Aluminium Release from Acidic Forest Soil following Deforestation and Maize Cultivation in Ghana, West Africa

C. Behrensdorff*, B. Elberling and L. Krogh
Institute of Geography, University of Copenhagen,Øster Voldgade 10, DK-1350 Copenhagen K, Denmark
**Corresponding author*

Abstract

Acidic tropical soils often have high Al^{3+} concentrations in soil solutions, which can be toxic to plants and, thereby, reduce agricultural yields. This study focuses on the impact of deforestation and cultivation on the short and long-term Al geochemistry of acidic soils in Ghana, West Africa. Site-specific investigations were made at two sites covered with forest and one site cultivated with maize (*Zea mays* L.). The capacity of soil to resist acidification was investigated in a leaching experiment and the corresponding release of aluminium quantified. Field results revealed a significant aacidification and Al mobility in the root zone of the cultivated site as compared to the forest sites. The leaching experiment showed that further acidification would significantly enhance Al-release and, consequently, the presence of Al^{3+} in soil solution. It is concluded that deforestation and cultivation in the study area has resulted in increasing levels of Al3+ and a lowering of the soils capacity to resists further acidification. This may be critical in relation to land-use management and long-term agricultural productions.

Introduction

Aluminium (Al) toxicity is one of the most important single factors limiting crop production in acidic tropical soils (Marschner, 1995; Noble, Gillman & Ruaysoongnern, 2000; Ritchie, 1995). Acidification accele-rates with deforestation and intensi-fied cultivation, which often reflect an increasing human population. Decreasing soil *p*H increases the instability of soil Al-minerals and thereby increases the concentration of total Al (Al_T) in solution. Speciation of Al depends on *p*H and a decrease in *p*H increases the relative amount of the plant toxic Al^{3+} ion relative to other Al-species (Marschner, 1995; Matzner *et al.*, 1998; Ritchie, 1989). At low *p*H (4–6) the concentration of Al^{3+} in soil solution is influenced by several processes; 1) decreas-ing amount of variable charge exchange sites, 2) exchange of Al^{3+} with H^+, 3) hydrolysis of Al with resulting increase in the concentration of Al^{3+}, 4) dissolution of gibbsite and release of Al^{3+}. Under advanced weathering as found in humid tropical soils, it is generally assumed that the activity of Al^{3+} is regulated by equilibrium with a gibbsite-like ($Al(OH)_3$) phase (Larssen *et al.*, 1999; Lindsay & Walthall, 1996; Ritchie, 1989). Precipitation or dissolution depends on the ion concentration and the solubility product (K_{sp}). For gibbsite the solubility product can be written as:

$$Al(OH)_3(s) \equiv Al^{3+} + 3OH^- , \qquad K_{gibbsite} = [Al^{3+}][OH^-]^3 = 10^{-32.64} \quad (1)$$

Equation (1) indicates that the activity of Al^{3+} in water depends on *p*H of the soil solution. At *p*H values below 5.5 the concentration of Al^{3+} increases due to the increasing solubility of gibbsite (Appelo & Postma, 1993). Al has a tendency to form hydroxy complexes, which can increase the solubility of gibbsite significantly. The total amount of dissolved Al in solution consists of both Al^{3+} ions and hydroxy complexes and can be described as a mass balance equation:

$$Al_{dissolved} = Al^{3+} + Al(OH)^{2+} + Al(OH)_2^{+} + Al(OH)_4^{-} \ (+ Al_{complexes}) \qquad (2)$$

Additionally, Al is able to form polynuclear Al species and complexes with fluoride, sulphate and organic matter (Ritchie, 1989; Vance, Stevenson & Sikora, 1996) but the majority of studies indicate that Al^{3+} appears to provide the most reliable estimate of toxic Al (Bertsch & Parker, 1996; Jardine & Zelazny, 1996; Parker, Zelazny & Kinraide, 1990). The physiological effects of Al toxicity at elevated Al^{3+} concentrations include restricted growth of roots and stems leading to increased susceptibility to drought and decreased use of subsoil nutrients (Foy *et al.*, 1993) and, in turn, reduced yields of agricultural crops (Collet *et al.*, 2002; Marschner, 1995; Parker *et al.*, 1990; Moustakas *et al.*, 1992). A large difference exists between various plants in their tolerance to acidity and Al toxicity but generally tropical crop species are adapted to elevated Al concentrations in contrast to maize, soybeans and wheat (Abruña-Rodriguez *et al.*, 1982; Marschner, 1995).

In many tropical soils (e.g. Oxisols) weathering processes over time have resulted in a high proportion of Al and Fe oxides. Weathering and leaching have removed base cations resulting in formation of acidic soils characterized by low buffer capacity and potential Al release. In natural forest ecosystems the magnitude of element cycling processes are greater than under forest vegetation. Removal of vegetation litter as part of cultivation reduces cycling of base cations from above ground vegeta-tion, which accelerate acidification and increase the potential Al toxicity due to a low soil *p*H (Fisher & Binkley, 2000; Greenland, Wild & Adams, 1992; Ross, 1993). Marked differences in soil *p*H have been found on cultivated and non-cultivated adjacent tropical soil, indicating the acidifying effect of cultivation and increasing risk of Al toxicity (Dolling, Porter & Robson, 1990; Noble *et al.*, 2000; Okusami, Rust & Alao, 1997; Xu *et al.,* 2002).

Most of the available knowledge of Al release from acid soils is based on laboratory experiments with homogenized soil samples, imitated soil solutions (Adams, Ali & Lewis, 1990; Moustakas *et al.*, 1992; Wheeler, Edmeades & Christie, 1992) and with soil from temperate areas (Berggren & Mulder, 1995; Zysset *et al.*, 1999; Lofts *et al.,* 2001). However, the impact of Al toxicity on plants and crop yield is more severe in humid tropical soils and under low-input agriculture. There is lack of knowledge regarding actual Al^{3+} concentrations in soil solutions of tropical forest- and cultivated soils, and the factors controlling present and long-term concentration of Al^{3+} in different soil-systems. Due to extensive changes of future land-use systems, site-specific observations are important to predict long-term changes in soil *p*H and plant available Al concentrations to minimize the potential risk of reduced yields.

The aims of this site-specific study are 1) to quantify the present concentration of total Al species in the soil solution, 2) to evaluate the environmental controls of the concentration of Al, and 3) to predict the amount of Al released to soil solutions due to a lower *p*H as a consequence of deforestation and continuous cultivation in acidic soil. Quantification of extractable Al gives an ecotoxic scenario of the capacity of soil to resist *p*H changes and estimates the amount of Al that is able to dissociate and mobilize from complexes to soil solution as a consequence of cultivation. Investiga-tion of both soil solids and *in situ* extracted soil solutions are further used to discuss the distribution of Al between solids and solution and, hence, elucidate the long-term impact of cultivation.

Materials and methods

Fieldwork was carried out in June 2000 at The Agricultural Research Station Kade, University of Ghana, West Africa (6° 09’ N; 0° 55’ W). The climate is humid tropical dominated by two rainy seasons. Average annual rainfall is 1179 mm with 80% falling from March to mid July and from September to November (Owusu-Bennoah *et al.*, 2000). Temperatures vary little during the year, reaching a maximum of 28-29 °C in February/March and a minimum of 25–26 °C in July/August (Christiansen & Awadzi, 2000). Soils in the study area consist mainly of argilliaceous sediments metamorphosed into phyllite. The soils are red, brown to yellow brown and progressively leached, and the dominant clay mineral is kaolinite (Owusu-Bennoah *et al.*, 2000). Soils consist of 40–60% particles finer than 2 µm with increasing contents with depth, indicating eluviation of clay-sized material forming an argillic B horizon (Owusu-Bennoah *et al.,* 2000). The main part of the Research Station is used for agricultural purposes but a small area is covered with semi-deciduous forest. The present study was conducted in a part of the forest and on agricultural soil used for maize production for 5 years.

