

Effects of soil acidification and subsequent leaching on levels of extractable nutrients in a soil

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Summary The effects of soil acidification (pH values from 6.5 to 3.8), and subsequent leaching, on levels of extractable nutrients in a soil were studied in a laboratory experiment. Below pH 5.5, acidification resulted in large increases in the amounts of exchangeable Al in the soil. Simultaneously, exchangeable cations were displayed from exchange sites and Ca, Mg, K and Na in soil solution increased markedly. With increasing soil acidification, increasing amounts of cations were leached; the magnitude of leaching loss was in the same order as the cations were present in the soil: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$.

Soil acidification appeared to inhibit nitrification since in the unleached soils, levels of NO_3^- clearly declined below pH 5.5 and at the same time levels of NH_4^+ increased greatly. Significant amounts of NH_4^+ and larger amounts of NO_3^- , were removed from the soil during leaching. Concentrations of NaHCO_3 -extractable phosphate remained unchanged between pH 4.3 and 6.0 but were raised at higher and lower pH values. No leaching losses of phosphate were detected. For the unleached soils, levels of EDTA-extractable Mn and Zn increased as the soil was acidified whilst levels of extractable Fe were first decreased and then increased greatly and those for Cu were decreased slightly between pH 6.5 and 6.0 and then unaffected by further acidification. Significant leaching losses of Mn and Zn were observed at pH values below 5.5 but losses of Fe were very small and those of Cu were not detectable.

Introduction

Slow natural acidification, as a process in soil development, is well known and documented²². Acidification of agricultural soils can also be a problem where continual applications of NH_4 -fertilizers have been made¹⁶. Renewed interest has been shown in the process and consequences of rapid soil acidification in recent years because of increasing concern regarding the effects of acid precipitation on the plant-soil system^{3,23}. Furthermore, with the increasing commercial cultivation of calcifuge (acid-loving) plants such as blueberries, cranberries, azalias, heaths and camellias, the rapid artificial acidification of soils is becoming increasingly prevalent. The major acidifying agents used are elemental S, aluminium and iron sulphates and ammonium fertilizers. Even more rapid acidification can be achieved with the direct use of sulphuric acid,

particularly when applied through irrigation water (*e.g.* through trickle systems). Rapid acidification results in the build-up of soluble salts in soil solution and subsequent leaching of these salts is required to maintain a fertile soil environment.

The consequences of natural soil acidification are normally determined from natural sequences with soils of different ages. However, rapid changes in soil properties as a result of artificial acidification have received little attention and there is surprisingly little work reporting changes in levels of available nutrients as soils are acidified. This study reports the effects of soil acidification, and subsequent leaching, on concentrations of cations in soil solution, levels of exchangeable cations and aluminium, and amounts of extractable mineral N, phosphate and micronutrient cations in a soil.

Materials and methods

The soil used in this study was the A horizon of Templeton silt loam¹⁷ (Eutric Cambisol; FAO) and was taken from a site which had not been used agriculturally and never received fertilizer applications. Some relevant properties of the soil were summarized previously¹².

The soil was air-dried and, after sieving, the less than 4 mm fraction was placed in plastic pots (1 kg air-dry soil per pot). Soils were moistened with increasing concentrations of dilute sulphuric acid to give a range of soil pH (CaCl₂) values between 6.0 and 3.5. One portion of soil was treated with Ca(OH)₂ to give a pH of 6.5 (CaCl₂). Six replicates of each pH value were prepared. Soils were thoroughly mixed and then incubated at room temperature at a moisture content of 70% of field capacity for 12 weeks. Three replicates of each pH treatment were then taken for analysis. The remainder of the samples was leached with two pore volumes of deionised water over a 24 h period in order to reduce soluble salts which had accumulated following acidification. Leachates were collected for analysis and the soils were then maintained at 70% field capacity for another four weeks after which samples were taken for analysis.

In the leachate, concentrations of Ca, Mg, K, Fe, Mn, Zn and Cu were determined by atomic absorption and Na and Al by atomic emission spectrophotometry. Leachate samples were analyzed for chloride by the modified mercuric thiocyanide method²⁰, ammonium by the phenol hypochlorite reaction²⁴, nitrate by the copperized cadmium reduction method⁹ sulphate by the BaCl₂-Tween 80 method¹⁸ and phosphate by the molybdenum blue method¹⁴.

