PII: S0269-7491(97)00088-2

SOIL SOLUTION NITROGEN AND CATIONS INFLUENCED BY (NH₄)₂SO₄ DEPOSITION IN A CONIFEROUS FOREST

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Abstract

The effects of chronically enhanced $(NH_4)_2SO_4$ deposition on ion concentrations in soil solution and ionic fluxes were investigated in a Picea abies *plot at Grizedale forest, NW England. Soil cores closed at the base and containing a ceramic suction cup sampler were 'roofed' and watered every 2 weeks with bulk throughfall collected in the field. Treatments consisted of the inclusion of living roots from mature trees in the lysimeters and increasing $(NH_4)_2SO_4$ deposition (NS treatment) to ambient + $75\,kg\,N\,ha^{-1}\,a^{-1}$. Rainfall, throughfall and soil solutions were collected every 2 weeks during 18 months, and analysed for major cations and anions. NO_3^- fluxes significantly increased following NS treatment, and were balanced by increased Al^{3+} losses. Increased SO_4^{2-} concentrations played a minor role in controlling soil solution cation concentrations. The soil exchange complex was dominated by Al and, during the experimental period, cores of all treatments 'switched' from Ca^{2+} to Al^{3+} leaching, leading to mean Ca/Al molar ratios in soil solution of NS treated cores of 0.24. The experiment confirmed that the most sensitive soils to acidification (through deposition or changing environmental conditions) are those with low base saturation, and with a pH in the lower Ca, or Al buffer ranges. © 1997 Elsevier Science Ltd*

Keywords: Aluminium, nitrification, ammonium sulphate, soil solution, acidification.

INTRODUCTION

In recent years the effects of anthropogenic changes in nitrogen (N) deposition to forest ecosystems have resulted in the concepts of excess N deposition, N saturation (see Aber *et al.*, 1989) and critical loads of N (e.g. Hornung and Skeffington, 1993). In contrast to the decreasing inputs of S to forest ecosystems, N deposition does not seem to be declining (Grennfelt and Hultberg, 1986) and this elevated N deposition has been related to

the forest dieback observed in Europe (Nihlgard, 1985). High NH_4^+ deposition may enhance nitrification, leading to soil acidification, NO_3^- and cation leaching, Al^{3+} mobilisation and root damage (e.g. Gundersen and Rasmussen, 1990). Nutrient imbalances due to an increased NH_4^+/cation ratio have also been related to forest decline (Roelofs *et al.*, 1985).

Early research into the acidifying role of air pollutants on forest ecosystems clearly identified the importance of nitrification in causing 'acidification pushes' in forest soils (Ulrich *et al.*, 1980), and the work of Van Miegroet and Cole (1984) identified the clear link between forest N status, nitrification and cation leaching. Nitrification affects soil acidification in two principal ways. Firstly, the process of nitrification results in the net release of H^+ ions. Secondly, leaching of the highly mobile product, NO_3^-, leads to an associated loss of soil cations (reviewed by Van Miegroet and Johnson, 1993). The pH, mineralogy and base exchange capacity of a soil dictate whether NO_3^- leaching is balanced by H^+, Ca^{2+}, Mg^{2+}, Al^{3+} or other cations.

Ulrich (1981) classified the responses of soils to acidification into a series of buffer ranges. Results from the first phase of the European project 'CORE' (described in CORE *et al.*, 1992) have largely confirmed this early classification of Ulrich (1981), through the reciprocal transplantation of forest soils in lysimeters across a European pollution gradient. The project demonstrated the clear boundary between the cation exchange and aluminium buffer ranges and the importance of soil pH in predicting the consequences of acidification for Al^{3+} leaching (Berg *et al.*, 1997). The work also indicated that certain soils may be 'poised' between buffer ranges, and would start to leach Al^{3+} as a consequence of any increases in nitrification rate (Raubuch, 1992). However, as for soil incubations, lysimeters in the early work of 'CORE' did not include living tree roots, effectively simulating nitrification responses in systems which are N-saturated (*sensu* Aber *et al.*, 1989, where 'availability of inorganic N is in excess of total combined plant and microbial nutritional demand') with regard to plant uptake.

In the current study, which was part of the second phase of the European network 'CORE', we examined the effects of enhanced $(NH_4)_2SO_4$ deposition on soil

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solution chemistry in the presence of living tree roots *in situ*, using a technique described by Anderson *et al.* (1990). In this paper we report the impacts of sustained increased $(NH_4)_2SO_4$ deposition on the soil solution chemistry of an acid forest soil with low base saturation.

METHODS

Site characteristics

The study site was located in Grizedale forest, NW England (National Grid Ref. SD326915) in a 42-year-old (in 1992) Norway spruce forest (*Picea abies*) with a tree density of approx. 3500 stems ha^{-1}. The stand was located on an acid brown soil with clay texture and slight seasonal waterlogging, with no ground vegetation within the forest. The altitude of the site was 170 m above sea level with a mean annual air temperature and rainfall of 12.8°C and 1556 mm (1989–1990), respectively. The area is remote from any major sources of sulphur or nitrogen pollution, but the site was within 20 km of the coast, with high rainfall levels resulting in high fluxes of sulphate in rainfall.

