

## The solubility of aluminum in acidic forest soils: Long-term changes due to acid deposition

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**Abstract**—Despite the ecological and pedogenic importance of Al, its solubility control in acidic forest soils is poorly understood. Here we discuss the solubility of Al and its development with time in three acid brown forest soils in The Netherlands, which are under extreme acidification from atmospheric deposition. All soil solutions (to a 60 cm depth) were undersaturated with respect to synthetic gibbsite ( $\text{Al}(\text{OH})_3$ ;  $\log K = 9.12$  at  $8^\circ\text{C}$ ), with the highest degree of undersaturation occurring in the surface soil. In about one third of the individual soil layers a significant positive correlation existed between the activity of  $\text{Al}^{3+}$  and  $\text{H}^+$ , but this relationship was far less than cubic. Kinetically constrained dissolution of Al is unlikely to explain the disequilibrium with respect to gibbsite, because undersaturation was highest through summer when water residence times were longest and temperatures greatest. Time series analysis of six year data sets for several soil layers revealed a significant annual decline in soil solution pH and Al solubility (defined as  $\log \text{Al} + 3 \text{ pH}$ ) despite a constant concentration of strong acid anions. The annual decline of both pH and Al solubility was greatest in the surface soil and was positively correlated with the relative depletion of reactive organically bound soil Al. The results support our earlier hypothesis that in strongly acidified forest soils complexation by solid phase organics controls the solubility of Al, even in mineral soil layers, relatively low in organic C. The data lend no support to the current widespread, and often uncritical use of gibbsite as a model for the Al solubility in highly acidic forest soils (pH < 4.5) of the temperate zone.

### INTRODUCTION

IN FOREST SOILS IN The Netherlands the rate of deposition of anthropogenically derived acidity is generally well above  $3 \text{ kmol ha}^{-1} \text{ y}^{-1}$ , which is among the highest in the world. Because Dutch forest soils are generally poor in weatherable minerals, acid neutralization is largely due to solubilization of potentially toxic Al (MULDER et al., 1987, 1989a). Insight into mechanisms controlling the solubility of Al is crucial for a quantitative understanding of soil acidification and its effects on biota. Currently, Al solubility controls are hotly debated (e.g., CRONAN et al., 1986; SEIP et al., 1989; WALKER et al., 1990; MATZNER and PRENZEL, 1992; ROBARGE and JOHNSON, 1992), with most acidification models (e.g., Birkenes, MAGIC, ILWAS, SMART) assuming Al activity regulation through cation exchange equilibrium or equilibrium with an  $\text{Al}(\text{OH})_3$  phase. Both mechanisms invoke a cubic relationship between the activity of  $\text{H}^+$  and  $\text{Al}^{3+}$ . Although common for modeling purposes, the latter mechanisms generally explain field observations with only marginal success (e.g., MULDER et al., 1987; NEAL et al., 1990; MATZNER and PRENZEL, 1992). To improve the simulation of the activity of dissolved Al in acidic forest soils empirical models with  $\text{H}^+$ - $\text{Al}^{3+}$  activity relationships significantly less than cubic have been applied (e.g., BLOOM and GRIGAL, 1985; REUSS et al., 1990). Others have explained disequilibrium with respect to Al containing phases by kinetically constrained dissolution (e.g., VAN GRINSVEN et al., 1989; MATZNER and PRENZEL, 1992).

Previously, batch studies have shown that, even in mineral soil horizons, dissolved Al largely originates in organically bound forms rather than in inorganic mineral phases (BLOOM et al., 1979; MULDER et al., 1989b; DAHLGREN and WALKER, 1993). MULDER et al. (1989b) hypothesized that the activity of Al in solution was controlled by complexation reactions

with (solid phase) soil organic matter rather than by equilibrium with  $\text{Al}(\text{OH})_3$ . If this hypothesis holds true, this has important consequences for the long-term Al solubility in acidified forest soils. Given the current high rate of Al mobilization and the generally small pool size of organically bound Al, a rapid depletion is to be expected. It can be shown theoretically that such a depletion would strongly decrease the Al solubility and consequently result in a steady decrease in soil solution pH. Alternatively, if  $\text{Al}(\text{OH})_3$  would control Al solubility, the pH would remain constant provided strong acid anion concentrations were constant. Only a complete removal of  $\text{Al}(\text{OH})_3$  would result in a loss of pH buffering and a marked decline in pH.

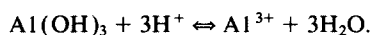
A rapid depletion of organically bound Al in acidified forest soils may have significant ecological implications. Although a gradual decrease in the concentration of potentially toxic inorganic Al may be considered as positive, its beneficial effect may be outweighed by increased concentrations of  $\text{H}^+$  and possibly Fe. Simultaneously, rapid decomplexation of Al could cause a decline in the ecologically relevant organic carbon (C) store in the mineral soil, due to increased rates of both mobilization (TIPPING and WOOF, 1990; MULDER et al., 1993) and microbial decomposition (MARTIN and HAIDER, 1986) of humic compounds.

The objective of this paper is to investigate the Al solubility in acid brown forest soils with high acid loadings and to test whether a significant long-term decrease in Al solubility and soil solution pH occurs. In addition, we tested if long-term changes in soil solution pH could be related to the depletion rate of the organically bound Al pool. The high rate of Al mobilization in Dutch forest soils, which presumably has persisted for decades, represents a unique case to study Al solubility controls in acidic forest soils. Here we present the results of a time series analysis of the Al solubility and pH

in soil solutions conducted at three woodland soil plots (Hackfort) in The Netherlands. The sites differ slightly in soil type and in content and distribution of organically bound Al within the profile. Sites also differ in atmospheric acid deposition and consequently in Al depletion rate. Soil solution data were collected monthly during a six year period. Previously, a time series analysis of  $\text{SO}_4$  and dissolved N compounds was conducted for soil solutions from the same sites (STEIN and VAN BREEMEN, 1993).

