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The effects of acid deposition on the biogeochemical cycles of major nutrients in miniature red spruce ecosystems

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Abstract. As part of an experimental study of air pollution effects on tree growth and health, we combined process studies with an ecosystem approach to evaluate the effects of acidic deposition on soil acidification, nutrient cycling and proton fluxes in miniature red spruce ecosystems. Ninety red spruce saplings were transplanted into 1-m diameter pots containing reconstructed soil profiles and exposed to simulated acid rain treatments of pH 3.1, 4.1 and 5.1 for four consecutive growing seasons. All the principal fluxes of the major elements were measured.

During the first year of treatments, the disturbance associated with the transplanting of the experimental trees masked any treatment effects by stimulating N mineralization rates and consequent high NO_3^-, cation, and H^+ flux through the soil profile. In subsequent years, leaching of base cations and labile Al was accelerated in the most intensive acid treatment and corresponding declines in soil pH and exchangeable pools of Ca and Mg and increases in exchangeable Al concentrations were observed in the organic horizon. Leaching of Ca^{2+} and Mg^{2+} also was significantly higher in the pH 4.1 than in the pH 5.1 treatment. Flux of Ca from foliage and soil was increased in response to strong acid loading and root uptake increased to compensate for foliar Ca losses. In contrast, K cycling was dominated by root uptake and internal cycling and was relatively insensitive to strong acid inputs. Cation leaching induced by acidic deposition was responsible for the majority of H^+ flux in the pH 3.1 treatment in the organic soil horizon whereas root uptake accounted for most of the H^+ flux in the pH 4.1 and 5.1 treatments. Although no measurable effects on tree nutrition or health were observed, base cation leaching was significantly accelerated by acidic deposition, even at levels below that observed in the eastern U.S., warranting continued concern about acid deposition effects on the soil base status of forested ecosystems.

Introduction

It is widely acknowledged that acid deposition can induce soil acidification by accelerating base cation leaching, a mechanism that is frequently cited as a potential cause of forest decline in both Europe and the eastern U.S. (e.g., Ulrich et al. 1980; Matzner & Ulrich 1987; Schultze 1989; Johnson & Lindberg 1992). Although the causal links in such a decline mechanism may be very complex, two likely effects of base cation leaching are prominent: (1) decreased availability of nutrient cations and consequent plant deficiencies (e.g., Schulze 1989), and (2) increased concentrations of labile Al with its toxic or inhibitory effects on plant roots (e.g., Reuss & Johnson 1986; Ulrich et al. 1980). Furthermore, increased N inputs from acid rain may stimulate tree growth and exacerbate the problem by increasing plant demands on the nutrient-poor soil, possibly leading to plant nutrient imbalances (Schultze 1989; Katzensteiner et al. 1992).

Although acid precipitation effects on soil acidification have been the focus of much research over the past decade, evidence linking anthropogenically induced soil acidification to forest health has been inconclusive (Irving 1991; Joslin et al. 1992). The cumulative effects of forest growth, natural soil processes, and forest management can affect the soil in ways similar to those ascribed to acidic deposition, thereby confounding efforts to quantify the impacts of atmospheric deposition on forested ecosystems (Krug & Frink 1983). For example, both the internal production of acids through natural processes and anthropogenic inputs of strong acids can cause cation leaching. Moreover, root uptake of nutrients and sequestration in plant biomass is an important mechanism leading to depletion of soil base cations, a condition which becomes permanent if biomass is removed from the site in forest management activities (Binkley & Richter 1987). Therefore, to assess the role of acid deposition in soil acidification, exogenous effects of strong acid loading need to be separated from soil-mediated processes.

We combined process studies with an ecosystem-level approach to evaluate the effects of acid deposition on soil acidification and plant nutrition in miniature red spruce ecosystems. Ninety red spruce saplings (approximately 10 years old) were transplanted from the field into individual pots with their original soil profiles intact, and these "ecosystems" were exposed to treatments of acid rain under controlled field conditions. Although simplified, these tree-soil systems contained many of the interacting components of a natural forested ecosystem, and the highly replicated experimental design offered a unique opportunity to analyze for differences in nutrient cycling processes under the different acid deposition regimes.

The objective of this study was to compare the influence of endogenous biological processes and exogenous acid inputs on soil acidification and nutrient cycles in these model red spruce ecosystems. We hypothesized that acid deposition would exacerbate the natural soil acidification processes associated with tree growth by promoting leaching of base cations. Consequent declines in soil fertility and increases in Al availability were expected to result in plant nutrient deficiencies and nutrient imbalances in the high acid treatment.

Methods

In 1985, 137 red spruce (*Picea rubens* Sarg.) saplings were collected from a site in northern Maine (60 km north of Millinocket) which had been clearcut in 1979. Soils at the site were Typic Haplorthods derived from glacial till. The trees averaged 1.3 m in height and 10 yr in age at the time of collection. Physical disturbances to the root system and upper soil horizons (Oi/e, Oa, E, and upper Bs horizons) were minimized by carefully trenching around the trees to the base of the major rooting zone (about 15 cm), lifting the trees by hand, and placing them into 0.92-m diameter pots which had been backfilled with mixed B horizon soil (referred to as bulk B_s soil) from the site. The potted trees were then transported by truck to our field research site in Ithaca, NY, USA, and 90 trees were selected for experimental use based upon similarities of photosynthetic rates and crown morphologies.

