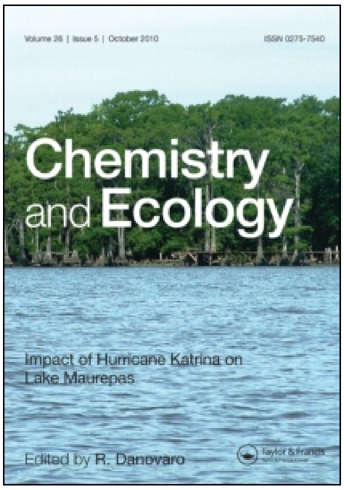

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A COMPARISON OF THE SHORT-TERM DYNAMICS OF SOIL "DAMAGE" DUE TO ENHANCED NITROGEN DEPOSITION AS AMMONIUM SULPHATE OR NITRIC ACID

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An experiment has been conducted to contrast the effects of enhanced oxidised and reduced nitrogen deposition upon key chemical parameters in a *Calluna* moorland podzol. A 40 cm deep podzol profile, derived from granite, was reconstructed in one hundred 4.2 cm diameter cores. For 20 weeks, the cores were subjected twice weekly to simulated rainfall containing either twice ambient nitrogen deposition in Aberdeen, or further enhanced nitrogen (further 2- and 6-fold increases) as nitric acid or ammonium sulphate. To quantify the dynamics of soil change in each horizon, randomly selected cores were destructively analysed every two weeks and the soils analysed. Increased nitrogen inputs, regardless of form, substantially and immediately reduced surface soil pH_{water} *via* the mobile anion or salt effect. For the higher nitrogen treatments, the pH reduction was seen throughout the profile. Longer term soil acidification was also seen in the $pH_{calcium\ chloride}$ results over the 20 weeks. At a given nitrogen deposition rate, the effects of ammonium sulphate and nitric acid on soil $pH_{calcium\ chloride}$ were similar. The ammonium sulphate treatments were especially effective at reducing base saturation throughout much of the profile, the direct base cation leaching being associated with substantial ammonium accumulation. The results suggest that the direct base cation leaching caused by ammonium deposition needs to be considered when assessing atmospheric pollution "damage" to heathland soils.

Keywords: Calluna moorland; podzol profile; nitrate; ammonium; enhanced N deposition; soil acidification

INTRODUCTION

Nitrogen is one of the most important macronutrients in terrestrial ecosystems. Low availability of nitrogen may limit tree growth. Excess

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*Corresponding author. e-mail: M.S.CRESSER@abdn.ac.uk inputs may stimulate growth and thereby lead to deficiencies of other nutrients, ultimately resulting in ecosystem malfunction, *e.g.*, decreased frost hardiness, disruption of mycorrhizal development and functions, and reduced root growth (Nihlgård, 1985). Although in pristine regions biological fixation of atmospheric nitrogen is the primary source of available nitrogen (Barsdate and Alexander, 1975), in large areas of Europe and North America which are under natural or semi-natural land use, pollutant deposition is a major input. Globally, pollutant emissions are estimated to exceed the total natural emissions and, in many areas, inorganic nitrogen input is greater than the ecosystem demand (Moldan *et al.*, 1995). In Scotland, current total anthropogenic deposition ranges from 10 to 30 kg a^{-1} yr^{-1}, and has been increasing over recent years (INDITE, 1994).

The concept of saturation was introduced by Aber *et al.* (1989) to describe the situation in which inorganic supply exceeds the nutritional demands of plants and microbes. In N-limited ecosystems, *e.g.*, forests in less polluted regions of Scandinavia and North America, the nitrogen cycle is very efficient, and as a result, little or no nitrate is lost to the water below the rooting zone. In areas where nitrogen deposition exceeds about 10–15 kg ha^{-1}, however, forest catchments show increased nitrogen leaching (Grennfelt and Hultberg, 1986; Hauhs *et al.*, 1989; Dise and Wright, 1995). Increasing concentration in surface waters is also commonly used as a quantitative manifestation of "N saturation" (Ågren, 1983; Andersen, 1986; Miller and Miller, 1988; Aber *et al.*, 1989). This has led naturally to the use of the concept of soil mass balance for setting soil nitrogen critical loads for forest soils in Europe.

Nitrogen deposition effects upon forest and agricultural ecosystems have been receiving much attention in recent years (Ashmore *et al.*, 1985; Edwards *et al.*, 1992; Sommer and Hutchings, 1995). In contrast, the widespread decline of heathlands throughout many areas of northern Europe has received considerably less research effort (Pitcairn *et al.*, 1995). Ecosystems such as heathlands and moorlands are generally perceived to be N-limited ecosystems, and thus act as efficient nitrogen sinks. However, in these unmanaged soils much of the input comes from the atmosphere and this can lead to serious effects in areas where levels of nitrogen deposited are elevated. For moorland ecosystems, however, soil-based methods for quantifying critical loads have not been established. Instead, empirical loads, based upon experimental studies and field observations are employed (Umweltbundesamt, 1996).