### THEORETICAL

In research on soil acidification due to atmospheric deposition, equilibrium with a gibbsite-like phase has often been reported to be an appropriate model for the solubility of Al (DAHLGREN et al., 1990; REUSS and JOHNSON, 1986; RO-BARGE and JOHNSON, 1992) even if gibbsite could not be detected mineralogically. Equilibrium with an  $\text{Al}(\text{OH})_3$  phase may be expressed as



Mathematically this equilibrium condition is a cubic relationship between  $\text{Al}^{3+}$  and  $\text{H}^+$ , according to

$$\{\text{Al}^{3+}\} / \{\text{H}^+\}^3 = \text{Constant}, \quad [1]$$

with curled brackets representing activities in soil solution. In a logarithmic form (base 10) the equilibrium equation becomes

$$\log \text{Al} + 3 \text{pH} = \log K, \quad [2]$$

where  $\log K$  is a constant. The  $\text{Al}(\text{OH})_3$  phases most frequently used as a model for the Al solubility include synthetic gibbsite ( $\log K = 8.11$  at  $25^\circ\text{C}$ ) and natural gibbsite ( $\log K = 8.77$  at  $25^\circ\text{C}$ ). Upon depletion of a gibbsite-like phase a new acid neutralizing compound might come into effect and buffer the acidity at a lower pH level. This new acid neutralizing compound could be another Al containing phase (with a lower Al solubility) or for example Fe containing materials. If the new acid buffer is an Al containing mineral,  $\log K$  in equation [2] is expected to decrease relatively quickly to  $\log K'$ . At constant acid loads a consecutive depletion of several gibbsite-type phases would result in stepwise decreases in  $\log K$  (Eqn. 2) as well as in stepwise decreases in pH.

Others have stressed the importance of soil organic matter in controlling the solubility of Al through complexation reactions (BLOOM et al., 1979; CRONAN et al., 1986; TIPPING et al., 1988; MULDER et al., 1989b; WALKER et al., 1990). In its simplest form complexation equilibrium may be represented by



Mathematically this equilibrium becomes

$$\{\text{Al}^{3+}\} / \{\text{H}^+\}^3 = \text{Constant} * (\{\text{Al}X\} / \{\text{H}_3X\}). \quad [3]$$

By contrast to Eqn. 1, the right-hand side of Eqn. 3 is a function of the composition of the complexation sites. In a logarithmic form Eqn. 3 becomes

$$\log \text{Al} + 3 \text{pH} = \log K + (\log \text{Al}X - \log \text{H}_3X). \quad [4]$$

With depletion of the pool of organically bound Al, the term ( $\log \text{Al} + 3 \text{pH}$ ) will decrease gradually. Note that even at fixed quantities of organically bound Al, the term ( $\log \text{Al} + 3 \text{pH}$ ) may decrease when pH values decline and thus  $\{\text{H}_3X\}$  increases due to protonation (e.g., WALKER et al., 1990). The gradual decrease in the Al solubility upon depletion of organically bound Al is in contrast to the discontinuous and decreases in  $\log K$  in the case of Al solubility control by inorganic mineral phases like gibbsite. The complexation reaction given here only serves as an example and also could have been written as a bidentate binding of Al to soil organic matter (e.g., TIPPING et al., 1988). However, also in the latter case the term ( $\log \text{Al} + 3 \text{pH}$ ) would decrease gradually upon Al depletion.

### MATERIALS AND METHODS

#### Study Sites

For this investigation we used existing data on the chemical composition of both the soil solid phase and soil solution from three woodland plots at Hackfort, in the alluvial plain of the river IJssel (eastern part of The Netherlands). Site characteristics were discussed in detail in previous publications (VAN BREEMEN et al., 1988). In brief, the research plots (HA, HB, and HC) are located in a small 3.2 ha oak-birch woodland (dominated by *Quercus robur* and *Betula pendula*) and have acid brown forest soils. Soils at the three plots are classified as Aeric Haplaquept (HA), Umbric Dystrochrept (HB), and Aquic Udipsamment (HC) (SOIL SURVEY STAFF, 1975). Total strong acid loads (in  $\text{kmol ha}^{-1} \text{y}^{-1}$ ) are 7.5 (HA), 5.0 (HB), and 3.0 (HC). The difference in acid loads between the plots is mainly due to differences in the rates of nitrification of atmospherically deposited  $\text{NH}_4$ . Average annual amounts of precipitation amount to 706  $\text{mm y}^{-1}$  and average annual drainage rates at the 60 cm soil depth range from 191  $\text{mm y}^{-1}$  at HA to 247  $\text{mm y}^{-1}$  at HC.

Soil sampling and analysis was conducted in 1980 at the beginning of the monitoring programme. All soils are acidic (Table 1) with  $\text{pH}(\text{H}_2\text{O})$  values in the surface soil ranging from 3.4 (HB) to 4.0 (HC) and below the rooting zone from 3.9 (HA) to 4.2 (HC). Base saturation values are generally well below 20%. Organic matter contents are low and differ significantly between the plots and between the soil layers, in general exhibiting a decrease with depth. Organic carbon in the surface 50 cm decreases in the order  $\text{HB} > \text{HA} \approx \text{HC}$ . Organically bound soil Al, as estimated via extraction with  $\text{Na}_4\text{P}_2\text{O}_7$  (BEGHEIJN, 1980), is highest in the upper soil layers of the HB site. At HA and HC the levels of organically bound Al are low. Particularly in the HA and HB soils, significant amounts of nonorganically bound free (secondary) Al are present. This Al, which is estimated by a dithionite-citrate-bicarbonate (DCB) extraction, is probably associated with Fe-oxides (PARFITT and CHILDS, 1988), but may also be due to a partial extraction of hydroxy-Al interlayers in the clay fraction. Clay contents at the three plots varies with depth between 6 and 14% (plot A), and between 2 and 8% (plots B and C). Clay mineralogy is dominated by 1.4 nm minerals, with some illite (1.0 nm) present below the 40 cm depth. The 1.4 nm minerals are mainly randomly interstratified chlorite/vermiculite at shallow depth and chlorite plus vermiculite at greater depth. This indicates that a significant amount of hydroxy-Al is present in interlayer positions (VAN BREEMEN et al., 1988).

#### Sampling and Analysis of Soil Solutions

Procedures are described in detail by MULDER et al. (1987) and VAN BREEMEN et al. (1988). Soil solutions were sampled monthly from type 1910 high flow porous ceramic cups (Soil Moisture Corp., Santa Barbara, California) at the 10, 20, 40, and 60 cm depths. At several positions duplicates were placed. Before installation, cups were leached with 0.001 M  $\text{HNO}_3$ , followed by prolonged leaching with demineralized water. Suction was applied either by evacuating the cups with a hand operated vacuum pump (when the soil was wet) or by connecting the cups to a 4-L PVC tank, previously evacuated

Table 1. Major soil chemical characteristics at Hackfort A (HA), Hackfort B (HB), and Hackfort C (HC). Soil data\* refer to the same soil pits as where solution lysimeters were installed (VAN BREEMEN et al., 1988). Beside an A horizon (between 0 and 5 cm depth) the three plots show few signs of soil development.

