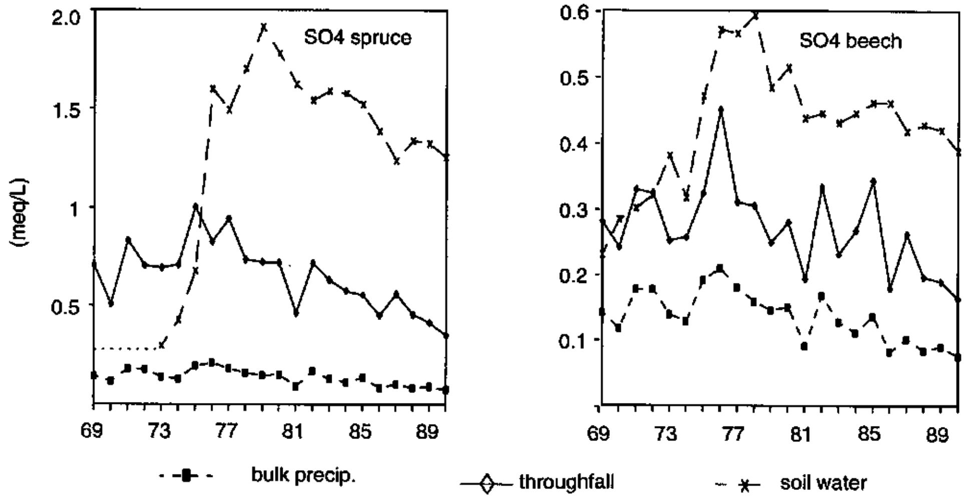

Figure 2. Annual volume-weighted concentrations of SO_4 in bulk deposition, throughfall and soil water (90 cm) under spruce and beech at Solling, Germany, from 1969 to 1990. Dotted line in left panel indicates estimated pre-monitoring SO_4 concentrations in spruce soil water.

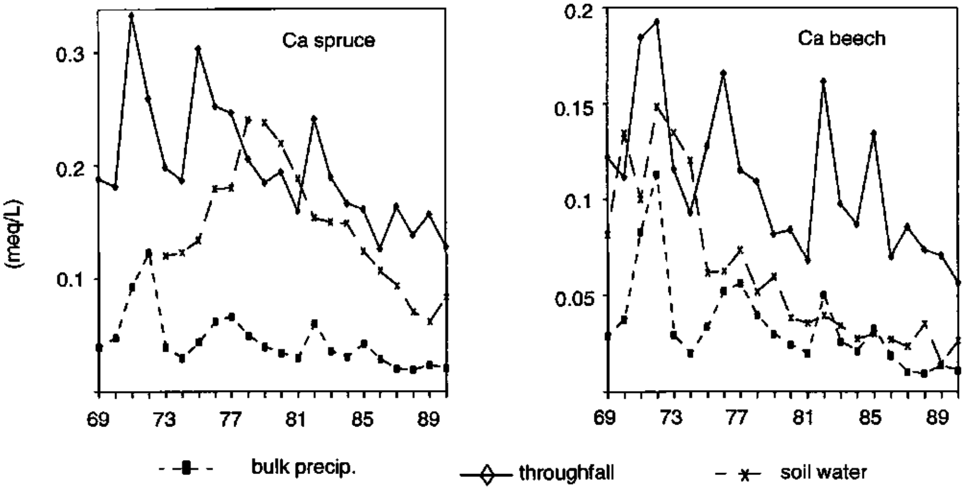

Figure 3. Annual volume-weighted concentrations of Ca in bulk deposition, throughfall and soil water (90 cm) under spruce and beech at Solling, Germany, from 1969 to 1990.

In the May months of 1989, 1990, and 1991, precipitation was very low (1.7, 0.9, and 0.9 cm of bulk precipitation, respectively), and solute concentrations were very high. In spite of the correction for effects of water flux, through the inverse proportional relation with solute concentrations (Eq. [1]), trends in throughfall under spruce after 1976 seemed obscured by these three data points. For the 1978-1988 period, concentrations of both Ca and Mg decreased significantly. In the soil solutions, SO_4 concentrations showed a strong and significant increase between 1969/1973 and 1978 under both spruce and beech, as did Na, K, H, and Al concentrations under beech and Na, Ca, Mg, H, and Al concentrations under spruce. After 1978, SO_4 concentrations in soil water decreased significantly at both sites together with Na, K, Ca, Mg, H, and Al concentrations in the beech soil and Na, Ca, Mg, H and Al concentrations in the spruce soil. Note, that time trends were corrected for changes in hydrological conditions (Eqs. [1] and [2]), therefore reflecting long-term changes in atmospheric inputs and/or soil chemistry.

Table 2. *Pools of exchangeable Base Cations*[a] *in keq/ha in the 0-50-cm mineral soil of the Spruce and Beech sites.*

		Ca	Mg	K	Na	ΣBC	N[b]	n[b]
1986	spruce	13.1 (1.7)	2.6 (0.3)	12.4 (0.5)	6.8 (0.6)	34.9	20	4
1973	spruce	12.9 (3.2)	2.5 (0.2)	7.6 (0.6)	5.3 (0.5)	28.3	15	3
1979	spruce	8.5 (1.5)	3.9 (0.3)	6.0 (0.3)	3.8 (0.2)	22.2	15	3
1983	spruce	5.0 (0.7)	3.1 (0.3)	7.9 (1.6)	4.3 (0.3)	20.3	20	4
1990	spruce	4.6 (1.7)	2.6 (0.8)	5.0 (0.8)	2.5 (0.8)	14.7	20	4
1966	beech	14.3	2.6	9.1	8.7[c]	34.7	12	2
1973	beech	9.1 (0.7)	2.8 (0.3)	9.1 (0.3)	6.8 (0.4)	27.8	15	3
1979	beech	13.6 (1.7)	4.9 (0.2)	8.6 (0.4)	2.9 (0.4)	29.5	15	3
1983	beech	5.9 (1.3)	2.9 (0.4)	7.1 (0.9)	5.8 (0.2)	21.7	20	4
1986	beech	6.7 (0.4)	3.2 (0.4)	8.1 (1.0)	5.6 (2.0)	23.6	20	4

[a] Data from 1966, 1968, and 1973 are reported by Ulrich et al. (4) and from 1979 and 1983 by Matzner (2). Data from 1986 and 1990 were obtained from the Forest Experimental Station, Göttingen, Germany (34).

[b] N refers to the number of samples taken, mostly from 10-cm depth intervals, which were mixed to n samples per depth interval for analysis. Standard deviations derived for *n* sampling profiles for the 0-50 cm depth are given in parentheses.

[c] A value of 1 keq/ha of exchangeable Na in 1966 is given by Ulrich et al. (4). Here, a value of 8.7 keq/ha was estimated from a re-analysis of two 1966 samples, carried out in 1986 (34).

As a reference point for SO_4 concentrations in spruce soil water, we estimated 'pre-monitoring' concentrations of dissolved SO_4 (Figure 2). We calculated an average SO_4 concentration of 0.29 meq/L. This value was obtained (a) assuming a total cumulative SO_4 deposition since the beginning of industrialization in 1850 of ca. 230 keq/ha (35), (b) substracting from this amount the present soil-bound inorganic SO_4 pool of 107 keq/ha (linearly extrapolated from 0-50 cm values (38)), obtaining a long-term SO_4 leaching of 123 keq/ha, and (c) assuming a constant annual water flux from the 90-cm soil of 350 mm.

Exchangeable Ca, K, and Na and the sum of exchangeable base cations under spruce decreased strongly from 1968 to 1990 (Table 2). Magnesium pools slightly increased until 1979 and decreased afterwards. The same trends were observed in the beech soil except for a high value of exchangeable Ca in 1979. Clearly, the net decrease in exchangeable K and Na, and the sum of exchangeable bases over the full time period was much less under beech than under spruce.

DISCUSSION

BULK PRECIPITATION AND THROUGHFALL

Decreased SO_4 concentrations in bulk precipitation and throughfall of spruce and beech after 1976 must be attributed to decreased SO_4 deposition in response to reduced SO_2 emissions in Europe (Table 4). Sulfate concentrations in throughfall under spruce showed a stronger decrease than under beech. Because the spruce canopy is a more effective scavenger of SO_4 deposition than the beech canopy (3), decreases in SO_4 deposition are expected to be stronger under spruce. The increase in NO_3 concentrations in spruce throughfall between 1969 and 1976 is also consistent with NOx emission patterns in this period (Table 4). The decrease in Cl concentrations in bulk precipitation after 1976 was, however, rather unexpected. Most of the Cl in precipitation is cyclic salt from seawater, which has presumably remained constant. Decreased Cl concentrations in bulk precipitation are possibly due to reduced industrial emissions too.

The declines in bulk deposition of Ca and Mg at Solling after 1976 are consistent with decreased dust emissions in Germany (Table 4). These result from controls on particulate emissions from fossil fuel combustion. Reduced particulate deposition may have a relatively strong effect on throughfall concentrations under spruce due to the greater scavenging by the spruce canopy. Table 3 shows that the downward trend in Ca concentrations in spruce throughfall was indeed much stronger than in beech throughfall.

Table 3. *Time Trends in Solute Concentrations.*

		BULK PRECIPITATION			
	1969-1976		1976-1991		
	Trend[a] (meq/L/yr)	R^2 [b]	Trend (meq/L/yr)	R^2	C_{avg} [c] (meq/L)
Na	0.00111	0.31	-0.00161	0.21	0.037
K	0.00017	0.48	-0.00004	0.39	0.011
Ca	-0.00301	0.51	-0.00166*	0.46	0.056
Mg	-0.00040	0.54	-0.00058**	0.53	0.016
NH_4	0.00273	0.20	-0.00124	0.19	0.095
H	0.00097	0.18	-0.00445***	0.22	0.075
Al	0.00111	0.31	-0.00094**	0.07	0.012
SO_4	-0.00010	0.53	-0.00819***	0.47	0.16
NO_3	0.00273	0.73	-0.00108	0.46	0.078
Cl	0.00235	0.23	-0.00245**	0.25	0.049
	(cm/yr)		(cm/yr)		(cm/yr)
J_{inp}	-0.1022	0.12	0.1309	0.05	103
		BEECH THROUGHFALL			
	1969-1976		1976-1991		
	Trend (meq/L/yr)	R^2	Trend (meq/L/yr)	R^2	C_{avg} (meq/L)
Na	0.00448	0.16	-0.00161	0.21	0.068
K	0.00103	0.23	0.00273	0.57	0.096
Ca	-0.00907(*)	0.56	-0.00373*	0.55	0.17
Mg	-0.00049	0.38	0.00026	0.71	0.045
NH_4	-0.00059	0.38	0.00461	0.54	0.15
H	0.00051	0.29	-0.00924***	0.23	0.10
Al	-0.00011	0.22	-0.00048	0.22	0.022
SO_4	-0.01401	0.39	-0.01480**	0.36	0.35
NO_3	0.00013	0.50	0.00057	0.33	0.15
Cl	0.00405	0.29	-0.00232	0.35	0.11
	(cm/yr)		(cm/yr)		(cm/yr)
J_{inp}	-0.1168	0.14	0.00325	0.15	87
		BEECH SOIL WATER 90 cm			
	1969-1978		1978-1991		
	Trend (meq/L/yr)	R^2	Trend (meq/L/yr)	R^2	C_{avg} (meq/L)
Na	0.00449***	0.82	-0.00136*	0.52	0.094
K	0.00122*	0.41	-0.00082**	0.17	0.016
Ca	-0.00638	0.47	-0.00279***	0.49	0.085
Mg	0.00074	0.47	-0.00090***	0.59	0.045
NH_4	-0.00138	0.53	0.00029	0.11	0.009
H	0.01331***	0.74	-0.00399***	0.55	0.070
Al	0.02411**	0.79	-0.00656*	0.27	0.31
SO_4	0.04222***	0.79	-0.01144**	0.71	0.40
NO_3	-0.00012	0.35	0.00176	0.17	0.044

Table* 3 *continued.

SPRUCE THROUGHFALL

	1969-1976 Trend (meq/L/yr)	R^2	1976-1991 Trend (meq/L/yr)	R^2	C_{avg} (meq/L)
Na	0.00656	0.23	-0.00147	0.24	0.11
K	0.00384	0.23	0.00032	0.35	0.12
Ca	0.00044	0.48	-0.00751*	0.31	0.265
Mg	0.00241	0.42	-0.00032	0.40	0.064
NH_4	0.01061	0.22	0.00092	0.14	0.18
H	0.00797	0.17	-0.03071***	0.15	0.39
Al	0.00312	0.21	-0.00183**	0.20	0.049
SO_4	0.00983	0.24	-0.04291***	0.23	0.78
NO_3	0.01620**	0.35	0.00135	0.33	0.26
Cl	0.01070	0.24	-0.00275	0.27	0.16
	(cm/yr)		(cm/yr)		(cm/yr)
J_{inp}	0.0425	0.16	0.0209	0.20	77
			1976-1988 (meq/L/yr)		
Ca			-0.0122*	0.24	
Mg			-0.00295**	0.27	

SPRUCE SOIL WATER 90 cm

	1973-1978 Trend (meq/L/yr)	R^2	1978-1991 Trend (meq/L/yr)	R^2	C_{avg} (meq/L)
Na	0.01157**	0.89	-0.00361**	0.58	0.21
K	0.00176	0.25	-0.00041	0.62	0.024
Ca	0.01035*	0.59	-0.01400***	0.89	0.15
Mg	0.01481***	0.92	-0.00455***	0.83	0.11
NH_4	-0.0066	0.24	0.00048	0.09	0.009
H	0.03011***	0.78	-0.00331***	0.42	0.085
Al	0.19982**	0.92	-0.01961**	0.45	1.33
SO_4	0.22801**	0.89	-0.04503***	0.52	1.34
NO_3	0.01731	0.75	0.00392	0.77	0.23

(*), *, **, *** is significant at the 90, 95, 99 and 99.9% confidence level

[a] Trend equals A_t in Eq. [1] and [2])

[b] R-squares of the regression models (Eq. [1], [2])

[c] average annual volume-weighted solute concentrations and average annual water fluxes for the whole observation period.

Table 4. *Emissions of SO_2, NO_x, Dust and NH_3 in the Western and Eastern part of Germany (in kgx10^6) in the 1970s and 1980s (37).*

Western Germany	70/75	76/80	81/85	86/89	89/90
SO_2	2700	3400	2700	1500	950
NO_x	1500	2850	2900	2800	2650
NH_3	-	-	-	-	720
dust	1050	730	600	500	450
Eastern Germany					
SO_2	-	4300	4800	5300	5000
NO_x	-	600	600	650	650
NH_3	-	-	-	-	350
dust	-	2600	2400	2100	1900

The same holds for Mg, where downward trends in beech throughfall were no longer significant. Atmospheric deposition as well as foliar leaching contribute to base cation concentrations in throughfall. These contributions may be separated with the method described by Ulrich (35). For the spruce forest, we calculated that foliar leaching of Ca (contributing ca. 38% to throughfall concentrations of Ca) did not significantly change after 1979. Foliar leaching of Mg decreased between 1976 and 1988 (-0.00185 meq/L/yr), but not significantly. Thus, reduced Ca and Mg concentrations in throughfall at Solling resulted largely from deposition changes. As rates of Ca weathering in the soils at Solling are very low (Table 1), atmospheric deposition is the main source of Ca to the Solling forests. Though rates of Mg weathering are higher, deposition still represents a considerable source of Mg to the ecosystem (Table 1) (2, 35).

SOIL WATER, ACID ANIONS

Initital SO_4 concentrations in the spruce soil are low compared to throughfall concentrations and close to the estimated 'pre-monitoring' SO_4 concentrations (Figure 2). The increases in dissolved SO_4 in the spruce soil and, to a lesser extent, in the beech soil from 1969/1973 to 1978, are much higher than changes in throughfall concentrations. We previously explained the increase in dissolved SO_4 in the spruce soil (19) by relating to 'peaking' SO_4 deposition loads in the mid-1970s (Figure 2). These entered a mineral soil where the SO_4 sorption capacity was nearly saturated (19, 36, 38). The rather steep breakthrough of SO_4 in the spruce soil is consistent with independently measured, steep SO_4 adsorption isotherms of the Solling soil (19, 38), which predict that dissolved SO_4 is maintained at low levels (below 0.4 meq/L) until around 95% of the SO_4-binding capacity is saturated. The subsequent decrease in dissolved concentrations of SO_4 in both the spruce and beech soil after 1978 is most likely due to reduced atmospheric inputs (19).

SOIL WATER, BASE CATIONS

Base cation chemistry in the spruce soil and, to a somewhat lesser extent, in the beech soil before 1978 is characterized by increased solution concentrations and decreased adsorbed pools (except for Mg). Model stage I (Figure 1) illustrates how a strong increase in SO_4 levels, measured in soil solutions in Solling, mobilizes Al from soluble hydroxide pools which displaces base cations from exchange sites- a very well known phenomenon of soil acidification. Increased exchangeable Mg between 1973 and 1979 at both sites may be explained by increased weathering of Mg under the influence of decreasing pH, which dropped in both soils by 0.6 units up to the mid-1970s. Magnesium weathering from illite is substantial in Solling (Table 1) and was found to be strongly pH-dependent ($R \approx [H^+]^{0.7}$, (21)).

After 1978, concentrations of most dissolved base cations decreased significantly as expected from stages II and III of our sample simulations (Figure 1). As discussed in the section theory, historical data on exchangeable pools are then crucial to identify how the following contribute: (a) decreasing acid anion concentrations, (b) base cation deposition and (c) continued depletion of base cations in the soil, forced by high acid anion levels. First, we will focus on the spruce soil. Table 2 shows that pools of exchangeable base cations in the spruce soil decreased in the 1980s. Therefore, the field data suggest that depletion of exchangeable bases in the spruce soil continued in the 1980s, while SO_4 levels decreased. Model stage IIIb shows that on the time scales and under the soil conditions considered, we expect atmospheric deposition of base cations to affect pools of exchangeable and dissolved base cations in the soil. Indeed, mass balance calculations show that since 1979, the Ca flux with throughfall under spruce decreased cumulatively in the order of around 3.0 keq/ha, and the pool of exchangeable Ca by 3.9 keq/ha: a strong indication that deposition has contributed to the decrease in exchangeable Ca after 1979. Note that Ca weathering at Solling is very low (Table 1) and contributes little to mass balance calculations. Furthermore, it was assumed that bio-element cycling of Ca was a constant factor (2).

For the Hubbard Brook case study, Kirchner (18) stressed the role of continued exchange of adsorbed base cations against Al, while acid anion concentrations decreased, a phenomenon illustrated by model stage II (Figure 1). This process may occur in the spruce soil where Na and K concentrations in throughfall showed no time trends. Still, Table 2 suggests a decrease of exchangeable Na and K in the 1980s. As for Ca, other biogeochemical processes affecting the water chemistry of Na and K were either insignificant (weathering, Table 1) or presumed constant with time (bio-element cycling (2)). Thus in addition to reduced deposition (Ca/Mg), continued depletion of base cations in the spruce soil may be forced by continuously high acid anion concentrations. In the adjacent beech soil, dissolved SO_4 concentrations are less than one-third of those in the spruce soil, and showed a comparatively strong decline in the 1980s. Furthermore, base cation concentrations in throughfall under beech declined less than under spruce. Modeling results for stage IIIa suggest that these factors may account for the slight recovery of exchangeable base cation pools observed in the beech soil (Table 2).

CONCLUSIONS

Long-term monitoring of water chemistry and exchangeable cations in the forested ecosystems at Solling were shown to be of great value, as various theoretical response stages of dissolved and exchangeable base cation pools in the soils, each with different deposition or soil processes dominating, could be identified from this field study. The effects of reduced base cation deposition and continued high SO_4 levels on dissolved and exchangeable base cations in the soil, as observed at Solling, are supported by other long-term studies at Hubbard Brook (7) and Birkeness (8), respectively. Continued present and future monitoring at Solling will be needed to verify the recovery of base saturation in response to reduced acid SO_4 deposition observed in the beech soil.

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Chapter 3

Mechanisms and rates of silicate weathering at Solling, Germany

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ABSTRACT

Weathering rates at the field scale generally are one to three orders of magnitude lower than rates inferred from experiments in the laboratory. Understanding these large discrepancies is a prerequisite for derivation of weathering rates from relatively cheap and reproducible laboratory studies. In this study we investigated illite weathering in an acid forest soil, in the German Solling area. Weathering rates in the field were estimated from input-output element budgets and elemental analysis of the soil profile. Factors that control weathering kinetics were manipulated in various types of dissolution experiments in the laboratory, where pH, temperature, mineral saturation and soil depth affected release rates of Mg and K. Analysis of the effect of temperature showed that K-release from illite was controlled by interlayer diffusion while Mg-release was chemically controlled. The results from the laboratory experiments were fitted with two equations, which were subsequently used to estimate weathering rates under field conditions. Predicted rates of K-weathering in the field were comparable to rates inferred from field methods, whereas Mg-weathering was overestimated by a factor 2 to 4. For both elements the original discrepancy with field rates was 2 orders of magnitude.

INTRODUCTION

Mineral weathering is an important nutrient source in terrestrial ecosystems, especially in ecosystems where pools of exchangeable base cation have been depleted, e.g. by soil acidification or intensive agricultural use. Weathering of parent material also strongly determines soil formation (Jenny, 1941) and ground water quality. So, quantification of weathering rates at field conditions is of importance to (i) asses the vulnerability of terrestrial ecosystems to, human, disturbances and (ii) understand and predict the time scales of soil formation.

There are several approaches to quantify rates of mineral weathering. At the field scale one may estimate 'historical' weathering from the bulk-chemistry of the soil; mineral pools are compared with the composition of a reference C-horizon or parent rock, taking a relatively stable mineral as an internal standard (Tarrah, 1988; Flehmig et al., 1990; Olsson and Melkerud, 1991). Weathering rates obtained with this method usually reflect thousands of years of weathering, but the environmental conditions during the past thousands of years may have been quite different from those today. Also, if a C-horizon is used as reference, its weathering status is often unknown. Present field weathering rates can be estimated from element budgets at the scale of a soil profile or catchment. Weathering rates are calculated from the balance of atmospheric input, output by net uptake in biomass, and output with drainage or stream water. At best, these studies extend over two decades (Matzner, 1989; Kirchner, 1992), however, they face considerable uncertainties in the input flux of dry atmospheric deposition and in changes in the pools of exchangeable cations.

At the field scale, manipulation and control of the soil system is difficult, especially when a slow process like mineral weathering has to be studied. Therefore, the most widely applied method to assess weathering rates, is to decrease the spatial scale to a soil column, or batch experiment in the laboratory. Often, the temporal scale of observation decreases concurrently. In the laboratory, experimental conditions can be controlled and a system can be manipulated to obtain information on rates and mechanisms of mineral weathering. A number of methods for studying weathering in the laboratory presented in the literature (for a review see van Grinsven and van Riemsdijk, 1992) have focussed on the role of pH (Sverdrup, 1990), organic molecules (Manley and Evans, 1986), flow rate (van Grinsven and van Riemsdijk, 1992), mineral pretreatment (Holdren and Berner, 1979) and surface characteristics (Anbeek, 1992). However, rates obtained from laboratory experiments are generally 1 to 3 orders of magnitude higher than rates obtained from field studies (e.g. Schnoor, 1990).

Appreciating the advantages and disadvantages of the several approaches to assess weathering rates, we remain with the question of how to explain the high rates of mineral weathering under laboratory conditions, and their discrepancies with rates observed in the field. Such an explanation could lead to a method to extrapolate weathering rates obtained at the laboratory scale to the field situation.

In this paper, we determine rates and mechanisms of silicate weathering from an acid forest soil in the German Solling area (Ellenberg, 1971; Matzner, 1989). Forests ecosystems in this area are strongly impacted by acid deposition. As a result the soils at Solling have been depleted in exchangeable base cations (base saturation <4%), which emphasizes the importance of quantifying base cation weathering rates. The soil under investigation is located in an experimental forest where the chemistry of bulk precipitation, throughfall and soil solution has been measured since 1969 (Matzner, 1989). At Solling, field observations also include repeated measurements of pools of exchangeable cations. Using this unique long-term data set we derive field weathering rates by calculating input-output mass balances. Furthermore, 'historical' weathering rates are estimated from elemental analysis of the soil profile.

Next, the effect of soil depth, solution chemistry (e.g pH), mineral saturation and temperature on mineral weathering, as determined in a number of laboratory experiments, is discussed. All these factors are considered to influence weathering rates in the field and are therefore potential parameters of a predictive weathering model. The weathering experiments focus on release of K and Mg from illite, the main reactive mineral source of these elements at Solling. The laboratory experiments are used to estimate parameters of proposed rate equations that describe release of Mg and K from illite. Subsequently, these rate equations are used to calculate K and Mg release at field conditions, and predictions are compared with the rates inferred from field methods.

THEORETICAL DESCRIPTION OF WEATHERING KINETICS

A general expression for the rate of mineral dissolution can be derived from transition state theory (Aagard and Helgeson, 1982; Nagy et al., 1991):

$$R_w = k \cdot \prod (a_i)^{m_i} \cdot (1 - e^{[\frac{n \Delta G}{RT}]^n}) \qquad [1]$$

R_w is the dissolution rate, k is a rate constant, a_i is the activity of species *i* in solution, ΔG is the energy of the overall reaction, R the gas constant and T the temperature, *m* and *n* are constants. For dissolution of silicates below pH5, the first term in Eq. [1] reduces to a_H^{mH} (Aagard and Helgeson, 1982), and Eq. [1] can be rewritten to:

$$R_w = k \cdot (H^+)^m \cdot (1 - [\frac{IAP}{Q_{eq}}]^n) \qquad [2]$$

where Q_{eq} is the equilibrium constant and IAP the ion activity product for the dissolution reaction. Eq. [2] was applied to illite weathering by van Grinsven et al. (1986); it describes a proton-dependent detachment rate of an activated complex on the mineral surface, with decreasing rate of detachment as solutions approach equilibrium with respect to a mineral phase (Nagy et al., 1991). Here Q_{eq} will be defined as the equilibrium product for the dissolution of a hypothetical Mg-Al-Si illitic phase :

$$Mg_aAl_bSi_{3.5}(s) + (2a+3b)H^+ \rightarrow aMg^{2+} + bAl^{3+} + 3.5Si$$

with

$$Q_{eq} = \frac{(Mg)^a \cdot (Al)^b \cdot (Si)^{3.5}}{(H)^{2a+3b}} \qquad [2a]$$

Diffusion controlled release of potassium from illite interlayers can be described by Fick's first law of diffusion: $J=D\cdot\partial x/\partial c$. The cumulative K release (M_K) during a time interval is equal to the time integral of J. For steady state diffusion it is written:

$$M_K = \int_0^t D\cdot\frac{\partial c}{\partial x} = k'\cdot(K_{crit}-K_{bulk})\cdot t \qquad [3a]$$

For non-steady state diffusion (Luce et al., 1972):

$$M_K = \int_0^t D\cdot\frac{\partial c}{\partial x} = k''\cdot(K_{crit}-K_{bulk})\cdot t^{0.5} \qquad [3b]$$

In both equations, a critical potassium concentration (K_{crit}) is defined, which may be regarded as the concentration of K close to the mineral surface (Mortland, 1958). K_{bulk} is the potassium concentration in the bulk solution. At solution concentrations below K_{crit}, a net release of K occurs, whereas above K_{crit} fixation in the illite interlayers occurs.