Experimental treatments

Open-top fumigation chambers fitted with moveable tops and rainfall nozzles were used in the study to allow controlled exposure to O_3 and simulated acid rain (Kohut et al. 1987). Trees were exposed to four O_3 treatments: charcoal-filtered air (0.5 × ambient), non-filtered air, and non-filtered air to which O_3 was added to levels of 1.5 and 2.0 times ambient. A chamber-free ambient "treatment" acted as a check for chamber effects. Each O_3 treatment was replicated three times for a total of 15 chambers. Generation and monitoring of the O_3 was carried out as described by Kohut et al. (1987).

Within each chamber three sub-plots, each containing two red spruce trees, were established. The sub-plots received treatments of simulated acid rain of pH 3.1, 4.1 or 5.1. Within each sub-plot, one tree was placed in a well on a weighing lysimeter, allowing continuous weight measurements of the tree-soil-pot system. Because no significant O_3 treatment effects nor any ozone-acid rain interaction effects were observed in these nutrient cycling studies, the results of the O_3 treatment are not explicitly presented in this report.

All ambient precipitation was excluded from the trees during the fumigation period, and simulated rain events were scheduled when the soil water status of the pots reached a critical level, as determined by weighing lysimeter and soil tensiometer readings. This procedure ensured that the trees did not experience pronounced water stress during the experiment. Simulated rain was prepared in batch tanks, distributed to chambers through a pressurized manifold system and delivered to each sub-plot through a nozzle mounted above the trees (Lauver et al. 1990). The simulated rain was prepared with a 2:1 sulfate to nitrate ratio (mass basis) and a constant background level of ions typical of Ithaca, NY (Kohut et al. 1987).

Soil analysis

At the field site in Maine, thirty soil blocks (15 × 15 cm) were taken to the depth of obstruction (rocks or fragipan) from the sampling site and transported to the laboratory for analysis. In addition, twenty random subsamples were taken of the soil that was used to back fill the pots (bulk B_s). Following volumetric estimation of bulk density, pretreatment soil samples were separated by horizon (O_a, E, B_s, and bulk B_s) and analyzed for organic matter content, pH, cation exchange capacity, SO_4 adsorption, and exchangeable bases. Organic matter concentration was estimated as loss-on-ignition by combusting samples in a muffle furnace for 4 hr at 500 °C. Soil pH was measured in 5:1 (solution:soil) ratio on samples in distilled water and 10 m$\underline{M}$ $CaCl_2$. Exchangeable nutrient pools were determined by equilibrating field moist soils with 0.1 $\underline{M}$ NH_4Cl (Johnson et al. 1991), and cation concentrations were measured in equilibrium solutions on an inductively coupled argon plasma emission spectrometer (ICP). Sulfate adsorption was determined for each soil horizon by equilibrating field moist soils (1.0 g dry weight equivalent) with K_2SO_4 solutions (10 ml) ranging from 1.0 to 1000 u$\underline{M}$ for 48 h. A constant ionic strength of 0.01 $\underline{M}$ was maintained by adding 0.1 ml of 1.0 $\underline{M}$ $KN0_3$ to all samples. Sulfate adsorbed or released was calculated by the difference between equilibrium solution concentrations of SO_4 and the added amount. All SO_4 determinations were made by ion chromotography. Exchange sites of field moist soils were saturated with NH_4^+ and displaced with K^+ to estimate CEC at field pH (Wada & Okamura 1980). Ammonium concentrations were measured colorimetrically on an Orion continuous flow autoanalyzer (CFA).

Soil cores (2.5-cm diameter) were taken from all the treatment pots in the fall of 1988, 1989, and 1990 and the pre-treatment soil analyses were repeated. Soil samples were pooled between replicate trees by soil horizon (O_a, B_s, and bulk B_s; there was not sufficient E horizon for analyses) resulting in a total of 45 samples per horizon per sampling date. Soil pH and exchangeable bases were measured as described above.

Nitrogen mineralization and nitrification rates were measured in the O_a and B_s soil horizons using an *in situ* buried bag method (Eno 1960). To minimize disturbance to the soils of the treatment trees, these measurements were obtained for eight untreated red spruce pots (adjacent to the treatment chambers but not utilized in the experiment) during the 1987 and 1988 seasons. During the final two years, N mineralization rates were measured in the pots of the experimental trees by the same *in situ* method. Soils were incubated for five 3-week intervals each season from May through October. Ammonium and NO_3 were extracted using 1.0 $\underline{M}$ KCl and concentrations analyzed on a CFA.

Tissue chemistry

In each year of experimental treatments, foliage and stem samples representing three different year classes (0, 1–2, 2+) were collected in October from standardized crown locations. Fine roots were collected by hand-sorting cores taken from the O_a and mineral soil horizons. Tissue samples were dried to constant mass at 70 °C and ground to pass a 20-mesh screen. Samples were dry-ashed in quartz crucibles, dissolved in concentrated HNO_3 plus 30% H_2O_2 and heated to dryness. The ash was then dissolved in a 10% HCl plus 10%

HNO_3 solution, centrifuged, and cations analyzed by ICP. Nitrogen was analyzed using a micro-kjeldahl digestion method. Suitable tissue standards were included in all runs.

Biomass estimates

The 45 experimental trees that were not on lysimeters were harvested after the third year of treatment applications for measurement of below- and aboveground biomass. The other 45 trees were harvested following the fourth and last year of experimental treatments.