The importance of nitrogen as a potentially acidifying agent and its direct and indirect adverse effects upon soil and water ecosystems are, however, taken into account when calculations of exceedance of critical loads of acidity are performed. Therefore the relationships between acid deposition and soil "damage" have been a major issue for decades. The various transformation processes are generally well understood and documented, though some uncertainties still remain, especially in the size and consequences of changes in organic pools and associated organic matter pools (van Breemen *et al.*, 1983; Posch *et al.*, 1995). Recently, however, the authors have found from a regional survey of pH_{water} values of soil horizons in podzol profiles evolved from rocks with very low weathering rates that the increase in mobile anion concentrations attributable to pollutant deposition has a significant role to play in the extent of direct soil acidification (White and Cresser, 1998). In such acidification-sensitive soils, soil pH_{water} is most relevant to biota supported by the soil. It seems likely, however, that on a mol_c for mol_c basis, inputs of ammonium sulphate could have just as much effect on immediate soil solution acidity and on base cation leaching as nitric acid inputs. This study attempts to gain greater insight into nitrogen species deposition effects in individual soil mineral horizons of a podzol subjected to elevated concentrations in both the oxidised (NO_3^--N) and reduced (NH_4^+-N) forms. It was designed to investigate the dynamics of soil "damage" manifestations, *e.g.*, decreases in pH, base cation saturation, increases in extractable aluminium, and nitrogen accumulation, as a function of depth in the soil profile.

METHODOLOGY

Experimental Aims and Approach

The underlying aim of this experiment was to contrast a soil profile's ability to buffer against increased levels of reduced and oxidised nitrogen deposition and to observe the effects of such deposition upon soil chemical characteristics of ecological relevance. The soil chosen came from Glen Dye, NE Scotland (NGR NO 627 838), and is known to receive moderate amounts of deposition (Tab. I). Extensive details of the experimental design have been presented elsewhere (White, 1996).

The soil profile was recreated in 42 mm internal diameter dark polythene tubes, allowing for 10 soil cores (*i.e.*, duplicates for each of 5 treatments) to be destructively analysed every 2 weeks over 20 weeks. The cores were placed in a timber rack in a controlled temperature room ($25 \pm 2°C$), where they were subjected to elevated nitrogen treatments. Total nitrogen was increased 2-, 4- and 12-fold, the extra nitrogen compared with the T1 treatment being added as either nitric acid or ammonium sulphate for the two sets of medium and highest treatments. Thus the 5 simulated treatments included twice ambient *i.e.*, N×2 (T1), medium nitrate *i.e.*, T1-N×2 (T2), high nitrate *i.e.*, T1-N×6 (T3), medium ammonium *i.e.*, T1-N×2 (T4) and high ammonium *i.e.*, T1-N×6 (T5). Table I summarises the deposition fluxes added to soil cores biweekly. The amount of "rainfall" applied was equivalent to 20 weeks of a typical wet August at the Glen Dye site. The rain was applied twice weekly using two Technicon II peristaltic pumps to deliver 25 ml/event at a rate of 1 ml min^{-1}.

Soil Analysis

Every two weeks, 36 hours after the final rain application, duplicate soil cores for each of the 5 rainfall treatments were destructively sampled. The soil was gently removed from each core and the horizons were separated and individual layers mixed thoroughly. The LFH soil was bisected into the upper, LFH_{top} and the lower LFH_{bottom} prior to analysis to observe the effects of enhanced deposition with depth at greater resolution. All soils were immediately analysed for moisture content, pH (both in water and calcium chloride pastes) and extractable nitrate, ammonium and aluminium, and within a few days for total nitrogen and total carbon, exchangeable base cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) and cation exchange capacity.

Statistical Analysis and Data Presentation

The data were tested for normality of distribution (Anderson–Darling, Cramer–von Mises and Watson critical norm tests) and

TABLE I Moorland deposition data for 1989–92 for the 20 km grid square including Glen Dye moorland (Fowler, pers. comm.) and the biweekly deposition fluxes being added to soil cores. Extra nitrogen was applied in T2–T5 as ammonium sulphate or as nitric acid, to increase total nitrogen by 2- or 6-fold compared with T1

	pH	NO_3^--*N*	NH_4^+-*N*	*Total N*	SO_4^{2-}-*S*	Ca^{2+}	Mg^{2+}	Na^+	Cl^-
deposition data ($kg\ ha^{-1}\ yr^{-1}$)									
	4.28	5.02	7.56	12.58	9.68	2.33	2.77	20.27	20.26
deposition data ($kg\ ha^{-1}$ (2-*weeks*)$^{-1}$)									
T1	4.05	0.435	0.657	1.092	0.962	0.202	0.241	1.756	3.768
T2	3.80	1.528	0.657	2.185	0.962	0.202	0.241	1.756	3.768
T3	3.34	5.897	0.657	6.554	0.962	0.202	0.241	1.756	3.768
T4	4.1	0.435	1.749	2.185	2.107	0.202	0.241	1.756	3.768
T5	4.15	0.435	6.119	6.554	7.108	0.202	0.241	1.756	3.768

consequently, when appropriate, logarithmic transformations were performed to make the variance independent of the mean. The effect of each treatment over the experimental time was tested using regression and the effects of the four highest elevated treatments were compared with those of the T1 treatment and each other using two-way analysis of variance on the total data set. All of the above statistics were performed using Genstat Release 2.2.