Sampling of soil and soil solutions

Soil profiles to a depth of 140–180 cm were excavated at three sites. Two of the study sites were situated in a forest on the upper gentle slopes of a catena (gradient 6%). The soil has probably not been disturbed for c. 50 years. According to the Soil Taxonomy System the soil at these two study sites are classified as a Typic Paleudult and a Kandic Paleudalf (Owusu-Bennoah *et al.*, 2000). According to the In the Ghanaian Soil Classification the soils belong to the Bekwai and Nzima Series, respectively. In the present study these sites are referred to as $Forest_B$ and $Forest_N$. The third study site was situated in an agricultural field cultivated with maize (*Zea mays* L.). Previously, this field has been cultivated with traditional slash and burn but this cultivation method is no longer allowed on Kade Research Station. The soil at this study site has been cultivated mainly with maize for c. 7 years. The soil is classified as a Kandic Paleudalf (according to Soil Taxonomy) and Nzima (according to in the Ghanaian Soil Classification). In the present study, the soil and study site is referred to as $Maize_N$.

Soil profiles were described in terms of soil horizon, structure and colour. For investigation of soil chemical properties, soil samples (300 cm3) were taken for every 10 to 15 cm from the surface to the bottom of the soil profiles without crossing horizon boundaries. Additional samples (347 cm^3, used for conduction of a leaching experi-ment) were taken in the A and B horizons at all three study sites (Fig. 1).

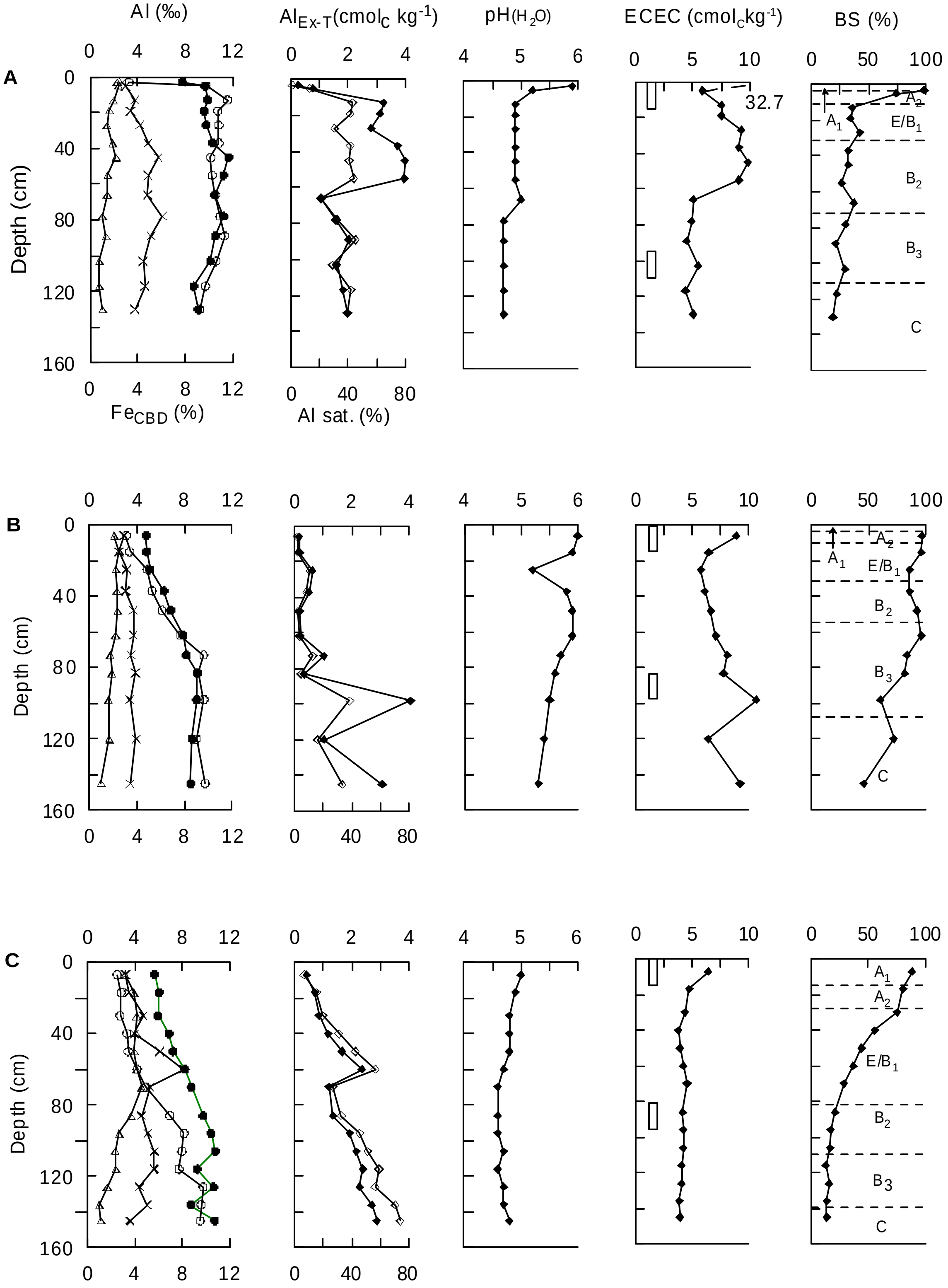

Fig. 1. Soil chemical properties of the three study sites: Forest$_B$ (A), Forest$_N$ (B) and Maize$_N$ (C). Al_{pyro} (open triangles), Al_{Ox} (crosses), Al_{CBD} (filled circles), Fe_{CBD} (open circles). Al_{Ex-T} = total exchangeable Al extracted by 1 M KCl (filled diamonds), $Al_{sat} = Al_{Ex-T}$ ´ 100/ECEC (open diamonds). BS = $\sum$ (Ca, Mg, K, Na) × 100/ECEC. Levels of horizons are shown as horizontal dashed lines. Vertical bars denote sampling of soil used for the leaching experiment.

Soil solutions were extracted by suction probes (PRENART®, diameter 21 mm and length 95 mm) installed horizontally at five depths in each soil profile. A vacuum of 500 mbar was established by a pump and soil solutions were collected 4 times during the next 2 months. The suction probes were coated with a paste-mixture consisting of soil from the representative horizon and distilled water before installation. The system was finally flushed approximately 20 times the dead-volume prior to soil solution was collectioned.

Soil analysis

Soil samples were air-dried and passed through a 2-mm sieve. Soil *p*H was determined in water *p*H(H_2O) at a solution ratio of 1:2.5. Exchangeable cations were extracted using a neutral (*p*H = 7.0) ammonium acetate *p*H 7 method (Sumner & Miller, 1996). The concentrations of Ca^{2+}, Mg^{2+}, K^+ and Na^+ in the extracts were measured using AAS. The contents of exchangeable H^+ and total concentration of exchangeable Al (Al_{Ex-T}) were determined by titration after extraction with 1 *M* KCl (Bertsch & Bloom, 1996). The results obtained by extraction with ammonium acetate and KCl were used for determination of ECEC, base saturation (BS) and Al saturation (Al_{Sat}). Determination of total carbon (C) and fractionation of Al and Fe were made on soil further crushed in a planetary ball mill. C was measured by determination of CO_2 following combustion of soil and NDIR detection using a Dohrman DC-190 (Nelson & Sommers, 1996).