Needle and stem dry weights were obtained for each tree by age class. Large root biomass (> 3.0 mm diameter) was measured for each tree and fine root biomass estimated by regression as follows. The entire root systems of ten trees were hand-picked and then separated and weighed by diameter size class (< 0.5, 0.5–1.0, 1.0–3.0, 3.0–10.0, and > 10.0 mm). Among these ten were five non-treatment trees, harvested in the fall of 1987, two non-treatment trees in fall, 1988, and three treatment trees in fall, 1989. These trees were subjectively chosen to represent a wide range of tree sizes with the aim of developing a regression equation between some easily measured tree dimension and fine root biomass. This analysis revealed a strong relationship ($Y = 120.29 + 0.83X$; $r^2 = 0.94$; $p < .001$) between fine root (< 3.0 mm) and coarse, lateral root biomass (> 3.0 mm). In the 1989 and 1990 tree harvests, the pots were cut away, the soil washed off the root systems using a high pressure hose, and the > 3.0 mm diameter roots collected, dried and weighed. Fine root biomass was then estimated using the above regression.

Litterfall mass was estimated with plastic dish collectors (20 × 20 cm) placed beneath each tree and collected on a regular basis. Litterfall was collected and pooled by rain pH treatment prior to each rain event and a seasonal total was obtained.

Solution chemistry

Experimental applications of simulated acid rain were initiated in July, 1987. Fifteen rain applications were made during the 1987 season, 28 in 1988, 26 in 1989, and 22 during the 1990 season. The rain was applied over a time period of approximately 2.5 h and the average deposition per rain event for all four years was 28 mm.

Precipitation samples were collected using funnel collectors with three collectors in each chamber, one in each pH treatment. Throughfall was collected from V-shaped troughs (2 cm × 92 cm) that were positioned randomly beneath the canopy of each tree and emptied into 1-L collection bottles. Precipitation and throughfall collectors were thoroughly washed and rinsed between events and put in place immediately prior to each rain event.

To obtain soil solutions, fritted-glass tension lysimeters (10-cm diameter; Arthur & Fahey 1993) were buried in the soil of each pot at two depths: two lysimeters just below the O_a horizon (approximately 5 cm deep) and two lysimeters at about 20-cm depth in the mineral soil. Pooled samples of the two lysimeters at each depth were obtained for each pot by applying 0.1 MPa of tension. Tension was applied to all lysimeters immediately prior to a simulated rain event. A spout was installed on the bottom of each pot to collect water that drained by gravity.

All water samples were collected immediately following rain events and returned to the laboratory for analysis of pH and NH_4^+ within 24 h. Solution pH was measured using a combination glass electrode on a Markson pH meter and NH_4^+ on a continuous flow analyzer (CFA) using the phenol-nitroprusside method. Subsamples were sealed in glass ampules for oxidation of dissolved organic carbon (Menzel & Vaccaro 1964) and subsequently analyzed on a CO_2 coulometer (Huffman 1977).

Total monomeric Al was determined within 48 h of collection on the CFA by the pyrocathecol violet method. Non-labile forms of monomeric Al (organic complexes) were fractionated using a cation exchange column and analyzed colorometrically (Driscoll 1984). Labile monomeric Al (inorganic Al complexes) was calculated as the difference between total and non-labile monomeric Al.

Inorganic anions (Cl^-, NO_3^-, and SO_4^{2-}) were stored at 10 °C and analyzed within 3 weeks of collection on an ion chromatograph (Dionex 2000i series instrument). Following storage at 10 °C for up to 9 months, cations were measured by ICP.

Nutrient flux through the plant-soil system was calculated from the product of elemental concentrations and estimated water flux for the different ecosystem strata. Rainfall and throughfall water flux were estimated from weight changes of the weighing lysimeters which allowed for volume corrections due to canopy evaporation (Sayre and Fahey, in preparation). Water flux from the bottom of the pot was measured directly as drainage water volume. Water volumes from lysimeter collectors were not considered adequate estimates of water flux in the soil, and a hydrologic model (Simmons 1991) for these pots was employed to estimate water flux through the soil profile. Element fluxes for each red spruce pot were summed over all rain applications to obtain a total seasonal flux and then averaged by pH treatment.

Nutrient and proton budgets

Nutrient budgets were calculated for each sample tree and averaged by pH treatment for each year of the study. Nutrient incorporation into new growth of stems, branches, roots, and foliage and changes in nutrient storage in older tissues were calculated by multiplying element concentrations of the various tissues by the total biomass for each year class. Coarse roots were assumed to grow at a rate proportional to aboveground woody stems ($r^2 = 0.43$; $p < 0.05$), and fine root biomass was estimated using the regression based on coarse root biomass.

Nutrient requirement was defined as the quantity of a nutrient incorporated into annual biomass increment plus canopy leaching (Waring & Schlesinger 1985). Nutrients for new growth are acquired by root uptake and by resorption of nutrients from old and senescing tissues. Nutrient resorption was calculated from the difference in nutrient concentrations between old and new tissues and between green and senescent needles (Fahey & Birk 1991). Resorption of nutrients from old to new tissues was determined for foliage and stems, but redistribution from senescing to live tissues was determined for foliage only. Resorption from roots was not considered. Nutrient uptake was calculated as the difference between nutrient requirement and resorption. Nutrient requirement, resorption, and uptake were calculated for each tree and averaged by rain pH treatment.

Soil nutrient pools were calculated as the product of measured exchangeable cation concentrations and soil mass for each horizon (O_a, B_s, and bulk B_s) for each of the weighing lysimeter pots. Measurements of the organic soil mass were made at the initiation of the experiment from depth measurements at several locations in each pot and bulk density measurements on soil cores from the field site. Mineral soil mass was determined by measuring the difference in pot weights at field capacity and at a water potential of −1.5 MPa and then converted to soil mass using data on bulk density and water holding capacity. The upper B_s horizon was assumed to be 10 cm deep in each pot, and the mass of the bulk B_s was calculated by difference.