Preparation of soil cores

Soil cores were constructed by fitting a Plexiglas cylinder (14.4 cm inner dia. ×24 cm deep) onto a metal cutter, and forcing into the ground. The detailed methodology of the apparatus and coring technique was described by Raubuch (1992) and Carnol *et al.* (1997). Any cores showing evidence of cracking or vertical smearing were discarded. The bottom of the soil core was carefully trimmed, so that the actual length of the soil column was 17.5 cm. A 5 cm depth of acid-washed fine quartz was then placed in the bottom of each core and a cap fitted and sealed with neutral silicone adhesive. A pre-washed ceramic cup (P80, Fa. KPM Berlin, Germany, 20 mm outer dia., 50 mm length, pore size: 1–2 mm), glued to perspex tubing (6 cm) and a tubing connector, was inserted diagonally into the sand at the base of each core, and connected to a glass bottle (2 litre capacity, thick walled) by PVC tubing. The whole experimental unit (soil core and ceramic cup) is referred to as a lysimeter. Prior to installation into the lysimeters, the ceramic cups were repeatedly rinsed under vacuum with distilled water, after soaking with hydrogen peroxide and conditioning in HCl (1N). Physical and chemical properties of the P80 cups were reported by Wenzel and Wieshammer (1995). The top 3 cm of the organic layer were gently separated and removed from all cores to permit placement of live roots in the F layer. This layer was returned to the appropriate lysimeter in the field, after introduction of the rooting systems (see below).

Field experimental design

Twenty-eight tension lysimeters were installed in the field level with the surrounding soil, in a randomised block design, with seven replicate lysimeters for each of the four treatments. Intact rooting systems, were inserted into each R and RNS lysimeter, after Anderson *et al.*

(1990). This process involved carefully 'teasing' out small (<2 mm dia.), healthy root branches from the forest floor and inserting them unbroken and undamaged through holes in the side of the lysimeter, into the organic horizon within each lysimeter. After placement, the holes were sealed with neutral silicone and the top 3 cm of the organic layer replaced over the intact root system. In this way root sinks were established which were attached to the adjacent mature trees. All lysimeters were destructively sampled at the end of the experiment, and root condition and mass determined. Each individual lysimeter was 'roofed' with a piece of Perspex (30×30 cm, 2 mm thickness) at 10 cm above the ground, to enable control of throughfall inputs whilst allowing air circulation above the lysimeter. Throughfall was replaced by bulked throughfall (C and R treatments) or an equal volume of bulked throughfall to which $(NH_4)_2SO_4$ additions had been made (NS and RNS treatments). The 'throughfall' treatments were applied manually at 2-weekly intervals on a *pro rata* volume basis, as determined from bulk throughfall collectors. The NS treatments were designed to provide an additional 75 kg N $ha^{-1} a^{-1}$ (addition of 2.88 kg N ha^{-1} at each watering to the NS and RNS lysimeters).

The resulting four lysimeter treatments were: non-rooted with control throughfall (C), non-rooted with $(NH_4)_2SO_4$ additions (NS), rooted with control throughfall (R), rooted with $(NH_4)_2SO_4$ additions (RNS). The throughfall needed for watering the lysimeters was collected in 10 large plastic bins covered with a 2 mm mesh to prevent litter and canopy debris from entering. They were pooled together for watering the lysimeters. The roofs excluded litter inputs to the lysimeters, and no fresh litter was added to the lysimeters during the experimental period. Sampling bottles were kept in small covered soil pits, and a suction of 0.065 MPa was re-established at each sampling. The volume of the bottles was sufficient to maintain a vacuum during the 2-week sampling period. Soil solution was sampled every 2 weeks and analysed for major cations and anions. Field trials showed that changes in soil solution chemistry during the 2-week storage interval were not significant (J. Poskitt, unpublished data). Lysimeters were first established in the field in Spring 1992, but the roots failed to survive, and new live root systems were inserted into the lysimeters in Autumn 1992. Consequently, $(NH_4)_2SO_4$ additions were started in September 1992 and applied during one year. Seven additional cores were collected for soil analysis in Autumn 1992.

Climate, rainfall and throughfall monitoring

Five rainfall collectors were installed in a nearby open field, and 10 throughfall collectors were installed beneath the canopy using random co-ordinates. The collectors consisted of a funnel (22 cm dia.) placed over a 10 litre polyethylene bottle at 1.5 m height. A nylon gauze was placed into the funnels to prevent debris contaminating the sample. At 2-weekly intervals, the funnels were cleaned, bottles and gauzes replaced, and

the throughfall samples returned to the laboratory for chemical analyses. Soil temperature was measured every hour at 5 cm depth using thermistors connected to a data logger (Grant Ltd., Squirrel 1200).

Chemical analyses

All water samples were collected every 2 weeks, and the volumes and pH (potentiometry) determined, prior to filtration (Whatman GF/C). They were then analysed for Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+} (inductively-coupled plasma spectrometry), NH_4^+-N (colorimetry), NO_3^--N, Cl^-, SO_4^{2-}-S (ion chromatography, Dionex). All analyses were performed by the Chemistry Section, ITE Merlewood. The integrity of the results supplied were checked by the use of certified reference materials and by regular participation in the 'Aquacheck's' bimonthly interlaboratory comparison programme for water analysis.

Soil pH was measured both in water and in 0.01 M $CaCl_2$, (1:2.5 fresh soil:water or $CaCl_2$) after 2 h of shaking. Total contents of Al, Ca, K and Mg in the organic horizons were determined after wet digestion, with C and N being measured using a Carlo–Erba total C/N analyser. Exchangeable cations were determined by atomic adsorption spectrometry after leaching the soil with a 1 N NH_4Cl solution, after Raubuch (1992).

Statistical analyses

Annual element fluxes (October 1992–October 1993) were calculated for individual lysimeters and the arithmetic means for replicate lysimeters calculated. These fluxes were tested for significant differences between treatments using one-way analysis of variance (ANOVA) and Tukey's Studentized Range Test (SAS Institute Inc., 1989). Soil solution concentrations are reported as arithmetic means of replicate lysimeters and comparisons of ionic concentrations between treatments over time were made using a two-way ANOVA with repeated measures on one factor (time), adjusting the error terms for mixed designs (Cody and Smith, 1991; SAS Institute Inc., 1989). Since interaction terms were significant, treatment effects were analysed at individual times, as recommended by Hatcher and Stepansky (1994), using one-way ANOVA and Tukey's studentized range test (HSD). Relationships between concentrations of ions in soil solution were analysed using Pearson's correlation coefficient.