Total "free" Al and Fe oxides as well as hydroxides contents in soil were extracted using Citrate-bicarbonate-dithionite (Al_{CBD}, Fe_{CBD}) method (Loeppert & Inskeep, 1996). The Al content adsorbed to organic compounds (Al_{Pyro}) was extracted using a 0.1 *M* sodium pyrophosphate ($Na_4P_2O_7$) solution overnight (18 h) (Bertsch & Bloom, 1996). Amorphous Al phases (Al_{Ox}) were extracted by acid ammonium oxalate (NH_4Ox-D) for 4 h in the dark (*p*H 3) using the procedure of Loeppert & Inskeep (1996). The concentrations of Al (CBD, Pyrophosphate and Oxalate) and Fe (CBD) in the extracts were determined by AAS using nitrous oxide/acetylene and air/acetylene, respectively.

Leaching experiment

A leaching experiment was conducted in the laboratory and acidification was carried out by a controlled addition of sulphuric acid (0.5 *M* H_2SO_4) into achieve a stepwise acidification process. The experiment was carried out with soil samples taken from the A and B horizons in $Forest_B$, $Forest_N$ and $Maize_N$ (Fig. 1). Soil samples were air-dried and passed through a 2-mm sieve. 10 Ten grams of each soil was placed in a centrifuge tube (85 ml) and 25 ml water added to establish a soil/water solution ratio of 1:2.5. For each soil sample six replicates were made. Initial *p*H-values were measured on all samples after 50 min shaking at 123 rpm and 24 °C. One of the replicates was centrifuged at 5000 rpm in 15 min and the supernatant decanted and collected. 100 µl 0.5 *M* H_2SO_4 was added to each of the remaining replicates to reduce *p*H of the soil solutions.

After the addition of sulphuric acid, the samples were shaken for 18 h at 123 rpm and 24 °C, and the *p*H measured immediately after. A second replicate was centrifuged for 15 min at 5000 rpm and the supernatant collected. 100 µl 0.5 *M* H_2SO_4 was added to each of the remaining four replicates and the samples were shaken for 18 h. Values of *p*H of the four replicates were measured and the third replicate was centrifuged and the supernatant decanted. The experiment was continued during the next few days reducing the number of replicates by one for every day until all replicates had been centrifuged and supernatants collected. The supernatants were stored at 5 °C in the dark until analysed. The extracts' content of Al_T was measured by AAS using nitrous oxide/acetylene.

The leaching experiment was repeated three times for each soil horizon and data were plotted as average values ± standard deviation. In addition, leaching of soil was conducted once with a shaking period of 36 h to test if equilibrium between soil particles and water had occurred. The results showed that there were no significant differences ($P < 0.05$) in the amount of extracted Al after 18 h and 36 h. It was, therefore, assumed that equilibrium between soil solution and soil particles had occurred within 18 h.

Soil water analysis

Soil solution *p*H was measured in the field when water was available. In addition, *p*H was determined in the laboratory after soil solution has reached equilibrium with atmospheric CO_2. Concentrations of total dissolved Ca^{2+}, Mg^{2+}, K^+, Na^+, Fe_T, Mn_T and Al_T of the soil solutions were determined by AAS. Concentrations of Cl^-, NO_3^- and SO_4^{2-} were determined using ion chromatography. Alkalinity was measured with 0.1 *M* HCl. Total carbon and inorganic carbon were determined by nondispersive infrared detector (NDIR) detection of released CO_2 following combustion of the water sample using a Dohrman DC-190. Total organic C was calculated by the difference between total and inorganic C.

Data evaluation

Soil chemical analyses were conducted in triplicate and reported as mean values ± standard deviation. Data was tested with Pearson correlation at 5% or 10% significance levels.

Results

Soil morphology

All three soil profiles had weak granular soil structures at the surface while subsoil structures were subangular blocky. Subsoil colours ranged from 2.5YR 4/8 to 10R 3/4 (Munsell colour chart), indicating a high degree of weathering and the presence of substantial amounts of secondary Fe oxides (Van Wambeke, 1994). Weathered stones of crystalline origin were found in all three profiles.

Soil chemical properties

Soil chemical data for the three soil profiles are presented in Fig. 1 (position of soil horizons are shown as dashed lines). Al_{CBD} correlated positively with Fe_{CBD} for $Forest_N$ ($r^2 = 0.94$) and $Maize_N$ ($r^2 = 0.81$) while a constant distribution of Fe with depth in $Forest_B$ resulted in poor correlation (Table 1). The concentration of Al_{CBD} and Fe_{CBD} increased with depth in $Forest_N$ and $Maize_N$ and, similarly, $Al_{Ex\text{-}T}$ increased with depth in these two profiles but no significant correlation between $Al_{Ex\text{-}T}$ and *p*H can be observed. However, a significant positive correlation was found between $Al_{Ex\text{-}T}$ and *p*H for the surface soil (0-40 cm; Table 1). In all three profiles, *p*H was positively correlated with base saturation (BS).

TABLE 1

Regression coefficients (r^2) between selected soil chemical properties (Pearson correlation)

Soil property	Fe_{CBD}	$Al_{Ex\text{-}T}$	$Al_{Ex\text{-}T}$ 0-40 cm	*BS*	Al_{sat}
$Forest_B$					
Al_{CBD}	0.46^{*}			0.27^{*}	
*p*H(H_2O)		0.18^{*}	0.76^{*}	0.89^{*}	0.65^{*}
BS		0.30^{*}			-0.79^{*}
$Forest_N$					
Al_{CBD}	0.94^{*}			0.41^{*}	
*p*H(H_2O)		0.30^{**}	0.71^{*}	0.53^{*}	0.42^{*}
BS		0.78^{*}			-0.86^{*}
$Maize_N$					
Al_{CBD}	0.81^{*}			0.87^{*}	
*p*H(H_2O)		0.25^{*}	0.63^{*}	0.66^{*}	0.23^{*}
BS		0.73^{*}			-0.71^{*}

Notes:

Levels of significance: $^{*}P < 0.05$; $^{**}P < 0.1$

CBD = Al/Fe extracted by Citrate-bicarbonate-dithionite

$Al_{Ex\text{-}T}$ = Total exchangeable Al extracted by 1 *M* KCl

BS = Base saturation

Al_{sat} = Al saturation

The *p*H-value of the topsoil was 6 in $Forest_B$ and $Forest_N$ while the cultivated soil $Maize_N$ had a surface *p*H of 5.0 (Fig. 1). Values of *p*H decreased with depth and the subsoil was acid ic with a *p*H of 4.9 and 4.6 in $Forest_B$ and $Maize_N$, respectively. Slightly higher *p*H-values of 5.3–5.9 were measured in the subsoil of $Forest_N$. ECEC was 6–10 $cmol_c\ kg^{-1}$ in the topsoil of $Forest_B$ (up to 32.7 $cmol_c\ kg^{-1}$ near the surface) and $Forest_N$ but lower values (4–6 $cmol_c\ kg^{-1}$) were registered in $Maize_N$. In all three soil profiles the high surface content of ions led to a BS level of almost 100%, declining rapidly in the subsoil to 15–35% in two Forest profiles and near 10% in the $Maize_N$. All profiles revealed a significant negative correlation ($P < 0.05$) between BS and Al_{Sat} (Table 1).