Soil pH was measured with a glass electrode in a 1:2.5 soil:distilled water slurry or a 1:2.5 soil:0.01 M CaCl₂ slurry. Exchangeable cations plus those in soil solution were extracted from moist unleached and leached soils with 1 M ammonium acetate (1:50 soil:solution ratio for 1 h) and Ca, Mg, K and Na were analysed as outlined above. Cations in soil solution were extracted from the moist soils under suction with a Buchner funnel after overnight equilibration with distilled water (1:2 soil:water ratio) and cations in extracts were analysed as outlined above. "Exchangeable" cations in soils were calculated by subtracting concentrations of cations in soil solution from those extracted with ammonium acetate. Exchangeable Al was extracted from soils with 1 M KCl (1:25 soil:extractant ratio for 1 h) and Al in extracts was analysed as outlined above. Effective CEC was calculated as the sum of exchangeable cations plus exchangeable Al; concentrations of exchangeable Al (and those in leachates) were calculated in terms of equivalents of Al³⁺.

Mineral-N was extracted from soils with 2 M KCl and extracts were analysed for ammonium and nitrate as outlined above. Available phosphate was extracted from soils with 0.5 M NaHCO₃ (1:100 soil:solution ratio for 16 h)⁶ and phosphate in the extract was determined by the molybdenum blue method. Micronutrient cations (Fe, Mn, Zn and Cu) were extracted from soils with 0.04 M EDTA (disodium salt adjusted to pH 6.0) using a 1:2.5 soil:solution ratio²⁶ and micronutrients in the extracts were determined as outlined above.

Results

Soil pH values in CaCl₂ were similar for the unleached and leached soils and these values are used throughout the paper. The pH values in water corresponding to 3.7 and 6.5 in CaCl₂ were: unleached 3.7, leached 3.9 and unleached 6.9, leached 7.2 respectively.

Levels of exchangeable Ca²⁺, Mg²⁺, K⁺, Na⁺ and to a lesser extent Al were less in leached than unleached soils (Fig. 1). Exchangeable Ca and Mg decreased greatly as the soil was acidified; the decrease was larger for the leached than unleached soil. There was a concomitant increase in exchangeable Al³⁺ as the soil was acidified. Levels of ex-

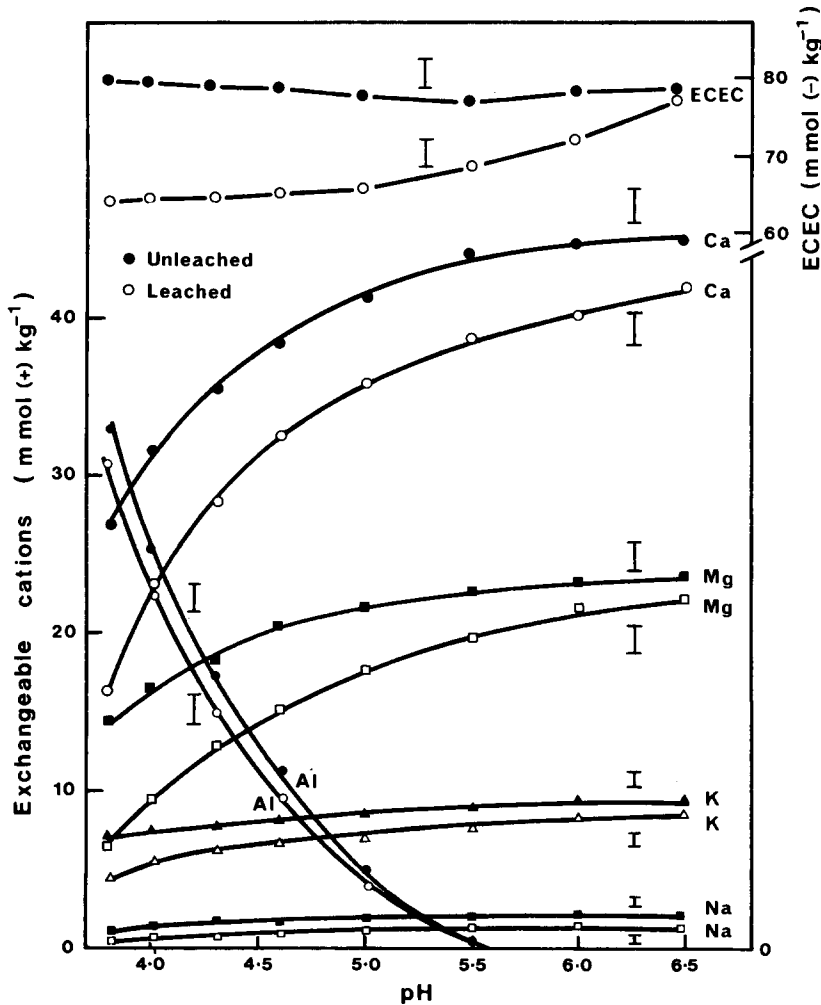


Fig. 1. Effects of soil acidification on levels of exchangeable Ca, Mg, K, Na and Al and effective cation exchange capacity (ECEC) in unleached (●) and leached (○) soils. Average 95% confidence intervals shown.