MATERIALS AND METHODS

All experimental data were obtained from a monitoring site in the Solling experimental forest, Germany. This site has been part of the International Biological Program (IBP) since the 1960s (Ellenberg, 1971). The site is located on the Solling plateau, 800 m above sea level. The soil was classified as a spodo-dystric Cambisol and carries a 110 years old spruce forest (Picea abies Karst.). A detailed site description is given by Ellenberg et al. (1971) and Matzner (1989). Our analysis focused on the upper 90 cm of the mineral soil. The upper 60 to 75 cm of the profile consists of loess deposited approximately 10,000 year ago, followed by a layer of loess mixed with weathered triassic sandstone down to 90 cm depth. The soil fraction <2mm contains approximately 10% feldspars and 18% illitic minerals. Mass fraction (%) of MgO increase from 0.35 at 5 cm depth to 1.03 at 75 cm depth. Mass fractions (%) of K_2O increase from 1.9 at 5 cm depth to 3.24 at 75 cm depth. X-ray analysis (Table 1) showed an increase of 1.0 nm illite minerals with depth with a concurrent decrease of vermiculite. The X-ray observations are consistent with a simple transformation if 1.0 nm illite to 1.4 nm vermiculite due to weathering or replacement of interlayer K. Most likely, chlorite was formed by Al-hydroxy interlayering of illite during soil formation (Tarrah, 1988). Minor amounts of kaolinite were found throughout the profile. There was no evidence of smectite presence. Hereafter, the illite/vermiculite/chlorite assemblage will be referred to as illite.

Table 1. *Mineralogy of Solling <2µm soil by X-ray powder diffraction.*

	Illite[1]	Vermiculite[2]	Chlorite[3]	Kaolinite[4]
5-10 cm	+	+++	-	+
10-15 cm	+	+++	(+)	+
40-50 cm	++	++	+	+
60-75 cm	+++	+	+	+

Identification criteria:

[1] 1.0 nm on Mg-saturation

[2] 1.4 nm on Mg-saturation, no changes on glycerolation, collapse to 1.0 nm on K-saturation at 150°C

[3] as 2 but no collapse on K-saturation at 150°C

[4] 0.7 nm on Mg-saturation, 0.7 nm on K-saturation at 150°C

Mineral presence ranges from minor amounts, (+), to abundant, +++.

Historical weathering

The bulk chemistry of 6 particle size fractions at depth intervals of approximately 10 cm was measured by X-ray fluorescence spectrometry (XRD) (Großkurth, 1993, unpublished data). Samples were air-dried, organic matter was removed by oxidation with H_2O_2 at room temperature, and particle size fractions were separated gravimetrically. Unfortunately, the Solling profile contains no C-horizon of loess material. A profile 30 km south-east of Solling (location Spanbeck; Tarrah, 1988), however, consists of a >180 cm deep homogeneous loess deposit with a mineralogy similar to that of the Solling site. We assumed that the bulk chemistry of the Spanbeck soil at 180 cm depth is representative of the parent material of the upper 60 cm loess layer at Solling. ZrO in the 6-60 µm particle size fraction, where it was most abundant, was used as an internal standard oxide. As no ZrO content was available for the reference C-horizon of the Spanbeck profile, it was calculated as $ZrO_{ref,180cm}=SiO_{2,ref,180cm}/SiO_{2,\ Solling\ 60cm}*ZrO_{Solling\ 60cm}$.

Weathering rates were calculated according to Eq. [4], exemplified for K:

$$R_w = \sum_{x=0cm}^{60cm} [\frac{M_{ref.ox,\,\Delta x}}{M_{ref.ox,\,rs}} \cdot M_{K_2O,\,rs} - M_{K_2O,\,\Delta x}] / M_{K_2O} 2 \cdot \rho_{\Delta x} \cdot \Delta X / \Delta T \cdot 10^3 \qquad [4]$$

where:

R_w = weathering rate (kmol$_c$ ha^{-1} yr^{-1})

Δx = layer of thickness Δx(cm), over which mineral contents were averaged

ΔT = assumed time period over which weathering occurred (yr)

ρ = bulk density of layer-Δx (g cm^3)

M = mass% of element oxides

rs = reference samples

Weathering from element budgets

The Solling data set provides an 18 year continuous time series of the chemistry of bulk precipitation, throughfall and soil water. For a detailed description of monitoring procedures we refer to Matzner (1989). Weathering rates were estimated from the balance of atmospheric inputs, output with drainage water at 90 cm depth, estimated output by net uptake in biomass, and measured changes of element storage in litter and exchangeable pools over the period 1979-1991. Matzner (1989) calculated weathering rates for the period 1973-1983 with this method. Here, we discarded the first 6 years of the observations in Solling, because during this period the pool of exchangeable base cations decreased appreciably (Matzner, 1988), which introduced large uncertainties in the calculation of (low) weathering rates. Weathering was calculated as:

$$R_{w,x} = -\sum_{1973}^{1991} J_{x,atmosp.} + \sum_{1973}^{1991} J_{x,\,90cm} + \sum_{1973}^{1991} J_{x,net\ upt.} + \Delta S_{x,litter} - \Delta S_{x,ex} \qquad [5]$$

where:

$R_{w,x}$ = weathering rate (kmol$_c$ ha^{-1} yr$^{-1)}$

X = elements Na, K, Ca, Mg and Al

$J_{x,atmosp}$ = Atmospheric deposition fluxes, calculated from measured monthly throughfall water fluxes, bulk deposition and estimated dry deposition as described by Matzner (1988, 1989).

$J_{x,90cm}$ = Solute drainage fluxes at 90 cm, calculated from measured monthly soil water concentrations and calculated water fluxes (Wesselink et al., 1994) .

$J_{x,net\ upt'}$ = Net uptake of elements in biomass, as given by Matzner (1988).

ΔS_{litter} = changes in element storage in litter, estimated from inventories in 1979 and 1983 (Matzner, 1989).

ΔS_{ex} = change in pools of exchangeable cations, estimated from inventories in 1973, 1979, 1983 (Matzner, 1988) and 1991.

Weathering from laboratory experiments

Background

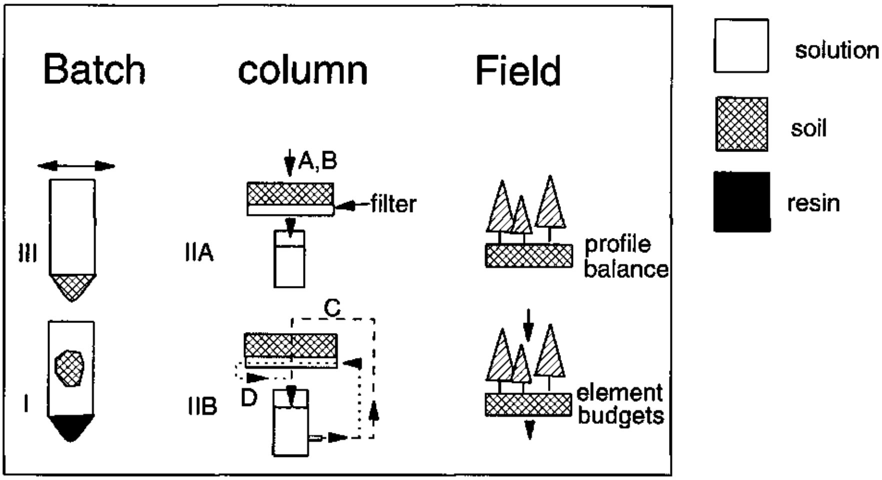

Figure 1. *Experimental methods used to measure weathering rates: I. batch-resin, IIA. column through-flow and IIB. column recirculation, III. batch-equilibrium, and field estimates from bulk chemistry of the soil (profile balance) and input-output element budgets. For detailed explanation of the experiments see text.*

Experimental methods used to study weathering in the laboratory are shown in Fig. 1. The experiments aimed at finding parameters for and testing of equations [2] and [3] that describe mineral weathering. In experiment I, a batch-resin experiment, solution chemistry was controlled at conditions strongly undersaturated with respect to all relevant mineral phases. From these experiments the rate constants *k* in Eq. [2] and [3] could be estimated. Also, at constant and very low concentrations of K_{bulk} (Eq. [3]), the cumulative release of K would show whether the release of K was linear with time (Eq. [3a]) or with the square root of time (Eq. [3b]). To account for the effects of temperature and soil depth on the rate constants, experiment I was carried out at 2 temperatures, 18°C and 5°C, with soil from 10 cm and 40 cm depth. In experiment IIA, a through-flow column experiment, the input solution chemistry was manipulated to estimate the pH-dependency of weathering and estimate parameter *m* in Eq. [2]. The flow-through columns of experiment IIA were recirculated in experiment IIB, which forced a continuous increase of reaction products in the system. Experiment IIB was carried out to estimate the parameters Q_{eq} and *n* in Eq. [2]. The occurrence of a 'critical' K-concentration (K_{crit}), as given in Eq. [3], was studied separately in experiment III. In a batch experiment, non-specifically bound K was removed, different initial K concentrations were added, and the kinetics of K-release or fixation with time were studied. Details on the experimental setup are given below.

experimental setup

Experiment I: Batch-resin experiments. Three grams of air-dried soil were put in a dialysis bag and subsequently in a small vessel with 20 ml of 10^{-3}M HCl. Two grams of H-saturated cation exchange resin (Dowex, 150-300μm) were added. The exchange resin controlled pH at 2.75 and accumulated cation released from the soil. Cation concentrations in solution remained low; after 4 weeks concentrations of K, Mg and Al in solution were 10, 3 and 300 ppb respectively. The aqueous pools of Mg and K were negligible compared to those accumulated on the exchange-resin. The first resin replacement after 14 days was discarded, because blank samples (with resin only) still contained adsorbed base cations. Probably, after the first extraction, a large part of exchangeable K and Mg was removed. Feigenbaum and Shainberg (1975) reported in a similar experiment that readily exchangeable K was removed within 2 hours. Hereafter, the resins were replaced after 21, 57 and 156 days. Reaction products adsorbed on the resin were retrieved by slow percolation with 25 ml of 2M HCl. K and Mg were analyzed by atomic absorption spectrometry (AAS) and Si was determined by colorimetry (blue silica molybdic acid complex). All batch experiments were carried out in duplicate with soil material from 10 cm and 40 cm depth at two temperatures: 5° and 18°C.
Experiment II: Column experiments. Air-dried soil from 40-50 cm depth was packed in soil columns (4.5 cm diameter, 1 cm height) which were leached under different percolation

conditions.

IIA. flow-through experiments. Before starting the actual experiments, the columns were percolated with 60 ml of 0.1 M $Ba(Cl)_2$ solution to remove exchangeable base cations, and for 3 days with HCl (pH 3.0) at a rate of approximately 2 ml h^{-1}. Subsequently, column A was percolated with HCl (pH 3.2) solution for 700 hours followed by a percolation with a $1 \cdot 10^{-3}$M $(Al)_2(SO_4)_3$ solution (pH 2.82) for 600 hours. Column B was percolated with a $0.4 \cdot 10^{-3}$M $(Al)_2(SO_4)_3$ solution (pH 2.82) for 700 hours followed by percolation with a $1 \cdot 10^{-3}$M $(Al)_2(SO_4)_3$ solution (pH 2.82) for 600 hours. Percolation rates were approximately 1.3 ml h^{-1} in these experiments.

IIB. recirculation experiments. In column C, the initial input solution of HCl (pH 3.2) was recirculated for 700 hours. Sampling was done from a recirculation vessel (Fig. 1). A similar experiment was carried out with column D, however, solution was not recirculated through the soil column but through a water reservoir connected to the soil column by a porous filter (Gelman, Versapor-200, 0.2µm pore size). Thus transport of reactants and reaction products in the soil column was by diffusion only (Fig. 1). In the column experiments, ultra pure water was used. Samples obtained during the experiments were stored at 3°C. Na, K, Ca and Mg were analyzed by atomic absorption on a Perkin-Elmer graphite tube auto-analyzer system. Al and Si were determined by colorimetry (measuring Al-pyrocatechol violet respectively blue silica molybdic acid complex).

Experiment III: Batch experiments. The effect of the K concentration in solution on release from or fixation in illite interlayers and the occurrence of a critical K-level (K_{crit}) was tested in batch experiments. Potassium in illite can be found 'fixed' in interlayers, specifically adsorbed on so-called 'wedge-sites' or non-specifically adsorbed on planar (external surface) sites (Fanning and Keramidas, 1977). Twelve samples of 2.5 grams of soil from 10 cm and from 40 cm depth were washed with 3 subsequent aliquots of 20 ml of 0.1M $Ba(Cl)_2$, to remove non-specifically adsorbed K. Next, 20 ml batches of 0, 5, 10, 30, 100 and $300 \cdot 10^{-6}$M KCl in a 0.01M $Ba(Cl)_2$ background were added to duplicate soil samples. Samples were gently shaken at room temperature. After 0.5, 2.5, 24, and 300 hours, samples were centrifuged and K-activity was measured with an Orion model 93-19 K-selective electrode. A linear calibration curve was obtained for the experimental concentrations range between $3.2 \cdot 10^{-6}$ and $0.3 \cdot 10^{-3}$M of K.

RESULTS AND DISCUSSION

FIELD

Table 2A. *Present weathering rates in the 0-90 cm Solling soil obtained from element budgets in the Solling spruce site for the period 1979-1991. Positive signs indicate sources, negative signs sinks.*

	Mg	K	Ca	Na	Al	
Σatmospheric input	3.1	2.4	10.3	8.5	3.2	($kmol_c$ ha^{-1})
Σdrainage output	-5.8	-1.1	-7.7	-10.4	-91.2	"
Σnet uptake	-1.1	-1.9	-3.9	*	*	"
Δlitter	-1.5	-1.0	-3.9	*	*	"
Δexchange	1.3	1.0	4.4	1.3	-8.0#	"
ΣWeathering	4.0	0.8	0.8	0.6	96	"
Weathering	0.33	0.06	0.06	0.05	8.0	($kmol_c$ ha^{-1} yr^{-1})

* assumed to be negligible
\# assumed to equal the sum of exchangeable base cation loss

Table 2B. *Historical weathering rates in the 0-60 cm Solling soil over the past 10,000 years and molar Mg:K:Al:Si ratios of weathering.*

	Mg	K	Ca	Na	Al	Si	
Weathering	0.30	0.20	0.083	0.077	1.60	1.46	($kmol_c.ha^{-1}.yr^{-1}$)
Molar ratios	0.36	0.47			1.3	3.5	

Historical and present field weathering rates calculated from Eq. [4] and [5] are given in Table 2. The calculation of weathering rates from element budgets involved uncertainties in all fluxes considered. Yet, positive weathering fluxes were calculated which were in the same order as the independently derived historical rates. The estimates of present weathering rates of Mg and K compare well with those given by Matzner (1989) calculated for the period 1973-1983 (0.36 and 0.08 $kmol_c.ha^{-1}.yr^{-1}$ respectively). Contrary to the 1973-1983 period (Matzner, 1989), positive weathering rates were calculated for Ca and Na in the 1979-1991 period.

Weathering rates of Ca, Na and K release for the past 10,000 years and for the present can be considered as low. For Ca, the annual release is even lower than the net annual storage of Ca in biomass (Matzner, 1989), which emphasises the role of atmospheric deposition as a source of Ca to the forest. As K-release from microcline feldspar is generally considered to be slower than Na-release from albite (e.g. Sverdrup, 1990), the estimated K release can be largely attributed to the weathering of illite. All Mg release is presumably from clay mineral dissolution, as the Solling soil contains no other Mg bearing minerals. Note, that the molar K:Mg:Al:Si ratio of illite in the C-horizon of the reference profile was estimated at 0.5:0.29:2.0:3.5 (Tarrah, 1989), whereas long-term weathering at Solling occurred at a ratio of 0.47:0.36:1.3:3.5 (see Table 2). Therefore, dissolution of illite appears to be non-stoichiometric and preferentially for Mg (Tarrah, 1989).

Interpretation of differences between historical and present rates of element release is difficult, because both pH and mineralogy will have changed considerably during the past 10,000 years. Present rates may be lower than historical rates due to depletion of mineral pools, which seems the case for K. On the other hand, the Solling soils receive high anthropogenic acid depositions (Matzner, 1989, 1989), which may have enhanced mineral weathering, as is probably the case for Mg. Enhanced weathering due to anthropogenic acidification obviously explains the present high rate of Al-release, which is 6 times higher than the average over the past 10,000 years.

LABORATORY

parameter estimation

Results of the laboratory experiments were used to estimate the parameters of the proposed rate Eq. [2] and [3] by means of non-linear regression (SPSS). k'' in Eq. [3b] was estimated from the cumulative K-release in experiment I (batch-resin) and IIA (column flow-through). Parameters a, b, and Q_{eq} in Eq. [2] were estimated from experiment IIB (column recirculation). Parameters k and m in Eq. [2] were estimated from experiments IIA (column flow-through) as well as from experiments I, IIa and IIb. As estimation of parameter n in Eq. [2] proved difficult, all experiments were used in its estimation. Results are given in Table 3.

Experiment I+II (batch resin and column-throughflow)

The cumulative release of K and Mg in the batch-resin experiments is shown in Fig. 2. Linear release curves were obtained for Mg, except for the 40cm/18°C samples, where the release seems to be curve-linear with time. For K, parabolic release curves were obtained, except for the 10cm/18°C samples. A pronounced effect of sampling depth was found on release rates of Mg. In the experiment at 5°C, the release from the 40 cm samples was 1.5x the release from the 10 cm samples, which compared well with the gradient of Mg-oxide with depth as obtained from the XRF analysis (mass fractions (%) of 0.38 for MgO at 10 cm and 0.61 for MgO at 40cm). The dependency of K-release on soil depth was minor at 18°C and it changed with time for the 5°C experiment. The low dependency of K-release on soil depth is also evident from the K_2O contents (XRF). Mass fractions (%) of K_2O were measured at 2.4 at 40cm depth and 1.97 at 10 cm depth. Fig. 2 shows a higher release rate of K and Mg in the 18°C experiments. A measure for the effect of temperature on reaction rate is given by the Arrhenius activation energy, E_a (e.g. Sparks, 1988). For Mg, E_a was calculated at ±61 kJ mol^{-1} in the 10 cm samples and ±76 kJ mol^{-1} in the 40 cm samples. For release of K, E_a was calculated at ±38 kJ mol^{-1} for the 10 cm samples and at ±18 kJ mol^{-1} for the 40 cm samples, during the first 57 days.

***Table 3.** Estimated parameters for Mg and K release according to Eq. [2] and [3b], Standard error of estimates, R^2 of model fit, number of observations, and experiments from which observations were obtained. Parameters refer to experiments at 18°C with soil material from 40/50cm depth.*

Eq. [2]		est.	Std.err.	R^2	n	Exp.
$\log(Q_{eq})$	-	-4.54	0.99	0.98	10	IIb
a	-	1.03	0.092	"	"	IIb
b	-	0.15	0.51	"	"	IIb
n	-	0.28	0.42	0.58	28	I, IIa, IIb
k	$mol^{-1}.kg^{-1}.h^{-1}$	$2.03 \cdot 10^{-5}$	$6.02 \cdot 10^{-5}$	0.39	14	IIa
m	-	0.69	0.37	"	"	IIa
k	$mol^{-1}.kg^{-1}.h^{-1}$	$2.08 \cdot 10^{-4}$	$3.04 \cdot 10^{-4}$	0.58	28	I, IIa, IIb
m	-	0.99	0.22	"	"	I, IIa, IIb
Eq. [3b]						
k"	$l.g^{-1}.h^{-1/2}$	0.435	0.025	0.89	13	I, IIA

Figure 3 shows the cumulative release of Mg, K, Al and Si from the flow-through column experiment (IIA) and the first observation points of the batch resin experiment I. Whereas the release of Mg responded strongly on pH, releases of K seemed unaffected (Fig. 3).

Dynamics of K and Mg release differed strongly in experiments I and II. The parabolic release curves of K are indicative for diffusion controlled release as described by Eq. [3] (Luce et al., 1972). Activation energies of K release were <40 kJ mol^{-1}, which is also indicative for diffusion controlled release (Sparks, 1988). Mortland and Ellis (1959) report an E_a of 15 kJ mol^{-1} for diffusion controlled release of K from vermiculite. The activation energy for Mg release was >40 kJ mol^{-1} suggesting chemically controlled release rates (Sparks, 1988).

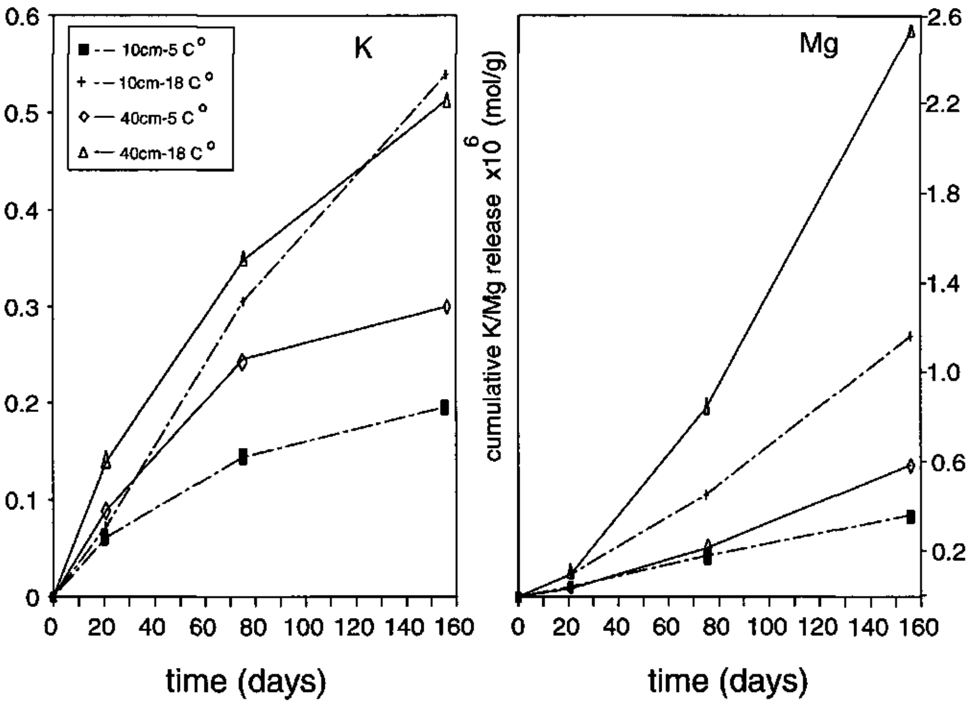

Figure 2. *Cumulative release of K and Mg in batch resin experiments. Samples from 10cm at 5°C (□), 10cm/18°C (+), 40cm/5°C (◊) and 40cm/18°C (Δ). Averages of duplicate measurements are shown.*

The different nature of Mg and K release is also apparant from their response to pH changes (Fig. 3). The effects of pH on K release from illite have been discussed extensively in the literature. Our results confirm those of e.g. Wells and Norrish (1968), who also concluded that pH was of minor importance in the replacement of interlayer K from illite. In a recent paper, Simmard et al. (1992) studied K and Mg release in mica containing soils. They found no relationship between the amount of K and Mg released with citric acid. In contrast to our experiments, however, these authors reported a parabolic release curve also for Mg.

Experiment IIB (column recirculation)

A general rate equation for chemically controlled release of Mg from illite is given by Eq. [2]. In experiment IIB the effect of the equilibrium term in Eq. [2] (IAP/Q_{eq}) on release of Mg was investigated. Solutions were recirculated (Fig. 1, column C+D) and dissolved reaction products were allowed to accumulate.

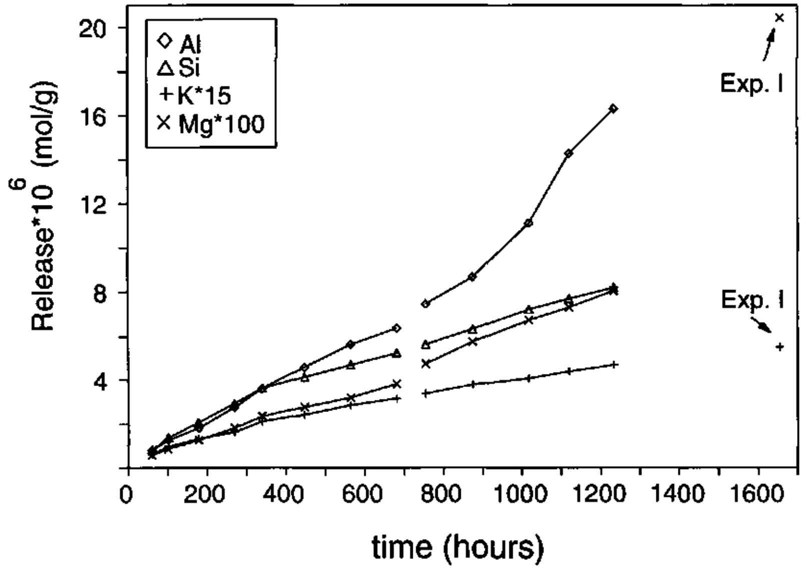

Figure 3. Cumulative release of K, Mg, Al and Si in flow-through column experiments, calculated as column output minus column input. 0-700h: input solution HCl (pH 3.2), output pH ≈3.8. 700-1300h: input solution $3.10^{-3}N\ Al_2(SO4)_3$, (pH 2.8), output pH ≈3.35. For K and Mg, releases from experiment I (pH 2.75) are also indicated.

Typically, concentrations of Mg, Al, Si, and pH in the recirculated solutions remained constant after 400 hours. Different equilibrium concentrations for Mg, Si, Al and pH were reached in columns C and D, after 400 hours. These equilibrium concentrations were used to estimate the stoichiometry and equilibrium solution activity product of the illitic phase controlling Mg release (Fig. 4). Parameters *a* and *b* give the reaction stoichiometry for the dissolution of a Mg-Al-Si illitic phase (Eq. [2a]). The molar ratios of dissolution obtained from experiment IIb (0.15:1.03:3.5) suggest non-stoichiometric dissolution of illite, as molar Mg:Al:Si ratios of illite in the surface soil of our reference profile (0-40 cm: Tarrah, 1989) were estimated at 0.14:2.4:3.3. Non-stoichiometric weathering was also apparent from the long-term, historic, weathering rates obtained for Solling (see *FIELD* discussion).