We constructed proton budgets for 1987 and 1990 for each red spruce "ecosystem" and averaged these by rain pH treatment to compare the effects of increased atmospheric loading on soil acidification in relation to acidity generated through internal nutrient cycling processes. We used the method described by Binkley (1992), which focuses on changes in the H-ion content of the soil exchange complex. The accounting scheme suggested by Binkley (1992) quantifies the replacement of base cations on the soil exchange complex by H-ions using six budgetary ($\mathrm{kmol_c\ ha^{-1}\ yr^{-1}}$) measurements:

(1) $H_{(in)}$ minus $H_{(out)}$
(2) $Al_{(in)}$ minus $Al_{(out)}$
(3) $NH_{4(in)}$ minus $NH_{4(out)}$
(4) $NO_{3(out)}$ minus $NO_{3(in)}$
(5) $SO_{4(out)}$ minus $SO_{4(in)}$
(6) Cation Increment

The fluxes are written so that a positive value indicates H-ion additions to the exchange sites and a negative value represents H-ion removal. The sum of the above elemental fluxes is a measure of the overall net H-ion load to the system. We calculated the H-ion budget for each of the three soil horizons as defined in our experimental system (O_a, B_s, and bulk B_s). In addition, we assessed canopy processing of acids using the flux relationships described above assuming that the same exchange mechanisms apply to foliage.

Statistical analysis

The experimental design was a 4 × 3 × 3 factorial conducted in split-plots with randomized blocks; the four levels of O_3 were the main plots and the three rain pH treatments were the sub-plots (Sokal & Rolf 1981). Orthogonal contrasts were used if the ANOVA indicated significant variation among treatments. All statistical analyses incorporated the above design and were performed using SAS on an IBM mainframe computer.

Results

Pre-treatment soil properties

Strong vertical stratification of the chemical and physical soil characteristics was observed with an especially abrupt change between the organic and mineral horizons (Table 1). Organic matter, exchangeable nutrient pools, and CEC were lower in the mineral soil horizons, and exchangeable Al concentrations and pH were higher in the mineral horizons. Calcium was the predominant cation on the exchange complex in the organic soil horizon, whereas Al occupied a greater proportion of the exchange sites in the mineral soil. All three soil horizons had a low affinity for SO_4^{2-} (Table 2).

Soil chemistry responses

Significant treatment effects of rain pH on soil pH were observed after the second year of treatments with significantly lower pH in the high acid treatment (Table 3). This was most pronounced in the organic soil horizon, but significant differences also were observed in the mineral soil. By 1990, soil pH in the high acid rain treatment was greatly depressed in both the organic and mineral soil. Soil pH changed little in the pH 4.1 and 5.1 treatments and no significant differences were detected.

Organic matter concentration (loss-on-ignition) in the organic horizon decreased in all treatments over the four-year study with significantly greater decreases in the pH 3.1 treatment (pH 3.1 = 34.9% O.M.; pH 4.1 = 40.6% O.M.; pH 5.1 = 45.7% O.M. in 1990). Organic concentration of the mineral soil remained constant among treatments and years.

Significant differences were observed in exchangeable pools of cations both among rainfall treatments and years. Calcium and Mg concentrations were significantly lower in the organic horizon of the pH 3.1 treatment as compared to the pH 4.1 and 5.1 treatments after the second year (1988, Fig. 1). Concentrations declined in subsequent years and strong rain pH treatment effects persisted throughout the study. Calcium and Mg concentrations in the mineral soil were variable among years, but no significant rain pH effects were observed. Soil pools of K were not influenced by rain pH treatments.

Table 1. Chemical and physical properties of three horizons of experimental soils prior to treatments of acid precipitation.

Soil horizon	Bulk density (kg/m^{-3})	Soil depth (m)	Loss on ignition (%)	pH (water)	CEC (cmol/kg)	% base saturation	Extractable elements (mmol/kg soil)			
							K	Ca	Mg	Al
O_a	180	0.04	72.5	3.85	8.21	82	4.05	47.90	11.30	0.48
B_s	770	0.10	12.0	4.79	3.55	11	0.51	2.60	0.50	9.80
Bulk Bs	770	0.28	9.6	5.20	2.79	30	1.30	5.91	0.97	6.60

Table 2. Sulfate adsorbed or released by three soil horizons equilibrated with solutions of differing sulfate concentrations prior to experimental applications of acid precipitation.

SO_4 added (mmol/kg)	SO_4 adsorbed/desorbed (mmol/kg)		
	O_a	B_s	Bulk B_s
0	-1.65	-0.47	-0.23
0.01	-1.75	-0.21	-0.16
0.05	-1.79	-0.31	-0.22
0.10	-1.94	-0.15	-0.27
0.50	-1.66	0.10	0.00
1.0	-1.36	0.27	0.16
5.0	-3.07	0.92	0.68
10.0	-5.39	1.12	0.94

Table 3. Soil pH of three soil horizons in red spruce pots measured prior to and during three years of exposure to rainfall of three different pH treatments.

Rain treatment	Soil horizon	1988	1989	1990
pH 3.1	O_a	4.19**	4.21**	4.03**
	B_s	4.94	4.84**	4.39**
	Bulk B_s	5.06	5.03	4.36**
pH 4.1	O_a	4.46	4.49	4.62
	B_s	5.12	5.07	4.87
	Bulk B_s	5.29	5.15	4.91
pH 5.1	O_a	4.50	4.44	4.89
	B_s	5.26	5.07	5.06
	Bulk B_s	5.25	5.20	5.12

** = significant differences; $P < 0.01$, between treatments of the same horizon.

Over time, concentrations of K in the O_a horizon increased markedly, while they decreased significantly in the upper B_s horizon in 1989, and remained constant in the deep mineral soil.