Analysis of C, N and P revealed variations between study sites, primarily in the surface contents (data not shown). The C concentration in the surface (0-10 cm) was 1.5–4.1% in $Forest_B$ and 1-1.9% and 1–1.8% in $Forest_N$ and $Maize_N$, respectively. In all three profiles, the concentration of C decreased rapidly to 0.4–0.7% in the subsoil. Total amount of C in the surface (0–10 cm) was 1.7 mg cm^{-3} and 1.0 mg cm^{-3} in $Forest_B$ and $Forest_N$ while 0.85 mg cm^{-3} was measured in $Maize_N$.

Leaching experiment

Fig. 2 shows the accumulated amount of released Al and *p*H as a function of added mmol H^+, revealing a wide variability between horizons and soils. In $Forest_B$ horizon A, *p*H was 4.3 after addition of 0.5 mmol H^+ while a *p*H value of 2.9 was measured in horizon B. A high magnitude in the amount of released Al was observed between horizons in $Forest_B$. 2.6 $mmol_c\ kg^{-1}$ Al was released from horizon A and 13.3 $mmol_c\ kg^{-1}$ from horizon B (Fig. 2A). A higher capacity to resist acidification was observed in soil from Forest_N (Fig. 2B). Total accumulated amount of released Al was low with values of 2.6–2.7 $\text{mmol}_c\ \text{kg}^{-1}$ and both horizons showed a drop of *p*H from 5.4 and 5.8 to 3.8 after addition of 0.5 mmol H^+. A high difference in released Al was also observed between horizons with soil from Maize_N (Fig. 2C). After addition of 0.5 mmol acid, 6.1 $\text{mmol}_c\ \text{kg}^{-1}$ and 13.9 $\text{mmol}_c\ \text{kg}^{-1}$ Al was released from horizon A and B, respectively.

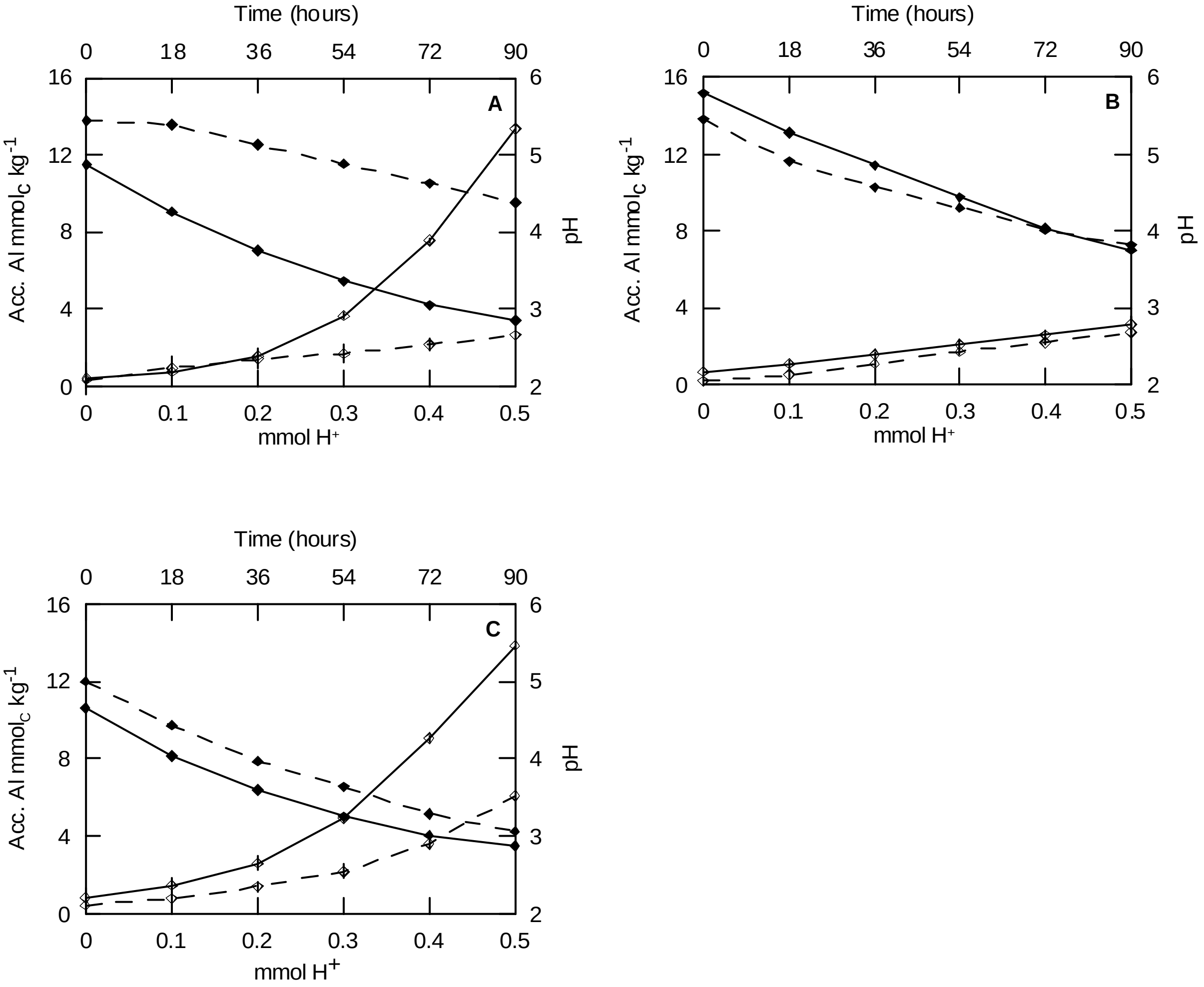

Fig. 2. Accumulated values of extracted Al_T (open diamonds) and corresponding *p*H (filled diamonds) as a function of added mmol H^+. Forest_B (A), Forest_N (B) and Maize_N (C). Dashed lines refer to A horizons and solid lines to B horizons. Standard deviations for extraction of Al denoted as vertical bars (n = 3). If not visible standard deviations are less than the size of measuring point.

Soil solutions

Charge balances and *p*H from field and laboratory measurements of *in situ* extracted soil solutions are shown in Fig. 3. Analysis of soil solutions collected over 2 months revealed variations in ion concentra-tions between succeeding extractions probably due to precipitation events. Data of measured ion concen-trations in Fig. 3 are the results of only one sampling that was representative for the average ion concen-trations for the sampling period (n = 4).