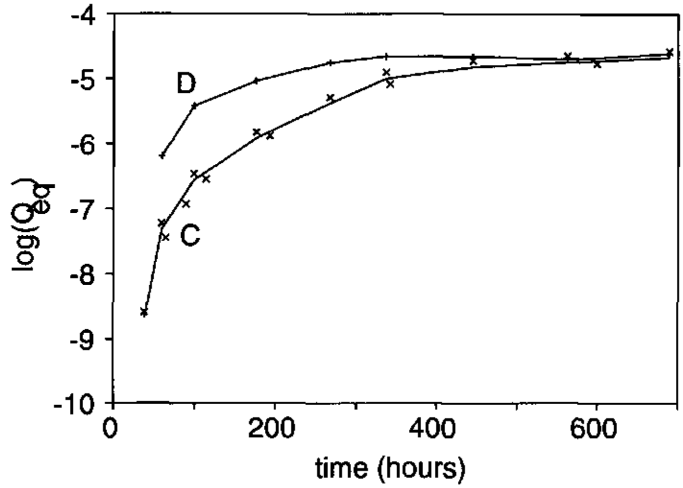

Figure 4. *Activity products of hypothetical illitic phase: $Q=(Mg)^a(Al)^b(Si)^{3.5}$, where brackets indicate solution activities. a and b were estimated at 0.15 and 1.03 respectively by minimizing the differences in Q-values from column C and D after 400 hours (Table 3).*

Experiment III (batch)

A general rate equation for diffusion controlled release of K from illite is given by Eq. [3]. Figure 5 shows the K concentrations in solution and the amounts of K released to, or retrieved from solution in the batch experiment III after 2.5, 24 and 300 hours. During the first 24 hours, kinetics of K release and fixation were fast compared to the batch-resin experiment I, probably due to ad- or desorption on selective 'wedge' sites (Fanning and Keramidas, 1977). From 24 hours on, the release slowed down, most likely due to diffusion controlled release or fixation of interlayer K. A 'critical' K-concentration is apparent from Fig. 5, which seems to confirm the validity of the proposed Eq. [3b] for K release. K_{crit} was estimated at $17 \cdot 10^{-6}$ M for the 40 cm samples and $27 \cdot 10^{-6}$M for the 10 cm samples. At bulk solution concentrations below K_{crit}, K was released to solution, whereas K was retrieved from solution when the K-concentration in the bulk solution was higher than K_{crit}.

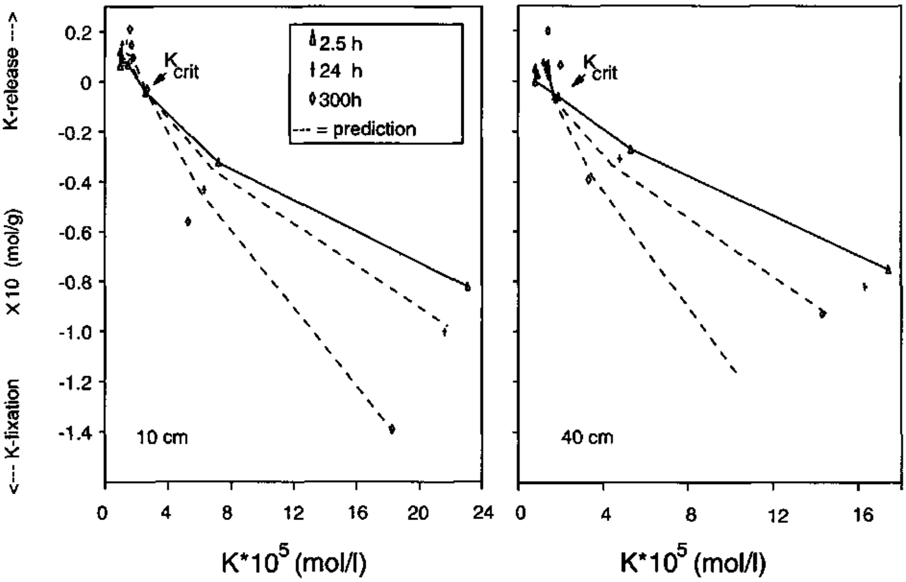

Figure 5. K-kinetics in batch-equilibrium experiment III. Shown is the quantity of K adsorbed (-) or released (+) by the Ba-saturated soil, against K activity measured in the bulk solution. Initial concentrations were: 0, 5, 10, 30, 100 and 300·10^{6}M KCl in a 0.01M Ba(Cl)$_2$ background. Averages of duplicate measurements and predicted K-dynamics are shown.

MODEL VALIDATION

Eq. [3b] was independently tested by using it to predict the slow kinetics of K-release in batch experiment III between 2.5 and 300 hours. Rate constant k'' in Eq. [3b] was estimated from the experiment I and IIa (Table 3), whereas the K_{crit} value obtained in experiment III was used. Potassium concentrations measured after 2.5 h in experiment III (Fig. 5) were used as initial values in Eq. [3b]. Predicted and measured K concentrations at 24 and 300 hours are shown in Fig. 5. Predictions seem to compare well with observations, except for the highest K-concentrations (>50·10^{-6}M) in the 40 cm samples. Bulk solution concentrations of K exceeding 50·10^{-6}M are, however, not representative for soil solutions in Solling, where K concentrations are in the range of 10 to 40·10^{-6}M.

Parameter of the Mg release model (k=2·10^{-5} and m=0.69, Table 3), obtained from the flow-through column experiments IIa, were used to predict release of Mg in the batch-resin experiment (40cm/18°C). The calculated release, however, underestimated the observations by a factor 3. Probably, release of Mg in the batch-resin experiments was enhanced compared to the column experiment, due to much lower Al-concentrations in the bulk solution. Sverdrup (1990) reported an increase of mineral weathering with decreasing Al concentrations. Also, dissolution of protective Al-coatings, or Al-interlayers, as reported by van Grinsven (1988) may have enhanced Mg-release. Because we had little certainty about the actual cause of the differences in Mg-release in experiment I and II, a second estimate of *k* and *m* was made, which included results from all experiments (Table 3).

Note, that estimates of *k*, *b* and *n* (Eq.[2]) were not significant (Table 3), which most probably results from an over-parameterization of Eq. [2], but may also result from an inappropriate model structure (i.e. Eq. [2]). Therefore, independent experiments to further test the validity of Eq. [2] are needed.

EXTRAPOLATION TO THE FIELD

To extrapolate laboratory observations to the field, Eq. [2] and [3b] were applied to field conditions. The predicted field rates were compared with the measured field rates shown in Table 2. Weathering rates were predicted for the upper 60 cm of the Solling soil. The predictions were carried out stepwise (Table 4) and started with the rates derived from experiment I (pH 2.8, 18°C). Next it was corrected for:

1) soil depth: from the batch-resin experiments with soil from 10 cm and 40 cm depth, it appeared that release of Mg was linearly related to contents of MgO. Therefore, a linear relation between rate constants *k* in Eq. [2] and MgO-contents was assumed. For K-release the dependency on depth of sampling was less clear. For the purpose of extrapolating to field conditions, it was assumed that *k''* in Eq. [3b] was independent of depth. Detailed data on bulk density were available (Großkurth, 1993, unpublished data).

2) temperature: to correct *k* and *k''* in Eq. [2] and [3b] for temperature, activation energies as derived in experiment I were used: 61 kJ mol^{-1} for Mg-release in the 0-30 cm soil and 76 kJ mol^{-1} for Mg-release in the 30-60 cm soil, 38 kJ mol^{-1} for K-release in the 0-30 cm soil and 15 kJ mol^{-1} for K-release in the 30-60 cm soil. The average soil temperature was assumed to match the long-term average air temperature in Solling at 6.5°C.

3) soil solution chemistry: soil solution chemistry is measured on a routine basis in Solling. Monthly values of chemistry at 10, 20, 40 and 90 cm depth were available for the 1982-1991 period (Matzner, 1988). Monthly solution chemistry at 60 cm depth was calculated as the average of 40 cm and 90 cm observations. K-release for the 1982-1991 period was calculated by averaging monthly predicted rates to annual rates. Similarly Mg-release at field pH was calculated. The correction for IAP/Q_{eq} at field conditions will be discussed separately.

Table 4 shows predictions of field weathering rates, subsequently corrected for soil depth, temperature, and solution chemistry at field conditions.

Table 4. *Stepwise extrapolation of rates of Mg and K-weathering inferred from laboratory experiments to field conditions. Units are $kmol_c.ha^{-1}.yr^{-1}$ for the 0-60 cm soil layer.*

	Mg	K
Exp. I	85	21
Stepwise corrections:		
soil depth	44	10.5
+		
temperature	11	5.6
+		
pH	0.58(1)	-
+		
IAP/K_{bulk}	#	0.25
field estimates	0.23-0.33	0.06-0.14

(1) see Table 3: used are $k=2.08\cdot10^{-4}$ and m=0.99. For $k=2.03\cdot10^{-5}$ and m=0.69, a field estimate of 0.93 $kmol_c.ha^{-1}.yr^{-1}$ is obtained after correction for soil depth, temperature and pH.
not estimated, see discussion.

The final K-release under field conditions between 1982 and 1991 was predicted at 0.25 $kmol_c\ ha^{-1}\ yr^{-1}$, which is close to the field estimates. The term (K_{crit}-K_{act}) in Eq. [3b] has a strong effect on the release rate of K, because concentrations of K in the field were close to the critical K concentration (K_{crit}) that we measured in the laboratory. Note, however, that on a monthly scale, predictions fluctuated considerably (maximum monthly release (+) or fixation (-) rates of 0.15 $kmol.ha^{-1}$ were calculated) as a result of deviations of soil solution K-concentrations from K_{crit}. Over longer periods, the monthly predictions balanced to an average release of 0.25 kmol ha^{-1} yr^{-1}. The rather high predictions of monthly K-release or -fixation at field conditions may be explained by an effective diffusion constant (k" in Eq.[3b]) in the field, that is lower than the value used in this study. Unsaturated moisture conditions and soil structure may increase the transport distance from the mineral surface to the bulk solution and therefore decrease the effective diffusion constant. Diffusion of K to the bulk solution can be considered as two sequential steps, (i) diffusion from the illite interlayer and (ii) diffusion on the inter-particle scale. The slowest of the two steps will determine the rate of K-release to the bulk solution. In experiment II, the second diffusion step was eliminated due to a sufficiently high convective mass transport. In experiment I, transport was by diffusion only, over a diffusion distance of approximately 2 cm. Still, similar release rates of K were observed in experiments I and II (see Fig. 3). This suggests that the largest resistance for K-transport was interlayer diffusion. Therefore, we expect a minor effect of unsaturated moisture conditions and soil structure on K-release at field conditions as long as these conditions do not effect interlayer diffusion. Indeed, Haagsma and Miller (1963) reported a small effect of moisture content on K-release in soil-resin mixtures at 5°C.

Predictions of Mg-release are most strongly affected by temperature and pH. After correction for pH and temperature, the extrapolations of laboratory data to field conditions were 2-4 times higher than the field estimates. The subsequent correction for mineral saturation, the $(1-[Q/IAP]^n)$-term in Eq.[2], was not possible at field conditions, as, unfortunately, the routine monitoring of soil water chemistry in Solling did not include the measurement of Si. However, in an adjacent plot where monitoring started in 1991, 20 samples from 40 cm and 70 cm depth respectively were obtained which included Si-measurements. The ion activity product (IAP) with respect to the hypothetical $Mg_{0.15}Al_{1.04}Si_{3.5}$ phase (Exp. IIB) was calculated for these samples and plotted in a stability diagram shown in Fig. 6, together with the stability lines of gibbsite, kaolinite, quartz and the hypothetical Mg-Al-Si phase proposed in this study. Also, the temperature dependency of the quartz, kaolinite and gibbsite lines are shown. From Fig. 6 it appears that soil water samples fall within the stability fields of gibbsite and quartz and are also close to the stability line of the hypothetical Mg-Al-Si mineral. Part of the 40 cm samples is oversaturated with respect to the hypothetical mineral phase which, in terms of Eq. [2], means that Mg tend to precipitate from solution. However, it also appears from Fig. 6 that the effect of temperature on mineral stability is distinct and can probably not be neglected for the hypothetical Mg-Al-Si phase. Unfortunately, the effect of temperature on the stability of the hypothetical Mg-Si-Al mineral, which was established at 18°C, is unknown.

CONCLUSIONS

Weathering of Mg and K from an illite-containing acid forest soil in Solling, Germany was investigated at field and laboratory conditions. Factors that were expected to control weathering in the field were varied at laboratory conditions. Mineral depletion, which was correlated with soil depth, temperature and solution chemistry proved to be important factors in controlling release rates of Mg and K from illite. Potassium release from illite was controlled by interlayer diffusion, whereas the release of Mg was chemically controlled.

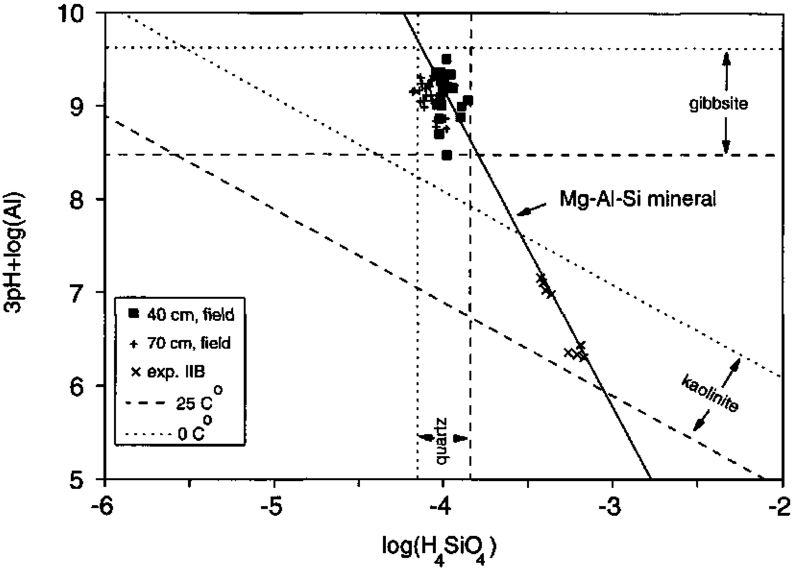

Figure 6. Stability of several aluminosilicates. Stability constants of quartz, kaolinite and gibbsite at 25°C are given by Robie et al. (1978). Stability constants at 0°C were calculated from constants at 25°C and standard enthalpy's of formation given by Robie et al. (1978). For the 'hypothetical' Mg-Al-Si phase and the soil samples, equilibrium with $5 \cdot 10^{-5}$M Mg^{2+} was assumed.

The proposed diffusion model for K-release predicted high potential rates of K release at field conditions. However, predicted actual field rates were much lower, and close to field estimates, because K-diffusion from interlayer space was limited by K concentrations in soil water, which were close to threshold values for interlayer release, obtained in the laboratory. Potential release rates of Mg at field conditions were a factor 2-4 higher than field estimates, after correction for temperature and pH. The remaining discrepancy between estimated and observed field rates of Mg-release may be caused by underestimation of the effect of saturation with the hypothesized reference mineral. To resolve this problem, the stability of the hypothetical Mg-Al-Si mineral needs further study.

The present study illustrates the potential of laboratory experiments to explain the apparent discrepancy between laboratory and field rates by differences in reaction conditions. Still, Mg-release was a factor 2 to 4 higher than observed at field conditions, which will cause a gross underestimation of the vulnerability of the forest ecosystems to external disturbances like acid rain. Therefore, present methods to obtain field weathering rates, i.e. from elemental analysis of the profile (historical weathering) and from input-output budgets (present weathering) remain necessary.

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Chapter 4

Processes controlling anion mobility in an acid forest soil at Solling, Germany

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ABSTRACT

A deterministic model was applied to simulate soil water chemistry data, collected during an 18-year period in an acid forest soil in Solling, Germany. In this paper, the hydrochemistry of Cl, NO_3 and SO_4 is discussed. Seasonal and long-term variations of Cl concentrations in soil solution were successfully simulated as a result of atmospheric deposition and hydrological processes. The marked increase of SO_4 concentrations at the 90 cm depth during the 1970s could be simulated satisfactorily using adsorption equilibrium. Here we assumed that high SO_4 deposition loads in the 1970s entered a soil which had reached a state of near saturation with respect to adsorbed SO_4 in the preceeding decades. In the 1980s, measured and simulated SO_4 concentrations at the 90 cm depth decreased, due to reduced SO_4 deposition. Modelled resupply of SO_4 to solution by desorption was less than observed, particulary in periods with high water fluxes. In wet periods, when observed N releases from the litter layer were high, simulated N concentrations in litter percolates were lower than observed values. Elevated N concentrations at the 90 cm depth occured when the N-input into the mineral soil exceeded approximately 4 kmol ha^{-1} yr^{-1}.

INTRODUCTION

Since the late 1960s element fluxes have been measured in a spruce and beech forest ecosystems in the Solling mountains of Germany (e.g. Ellenberg, 1971; Matzner, 1989). These measurements showed that spruce and beech forests have received high amounts of acid atmospheric deposition. In the spruce forest this amounted to an average of 4.8 $kmol_c$ ha^{-1} yr^{-1} of S and 3.3 $kmol_c$ ha^{-1} yr^{-1} of N in the 1973-1991 period (Ulrich, 1994). These inputs caused a strong soil acidification (present base saturation <4%). Monitoring of monthly rainfall-, throughfall- and soil solution chemistry in the Solling spruce and beech forest ecosystems still continues, creating a unique long-term data set, one of the longest of its kind, worldwide. The element budget approach, which analyses the input and output of solutes from several 'compartments' in the ecosystem, has elucidated the role of atmosphere, mineral soil, forest-floor and forest stand as a sink or source of elements in the Solling forest ecosystems (for a review see Matzner, 1989). Based on these studies, several underlying mechanisms have been proposed, e.g. spatial and temporal decoupling of N uptake and mineralization causing so called seasonal acidification phases (Ulrich, 1981; Matzner, 1989) and formation and dissolution of basic aluminum sulphates in acid forest soils (e.g. Prenzel, 1983).

Computer models have been applied to the Solling data to model hydrology (Benecke, 1984; Salihi, 1984; Manderscheid, 1992) and, for the beech site, bioelement cycling (Ulrich et al., 1973). Förster (1987) used a multicomponent transport model which included cation exchange and $AlOHSO_4(s)$ to describe the dynamics of SO_4 and Al in the sub-soil of the Solling spruce site. Unfortunately, to date no comprehensive model has been applied on the Solling spruce data set to study the integrated effects of hydrology, deposition and biogeochemical processes like SO_4-adsorption, bioelement cycling, cation-exchange and weathering.

This paper reports simulations of soil solution chemistry of the Solling spruce site, by using a comprehensive soil chemistry model and field data. Here, we focus on the dynamics of dissolved Cl, NO_3,and SO_4, the major anions in soil solution. In separate papers (Wesselink et al., 1994; Wesselink and Mulder, 1994) the chemistry of cations is discussed.

Important processes concerning the chemistry of anions at the Solling Spruce site include:

1) Hydrological processes, i.e. the dynamic effect of rainfall, evapo-transpiration and percolation on solute concentrations. To test the hydrology sub-model, we used observed Cl concentrations in soil solution, because these primarily depend on atmospheric deposition and hydrology.

2) Retention and release of SO_4 in the mineral soil. Here the main aim was to better understand the short-term and long-term dynamics of SO_4.

3) Nitrate production in the surface soil. We investigated to what extent the occurrence of NO_3 peaks (seasonal acidification phases) could be explained by atmospheric deposition of N, by hydrology and by the biological processes of N mineralization and uptake. Furthermore the model was used to study which factors governed observed long-term changes in NO_3 concentrations at the 90 cm depth in the mineral soil.

SITE DESCRIPTION

The monitoring site is located at the plateau of the Solling mountains in Germany (9°30' East, 51°40' North), 500 m above sea level. The soil is classified as a spodo-dystric cambisol (Ulrich, 1989) and carries a 105-year old Norway Spruce (Picea abies) stand. The soil profile consists of an organic litter layer of ca. 8 cm thickness, followed by a 60-80 cm loess mineral layer lying on soliflucted material from weathered triassic sandstone. The clay content is approximately 17% in the loess layer and 23% in the weathered sandstone. The clay fraction consists of mainly illite and vermiculite.

Rainfall, throughfall and soil solution at the 0 cm depth, i.e. below the litter layer, were collected since 1969 and soil solution at the 90 cm depth since 1973. From 1973 to 1975, the soil solution was also sampled at the 40 cm depth. Monitoring at the 10, 20, 40 and

80 cm depth started in 1981. Solutions were sampled continuously and sample bottles were replaced monthly. Monthly rainfall and throughfall were collected from fifteen collectors and pooled to make three samples for analysis. Solutions obtained from the litter layer and at the 40 cm and the 90 cm depth were extracted using ceramic plates (three below the litter and seven at the 90 cm). Plates below the litter layer and at the 90 cm depth were renewed in January 1976, whereas sampling at the 40 cm depth stopped after 1975. Sampling at the 10, 20, 40 and the 80 cm depth was carried out with ceramic cups (six at each depth), installed close to the 0 cm and 90 cm plates. If sample volume was enough for analysis, three (pooled) samples were analyzed from the 10, 20, 40 and the 80 cm depth. At the 0 cm depth, i.e. below litter, the number of monthly analyzed samples varied between two and five. At the 90 cm depth samples from all seven plates were analyzed from 1978 until 1980, whereas in other periods samples were pooled to make three or four samples for analysis. Suction pressures for plates and cups were frequently adapted by hand, to match measured soil matrix potentials.

Methods for the analysis of solutions are given by Meiwes et al. (1984) and König et al. (1989) and are shortly described hereafter. Until 1982, SO_4 was determined by precipitation with Ba and analyzing excess Ba by potentiometric titration with EDTA, using a wolfram electrode (Grether, 1965). From 1982 onwards, SO_4 was analyzed colorimetrically using methyl thymol blue (Meiwes et al., 1984). Ammonium and NO_3 were determined colorimetrically with indophenol green and K-perrhenate, respectively, until 1981 (Holz, 1971; Holz and Kremers, 1973). From 1982 on, NH_4 was analyzed with Na-salicylate and Na-dichlorcyanurate, while NO_3 was determined with the Cadmium reduction method (Meiwes et al., 1984). Until 1980, Cl was determined by potentiometric titration with a $AgNO_3$ solution in a system with a glass- and an Ag-AgCl electrode. After 1980, Cl was determined by the ferricyanide method (Meiwes et al., 1984). pH was measured with a glass combination electrode. Aluminum was measured colorimetrically until 1982 and by atomic adsorption afterwards (König et al., 1989). Typically, the performance of any new analytical method was tested parallel to the old method in a large number of samples.

MODEL DESCRIPTION

Process formulations in the model are summarized in Appendix 1 of this chapter.

Hydrology

An empirical flow model was used to describe vertical water flow. In this model the water flow from a layer does not depend on the hydraulic gradient to the next layer, as commonly used (e.g. Benecke, 1984) but depends on the moisture content of the layer itself. With a similar approach, Lindström and Rohde (1992) successfully described transit times of ^{18}O tracers in soil lysimeters. Water flow depends non-linearly on soil moisture content. Flow was assumed to be downward at soil moisture contents above field capacity and upward (capillary rise) when the soil was below field capacity. Water uptake was driven by potential transpiration and reduced when the moisture content was below field capacity. The mass balance was solved explicitly and time steps of 0.1 day were used. Water fluxes to and from each layer and soil moisture contents were output to the chemistry model. The frequency of output to the chemistry model was dependent on rainfall intensity, and varied between 0.25 day in periods of fast flow and 2 days in dry periods.

Input data. Boundary conditions for the hydrology model include daily amounts of throughfall water and potential evapotranspiration. Daily throughfall was calculated from monthly measured cumulative throughfall in the Solling spruce forest and daily rainfall frequency distribution from a nearby weather station (Holzminden-Silberborn). Potential evapotranspiration was input to the model and was calculated with the Penman-Monteith equation from daily values of air temperature, hours of sunshine and air moisture saturation from the nearby weather station (from Manderscheid, 1992, 1994). Soil evaporation and snow formation was not considered. Daily throughfall and potential evapotranspiration were evenly distributed over the day. Moisture contents at wilting point, field capacity and saturation were obtained from Θ-pF curves at pF 4, pF 2.5 and pF 0 respectively (Benecke, 1984).

The distribution of water uptake in the soil profile (*fwu*, Table 1, App. 1) was based on measured concentrations of Cl. Chloride was regarded as chemically inert in the soil solution. Consequently the increase in the concentration of Cl with depth (throughfall, 0, 10, 20, 40 ,90 cm) could be used to calibrate the distribution of potential water uptake in the soil. Calibration was done by minimizing the sum of squared differences between average observed and simulated Cl concentrations at the different soil depths for the 1981 until 1990 period.

Initial conditions. Simulations started in January 1973, with soil moisture contents at field capacity.

Soil Chemistry

The model describes the following biogeochemical processes: SO_4 adsorption, release of nutrients through mineralization, nutrient uptake, nitrification, cation exchange, complexation in solution, and mineral weathering. The chemical species considered are indicated in App. 1.

Input data. Measured monthly averaged throughfall chemistry in the Solling spruce forest was used as model input. In months where throughfall chemistry was lacking, long-term monthly averaged chemistry was used. Inputs of organic-N, estimated from Kjeldahl-N minus NH_4^+-N, were added to NH_4^+-N as input to the model. From the hydrology model, water fluxes and soil moisture contents for each time step were used.

Freundlich adsorption constants (see Table 1 and Fig. 4) were derived from data of Meiwes (1979) and Meiwes et al. (1980). We assumed the sub-soil at the 40-90 cm depth to have adsorption characteristics similar to those at the 40-50 cm soil depth. Sulfate adsorption isotherms at the 0-10 cm, 10-20 cm, and 40-50 cm depth and approximate equilibrium pH of 3.8 (0-10 cm), 4.05 (10-20 cm) and 4.3 (40-50 cm) are given in Fig. 4. pH dependency of SO_4 adsorption at the 40-50 cm depth is also shown in Fig. 4. For the 40-90 cm soil layer we used three types of adsorption isotherms. Firstly, pH independent adsorption (Table 1 and App. 2, A and B constant). Secondly, assuming Freundlich exponent B constant and parameter A dependent on pH. By fitting isotherms through the data points in Fig. 4 we arrived at $A=(-2.07\times pH+16.9)\times 10^{-3}$. Thirdly, and more empirically, we assumed pH-dependent behaviour of both Freundlich parameters. The exponent B in the Freundlich equation decreases with pH when comparing isotherms at the 0-10 cm, 10-20 cm and 40-50 cm depth in Fig. 4. Assuming this decrease is due to pH only we derived the relationship $B=-0.32\times pH+1.46$. Next, 40-50 cm isotherms were fitted through the data points indicated in Fig. 4 to arrive at the relationship $A=(3.78\times pH-8.77)\times 10^{-3}$. When pH-dependent SO_4 adsorption was calculated for the 40-90 cm depth, measured pH concentrations (3rd order moving averages) at the 90 cm depth were used as input to the model.

The annual average N mineralization in the litter layer ($J_{min,avg}$, Table 1, App. 1) was calibrated to obtain a value of 1.6 kmol ha^{-1} yr^{-1} as estimated by Matzner (1988). In the 0-10 cm soil its value was set at 0.4 kmol ha^{-1} yr^{-1}. Annual average N-uptake from the litter layer was calculated from the N input-output budget of the litter layer and amounted to long-term average value of 0.9 kmol ha^{-1} yr^{-1} (in kmol ha^{-1} yr^{-1}: 3.2 (throughfall-N) + 1.6 (mineralization) - 3.9 (litter percolates) = 0.9). To estimate total N-uptake from the soil ($J_{nu,avg}$, Table 1, 2), we assumed N-uptake proportional to water uptake. Thus, at an average N-uptake of 0.9 kmol ha^{-1} yr^{-1} and on average 25% of total water uptake from the litter layer, a total N-uptake of 0.90/0.25=3.6 kmol ha^{-1} yr^{-1} was calculated. Although uptake of N is modelled proportional to water uptake (Table 1, App. 1), uptake may be reduced when it exceeds N-stores in solution during a time step. The nitrification rate constant (K_{nitr}, Table 1, App. 1) was estimated from measured average annual fluxes of NH_4 in throughfall minus leaching of NH_4 from the litter layer plus net mineralization of N in the litter layer. Uptake and mineralization of S were not modelled, as we assumed a steady state situation in which uptake equalled mineralization.