For maximum resolution and visual clarity, the time series plots for each soil horizon presented in this paper are shown without individual error bars. Each point is a mean of at least four replications with a percent coefficient of variation $<5\%$ and trends are generally described as significant at the $\geq 95\%$ level (*i.e.*, $P \leq 0.05$), with actual probability values shown in summary tables (Tabs. II and III).

RESULTS AND DISCUSSION

Table I summarises the total deposition flux data and pH for the control and elevated nitrogen treatments on a biweekly basis. Table II summarises the significant changes (*F* probability values) of key soil chemical parameters determined and Table III summarises the significant differences (*F* probability values) observed between the elevated nitrogen treatments and the lowest treatment (T1) for each soil horizon.

Effects of Enhanced Nitrogen Deposition on Soil pH

Figures 1 and 2 show the temporal changes in pH for each horizon, measured in water and in calcium chloride, respectively. As discussed earlier, the LFH horizon was split into upper (LFH_{top}) and the lower ($\text{LFH}_{\text{bottom}}$) halves prior to analysis, to observe the effects of enhanced deposition with depth at higher resolution. For the highest nitrate treatment, T3, soil pH_{water} values were significantly ($\geq 95\%$) lower than the T1 pH_{water} in every horizon down the profile (Tab. III). The highest ammonium treatment, T5, also resulted in significantly lower soil pH_{water} values, but only in the LFH_{top} and the E, B and C horizons. All of the elevated N treatments resulted in significant decreases in pH_{water} over time.

TABLE II Significance of changes in soil chemical parameters with time. *F* probability values represent significance levels and $_{\uparrow}$ and $_{\downarrow}$ represent an increase and decrease respectively. Treatments (T1 – T5) are as specified in the text

		Soil horizon					
	Treatment	LFH_{top}	LFH_{bott}	*A*	*E*	*B*	*C*
pH_{water}	T1	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$
	T2	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$
	T3	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$
	T4	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$
	T5	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$
pH_{CaCl_2}	T1	$0.006_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$
	T2	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$
	T3	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$0.003_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$
	T4	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$
	T5	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$
extractable Al^{3+}	T1	$<0.001_{\uparrow}$	$0.010_{\uparrow}$	$0.006_{\uparrow}$	$0.552_{\uparrow}$	$0.041_{\uparrow}$	$0.004_{\uparrow}$
	T2	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$	$0.008_{\uparrow}$	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$
	T3	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$
	T4	$0.937_{\uparrow}$	$<0.001_{\uparrow}$	$0.004_{\uparrow}$	$0.006_{\uparrow}$	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$
	T5	$0.130_{\uparrow}$	$<0.001_{\uparrow}$	$0.026_{\uparrow}$	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$
percent base saturation	T1	$0.034_{\downarrow}$	$0.007_{\downarrow}$	$0.006_{\downarrow}$	$0.121_{\downarrow}$	$0.009_{\downarrow}$	$0.112_{\downarrow}$
	T2	$0.016_{\downarrow}$	$0.069_{\downarrow}$	$0.011_{\downarrow}$	$0.003_{\downarrow}$	$0.014_{\downarrow}$	$0.504_{\downarrow}$
	T3	$0.162_{\downarrow}$	$0.002_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$<0.001_{\downarrow}$	$0.020_{\downarrow}$
	T4	$0.130_{\downarrow}$	$0.002_{\downarrow}$	$0.007_{\downarrow}$	$<0.001_{\downarrow}$	$0.022_{\downarrow}$	$0.169_{\downarrow}$
	T5	$0.262_{\downarrow}$	$<0.001_{\downarrow}$	$0.008_{\downarrow}$	$<0.001_{\downarrow}$	$0.008_{\downarrow}$	$0.105_{\downarrow}$

TABLE II (Continued)