Code	Depth (cm)	C	Al <sub>2</sub> O <sub>3,org</sub> -----%	Al <sub>2</sub> O <sub>3,DCB</sub> -----%	pH(H <sub>2</sub> O)	CEC <sup>1</sup> meq/kg	BS <sup>1</sup> -----%	AlS <sup>1</sup>
HA	0-10	3.7	0.17	0.62	3.8	63	11	31
	10-20	0.9	0.17	0.83	3.7	45	3	33
	20-30	0.5	0.11	0.83	3.9	39	2	44
	30-40	0.3	NA	0.77	3.8	NA	NA	NA
	40-50	0.2	0.10	0.71	3.9	33	4	38
	50-60	0.1	0.07	0.58	4.1	36	36	25
HB	0-3	7.8	NA	0.30	3.4	52	10	74
	3-15	2.2	0.31	0.58	3.9	52	15	74
	15-25	2.3	0.36	0.59	4.1	41	7	44
	25-35	1.0	0.44	0.68	4.0	24	17	71
	35-45	0.6	0.33	0.59	4.0	15	10	76
	45-55	0.2	0.04	0.26	4.1	20	14	81
	55-65	0.2	NA	0.40	4.0	16	14	80
HC	0-10	3.2	0.05	0.49	4.0	40	29	22
	10-15	1.0	NA	0.41	4.1	26	16	34
	15-25	0.7	0.22	0.89	4.2	28	10	43
	25-40	0.3	0.12	0.88	4.1	18	5	45
	40-50	0.2	0.07	0.66	4.2	15	5	35
	50-57	0.2	NA	0.54	4.2	12	8	42
	57-70	0.0	NA	0.52	4.2	9	8	39

\* Not available data are designated NA

<sup>1</sup> Saturation of the cation exchange sites with base cations (BS) and Al (AlS), as well as the cation exchange capacity (CEC) were determined in 0.1 M BaCl<sub>2</sub>. CEC is calculated as the sum of exchangeable base cations and exchangeable acidity.

in the laboratory (when the soil was moist to dry). Within 24 h after evacuating the cups, the water collected in the cups (usually 10 to 100 cm<sup>3</sup>) was sampled by suction in a 100 cm<sup>3</sup> polyethylene bottle and brought to the laboratory. After prolonged periods without rain in summer the surface 60 cm of the soil was often too dry to collect water.

Analytical methods (BEGHEIJN, 1980) include the potentiometric determination of pH and measurement of electrical conductivity (EC). Both parameters were determined upon return in the laboratory. Inorganic and total dissolved C concentrations were measured by infrared spectrometry (Carbon analyzer, Beckman 915B). Fluoride, Cl, NO<sub>3</sub>, and SO<sub>4</sub> were determined by ion chromatography (Dionex IC 10). Concentrations of Ca and Mg were measured by atomic absorption (Perkin Elmer AAS/AES type 560), with LaCl<sub>3</sub> added to reduce interferences. Sodium and K were analyzed by flame emission, with Al added to control ionization. Ammonium, PO<sub>4</sub>, Al, and Si were determined by auto analyzer. Ammonium was determined with salicylate, nitroprusside hypochlorite. Phosphate was determined with ammonium molybdate, antimony-potassium tartrate, and ascorbic acid as reagents. Dissolved Si was estimated using ammonium molybdate and ascorbic acid (BEGHEIJN, 1980).

Total dissolved Al was assumed to equal measured Al in pre-acidified samples. The analysis was conducted using pyrocatechol violet and an ammonium acetate/acetic acid buffer (BEGHEIJN, 1980). Efforts to also measure monomeric organic Al, using the fractionation procedure of DRISCOLL (1984) failed to give accurate results, because of the high concentration of inorganic monomeric Al, which swamps the organically complexed forms (MULDER et al., 1989a). In all computations total dissolved Al was assumed to equal inorganic monomeric Al. Particularly at the 10 cm soil depth, where average dissolved organic carbon (DOC) concentrations are high (on average ranging from 50 to 67 mg/L) but pH is low (Table 2), this assumption may lead to an overestimation of inorganic monomeric Al. MULDER et al. (1987) estimated that organic complexes contribute about one third of the total monomeric Al at the 10 cm depth and <20% in the deeper soil layers.

#### Soil Temperature

Soil temperature was measured biweekly (to January 1982) or monthly (from January 1982 onwards, simultaneously with the col-

lection of soil solutions), by means of copper-constantan thermocouples, which were permanently installed at the 5, 10, 20, 50, and 100 cm soil depths. Measurements were done using a Comark type 1624 electric thermometer, with an ice-water mixture as a reference. One set of five thermocouples was placed in each plot.

#### Computational Procedures

Ionic strength of the individual soil solutions as well as the activity of Al<sup>3+</sup> was estimated using the chemical equilibrium program AL-CHEMI (SCHECHER and DRISCOLL, 1987). The program accounts for free (aquo) Al<sup>3+</sup>, as well as monomeric hydrolysed forms of Al and complexes with SO<sub>4</sub> and F. Activity calculations were corrected for temperature and ionic strength. Thermodynamic constants were according to SCHECHER and DRISCOLL (1987, 1988). For many of the calculations as outlined below the estimated cation activity values were transformed to their logarithm with a base of 10.

Using the estimated activities the Al solubility (expressed as log × Q) was calculated for each individual soil solution according to

$$\log Q = \log_{10} (\{Al^{3+}\} / \{H^+\}^3) = \log Al + 3 pH \quad [5]$$

and compared with log K values reported for the various Al(OH)<sub>3</sub> phases (Eqn. 2). With respect to the mineral phase under consideration soil solutions can be undersaturated (log Q < log K), saturated (log Q = log K), or oversaturated (log Q > log K).

Time series analyses, conducted to detect long-term time trends in pH, log Al, log Ca, and log Q, were performed using a linear regression model with autocorrelated errors (GALLANT and GOEBEL, 1976). This procedure permits the estimation of model parameters when the data are time series and the error term is an autoregressive process. Several steps are distinguished.