Table 1. Model Parameters.

Depth (cm)	layers (nr.)	Buld dens. (kg dm^{-3})	$\Theta^*_{s,fc,wp}$	K^*_{sat} (dm day^{-1})	fwu$^{\$}$ <1979	fwu$^{\$}$ >1979	$J_{Nu,avg}{}^{\&}$ (kmol ha^{-1} yr^{-1})	$J_{Nmin,avg}{}^{\&}$ (kmol ha^{-1} yr^{-1})	A§ (mol kg^{-3} soil)	B§
8-0	2	0.3	0.65/0.45/0.16	2.5	0.50	0.20	$fwu_{8\text{-}0cm} \times 3.6$	1.64$^{(a)}$	0	0
0-10	1	0.9	0.55/0.45/0.16	0.175	0.075	0.075	$fwu_{0\text{-}10cm} \times 3.6$	0.4	1.4×10^{-3}	0.24
10-20	1	1.0	0.47/0.38/0.16	0.175	0.125	0.125	$fwu_{10\text{-}20cm} \times 3.6$	0	5.1×10^{-3}	0.14
20-40	2	1.0	0.42/0.32/0.16	0.175	0.175	0.175	$fwu_{20\text{-}40cm} \times 3.6$	0	5.1×10^{-3}	0.14
40-90	5	1.6	0.38/0.32/0.16	0.175	0.125	0.425	$fwu_{40\text{-}90cm} \times 3.6$	0	7.8×10^{-3}	0.078
$pK_{AlOH2+}{}^{(b)}$		-5.02								
$pK_{Al(OH)2+}{}^{(b)}$		-9.30								
$pK_{AlSO4+}{}^{(b)}$		3.20								
K_{nit}		6×10^{-6} (mol dm^{-3} day^{-1})								

[*] Θ = moisture contents at saturation, field capacity and wilting point, K_{sat} = saturated hydraulic conductivity

[$] fwu= fraction of water uptake,

[&] $J_{Nu,avg}$ = average annual N uptake and $J_{Nmin,avg}$ = average annual N mineralization.

[§] Freundlich adsorption parameters, pH-independent, from Meiwes (1979)

(a) from Matzner (1988), (b) from Lindsay (1979).

The process of denitrification was not included in the model, as measurements have indicated that NO_2 fluxes from the Solling soil are relatively low (Brumme and Beese, 1992).

Initial conditions. The measured chemical composition of the soil solution at the 0, 40 and the 90 cm depth in January 1973 was taken as the starting point for the simulations.

For each time step the chemical mass balance in each soil layer, resulted in twelve equations with twelve unknown concentrations of solutes (H, K, Na, Ca, Mg, Mn, Al, NH_4, Cl, SO_4, DOC, NO_3). This set of equations was solved with a Gauss-elimination procedure. Numerical dispersion due to discretization of time steps and soil layers is given as $D_N=0.5\times V_w\times(\Delta z-V_w\times\Delta t)$ (Goudriaan, 1973), where Δz is the layer thickness, Δt the time step and V_w the pore water velocity. In our simulations, D_N equalled 1.45 cm at an average percolation rate of 0.3 cm day^{-1} and 5 cm at occasional peak flow at the maximum saturated conductivity of 1.0 cm day^{-1}.

RESULTS AND DISCUSSION

HYDROLOGY AND CHLORIDE

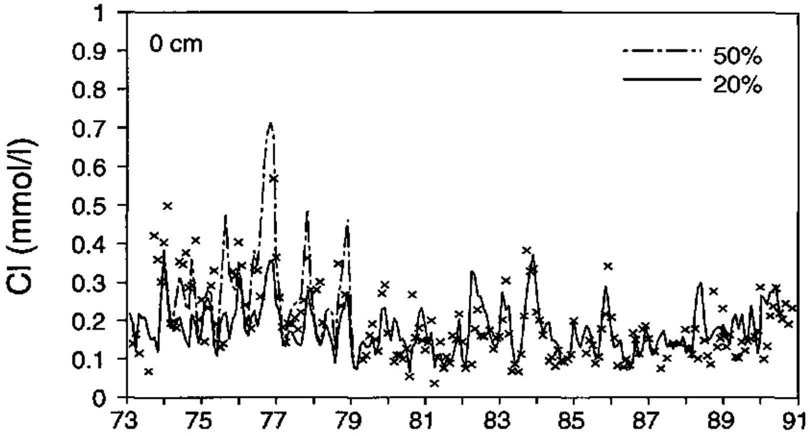

Figure 1. *Predicted Cl concentrations in percolates from the litter layer, with 50% (1973-1978, -·-·-) and 20% (1973-1990, ———) of total water uptake occurring in the litter layer. Average observed Cl concentrations in the litter layer are indicated as (×).*

The calibrated distribution of the potential water uptake with depth is shown in Table 1 (*fwu*). For the 1980s, a large uptake of water from deeper soil layers was calibrated. Using the same water uptake distribution for the 1973-1979 period, however, resulted in an underestimation of Cl concentrations in litter percolates in that period (Fig. 1). An increase in water uptake from the litter layer from 1973 until 1979, at the cost of water uptake from the mineral soil (Table 1), improved the prediction of Cl concentrations in litter percolates in that period. The high uptake of water from the litter layer in the 1970s is in accordance with measured fine root mass which concentrates in the litter layer and in the 0-10 cm mineral soil (Ulrich, 1994). The apparent shift to increased water uptake from deeper soil layers in the 1980s is remarkable and does was far was we know not coincide with a change in fine root distribution. Possibly, the surface soil was relatively important for water uptake in the mid-1970s because of drought. From 1975 until 1979 , measured inputs of throughfall water were 650, 550, 706 and 645 mm yr^{-1} respectively, whereas the long-term average was 769 mm yr^{-1}. The shift in water uptake to the sub-soil in the wetter 1980s may reflect to importance of large roots. Tiktak and Bouten (1990) reported a relatively large water uptake by few, active, large roots for a sandy soil in the Netherlands.

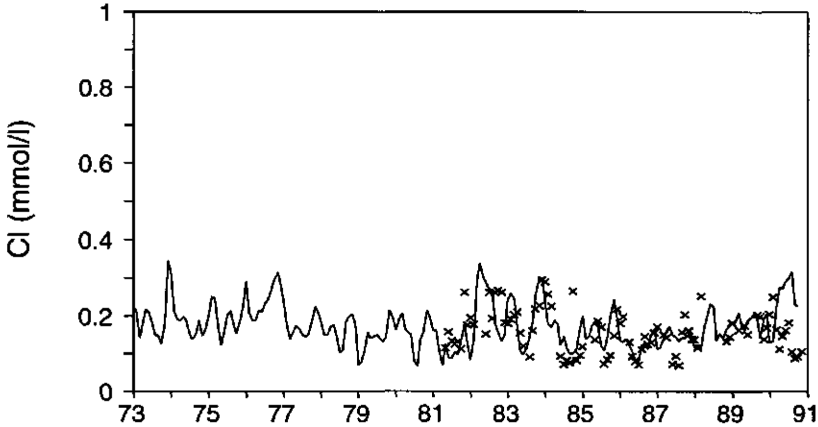

***Figure 2.** Predicted (—) and average observed Cl concentrations (×) at the 10 cm depth.*

Modelled monthly drainage fluxes at 90 cm depth are compared with fluxes calculated with Darcy models as given by Benecke (1984) for the period 1973-1975 and Salihi (1984) for the period 1976-1981 (Fig. 3). Drainage fluxes at the 90 cm depth varied seasonally, with small fluxes during summer months when transpiration was high and large drainage fluxes in winter months, when the transpiration was low. A recent compilation of drainage water fluxes at the 90 cm depth as calculated with Darcy-models over the 1973-1991 period is given by Manderscheid et al. (1994) and Ulrich (1994). For the period 1973-1990 we calculated an average annual drainage of 40.5 cm which was 10.5% lower than the average annual drainage calculated with Darcy models (Manderscheid et al., 1994). Consequently, we also calculated slightly different Cl input-output budgets. Manderscheid et al. (1994) reported average Cl outputs of 1.19 $kmol^{-1}$ ha^{-1} yr^{-1} (1973-1990), whereas the average input in throughfall is 1.13 $kmol^{-1}$ ha^{-1} yr^{-1}. In our calculations, we estimated and average Cl output of 1.08 $kmol^{-1}$ ha^{-1} yr^{-1}. Our slightly lower estimates of water fluxes resulted from higher transpiration rates, most probably due to a more efficient water uptake from deeper soil layers in the 1980s.

Chloride in throughfall had a distinct seasonal pattern, with maximum concentrations in November and December (not shown), which was attributed to the increased aerosol deposition of NaCl in fog and dew in these periods (Matzner, 1988). In the mineral soil, these seasonal variations showed a shift due to hydrological processes. Maximum correlations between simulated Cl concentrations in soil solution and measured throughfall concentrations were found with a time lag of 1 month at 0 cm, 2 months at 10 cm, 3-4 months at 40 cm and 10-11 months at 90 cm depth. The time lag indicates the average transit time of Cl in the soil as determined by percolation fluxes, average soil moisture contents and soil depth. With depth, variations in Cl concentrations within the years were dampened, and variability between the years became more pronounced (Fig. 3). At the 90 cm depth, these long-term changes, expressed as annual averaged Cl concentrations, varied as a function of annual throughfall concentrations of Cl and water fluxes at 90 cm ($Cl_{90cm,yr}=0.197+1.097\times Cl_{tf,yr-1}-0.02165\times J_{90cm,yr-1}$, with Cl in mmol l^{-1}, J in dm yr^{-1}, $R^2=0.7$, $p<0.001$, both variables contribute sign. to Cl_{90cm}, $p<0.05$).

The spatial variation in Cl concentrations at the 90 cm depth was high (Fig. 3). Approximately 35% of this spatial variation could be explained from variation in Cl concentrations in throughfall. This was indicated by running the model with monthly minimum and maximum measured Cl concentrations in throughfall. As Cl concentrations at the 90 cm depth also depend on changes in water fluxes (see regression equation above), spatial variations of this water flux may explain the remainder of the observed variation in Cl concentrations at the 90 cm depth.

In summary, it appears that the hydrology model was able to reproduce water fluxes calculated with a Darcy-model, as well as seasonal and long-term variations in Cl concentrations in soil solution. The large shift in the distribution of water uptake in the soil profile after 1979 remains difficult to explain, however.

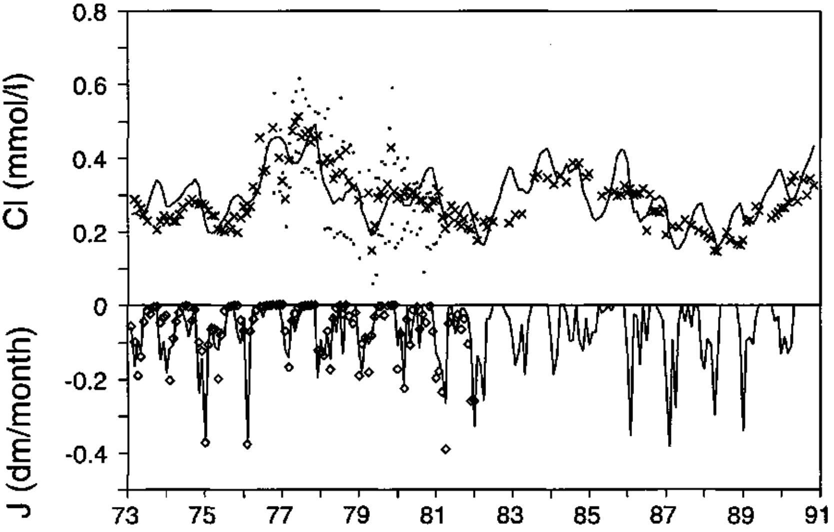

Figure 3. Predicted (—), average (×) and minimum and maximum observed Cl concentrations (·) at the 90 cm depth (upper panel). Monthly water fluxes at 90 cm depth, calculated with the present model (—) and with Darcy models (◊) (Benecke, 1984; Salihi, 1984) (lower panel).

SULFATE

One of the most striking features of the time series at the 90 cm depth is the strong increase of SO_4 concentrations in the 1970s (Fig. 6). We believe that the key to understand this increase is given in Fig. 4. This figure indicates that the major part of the SO_4 adsorption capacity was filled at the, measured, initial solution concentrations of 1973. As a consequence, from 1973 onwards, the model predicted SO_4 concentrations in the soil solution that quickly adapted to atmospherically deposited SO_4 (Fig. 6, run I). However, this modelled increase of SO_4 concentrations (Fig. 6, run I) was more smooth than the observed increase. Simulations of the seasonal variation in SO_4 concentrations at 90 cm before 1977 could be improved by introducing pH-dependent Freundlich adsorption (Fig. 6, run III).

Between 1977 and 1982, SO_4 concentrations at the 90 cm depth reached high values of about 2 $mmol_c.l^{-1}$. These resulted from high deposition fluxes in the 1970s (Matzner and Meiwes, 1993) and comparatively strong concentration increases in the soil due to high transpiration and low percolation in the mid 1970s (not shown). Figures 5 and 6 demonstrate how elevated SO_4 concentrations in litter in the mid-1970s resulted in peak concentrations at the 90 cm depth about 2,5 years later.

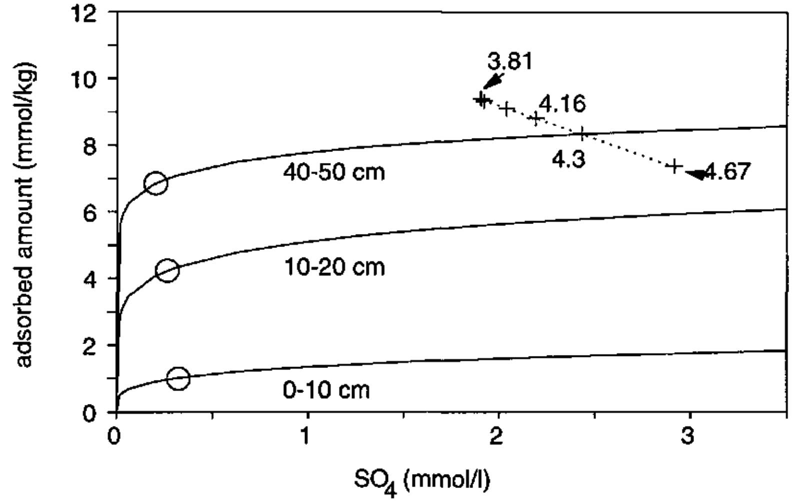

Figure 4. *Sulfate adsorption isotherms measured by Meiwes (1979). pH dependency of SO_4 adsorption in samples from the 40-50 cm depth was obtained from Meiwes et al. (1980) and indicated in the figure (+). Measured approximate SO_4 concentrations in soil solution at the start of simulations in 1973 are indicated (O).*

The response time of dissolved SO_4 at the 90 cm depth was some 1,5 years longer than that of Cl, due to sorption processes. Note, that the time delay of 2,5 years for the elevated SO_4 concentrations in litter to reach the 90 cm depth resulted in strongly negative annual SO_4-budgets (i.e output>input) for the years 1979 until 1982, in which S deposition had decreased compared to the mid 1970s.

In the 1980s, observed SO_4 concentrations at the 90 cm decreased significantly (-0.045 $mmol_c\ l^{-1}\ yr^{-1}$, $p<0.001$), concurrent with declines in SO_4 deposition (-0.043 $mmol_c\ l^{-1}\ yr^{-1}$, $p<0.001$, Wesselink et al., (1994)). The model simulated decreasing SO_4 concentrations at the 90 cm depth (Fig. 6, run I) more rapidly than was observed, however. This was particulary so in 1982, 1983 and from 1987 until 1990. Apparently, Freundlich adsorption insufficiently described desorption of SO_4 in the 1980s. Note, that also pH dependent adsorption of SO_4 did not improve SO_4 predictions during these periods (Fig. 6, run II,III).

A possibility that litter acted as a source of SO_4 was evaluated by using measured SO_4 concentrations in litter percolates as model input to the mineral soil. However, this had minor effects on predicted SO_4 concentrations at the 90 cm depth. This confirms our model assumption that the litter layer is a negligible source of SO_4 to soil solution. Release of organically bound SO_4 from the mineral soil seems also unlikely, as stores of organic-S are rather low (31 $kmol_c$ ha^{-1} in the 0-50 cm soil layer, Meiwes and Khanna, (1981)).

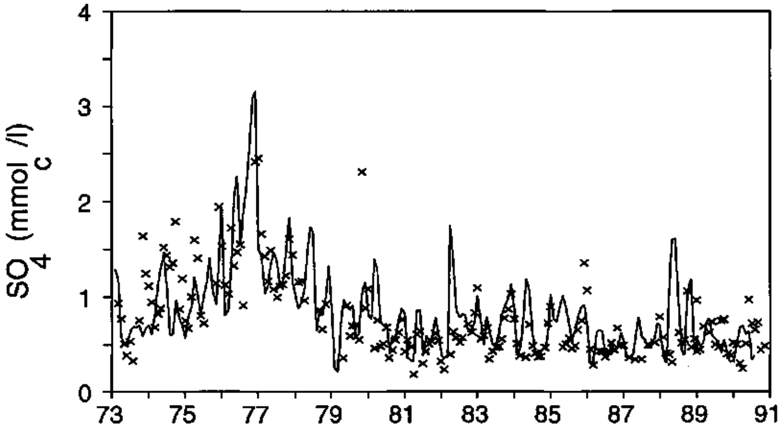

Figure 5. *Predicted (——) and average observed total SO_4 concentrations (×) in percolates from the litter layer.*

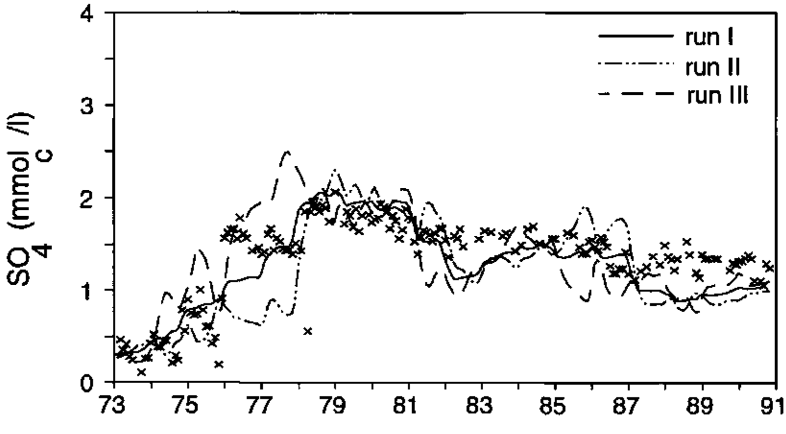

Figure 6. *Predicted and average observed total SO_4 concentrations (×) at the 90 cm depth. Run I with pH independent Freundlich parameters as given in Table 2. Run II with Freundlich parameter A in the 40-90cm mineral soil dependent on measured monthly pH's at the 90 cm depth (see Input data). Run III with both Freundlich parameters in the 40-90cm mineral soil dependent on measured monthly pH's at the 90 cm depth (see Input data).*

An alternative description for SO_4 retention and release in forest soils under high sulfur deposition is the formation and dissolution of the mineral $AlOHSO_4$ (jurbanite) (Prenzel,1983 and 1994; Khanna et al., 1987; Ulrich, 1989). The following reaction scheme was proposed (Prenzel, 1983):

$$H_2SO_4 \quad <==> \quad 2H^+ + SO_4^{2-} \qquad (1)$$
$$AlOH_3(s) + 3H^+ \quad <==> \quad Al^{3+} + 3H_2O \qquad (2)$$
$$Al^{3+} + SO_4^{2-} + H_2O <==> AlOHSO_4(s) + H^+ \qquad (3)$$

$$AlOH_3(s) + H_2SO_4 \quad <==> \quad AlOHSO_4(s) + 2H_2O \qquad (4)$$

where reaction (2) may be replaced by exchange of protons against Al on the exchange complex (Förster, 1986; 1987). The jurbanite reaction scheme was tested on Solling field data by Förster (1987). Using a multicomponent transport model and measured atmospheric deposition and precipitation surplus as input to the model, this author found an increase in solution concentrations of SO_4 and Al in the sub-soil during the 1970s, due to jurbanite dissolution. However, the increases were much more gradual than observed. Moreover, simulated SO_4 concentrations remained high after 1980, due to continued jurbanite dissolution (reaction (3)), whereas measured concentrations decreased (see Fig. 6).

Ion-activity-products (IAP) for jurbanite at the 90 cm depth were, however, not constant with time as a equilibrium with a single mineral phase would require (Khanna et al.,1987; Matzner and Prenzel, 1992; this paper Fig. 7). Therefore, the hypothesized equilibrium with jurbanite could only explain the observations if jurbanite was considered a solid-solution mixture of $Al(OH)_3$ and $AlOHSO_4$ (Khanna et al., 1987). Thus, these authors explained qualitatively the increase of the IAP of jurbanite from $\log K \approx -18$ to $\log K \approx -16.8$ in the 1970s (Fig. 7) by a gradual increase in the mol fraction of $AlOHSO_4(s)$ in the solid solution mixture, at the expense of $Al(OH)_3$ (reaction (4) to the right). Here, the logK value of approximately -16.8 represents the $AlOHSO_4$ end-member of the solid solution mixture.

From a modelling point of view, however, a dynamic description of solid solution mixtures, under field conditions, is less desirable. This is because additional, unknown, parameters are introduced in a model. Moreover, Freundlich adsorption/desorption, with independently measured adsorption constants, explained SO_4 dynamics in the 1970s well. Even though in the 1980s SO_4 adsorption equilibria described S dynamics with less succes, the jurbanite solid solution concept is unlikely to do much better. The measured input-ouput budget of SO_4 (Manderscheid et al., 1994; Ulrich et al., 1994) indicates that the soil is a continuous source of SO_4 after 1978. According to the solid solution concept, continuous desorption, or dissolution, of SO_4 should result in a decrease of the IAP of jurbanite. This is, however, not apparent from the observations (Fig. 7).

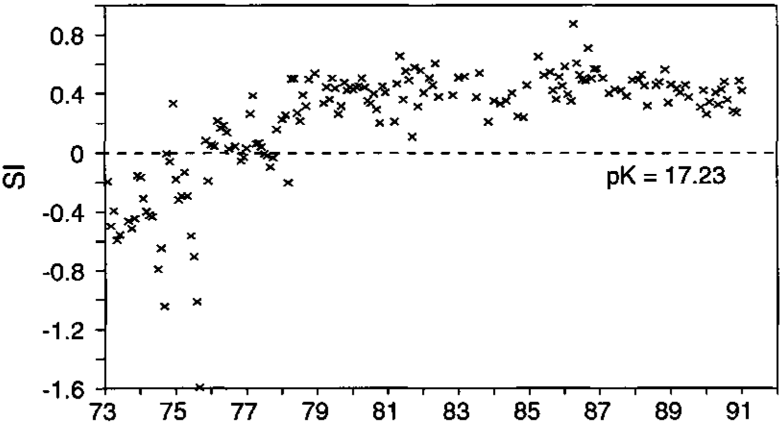

Figure 7. Saturation indices (SI) of jurbanite at the 90 cm depth. SI= log(IAP)-log($K_{jurbanite}$), where IAP= ion-activity-product = (Al)(SO_4)(OH) and brackets refer to solute activities calculated with the chemical equilibrium model ALCHEMI (Schecher and Driscoll, 1987) assuming a constant soil temperature of 7°C.

NITROGEN

With respect to N, two simulations were made, one in which mineralization and uptake of N were not considered and thus throughfall inputs changed due to hydrology only. In a second scenario, uptake and mineralization of N was included. Average N-concentrations in litter percolates are shown in Fig. 8. It should be noted that the spatial variability in monthly N-concentrations was high (coefficients of variation: 20-50% in winter months and 80-250% in summer months during 1981 until 1987). Total N concentrations in litter percolates consisted for approximately 70% of NO_3, 15% of NH_4 and 15% of N_{org}.

Typically, in summer and autumn months, simulated mineralization in the litter layer was higher than uptake (not shown). From 1975 until 1978, however, the annual uptake of N from the litter layer exceeded mineralization. This was due to an increased water uptake from the litter layer in this period (see 'Hydrology and Chloride' section) and the assumed proportional increase of N-uptake. Therefore, increased water uptake from the litter layer had contrasting effects on different anions: Concentrations of Cl and SO_4 rose due to increased water uptake and decreased percolation, whereas N concentrations decreased due to a concurrent increase in N-uptake. Simulations of N-concentrations in litter matched observations with variable success. In a number of years the simulated increase of N-concentrations in the litter layer in late summer matched observations. However, in other years (1979/80, 1986/87) N concentrations were underestimated.

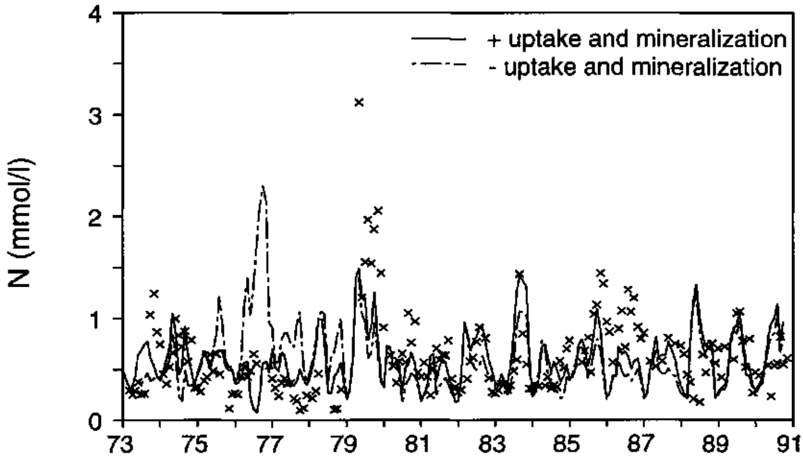

Figure 8. *Predicted and average observed (×) total N concentrations (NH_4+NO_3+N_{org}) in percolates from the litter layer. (———) is model run including uptake and mineralization and (—— —) is model run without uptake and mineralization.*

In the mineral soil, dissolved N is largely present as NO_3. Figure 9 shows how mineralization and uptake contributed to N concentrations at the 10 cm depth. Elevated NO_3 concentrations in warm and dry years have often been used to demonstrate the occurrence of seasonal acidification phases due to excess nitrification of NH_4 from deposition and mineralization (Matzner, 1988; 1989; Ulrich, 1981). In the comparatively warm and dry years of 1982, 1983, 1985 and 1990, however, the net contribution from mineralization and uptake to N concentrations at the 10 cm depth appeared to be rather small. In these years, modelled mineralization of N was largely balanced by uptake and elevated N concentrations at the 10 cm depth were primarily controlled by N deposition and hydrology.

From 1986 until 1990, simulations and observations of N at the 10 cm depth did not match well. Most likely, this was due to poor predictions of N concentrations in litter percolates in these periods, as apparent from underestimated N concentrations in both litter and at 10 cm depth in 1986 and 1987 (Figs. 8, 9). Consequently, predicted N concentrations at the 90 cm depth poorly resembled the observations (not shown). At this depth, four prolonged periods of elevated N concentrations were observed, intermitted by periods with low concentrations (Fig. 10).