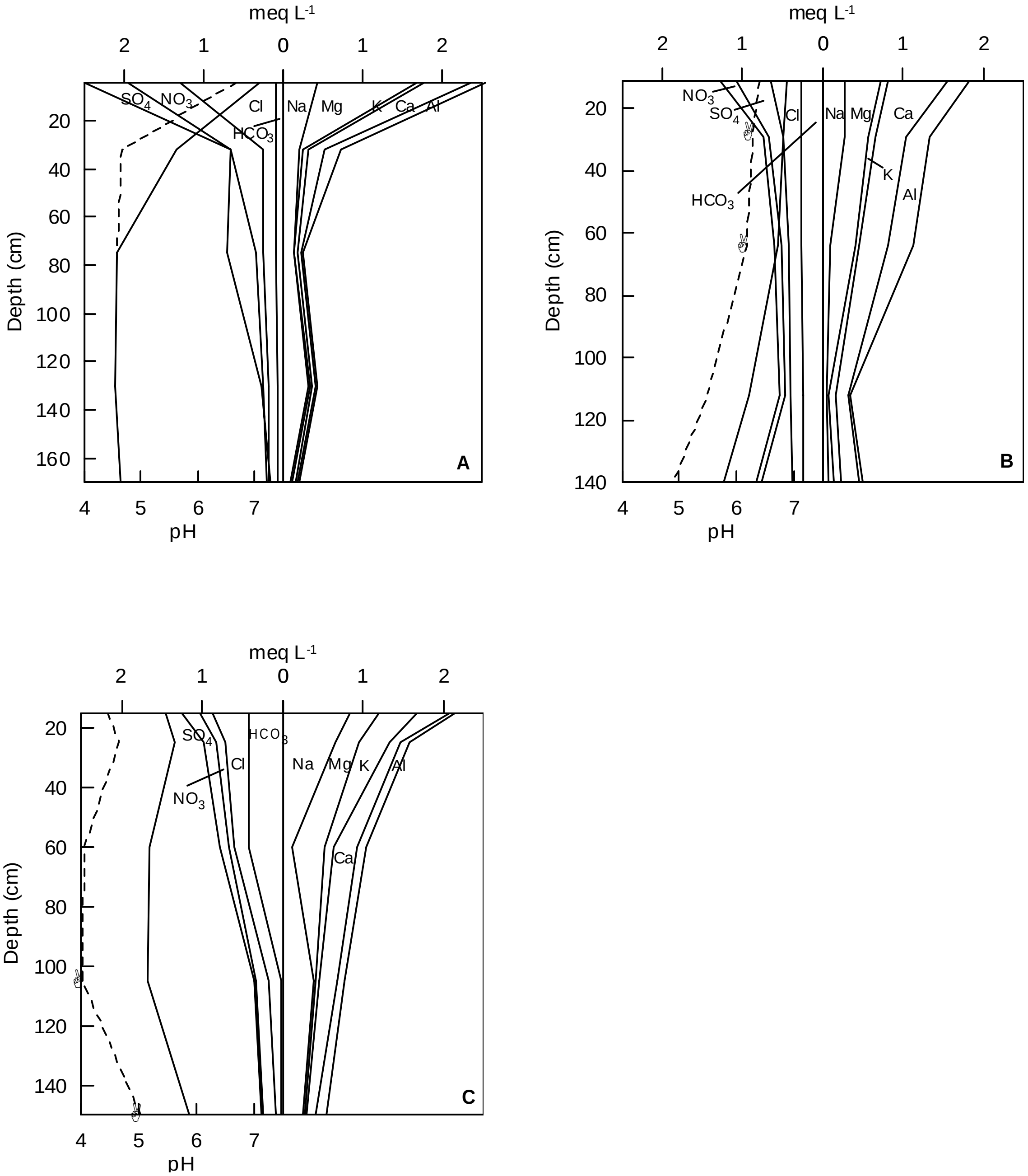

Fig. 3. Charge balance and pH of extracted soil solutions. Solid bold line is $p\mathrm{H}_{\mathrm{lab}}$ and dashed bold line $p\mathrm{H}_{\mathrm{field.}}$ Forest$_{\mathrm{B}}$ (A), Forest$_{\mathrm{N}}$ (B) and Maize$_{\mathrm{N}}$ (C). Filled stars refer to calculated $p\mathrm{H}_{\mathrm{field}}$ values.

When soil solutions are exposed to atmospheric pressure of carbon dioxide, CO_2 degases which tend to increase the pH values (Elberling & Jakobsen, 2000). The $p\mathrm{H}_{\mathrm{lab}}$ -values are, therefore, biased and $p\mathrm{H}_{\mathrm{field}}$ values are shown (Fig. 3). Sometimes the availability of water in the field was limited and $p\mathrm{H}_{\mathrm{field}}$ values have consequently been calculated based on $p\mathrm{H}_{\mathrm{lab}}$ values which are available for all samples. This has been possible as significant correlation existed between ΔpH ($p\mathrm{H}_{\mathrm{lab}} - p\mathrm{H}_{\mathrm{field}}$) and pH measured in the laboratory ($r^2 = 0.95$, $P < 0.005$). Thus, pH values have been calculated based on the correlation between $p\mathrm{H}_{\mathrm{lab}}$ and Δ pH shown as filled stars in Fig. 3.

Highest ion concentrations were measured in the surface with values in the range of 1-2.5 meq l^{-1} (Fig. 3). In all three profiles, concentrations of anions and cations declined to less than 1 meq l^{-1} below 40 cm. The highest ion concentrations were measured in the surface of Forest$_{\mathrm{B}}$ where the $p\mathrm{H}_{\mathrm{field}}$ of the soil water was 6.7, declining to 4.6 below 40 cm. The soil solution of Forest$_{\mathrm{N}}$ had a $p\mathrm{H}_{\mathrm{field}}$ of 6.4 and the value decreased slightly with depth. A low $p\mathrm{H}_{\mathrm{field}}$ of 4–4.5 was observed throughout the Maize$_{\mathrm{N}}$ profile. In all three profiles, Ca, Mg and Na were the dominating cations and the concentration of Al was 0.02-0.24 meq l^{-1}. The soil solutions extracted from the surface soil (0-30 cm) of Forest$_{\mathrm{N}}$ and Maize$_{\mathrm{N}}$ have a dissolved organic carbon (DOC) concentration of 8–16 mg l^{-1} (data not shown). The soil water from the topsoil of Forest$_{\mathrm{B}}$ contained up to 47 mg l^{-1} but concentrations decreased rapidly below 10 cm. In all three profiles, the concentration of DOC decreased to 5 mg l^{-1} below 60 cm.

Discussion

Soil chemical characteristics

The two forest sites (Forest$_B$ and Forest$_N$) are only a few 100 m apart. Despite of that soil chemical data areon the catena, they show different drainage conditions resulting in highly natural soil variableility as shown as expressed as spatial variations in *p*H, nutrient status and Al content (Fig. 1). This variability adds to the complexity of separating natural spatial variations and effects of land use changes. In studies of the same area, Lawson, Armstrong-Mensah & Hall (1970) and Owusu-Bennoah *et al.,* (2000) found a similar variability in the soil system. As Forest$_N$ and the cultivated soil Maize$_N$ are alike in soil type, colour and drainage conditions, the following discussion on effects of a land use will be based primarily on these two soils.

The soil chemical data show that cycling of nutrients resulted in higher values of *p*H, ECEC and BS in the surface soil than in the subsoil. This effect was more pronounced in the forest profiles where nutrients are added continuously. Deforestation and cultivation of the maize field (Maize$_N$) has reduced this effect and is probably the most important factor resulting in a *p*H of 5 in the surface soil of Maize$_N$, which is 1 unit lower than in the surface soil of Forest$_N$. Soil litter is limited on the cultivated site compared to forest sites as parts of crops residues are used for feeding livestock. Limited cycling of nutrients from vegetation has previously been shown to result in a lower near-surface soil *p*H (Fisher & Binkley, 2000; Greenland, Wild & Adams, 1992; Ross, 1993) and *p*H values are consistent with other studies of cultivated and non-cultivated tropical soils indicating the reducing effect of anthropogenic activities on *p*H (Noble, Gillman & Ruaysoognern, 2001; Okusami, Rust & Alao, 1997; Porter, McLay & Dolling, 1995; Xu *et al.*, 2002).

A significant positive correlation was found between *p*H and Al$_{Ex-T}$ in the surface soil (Table 1), indicating anthe increasing solubility of Al with decreasing *p*H. Translocation of Al (and Fe) oxides was the main reason for of a poor correlation between *p*H and Al in the subsoil but show that these soils are progressively leached.