For pH and the logarithms of the activity of Al<sup>3+</sup>, and Ca<sup>2+</sup>, as well as for log Q (Eqn. 5), we applied a regression model for time t according to

$$\{pH, \log Al, \log Ca, \log Q\}_t = \alpha + (\beta * t) + (\gamma * T_t) + (\delta * IS_t) + v_t, \quad [6]$$

where α, β, γ, and δ are model parameters, v<sub>t</sub> the autocorrelated error term, t the time (in years), T<sub>t</sub> the temperature of the solution (in

Table 2. Average values and standard deviations of selected parameters as observed in individual soil solution lysimeters at Hackfort A (HA), Hackfort B (HB), and Hackfort C (HC) between 1981 and 1987. i and ii represent replicates. The total concentration of strong acid anions (SAA) represents the summed concentration of  $\text{NO}_3$ ,  $\text{SO}_4$  and  $\text{Cl}$ .

Site	dpth		pH <sup>1</sup>		Al		Ca		SAA	
	(cm)	obs			$\mu\text{mol L}^{-1}$		$\mu\text{mol L}^{-1}$		$\mu\text{eq L}^{-1}$	
HA(i)	10	46	3.32	0.17	204	111	344	324	2658	739
	20	53	3.51	0.13	364	169	256	94	2784	856
	40	52	3.75	0.15	822	351	298	124	4158	1530
HA(ii)	10	27	3.60	0.37	207	90	371	149	2484	692
	40	27	4.02	0.58	580	260	339	116	3091	824
HB(i)	10	49	3.37	0.16	134	102	179	92	1990	645
	40	51	3.99	0.11	634	288	182	52	2902	958
HB(ii)	10	42	3.26	0.18	170	162	216	116	2326	876
	20	56	3.37	0.15	350	126	268	97	2868	795
	40	60	3.90	0.15	581	217	240	80	2840	899
	60	58	4.00	0.16	711	207	240	69	3184	840
HC(i)	10	41	3.70	0.25	247	96	182	69	2074	614
	60	62	4.02	0.18	382	155	184	42	2273	527
HC(ii)	10	54	3.63	0.16	132	55	144	54	1535	540
	20	62	3.64	0.16	163	65	116	40	1615	530
	40	61	3.91	0.15	308	150	128	64	1866	734
	60	58	4.09	0.15	303	123	152	46	2089	633

<sup>1</sup> arithmetic mean

degrees C) at time  $t$ , and  $IS_t$  the ionic strength of the solution at time  $t$ . Autoregressive parameters are fitted for lags of 1 and 12 months:  $v_t = \eta_1 v_{t-1} + \eta_{12} v_{t-12}$ , since observations are likely to be most highly influenced by observation 1 month and 12 months earlier. This model is equivalent to an autoregressive process of order 2, AR(2). The parameters  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  are structural model parameters, which are estimated, following a Yule-Walker procedure (HARVEY, 1981; CHATFIELD, 1989): an initial guess is made, assuming independence (i.e., with  $v_t$  being an independent white noise process), using ordinary least squares. Next estimates for  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ , as well as for  $\eta_1$  and  $\eta_{12}$  are used to transform the data, and subsequently new estimates are obtained by means of generalized least squares. The quality of the fit of the structural part of the model after transforming for the autocorrelation is given by the  $R^2$  value, defined as  $1 - \text{SSE}_T / \text{SST}_T$ , where  $\text{SST}_T$  is the total sum of squares of the transformed response and  $\text{SSE}_T$  is the error sum of squares for the transformed regression model. In principle, this procedure can be iterated until convergence is achieved. In this study we used just one iteration step to facilitate the calculations. Additional iteration steps were found to modify the analytical results only slightly.

The main purpose of our time series analysis was to test whether significant changes with time occurred in the parameters of interest. Note that no attempts were made to improve explanation of the parameter variability (increase  $R^2$  values), which could probably be achieved by including more parameters in the right-hand side of Eqn. 6. However, such additional parameters may be time dependent themselves, so that including them in the analysis could cause an erroneous underestimation of the long-term change  $\beta$  in pH, log Al, log Ca, and log  $Q$ .

To investigate the relationship between log Al and pH we used a linear regression model with an autocorrelated error term to allow corrections for long-term trends and systematic changes with soil solution temperature:

$$\log \text{Al}_t = \alpha + (\beta * t) + (\gamma * T_t) + (\delta * \text{pH}_t) + v_t. \quad [7]$$

Model parameters were obtained in a similar way as discussed for Eqn. 6.

## RESULTS AND DISCUSSION

### General

All three plots had high concentrations of strong acid anions ( $\text{NO}_3$ ,  $\text{SO}_4$ , and  $\text{Cl}$ ; Table 2). This pattern is consistent

with the elevated inputs of acid deposition. Because the soils have a low acid-buffering capacity, soil solutions were extremely acidic, with average pH values ranging from 3.2 to 3.7 at the 10 cm soil depth. Even at the 60 cm depth soil solution pH values were as low as 4.0. Aluminum, which was the dominant cation in solution on a charge basis, reached average concentrations between 132 and 247  $\mu\text{mol L}^{-1}$  at the 10 cm soil depth. Increasing neutralization of  $\text{H}^+$  with depth by Al solubilization caused Al concentrations to increase to values between 303 and 711  $\mu\text{mol L}^{-1}$  at the 60 cm depth (MULDER et al., 1987; VAN BREEMEN et al., 1988). These observations are in accordance with earlier findings that Al dissolution is the major acid neutralizing process accounting for more than 75% of the acid neutralization in the Hackfort soils (MULDER et al., 1987). For comparison, average Ca concentrations are also included in Table 2. In the surface layers concentrations of Ca and Al were similar, when expressed on a molar basis. However, by contrast to Al the concentration of Ca was fairly constant with depth. Earlier, VAN BREEMEN et al. (1988) demonstrated that most of Ca in soil solutions is related to nutrient cycling and only to a lesser extent due to dissolution of the Ca pool in the soil. Cycling of Ca is particularly high at the HA plots, which have a calcareous subsoil (below the 60 cm soil depth).