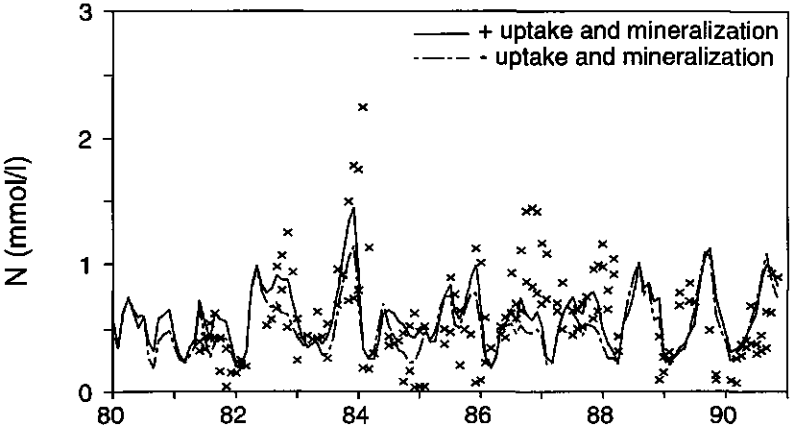

Figure 9. Predicted as well as minimum and maximum observed (×) N concentrations (NH_4+NO_3+N_{org}) at the 10 cm depth. (———) is model run including uptake and mineralization and (—— —) is model run without uptake and mineralization.

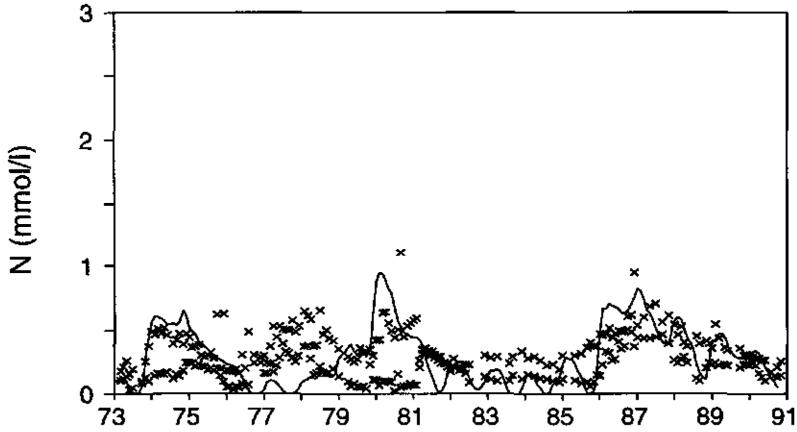

Figure 10. Predicted (———) as well as minimum and maximum observed (×) N concentrations (NH_4+NO_3+N_{org}) at the 90 cm depth. The model used measured N concentrations in litter percolates as input to the first mineral soil layer.

To investigate the dynamics of these long-term changes, we carried out an additional simulation where the model used measured N concentrations in litter percolates as input to the first mineral soil layer. Three periods with elevated N concentrations at the 90 cm depth were simulated. These elevated N concentrations were due to high N levels in litter percolates in the years 1973-74, 1979-81 and 1985-88, which reached the 90 cm depth after a transport time of approximately one year. The close coupling of N-leaching at the 90 cm and N-input into the mineral soil in the previous years was surprising, as on the average around 75% of N entering the mineral soil is taken up by the trees. From the observations in the 1980s, where simulated N-concentrations at the 90 cm matched best with observations, it could be derived that when a critical N-input into the mineral soil of about 4 kmol ha^{-1} yr^{-1} was exceeded, this resulted in increased leaching of N at the 90 cm depth.

Calculated input-output budgets of N for the litter layer (Fig. 11) show that in the years 1973-74, 1979-81 and 1985-1988 litter was a relative large source of N. Note, that the long-term net release of N from litter of approximately 0.9 kmol ha^{-1} yr^{-1} is small compared to the average annual N-flux of 3.3 kmol ha^{-1} yr^{-1} in litterfall (Matzner, 1988). This has resulted in strong accumulation of N in litter with time (store of 145 kmol ha^{-1} in 1983, Matzner (1988)). The annual input-output budgets of N in the litter layer were positively correlated with annual amounts of throughfall water (N_{out}-N_{in}=$J_{water,tf(dm)}$×0.685-4.8, R^2=0.42, $p<0.01$) and negatively, though not significantly, with annual average air temperatures (N_{out}-N_{in}=-1.49×T_{avg}+12.04, R^2=0.19). Obviously, periodic high N releases from litter resulted from decoupling of N mineralization and uptake processes (Ulrich, 1981). After Ulrich (1981, 1994), such decoupling is expected to be strongest in warm/dry years. Contrary, in the litter layer of Solling, decoupling appeared to be strongest during relatively wet years.

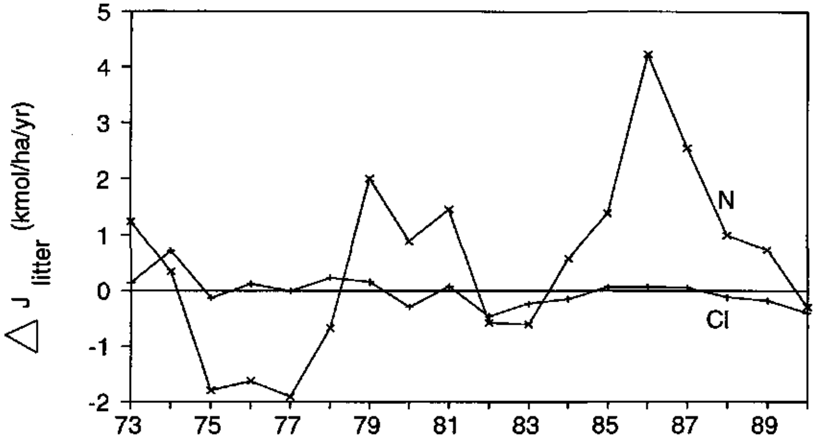

Figure 11. *Input-output budgets for Cl and N (NH_4+NO_3+N_{org}) in the litter layer. Fluxes into the litter layer were calculated from observed throughfall concentrations and observed water fluxes. Fluxes from the litter layer were calculated from observed concentrations in litter percolates and calculated water fluxes. The input-output budget was calculated as annual output flux minus annual input flux (ΔJ_{litter}).*

Note, that elevated NO_3 concentrations at the 90 cm depth in 1977 and 1978 were not captured by the simulations. The measured N-fluxes from the litter layer and at the 90 cm depth showed that in 1976 and 1977 a total N-flux of 3.2 kmol ha^{-1} entered the mineral soil, whereas, after a transport time of approximately one year, 2.5 kmol ha^{-1} of N was drained at the 90 cm in 1977 and 1978. Thus, by contrast to our predictions, only minor amounts of N were taken up from the mineral soil during this period. Probably, the assumed N uptake from the mineral soil (50%, Table 1) was too large. Alternatively, rewetting of the mineral soil after the very dry year of 1976 may have triggered mineralization of N in the mineral soil (e.g. Ulrich, 1989), something which was not accounted for in the model.

CONCLUSIONS

The present model analysis improved data explanation of the 18-year Solling data set. Dynamics of Cl, SO_4 and N were investigated, using a comprehensive and dynamic model. In the model, we considered the integrated effects of throughfall composition, hydrology and biogeochemical processes on soil water chemistry. Chloride and SO_4 concentrations in soil solutions were generally well predicted. The observed time series of SO_4 at the 90 cm depth exhibited three typical phases: (1) strongly increasing SO_4 concentrations until the mid-1970s, where solution concentrations adapted to atmospherically controlled levels due to saturation of adsorption sites, (2) maximum SO_4 concentrations from 1978 until 1981 controlled by the, retarded, arrival of high SO_4 depositions at the 90 cm depth, and (3) from 1982 onwards, declining SO_4 concentrations in response to reduced SO_4 deposition levels. The modelled Freundlich SO_4-sorption isotherms, however, underestimated SO_4 desorption during the last phase. Simulated N concentrations in litter percolates underestimated observations in wet periods, probably due to a stronger decoupling of mineralization and uptake of N than anticipated in the model. Because N concentrations in the mineral soil appeared highly sensitive to inputs of N with litter percolates and because N stores in litter in the Solling spruce forest are large (145 kmol ha^{-1} in 1983), a proper modelling of N release from litter needs major attention. The use of measured N concentrations in litter percolates as model input to the mineral soil improved the predictability of long-term changes in N concentrations at the 90 cm depth and might be considered in other model studies.

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Appendix 1. Model processes, hydrology

HYDROLOGY

Processes in each layer l, during timestep Δt:

percolation:

$$J_p = K_{sat} \times \Delta t \times \frac{(\Theta-\Theta_{fc}) \times (\Theta-\Theta_{wp})}{(\Theta_s-\Theta_{fc}) \times (\Theta_s-\Theta_{wp})} \times \alpha \quad \text{in litter } J_p = K_{sat} \times \Delta t \times \frac{(\Theta-\Theta_{fc})}{(\Theta_s-\Theta_{fc})}$$

if $\Theta > \Theta_{fc}$ then $\alpha = 1$ else $\alpha = [(\Theta_{l+1,t-\Delta t} - \Theta_{wp,l+1})/(\Theta_{s,l+1} - \Theta_{wp,l+1})]^2$. if Θ-litter$<\Theta_{fc}$ then $J_p = 0$

where Θ = volumetric moisture content, fc = field capacity, wp = wilting point, s = saturated and K_{sat} = saturated conductivity

water uptake:

$$J_{wu} = (T_{pot}) \times \Delta t \times fwu_l \times \frac{(\Theta-\Theta_{wp})}{(\Theta_{fc}-\Theta_{wp})}$$

where T_{pot} = potentential transpiration (Manderscheid, 1992), fwu_l = fraction of water uptake from layer l ($0 < fwu_l < 1$). If $\Theta > \Theta_{fc}$ then $J_{wu} = (T_{pot}) \times \Delta t \times fwu_l$, if $\Theta < \Theta_{wp}$ then $J_{wu} = 0$

Mass balance for layer l with thickness D:

$$\Theta_{l,t} = (\Theta_{l,t-\Delta t} \times D + J_{p,l-1} - J_{p,l} - J_{wu,l})/D$$

Appendix 1. Model processes, chemistry

CHEMISTRY

Components: H, K, Na, Ca, Mg, Al, NH_4, Mn, Cl, SO_4, NO_3, DOC
Species: Al: Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $AlSO_4^+$, SO_4: SO_4^{2-}, $AlSO_4^+$

Processes in each layer l, during timestep Δt:

Sulphate adsorption:

$\{SO_4\}_a = A \times [SO_4]^B$ (Freundlich)

where { } = adsorbed concentrations (mol dm^{-3} soil)
and [ ] = solution concentration (mol l^{-1})

Uptake by vegetation:

$J_{nu} = J_{wu,l,\Delta t} / \Sigma J_{wu,l} \times yrs \times (J_{nu,avg})$

where $\Sigma J_{wu,l}$ = cumulative water uptake from layer l during simulation period, $J_{nu,avg}$ = long-term annual average nutrient uptake from the soil, and $J_{nu} <=$ (pool of nutrient in solution).

Mineralization:

$J_{min} = k \times T^2 \times f \times \Delta t \times (J_{min,avg})$

where T= temperature in °C, if T<2°C $J_m=0$, k=rate constant, $J_{min,avg}$ = long-term annual average mineralization from litter. If $\Theta < \Theta_{fc}$ then $f = (\Theta - \Theta_{wp}) / (\Theta_{fc} - \Theta_{wp})$ else f=1.

Nitrification:

$J_{nit} = K_{nit} \times \Delta t \times [NH^{4+}] / (10^{-4} + [NH^{4+}])$ (Michaelis-Menten)

where K_{nit} = nitrification rate constant

Cation-exchange equilibrium:

$2\{X^{n+}\} + n(Ca^{2+}) <---> n\{Ca^{2+}\} + 2(X^{n+})$ (Gaines-Thomas)

where X= H^+, Mg^{2+}, K^+, Na^+ Al^{3+}, NH^{4+}, Mn^{2+}, {} = adsorbed equivalent fractions, () = molar activities in solution

Appendix 1 (continued). Model processes, chemistry

Weathering of base cations and Mn:

$J_{w,b} = K_w \times \Delta t \times M_b \times (H^+)^p$

where b= Ca^{2+}, Mg^{2+}, K^+, Na^+, Mn^{2+}, M= element mass and $0<p<1$ and K_w= weathering rate constant

Al-weathering:

$J_{w,Al} = K_w \times \Delta t \times (1-[IAP]/K_{AlOH3})$

where K_{AlOH3} = solubility constant of Al-trihydroxide
and IAP= ion activity product in solution = $(Al^{3+})/(H^+)^3$, with () = molar activities

Complexation in solution:

$Al^{3+} + H_2O \;\; <--> AlOH^{2+} \; + H^+$
$Al^{3+} + 2H_2O \;\; <--> Al(OH)_2^+ + 2H^+$
$Al^{3+} + SO_4^{2-} \;\; <--> Al(SO_4)^+$

Balances for layer l with thickness D:

Mass balance for each component except H:

$Ctot_t = (Ctot_{t-\Delta t} + Sink/D - Source/D)/\Theta_t$ (mol dm^{-3} soil)

where Ctot = $[C] \times \Theta + \{C\}$ i.e solution plus adsorbed concentration (mol dm^{-3} soil)
Sink = $J_{nu} + J_{p,l,t-\Delta t} \times [C]_{l,t-\Delta t}$ (+ J_{nit}, in case of NO_3)
Source = $J_{min} + J_w + J_{p,l-1,t-\Delta t} \times [C]_{l-1,t-\Delta t}$ (+ J_{nit}, in case of NH_4)

Proton concentration from charge balance:

$H_{tot} = CEC - \Sigma\{C_{cat}\} - \Sigma([C_{cat}] \times Val_{cat}) + \Sigma([C_{an}] \times Val_{an})$ (mol dm^{-3} soil)

where H_{tot} = concentration of H^+ adsorbed and in solution, $\{\Sigma C_{cat}\}$ = sum of all adsorbed cations except H, Val = Valency, $\Sigma([C_{cat}] \times Val_{cat})$ = sum of all cations in solution except H.

Chapter 5

Aluminum solubility controls in acid forest soils (I): testing hypothesis on data from Solling, Germany

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ABSTRACT

Hypotheses for controls of the Al solubility in acid forest soils were tested, using the large data set of soil- and solution chemistry of the Solling Spruce site (Germany). The observed low Al^{3+}-H^+ reaction stoichiometries (±0.3) as well as the measured increase of CEC in the surface soil with time, support the hypothesis of Al solubility control by complexation to soil organic matter (SOM). Incorporation of Al-SOM equilibrium in a comprehensive soil acidification model improves simulations of seasonal and long-term pH changes in soil solutions at Solling.

INTRODUCTION

Soils in the Solling area in Germany are strongly acidified due to high atmospheric inputs of acids from anthropogenic sources (Matzner 1989). Inputs of strong acids are largely neutralized in the mineral soil by release of Al from reactive soil pools. At present, base saturation of the mineral soil is below 4% and Al-species constitute over 70% of the cationic charge in solution. Recent evidence suggests that dissolved Al is toxic to terrestrial and aquatic biota. Despite the ecological relevance of Al and its omnipresence in solution, the mechanism(s) that control the solubility of Al are still poorly understood.

In two previous paper (Wesselink et al. 1994a, 1994b), principles and key equations of a soil acidification model were outlined, and the processes that regulate the chemistry of the major anions (Cl, SO_4 and NO_3) and base cations in soil solutions at the Solling spruce site were discussed in detail. In the present paper we will focus on Al and H.

Most soil acidification models use gibbsite equilibrium as an Al solubility control in soil solutions (e.g. ILWAS, MAGIC, STEADQL). Yet, in soils with high rates of Al-mobilization, equilibrium with $Al(OH)_3$ seems exception rather than rule (Prenzel & Schulte-Bisping 1991, Matzner & Prenzel 1993, Mulder & Stein 1993). To better explain the data, time dependent release of Al has been proposed (van Grinsven et al. 1992, Matzner & Prenzel 1993) and was incorporated in models like NUCSAM and ILWAS. By contrast, Cronan et al. (1986) found that in organic soil horizons Al-solubility was controlled by complexation of Al to soil organic matter. More recently, a similar mechanism was hypothesized for mineral soils (Mulder et al. 1989), even when low in organic matter content (Mulder & Stein 1994).

In this paper, data from Solling were used to test several mechanisms that may control the solubility of Al. Data included extensive sets of soil solution composition and soil chemistry records. The model WHAM (Tipping 1993) describing metal complexation to humic compounds was used to study the possibility of Al solubility control by humic compounds. A derivation of this model was incorporated in a comprehensive soil acidification model (WATERSTOF, Wesselink et al. 1994a) to simulate the dynamics of all major cations and anions at the Solling spruce site during the 1973-1991 period. In addition, two deposition scenarios were analyzed.

MATERIALS AND METHODS

To study Al^{3+}-H^+ relationships in soil solutions, the speciation of dissolved Al was calculated with the chemical equilibrium model ALCHEMI (Schecher & Driscoll 1987). Al-F species were not accounted for, because F concentrations were not measured. Fluoride concentrations are probably low compared to total Al, however, and therefore of minor importance for the speciation of Al. Complexation of dissolved Al to DOC was not considered, as in Solling dissolved Al is predominantly in the inorganic from (>95%) even at the 10 cm depth (Dietze & Ulrich 1992). Calculations were done with a constant soil temperature of 8°C. The logarithmic form of the ion-activity-product for Al-trihydroxide was calculated as $\log(Al^{3+})-3\times\log(H^+)=\log Q$, where brackets denote solutions activities.

Modelling Al complexation to soil organic matter

To study Al solubility control by complexation to soil organic matter, we used the model WHAM (Tipping 1993). WHAM is derived from Model V (Tipping and Hurley 1992), and describes proton and metal binding to humic substances (fulvic and humic acids). The model considers bidentate and monodentate complexation of metals to discrete sites and non-specific binding in the diffuse double layer. Precipitation of $Al(OH)_3$ is assumed, in case the $Al(OH)_3$ solubility is exceeded. Calculations were done with 1 gr fulvic acids per liter, with a carboxylic acidity of 4.73×10^{-3} mol_c gr^{-1} fulvic acid and Al additions (Al_t) of 8, 16 and 22×10^{-4} mol l^{-1}. Assuming a fulvic acid carbon content of 50%, this corresponds to molar Al_t/C ratios of 0.024, 0.048 and 0.068. The equilibrium chemistry of this system was calculated at various HCl or NaOH additions and at constant $MgCl_2$ concentration of 1×10^{-3} M. Intrinsic protonation constant for type A, carboxylic, acids was set at pKA=3.26, for type B, phenolic, acids at pKB=9.46. The monodentate Al-carboxyl complexation constant, pK_{MHA} was set at 0.4 and pK_{MHB} at 1.6. WHAM calculates bidentate equilibrium constants by multiplying the given monodentate site equilibrium constants. It was assumed that 40% of the monodentate complexation sites on fulvic acids can potentially form bidentate complexes with metals. A temperature of 8°C was used in the equilibrium calculations. For details on WHAM refence is made to Tipping & Hurley (1992) and Tipping (1993).

Modelling chemistry of major anions and cations in Solling

In a recent paper (Wesselink et al. 1994a) a model for the simulation of biogeochemical and hydrological processes in forest soils was outlined. A brief description of model processes is given in Appendix 1. The model was used to calculate the concentrations of all major anions and cations in soil solutions at Solling over the period 1973-1991. In addition, the model was run with two different deposition scenarios. In the 'business as usual' scenario, the monthly input in throughfall and hydrology in the period 1973-1990 was repeated 5 subsequent 18-year periods. In the 'improved environment' scenario the monthly depositions of H, SO_4, NH_4 and NO_3 in 1990 were reduced by 7.5% each year until the year 2000 and were kept constant thereafter. Deposition of Mg and of Ca were reduced with the same percentage. In the 'improved environment' scenario, the hydrology of the 1981-1990 period was repeated each decade after 1990.

RESULTS AND DISCUSSION

AI-SOLUBILITY CONTROLS AT SOLLING, FIELD DATA AND MODEL CONCEPTS

surface soil

Solutions in the upper 20 cm of the mineral soil (Table 1) are strongly undersaturated with respect to synthetic gibbsite (logK=9.1 at 8°C). Laboratory experiments (Matzner 1992) indicate that this may be due to solubility control of Al by complexation to soil organic matter. Indeed, at Solling, secondary, reactive, soil Al in the surface soil is largely associated with soil organic matter, as pyrophosphate and oxalate extract (Table 3) similar amounts of Al (Mulder et al. 1989). Kinetically constrained Al dissolution has also been suggested to explain the undersaturation with respect to gibbsite (Matzner & Prenzel 1992). However, with kinetically controlled release, it may be expected that mineral saturation is approached when residence time of soil solutions increase, i.e. in summer months. This was, however, not apparent from the soil solution data.

Table 1. *Average logQ^{+} values (see text) for the Solling spruce site. Slope, R^2 and level of significance refer to the linear regression of pH-pAl relationships in soil solutions.*

depth	period	logQ	slope	R^2
0 cm	69-73/79-91	5.3	0.28	0.16***
10 cm	81-91	6.9	0.11	0.02
20 cm	81-91	8.1	0.24	0.11**
40 cm	81-91	8.9	0.33	0.17***
90 cm	78-91	8.7	0.25	0.30***

+ $\log Q = \log(Al^{3+}) - 3 \times \log(H^{+})$

*** is significant at the 99.99% confidence level

** is significant at the 99.9% confidence level

sub-soil

Below the 20 cm depth, soil solutions at Solling seem to approach a constant $Al(OH)_3$ ion-activity product (expressed as logQ in table 1). Yet, on average, solutions remain undersaturated with respect to synthetic gibbsite (logK=9.1 at 8°C). Furthermore, logQ values vary strongly on a monthly time scale (±1.5 log units, Matzner & Prenzel 1992) and do not indicate equilibrium with an $Al(OH)_3$ phase. This is further illustrated for the 90 cm soil depth in Fig. 3. There, equilibrium with $Al(OH)_3$ would result in a pH buffered in a narrow range of ca. 0.4 units. This is because any change in total acidity is be largely transmitted to changes in Al and less to changes in H^+. By contrast, measured pH at the 90 cm depth varies almost one unit.

The slope of H^+-Al^{3+} relationships in soil solutions are similar at all depths. Linear regression of pAl versus pH values for individual soil layers indicate a slope of ca. ±0.3 (Table 1). This suggests that the Al solubility in sub- and surface soil is controlled by a similar mechanism. In the next section, we will show that observed H^+-Al^{3+} relationships can be explained by equilibrium complexation to soil organic matter. In this perspective, the laboratory experiments of Prenzel (1982) are of interest. This author carried out batch equilibrium experiments with soil from the 40-50 cm depth at Solling. After equilibration with many different dilute salt solutions ($I=10^{-3}$ M) logQ values varied between 7.2 and 8.7, where logQ values decreased (i.e. solutions more undersaturated) with decreasing pH. These experiments support field observations as most clearly demonstrated for the 90 cm depth (Fig. 1). Visual inspection of H^+-Al^{3+} relations in the batch experiments of Prenzel (1982, Fig. 4.2-1) indicates a H^+-Al^{3+} reaction stoichiometry of ±0.6.

Equilibrium with solid phase humic compounds: solution chemistry

The model WHAM (Tipping 1993) was applied to study how complexation of Al to humic compounds may explain the Al^{3+}-H^+ relationships observed in Solling. Here, we will use a more general expression for complexation of Al to soil organic matter (Berggren 1992) to explain the pH-pAl curves modelled with WHAM:

$$\text{SOM-Al}^{m} + n\text{H}^{+} \Longleftrightarrow \text{SOM-H}_{n}^{(m+n-3)} + \text{Al}^{3+} \qquad (1)$$

where *SOM* is soil organic matter, *m* is the charge of the Al-humic complex and *n* the number of reacting protons, equal to or smaller than three. Eq. (1) can be expressed as :

$$(\text{Al}^{3+})/(\text{H}^{+})^{n} = K'_{\text{Al-SOM}}\times[\text{SOM-Al}]/[\text{SOM-H}_{n}]=K''_{\text{Al-SOM}} \qquad (2)$$

and $K'_{\text{Al-SOM}}=K_{\text{Al-SOM, intr.}}\times e^{-(3-n)wZ}$

where brackets indicate molar activities, squared brackets indicate molar fractions and $K_{\text{Al-SOM, intr}}$ is the intrinsic equilibrium constant. The factor $e^{-(3-n)wZ}$ accounts for the effect of the electrostatic field on binding strength, where Z is the net charge of the humic compound and *w* an electrostatic interaction factor (Tipping & Hurley 1992). pH-pAl relationships in the fulvic acid model system were calculated at three Al additions when titrating with mineral acid or base (Fig. 1). At relatively low Al additions ($Al_t/C=0.024$), bidentate binding of Al dominates (Eq. (1,2), n=2). However, upon acid addition non-complexed SOM sites are protonated. This results in a decrease of the charge (Z) of SOM and of the apparent solubility $K'_{\text{Al-SOM}}$. Consequently, the net H^+-Al^{3+} reaction stoichiometry is only around one. Equation (2) also shows that $K'_{\text{Al-SOM}}$ increases with the degree of Al complexation. This explains the shift of the pH-pAl curves to lower pAl and higher pH values in Fig. 1 upon addition of Al. At relatively high Al addition, bidentate binding sites gradually become saturated and monodentate binding of Al becomes more important (Eq. (2), *n*=1). Again, upon acid addition SOM protonation will cause a decrease in both the charge (Z) of SOM and in $K'_{\text{Al-SOM}}$, resulting in a net H^+-Al^{3+} reaction stoichiometry between zero and one.

The shift of the modelled pH-pAl curves with Al saturation of SOM is qualitatively in agreement with field data. Field data indicate that the saturation of SOM with Al, as estimated from measured Al_{pyr}/C ratios, increases with depth (Table 3). In the sub-soil, measured Al_{pyr}/C ratios increase to ±0.15, which suggests a full saturation of organic matter complexation sites with Al, i.e. one Al per carboxylic group (Buurman 1985). WHAM calculations with Al_t/C ratios of 0.15, however, resulted in much higher Al concentrations in solution than observed. Possibly, more than the assumed 40% of complexation sites can from bidentate complexes, which would increase the Al complexation to SOM. Alternatively, solutions in the sub-soil may be in local equilibrium with SOM which is relatively depleted in Al and therefore has lower Al_t/C ratios than the bulk soil.

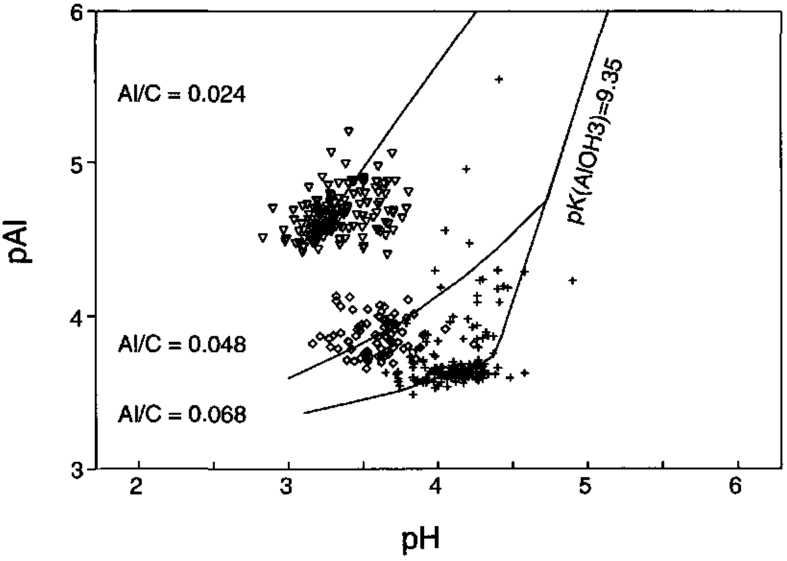

Figure 1. pH and pAl relations observed in litter percolates (∇), 10 cm (◊) and the 90 cm depth (+). Lines indicate simulations with WHAM.