Input and output volume budgets were used to assess the hydrological integrity of each lysimeter, with blocked or leaking lysimeters being discarded from all subsequent analyses. On any occasions when the suction cup vacuum was not maintained over the 2-weekly sampling period, and was accompanied by a low volume of leachate (less than 75% of applied volume), this indicated that the suction system had leaked. Such lysimeters were excluded from subsequent calculations of mean concentrations for that sampling. Lysimeters with root implants in which the roots were not viable at the end of the experiment were also discarded, with the resulting number of replicates per treatment varying between four and seven.

RESULTS

Site characteristics

The mean 2-weekly soil temperature (5 cm below ground) varied between 1 and 13°C, showing a strong seasonal trend with similar summer maxima (August/September) for both years (Fig. 1). The average temperature during the 18 months of study was 8.8°C (yearly average 7.8°C), whilst rainfall totalled 1906 mm per annum.

The total element contents of the organic horizons, and exchangeable cations of the mineral horizons, are shown in Tables 1 and 2, together with the pH_{H_2O} and pH_{CaCl_2} profiles. Total element contents of the organic horizons showed an increase in Al content with depth, with a sharp decrease in Ca (Table 1). This was paralleled by high exchangeable Al in the mineral soil layers (Table 2), with Al constituting >90% of the total exchangeable cation pool. The amount of total exchangeable cations was moderately high, but Ca represented only a small fraction of the exchange complex (<3.5%). The pH data also showed that the soil was strongly acidified, with a minimum pH_{H_2O} of around 3.6 in the humus and upper mineral soil horizons.

C/N ratios were relatively high in the organic layers, characteristically declining with depth attaining values typical for moder type soils (Duchaufour, 1977).

Soil solution chemistry

Two-weekly mean Ca^{2+}, Al^{3+} and NO_3^- concentrations in soil solution are shown in Fig. 2(a)–(d). At the beginning of the experiment, mean Ca^{2+} concentrations across all treatments were around 0.6 meq litre^{-1}, whilst Al^{3+} concentrations were below 0.05 meq litre^{-1}. The behaviour of Ca^{2+} was very similar in all treatments (Fig. 2(a)–(d)), showing a slight initial rise in concentration, followed by a steady decline during the subsequent year of observation. At the end of the experiment
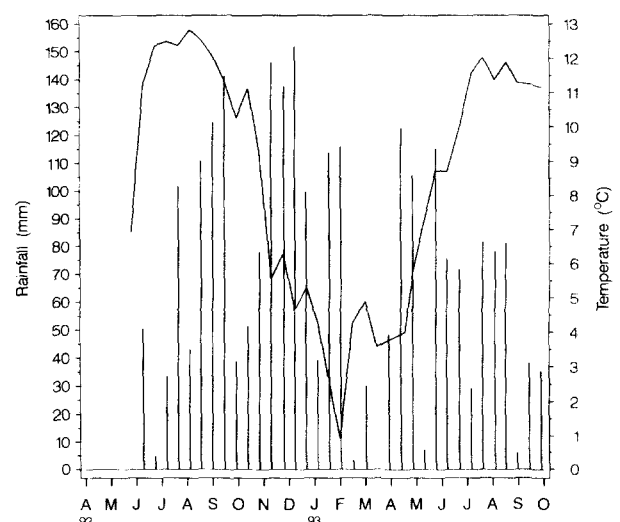

Fig. 1. Climatic conditions during the experiment. Temperatures (line) are for the soil at 5 cm depth, with hourly data averaged over 14 days, and rainfall volumes (bars) are totals for 14 days (means of five replicates).

Table 1. Total element (μg g^{-1}), C, and N contents (%), and pH profiles of the organic layers. Means of seven replicates and SD are given

	Al	Ca	K	Mg	C (%)	N (%)	C/N	pH$_{H_2O}$	pH$_{CaCl_2}$
Ol mean	3199	1462	1008	573	43.9	1.50	29.7	4.1	3.2
SD	2672	445	423	164	5.6	0.20	3.3	—	—
Of mean	2372	1107	616	560	45.3	1.60	28.6	3.9	2.8
SD	662	178	105	84	1.3	0.04	1.4	—	—
Oh mean	5394	298	793	588	34.1	1.90	18.0	3.6	3.0
SD	1673	59	220	175	2.8	0.20	0.8	—	—

Table 2. Exchangeable cations (μeq g^{-1}), percentage on total exchangeable cations (%) and pH in the mineral horizons. Means of seven replicates and SD

		Al	Ca	K	Mg	Na	Total	C (%)	N (%)	C/N	Ca/Al (mol mol^{-1})	pH$_{H_2O}$	pH$_{CaCl_2}$
0–5 cm	Mean	113	4.3	1.2	3.6	1.3	123.0	30.7	1.9	15.8	0.04	3.7	3.2
	SD	23	0.5	0.4	0.9	0.5	5	3.3	0.1	1.2	0.01		
	%	91	3.6	1.0	2.9	1.1							
	SD	1	0.7	0.3	0.6	0.3							
5–8 cm	Mean	112	3.7	0.9	3.2	0.9	121.0	34.0	2.1	16.4	0.03	3.8	3.3
	SD	27	0.8	0.5	1.2	0.7	3	3.6	0.3	1.3	0.01		
	%	93	3.2	0.7	2.6	0.7							
	SD	1	0.7	0.3	0.7	0.5							

the Ca^{2+} concentrations were between 0.1–0.3 meq litre^{-1}, with slightly greater variability in the rooted lysimeters. In contrast, the Al^{3+} concentrations increased in all treatments, rising to molar charge concentrations similar to those initially found for Ca^{2+}. However, C and R lysimeters (Figs 2(a) and (b)) behaved differently to NS treated ones (Figs 2(c) and (d)). Al^{3+} concentrations stabilised after 6–9 months in the lysimeters not receiving additional N and S, whilst they continued to rise in the NS treatments, leading to significantly ($p < 0.05$) higher Al^{3+} concentrations for the NS treated lysimeters, compared to controls at the end of the experiment. NO_3^- concentrations ranged between 0.3–0.4 meq litre^{-1} at the beginning of the experiment, and showed a similar evolution for the four treatments. After an initial rise during summer, up to an optimum in autumn, concentrations decreased during the winter months. Concentrations rose again in spring, but maximum values attained where lower than in the previous year (except for RNS lysimeters). In NS and RNS lysimeters, NO_3^- concentrations were significantly ($p < 0.05$) increased, compared to controls, 4 months after the beginning of the $(NH_4)_2SO_4$ applications.