		Soil horizon					
	Treatment	LFH_{top}	LFH_{bott}	*A*	*E*	*B*	*C*
extractable NH_4^+-N	T1	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$	$0.001_{\uparrow}$	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$	$0.146_{\uparrow}$
	T2	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$	$0.001_{\uparrow}$	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$	$0.007_{\uparrow}$
	T3	$0.002_{\uparrow}$	$<0.001_{\uparrow}$	$0.001_{\uparrow}$	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$	$0.247_{\uparrow}$
	T4	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$	$0.001_{\uparrow}$	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$	$0.002_{\uparrow}$
	T5	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$	$0.001_{\uparrow}$	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$
extractable NO_3^--N	T1	$<0.001_{\uparrow}$	$<0.001_{\uparrow}$	$0.003_{\downarrow}$	$0.020_{\uparrow}$	$0.110_{\downarrow}$	$0.117_{\downarrow}$
	T2	$<0.001_{\uparrow}$	$0.002_{\uparrow}$	$0.003_{\downarrow}$	$0.115_{\downarrow}$	$0.009_{\downarrow}$	$0.010_{\downarrow}$
	T3	$<0.001_{\uparrow}$	$0.030_{\uparrow}$	$0.049_{\downarrow}$	$0.043_{\uparrow}$	$0.205_{\downarrow}$	$0.250_{\downarrow}$
	T4	$<0.001_{\uparrow}$	$0.003_{\uparrow}$	$0.021_{\uparrow}$	$0.005_{\uparrow}$	$0.015_{\uparrow}$	$0.017_{\uparrow}$
	T5	$<0.001_{\uparrow}$	$0.061_{\uparrow}$	$0.071_{\downarrow}$	$0.779_{\uparrow}$	$0.119_{\downarrow}$	$0.139_{\downarrow}$

TABLE III Summary of the significance of differences between the elevated nitrogen treatments, T2–T5, and the T1 treatment for every soil horizon (*F* probability values). Treatments (T1–T5) are as specified in the text

		Soil horizon					
	Treatment	LFH_{top}	LFH_{bott}	*A*	*E*	*B*	*C*
pH_{water}	T2	0.001	0.066	0.101	0.711	0.710	0.620
	T3	<0.001	0.014	0.012	0.001	0.001	0.001
	T4	0.010	0.119	0.357	0.597	0.497	0.447
	T5	<0.001	0.066	0.082	0.020	0.010	0.020
pH_{CaCl_2}	T2	0.118	0.281	0.262	0.354	0.284	0.735
	T3	0.005	0.091	0.041	0.106	0.055	0.228
	T4	0.298	0.240	0.342	0.207	0.256	0.508
	T5	0.009	0.057	0.037	0.094	0.048	0.133
extractable Al^{3+}	T2	0.795	0.496	0.699	0.151	0.841	0.477
	T3	0.904	0.530	0.560	0.656	0.704	0.901
	T4	0.970	0.973	0.201	0.990	0.733	0.652
	T5	0.708	0.003	0.675	0.991	0.944	0.581
percent base saturation	T2	0.682	0.008	0.443	0.001	0.847	0.730
	T3	0.399	0.769	0.732	<0.001	0.772	0.253
	T4	0.791	0.953	0.044	<0.001	0.967	0.052
	T5	0.818	0.069	0.021	<0.001	0.219	0.165
extractable NH_4^+-N	T2	0.757	0.896	0.813	0.782	0.852	0.673
	T3	0.228	0.189	0.175	0.163	0.188	0.379
	T4	0.011	0.015	0.007	0.006	0.011	0.541
	T5	<0.001	<0.001	<0.001	<0.001	<0.001	0.896
extractable NO_3^--N	T2	<0.001	<0.001	0.116	0.033	0.188	0.030
	T3	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
	T4	0.530	0.064	<0.001	0.376	0.041	0.001
	T5	0.855	0.070	0.534	0.018	0.859	0.753

The pH measured in calcium chloride pastes (Fig. 2) decreased significantly over time for all treatments, and significant (≥95%) differences between the T1 and the other elevated treatments were observed for the soils receiving the two high treatments (T3 and T5) in the LFH_{top} and A and, for T5, B horizons only (Tab. III). The greater incidence of significant differences for the soil pH_{water} values compared with the soil $pH_{calcium\ chloride}$ values suggests that a substantial mobile anion or salt effect contributes, at least in part, to the pH trends seen. The fact that the effects of pH_{water} are clearly discernible even in week 2 (Fig. 1) demonstrates clearly the importance of this effect. In marked contrast, the slowly increasing $pH_{calcium\ chloride}$ gap over time between the T1 and T2/T4 or T3/T5 plots (Fig. 2) is a clear indication of the longer term soil acidification effect.