changeable K^+ and Na^+ decreased at a lesser rate than those of Ca and Mg as the pH was lowered. As the soil was acidified there was a decrease in effective CEC in the leached soil (Fig. 1) but no such effect was observed in the unleached soil.

In the unleached soil, levels of Ca and Mg in soil solution increased exponentially as the pH was lowered from 6.5 to 3.8 (Fig. 2) whilst levels

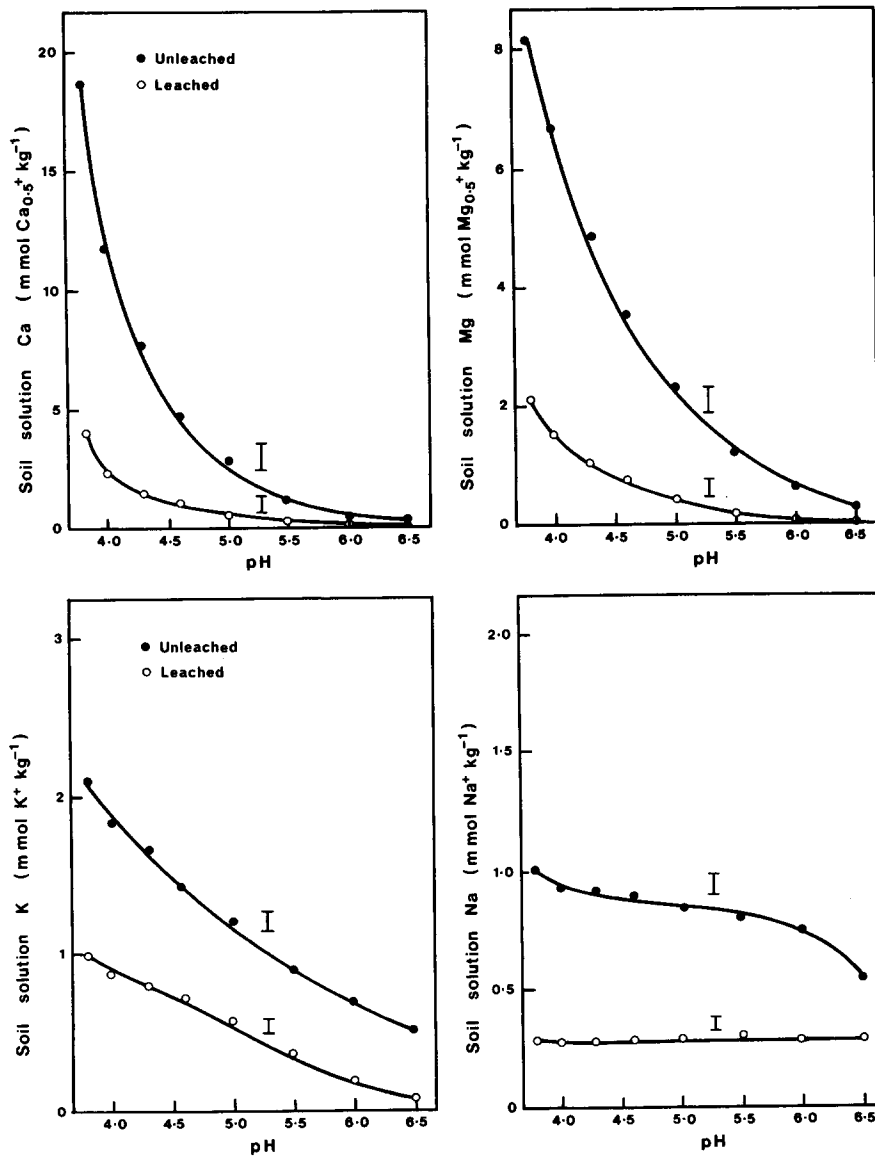


Fig. 2. Effect of soil acidification on levels of Ca, Mg, K and Na in soil solution in unleached (●) and leached soils (○) soils. Average 95% confidence intervals shown.