The strong relationship between NO_3^- and $Ca^{2+} + Al^{3+}$ concentrations in soil solution is shown in Fig. 3(a) ($r^2 = 0.45$, $p < 0.001$). The correlation between SO_4^{2-} and $Ca^{2+} + Al^{3+}$ concentrations in soil solution was significant ($r^2 = 0.19$, $p < 0.001$), but of low explanatory power (Fig. 3(b)). Although SO_4^{2-} was always an important ion in the leachate, NO_3^- was the only anion to make a significant contribution to the increase observed in either Ca^{2+} or Al^{3+} concentrations.

Ionic balances

The annual cation-anion fluxes (keq ha^{-1}) for inputs and outputs to the lysimeters are shown in Fig. 4,

representing totals for 1 year from the start of the NS treatments. This figure compares rainfall and throughfall fluxes at the site with the actual inputs (bulked throughfall) to the lysimeters. The slight differences between the chemistry of the 'throughfall' and 'bulked throughfall' fluxes were due to spatial variability in the quality of throughfall from the various sampling points. Cations and anions were balanced in all solutions analysed, indicating that all major ions had been measured in the chemical analyses.

Precipitation chemistry was dominated by Na^+ and Cl^-, probably resulting from the proximity of the site to the sea (*ca* 20 km) in the direction of the prevailing wind. Throughfall was enriched in most ions, principally explained by aerosol deposition onto the canopy (Na^+, Cl^-), dry deposition (SO_4^{2-}, H^+) and leaching from the needles (K^+, Ca^{2+}, Mg^{2+}). The bulked throughfall solution closely resembled throughfall composition, indicating that the bulking approach to standardising throughfall was effective in that the throughfall chemistry at the site was largely maintained in the treatments, whilst ensuring uniformity of treatments.

The NS treatment, in which ammonium sulphate was added to the bulked throughfall, resulted in a total deposition of 5.66 keq ha^{-1} a^{-1} NH_4^+ (79.3 kg N ha^{-1} a^{-1}) and 7.33 keq ha^{-1} a^{-1} SO_4^{2-} (117.5 kg S ha^{-1} a^{-1}), compared to 0.62 keq ha^{-1} a^{-1} NH_4^+ (8.7 kg N ha^{-1} a^{-1}) and 2.19 keq ha^{-1} a^{-1} SO_4^{2-} (35.1 kg S ha^{-1} a^{-1}) for the C treatment (Fig. 4). The ionic fluxes for the control (C) lysimeters clearly showed that nitrification occurred in this soil (Fig. 4 and Table 3). NO_3^- leaching in control lysimeters was mainly balanced by Al^{3+}, but also resulted in a slight increase in Ca^{2+}, Mg^{2+}, and H^+ leaching, compared to throughfall inputs. Total NO_3^- leaching was 5.5 keq ha^{-1} a^{-1} (77.0 kg N ha^{-1} a^{-1}). The fluxes of Na^+, Cl^- and SO_4^{2-}–S from the C lysimeters
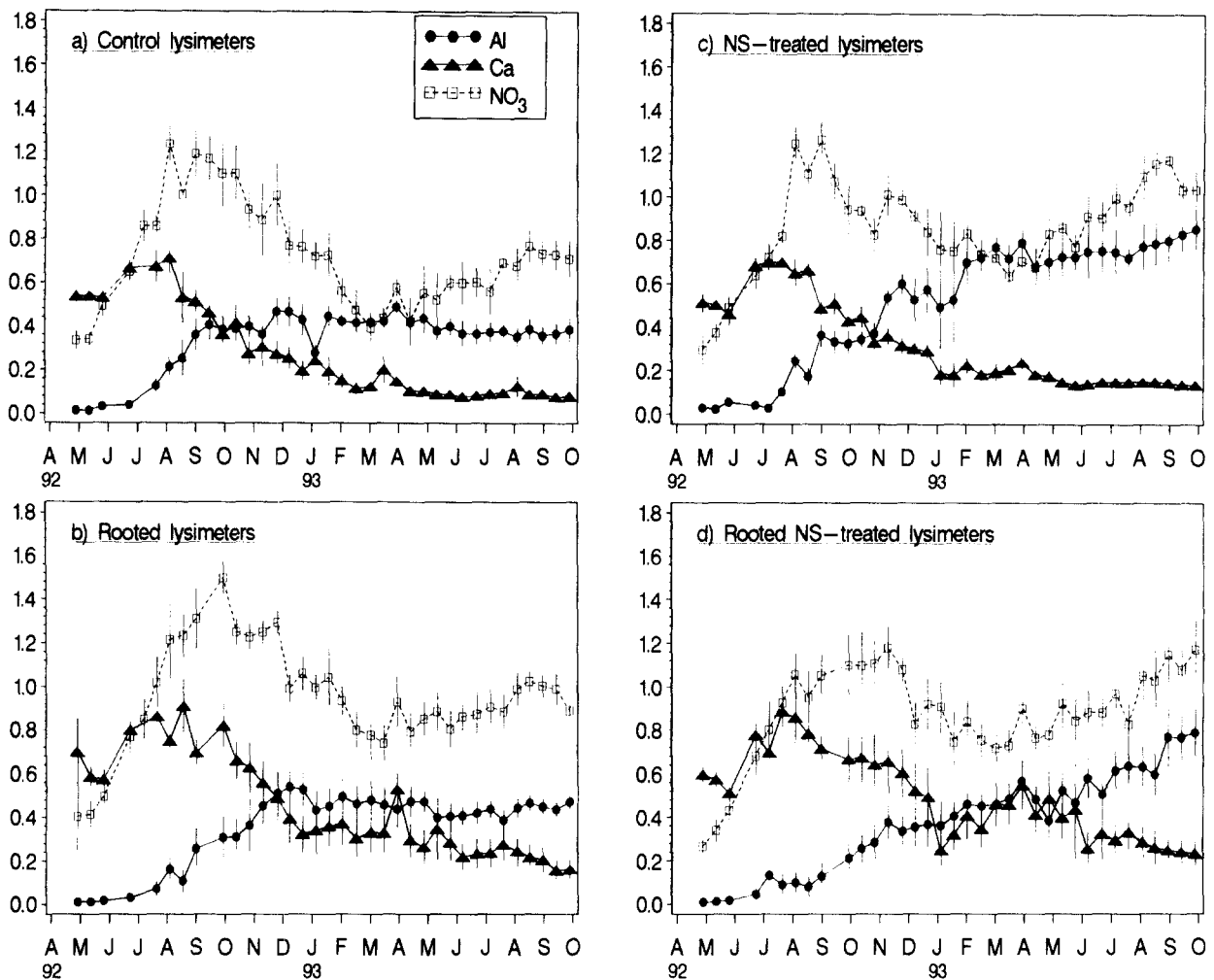
Fig. 2. Two weekly mean Ca^{2+} (▲), Al^{3+} (●) and NO_3^- (□) concentrations (meq litre^{-1}) in the soil solution for the four treatments. $(NH_4)_2SO_4$ additions began in September 1992. Means of four to seven replicates are presented, and bars represent SE.