Equilibrium with solid phase humic compounds: soil chemistry

As follows from Eq. (1), decomplexation of Al will decrease the positive charge of the complexing surface ligand (e.g from $SOM\text{-}Al]^+$ to $SOM\text{-}H_2]^0$ in case of bidentate binding). Where the bulk of SOM is probably negatively charged at pH>2 (de Wit 1992), decomplexation of Al, i.e. local removal of positive charge, may increase the bulk negative charge of SOM. At Solling, we find field evidence for this phenomenon. From table 2, we calculate the total release of organically complexed Al from 1979-1991 as the sum of the solute flux of Al plus the increase of NH_4Cl exchangeable Al. The total Al release of ±72 $kmol_c\ ha^{-1}$ or 24 $kmol\ ha^{-1}$, coincides with an increase in CEC of ±33 $kmol_c\ ha^{-1}$. Therefore, with each mol of released Al the CEC increases 1.4 equivalents, which is consistent with an intermediate of a bidentate and monodentate complexation reaction. Though this calculation is tentative, given the uncertainties in both CEC measurements and solute flux estimates, it is, in our view, yet another indication for Al-solubility control by binding to soil organic matter. The hypothesized release of Al from organically bound pools (see also Chapter 6 of this thesis) and concurrent increase of NH_4Cl exchangeable Al^{3+} suggest that part of the decomplexed Al is re-adsorbed in a more readily exchangeable, probably electrostatically bound, form. Note, that an increase of CEC due to dissolution of Al-hydroxy interlayer from clay minerals (e.g. Süsser 1987, Prenzel & Schulte-Bisping 1992) is unlikely in our case, as X-ray analysis detected no hydroxy interlayering in clay minerals in the upper 10 cm soil and only traces in the 10-15 cm soil (Wesselink et al. 1994c).

Table 2. *Cation exchange capacity (CEC) and pools of exchangeable Al and H in 1979 and 1991. In addition, the change in CEC and exchangeable Al and H is indicated as well the cumulative solute flux of Al. All data refer to the 0-10 cm soil.*

$kmol_c\ ha^{-1}$	CEC†	Al_{ex}†	H_{ex}	Σsolute flux‡
1979	102	77	9.5	
1991	135	95	23	
Time trend	+33	+18	+14	+54

†) Exchangeable cations were determined by percolation with 1N NH_4Cl, exchangeable protons were calculated, correcting for hydrolysis of exchanged Al (Prenzel & Schulte-Bisping 1991). CEC was calculated from the sum of exchangeable cations.

‡) calculated from observed Al concentrations at the 10 cm depth (1981-1991) and calculated water fluxes. For the years 1979 and 1980 the average flux from the period 1981-1991 was taken.

MODELLING SOLUTION CHEMISTRY AT SOLLING WITH WATERSTOF

In WATERSTOF, the Al-SOM equilibrium was modelled as:

$$(Al^{3+})/(H^+)^n = K''_{Al\text{-}SOM}$$

The increase of $K''_{Al\text{-}SOM}$ with increased Al saturation of SOM (Eq. (2)) was estimated from average observed $K''_{Al\text{-}SOM}$ values and Al_{pyr}/C ratios with depth (Table 3). In case Al equilibrium concentrations exceeded the solubility of $Al(OH)_3$, precipitation of $Al(OH)_3$ was enforced. For Solling, *n* was approximated at a value of 0.3 (Table 1).

Table 3. Selected field data from the Solling Spruce soil.

	C[†] (%)	Al_{pyr}[‡] ($mmol\ kg^{-1}$)	Alox[‡] ($mmol\ kg^{-1}$)	Al_{pyr}/C (mol/mol)	$Al/H^{0.3}=K''_{Al\text{-}SOM}$[§]
litter	50	-	-	0.0034	2.2×10^{-4}
0-10 cm	4.2	64	71	0.018	1.7×10^{-3}
10-20 cm	2.1	89	91	0.05	2.7×10^{-3}
20-40 cm	1.2	133	190	0.13	3.2×10^{-3}
40-90 cm	0.5	74	141	0.18	3.8×10^{-3}

†) from Allewel (1991)

‡) Al_{pyr} is pyrophosphate extractable Al and Al_{ox} is NH_4-oxalate extractable Al. 0-20 cm samples were taken in the F1 plot in 1991, 20-90 cm samples from the 'roof-plot' adjacent to the F1-site in 1990. Extractions were done parallel in separate samples. Al/C in litter was calculated from total Al as given by Matzner (1988).

§) By linear regression with zero intercept the model relationship $K''_{Al\text{-}SOM}=0.059\times Al_{pyr}/C$ ($R^2=0.9$, n=3) was obtained at $Al_{pyr}/C<=0.05$. At $Al_{pyr}/C>0.05$ $K''_{Al\text{-}SOM}$ in the model was assumed independent of the Al_{pyr}/C ratio and set at an average value of 3.4×10^{-3}.

business as usual scenario

As discussed, reactive soil Al in the surface soil is probably largely organically bound. At the current high acid deposition levels, Al mobilization rates from these pools may exceed resupply from primary mineral weathering, and depletion may occur. To evaluate this, the scenario of unchanged deposition levels was run for the period 1991-2060.

Fig. 2 shows decreasing pH and increasing pAl with time at the 10 cm depth. These changes are due to decreasing solubility of soil organic Al which is depleted with time, as modelled with the linear relationship between K''_{AlSOM} and Al_{pyr}/C ratios. The simulated annual decrease in pH until 2010 (ca. 0.015 units) is similar to that currently observed at Hackfort (the Netherlands), which receives about the same acid load (Mulder & Stein 1993). Note, that soil carbon pools were not modelled dynamically, and therefore $K''_{Al\text{-}SOM}$ decreased due to depletion of Al_{pyr} only. The main primary mineral source of Al and base cations (K and Mg) at Solling is illite. Aluminum release from illite was calibrated at 0.4 kmol ha^{-1} in the 1980s. This value was obtained from an estimated Mg release from illite of 0.1 kmol ha^{-1} yr^{-1} in the upper 10 cm and a Mg:Al molar release ratio of 1:4 (Wesselink et al. 1994c). Furthermore, illite weathering was found to be strongly dependent on pH ($R\approx(H)^{0.8}$, Wesselink et al. 1994c). At the end of the simulated time period a steady state is approached, where weathering of Al from illite has increased to 0.8 kmol ha^{-1} yr^{-1}, due to decreased pH, which is sufficient to resupply the Al released from SOM. Concurrently, modelled (Mg+Ca)/Al molar ratios increases from about 0.9 to 2.1, due to decreasing Al concentrations (Fig. 2) and increased

Mg weathering.

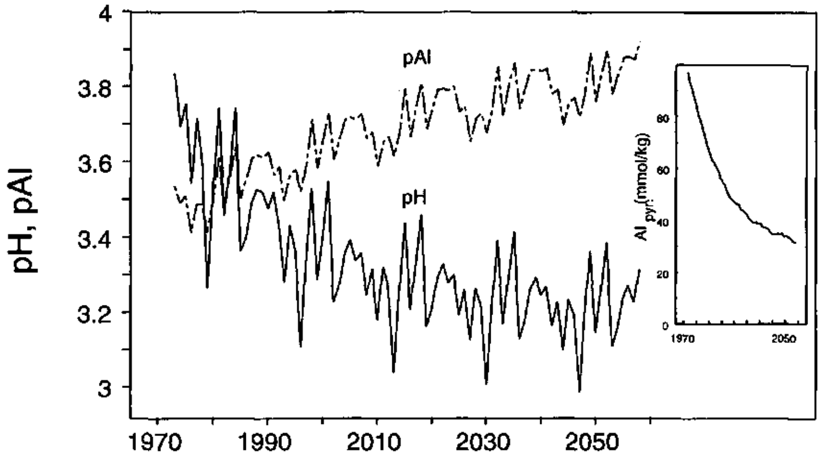

Figure 2. *pH and -log(Al_t) (pAl) with time at the 10 cm depth in the 'business as usual scenario'. Inset shows the size of the organically bound Al pool with time.*

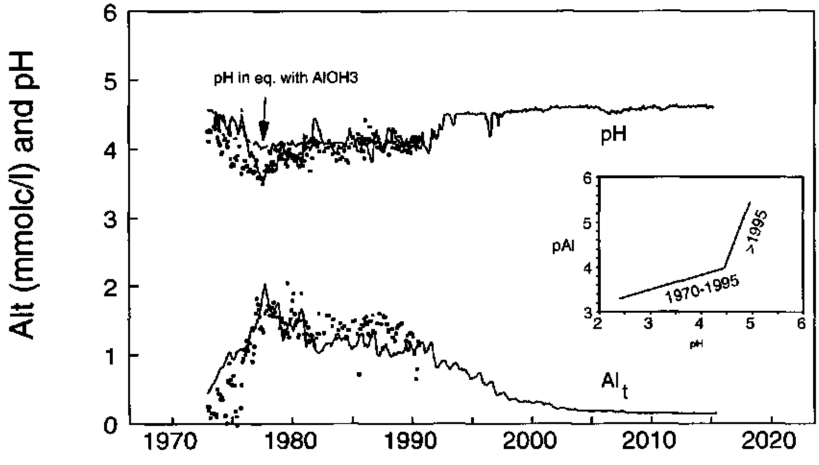

Figure 3. *Observed (■) and simulated pH total dissolved Al at the 90 cm depth during the 1973-1990 period, followed by the 'improved environment' scenario. The pH in equilibrium with Al(OH)$_3$ was not modelled with WATERSTOF. Instead, it was calculated by adding monthly measured Al^{3+} and H^+ activities and redistributing these species as governed by Al(OH)$_3$ equilibrium, where pK_{AlOH3} was set at the average observed value of 8.5 (Table 1). Inset shows time path of pAl-pH relationship.*

Improved environment scenario

In the 1973-1990 period, modelled Al solubility is controlled by organic Al, throughout the soil profile. As apparent from Fig. 3, simulations of pH dynamics are improved compared to $Al(OH)_3$ solubility control. Concentrations of Al are somewhat underestimated in the 1980s, because predicted SO_4 concentrations were lower than observed (Wesselink et al. 1994a). In the 'improved environment' after 1990, salt levels at the 90 cm depth quickly adjust to reduced atmospheric inputs. As was demonstrated with the model WHAM (Fig. 1), a sharp transition from Al-SOM to $Al(OH)_3$ solubility control may occur at lower acidity levels. This rapid transition was simulated in the sub-soil at Solling in the improved environment scenario where solutions at the 90 cm depth reach $Al(OH)_3$ equilibrium after 1995. As a consequence of, regained, $Al(OH)_3$ solubility control the predicted pH changes after 1995 are small compared to the preceeding period, were organic complexation controlled Al solubility.

CONCLUSIONS

At present, the Al solubility at Solling is not controlled by a mineral $Al(OH)_3$ phase. Alternatively, the low Al^{3+}-H^+ relationships in soil solution of the Solling spruce site were explained by Al complexation to soil organic matter. Further support for this mechanism was found in the observed CEC increase in the surface soil, associated with decomplexation of Al. Due to the low Al^{3+}-H^+ stoichiometry that results from equilibrium complexation of Al to soil organic matter, the pH in soil solutions responds strongly to changes in acid anion concentrations. This explains observed seasonal and long-term pH fluctuations of about one unit. The large temporal flucutations of pH implies a potential danger of proton stress to roots (Matzner 1989). A proper description of pH-dynamics is therefore of importance for models that simulate proton stress (e.g. SOILVEG, Berdowski et al. 1991). Also, the low Al^{3+}-H^+ relationships as observed in Solling appear much more common in acid forest soils than previously assumed (Mulder & Stein 1993, Prenzel & Schulte-Bisping 1991). Therefore, solubility control by Al complexation to soil organic matter should be included in soil acidification models. The empirical Al^{3+}-H^+ relationship used in our hydro-biogeochemical model may be easily incorporated in other acidification models that presently calculate $Al(OH)_3$ equilibrium only.

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The use of the educational software package 'Simulation of Soil Forming Processes' (Meijer, E.L & T.C.J. Feijtel, 1993. Department of Soil Science and Geology, Wageningen) was very helpful in gaining insight in Al-SOM complexation reactions. We thank Ed Tipping for kindly providing the model WHAM.

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Appendix 1.

Model processes, hydrology (see chapter 4)

Model processes, chemistry (for full description see Chapter 4)

CHEMISTRY

Components: H, K, Na, Ca, Mg, Al, NH_4, Mn, Cl, SO_4, NO_3, DOC
Species: Al: Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $AlSO_4^+$, SO_4: SO_4^{2-}, $AlSO_4^+$

Processes in each layer l, during timestep Δt:

Cation-exchange equilibrium:

$2\{X^{n+}\} + n(Ca^{2+}) <---> n\{Ca^{2+}\} + 2(X^{n+})$ (Gaines-Thomas)

where X= Mg^{2+}, K^+, Na^+ Al^{3+}, NH^{4+}, Mn^{2+}, { } = adsorbed equivalent fractions, () = molar activities in solution

Primary mineral weathering of base cations and Al:

$J_{w,b}= K_w \times \Delta t \times M_b \times (H^+)^p$

where b= Ca^{2+}, Mg^{2+}, K^+, Na^+, Al^{3+}, M= element mass and $0<p<1$ and K_w= weathering rate constant

Al solubility control by complexation to soil organic matter:

$(Al)/(H)^n=K''_{Al\text{-}SOM}$

where $0<n<3$, $K''_{Al\text{-}SOM}=k \times Al_{pyr}/C$, Al_{pyr} is the pool of pyrophosphate extractable soil Al, and C total soil carbon. If $(Al)/(H)^n > K''_{AlOH3}$ then Al solubility is calculated as: $(Al)/(H)^3=K_{AlOH3}$.

Complexation in solution:

$Al^{3+} + H_2O <--> AlOH^{2+} + H^+$
$Al^{3+} + 2H_2O <--> Al(OH)_2^+ + 2H^+$
$Al^{3+} + SO_4^{2-} <--> Al(SO_4)^+$

Mass and charge balances for layer l with thickness D:

Mass balance for each component except H and Al:

$Ctot_{t+\Delta t} = (Ctot_t + Sink_t/D - Source_t/D)/\Theta_{t+\Delta t}$ (mol dm^{-3} soil)

where Ctot $= [C] \times \Theta + \{C\}$ i.e solution plus adsorbed concentration (mol dm^{-3} soil)
Sink $= J_{nu} + J_{p,l} \times [C]_l$ (+ J_{nit}, in case of NO_3)
Source $= J_{min} + J_w + J_{p,l-1} \times [C]_{l-1}$ (+ J_{nit}, in case of NH_4)

Proton concentration from charge balance:

$H_{tot} = CEC - \Sigma\{C_{cat}\} - \Sigma([C_{cat}] \times Val_{cat}) + \Sigma([C_{an}] \times Val_{an})$ (mol dm^{-3} soil)

where H_{tot} = concentration of H^+ adsorbed and in solution, $\{\Sigma C_{cat}\}$ = sum of all adsorbed cations except H, Val = Valency, $\Sigma([C_{cat}] \times Val_{cat})$ = sum of all cations in solution except H.

pool of reactive soil Al, Al_{pyr}, from Al mass balance:

$Al_{pyr,t+\Delta t} = Al_{pyr,t} + J_{w,Al} - [\ (J_{p,l,t} \times [Al]_{l,t} - J_{p,l-1,t} \times [Al]_{l-1,t}) + (Ctot_{t+\Delta t} - Ctot_t)\ ]$

where [Al] is total Al concentration in solution and Ctot is dissolved plus adsorbed Al

Chapter 6

Aluminum solubility controls in acidic forest soils (II): predicting aluminum activities

Bart Wesselink, Nico van Breemen and Jan Mulder

(European Journal of Soil Science, *submitted*)

ABSTRACT

We have derived and tested a simple model for competitive binding of Al and protons on soil organic matter. Results have given further evidence that Al activities in soil solutions of mineral acid forest soils are controlled by equilibrium complexation to soil organic matter. The model has successfully explained relationships observed between pH and dissolved Al activities for a number of different forest soils. Furthermore, we have found evidence that pools of organically bound Al may be depleted on relatively short time scales. Our data suggest that also inorganic soil Al compounds may dissolve significantly. However, this does not seem to affect the Al solubility control though organic complexation reactions. The previously reported decrease of Al solubility that parallels measured declines in organically bound soil Al in three of the Dutch soils was quantitatively consistent with the organic Al model proposed here.

INTRODUCTION

Mobilization of soil Al is the main acid neutralizing process in acid forest soils low in base cations (Mulder, 1988). Solution data from surface soils indicate that at pH<4.3 undersaturation with respect to Al-containing minerals is common (Prenzel and Schulte-Bisping, 1991), thus ruling out solubility control by these minerals. Alternatively, control of the solubility of Al may be explained by, (i) equilibrium complexation reactions with soil organic matter (humus), or (ii) kinetically controlled release of Al from inorganic Al compounds. The importance of complexation reactions in controlling the Al solubility has previously been discussed in studies of organic O-horizons (Bloom et al., 1979; Cronan et al., 1986; Walker et al.,1990). By contrast, the hypothesized kinetically constrained dissolution of Al is based on experiments with samples from deeper soil layers with low soil organic C levels (Van Grinsven et al., 1992). In acid forest soils, however, Al is mobilized primarily in the mineral surface soil, rather than in the organic layer or in deeper soil horizons (Mulder, 1988). Increasing evidence indicates that organically bound soil Al plays a major role in controlling Al activities in these soil layers (Mulder et al., 1989b; Mulder and Stein, 1994; Dahlgren and Walker, 1993; Wesselink and Mulder, submitted; Berggren, 1992; Bloom et al., 1979). Cronan et al. (1986) derived an empirical model for organic O-horizons to describe the solubility of Al controlled by complexation with organic matter. For Al proton exchange on organic matter in mineral soils, Bloom and Grigal (1985) suggested an empirical relationship, $Al=K_A\cdot(H)^a$ with an exponent *a* of about 1.66. A similar relationship was used by Reuss et al. (1990). However, this model is not generally applicable, as K_A and *a* vary with soil and horizon (Bloom and Grigal, 1985; Mulder and Stein, 1994; Wesselink and

Mulder, submitted). Therefore, our first objective in this study was to derive and test a more generally applicable and yet simple model to describe the solubility of Al in mineral surface soils as controlled by binding to soil organic matter. Field data were available from acid forest soils in the Netherlands, Germany, Denmark and Sweden.

When complexation with soil organic matter controls activities of dissolved Al, depletion of the organically bound Al pool will reduce its solubility (Cronan et al., 1986; Mulder and Stein, 1994). In surface horizons of acid forest soils of the Netherlands and Germany, pools of organically bound soil Al are often low and the rates of Al mobilization relatively high due to high rates of acid atmospheric deposition. In these soils, pools of organically bound soil Al may become depleted in the coming decades (Mulder et al., 1989b), so that gradual decreases in pH and Al concentrations are to be expected. This could cause a significant change in solution chemistry of acid forest soils, with uncertain ecological consequences. Unfortunately, to date no direct evidence for decreasing pool sizes of organically bound Al under field conditions has been reported. Therefore the second objective of this study was to test the Al depletion hypothesis directly by comparing past and present pools of organically bound soil Al in forest soils in the Netherlands and Germany; all these soils have reveived high atmospheric acid inputs. For this purpose, we selected seven sites. These included the three Hackfort sites studied by Mulder and Stein (1994) and two sites at Gerritsfles all five in The Netherlands (Mulder, 1988; Van Dobben et al., 1992), as well as two sites in Solling, Germany (Matzner, 1988). For these sites, the Al contents in 'old' (taken from about 1980) and 'new' (taken in 1991 or 1993) soil samples were compared.

THEORETICAL

Aluminum complexation to soil organic matter

The neutralization of acid atmospheric deposition through release of Al from organic matter binding sites may be illustrated by the following equilibrium reaction (Berggren, 1992; De Wit, 1992):

$$]SAl^{(3-x)+} + xH^{+} \longleftrightarrow\ ]SH_{x} + Al^{3+} \qquad [1]$$

where $]S\text{-}Al$ and $]S\text{-}H_x$ represent Al-bound and protonated humic binding sites, respectively. Mathematically Eqn. [1] can be written as:

$$(Al)/(H)^x = K_{H\text{-}Al}\{]S\text{-}Al^{(3\text{-}x)+}\}/\{]SH_x\} \qquad [2]$$

where round brackets indicate solution activities, braces molar fractions, $K_{H\text{-}Al}$ the exchange constant and x the reaction stoichiometry. Theoretically, the reaction stoichiometry x in Eqn. 1 may have an integer value of 2 or 1, determined by the type of binding of Al to soil organic matter, e.g. monodentate binding to a carboxyl group or bidentate binding to adjacent carboxyl groups, adjacent phenol groups or an adjacent carboxyl and a phenol group (Tipping and Hurley, 1992). In practice, though, x may have a non-integer value between 2 and 0 due to: (i) heterogeneity in binding sites each with a specific binding stoichiometry and (ii) a dependency of $K_{H\text{-}Al}$ on the net charge of the humic compound, which is altered by metal binding, as illustrated by Eqn. 1 (Tipping and Hurley, 1992; De Wit, 1992, chap. 6).

For soils, data on Al and proton activities (Eqn. 2) are available from routine monitoring of soil water chemistry (e.g van Breemen et al., 1988). Parameters needed in the right-hand side of Eqn. 2 —the binding site density of soil organic matter and the fractions of the binding capacity that are Al- and proton-bound— may be difficult to obtain for (poorly defined) soils. We therefore propose, as a first approximation, a simplified alternative for Eqn. 2. Specific soil extraction procedures (Mokma and Buurman, 1982) will be used to estimate the amount of Al bound to humus, Al_{org}, and $]SH_x$ is estimated from the total carbon content of the soil. Thus Eqn. 2 is rewritten to:

$$(Al)/(H)^x = K_{H\text{-}Al}*Al_{org}/C \qquad [3]$$

Eqn. 3 can be rewritten as:

$$pY = pK_{H\text{-}Al} + x pH \qquad [4]$$

where $pY=p[(Al)*C/Al_{org}]$ and p indicates -log. When the validity of Eqns. 1-3 is to be tested against an arbitrary set of data, pY plotted against pH should yield a straight line with slope x and intercept $pK_{H\text{-}Al}$.

Figure 1 illustrates how, for a hypothetical case, depletion of the organically bound Al pool, resulting in a decrease in the right-hand side term of Eqn. 3, will shift the pH-pAl relationship, and decrease the solubility of Al.

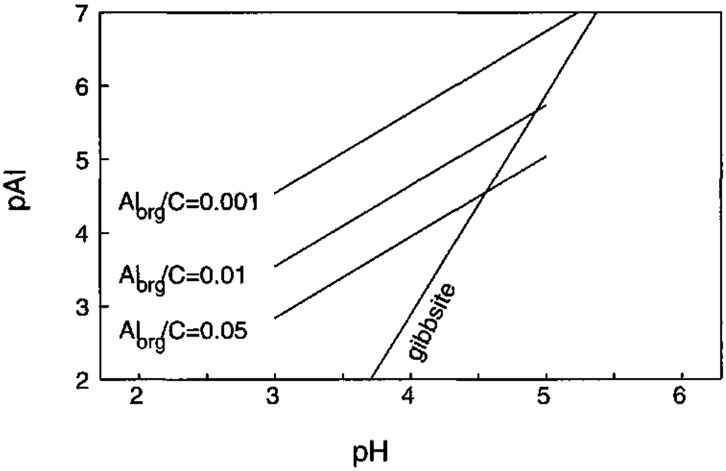

Figure 1. *Theoretical example of pAl vs. pH relationships as calculated using the model:* $\{Al\}/\{H\}^{1.1}=10^{1.76}*Al_{org}/C$, *at molar (bound-Al):C of 0.05, 0.01 and 0.001. The gibbsite equilibrium line (pK=9.12 at 8°C) is also indicated.*

MATERIALS AND METHODS

Study sites

As part of this study we used 'old' samples; further we resampled soils at Hackfort and Gerritsfles in the Netherlands, and Solling in Germany. In addition, we used existing data on the soil solution composition at these sites. For detailed site characteristics, we refer to Van Breemen et al. (1988) for Hackfort, Van Dobben et al. (1992) for Gerritsfles and Matzner (1988) for the Solling sites.

The Hackfort site is a small 3.2-ha oak-birch woodland (dominated by *Quercus robur* and *Betula pendula*) in the eastern part of the Netherlands with acid brown forest soils. Three plots (HA, HB, HC) were selected and soils classified as Aeric Haplaquept (HA), Umbric Dystrochrept (HB) and Aquic Udipsamment (HC) (according to Soil Survey Staff, 1975). The soils have developed in sandy loam (HA), loamy fine sand (HB) and fine to medium sand (HC). Clay content accounts for 14% (HA), 8% (HB) and 4% (HC) in the upper 20 cm. Clay mineralogy is dominated by 1.4 nm hydroxy-Al interlayered vermiculites. In each plot, atmospheric input and soil solution chemistry was monitored in duplicate (indicated with subscript *i* or *ii*) from 1981 until 1988. Total acid loads ranged from 7.5 (HA), through 5.0 (HB) to 3.0 (HC) $kmol_c\ ha^{-1}\ yr^{-1}$, where differences are mainly due to different rates of nitrification of atmospherically deposited NH_4.

Gerritsfles is a driftsand area in the central part of the Netherlands, where two plots have been established, one with a forest vegetation (GF) dominated by *Pinus sylvestris* and one with bare sand (GB). Upon resampling in 1993, the bare plot was fully covered with algae and mosses. Both soils are Typic Udipsamments (without distinct characteristics of soil formation) in well-sorted fine sand. Hydrochemistry at both sites was monitored from 1982 to 1987. Total acid loads were 5.0 $kmol_c\ ha^{-1}\ yr^{-1}$ on the forest (GF) and 2.0 $kmol_c\ ha^{-1}\ yr^{-1}$ on the bare sand (GB). Differences in acid loads are due to the presence of a dry deposition enhancing forest cover at the GF plot.

The Solling site is located 500 m above sea level in central Germany. At Solling, two plots have been studied, one forested with *Fagus silvatica* (B1) and one with *Picea abies* (F1). At both plots soils are Typic Dystrochrepts which have developed in a 60-80-cm loess layer overlying soliflucted material from weathered triassic sandstone. Clay mineralogy is dominated by illite and vermiculite; no Al interlayering was detected (Wesselink et al., 1994b). Hydrochemical measurements were started in 1969. Initially, the soil solution chemistry was only measured at 0-cm and 90-cm soil depths. Monitoring of the soil solution chemistry at intermediate depths started in 1981. Total acid loads at Solling were ca. 8.0 (F1) and 3.0 (B1) $kmol_c\ ha^{-1}\ yr^{-1}$. The total acid load at the F1 plot is much higher than at B1 due to more efficient scavenging of acid atmospheric deposition by the spruce canopy, and higher NO_3 and SO_4 leaching rates from the spruce soil.