of K^+ in soil solution increased at a more-or-less linear fashion and those for Na tended to increase. Chemical analysis showed that immediately after leaching, levels of cations in soil solution were all very low ($< 2 \text{ m mol (+) kg}^{-1}$) (Data not shown). After leaching and equilibration for a further period of four weeks, soil acidification resulted in an increase in concentrations of soluble Ca^{2+} , Mg^{2+} and K^+ but the increase was considerably less in magnitude than that in the unleached soils (Fig. 2). Levels of Al in soil solution were very low ($< 0.11 \text{ m mol Al}_{(0.33)} \text{ kg}^{-1}$) even from samples of pH below 4.0. The approximate ionic strength in soil solution in leached and unleached soils was 0.003 M and 0.014 M at pH 6.5 and 0.048 M and 0.201 M at pH 3.8 respectively.

In the unleached soil, levels of NO_3^- -N declined greatly below pH 5.0 and levels of NH_4^+ -N increased greatly (Fig. 3). In the leached soil levels of NH_4^+ -N were less than those for the unleached soils and concentrations of NO_3^- -N were all relatively low although they declined with decreasing pH (Fig. 3). Concentrations of $NaHCO_3$ -extractable phosphate remained unchanged between pH 6.0 and 4.3 but were increased at higher and lower pH values (Fig. 3). The amounts of $NaHCO_3$ -extractable phosphate in the soil were low since critical levels for pastures are between 22 and $48 \mu\text{g P g}^{-1}$ ¹³.

As observed in a previous study¹², soil acidification resulted in increases in levels of EDTA-extractable Fe, Mn and Zn but had little effect on levels of extractable Cu (Fig. 3). However, below pH 5.5 levels of EDTA-extractable Mn and Zn were markedly lower in leached than unleached soils but there were no significant differences for EDTA-extractable Fe and Cu.

The amounts of cations and anions leached from the soils at soil pH values of 6.5, 6.0, 5.5, 4.6 and 3.8 are shown in Table 1. With increasing soil acidification increasing amounts of Ca^{2+} , Mg^{2+} and K^+ were leached along with the applied SO_4^{2-} -S. The magnitude of cation losses were $Ca^{2+} > Mg^{2+} > K^+ > Na^+$. At low soil pH, significant leaching losses of NH_4^+ occurred. Considerable quantities of NO_3^- were leached at high soil pH. In the high pH treatments (pH 6.0 and 6.5), NO_3^- was the major anion leached. With increasing soil acidification increasing amounts of Fe, Mn and Zn were leached. Concentrations of Cu in leachates were not detectable ($< 0.09 \mu\text{g g}^{-1}$).

Discussion

The large increases in levels of Ca^{2+} and Mg^{2+} , and to a lesser extent K and Na, in soil solution as the soil was acidified were the result of replacement of cations on exchange sites by added H^+ and solubilized Al species^{3,22}. Thus the ratio of bases in soil solution to exchangeable bases