mirrored those in the input solutions and these ions appeared to be largely unaffected by passage through the soil.

Results of ANOVA statistics (Table 3) showed that total soil solution water fluxes were significantly reduced by the presence of roots in the RNS treatments,

compared to NS. Water fluxes from R were also lower than for C, but the difference was not significant. Na^+, K^+, H^+ and Cl^- fluxes in soil solution were not significantly influenced by either the presence of roots (R) or the NS treatments (Table 3). The presence of roots in the RNS lysimeters led to a significant increase in the
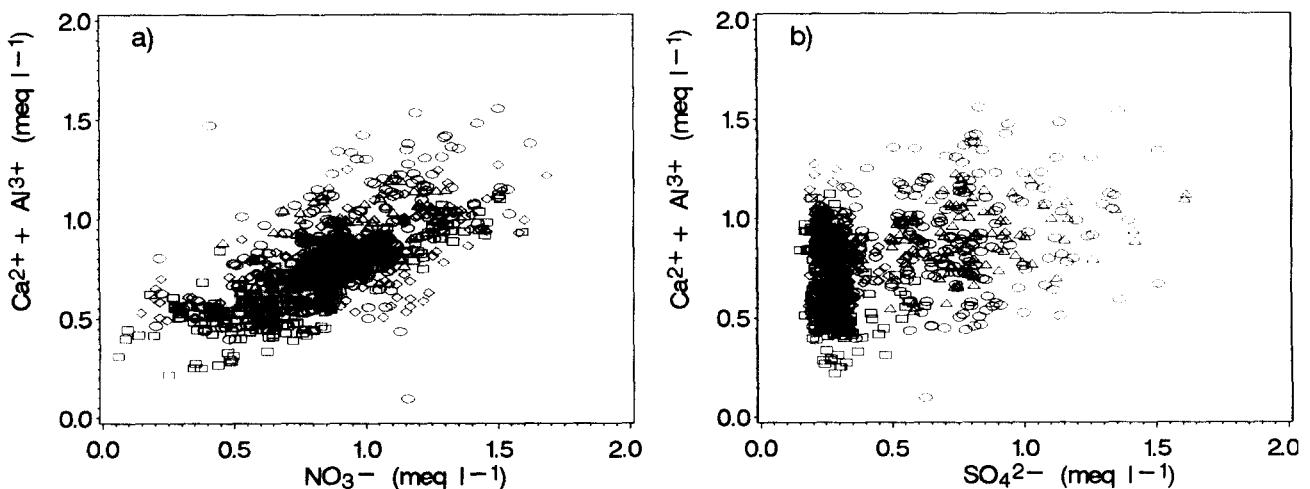