Soil chemical properties show that the soils are highly weathered and poor in nutrients. The general nutrient deficiency of tropical soils is attributable to the intensive weathering under conditions of high temperature and moisture, resulting in a high proportion of kaolinitic clays and Fe and Al hydroxides (Ross, 1993; Van Vambeke, 1994). These variable charged particles with low exchange capacity cause an easy loss of cations with decreasing *p*H. Differences in capacity to resist acidification according to site-specific conditions are shown in the leaching experiment (Fig. 2). The effects of added H$^+$ ions, as an indication of continuous or intensive cultivation, reveals that acidification resulted in an increase in the concentration of Al in solution due to exchange of H$^+$ with Al^{3+} and below *p*H 5.5 by dissolution of gibbsite (Equation 1). The observed increase in extractable Al with decreasing *p*H is in accordance with other studies of acid soils (Johnson & McBride, 1991; Larssen *et al.,* 1999; Lofts *et al*., 2001; Xu *et al.,* 2002).

The soil's capacity to resist acidification and the corresponding release of Al showed a marked variation between A horizons. The A horizon of Maize$_N$ had a remarkably lower *p*H and a higher amount of released Al. The initial *p*H was 5, ECEC was c. 4 cmol$_c$ kg^{-1} (Fig. 1) and the low starting point of *p*H facilitated a rapid Al increase (Fig. 2C). An initial lower *p*H of the surface horizon probably caused by cultivation is the main cause of a higher amount of released Al with increasing acidification compared to forest soil. However, factors other than *p*H affect the concentration of released Al including type and amount of clay minerals, organic material contributing to CEC, amount of adsorbed base cations and Al saturation. The amount of adsorbed Ca^{2+} and Mg^{2+} ions were higher in the A horizon of Forest$_N$ (5.9 and 2.3 cmol$_C$ kg^{-1}) than in Maize$_N$ (4.0 and 1.4 cmol$_C$ kg^{-1}), indicating that cations acted as an important buffer mechanism and prevented lowering of *p*H to some extent as observed in the A horizon of Maize$_N$. In a study of cultivation of Oxisols, Noble, Gillman & Ruaysoongnern (2001) found that soil *p*H, organic C levels and exchangeable cations decreased drama-tically on a disturbed site due to reduced nutrient cycling and continuous stirring of soil compared with adjacent undisturbed forest soil. The reduced concentration of nutrients in the surface soil of Maize$_N$ causing a low *p*H was due to restricted bio-cycling of ions due to cultivation resulting in a lower capacity of the surface soil (A horizon) to resist acidification, increasing the Al in solution.

Leaching of soil from the B horizon of Maize$_N$ resulted in a rapid increase in the release of Al due to a highly acidic soil with low ECEC (below 4 cmol$_C$ kg^{-1}) and low BS of 15%, indicating that the subsoil is progressively leached (Fig. 1). The B horizon had an Al$_{sat}$ of 30-50% and hence the release of Al is higher than from Forest$_N$ where Al$_{sat}$ was 5–38%. The high amount of base cations in Forest$_N$ (base saturation of 60-83%) was responsible for cation ex-change being the most important buffer mechanism even at a *p*H value where gibbsite dissociates. However, the large reserve acidity in these soils in the form of Al^{3+} ions in gibbsite can easily be released by a *p*H decrease as shown by the leaching experiment. Part of the Al^{3+} ions may also originate from kaolinite, which constitutes the main part of the clay fraction (Owusu-Bennoah *et al.*, 2000).

The distinct variation in *p*H and Al release between Forest$_B$ and Forest$_N$ must be attributed to small differences in parent material, nutrient status and drainage conditions of the forest soils. Similar short distance differences in soil chemical properties of Ustalfs in Niger were found by Scott-Wendt, Chase & Hossner (1988) along a transect of 15 m. Soil chemical variations resulted in extreme variability in yield when soils were cultivated and Al toxicity was the main reason limiting plant growth (Scott-Wendt, Chase & Hossner, 1988). Despite the differences in soil chemical properties the leaching experiment showed that the soils responded similarly to acidification at a given *p*H. Fig. 4 shows that the amount of Al released during the leaching experiments, as function of *p*H, is almost the same for all three soils. Al being released is presumably a result of gibbsite dissolution primarily controlled by *p*H. It is beyond the scope of this study to evaluate the proportion of various gibbsite types in these soils and, thus, at which *p*H value the Al-source will be depleted. However, it is likely that most nutrient-poor soils, like Forest$_B$, will be most affected by an acidification.

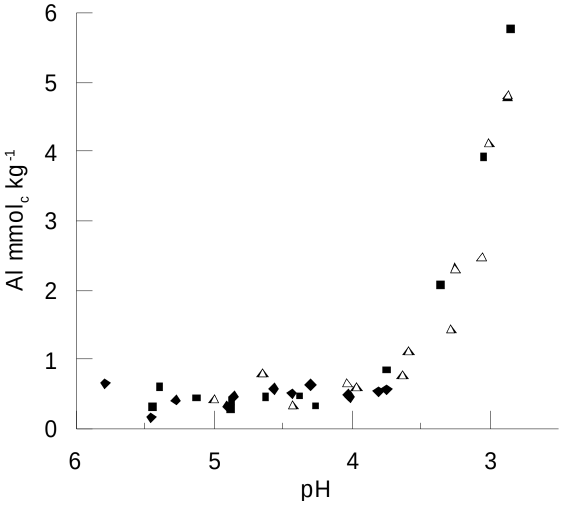

Fig. 4. Release of Al$_T$ as a function of *p*H during the leaching experiment. Forest$_B$ (filled squares), Forest$_N$ (filled diamonds) and Maize$_N$ (open triangles).

Soil solution chemistry and Al-speciation

Results of soil solution analysis showed that total ion concentrations were above 1 meq l^{-1} in solutions extracted from the soil surface and concentrations declined to 0.2–1 meq l^{-1} below 50 cm (Fig. 3). The higher ion concentrations in the surface were due to nutrient cycling (driven by litter turnover) and consistent with the higher surface *p*H of forest profiles. In Maize$_N$ ions concentra-tions were slightly higher in the surface than in the subsoil but *p*H$_{lab}$ was constantly 5–6 throughout the soil, which is an indication of a reduction in ion cycling (Fig. 3C).

The *p*H values measured in the field (*p*H$_{field}$) were generally below 5 and, on average, 1 *p*H unit lower than measured those in the laboratory, which indicate degassing of CO_2 prior to *p*H measurements in the laboratory. Consequently, *p*H$_{lab}$ measurements in the laboratory underestimated the ongoing soil acidification process. This emphasises the importance of using an appropriate *p*H methodology, particularly, when evaluating potential Al problems.

The concentration of total dissolved Al measured in extracted soil solutions from Forest$_N$, is higher than measured in extracted solution from Forest$_B$ and Maize$_N$. However, in order to relate total Al concentrations to Al toxicity, the fraction of Al^{3+} must be simulated since the intensity of Al toxicity is assumed to be proportional to the Al^{3+} concentration (Hue, Craddock & Adams, 1986; Lindsay & Walthall, 1996; Marschner, 1995). Assuming Al$_T$ is equal to the Al species in equation 2 and ignoring Al-organic complexation, the speciation model PHREEQE (Parkhurst, Thorstenson & Plummer, 1980) has been used to predict Al^{3+} concentrations of the extracted soil solutions from Forest$_N$ and Maize$_N$ sites. These simulations (using pH$_{field}$) suggest that Al^{3+} constitutes a negligible percent of the total Al in soil solution extracted from Forest$_N$ site. In contrast, soil solution extracted from the Maize$_N$ site with a *p*H of 5.2 contained 3–7.5 μ*M* Al$_T$ of which 10–30% is present as Al^{3+} . The near-surface low *p*H values at the Maize$_N$ site were the main reason for differences in Al speciation between Forest$_N$ and Maize$_N$. However, it is worth noting that PHREEQE simulations may overestimate the Al^{3+} concentrations as soil solutions extracted had a total dissolved carbon (DOC) concentrations between 8–47 μ*M* and since complexation of Al^{3+} ions with organic ligands may have a detoxifying effect (Adams, Ali & Lewis, 1990; Jones & Kochian, 1996; Ritchie, 1989).