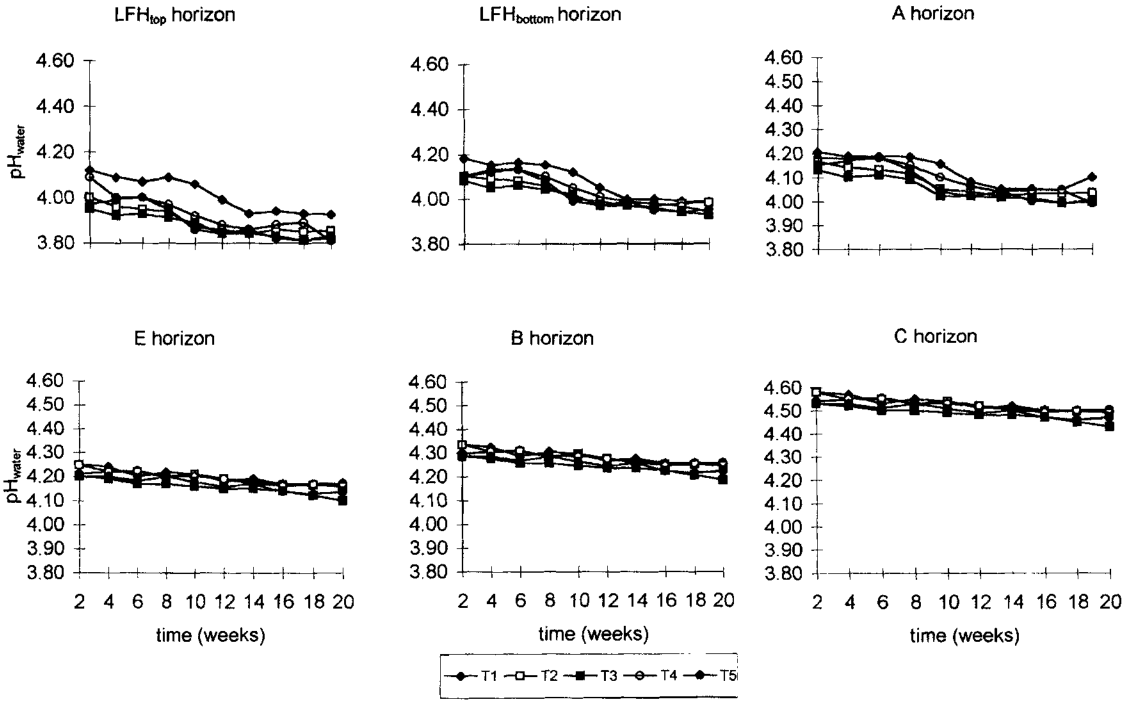

FIGURE 1 Changes in soil pH in water for the LFH$_{top}$, LFH$_{bottom}$, A, E, B and C horizons over time for the twice ambient-N treatment (T1) and the further 2- and 6-fold elevated nitrogen treatments (T2–T5). Points are means of four replicate determinations.

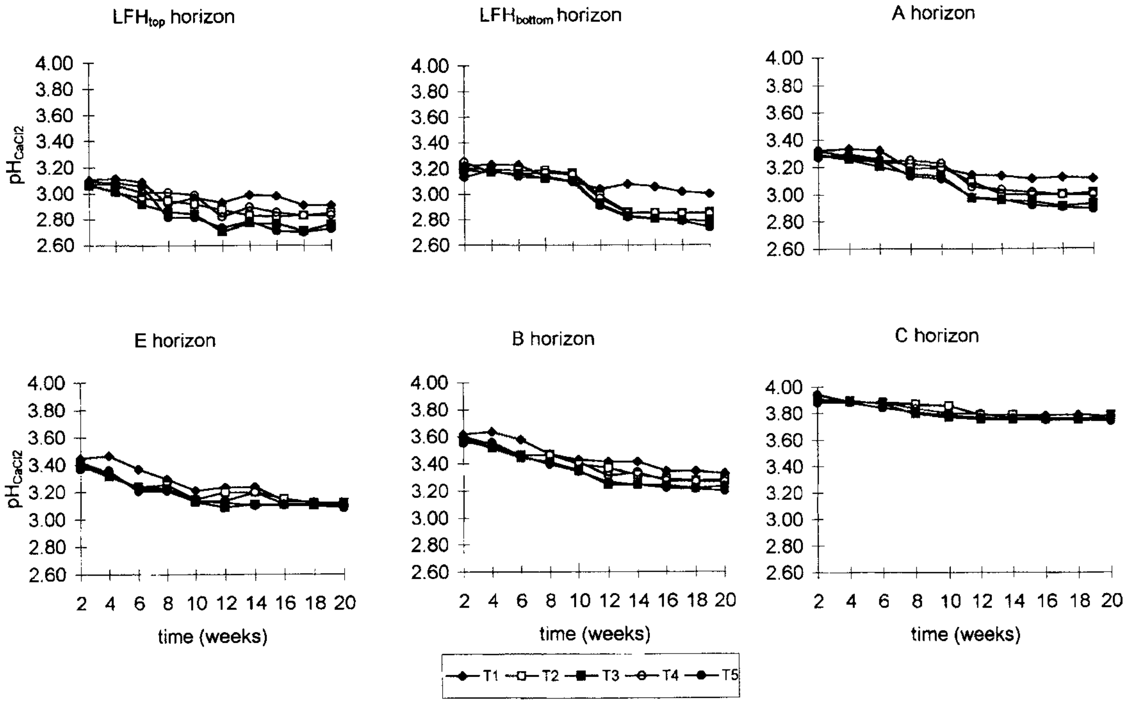

FIGURE 2 Changes in soil pH in calcium chloride for the LFH$_{top}$, LFH$_{bottom}$, A, E, B and C horizons over time for the twice ambient-N treatment (T1) and the further 2- and 6-fold elevated nitrogen treatments (T2–T5). Points are means of four replicate determinations.