Exchangeable pools of Al increased significantly in the organic soil in response to strong acid loading (Fig. 1). Exchangeable pools of aluminum in the mineral soil increased each year and, although no significant rain pH treatment effects were detected, concentrations tended to be higher in the low pH treatment.

High rates of nitrogen mineralization and nitrification were observed in the Oa horizon of the untreated pots in 1987 and 1988 (mean mineralization rate = 403 mg N kg^{-1} soil yr^{-1} and mean nitrification rate = 300 mg N kg^{-1} soil yr^{-1}) with much lower rates in the mineral soil (mean mineralization rate = 87 and nitrification = 67 mg N kg^{-1} soil yr^{-1}). Measured rates were significantly lower in both the organic and mineral soil horizons in 1989 and 1990. In the organic horizon, N mineralization averaged only 174 mg N kg^{-1}

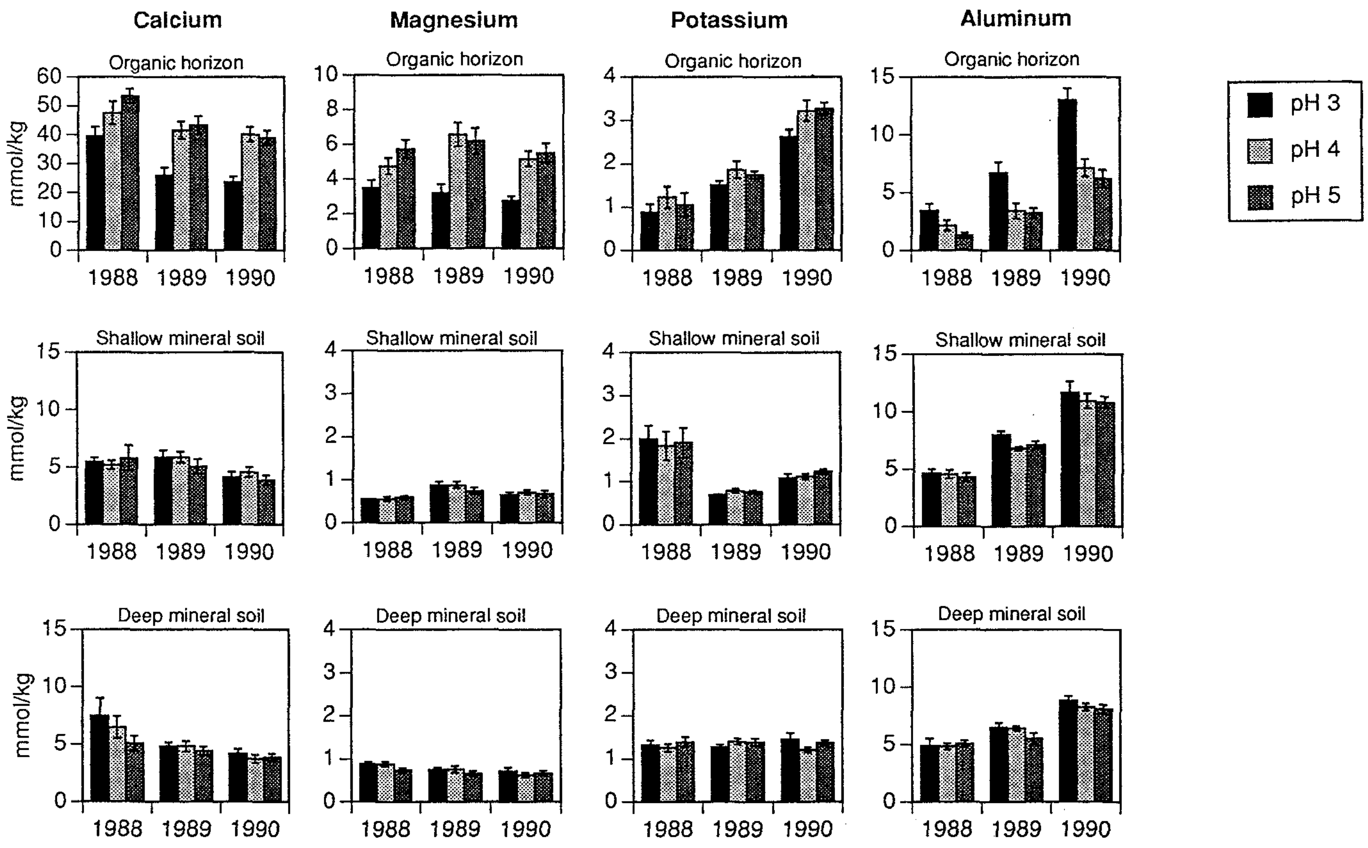

Fig. 1. Exchangeable cation concentrations (mmol kg^{-1}) of three soil horizons in miniature red spruce ecosystems exposed to precipitation of pH 3.1, 4.1, and 5.1 for two (1988), three (1989) and four (1990) years. Error bars indicate standard error of the mean.

soil yr^{-1} and nitrification only 67 mg N kg^{-1} yr^{-1} in 1989 and 1990. Nitrogen mineralization rates in the mineral soil were 14.0 mg N kg^{-1} soil yr^{-1} and nitrification averaged 8 mg N kg^{-1} yr^{-1}. No differences among rain pH treatments were observed.

Throughfall chemistry

A detailed analysis of the throughfall chemistry data is presented elsewhere (Sayre & Fahey, in preparation), and we present only a brief summary here. Throughfall solutions were enriched relative to rainfall solutions for most elements and consistent patterns were observed among years (Table 4). Rain pH treatments significantly affected throughfall chemistry for most solutes. Canopy leaching was enhanced in the pH 3.1 treatment and no significant differences were observed between the pH 4.1 and 5.1. The higher solute concentrations observed for elements in 1989 and 1990, as compared to 1987, can be attributed in part to the larger canopy biomass and surface area.