At all depths soil solutions were, on average, undersaturated with respect to synthetic gibbsite ( $\log K = 9.12$  at 8°C; Fig. 1). This was particularly evident in the surface soil layers, but even at the 60 cm soil depth a considerable degree of undersaturation occurred. Individual data points for three selected soil layers (Fig. 2) indicate that even for individual lysimeters, log Al and pH values were not well correlated. Similar observations were reported for the German Solling site (MATZNER and PRENZEL, 1992). Clearly, the predictive capabilities of the synthetic gibbsite equilibrium model for dissolved Al are rather poor at these sites. Note, however, that our data have as yet not been corrected for possible long-

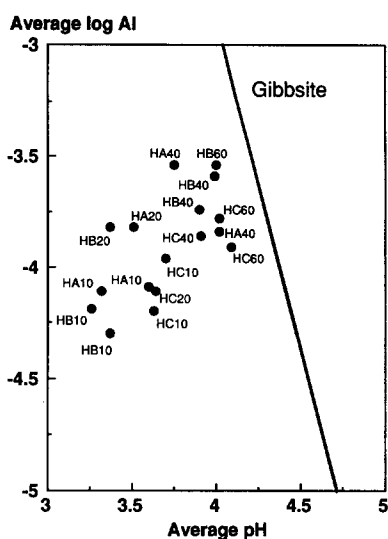


FIG. 1. Log Al vs. pH at Hackfort A (HA), Hackfort B (HB), and Hackfort C (HC). The code further indicates lysimeter depth (in cm). All data points represent average values for one soil solution lysimeter (see also Table 2). The solid line indicates the solubility of (synthetic) gibbsite at 8°C ( $\log K = 9.12$ ). At all depths the average soil temperature is ca. 8°C.

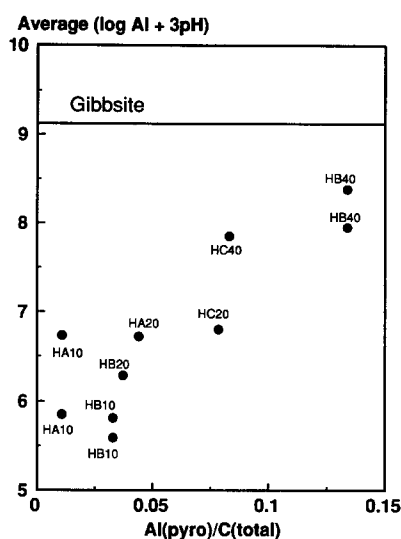


FIG. 3. Average values for  $\log Q (= \log Al + 3 pH)$  against the molar ratio of pyrophosphate extractable Al and total organic C. Data points are given per soil layer. The codes of the data points are explained in Fig. 2. Soil layers with either pyrophosphate extractable Al below 20  $\text{mmol kg}^{-1}$  or with less than 0.2% organic C were excluded from the figure, because of low analytical precision. The solid line indicates the solubility of (synthetic) gibbsite at 8°C ( $\log K = 9.12$ ).

term changes in Al solubility. Below we will use time series analysis to correct the pH and log Al data for long-term trends and variations in Al solubility due to temperature changes.

Values for  $\log Q$  were positively correlated with the amount of complexed Al per mol organic C in the soil solid phase (Fig. 3). This pattern suggests that  $\log Q$  values decrease (Al solubility decreases) with decreasing Al saturation of the organic complexation sites. Similar findings concerning the importance of soil organic matter as an Al solubility control in mineral soil horizons were reported previously from batch experiments (BLOOM et al., 1979; MULDER et al., 1989b; WALKER et al., 1990).

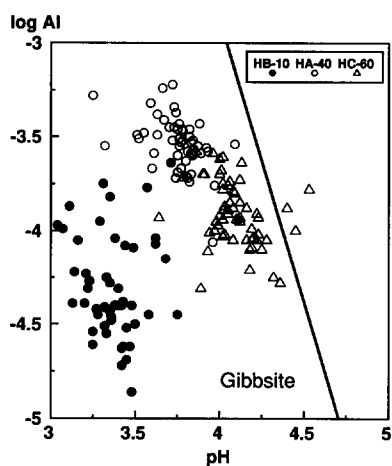


FIG. 2. Log Al vs. pH for three individual soil solution lysimeters (Hackfort B (10 cm depth), Hackfort A (40 cm depth), and Hackfort C (60 cm depth), respectively). Data points represent all available monthly values between 1981 and 1987. The solid line indicates the solubility of (synthetic) gibbsite at 8°C ( $\log K = 9.12$ ). Soil temperatures vary between 0°C and 16°C at the 10 cm depth and between 3°C and 13°C at the 40 cm and 60 cm soil depth.

#### Time Series Analysis

Recently STEIN and VAN BREEMEN (1993) conducted a time series analysis of the concentration of  $\text{SO}_4$  and  $\text{NO}_3$  at the Hackfort sites. Results indicate that  $\text{SO}_4$  concentrations in soil solutions at Hackfort decrease slightly, whereas  $\text{NO}_3$  concentrations show a minor increase. At most depths long-term trends are not significant at the 90% confidence level, however. Consequently, the summed concentration of strong acid anions (SAA in Table 2) does not change significantly with time. This trend is in contrast to other investigations in both Europe (CHRISTOPHERSEN et al., 1990; WESSELINK et al., 1993) and North America (DRISCOLL et al., 1989) where  $\text{NO}_3$  concentrations are generally low, but where a significant decrease in  $\text{SO}_4$  concentrations occurred during the 1980s.

Despite the constancy of the summed concentration of  $\text{SO}_4$  and  $\text{NO}_3$ , pH values decreased significantly in the surface layers of all three soil plots (Table 3a). Decreases in soil solution pH in the upper 10 cm of the soils ranged from 0.05 to 0.14 units per year. At the 20 cm soil depth pH decreased between 0.03 and 0.04 units per year. At the 40 and 60 cm soil depth the long-term change in soil solution pH was generally not significant. Soil solution pH values decreased with increasing soil temperature but generally this correlation was not significant. Not surprisingly, pH values decreased significantly with increasing ionic strength.

In general,  $\log Ca$  values in soil solutions decreased with time (Table 3b). By contrast to pH, however, this long-term change was not significant in the surface soil layers but rather at greater depths. At the 40 and 60 cm soil depth  $\log Ca$  decreased up to 0.04 units per year. Possibly the lack of significance of the decrease in  $\log Ca$  in the surface soil is due to noise introduced by Ca cycling (e.g., VAN BREEMEN et al., 1988). Similarly to soil solution pH, temperature did not affect  $\log Ca$  values significantly, whereas  $\log Ca$  increased

Table 3a. Estimated model parameters  $\beta$ ,  $\gamma$ , and  $\delta$  for equation [6],  

$$\text{pH}_i = \alpha + (\beta * t) + (\gamma * T_i) + (\delta * \text{IS}_i) + v_i$$
 with  $t$  is time (year),  $T$  is temperature ( $^{\circ}\text{C}$ ), and  $\text{IS}$  is ionic strength (M). One, two and three asterixes indicate significance at the the 99.9 %, 99 %, and 95 % confidence level.