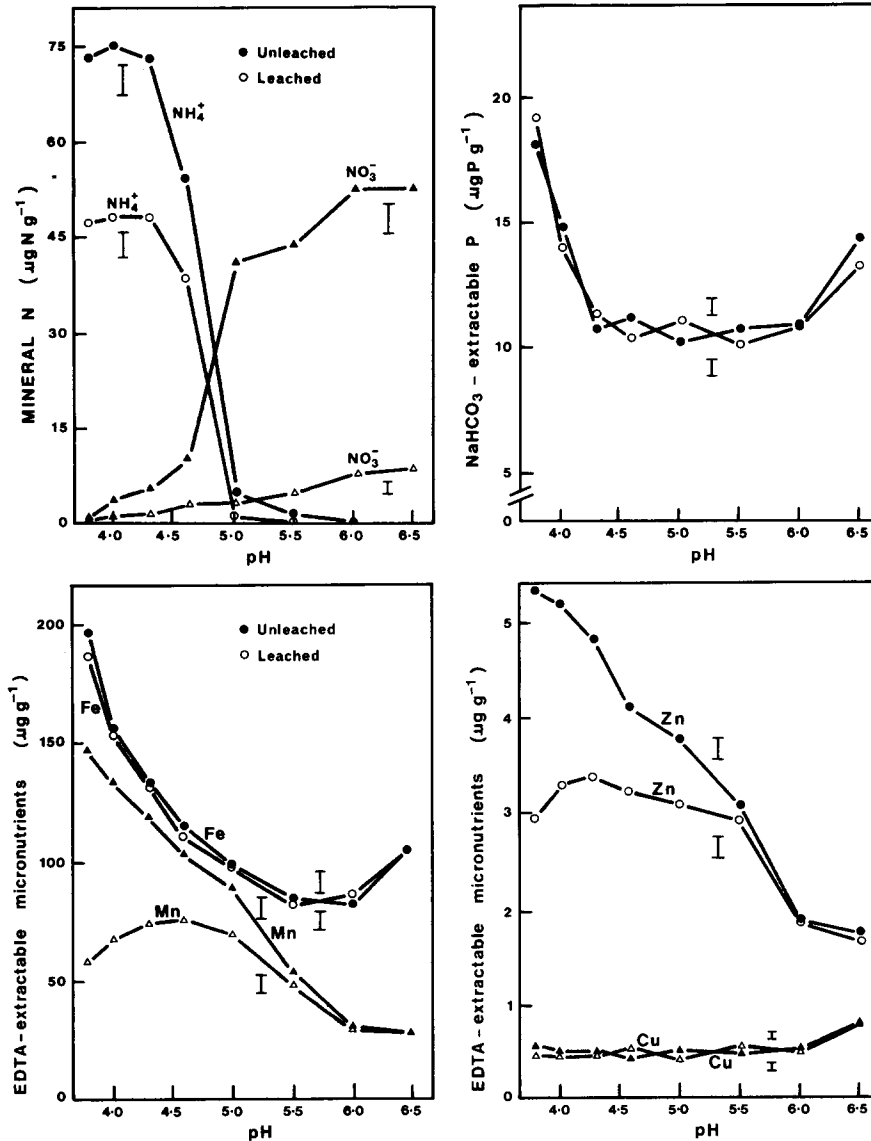


Fig. 3. Effect of soils acidification on levels of potassium chloride-extractable NH_4^+ - and NO_3^- -N, sodium bicarbonate-extractable P and EDTA-extractable Fe, Mn, Zn and Cu in unleached (●) and leached (○) soils. Average 95% confidence intervals shown.

increased as levels of exchangeable Al increased. As the soil was acidified, increasing amounts of Ca^{2+} , Mg^{2+} , K^+ and Na^+ were leached as counterions for the added SO_4^{2-} -S. However, for the soils that were not acidified (pH 6.0 and 6.5), NO_3^- was the dominant anion leached. Indeed, under normal conditions, significant leaching of cations does not

Table 1. Effect of soil acidification on the amounts of nutrients leached from the soils

Nutrient	Soil pH				
	3.8	4.6	5.5	6.0	6.5
<i>Cations* m mol (+) kg⁻¹</i>					
Ca ²⁺	24.9	9.8	6.1	3.5	3.6
Mg ²⁺	10.8	7.9	3.7	1.6	1.8
K ⁺	3.9	2.4	1.6	1.1	1.1
Na ⁺	1.4	1.3	1.3	1.1	1.0
Al ³⁺	2.7	1.8	—	—	—
Mn ²⁺	3.3	1.5	—	—	—
NH ₄ ⁺	1.6	1.2	—	—	—
∑ Cat	48.6	25.9	12.7	7.3	7.5
<i>Anions m mol (-) kg⁻¹</i>					
SO ₄ ²⁻	44.8	24.4	7.0	1.3	1.3
NO ₃ ⁻	—	—	3.2	3.8	3.8
Cl ⁻	1.8	1.7	1.9	1.8	1.9
∑ An	46.6	26.1	12.1	6.9	7.0
<i>Micronutrients μg g⁻¹</i>					
Fe	1.0	0.3	0.2	0.2	0.2
Mn	96	25	0.15	0.11	0.10
Zn	2.7	0.88	0.05	0.04	0.05

*Quantities of exchangeable cations initially present in the soil were Ca, 40; Mg, 24; K, 10 and Na 2 m mol (+) kg⁻¹

occur unless NO₃⁻ accumulates and leaches through the soil²¹. The magnitude of leaching loss of individual cations was, as expected, in the same order as they were present in the soil: Ca²⁺ > Mg²⁺ > K⁺ > Na⁺. Significantly larger amounts of Ca²⁺, Mg²⁺, K⁺ and Na⁺ were leached than were present in soil solution before leaching. Apparently, as cations in soil solution were leached from the soil, more exchangeable cations moved into solution and were also removed during leaching. At low pH values (less than 5) significant losses of Al, Mn and NH₄⁺ also occurred as Al and Mn became solubilized and nitrification was inhibited.