Soil solution chemistry

Concentrations of NO_3^- in soil solutions were initially very high in all treatments; despite greater than fifteen-fold differences in NO_3^- loading, NO_3^- concentrations were not different between treatments in 1987 (Table 4). However, during the final two years of experimental treatments, significant effects were observed with greater NO_3^- concentrations in the pH 3.1 treatment; NO_3^- concentrations in the pH 4.1 and 5.1 treatments were near detection limits.

Sulfate concentrations were significantly higher in the pH 3.1 treatment at all soil depths reflecting the high SO_4^{2-} in that treatment (Table 4). Concentrations increased significantly from 1987 to 1989–1990 in the pH 3.1 treatment (Table 4). Despite relatively small differences in SO_4^{2-} loading between the pH 4.1 and 5.1 treatments, mineral soil solution SO_4^{2-} concentrations were significantly higher in the pH 4.1 treatment during the latter years. Concentrations of Cl and DOC did not exhibit any response to rain pH treatments over the four years.

No significant rain pH treatment effects on the base cations were detected during the 1987 season, but in subsequent years, increased leaching of Ca^{2+}, Mg^{2+}, and to a lesser extent K^+, was observed in the low pH treatment (Table 4). There were also significantly higher concentrations of Ca^{2+} and Mg^{2+} in the pH 4.1 than the pH 5.1 treatment for the mineral soil solutions. Calcium was the predominant cation in all soil solutions throughout the duration of the study. No pH treatment effects were detected for concentrations of Na.

Soil solution pH was significantly lower in the pH 3.1 treatment than the pH 4.1 and 5.1 treatments in all years whereas no differences were detected between the latter treatments (Table 4). The pH of forest floor leachate and drainage solutions decreased significantly from 1987 to 1989–1990, especially in the pH 3.1 treatment.

Total and labile Al concentrations exhibited a strong response to rain pH treatments in 1989–1990, whereas the organically bound Al fraction showed no response (Table 4). Again, the pH 3.1 treatment was significantly different from the higher pH treatment. There was also a significant early response (i.e. in 1987) of total and labile Al concentrations in the drainage solutions. Soil solution concentrations of Al increased over the four year study in the pH 3.1 treatment.

Biomass and foliage chemistry

The red spruce saplings grew rapidly over the four-year study, and average total biomass more than doubled from an initial dry weight of 2660 g (range = 1414–4881 g) to 6492 g (range = 4867–8817 g) after the final year of treatments. Biomass increment was not different among rain pH treatments during the first three years. In 1990, aboveground biomass increment in the pH 3.1 treatment (715.3 ± 32.9 g) was significantly higher, but no differences between the pH 4.1 and 5.1 treatments were detected (596.5 ± 22.5 and 628.0 ± 32.2 , respectively).

Root expansion was restricted by confinement in the pots. After rapid inital growth in 1986 and 1987, root growth slowed as no new soil was available for exploitation. Excavations of the root systems of the experimental trees showed that a very large root mass had developed throughout the Bulk B_s horizon. Because this horizon was root-free at the beginning of the experiment, these were all new roots. Coarse roots (> 1.0 mm diameter) were primarily limited to the surface organic horizons (85%) whereas a higher proportion of the fine roots (71%) was distributed in the mineral soil. No quantitative information was available on longevity or turnover rates of fine roots in this study.

Averaged over pH treatments, concentrations of N in foliage showed a significant decline from 1.9% in 1987 to 0.7% in 1990 and K concentrations decreased from 0.67% to 0.4%. Calcium concentrations (0.39%) showed an initial decrease but then remained relatively constant (0.30%) and S concentrations (0.12%) did not change throughout the study. Nutrient concentrations in the fine roots showed similar changes as the foliage with the exception of Al which increased in the mineral soil fine roots as the study progressed (0.4% in 1987 and 0.9% in 1990). The only significant rain pH treatment effect was observed on foliage and root tissue N concentrations in 1989 with higher concentrations in the low pH treatment ($p < 0.05$).

Nutrient budgets

Nutrient budgets were calculated for Ca, K, and N for the 1987 and 1990 seasons to compare nutrient flux, uptake, and changes in soil pool size across

Table 4. Changes in solute concentrations during passage through red spruce "ecosystems" as affected by rain pH treatments.