Site	depth (cm)	$\beta$	$\gamma$	$\delta$	$R^2$
Hackfort Ai	10	-0.054 **	-0.009	- 69.7 ***	0.34
	20	-0.033 ***	-0.013 **	- 29.9 **	0.41
	40	+0.001	-0.008	- 28.4 ***	0.39
Hackfort Aii	10	-0.148 *	-0.033	- 75.6	0.30
	40	+0.131	-0.049	-194	0.31
Hackfort Bi	10	-0.053 ***	-0.011 *	- 41.7 *	0.39
	40	-0.004	-0.004	- 21.5 *	0.13
Hackfort Bii	10	-0.059 **	-0.010	- 49.1 **	0.34
	20	-0.038 **	-0.013 **	- 48.0 **	0.34
	40	-0.002	-0.004	- 36.9 **	0.14
	60	+0.004	-0.006	- 27.5	0.06
Hackfort Ci	10	-0.103 ***	-0.009	- 53.8	0.55
	60	-0.021	-0.015 *	- 36.4	0.14
Hackfort Cii	10	-0.063 ***	-0.005	- 59.5 **	0.57
	20	-0.041 ***	-0.009 *	- 93.9 ***	0.39
	40	-0.032 **	-0.009	- 51.0 **	0.29
	60	-0.005	-0.011	- 47.5 *	0.17

significantly with ionic strength. The observed decrease in Ca concentration at depth is consistent with decreases in dissolved Ca at Hubbard Brook (DRISCOLL et al., 1989) and at Birkenes (CHRISTOPHERSEN et al., 1990). At Birkenes this decrease in Ca concentration has been attributed to the depletion of both exchangeable and weatherable pools of Ca. By contrast, at Hubbard Brook this pattern was attributed to either a decline in leaching of exchangeable Ca pools, due to decreases in  $\text{SO}_4$  inputs and/or to decreases in atmospheric input of Ca.

Long-term trends in log Al (Table 3c) tended to be negative for the surface soil and positive for the deeper soil layers, but trends were not consistently significant for any of the depths. The effect of temperature and ionic strength on log Al were similar to that for log Ca.

Our results indicate that pH in the surface soil layers decreased gradually with time, notwithstanding a constant SAA. Consequently, other cations, notably Al, being the dominant cation on a charge basis, had to decrease in concentration at the same rate because of charge balance constraints. However,

Table 3b. Estimated model parameters  $\beta$ ,  $\gamma$ , and  $\delta$  for equation [6],  

$$\log \text{Ca}_i = \alpha + (\beta * t) + (\gamma * T_i) + (\delta * \text{IS}_i) + v_i$$
 with  $t$  is time (year),  $T$  is temperature ( $^{\circ}\text{C}$ ), and  $\text{IS}$  is ionic strength (M). One, two and three asterixes indicate significance at the the 99.9 %, 99 %, and 95 % confidence level.

Site	depth (cm)	$\beta$	$\gamma$	$\delta$	$R^2$
Hackfort Ai	10	-0.014	+0.005	+ 93.4 ***	0.63
	20	-0.050 ***	+0.000	+ 72.8 ***	0.72
	40	-0.018 *	-0.001	+ 47.5 ***	0.65
Hackfort Aii	10	-0.018	-0.002	+ 96.3 ***	0.70
	40	+0.029	-0.002	+ 36.1	0.13
Hackfort Bi	10	+0.019 *	+0.008 *	+ 14.0 ***	0.80
	40	-0.043 ***	+0.012 *	+ 16.1 *	0.44
Hackfort Bii	10	-0.007	+0.008	+106 ***	0.83
	20	-0.026 ***	+0.001	+ 91.0 ***	0.74
	40	-0.038 ***	+0.003	+ 48.5 ***	0.57
	60	-0.028 ***	+0.015 ***	+ 59.6 ***	0.72
Hackfort Ci	10	-0.013	+0.002	+122 ***	0.74
	60	-0.027 ***	-0.007	+ 73.4 ***	0.36
Hackfort Cii	10	+0.017	+0.011 **	+190 ***	0.69
	20	+0.019	+0.000	+166 ***	0.52
	40	-0.037 *	+0.005	+105 ***	0.50
	60	-0.013	+0.009	+ 92.2 ***	0.44

Table 3c. Estimated model parameters  $\beta$ ,  $\gamma$ , and  $\delta$  for equation [6],  
 $\log A_i = \alpha + (\beta * t) + (\gamma * T_i) + (\delta * IS_i) + v_i$ ,  
 with  $t$  is time (year),  $T$  is temperature ( $^{\circ}C$ ), and  $IS$  is ionic strength (M). One, two and three asterixes indicate significance at the the 99.9 %, 99 %, and 95 % confidence level.

Site	dpth (cm)	$\beta$	$\gamma$	$\delta$	$R^2$
Hackfort Ai	10	-0.003	+0.005	+135 ***	0.67
	20	+0.021	+0.007	+ 77.6 ***	0.41
	40	+0.005	+0.001	+ 49.0 ***	0.72
Hackfort Aii	10	+0.047 *	+0.008	+146 ***	0.65
	40	-0.153	+0.056	+391	0.29
Hackfort Bi	10	-0.060 ***	+0.007	+186 ***	0.78
	40	+0.001	-0.004	+ 69.1 ***	0.81
Hackfort Bii	10	+0.012	+0.007	+177 ***	0.83
	20	-0.005	-0.003	+ 92.2 ***	0.80
	40	+0.060	+0.142 ***	+173 *	0.27
	60	+0.013 ***	-0.003	+ 55.8 ***	0.86
Hackfort Ci	10	-0.003	-0.006	+157 ***	0.60
	60	+0.018 **	-0.006 *	+144 ***	0.85
Hackfort Cii	10	-0.054 ***	+0.012 **	+104 ***	0.63
	20	-0.031 ***	+0.005	+153 ***	0.71
	40	+0.027 ***	-0.004	+116 ***	0.74
	60	+0.017	-0.003	+ 88.4 ***	0.53

at the relatively high concentrations of Al (Table 2), it may prove difficult to detect the significance of such relatively small changes.