In this study, we also used data on the chemical composition of soils and soil water chemistry from (i) sites at Tongbersven and Hasselsven, two sandy spodosols in the Netherlands (Mulder, 1988; Van Dobben et al., 1992), and (ii) three cambisols and three spodosols in southern Sweden (Berggren, 1992).

In all soils studied here, acid loads are largely neutralized through dissolution of Al in the upper 20 cm of the mineral soil.

Sampling and analysis of soil solutions

A detailed description of the sampling and analytical procedures has previously been given by Van Breemen et al. (1988) (Hackfort), Van Dobben et al. (1992) (Gerritsfles, Tongbersven and Hasselsven), Matzner (1988) (Solling), and Berggren (1992) (all Swedish sites). In brief, the following procedures were used:

At Hackfort, soil solutions were sampled monthly from type 1910 high-flow porous ceramic cups (Soil Moisture Corp., Santa Barbara, California) after evacuating (50 kPa) overnight. At Gerritsfles, Tongbersven, Hasselsven soil solutions were collected continuously from polyacrylate filter plates (Driscoll et al., 1985) by constant low suction (ca. 10 kPa) and analyzed monthly. At Solling soil solutions were sampled continuously from porous ceramic cups (type P 80, Hetsch et al., 1979) by continuous low suction and analyzed monthly. At the Swedish sites, solutions were sampled continuously from plexiglass zero-tension column lysimeters (Berggren, 1992) and analyzed every 7-12 weeks (Berggren, 1992).

At Hackfort and Gerritsfles Al was analyzed colorimetrically using pyrocatechol violet after acidifying solutions to pH 2 (Velthorst, 1993). At the Solling and the Swedish sites, Al was measured by atomic absorption spectrometry (König et al., 1989; Berggren, 1992). Soil solution chemistry data used in the present study comprised 6 (Hackfort), 5 (Gerritsfles, Tongbersven, Hasselsven), 9 (Solling) and 1.5 years (Swedish sites) of monitoring data.

Resampling of selected soils in the Netherlands and Germany

The Hackfort soils were sampled in 1980 and the Gerritsfles soils in 1982, both at the beginning of the monitoring programmes. Single mixed soil samples were taken at varying depth intervals from the walls of soil pits in which ceramic cups were installed afterwards. These sampling points are well documented (Van Breemen et al., 1988, Van Dobben et al., 1992) and old pits could be traced back accurately for resampling. In 1993 single samples were obtained from the same depths as the old samples by mixing triplicate auger probes taken within 0.5 m of the old sampling location. At Solling, old (1979) and new (spruce 1991, beech 1993) samples which were routinely taken for inventories were used. Four or five samples were taken from the 100×100 m^2 plots (Matzner, 1988; Wesselink et al., 1994c), each sample was mixed from 5 sub samples obtained by auger. The sampling points were evenly distributed over the sites. From the 1979 sampling, 2 to 3 mixed samples were still available for the present analysis. All samples, 'old' and 'new', were air-dried, sieved (2 mm) and stored in small plastic containers.

Analysis of soils

Soil Al in old and new samples from Hackfort, Gerritsfles and Solling was extracted with: 1) *Na*-pyrophosphate: 1 g of air-dried soil with 100 ml 0.1M sodium pyrophosphate for 16 h and 2) *NH_4* oxalate: 1 g of air-dried soil with 50 ml 0.1M NH_4 oxalate adjusted to pH 3, 4 h in the dark (Van Lagen, 1993). In the pyrophosphate extracts superfloc was added before centrifugation to stimulate settling of colloidal particles. Extractions 1 and 2 are operationally defined estimates of secondary Al. Pyrophosphate (at pH 10) extracts organically bound Al and minor amounts of amorphous hydrous oxides (McKeague, 1967). Oxalate (at pH 3) extracts amorphous Al from hydrous oxides and organic matter and minor amounts of non-silicate crystalline Al (Mokma and Buurman, 1982). In both extracts, dissolved Al was analyzed with atomic adsorption spectroscopy (AAS). Old and new samples were extracted pair-wise to minimize differences in experimental conditions. Total soil C in old and new samples was measured using an element analyzer (Carlo Erba).

For study sites where soils were not resampled, soil chemical data were obtained from the literature. Pyrophosphate extractable Al data at Tongbersven and Hasselsven is given by Mulder et al. (1989b) and Mulder (1988) and for the Swedish sites by Berggren (1992). In cases where extraction with pyrophosphate was done sequentially, i.e. following KCl extraction, the generally minor amounts of Al extracted by KCl were included in the Al_{pyr} values used in this study.

Computations

Aluminum activities in soil solutions of the Dutch and German sites were calculated using ALCHEMI (Schecher and Driscoll, 1987), assuming a constant temperature of 7°C and correcting for ionic strength. Complexation of Al to dissolved organic matter in soil solution was not considered. At Hackfort (10 cm) this assumption may lead to an overestimation of the free Al activity of around 30% (Mulder and Stein, 1994). At Solling and also in the deeper soil layers at Hackfort, dissolved Al was predominately found in an inorganic form (Dietze and Ulrich, 1992; Mulder et al., 1987). For the Swedish sites, arithmetic mean Al activities and pH over the sampling period were obtained from Berggren (pers. comm., and Berggren, 1992). Complexation of Al to DOC was accounted for in these data.

Aluminum leaching that occurred in the various soil layers at Hackfort, Gerritsfles and Solling between ca. 1980 ('old' samples) and 1992 ('new' due to resampling) was estimated from annual average fluxes reported by Van Breemen et al. (1988) (Hackfort) and Mulder et al. (1989a) (Gerritsfles). These values were compared with the losses of solid-phase Al, as estimated from the different soil extractions. Only cases where the sampling depth intervals of soil and solutions were the same, or nearly so, were considered. For Solling, Al fluxes in the surface soil have not been reported. As a first approximation, we assumed that annual average Al fluxes reported for the 90-cm depth at Solling (Matzner, 1988), were mobilized in the upper 20 cm of the mineral soil. This assumption seems reasonable in the light of the rather constant Al concentrations below the 20-cm depth (Matzner and Prenzel, 1992).

Statistics

Differences in extractable soil Al in old and new sample pairs were compared using the Student's *t*-test for paired samples (Snedechor and Cochran, 1980). This test was used assuming that differences in the individual sample pairs (D_i) were normally distributed around the average difference between old and recent samples (μ_D) (Snedechor and Cochran, 1980).

RESULTS

Solution chemistry

Solutions from the Dutch and German soils (Fig. 2, 1-19) were undersaturated with respect to synthetic gibbsite, except for the sub soil (40-cm depth) at the bare Gerritsfles driftsand plot (Fig. 2, nr 10). Solutions from the Swedish soils (Fig. 2, 20-28) were found close to the gibbsite equilibrium line. For individual horizons H^+-Al^{3+} relationships were estimated from the slope of a linear regression of monthly measurements of pH against pAl (x in Table 1). Slopes were always less than one and in about half the cases significantly different from zero. Although the Swedish soils were on average found close to the gibbsite equilibrium, Berggren (1992) reported slopes of ca. 1.5, contrary to the cubic relationship (i.e. slope of three) predicted by gibbsite equilibrium. A regression of average pAl vs. pH values from the 28 soil layers included in this study indicates that there is no simple linear relationship between average pAl and pH values (Fig. 2, $pAl=0.16*pH+3.4$, $R^2=0.04$). We therefore tested the proposed equilibrium in Eqn. 1 on our data.

Test using the model

To test the proposed equilibrium in Eqn. 1 on our data, we calculated values of pY, (Eqn. 3) for the 29 soil layers in our study. For soils that were resampled in this study (Gerritsfles, Hackfort and Solling), we calculated average C content from 'old' and 'new' values (Table 1). Carbon contents for the other sites are given in Table 4. For soils that were resampled the average organically bound Al pools (Al_{org}, Eqn. 3) were estimated from 'old' and 'new' Al_{ox} values (Table 1, see also *'Resampling of soils'* below). Organically bound soil Al for the other sites was estimated from Al_{pyr} values (Table 4). In calculating pY values (Eqn. 3) molar $C:Al_{org}$ ratios were used. Data are shown in Fig. 3.

Table 1. *Average values of selected soil and solution parameters at Hackfort (HA, HB, HC), Gerritsfles (GF, GB) and Solling (F1, B1). The code numbers refer to Fig. 2-4.*

Site no.	Code	Depth (cm)	pH	pAl	*n*	x[1]	Al_{ox}[2] .... % ...	C[2]
1	HAi	10	3.28	4.07	46	0.43*	0.075	4.0
2	HAi	20	3.49	3.79	53	0.29	0.095	1.9
3	HAii	10	3.52	4.04	27	0.32***	0.08	3.7
4	HBi	10	3.34	4.21	49	0.36	0.095	4.7
5	HBii	10	3.22	4.08	42	0.55	0.072	8.1
6	HCi	10	3.64	3.93	41	0.29	0.03	3.8
7	HCii	10	3.60	4.17	54	0.18	0.02	2.6
8	HCii	20	3.61	4.09	62	0.29***	0.02	0.2
9	GF	40	3.98	3.58	88[3]	0.93***	0.045	0.5
10	GB	40	4.43	4.29	47	0.37*	0.04	0.24
11	F1	10	3.55	3.89	73	0.11	0.21	3.6
12	F1	20	3.98	3.77	73	0.24**	0.27	2.1
13	B1	10	3.84	4.14	82	0.28***	0.17	4.2
14	B1	20	4.19	4.06	82	0.29***	0.22	2.1

[1] x is the slope of a linear regression of n monthly measurements of pH against pAl. x values for Hackfort (HA, HB, HC) are reported by Mulder and Stein (1994), and for Solling (F1) by Wesselink and Mulder (subm.)

[2] average of values measured in old (around 1980) and recent (1991/1993) samples

*, **, *** indicate slopes (x) significantly different from zero at the 95%, 99% and 99.9% confidence level, respectively

[3] from duplicate lysimeter measurements

Table 2. *'free' soil Al and C contents in old (around 1980) and new (1991/1993) samples from Hackfort (HA, HB, HC), Gerritsfles (Gf, Gb) and Solling (F1, B1)*

		old			**recent**		
Code	Depth (cm)	Al_{ox}	Al_{pyr}	C	Al_{ox}	Al_{pyr}	C
		.... g/100g			.... g/100g		
HAi	0-10	0.08	0.10	5.2	0.07	0.08	2.9
HAi	10-20	0.10	0.10	2.4	0.09	0.12	1.4
HAii	0-8	0.09	0.09	4.2	0.07	0.09	3.1
HAii	8-20	0.10	0.11	1.2	0.09	0.12	1.3
HBi	0-3	0.10	0.14	9.6	0.09	0.15	5.9
HBi	3-15	0.12	0.15	3.9	0.14	0.21	2.9
HBii	0-4	0.08	0.08	8.2	0.07	0.09	17.1
HBii	4-8	0.08	0.08	4.0	0.06	0.07	6.4
HCi	0-10	0.03	0.04	4.5	0.03	0.03	3.0
HCi	10-15	0.04	0.04	1.1	0.02	0.02	0.4
HCii	0-10	0.02	0.03	2.6	0.02	0.02	2.6
HCii	10-20	0.02	0.02	0.2	0.02	0.02	0.2
Gf	0-0.5	0.04	0.06	6.1	0.03	0.04	3.8
Gf	0.5-25	0.05	0.060	0.6	0.04	0.05	0.4
Gb	0-0.5	0.04	0.03	0.7	0.03	0.02	0.4
Gb	0.5-25	0.04	0.03	n.d[1]	0.04	0.03	n.d
F1	0-10	0.24	0.22	3.5	0.19	0.17	3.7
F1	10-20	0.30	0.30	2.2	0.25	0.24	1.9
B1	0-10	0.17	0.13	4.0	0.17	0.13	4.4
B1	10-20	0.22	0.19	1.9	0.22	0.21	2.4

[1] Not detectable. A value of 0.24 reported by Mulder et al.(1989) was used.

Table 3. *Changes in organically bound soil Al (Al_{ox}) and estimated Al solute fluxes at Hackfort (HA, HB, HC), Gerritsfles (GF, GB) and Solling (F1, B1) between past (HA, HB, HC, GF, GB: 1982; F1, B1: 1979) and recent (HA, HB, HC, GF, GB, B1: 1993; F1: 1991) sampling*

Code	Depth (cm)	Bulk dens. (kg dm^{-3})	$Al_{ox,past}$	$Al_{ox,recent}$	$Al_{ox,past-recent}$	Al solute fluxes
			<......	(mmol kg^{-1})		......>
HAi	0-10	0.92	30	26	-4	-15
HAi	10-20	1.22	37	33	-4	-3.2
HAii	0-8	0.95	33	26	-7	-19
HAii	8-20	1.15	37	33	-4	-2.8
HBi	0-15	1.02	42	46	+4	-9
HBii	0-8	1.03	30	24	-6	-13
HCi	0-10	0.93	11	11	0	-13
HCii	0-10	1.07	7.5	7.5	0	-12
HCii	10-20	1.47	7.5	7.5	0	0
GF	0-25	1.37	19	15	-4	-3.8
GB	0-25	1.60	19	19	0	-1.3
F1	0-10	0.93	89	70	-19	-13.5
F1	10-20	1.14	111	93	-18	-11.0
B1	0-10	1.15	77	77	0	-4.8
B1	10-20	1.15	81	81	0	-4.8

Table 4. *Average values of selected soil and solution parameters in soils from Hasselsven (HH) and Tongbersven (TF) in the Netherlands, Lund in Sweden (Spod and Scam) and the sub soil at the Solling spruce site. The code numbers refer to Figs. 2-4.*

Site no.	Code[1]	pH[2]	pAl[2]	C	Al_{pyr}
				...... g/100g	.....
15	TF-12	3.42	4.80	2.1	0.017
16	TF-35	4.02	3.68	4.5	0.57
17	TF-57	4.06	3.56	0.6	0.095
18	HH-7	3.52	4.24	2.5	0.05
19	HH-22	4.21	4.02	1.2	0.19
20	Spod-spr/50	4.25	3.95	1.6	0.23
21	Spod-bch/50	4.25	3.76	1.3	0.26
22	Spod-br/50	4.85	4.93	1.4	0.26
23	Scam-spr/15	3.95	4.08	1.8	0.21
24	Scam-bch/15	4.35	4.41	1.7	0.19
25	Scam-br/15	4.59	4.83	1.4	0.19
26	Scam-br/50	4.56	4.67	0.8	0.185
27	Scam-spr/50	4.23	3.28	0.4	0.19
28	Scam-bch/50	4.44	4.21	0.8	0.26
29	F1-90	4.15	3.75	0.5	0.20

[1] site, followed by depth (cm), horizon, or vegetation type/depth (spr=spruce, bch=beech, br=birch)

[2] for TF and HH from Mulder (pers. comm.). For the Swedish sites (nos. 20-28) from Berggren (pers. comm.) for F1 from Wesselink and Mulder (subm.). pAl refers to free Al^{3+}. Complexation of dissolved Al to DOC was accounted for on the Swedish sites.

Resampling of soils

Pyrophosphate and oxalate extractable Al in old and new samples from the Dutch and German sites is given in Table 2. Coefficients of variation in standard samples were ca. 6% for the oxalate extraction (*n*=4, average Al_{ox} content 0.75 g/100g) and 10% for the pyrophosphate extraction (*n*=3, average Al_{pyr} content 0.26 g/100g). We found that the two extractants removed similar amounts of Al from the soil samples. In the Hackfort samples Al_{pyr} was equal to or somewhat higher (10-40%) than Al_{ox}, while in the Solling samples Al_{pyr} was somewhat lower than Al_{ox}. The close similarity of Al_{pyr} to Al_{ox} indicates that Al extracted with oxalate is largely associated with soil organic matter and that inorganic amorphous Al levels are low. Theoretically though, Al_{pyr} values are not expected to exceed Al_{ox} values, as observed at Hackfort. Slow settling of soil colloids (including clay particles and organics) due to strong dispersion at high pH and Na saturation in the $Na_4P_2O_7$ may have affected Al_{pyr} extractions in particular in the Hackfort samples HA and HB. We decided, therefore, to use the more reproducible Al_{ox} values rather than Al_{pyr} in comparing past and recent organically bound soil Al content at all our sites (Table 2).

Differences between old and new values of Al_{ox} (Table 2) were significant at the $p<0.01$ level (Student's *t*-test for paired samples). In 13 out of 20 cases, current Al_{ox} content was equal to or lower than past values and in 6 out of 20 cases present Al_{ox} content was equal to past content.

Carbon content differed more between past and recent sample pairs (up to a 150% difference, Table 2) than Al_{ox}. However, the Student's *t*-test, for paired samples, revealed no significant differences between C content in past and recent samples, indicating that differences in C content between past and recent samples are governed by other factors than time. One factor that may account for the variation in C content in past and recent samples from the same soil horizon is mixing of the mineral soil with minor amounts of humus from the O-horizon as a result of sampling or biological activity. This may strongly affect organic C content of the soil sample but will due to the low Al contents of O-horizon humus hardly affect Al_{ox} content.

Table 3 compares changes in Al_{ox} with Al solute fluxes between past (about 1980) and recent (ca. 1992) sampling. In the soils at Hackfort, depletion of Al_{ox} was, in most cases, lower than solute fluxes of Al. At Solling-F1, decreases in Al_{ox} were somewhat larger than inferred from solute fluxes, whereas no changes in Al_{ox} were observed in the beech site.

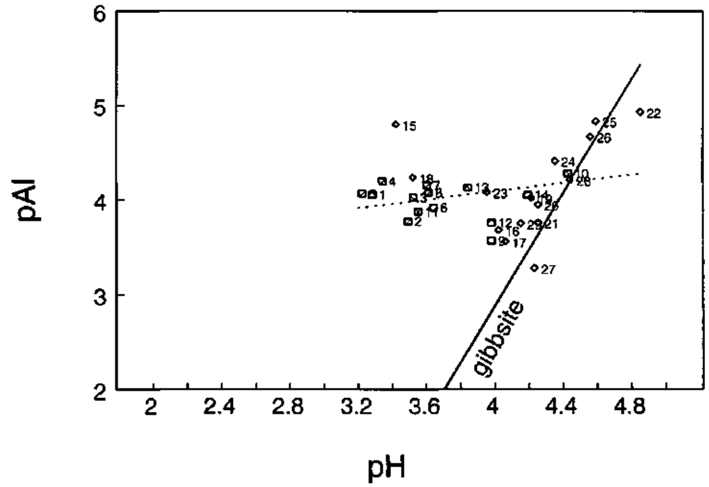

***Figure 2.** Relationship of $-\log\{Al^{3+}\}$ to pH in soil layers from research sites in the Netherlands, Germany, and Sweden. Numbers represent site codes (Table 1, 4). Solid line indicates gibbsite equilibrium ($pK=9.12$ at 8°C); dotted line indicates linear regression through the data ($pAl=0.16*pH+3.4$, $R^2=0.04$).*

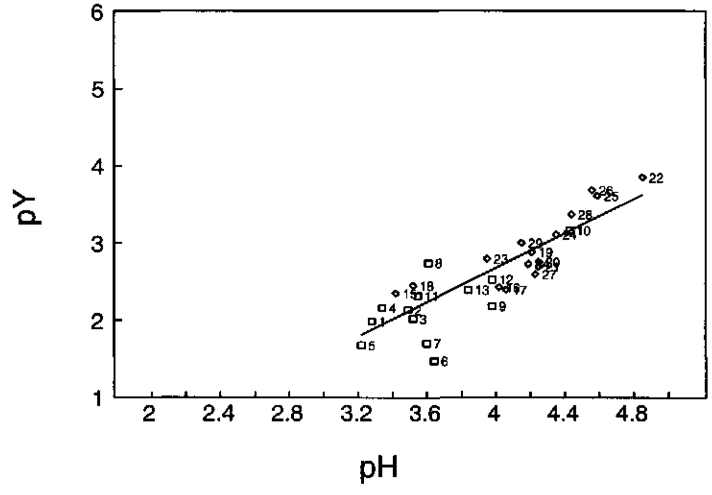

***Figure 3.** Relationships of pY ($-\log(\{Al^{3+}\}*C/Al_{org})$ to pH in soil layers from research sites in the Netherlands, Germany and Sweden. Numbers represent site codes given in tables 1 and 4. Linear regression through all data gave $pY=1.16*pH-1.98$, $R^2=0.74$. For the regression line shown, site numbers 6-8 were excluded: $pY=1.11*pH-1.76$, $R^2=0.82$.*

DISCUSSION

Predicting activities of dissolved Al

Solubility controls of Al have been discussed previously for Hackfort (Mulder and Stein, 1994), Solling (Wesselink and Mulder, subm.), Gerritsfles, Tongbersven and Hasselsven (Mulder et al., 1989a), and the Swedish soils (Berggren, 1992). In these studies regulation of dissolved Al was attributed to complexation of Al to soil organic matter, not to equilibrium with gibbsite. This was based on (i) undersaturation of solutions with respect to synthetic gibbsite (Fig. 1), (ii) H^+-Al^{3+} activity relationships less than cubic (x in Table 1), (iii) reactive soil Al being largely present in an organically bound form rather than in inorganic mineral phases (Table 2) and (iv) a small temperature sensitivity of pH-pAl relationships (Berggren, 1992).

We tested the proposed Al-proton exchange equation (Eqn. 1) by plotting individual pY vs. pH values for a range of soils with different soil and solution chemistry (Fig. 3). We found a significant linear relationship (R^2=0.74, p<0.001, n=29) with a slope x of 1.16 and an intercept $pK_{H\text{-}Al}$ of -1.98 (Fig. 2). Notable outliers from the regression line in Fig. 2 are numbers 6, 7 and 8 from the HC profiles. Van Breemen et al. (1988) reported that this soil had been disturbed (centuries ago) by bringing relatively unweathered subsoil to the surface, which may explain the low Al_{ox} content, and therefore low pY values, of the HC horizons nos. 6 and 7. Omitting site numbers 6 to 8 from the regression analysis in Fig. 3 improves the fit (Fig. 3, pY=1.11*pH-1.76, R^2=0.82) and results in a slightly changed slope and intercept.

Depletion of organically bound soil Al, consequences for Al solubility

The decrease in pools of organically bound soil Al in the Hackfort-A and -B surface soil in the 1980s coincides with significant decreases in Al solubility in the same period, as recently reported by Mulder and Stein (1994). Both phenomena can, in a qualitative way, be accounted for by the organic Al model, as was illustrated in Fig. 1. We tested whether changes in soil and solution chemistry of Al observed at HA and HB were also quantitatively consistent with the proposed organic Al model. This was done by estimating past and present pairs of pY and pH values, which should both be plotted on the derived regression line (Fig. 3). Past pY-pH pairs were estimated from Al_{ox} in samples from 1980 and average solution chemistry in 1981 (Mulder, 1994, unpublished data). Present pY-pH pairs were calculated from Al_{ox} pools measured in 1993 and average solution chemistry in 1987, the final year of hydro-chemical monitoring at Hackfort (Mulder, 1994, unpublished data). Given the variation in new and old organic C values from the same soil layers, it was in our view most appropriate to use only average (from old and new samples) C contents in the calculation of 'old' and 'recent' pY values. Despite the uncertainty in the assesment of 'old' and 'new' soil chemical data, observed changes in pY and pH over time at HAi, HAii and HBii appear to be consistent with the proposed model as indicated in Fig. 4.

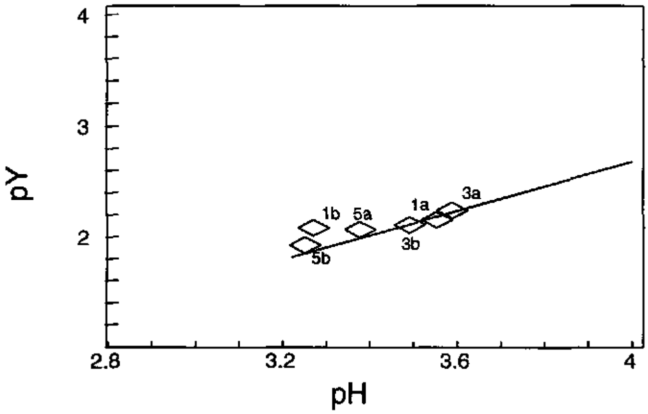

Figure 4. *Relationship of pY (-log((Al^{3+})*C/Al_{org}) to pH at HAi-10 (1), HAii-10 (3), and HBii-10 (5) about 1980 (a) and 1990 (b). Linear regression line through data as derived in Fig. 3 (pY=1.11*pH-1.76) is indicated.*

Depletion of soil Al in the field

Analysis of Dutch and German soils sampled in a time interval of 12 to 14 years revealed a significant depletion of organically bound soil Al. In the soils at Hackfort, depletion of Al_{ox} was generally lower than expected from solute fluxes of Al (Table 3). The errors involved in the Al solute fluxes are in the order of 10-30% (coefficients of variation (CV), van Grinsven et al., 1987) while those of Al_{ox} may be estimated at about 12% (twice the CV of 6% from standard Al_{ox} samples). Even when considering these errors, it seems unlikely that the Al fluxes at Hackfort are solely explained by dissolution of Al_{ox}.

Average Al removal with drainage water from the 0-10 cm soil layers at Hackfort (HA_i, HA_{ii}, HB_{ii}, HC_i, HC_{ii}) was about 1.2 kmol ha^{-1} yr^{-1} between 1982 and 1993 (derived from Table 3, at an average bulk density of 1 kg dm^{-3}). Depletion of Al_{ox} explained only about 0.3 kmol ha^{-1} yr^{-1} of the Al flux. Silicate weathering may be another source of dissolved Al. Indeed, the discrepancy between Al removal by drainage and decrease of Al_{ox} is greatest at HC, where, as mentioned above, unweathered subsoil material has been brought to the surface. Assuming that (i) illite is the dominant source of silicate Al at Hackfort, (ii) illite dissolves congruently ($K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$, van Grinsven et al., 1986), and (iii) rates of K and Mg weathering are 0.4 and 0.15 kmol ha^{-1} yr^{-1} respectively for a 90-cm profile (Van Breemen et al., 1988), silicate weathering of Al at Hackfort is estimated at 1.5 kmol ha^{-1} yr^{-1} for a 90-cm soil layer. Furthermore, assuming a linear pH gradient with soil depth ranging from 3.4 at 10 cm to 4.2 at 90 cm (Mulder and Stein, 1994), and estimating the pH dependency of illite weathering at $R \approx (H^+)^{0.8}$ (Van Grinsven et al., 1986), we estimate that around 0.30 $kmol^{-1}$ ha^{-1} yr^{-1} of Al release from illite may occur in the upper 10 cm of the soil profile. Thus silicate weathering may explain another 30% of the Al flux. Because depletion of Al_{ox} and silicate weathering together explain only 50% of the observed Al flux, other Al pools, perhaps dithionite extractable Al (Mulder and Stein, 1994), appear to be involved as well.

The contribution of inorganic Al pools to mobilization of Al is different from findings of Mulder et al. (1989b) who, in laboratory experiments, showed that organically bound soil Al was the dominant source of dissolved Al. The study of Mulder et al. (1989b), however, i) focused on sandy podzolic soils with small pools of inorganic Al hydroxides, and ii) was carried out over relatively short time periods. The present results of the Hackfort sites suggest that under field conditions inorganic Al pools may contribute significantly to mobilization of Al.