Fig. 3. $Ca^{2+} + Al^{3+}$ versus NO_3^- (a) and SO_4^{2-} (b) concentrations in leachates of control (□), $(NH_4)_2SO_4$ treated (△), rooted (◇) and rooted $(NH_4)_2SO_4$ treated (○) lysimeters.
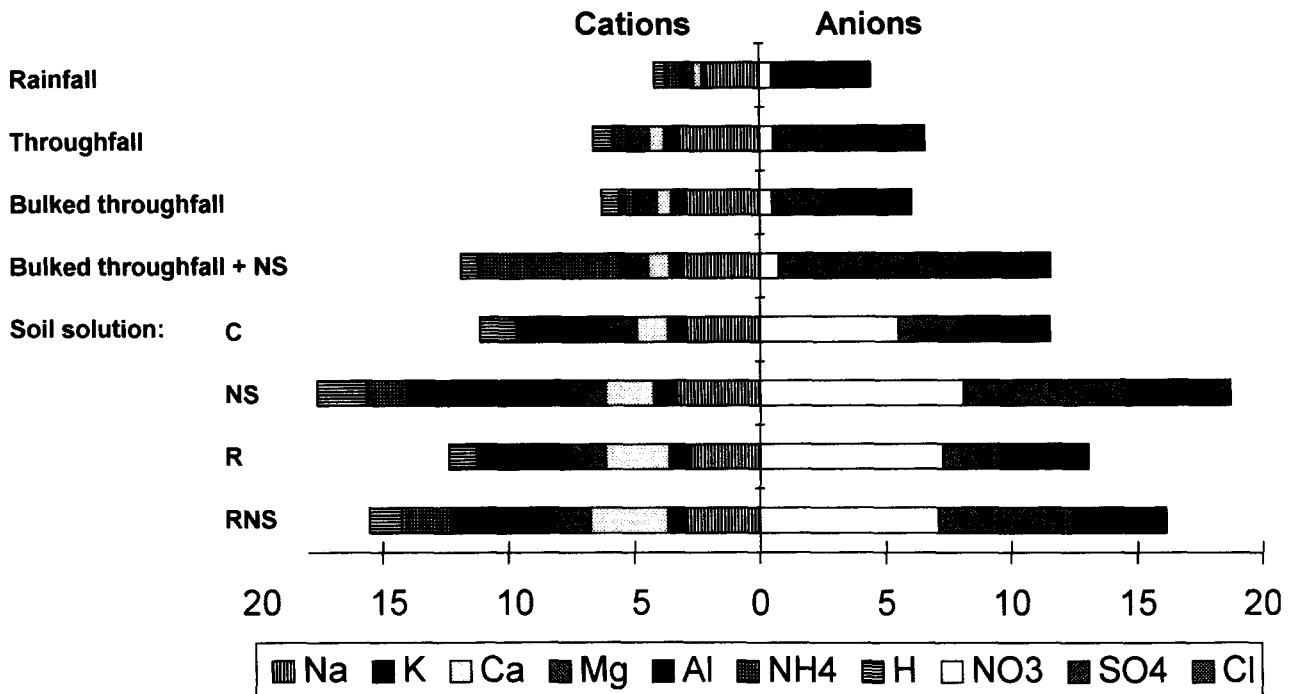
Fig. 4. Annual ionic deposition (rainfall, throughfall) from October 1992 to October 1993, inputs to lysimeters by watering solutions (bulked throughfall, bulked throughfall + NS), and outputs from control (C), $(NH_4)_2SO_4$ treated (NS), rooted (R) and rooted $(NH_4)_2SO_4$ treated (RNS) lysimeter leachates $(keq\,ha^{-1}\,a^{-1})$. Values are means of four to seven replicates (see text).

Ca^{2+} flux, but, in comparison with NS, decreases in Al^{3+} and SO_4^{2-}–S. No significant differences were found between rooted and control lysimeters for any ion, but there appeared to be a trend to higher NO_3^-, Ca^{2+} and Mg^{2+} leaching from lysimeters containing roots. In contrast, the NS treatment significantly increased NO_3^-–N, SO_4^{2-}–S, NH_4^+–N, Al^{3+} and Mg^{2+} leaching, with NO_3^- leaching being increased by $2.6\,keq\,ha^{-1}\,a^{-1}$ $(36.4\,kg\,N\,ha^{-1}\,a^{-1})$ and Al^{3+} leaching by $2.69\,keq\,ha^{-1}\,a^{-1}$ $(24.2\,kg\,ha^{-1}\,a^{-1})$ when compared to the control (C). The increase in Mg^{2+} was relatively small $(0.57\,keq\,ha^{-1}\,a^{-1}$; 6.9 kg $ha^{-1}\,a^{-1})$ and comparisons of these increases on an equivalence basis suggest that the increase in Al^{3+} was almost entirely matched by increased NO_3^- fluxes (Fig. 4).

Table 3. Water and ionic fluxes $(kg\,ha^{-1}\,a^{-1})$ from October 1992 to October 1993, for control (C), NS-treated (NS), rooted (R) and rooted NS-treated (RNS) lysimeter leachates. Different letters denote significant differences $(p < 0.05)$ between treatments (Tukey)

	C	NS	R	RNS	p
Volume (litre lysimeter^{-1})	13.5^{ac}	14.6^a	12.2^{ac}	12.2^{bc}	0.0297
Na$^+$	67.1^a	76.3^a	65.4^a	67.2^a	n.s.
K$^+$	28.7^a	35.1^a	29.8^a	29.1^a	n.s.
Ca^{2+}	25.2^a	39.1^a	51.1^a	62.3^b	0.0433
Mg^{2+}	16.0^a	22.9^b	18.7^{ac}	22.0^{bc}	0.0002
Al^{3+}	29.4^a	53.6^b	29.9^a	33.0^a	0.0112
NH$_4^+$–N	2.3^a	22.6^b	3.3^a	27.6^b	0.0003
H$^+$	1.5^a	2.0^a	1.1^a	1.3^a	n.s.
NO$_3^-$–N	77.0^a	113.4^b	102.0^{ab}	99.4^{ab}	0.0327
Cl$^-$	127.9^a	140.1^a	124.6^a	120.2^a	n.s.
SO$_4^{2-}$–S	38.9^a	106.9^b	36.6^a	91.0^c	0.0001

DISCUSSION

Forest soil solution chemistry is subject to high spatial and temporal variability (Manderscheid and Matzner, 1995a,b), often associated with the influence of stemflow and the non-uniform distribution of rooting systems (Seiler and Matzner, 1995; Koch and Matzner, 1993). The spatial distribution of throughfall water concentrations and fluxes (Gundersen *et al.*, 1995; Beier *et al.*, 1993) also contributes to this heterogeneity, and can confound the detection of potential experimental impacts on soil solution chemistry, as noted by Raubuch (1992). The roofing of experimental units, coupled with the replacement of the throughfall by a representative, controlled bulk throughfall solution from the site, provides a powerful means of reducing this natural heterogeneity whilst maintaining throughfall inputs realistic in volume and chemistry. This enables the calculation of exact input and output fluxes for each experimental unit. However, the exact timing of inputs was not maintained, and could have induced some changes in the 'climate' of the lysimeters, causing increased mineralisation/nitrification (see below). Additionally, this watering method may induce lower residence times for the water in the soil layers. However, contact times were sufficient for the watering solution to interact with the soil, as demonstrated by almost complete retention of NH_4^+ for other soil types, using an identical experimental protocol (Carnol *et al.*, 1997).