	Rainfall			Throughfall			O_a soil horizon		
	pH 3.1 ± s.e.	pH 4.1 ± s.e.	pH 5.1 ± s.e.	pH 3.1 ± s.e.	pH 4.1 ± s.e.	pH 5.1 ± s.e.	pH 3.1 ± s.e.	pH 4.1 ± s.e.	pH 5.1 ± s.e.
1987 Season									
pH	3.10 a	4.10 b	5.10 c	3.20 a	4.30 b	5.10 c	4.21 a	4.64 b	4.53 b
K	0.17 ± 0.05	0.20 ± 0.05	0.18 ± 0.05	0.97 ± 0.10	0.88 ± 0.09	0.96 ± 0.08	3.64 ± 0.37	4.02 ± 0.46	2.51 ± 0.35
Ca	0.34 ± 0.02	0.39 ± 0.02	0.30 ± 0.03	2.81 ± 0.34a	1.53 ± 0.15b	1.83 ± 0.45b	25.41 ± 1.84	25.08 ± 3.47	18.58 ± 2.69
Mg	0.05 ± 0.00	0.06 ± 0.01	0.05 ± 0.01	0.45 ± 0.07a	0.24 ± 0.03b	0.26 ± 0.04b	6.06 ± 0.62	5.29 ± 0.75	4.18 ± 0.71
Al-total	0.03 ± 0.00	0.03 ± 0.01	0.03 ± 0.01	0.04 ± 0.01	0.04 ± 0.04	0.04 ± 0.04	0.89 ± 0.13	0.59 ± 0.31	0.49 ± 0.16
Al-organic	–	–	–	–	–	–	0.26 ± 0.03	0.35 ± 0.04	0.40 ± 0.04
Al-labile	–	–	–	–	–	–	0.68 ± 0.14	0.24 ± 0.19	0.09 ± 0.04
Na	0.68 ± 0.00	0.63 ± 0.01	0.54 ± 0.01	1.08 ± 0.05	0.91 ± 0.05	0.86 ± 0.04	7.25 ± 0.88	7.85 ± 1.74	6.57 ± 1.10
Cl	0.26 ± 0.03	0.30 ± 0.03	0.29 ± 0.05	0.55 ± 0.05	0.68 ± 0.04	0.76 ± 0.05	5.49 ± 0.78	6.06 ± 1.08	5.63 ± 1.07
NO_3-N	3.39 ± 0.10a	0.54 ± 0.07b	0.27 ± 0.06c	4.09 ± 0.22a	0.95 ± 0.11b	0.71 ± 0.14c	13.38 ± 2.72	20.44 ± 8.12	15.27 ± 6.04
SO_4-S	9.98 ± 0.31a	1.75 ± 0.29b	0.61 ± 0.11c	10.29 ± 0.11a	1.92 ± 0.05b	1.20 ± 0.10b	12.44 ± 0.65a	4.88 ± 0.49b	3.40 ± 3.88b
NH_4-N	0.32 ± 0.02	0.32 ± 0.03	0.33 ± 0.07	0.73 ± 0.04a	0.50 ± 0.03b	0.43 ± 0.03b	1.37 ± 0.38	0.73 ± 0.29	1.42 ± 0.45
DOC	0.64 ± 0.06	0.64 ± 0.05	0.74 ± 0.18	17.34 ± 4.06	17.99 ± 3.08	19.57 ± 4.36	25.78 ± 3.18	27.04 ± 8.45	37.83 ± 3.77
1989 + 1990 Season									
pH	3.10 a	4.10 b	5.10 c	3.20 a	4.48 b	5.01 c	3.79 a	4.27 b	4.24 b
K	0.19 ± 0.05	0.17 ± 0.05	0.19 ± 0.05	1.81 ± 0.16	1.92 ± 0.25	1.86 ± 0.28	1.31 ± 0.22	1.08 ± 0.24	0.82 ± 0.18
Ca	0.35 ± 0.02	0.35 ± 0.02	0.32 ± 0.03	3.26 ± 0.17a	2.10 ± 0.08b	1.70 ± 0.09c	19.48 ± 0.83a	7.24 ± 0.61b	6.34 ± 0.45b
Mg	0.06 ± 0.00	0.06 ± 0.01	0.06 ± 0.00	0.38 ± 0.02a	0.28 ± 0.01b	0.25 ± 0.02b	2.91 ± 0.17a	1.04 ± 0.08b	1.15 ± 0.12b
Al-total	0.05 ± 0.00	0.05 ± 0.01	0.05 ± 0.01	0.06 ± 0.01	0.07 ± 0.00	0.06 ± 0.00	1.60 ± 0.30a	0.92 ± 0.05b	0.85 ± 0.06b
Al-organic	–	–	–	–	–	–	0.58 ± 0.05	0.55 ± 0.05	0.55 ± 0.06
Al-labile	–	–	–	–	–	–	1.02 ± 0.09a	0.38 ± 0.06b	0.31 ± 0.03b
Na	0.56 ± 0.00	0.55 ± 0.01	0.51 ± 0.01	0.24 ± 0.01	0.26 ± 0.02	0.26 ± 0.02	3.06 ± 0.26	1.95 ± 0.24	2.23 ± 0.29
Cl	0.22 ± 0.03	0.23 ± 0.03	0.23 ± 0.05	1.65 ± 0.01	1.02 ± 0.06	1.26 ± 0.09	2.95 ± 0.29a	2.21 ± 0.27b	2.33 ± 0.28b
NO_3-N	3.41 ± 0.10a	0.55 ± 0.07b	0.31 ± 0.06c	3.50 ± 0.09a	0.93 ± 0.06b	0.69 ± 0.05c	1.87 ± 0.20a	0.14 ± 0.03b	0.10 ± 0.03b
SO_4-S	9.75 ± 0.31a	1.73 ± 0.27b	0.55 ± 0.10c	13.10 ± 0.18a	2.64 ± 0.06b	1.60 ± 0.07c	19.81 ± 0.86a	5.01 ± 0.43b	4.16 ± 0.37b
NH_4-N	0.29 ± 0.02	0.28 ± 0.03	0.30 ± 0.07	1.29 ± 0.07a	1.18 ± 0.22b	1.03 ± 0.27b	0.07 ± 0.02	0.01 ± 0.00	0.00 ± 0.00
DOC	0.68 ± 0.06	0.71 ± 0.05	0.65 ± 0.18	18.73 ± 2.88	20.46 ± 3.14	18.30 ± 2.95	35.09 ± 5.59	28.88 ± 2.26	32.13 ± 3.47

Table 4. (Continued).