At Solling, changes in Al_{ox} were either larger (F1) or smaller (B1) than inferred from solute fluxes. This is possibly due to the spatially distributed sampling of 'old' and 'new' samples at Solling, and the fact that only half the old soil samples were still available for the present study.

Predicting monthly variations in Al activities and pH in soil solutions

To further test the validity of our organic,Al model, we hindcasted observed monthly values of pH and Al activities in soil solutions available from the monitoring sites. As an example we selected the Hackfort A (HA*i*) profile at the 10-cm and 20-cm depth, and the Tongbersven profile at the 35-cm depth. Calculations were conducted by adding monthly measured H and Al activities, $(Al^{3+} + H^+)_{meas.}$, and redistributing these over Al^{3+} and H^+ using Eqn. 3. For the HA*i* profile and the Tongbersven soil (35-cm depth), the right-hand side in Eqn. 3, $K\text{-}_{H\text{-}Al}*C/Al_{org}$, was presumed constant with time. Values were estimated from average chemistry data given in Table 1 and $K_{H\text{-}Al}$ as derived in Fig. 2. For HA*i*-20, $K_{H\text{-}Al}$ was adjusted to better match observed and predicted monthly data ($\log K_{H\text{-}Al}$ 2.3 instead of 1.76). For the 10-cm depth at Hackfort-A*i*, the right-hand side of Eqn. 3 was assumed to change linearly with time according to measured depletion of Al_{ox}. Simulated values for pH and pAl are shown in Fig. 5. Predicted and measured pH compare well (R^2=0.96 using all data). Although pAl values are not as well predicted, correlation with observations is still good (R^2=0.71).

That observed short-term variations in both pH and pAl are predicted well is important in practice. These variations may result for example from seasonal changes in supply of (H)NO_3 to the soil solution as a result of mineralization or atmospheric deposition processes, and are important potential stress factors to the forest (so-called 'seasonal acidification phases', e.g. Ulrich, 1989; Matzner, 1988, 1989).

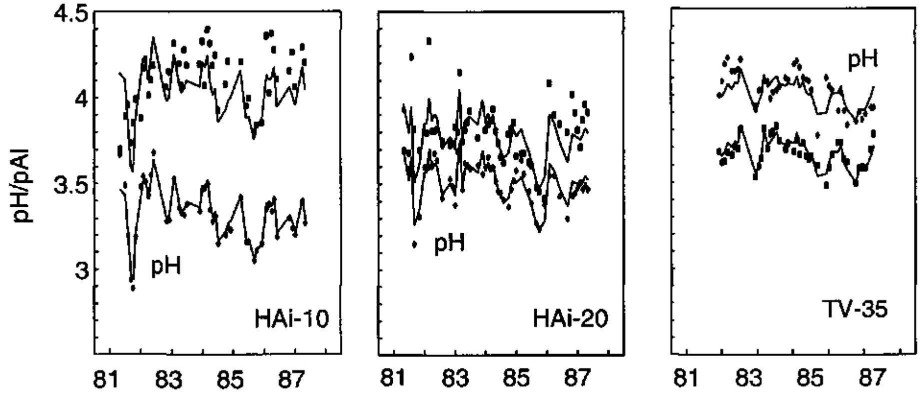

Figure 5. *Observed and predicted monthly pAl (-log{Al^{3+}}) and pH values at HAi-10, HAi-20 and TV-35 in the Netherlands. Squares indicate pH, diamonds pAl and lines predictions using the model.*

CONCLUSIONS

Using data from a range of acid forest soils, we derived a simple equilibrium model of Al proton exchange on soil organic matter to predict activities of dissolved Al. Such a control on Al activities has previously been proposed for organic surface horizons; here we showed that it also applies to mineral horizons, even when low in soil organic carbon. The model, based on data from a range of field studies, explains differences in Al activities between sites, as well as monthly observed variations in Al and proton concentrations. The model seems generally applicable and useful for site specific as well as regionalized soil acidification models.

We measured significant decreases in organically bound soil Al over a period of 12 to 14 years in soils of the Netherlands and Germany where pools are low and release rates high. However, depletion rates at Hackfort, The Netherlands, was less than inferred from long-term monitoring of Al solute fluxes. This indicates that pools other than organically bound Al, i.e. silicates and inorganic Al hydroxides, may contribute to Al mobilization as well. Release from these pools is most likely kinetically constrained (Van Grinsven et al., 1992; De Vries, subm.). Currently, there is discussion on whether Al activities in solutions of acid forest soils are controlled by kinetically constrained (time-dependent) dissolution of inorganic Al hydroxides or by equilibrium-binding to soil organic matter (Mulder and Stein, 1994; De Vries, subm.; Van Grinsven et al., 1992; Matzner, 1992). From our study we conclude, (i) that Al activities in soil solution are controlled by equilibrium-binding to soil organic matter but (ii) that both kinetic release from inorganic Al pools and equilibrium release from organic Al pools contribute to Al mobilization (Fig. 6). This indicates that the rate of depletion of the organically bound Al pool (and consequently decrease in its solubility) depends on rates of resupply by kinetically constrained dissolution from inorganic Al pools.

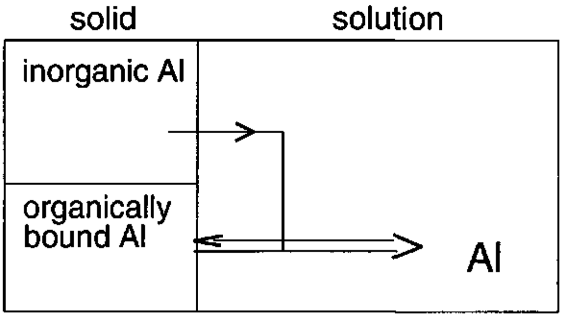

Figure 6. *Scheme showing contributions of both kinetic and equilibrium release of Al to acid neutralization, and dissolved Al activities controlled by equilibrium-binding to soil organic matter.*

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Chapter 7

SUMMARY AND CONCLUSIONS

SUMMARY

The effects of acid atmospheric deposition on forest ecosystems have been studied intensively in the past two decades. Measurements of element budgets in forested ecosystems throughout the world have shown that acid deposition may deplete stores of exchangeable base cations in the soil, decrease the soil pH, increase rates of mineral weathering, and release potentially toxic Al into the soil solution. In summary, acid atmospheric deposition can strongly alter the chemical environment for living organisms.

In this thesis the mechanisms that may control those phenomena are studied, with emphasis on soil chemical processes. Central in this study are long and comprehensive data sets from continuous measurements (monitoring) of element fluxes in forest ecosystems, specifically from the Solling experimental forest in Germany.

Base Cations

Using over 20 years of data on deposition and soil chemistry at Solling, chapter 2 discusses how long-term changes in atmospheric deposition of acid anions and base cations affect dissolved and exchangeable pools of base cations in the soil, through the process of cation exchange. Positive effects of declining SO_4 deposition in the 1980s, which potentially reduces leaching of base cations from the soil, were partially offset by (i) continued high concentrations of dissolved SO_4 in the soil and (ii) declining deposition of the base cations Ca and Mg. The latter appears to result from stricter controls on particle emissions from fuel combustion and industrial processes. Recent studies indicate that declining deposition of base cations is observed in other regions of Europe and North America as well. This is a matter of concern as forests may be sensitive to changes in base cation deposition which is, together with mineral weathering, the most important source of nutrients to forests on acidified soils.

In chapter 3 we quantified rates of mineral weathering at Solling, as a source of nutrients and acid neutralization. Estimates of field weathering rates were obtained from, (i) long-term input-output mass balances, correcting for changes in stores of exchangeable base cations in the soil, and (ii) elemental analysis of the soil profile. At Solling, rates of supply of Ca, K and Na by weathering are much lower than by atmospheric deposition; for Mg the contributions are of similar magnitude. This emphasizes (i) the relevance of atmospheric deposition of base cations as a nutrient source to the Solling forests, and (ii) the concern with respect to its present decline. To investigate mechanisms of mineral weathering of Mg and K, a series of laboratory weathering experiments with soils from Solling were conducted.

These focused on weathering of illite, the dominant mineral source of K and Mg. A major problem in quantifying rates of mineral weathering is the large discrepancy in rates obtained in laboratory studies and field estimates, with laboratory rates being generally one to three orders higher. In the laboratory, effects of pH, temperature, and soil solution composition on illite weathering were studied. Corrected for the effects of these factors, Mg and K release rates from illite measured in the laboratory were comparable (K) or a factor 2 to 4 higher (Mg) than rates inferred from field methods. It is concluded that field estimates of weathering rates, from elemental analysis of the soil profile or input-output flux balances, remain necessary to obtain reliable estimates of base cation weathering rates.

Anions

In a simplified way, anions in the soil solution can be regarded as carriers of base and acid cations, through charge balance constraints. Understanding the processes that determine dissolved concentrations of these components in the soil is therefore of prior importance. In chapter 4 we discussed the processes that govern the mobility of dissolved Cl, SO_4 and NO_3 in the Solling spruce soil over a period of 18 years. For this purpose a simulation model describing soil hydrology and a number of biogeochemical processes was introduced. Using throughfall water and concentrations as input to the model, concentrations of Cl in soil solutions were successfully simulated, a requirement to further study components that interact chemically or biologically with the soil.

Sorption of SO_4 is of significance in the soils at Solling due to comparatively high contents of Al and Fe oxides. By contrast, in the mineralogically poor sandy soils in the Netherlands SO_4 often behaves chemically nearly conservative. The steep increase in dissolved SO_4 in the Solling spruce soil during the mid-1970s was modelled adequately using adsorption parameters reported in literature, and was explained by a steep adsorption isotherm and a state of near saturation of SO_4 sorption sites in the early 1970s, at the start of the monitoring program. Rates of desorption of SO_4 in the 1980s in response to declining SO_4 deposition, described by the same model, were less than those measured in the field. In the absence of evidence for alternative controls on dissolved SO_4, like jurbanite ($AlOHSO_4$) dissolution, the mechanism of SO_4 desorption remains unclear.

The model increased our understanding of the processes that control repeated 3-year cycles of high and low concentrations of NO_3 in deeper layers (90 cm) of the Solling spruce soil. Recently, there is increasing interest in N-dynamics in forest ecosystems, as N-saturation has been hypothesized as an additional cause of forest decline. In the Solling spruce soil, concentrations of NO_3 water leaving the soil profile increased when the N-flux into the *mineral* soil, from deposition and net mineralization, exceeded the N uptake capacity of the forest at a threshold value of around 4 kmol ha^{-1} yr^{-1}. At present, total deposition of N on the spruce forest amounts to 3.3 kmol ha^{-1} yr^{-1} and is close to this threshold value. This points to the critical role of N mineralization processes in the litter layer, where large stores of N have accumulated over the past 25 years. The annual release of N from the spruce litter layer was positively correlated with rainfall. This was apparent from large N releases from litter in relatively wet years which subsequently increased NO_3 concentrations at the 90 cm depth.

Aluminum

The main acid neutralizing process in acid forest soils under high acid loads is the release of Al to the soil solution. Soil acidification models generally describe the solubility of reactive soil Al by equilibrium or kinetic dissolution of Al-trihydroxide ($Al(OH)_3$). In chapters 5 and 6, we scrutinized the evidence for this reaction mechanism from extensive sets of field data, but found little support for the gibbsite model. By contrast, evidence points to Al binding to soil organic matter as a control of dissolved Al, even when organic matter contents are low. In chapter 6 a new, mechanistic, and yet simple model was presented that explained much of the spread in Al-solubility, as observed in 29 different soil layers from 18 forest soils. The model describes Al-solubility as a function of the degree to which humus binding sites are saturated with Al. It involves only two soil specific parameters, the organic C content of the soil and an estimate of the pool of organically bound soil Al, and may therefore be easily incorporated in current soil acidification models.

The soils studied in this thesis generally receive high loads of acid deposition, and acidity is largely neutralized by release of Al in the upper 20 cm of the mineral soil. It has been suggested that in surface layers of these soils depletion of reactive soil Al may result within decades. The depletion hypothesis was put to test by measuring pools of organically bound soil Al in old (around 1980) and new (around 1993) samples from research sites at Hackfort and Gerritsfles in the Netherlands, and Solling in Germany. Indeed, significant decreases with time were found. Independently measured depletion of organically bound soil Al and declining Al solubility, as observed previously from 6 years of field monitoring at Hackfort in the 1980s, proved to be consistent with the humus-Al model presented in this thesis. Rates of depletion of organically bound soil Al at Hackfort, the Netherlands, during a period of about 13 years were lower than expected from long-term monitoring of Al solute fluxes. This suggests that pools other than organically bound Al, i.e. silicates and inorganic Al hydroxides, may contribute to Al mobilization as well. Literature indicates that release of

Al from these pools may be kinetically constrained. The current discussion on whether Al activities in solutions of acid forest soils are controlled by kinetically constrained (time dependent) dissolution of inorganic Al hydroxides or by equilibrium binding to soil organic matter is, in my view, clarified when the kinetic and the equilibrium process are regarded as sequential; kinetic release supplying Al to the organic exchanger, which equilibrates with the soil solution.

GENERAL CONCLUSIONS

1. In the recent past, deposition of SO_4, Ca and Mg on the German Solling forests has declined significantly as a result of reduced industrial emissions.
2. Results from Solling indicate that soil de-acidification, i.e. an increase in the pool of exchangeable base cations, as a result of declining SO_4 deposition may be offset by i) continuous release of sorbed SO_4 from the soil and ii) declining deposition of base cations.
3. Weathering rates of Ca, K and Na at Solling, Germany, are much lower than their supply by atmospheric deposition; for Mg the contributions of deposition and weathering are of similar magnitude.
4. Illite is the main mineral source of Mg and K at Solling. Although coming from the same mineral source, the two cations are released by different mechanisms. Magnesium release is controlled by chemical kinetic processes and its release is highly pH dependent ($R \approx (H^+)^{0.8}$), whereas K is released from interlayers by diffusion, a process that showed independent of pH.
6. A six-fold increase of dissolved SO_4 in the Solling spruce soil (90 cm) in the mid-1970s, and continuously high concentrations thereafter, is explained by 'peaking' SO_4 deposition loads in the mid-1970s that entered a mineral soil where the SO_4 sorption capacity was nearly saturated.
6. Repeated 3-year cycles of high and low concentrations of NO_3 in deeper layers (90 cm) of the Solling spruce soil are related to excess release of N from the litter layer in comparatively wet years.
7. Strong changes in pH and less strong changes in pAl ($-\log\{Al^{3+}\}$) in response to varying acid anion concentrations, generally observed in acid forest soils, and the measured increased of CEC with time in the surface soil of the Solling spruce sites, support the hypothesis of Al solubility control by complexation to soil organic matter.

8. Data from 29 soil layers of 18 forest soils, covering a range in soil pH, Al activities, and reactive soil Al pools indicate that Al solubility control by complexation to soil organic matter is a general phenomenon, even when organic C contents are low.
9. Much of the variation in Al solubility observed in 29 different soil layers of 18 forest soils is explained by the organically bound Al: soil C ratio.
10. In surface soils where stores of organically bound Al are low and release rates high depletion of reactive, organically bound, soil Al is significant on a time scale of 12 to 14 years only.
11. Independently measured declines in (i) Al solubility in surface soils at Hackfort the Netherlands, from 6 years of monitoring of soil water chemistry and (ii) pools of organically bound soil Al, are consistent with the Al-humus equilibrium model proposed in this thesis.
12. In acid forest soils where dissolved Al activities are controlled by equilibrium complexation to soil organic matter, kinetically constrained release of Al from inorganic Al pools may well contribute to acid neutralization.

SAMENVATTING

In de afgelopen 20 jaar zijn de effecten van zure atmosferische depositie op bosecosystemen intensief bestudeerd. Metingen in verschillende bosecosystemen hebben aangetoond dat zure atmosferische depositie kan leiden tot uitputting van de voorraad aan omwisselbare basische kationen (Ca, Mg, K, Na), daling van de bodem pH, toename in de verweringssnelheid van bodemmineralen, en vrijzetting van Al uit de vaste fase van de bodem. Kortom, zure atmosferische depositie kan het bodemchemisch milieu van het bos drastisch veranderen, met als mogelijk gevolg grootschalige schade aan bosecosystemen.

In dit proefschrift is onderzocht welke mechanismen de bovengenoemde bodemchemische veranderingen sturen. Centraal daarbij stonden veldmetingen in bosecosystemen, met nadruk op lange meetseries (tot 20 jr) van de chemische samenstelling van atmosferische depositie, bodemwater, en de vaste fase van de bodem. In dit onderzoek is vooral gebruik gemaakt van gegevens uit de Duitse boslocatie Solling.

In het proefschrift zijn de processen besproken die de bodemchemie van basische kationen, anionen en aluminium reguleren.

Basische kationen

Gebruik makend van 20 jaar meetgegevens van de locatie Solling is in hoofdstuk 2 besproken, i) in hoeverre er op lange termijn veranderingen in atmosferische depositie van zure en basische componenten waren, en ii) hoe deze veranderingen in depositie leidden tot lange termijn veranderingen in concentraties aan omwisselbare en opgeloste basische kationen (=nutriënten) in de bodem. Uit de gegevens van de locatie Solling bleek dat de zure depositie door SO_x sinds de jaren '80 sterk is afgenomen. Dit leidde op deze locatie echter niet direct tot een omkering van het bodemverzuringsproces ('ontzuring'). Theoretisch werd dit wel verwacht indien de afname in SO_4 depositie zou hebben geleid tot een equivalente afname in SO_4 uitspoeling uit de bodem. Twee processen bleken de 'ontzuring' tegen te werken, i) desorptie van aan de bodem gebonden SO_4, waarbij zuur vrijkomt, en ii) een afname in de atmosferische depositie van Mg en met name Ca (ca. 30% sinds begin jaren '80). Deze bevindingen sluiten aan bij een recente publikatie waarin voor meerdere lokaties in Noord-Europa, waaronder Nederland, en Noord-Amerika een dalende trend in concentraties van basische kationen in regenwater werd gerapporteerd. Deze trend lijkt het gevolg te zijn van een gereduceerde uitstoot van stofdeeltjes uit kolenverbrandingsinstallaties en andere industrieën.

In hoofdstuk 3 is de lange termijn bijdrage van verwering van bodemmineralen aan de toevoer van basische kationen naar het bos geschat. Naast atmosferische depositie is verwering op de lange termijn de enige bron van basische kationen voor het bos. Veldverweringssnelheden in het bodemprofiel van Solling werden afgeleid uit, i) de massabalans van elementfluxen in en uit het bosecosysteem, en ii) element analyse van het bodemprofiel, waarbij de huidige vaste fase samenstelling van de bodem werd vergeleken met die van een relatief onverweerde referentiebodem. In Solling bleek de toevoer van K en Ca uit verwering kleiner dan de bijdrage van deze componenten uit atmosferische depositie. Voor Mg waren de bijdragen vergelijkbaar groot. Dit gegeven benadrukt het belang van atmosferische depositie als bron van nutriënten voor bossen. Omdat de voorraden aan omwisselbare kationen in zure bodems klein zijn, zijn bossen gevoelig voor veranderingen in depositie van basische kationen. De dalende trend in de depositie van deze componenten is daarom een ongewenste ontwikkeling.

De volgens boven genoemde methoden geschatte verweringssnelheden in het veld zijn vergeleken met snelheden gemeten in laboratoriumexperimenten. Hierbij lag de nadruk op de verwering van het illiet, de belangrijkste minerale bron van Mg en K in de Solling bodem. Een algemeen probleem is dat in laboratoriumexperimenten vaak verweringssnelheden worden gemeten die 1 tot 3 orden van grootte hoger zijn dan die in het veld. Om inzicht te krijgen in de factoren die dit verschil veroorzaken werd in laboratoriumexperimenten de invloed van pH, temperatuur, bodemdiepte en bodemvochtsamenstelling op de verwering gemeten. Na correctie voor de genoemde factoren bleek de verweringssnelheid van K zoals gemeten in het laboratorium vergelijkbaar met die in het veld, terwijl de Mg verwering een factor 2 tot 4 hoger was. In hoofdstuk 3 werd geconcludeerd dat, vooralsnog, veldmetingen de meest betrouwbare schattingen van verweringssnelheden geven.

Anionen

Anionen in de bodemoplossing kunnen, sterk vereenvoudigd, worden voorgesteld als 'dragers' van basische en zure kationen, omdat de som van de ladingen van opgeloste kationen en anionen gelijk moeten zijn. Om het gedrag van de kationen in de bodem te modelleren is begrip van de processen die de concentraties van anionen in de bodem reguleren daarom noodzakelijk. In hoofdstuk 4 werd een simulatiemodel geïntroduceerd dat hydrologische en biochemische processen in bosbodems beschrijft. Met behulp van dit model werd het gedrag van Cl, SO_4 en NO_3 in de bodemoplossing van de Solling fijnspar locatie over een periode van 18 jaar geanalyseerd. Met het model konden Cl concentraties in het bodemvocht goed voorspeld worden, waarbij maandelijks gemeten concentratie en hoeveelheden van het lekwater uit het kronendak ('doorvalwater') als invoer voor het model fungeerden. Omdat Cl biochemisch inactief ('conservatief') is, werd hiermee het hydrologische deelmodel gevalideerd.

Sorptie van SO_4 is in de Solling bodem van belang, vanwege relatief hoge Al en Fe-(hydr)oxyde gehaltes, dit in tegenstelling tot bijvoorbeeld de arme Nederlandse zandgronden waar SO_4 zich in het algemeen 'conservatief' gedraagt. De scherpe toename in concentraties opgelost SO_4 in de ondergrond van de Solling bodem in het midden jaren van de jaren '70 werd adequaat voorspeld met onafhankelijk bepaalde adsorptie parameters voor SO_4 en werd verklaard door, i) een zeer steile adsorptie isotherm, en ii) het bijna verzadigd zijn van SO_4 bindingsplaatsen bij het begin van de monitoring in de locatie Solling. De door het model voorspelde desorptie van SO_4 in de jaren '80, als reactie op verlaagde SO_4 depositie, was geringer dan veldmetingen in de Solling bodem aangaven. Vooralsnog blijft onduidelijk welk mechanisme de afgifte van SO_4 naar de bodemoplossing, zoals waargenomen in de jaren '80, reguleert.

Met behulp van het model werd meer inzicht verkregen in de processen die herhaalde 3-jarige cycli van hoge en lage NO_3 concentraties in de ondergrond van de Solling locatie (90 cm) over een periode van 18 jaar, reguleren. Inzicht in de processen die NO_3 concentraties reguleren is van belang, omdat zogenaamde N-verzadiging van bosecosystemen wordt gezien als een extra oorzaak van bosschade en -sterfte. Concentraties in de ondergrond van de Solling fijnspar locatie bleken sterk toe te nemen wanneer de N-flux naar de *minerale* bodem bij een drempelwaarde van ca. 4 $kmol.ha^{-1}.yr^{-1}$ de N-opname capaciteit van het bos overschreed. De N-flux naar de minerale bodem bestaat uit twee componenten, atmosferische depositie en een netto mineralisatie flux van N in de humuslaag. De totale atmosferische depositie van N in de Solling fijnspar locatie is op dit moment ca. 3.3 $kmol.ha^{-1}.yr^{-1}$. Een kleine verhoging van de netto mineralisatie in de humuslaag, waar de voorraad opgeslagen N in de afgelopen 25 jaar is verdubbeld, kan daarmee leiden tot een overschrijding van de eerder genoemde drempelwaarde. Uit de gegevens van de Solling fijnspar locatie bleken periodieke overschrijdingen van de drempelwaarde door een verhoogde netto mineralisatie in de humuslaag positief gecorreleerd met de jaarlijkse hoeveelheid neerslag.

Aluminium

Het belangrijkste zuur neutraliserende proces in bosbodems is het vrijkomen van bodemgebonden Al in de bodemoplossing. In dit proefschrift is nader ingegaan op het mechanisme dat de Al concentraties in de bodemoplossing reguleert. Gebruik makend van veldgegevens uit verschillende lokaties in Duitsland (Solling), Nederland en Zweden werd aangetoond dat Al concentraties in zure bosbodems (pH< ca. 4.5) worden gereguleerd door binding van Al aan organische stof in de bodem. Uit de veldgegevens werd een nieuwe en eenvoudige procesbeschrijving afgeleid, die het schijnbare verschil in de oplosbaarheid van Al in de verschillende lokaties verklaart uit de mate waarin bindingsplaatsen aan organische stof met Al zijn bezet. De afgeleide procesbeschrijving kan eenvoudig in bestaande bodemverzuringsmodellen worden toegepast.

In de bovengrond van zure, mineralogisch arme bosgronden zijn de voorraden van organisch gebonden Al beperkt. In theorie kunnen op een termijn van enkele tientallen jaren deze voorraden uitgeput raken als gevolg van voortschrijdende buffering van zure depositie. Hierdoor verliest de bodem haar 'snelle' buffercapaciteit en kan de pH drastisch dalen. Deze uitputtingshypothese werd getest door in verschillende boslocaties de hoeveelheden organisch gebonden Al in de bovengrond in monsters uit begin jaren '80 te vergelijken met die in 1993. Hierbij werd een significant afname in de tijd geconstateerd. In een recente publikatie toonden andere onderzoekers aan dat de pH in het bodemwater in diverse plots binnen één van de herbemonsterde lokaties, Hackfort (Gelderland, NL), in de jaren '80 significant daalde. In dit proefschrift is aangetoond dat de afnemende buffering van pH in deze locatie gekoppeld is aan een uitputting van de voorraad organisch gebonden Al. De afname van de voorraad organisch gebonden Al in deze locatie was echter ca. 30% kleiner dan de geschatte totale hoeveelheid Al die tussen 1980 en 1993 uit de bovengronden uitspoelde. Geconcludeerd wordt dan ook dat verwering van Al uit andere Al-voorraden in de bodem (secundaire Al-mineralen) voor aanvulling van de voorraad organisch gebonden Al zorg kan dragen.

Curriculum vitae

Bart Wesselink werd geboren op 19 september 1964 te Dalfsen, Overijssel. In 1982 behaalde hij zijn eindexamen Atheneum aan het College Noetsele te Nijverdal. In dat zelfde jaar begon hij zijn studie Bodemkunde aan de Landbouwuniversiteit te Wageningen. Zijn praktijktijd bracht hij door aan Cornell University (Ithaca, NY) bij Prof. M.B. McBride. In 1988 studeerde hij met lof af met als afstudeervakken bodemscheikunde, bodemvorming en ecopedologie, en bodemmineralogie. Na zijn afstuderen werkte hij 3 maanden als toegevoegd onderzoeker op de vakgroep Bodemkunde en Plantevoeding (LUW) aan de ontwikkeling van het simulatie model DYNAMITE. In 1989 begon hij als Assistent in Opleiding aan het onderzoek dat in dit proefschrift resulteerde. De eerste 1.5 jaar van dit onderzoek werden uitgevoerd aan het Institut für Bodenkunde und Waldernährung in Göttingen, Duitsland, onder Prof. Dr. Dr. h.c. Ulrich. Daaropvolgend was hij werkzaam aan de vakgroep Bodemkunde en Geologie in Wageningen onder leiding van Prof. Dr. N. van Breemen. Sinds december 1993 is hij werkzaam als deskundige bouw- en afvalstoffen bij het Laboratorium voor Afvalstoffen en Emissies (LAE) van het Rijksinstituut voor Volksgezondheid en Milieuhygiëne (RIVM) te Bilthoven.