No fresh litter was added to the soil cores, to permit comparison across the European sites used in this study without confounding effects (Carnol *et al.*, 1997). *Picea abies* litter has a high C:N ratio of 40–50, usually associated with low decomposition rates and net N

immobilisation. However, data derived from Wedraogo *et al.* (1993) would predict leaching of 8.7 kg ha^{-1} a^{-1} of NO$_3^-$–N from *P. abies* litter during the first year of decomposition. The litter of Wedraogo *et al.* (1993) was incubated in an open field, and decomposition rates under the dense canopy in Grizedale forest can be expected to be lower. A decomposition experiment, using *P. abies* litter, under the forest canopy has shown a loss of 3.3 kg N ha^{-1} during the first 10 months (Parmentier and Remacle, 1981), with subsequent immobilisation, totalling a net loss of 1.15 kg N ha^{-1} after 3 years. Contribution of fresh litter to N fluxes can thus be expected to be small, compared to fluxes observed in our 18-month study. Additionally, as fresh litter was excluded in all lysimeters, treatments are comparable. Some remaining variation between rooted lysimeters could be explained by the degree of root functioning. Water fluxes were significantly reduced in RNS lysimeters, but not in the rooted only lysimeters (R). Root mass and condition showed high variability between lysimeters, but differences between R and RNS treatments were not significant (Carnol *et al.*, 1997).

Lysimeter units used in this study combined tension lysimetry with the use of defined experimental units. The major advantage of this approach was the exact control of inputs to a certain surface, enabling flux calculation without the use of water flowpath models. Tension lysimeters have been criticised for collecting soil water from non-representative fractions of the soil matrix (see review by Litaor, 1988) or influencing the soil solution elemental concentration, particularly through Al contamination (Raulund-Rasmussen, 1989) or cation retention. These problems, however, depend on the materials used for the construction of the suction cups (Wenzel and Wieshammer, 1995). The ceramic P80 cups, used in this study, have been tested for structural changes in the surrounding soil (Beckmann *et al.*, 1992), influence on the chemical composition of a typical soil solution (Hetsch *et al.*, 1979; Beier and Hansen, 1992), and trace metal adsorption (Wenzel and Wieshammer, 1995, and references therein). Results showed no significant differences between soil solution concentrations sampled by means of P80 and PTFE (considered inert) cups (slight differences for Mg^{2+}), and suitable reproduction of test solution concentrations for major elements, except phosphate. Wenzel and Wieshammer (1995) reported significant adsorption of trace elements by P80 cups, but in the ppb range; at higher concentrations no adsorption has been found for acid solutions (Grossmann and Udluft, 1991).

Possible contamination from the cup material with aluminium is overcome by acid washing of the ceramic cups (Wenzel and Wieshammer, 1995; Hughes and Reynolds, 1988). We found very low aluminium leaching from other forest soils using the same methodology (Berg *et al.*, 1997; Carnol *et al.*, 1997), and consider that Al contamination was insignificant. Additionally, the soil/cup contact was improved by embedding in acid-washed sand, as recommended by Beckmann *et al.* (1992). This also removed concerns of sampling soil

matrix water around the cups. The tension applied simulated the groundwater table at greater depth than the 22 cm of the soil core, drawing the conditions closer to the natural environment than by using free-draining lysimeters (Raubuch, 1992).

The total exchangeable cation content of the soil was large (123 µeq g^{-1}), and was characterised by Al saturation (>90%) and little Ca on the exchange complex (<3.5%). These values are in the range described by Foth (1990) for highly weathered soils and this could be the result of the high volumes of precipitation at this site (annual total: 1906 mm). Mean soil pH$_{H_2O}$ for the different soil layers varied between 3.6 and 4, indicating that the soil was situated in the upper region of the aluminium buffer range (pH 2.8–4.2; Ulrich, 1987). The lower pH$_{CaCl_2}$ was due to the displacement of acidic cations from the exchange complex (Binkley *et al.*, 1989) and indicated the potential response of the soil to acid stress (Ulrich, 1981). Although the different buffer ranges have frequently been discussed in the literature (e.g. Ulrich, 1987), and marked shifts in soil pH observed over long time scales (Johnston *et al.*, 1986), the actual change from one range to the next has never been clearly demonstrated in this form. We report a decrease in pH and a concurrent 'switch' from Ca to Al dominated soil solutions in all treatments, during an 18-month study with 2-weekly soil solution data. Soil solution SO$_4^{2-}$ concentrations increased from 0.25 meq litre^{-1} to 0.50–1.0 meq litre^{-1} in NS treated lysimeters (Carnol *et al.*, 1997), but as the switch was observed under all treatments, it could not be attributed to a 'salt effect', associated with increased soil solution mobile anion concentrations in the NS treatments (see Binkley *et al.*, 1989; Reuss and Johnson, 1986). However, the significantly ($p < 0.05$) higher Al^{3+} concentrations reached by the NS treatments at the end of the experiment could well be, at least partially, explained by this effect. Alternatively this effect could be due to acidification through cation exchange (against H$^+$) of deposited NH$_4^+$. But the marked correlation between Al^{3+} + Ca^{2+} and NO$_3^-$ soil solution concentration indicated that nitrification was the main driving force (see below).