Aluminium toxicity and implication for soil management

The measured concentrations of total dissolved Al of 7.5 µ*M* (*p*H 5.2) in soil solutions extracted from Maize_N are not high enough to decrease yield substantially. However, lower yield and morphological changes of plant roots have been reported in soil solutions with Al concentrations of 1-37 µ*M* (Marschner, 1995; Wheeler, Edmeades & Christie, 1992). Generally, toxicity varies with plant species. Nevertheless, the ability for maize plants to be influenced by Al toxicity is quite possible due to progressive acidification and Al_{sat} of 20–56% within Maize_N (30–60 cm, Fig. 1C) and since yield reduction have been reported when Al_{Sat} is > 30% in the surface soil (Abruña-Rodriguez *et al.*, 1982; Marschner, 1995; Ritchie, 1989).

An equal release of Al in the leaching experiment at a given *p*H reveals that site-specific conditions (other than *p*H) do not influence the processes controlling the release of Al (Fig. 4). Differences in Al release between Forest_N and Maize_N may be due to a lower buffering capacity by the maize soil than the forest soil and variability with respect to soil mineralogy. But nevertheless, the same combination of processes is likely to control the release of Al in all three soils and the strong dependence of *p*H suggests that equilibrium with gibbsite was responsible for the Al release. Results of the leaching experiment showed no signs of depletion of gibbsite at *p*H 3. Results of the leaching experiment should not be compared directly to concentrations of Al observed in the field as conditions in the laboratory are not similar to field conditions. Soil moisture and vacuum during extraction are factors which could be important for deviations in measured Al concentrations based on field collected water and laboratory extractions.

To minimize soil acidification and potential Al release in near-surface layers (root zone) of cultivated soils lime can be added. However, lime is expensive and may not be an economical feasible solution for farmers. Application of litter or other forms of organic matter can serve the purpose since topsoil organic matter is enriched in ions that will be released during the recycling process and, thereby, diminish further soil acidification. Several cropping techniques that minimize acidification are well known. Examples are agro-forestry, rotational cropping or ground cover planting in combination with perennial pastures (Cregan, Hirth & Conyers, 1989). Cultivation of native species that are tolerant to Al toxicity and soil acidity is also another intervention (Abruña-Rodriguez *et al.*, 1982; Marschner, 1995).

Conclusion

Investigations on soil chemical data and soil solutions show that the short-term effect of maize cultivation may result in acidification of surface soil compared to two adjacent forest soils. Field observations of the total amount of dissolved Al in *in situ* extracted soil solutions reveal that concentrations are not high enough to decrease yield substantially. But enhanced soil acidification of the cultivated soil, compared to the forest site, suggests that ongoing acidification is increasing not only the concentration of total Al in solution but also the fraction of Al^{3+} in soil solution. A laboratory leaching experiment reveals that the two forest soils have a better capability to resist acidification, but also that a significant amount of Al can be released to the soil solution from all three soil types as soil *p*H decreases to values below 4. In combination, results suggest that Al may be released similarly from all three soil types due to a progressive acidification, but that the release is likely to be accelerated due to cultivation. And furthermore, that long-term effects of deforestation and cultivation of these soils may be increasing levels of Al^{3+} and soil *p*H, and soil solution *p*H measured in the field seem to be the most simple and important indicator for potential Al problems.

. Acknowledgement

The study was funded by the Danish Natural Science Research Council Steno grant (Reg. No. 1235; B. Elberling) and the ENRECA project “Laboratory for Ecological Studies with Special Emphasis on Nutrient and Water cycling in Ghanaian Ecosystems”. The authors wish to thank the Principal Responsible Party of the ENRECA project, Professor H. Breuning-Madsen, Institute of Geography, University of Copenhagen. They also thank the staff at the Department of Geography and Resource Management, University of Ghana, Legon, especially the director of ECOLAB at the Soil Science Department, Prof. S. K. A. Danso and Mr T. W. Awadzi for assistance during field work. They are grateful to the staff at Kade Agricultural Research Station for their cooperation and for the permission to work on the soils at Kade Research Station.

References

Abruña-Rodriguez F., Vicente-Chandler J., Rivera E. and **Rodriguez J.** (1982). Effect of soil acidity factors on yields and foliar composition of tropical root crops. *Soil Sci. Soc. Am. J.* **46:** 1004–1007.

Adams W. A., Ali A. Y. and **Lewis P. J.** (1990). Release of cationic aluminium from acidic soils into drainage water and relationships with land use. *J. Soil Sci.* **41**: 255–268.

Appelo C. A. J. and **Postma D.** (1993). *Geochemistry, groundwater and pollution*. Rotterdam, Holland: A. A. Balkena.

Berggren D. and **Mulder J.** (1995). The role of organic matter in controlling aluminium solubility in acidic mineral soil horizons. *Geochim. cosmochim. Acta* **59**: 4167–4180.

Bertsch P. M. and **Bloom P. R.** (1996). Aluminium. In *Methods of soil analysis, Part 3 – Chemical methods*. (D.L. Sparks, ed.), pp. 517–550. Madison, USA: Soil Science Society of America Book Series.

Bertsch P. M. and **Parker D. R.** (1996). Aqueous polynuclear aluminium species. In *The environmental chemistry of aluminium.* (G. Sposito, ed.), pp. 117–168. USA: Lewis Publishers, Boca Raton.

Christiansen E. and **Awadzi T. W.** (2000). Water balance in a moist semi-deciduous forest of Ghana. *W. Afr. J. appl. Ecol.* **1**: 11–21.

Collet L., de Leon, C., Kollmeier M., Schmohl N. and **Horst W. J.** (2002). Assessment of aluminium sensitivity of maize cultivars using roots of intact plants and excised root tips. *J. Pl. Nutr. Soil Sci.* **165**: 357–365.

Cregan P. D., Hirth J. R. and **Conyers M. K.** (1989). Amelioration of soil acidity by liming and other amendments. In *Soil acidity and plant growth*. (A.D. Robson, ed.), pp. 205–264. Sydney, Australia: Academic Press.

Dolling P. J., Porter W. M. and **Robson A. D.** (1990). Soil pH and aluminium and their spatial variation in Western Australian acidic soils. *Aust. J. exp. Agric.* **30**: 637–643.

Elberling B. and **Jakobsen B. H.** (2000). Soil solution pH measurements using in-line chambers with tension lysimeters. *Can. J. Soil Sci.* **80**: 283–288.

Fisher R. F. and **Binkley D.** (2000). *Ecology and management of forest soils,* 3rd edn. New York, USA: John Wiley and Sons.

Foy C. D., Duncan R. R., Waskom R. M. and **Miller D. R.** (1993). Tolerance of sorghum genotypes to an acid, aluminum toxic Tatum subsoil. *J. Pl. Nutr.* **16**: 97–127.

Greenland D. J., Wild A. and **Adams D.** (1992). Organic matter dynamics in soils of the tropics – From myth to complex reality. In *Myth and science of soils of the tropics.* (R. Lal and P. A. Sanchez, ed.), pp. 17–33. American Society of Agronomy Division A-6, World Association of Soil and Water Conservation.