As follows from the time series analysis of log Al and pH, negative long-term changes in log Q (= log Al + 3 pH) occurred in the surface soil layers (Table 3d; Fig. 4). This pattern indicates that the solubility of Al decreased gradually with time. At the 10 cm soil depth the annual decrease in log Q ranged from 0.15 to 0.4 units, while at the 20 cm soil depth

this ranged from 0.08 to 0.14 units. At greater depth long-term changes in log Q were generally not significant. These results suggest that the Al solubility in these soil solutions is not controlled by equilibrium with a single mineral phase like gibbsite. Values for log Q were generally negatively correlated with temperature (i.e., solutions were more undersaturated at higher temperature; Table 3d), but only in five soil layers this correlation was significant. Our data indicate that the temperature dependence of the log K of synthetic

Table 3d. Estimated model parameters  $\beta$ ,  $\gamma$ , and  $\delta$  for equation [6],  
 $\log Q_i = (\log Al + 3pH)_i = \alpha + (\beta * t) + (\gamma * T_i) + (\delta * IS_i) + v_i$ ,  
 with  $t$  is time (year),  $T$  is temperature ( $^{\circ}C$ ), and  $IS$  is ionic strength (M). One, two and three asterixes indicate significance at the the 99.9 %, 99 %, and 95 % confidence level.

Site	dpth (cm)	$\beta$	$\gamma$	$\delta$	$R^2$
Hackfort Ai	10	-0.157 **	-0.023	- 70.8	0.22
	20	-0.081 *	-0.033 *	- 8.8	0.19
	40	+0.007	-0.024	- 37.6	0.15
Hackfort Aii	10	-0.405 *	-0.090	- 98.1	0.29
	40	+0.237	-0.092	-204	0.33
Hackfort Bi	10	-0.220 ***	-0.026	+ 56.8	0.46
	40	-0.008	-0.016	+ 5.0	0.03
Hackfort Bii	10	-0.168 **	-0.025	+ 22.1	0.24
	20	-0.115 **	-0.042 **	- 50.1	0.25
	40	+0.079	+0.141 **	+ 88.5	0.16
	60	+0.025	-0.021	- 27.0	0.03
Hackfort Ci	10	-0.311 ***	-0.033	- 23.4	0.57
	60	-0.045	-0.050 *	+ 35.6	0.08
Hackfort Cii	10	-0.242 ***	-0.003	- 72.1	0.60
	20	-0.147 ***	-0.019	-120	0.31
	40	-0.068 *	-0.030 *	- 37.8	0.14
	60	+0.001	-0.027	- 27.5	0.06

gibbsite (a decrease of 0.059 units per degree C) is higher than that of  $\log Q$ . This modest temperature dependence of  $\log Q$  also suggests the importance of ion exchange reactions in controlling the solubility of Al (WALKER et al., 1990). Ionic strength did not affect  $\log Q$  significantly.

Many authors have explained the apparent undersaturation with respect to gibbsite in the mineral horizons at the soil surface by kinetically constrained mineral dissolution (e.g., VAN GRINSVEN et al., 1992). However, this hypothesis is not supported by our data (Fig. 4). Here, values of  $\log Q$  tended to reach a minimum in summer and a maximum in winter. Given the low contents and fluxes of water, the residence time of soil water was longest in summer (e.g., VAN GRINSVEN et al., 1987). Also, the soil temperatures are highest in summer. The coincidence of a lower apparent solubility of Al with longer water residence times and higher temperatures in summer, is the reverse of the relationship expected from kinetically constrained dissolution of Al.

Using the time series model in Eqn. 7, only five out of the seventeen soil layers investigated at Hackfort showed a negative effect of pH on  $\log Al$  (values of  $\delta$  ranging from  $-0.29$  to  $-1.62$ , Table 4). The incidental high value of  $-1.62$  at the 40 cm depth of HAii should be seen in the light of the (unique) significant long-term decrease of SAA for this soil layer ( $-209 \mu\text{mol l}^{-1} \text{y}^{-1}$ ). All values differed considerably from the theoretical value of  $-3$ , as given in Eqn. 2. This means that variations in  $\text{SO}_4$  and  $\text{NO}_3$  concentrations, and thus variations in the concentrations of acidic cations, resulted in a stronger change in pH and a lesser change in  $\log Al$  than predicted by the gibbsite equilibrium model. For example, soil solutions became more undersaturated with respect to gibbsite ( $\log Q$  decreases) with increasing concentrations of  $\text{SO}_4$  and  $\text{NO}_3$  (e.g., in the relatively dry summer period). This finding is similar to that reported for batch experiments by BLOOM et al. (1979).

Previously, polymeric hydroxy-Al precipitates (e.g., hydroxy-Al interlayers), which would result in a slope in the

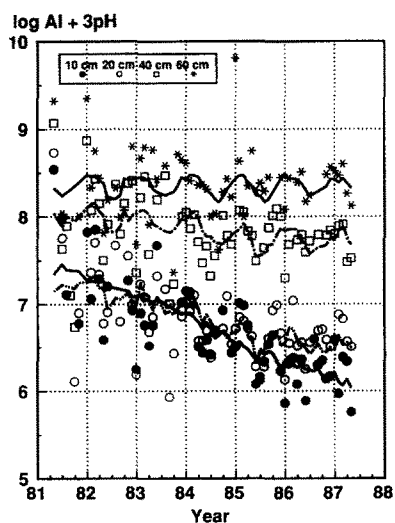


FIG. 4. The time series of  $\log Q$  ( $= \log Al + 3pH$ ) at the HC(ii) plot. Data points are observations, whereas solid and broken lines represent the result of the regression analysis.

Table 4. Values for  $\delta$  in  $\log Al = \alpha + (\beta * t) + (\gamma * T_s) + (\delta * pH) + v$ , (Equation [7]). One, two and three asterixes indicate significance at the the 99.9 %, 99 %, and 95 % confidence level.

Site	depth (cm)	$\delta$
Hackfort Ai	10	-0.43 *
	20	-0.29
	40	-0.21
Hackfort Aii	10	-0.32 ***
	40	-1.62 ***
Hackfort Bi	10	-0.36
	40	-0.12
Hackfort Bii	10	-0.55
	20	-0.21
	40	-0.22
	60	-0.05
Hackfort Ci	10	-0.29
	60	+0.01
Hackfort Cii	10	-0.18
	20	-0.29 ***
	40	-0.32 **
	60	-0.13

$\log Al$ -pH diagram of ca.  $-2.7$  (BLOOM et al., 1977; DAHLGREN and WALKER, 1993), have been proposed to control the Al activity in soils at pH values greater than 4.5 (CRONAN et al., 1986; DAHLGREN and UGOLINI, 1989; DAHLGREN et al., 1989; DAHLGREN et al., 1990; WALKER et al., 1990). However, in more acidic conditions like those at Hackfort, control of the Al solubility by polymeric hydroxy-Al is unlikely as is indicated by the slopes ( $\delta$  value) close to zero in Table 4.