Levels of Al in soil solution were very low even at low pH and leaching losses of Al were very small especially in comparison with the amounts of exchangeable Al present at low pH. This reflects the strong affinity that Al species generally have for the cation exchange surfaces of soils and the ability of the Al to strongly complex with organic matter.

Permanently changed clay minerals predominated in the soil used in this study⁵ and organic colloids are likely to have been the dominant variably charged surfaces contributing to the small decrease in effective CEC in the leached soil as it was acidified⁵. In the unleached soil, effective CEC was unaffected by pH and this was probably the result of the

increasing ionic strength in soil solution caused by acidification counteracting the effect of decreasing pH. The net result was that the charge on the variably charged soil surfaces remained relatively unchanged.

The large decrease in NO_3^- -N which occurred concomitantly with NH_4^+ -N accumulation, as the unleached soil was acidified, was presumably the result of inhibition of autotrophic nitrification which is characteristically impeded at low pH^{7,8,19}. Nonetheless, such an effect may only be short-term in nature since in the long-term acid-tolerant nitrifiers may develop and/or slow heterotrophic nitrification may prevail^{7,19}. The higher concentrations of NH_4^+ -N present at low pH (3.8 to 4.7) compared to those of NO_3^- -N at high pH (5.5–6.5) suggest that greater net mineralization occurred at low pH. Decreased immobilization of N at low pH or even losses of NO_3^- at higher pH values through denitrification are possible explanations for such a phenomenon. Certainly, the distribution of species within the diverse microbial population involved in decomposition of soil organic nitrogen will be altered by acidification since the population characteristically shifts from bacteria to actinomycetes to fungi as the pH declines although acid tolerance of individual species varies widely¹. Results of this study are in some respects similar to those of Strayer *et al.*¹⁹ since they observed that acidification of soils of pH above 5.5 either stimulated or did not affect net mineralization but strongly inhibited nitrification of added NH_4^+ .

As often occurs over the normal pH range of soils (*i.e.* 4.3–6.0), pH had little effect on levels of extractable phosphate¹⁰. Increases in phosphate extractability at high and low pH values have also been observed by some other workers^{2,25}. The increase in extractable phosphate at very low pH (4.0 and 3.7) was probably caused by dissolution of amorphous Al and Fe adsorption surfaces (as indicated by the rapid increase in exchangeable Al and extractable Fe) causing the release of previously adsorbed phosphate. Although precipitation of Al phosphate can occur at low pH values (thus decreasing phosphate availability) such an effect was probably not important in this soil since levels of extractable phosphate were initially low. The higher levels of extractable phosphate at pH 6.5, compared to those between pH 4.3 and 6.0, were probably due to desorption of adsorbed phosphate which characteristically occurs at high pH⁴.

Significant leaching losses of Mn and Zn occurred, particularly at low pH, and these losses were reflected in differences in levels of EDTA-extractable Mn and Zn in the leached and unleached soils. Indeed, at low pH, Mn and Zn were relatively mobile in the soil whilst Fe and Cu were not. It seems probable that the ability of Fe and Cu (like Al) to complex strongly with soil organic matter^{11,15} tended to greatly reduce leaching losses of these elements at low pH relative to those of Mn and Zn.

It is evident that the overall result of acidification and subsequent leaching was a soil low in exchangeable bases, high in exchangeable Al and, at least in the short-term, with a predominance of NH_4^+ - rather than NO_3^- -N. Whilst calcifuge plants have adapted to grow well under such conditions, most plant species will find the conditions detrimental to their growth.

Conclusions

This study provides an example of the changes in soil properties that can occur when a soil is rapidly acidified and subsequently leached. The increases in concentrations of cations in soil solution, large increases in levels of exchangeable Al and decreases in levels of exchangeable Ca^{2+} , Mg^{2+} , K^+ and Na^+ as the soil was acidified were all reasonably predictable. Nonetheless, the large decrease in NO_3^- concentrations and the correspondingly even larger increase in concentrations of NH_4^+ as the soil was acidified were surprisingly marked whilst the increases in extractable phosphate at both high and low pH values were unexpected. The significant leaching losses of Mn and Zn at low pH were also surprising whilst in contrast, losses of Fe and Cu were very small or undetectable presumably because of their ability to complex strongly with organic matter.

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