Effects of Enhanced Nitrogen Deposition on Soil Aluminium

Base cation leaching is an indicator, at least in the short term, of a soil's ability to neutralise acidity. Aluminium, rather than the base cations, dominated these soils, and subsequently aluminium was the dominant cation leaching. The extractable aluminium was expected to increase with decreases in soil pH. Figure 3 shows the trends in soil extractable aluminium over the experimental period, where a progressive increase in KCl-extractable aluminium was observed in all the horizons as soil pH_{water} fell. The two elevated NOC_3^--N treatments (T2 and T3) resulted in very significant increases in extractable aluminium in all horizons down the profile over time (Tab. II). The two higher NH_4^+-N treatments (T4 and T5) resulted in significant increases in extractable aluminium over time in all but the LTH_{top} horizon, and the T1 treatment in all but the E horizon (Tab. II). Surprisingly, the T2–T5 treatment effects on extractable aluminium generally did not differ significantly from the T1 treatment effect (Tab. III).

Effects of Enhanced Nitrogen Deposition on Soil Base Saturation

Increased base cation leaching and subsequent reduction in the soil base cation status is probably one of the most detrimental effects of acid deposition. Although there was a general decrease in base saturation for all horizons with time, it was not always significant (see Tab. II). Few readily explicable effects on the percent base saturation of the soils attributable to effects of the different treatments were found (Tab. III). This is because base saturation in these soils will be influenced not only by base cation leaching, but also by changes in pH-dependent CEC and by mineralisation of soil organic matter. Moreover, and perhaps more importantly, over a few weeks, enhanced base cation leaching from upper soil horizons will function as a base cation input to lower horizons. Such base cation translocation would, in the short term at least, help buffer against a fall in soil pH at depth for modest nitrogen inputs. Nevertheless, the elevated ammonium treatments, T4 and T5, reduced base saturation very significantly for the A and E horizons (Tab. III).

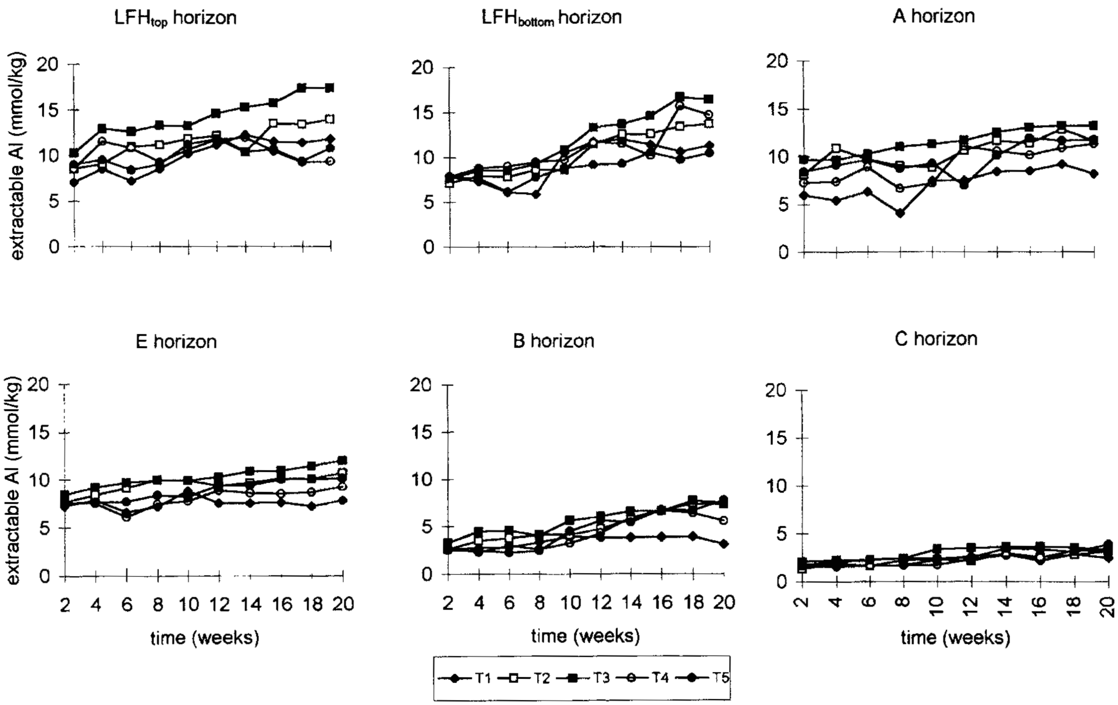

FIGURE 3 Changes in concentrations of soil extractable aluminium (mmol kg^{-1}) for the LFH_{top}, LFH_{bottom}, A, E, B and C horizons over time for the twice ambient-N treatment (T1) and the further 2- and 6-fold elevated nitrogen treatments (T2–T5). Points are means of four replicate determinations.