Recently developed deterministic models describing complexation of Al by humic substances (e.g., TIPPING and HURLEY, 1988; DE WIT et al., 1990) in dilute suspensions also predict relationships between the activities of  $H^+$  and  $Al^{3+}$  significantly less than cubic. However, model predictions of this relationship appear to be highly sensitive to assumed type of binding (e.g., monodentate, bidentate) and assumptions concerning hydrolysis of complexed Al. These assumptions warrant further investigation for soil systems, which even in batch experiments, are much more concentrated than the systems originally used for model development.

The estimated annual decrease in  $\log Q$  correlates well with the calculated annual export of Al from each soil layer (Fig. 5). At Hackfort  $\log Q$  decreased approximately 0.75 units per mole of leached Al per  $m^2$ . This trend suggests that the Al solubility is strongly related to the reactive Al pool. Earlier we have reported that this active pool consists predominantly of organically bound Al (MULDER et al., 1989b). Assuming that the annually exported Al originates in the organically bound pool we estimated the annual relative decrease of the organically bound Al pool. Values for  $\log Q$  appeared to decrease between 0.03 and 0.04 units per 1% decrease of the organically bound Al pool (Fig. 6). A similar significant positive correlation between pyrophosphate extractable (organically bound) soil Al and  $\log Q$  was reported



from equilibrium batch experiments by MULDER et al. (1989b).

### Comparison with Other Studies

Other studies in strongly acidified systems have also found pH-log Al relationships far less than cubic (e.g., BLOOM et al., 1979; BLOOM and GRIGAL, 1985; NEAL et al., 1990; BERGGREN, 1992). Unfortunately, very few long-term soil solution data sets exist, so that our hypothesis of the importance of organically bound Al as a dominant Al activity control in acidic mineral soil horizons could not be tested rigorously on other sites. Only for the Solling site (Germany) an extensive data set is available and the Al chemistry was recently discussed by MATZNER and PRENZEL (1992). These authors explained undersaturation with respect to gibbsite in the surface soil of both spruce and beech stands by assuming kinetically constrained Al dissolution. However, similar to our observations their data (Fig. 2 of MATZNER and PRENZEL, 1992) show undersaturation with gibbsite reaching its maximum in summer. Again this weakens the argument of the importance of kinetic constraints. Interestingly enough their log  $Q$  for the 10 cm soil depth decreased between 1981 and 1985 by approximately 0.25 units per year. With an estimated annual Al leaching rate from the surface 10 cm of the Solling spruce stand of ca.  $0.16 \text{ mol m}^{-2} \text{ y}^{-1}$  the decrease in log  $Q$  is somewhat high compared to our own observations (Fig. 5). The relatively large annual decrease in log  $Q$  at Solling may have been amplified by a slight increase in  $\text{SO}_4$  during this four year period (WESSELINK et al., 1993). After 1985, MATZNER and PRENZEL (1992) reported a gradual increase in log  $Q$ . Although the latter seems to contradict our hypothesis, it may be explained by the apparent decline in  $\text{SO}_4$  concentrations after 1985. Presumably, the log  $Q$  increase caused by the decrease in  $\text{SO}_4$ , has overridden the tendency

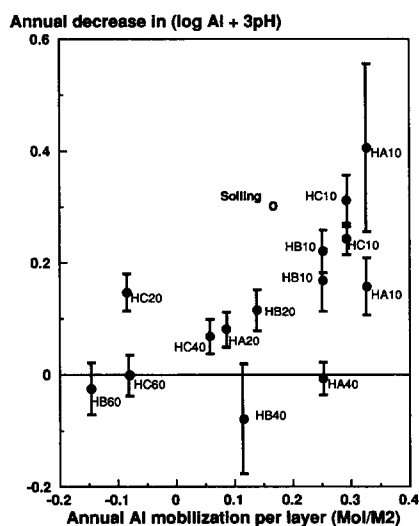


FIG. 5. The annual decrease in log  $Q$  (also given in Table 3d) against the average annual amount of leached Al per soil layer (VAN BREEMEN et al., 1988). The codes of the data points are explained in Fig. 2. Bars indicate standard errors. The open circle represents the Solling spruce site at the 10 cm soil depth as estimated from MATZNER and PRENZEL (1992).

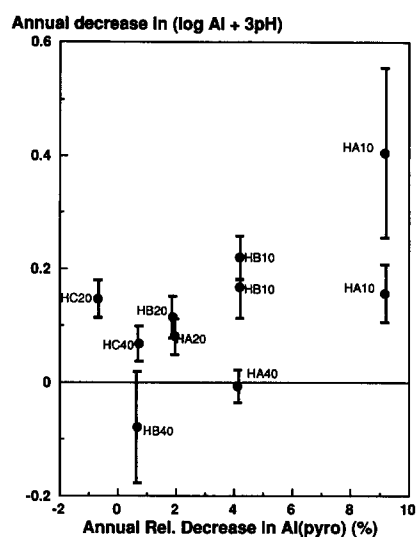


FIG. 6. The annual decrease in log  $Q$  (also given in Table 3d) against the relative annual decrease of pyrophosphate extractable Al. Here we assumed that all leached Al originates in the pyrophosphate extractable (organically bound) pool (MULDER et al., 1989b). The codes of the data points are as in Fig. 2. Bars indicate standard errors.

of log  $Q$  to decrease due to Al leaching. Similarly to our findings for the Hackfort sub-soils a long-term trend in log  $Q$  was less apparent at the 80 cm soil depth of the Solling spruce stand.

### CONCLUSIONS

Six years of soil solution data from the highly acidic Hackfort soil plots in The Netherlands demonstrate that neither equilibrium with a gibbsite-like phase nor kinetically constrained dissolution explains Al activities very well. Instead, the Al solubility is positively correlated with organically bound Al in the soil solid phase. To test if the long-term decrease of the pool of organic soil bound Al coincides with a declining Al solubility, we applied a time series analysis on pH, log Al, log Ca, and Al solubility (log  $Q = \log \text{Al} + 3 \text{pH}$ ). Results indicate that leaching of Al, due to acidification, leads to a gradual but significant decrease in pH and Al solubility. Both the leaching of Al and the decrease in log  $Q$  values are strongest in the surface 10 cm of all three soil plots. The data support our hypothesis of equilibrium control of the Al activity in soil solution of acidic soils (pH < 4.5) by organically bound solid phase Al.

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