Although there were no significant differences in soil solution pH concentrations between treatments, there was a significant ($p < 0.05$) decrease over time for all treatments from pH 4.9 (1 month after installation) to pH 3.8 (last sampling). Input solution pH was 4.1 for both control and NS treatments. Based on the solubility of gibbsite and the exchange equilibrium between Al^{3+} and H$^+$, Reuss and Johnson (1986) would predict the constancy for 3pH–pAl (pAl: negative logarithm of molar activity of Al^{3+}) for a given soil. Our data, however, showed pAl decreasing linearly with pH ($p < 0.001$, $r^2 = 0.72$–0.89 in the four treatments), and the selectivity coefficient, calculated as in Reuss and Johnson (1986) would have changed from 9 to 5.3 during the experiment, assuming fractions of Ca and Al on the exchange complex to be constant. Although these authors state that significant changes in exchangeable

cations resulting from acid deposition would require years or decades, their chemical equilibrium model predicts an abrupt transition between Ca and Al dominated soil solutions occurring at low Ca saturation. Similarly, maximum sensitivity to pH changes is predicted at low base saturation and CEC. The relationship between Ca and Al soil solution concentrations in this study did not follow the Gaines–Thomas equation, but showed a decreasing exponential relationship, as for the modelled Al concentrations in function of Ca saturation of the exchange complex (Reuss and Johnson, 1986). We suggest, therefore, that the observed switch was due to chemical equilibrium processes, responding to acidification and reduction of the already low Ca saturation. The significant correlation between $Al^{3+} + Ca^{2+}$ and NO_3^- soil solution concentration indicates that the observed acidification was probably due to nitrification.

The data clearly show that important changes in soil solution concentrations can occur over relatively short time scales, and could represent a short term switch caused by environmental or experimental influences (Ulrich et al., 1980). In any case, the Ca/Al ratios reached were very low (from 0.24 ± 0.08 for NS to 0.57 ± 0.64 in RNS). Following an extensive literature review, Cronan and Grigal (1995) concluded that there would be a 75–100% risk of adverse impacts on tree growth or nutrition with a soil solution Ca/Al ratio of 0.5 and 0.2, respectively. The Al^{3+} concentrations reached at the end of this experiment have been reported to decrease fine root biomass and adversely affect nutrient uptake (Majdi and Rosengren-Brinck, 1994; Boxman et al., 1991; Van Praag et al., 1985).

S inputs in this study were high in comparison to natural throughfall deposition, even in polluted areas. However, acidity transferred by the $(NH_4)_2SO_4$ to the soil was mainly associated with NH_4^+. SO_4^{2-} behaved as a conservative ion with 90% of the input being leached (Carnol et al., 1997), and balanced by Na^+, NH_4^+ and some base cations. Changes observed in the soil solution ionic concentrations were either related to NO_3^- (see below), or not due to the experimental treatment. The contribution of the large S input to the chemical processes reported in this study was therefore minor.

NO_3^-–N leaching losses, ranging from 77 to 113 kg ha^{-1} a^{-1}, were relatively high, compared to exports via streamwater in catchments (Hornung et al., 1990), where the highest export was reported to be 31 kg ha^{-1} a^{-1} from the Hafren catchment in Plinlymon. Similarly, average export from the Hubbard Brook Experimental Forest was only 17 kg ha^{-1} a^{-1} (Likens and Bormann, 1995), and 13.4–19.8 kg ha^{-1} a^{-1} from the Robinette catchment in the Belgian Ardennes (Hornung et al., 1990). However, leaching data from the root zone are often reported to be higher than streamwater concentrations, due to removal of nitrate at greater depth (Van Breemen et al., 1987). Tietema et al. (1993) reported NO_3^-–N leaching of 50 kg ha^{-1} a^{-1} from the organic horizons of a Douglas fir plot, and stagnopodzols within the NITREX study sites showed NO_3^-–N

leaching up to 33 kg ha^{-1} a^{-1} (Emmett et al., 1995b). A compilation from 64 European plot-scale studies (49 coniferous sites) reported NO_3^-–N leaching losses between 0–85 kg ha^{-1} a^{-1} (Gundersen, 1995). In contrast to these data, where exports were higher than inputs at only four sites, NO_3^-–N leaching was greater than total N inputs in our study. Johnson et al. (1995) have questioned the usefulness of laboratory lysimeter studies, due to high N mineralisation after soil disturbance. In our field study, these disturbances were minimised, as the soil was neither sieved nor mixed, and data used for flux calculations were derived from soil solutions collected from 6 months after initial perturbation. Yet, the prolonged dry periods (2 weeks), caused by roofing and manual watering, could have improved the conditions for microorganisms at this usually wet site, causing increased mineralisation/nitrification. During the previous phase of the CORE project, roofed lysimeters of a clay–loam soil (placed in Grizedale forest) with 2-weekly manual watering showed similar nitrate outputs to those receiving the throughfall at natural frequency (Berg et al., 1997; Raubuch, 1992). However, the Grizedale soil, moved to forested sites in different countries, showed NO_3^-–N leaching between 27.3 (in Grizedale) and 79.4 kg ha^{-1} a^{-1} (Berg et al., 1997) under natural throughfall frequency, supporting the hypotheses that our watering method induced increased mineralisation/nitrification for this clay soil.

The potential effects of increased N deposition in the absence of tree uptake are demonstrated by the results from the 'control non-rooted lysimeters'. NO_3^-–N leaching was increased by 36 kg ha^{-1} a^{-1} and was balanced by Al^{3+} leaching. This increase was apparent 4 months after the start of the treatments (Carnol et al., 1997). In contrast, NH_4NO_3 applications did not lead to apparent nitrification of the applied NH_4 in a Sitka spruce plantation in Wales (Emmett et al., 1995b). This could be explained by a difference in soil %N between these two sites, with the Welsh site being below the 1.7% threshold for nitrification of incoming NH_4^+ (Emmett et al., 1995a), and the current site being above this threshold.

This study suggests that in moderately acid soils with low base saturation, acidification can induce an abrupt switch from Ca^{2+} to Al^{3+} dominated soil solutions, leading to Ca/Al ratios reported to be damaging to tree growth and nutrition. Base saturation could therefore constitute an indicator of sensitivity with regards of establishment of critical loads for forest soils.

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