Evidence of Nitrogen Accumulation

A full understanding of the effects of nitrogen deposition requires a knowledge of how much is accumulating, and in what forms, at various points within the soil profile. Therefore it was deemed important to section the profiles and examine species concentration as a function of depth. Figures 4 and 5 show the observed trends in soil extractable NH_4^+-N and NO_3-N, respectively, in all horizons. For all horizons and all treatments, except the C horizon for T1 and T3, extractable NH_4^+-N increased significantly over time (Tab. II). Compared with the T1 and middle nitrate (T2) treatments, both the elevated ammonium treatments resulted in significantly more NH_4^+-N in all horizons but the C horizon (Tab. III). Similar results, but for forest soils in the field, were reported by Gundersen and Rasmussen (1995), who found enhanced retention of NH_4^+-N in the organic layer and upper mineral soil. They also reported increases in extractable NO_3^--N with depth. The high NO_3^--N treatments did not significantly enhance extractable ammonium concentrations compared to the T1 treatment (Tab. III). Thus it does not appear that nitrate retention by biomass leads relatively rapidly in this soil to enhanced ammonium production by subsequent ammonification.

The soil extractable NO_3^--N results showed less clear trends, apart from obvious and significant increases in NO_3^--N present, compared with the T1 treatment, for the highest NO_3^--N treatment (T3) in all soil horizons (Tab. III). This suggests that not all the nitric acid input can be used by biomass, an observation previously made for ombrotrophic peats in Scotland (Black *et al.*, 1993). An earlier study from this laboratory (Duckworth and Cresser, 1991) suggests that the extent to which nitrate is retained from high rates of nitrate-N deposition is temperature dependent, being greater at higher temperature. Throughout the experiment and in all soil horizons, the highest NO_3^--N treatment (T3) was associated with obviously higher soil extractable NO_3^--N concentrations than all the other treatments. However, the effect is especially large in the surface horizons, and declines with depth. No clear trends for the soil total carbon and nitrogen concentrations were found, and therefore these results are not discussed in this paper.

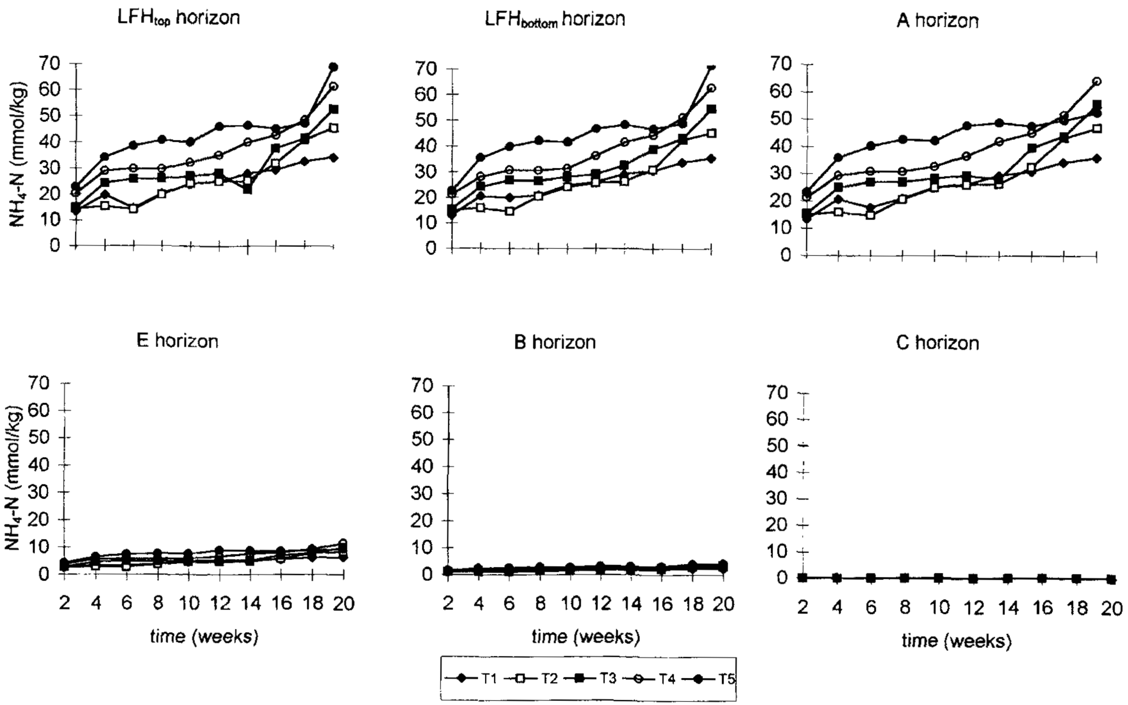

FIGURE 4 Changes in concentrations of soil extractable NH_4^+-N (mmol kg^{-1}) for the LFH_{top}, LFH_{bottom}, A, E, B and C horizons over time for the twice ambient-N treatment (T1) and the further 2- and 6-fold elevated nitrogen treatments (T2–T5). Points are means of four replicate determinations.