Hue N. V., Craddock G. R. and **Adams F.** (1986). Effect of organic acids on aluminium toxicity in subsoils. *Soil Sci. Soc. Am. J.* **50**: 28–34.

Jardine P. M. and **Zelazny L. W.** (1996). Surface reactions of aqueous aluminium species. In *The environmental chemistry of aluminium.* (G. Sposito, ed.), pp. 221–270. Boca Raton, USA: Lewis Publishers.

Johnson M. G. and **McBride M. B.** (1991). Solubility of aluminium and silicon in acidified spodosol: Evidence for soluble aluminosilicate. In *Plant-soil interactions at low* p*H: proceedings of the 2nd. International Symposium on Plant-Soil Interactions at Low* p*H.* (R. J. Wright, V. C. Baligar and R. P. Murrmann, ed.), pp. 15–24. Dordrecht, Holland: Kluwer Academic Publishers.

Jones D. L. and Kochian L. V. (1996). Aluminium-organic acid interactions in acid soils. *Pl. Soil* **182**: 221–228.

Kuo S. (1996). Phosphorus. In *Methods of soil analysis. Part 3 – Chemical methods.*(D. L. Sparks, ed.), pp. 869–919. Madison, USA: Soil Science Society of America Book Series.

Lawson G. W., Armstrong-Mensah K. O. and **Hall J. B.** (1970). A catenea in tropical moist semi-deciduous forest near Kade, Ghana. *J. Ecol.* **58:** 371–398.

Larssen T., Vogt R.D., Seip H.M., Furoberg G., Liao B., Ziao J. and **Xiong J.** (1999). Mechanisms for aluminium release in Chinese acid forest soils. *Geoderma* **9:** 65–86.

Lindsay W. L. and **Walthall P. M.** (1996). The solubility of aluminium in soils. In *The environmental chemistry of aluminium*. (G. Sposito, ed.), pp. 333–361. USA: Lewis Publishers, Boca Raton.

Lofts S., Woof C., Tipping E., Clarke N. and Mulder J. (2001). Modelling *p*H buffering and aluminium solubility in European forest soils. *Eur. J. Soil Sci.* **52**: 189–204.

Loeppert R. H. and **Inskeep W. P.** (1996). Iron. In *Methods of soil analysis. Part 3 – Chemical methods.* (D. L. Sparks, ed.), pp. 639–664. Madison, USA: Soil Science Society of America Book Series.

Marschner H. (1995). Adaption of plants to adverse chemical soil conditions. In *Mineral nutrition of higher plants*, 2 edn, pp. 596–657. London. England: Academic Press.

Matzner E., Pijpers M., Holland W. and **Manderscheid B.** (1998). *Soil Sci. Soc. Am. J.* **62**: 445–454.

Moustakas M., Yupsanis T., Symeonidis L. and **Karataglis S.** (1992). Aluminum toxicity effects on durum wheat cultivars. *J. Pl. Nutr.* **15**: 627–638.

Nelson D. W. and Sommers L. E. (1996). Total carbon, organic carbon, and organic matter. In *Methods of soil analysis. Part 3 – Chemical methods.* (D.L. Sparks, ed.), pp. 961–1010. Madison, USA: Soil Science Society of America Book Series.

Noble A. D., Gillman G. P. and **Ruaysoongnern S.** (2000). A cation exchange index for assessing degradation of acid soil by further acidification under permanent agriculture in the tropics. *Eur. J. Soil Sci.* **51**: 233–243.

Noble A. D., Gillman G. P., Nath S. and **Srivastava R. J.** (2001). Changes in the surface charge characteristics of degraded soils in the wet tropics through the addition of beneficiated bentonite. *Aust. J. Soil Res.* **39**: 991–1001.

Okusami T. A., Rust R. H. and **Alao A. O.** (1997). Red soils of different origins from southwest Nigeria: Characteristics, classification, and management considerations. *Can. J. Soil Sci.* **77**: 295–307.

Owusu-Bennoah E., Awadzi T. W., Boateng E., Krogh L., Breuning-Madsen H. and **Borggaard O.K**. (2000). Soil properties of a toposequence in the moist semi-deciduous forest zone of Ghana. *W. Afr. J. appl. Ecol.* **1**: 1–10.

Parker D. R., Zelazny L. W. and Kinraide T. B. (1990). Chemical speciation and plant toxicity of aqueous aluminium. In *Environmental chemistry and toxicology of aluminium*. (T. E. Lewis, ed.), pp. 117–145. Chelsea. England: Lewis Publishers.

Parkhurst D. L., Thorstenson D. C. and **Plummer L.N.** (1980). P*HREEQE – A computer program for geochemical calculations*. U.S. Geol. Surv. Water Resour. Inv. pp. 80–96.

Porter W. M., McLay C. D. A. and **Dolling P. J.** (1995). Rates and sources of acidification in agricultural systems of southern Australia. In *Plant-soil interactions at low* p*H: Principles and management: proceedings of the 3rd International Symposium on Plant-Soil Interactions at Low* p*H*. (G. E. Date, G. E. Grundon and M. E. Probert, ed.), pp. 75–83. Dordrecht, Holland: Kluwer Academic Publishers,.

Ritchie G. S. P. (1989). The chemical behaviour of aluminium, hydrogen and manganese in acid soils. In *Soil acidity and plant growth.* (A. D. Robson, ed.), pp. 1–60. Sydney, Australia: Academic Press.

Ritchie G. P. S. (1995). Soluble aluminium in acidic soils. Principles and practicalities. In *Plant-soil interactions at low pH: Principles and manage-ment: proceedings of the 3rd. International Symposium on Plant-Soil Interactions at Low* p*H*. (G. E. Date, G. E. Grundon and M. E. Probert, ed.), p. 23–33. Dordrecht, Holland: Kluwer Academic Publishers.

Ross S. M. (1993). Organic matter in tropical soils: current conditions, concerns and prospects for conservation. *Pro. phys. Geogr.* **17**: 265–305.

Scott-Wendt J., Chase R. G. and **Hossner L. R.** (1988). Soil chemical variability in sandy Ustalfs in semiarid Niger, W. Afr.. *Soil Sci.* **145**: 414–419.

Sumner M. E. and **Miller W. P.** (1996). Cation exchange capacity and exchange coefficients. In *Methods of soil analysis. Part 3 – Chemical methods.* (D. L. Sparks, ed.), pp. 1201–1229. Madison, USA: Soil Science Society of America Book Series.

Vance G. F., Stevenson F. J. and **Sikora F. J.** (1996). Environmental chemistry of aluminium-organic complexes. In *The environmental chemistry of aluminium.* (G. Sposito, ed.), pp. 169–220. Boca Raton, USA: Lewis Publishers.

Van Wambeke A. (1994). *Soils of the tropics.* New York, USA: McGraw-Hill.

Wheeler D. M., Edmeades D. C. and **Christie R. A.** (1992). Effect of aluminum on relative yield and plant chemical concentrations of cereals grown in solution culture at low ionic strength. *J. Pl. Nutr.* **15:** 403–418.

Xu R. K., Coventry D. R., Farhoodi A. and **Schultz J. E.** (2002). Soil acidification as influenced by crop rotations, stubble management, and application of nitrogenous fertilizer, Tarlee, South Australia. *Aust. J. Soil Res.* **40**: 483–496.

Zysset M., Blaser P., Luster J. and **Gehring A. U.** (1999). Aluminium solubility control in different horizons of a podzol. *Soil Sci. Soc. Am. J.* **63**: 1106–1115.