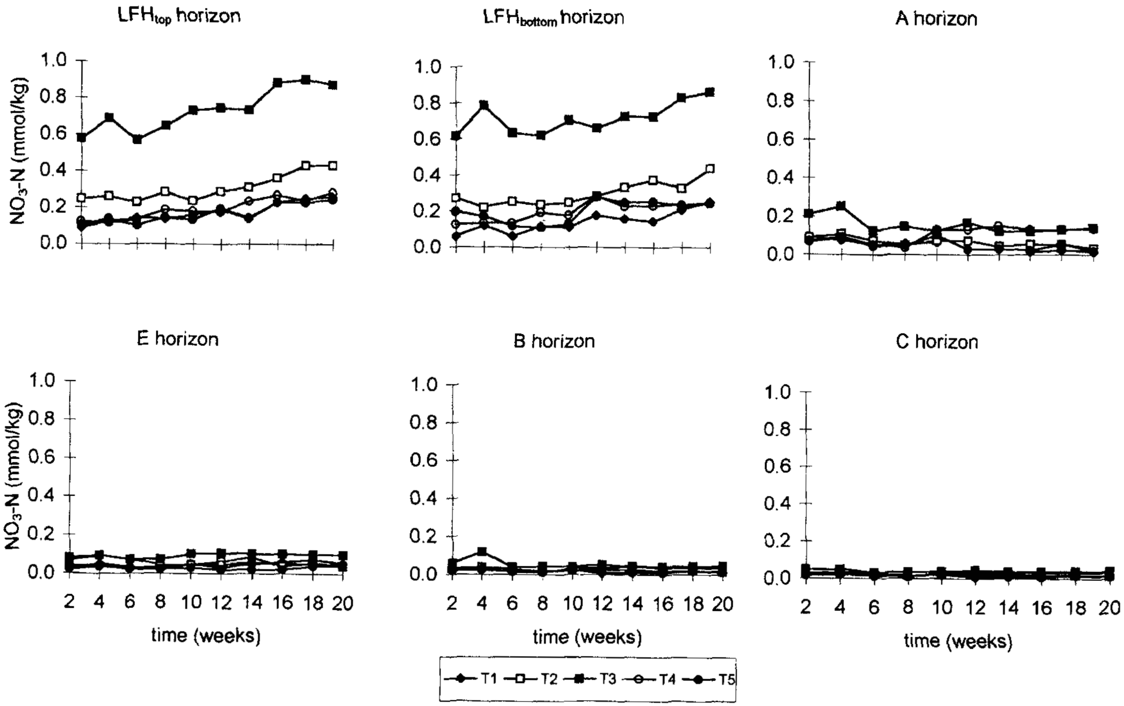

FIGURE 5 Changes in concentrations of soil extractable NO_3^--N (mmol kg^{-1}) for the LFH$_{top}$, LFH$_{bottom}$, A, E, B and C horizons over time for the twice ambient-N treatment (T1) and the further 2- and 6-fold elevated nitrogen treatments (T2–T5). Points are means of four replicate determinations.

CONCLUSIONS

From the acidification point of view, this experiment demonstrates that ammonium inputs may cause direct base cation leaching and may, by displacing hydrogen from cation exchange sites, be almost as directly acidifying as nitric acid inputs in the short term. Thus instantaneous soil pH effects of immediate relevance to soil biota may occur as a consequence of ammonium adsorption. In the context of soil "damage", the mobile anion or salt effect therefore is important, especially when considering soil pH_{water}. The latter reflects the chemical environment under field conditions in acidification-sensitive soils more closely than soil $pH_{calcium\ chloride}$.

In previous publications by the authors, the importance of base cation inputs from the atmosphere and in laterally flowing water to such sensitive soils has been emphasised (White and Cresser, 1995). In the present study, the ameliorative effects of atmospheric base cation inputs were included in the simulation. However, loss of effects of base cations in laterally flowing water could be significant. Both decreasing pH and more direct effects of mobile anions probably contribute to the increasing pool of available aluminium in these soils over time. Overall, the experiment highlights the need for reliable and comprehensive quantitative information on nitrogen deposition effects, and for more work on the interactions between deposition and all aspects of the soil organic matter-pool. This would then allow a better assessment of the relative merits of using nitrogen mass balance, acidification effects of deposition, and empirical values based upon field observations and/or simulation experiments for assigning deposition critical loads.

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