	B soil horizon			Drainage		
	pH 3.1 ± s.e.	pH 4.1 ± s.e.	pH 5.1 ± s.e.	pH 3.1 ± s.e.	pH 4.1 ± s.e.	pH 5.1 ± s.e.
1987 Season						
pH	4.47	4.20	4.51	4.85 a	5.06 b	5.24 c
K	4.27 ± 0.21	3.60 ± 0.21	4.00 ± 0.23	2.85 ± 0.28a	1.46 ± 0.22b	2.36 ± 0.22b
Ca	36.68 ± 1.22	34.26 ± 1.63	30.69 ± 1.57	19.27 ± 1.60a	8.32 ± 0.68b	10.27 ± 1.57b
Mg	7.10 ± 0.21	6.24 ± 0.29	6.03 ± 0.29	3.26 ± 0.16a	1.59 ± 0.13b	1.69 ± 0.15b
Al-total	1.92 ± 0.10	1.49 ± 0.15	1.61 ± 0.11	0.57 ± 0.05a	0.45 ± 0.04b	0.36 ± 0.02c
Al-organic	0.24 ± 0.02	0.27 ± 0.01	0.25 ± 0.02	0.25 ± 0.03	0.34 ± 0.01	0.30 ± 0.02
Al-labile	1.68 ± 0.18	1.24 ± 0.16	1.36 ± 0.19	0.32 ± 0.09a	0.11 ± 0.02b	0.06 ± 0.02b
Na	6.80 ± 0.24	7.36 ± 0.25	6.69 ± 0.28	2.61 ± 0.21	3.01 ± 0.17	2.21 ± 0.20
Cl	8.39 ± 0.43	9.62 ± 0.49	9.10 ± 0.44	2.50 ± 0.21	1.69 ± 0.25	2.35 ± 0.19
NO_3-N	30.74 ± 1.30	27.90 ± 2.88	26.25 ± 3.32	10.82 ± 1.65a	4.18 ± 0.93b	5.05 ± 1.82b
SO_4-S	6.19 ± 0.23a	3.97 ± 0.11b	3.26 ± 0.13c	7.54 ± 0.63a	4.72 ± 0.58b	3.79 ± 0.14b
NH_4-N	0.27 ± 0.04	0.19 ± 0.04	0.33 ± 0.14	0.28 ± 0.21	0.23 ± 0.15	0.38 ± 0.23
DOC	16.72 ± 1.11	17.10 ± 0.84	18.74 ± 4.46	17.67 ± 1.40	18.66 ± 1.09	15.61 ± 1.35
1989 + 1990 Season						
pH	4.39	4.29	4.51	4.25 a	4.90 b	5.19 c
K	0.92 ± 0.13a	0.57 ± 0.05b	0.54 ± 0.09b	1.31 ± 0.07a	0.98 ± 0.05b	0.95 ± 0.04b
Ca	18.19 ± 0.85a	11.23 ± 0.86b	6.69 ± 0.44c	11.15 ± 0.26a	3.64 ± 0.16b	4.94 ± 0.44b
Mg	2.85 ± 0.21a	1.63 ± 0.16b	1.06 ± 0.08c	1.16 ± 0.04a	0.50 ± 0.03b	0.56 ± 0.03b
Al-total	1.68 ± 0.10	1.06 ± 0.06	1.84 ± 0.05	1.28 ± 0.07a	0.39 ± 0.02b	0.29 ± 0.02b
Al-organic	0.37 ± 0.03	0.35 ± 0.02	0.41 ± 0.15	0.24 ± 0.01	0.19 ± 0.01	0.17 ± 0.01
Al-labile	0.85 ± 0.08a	0.48 ± 0.03b	0.43 ± 0.04b	1.04 ± 0.06a	0.20 ± 0.01b	0.13 ± 0.01b
Na	5.56 ± 0.53	6.19 ± 0.72	3.37 ± 0.32	1.89 ± 0.15a	1.31 ± 0.12b	1.31 ± 0.10b
Cl	3.15 ± 0.25	3.58 ± 0.35	3.20 ± 0.31	2.27 ± 0.18a	1.71 ± 0.12b	1.85 ± 0.12b
NO_3-N	0.63 ± 0.07a	0.11 ± 0.04b	0.09 ± 0.03b	0.99 ± 1.11a	0.22 ± 0.03b	0.15 ± 0.02b
SO_4-S	17.78 ± 0.95a	8.26 ± 0.51b	5.97 ± 0.37c	13.18 ± 0.33a	3.42 ± 0.12b	3.07 ± 0.28b
NH_4-N	0.01 ± 0.01	0.00 ± 0.00	0.02 ± 0.01	0.12 ± 0.02	0.07 ± 0.02	0.05 ± 0.01
DOC	17.87 ± 1.00	21.66 ± 1.50	18.97 ± 1.43	10.45 ± 0.51	11.62 ± 0.52	12.61 ± 0.64

Data are presented for the first year of treatment (1987) and the average of the final two years. All concentrations are in mg/l except pH. Different letters following concentrations indicate significant differences among treatments ($p < 0.05$); no letters indicate no significant differences among treatments.

rain pH treatments (Fig. 2). Nutrient budgets were compiled for each pot and then means and standard errors calculated by rain pH treatment.

Root uptake and leaching flux of Ca in the organic soil horizon exceeded inputs via throughfall and litterfall in all treatments, and over the 4-year treatment period, Ca pools decreased by approximately 50% in the organic horizon in the low pH treatments, and by about 25% in the pH 4.1 and 5.1 treatments (Fig. 2a). Calcium pools increased in the shallow mineral soil over the period of study indicating that some of the Ca from the organic soil horizon was redistributed to the mineral soil. Calcium budgets also suggested the gross transport of Ca to the deep mineral soil, where it was partly retained.

During the 1987 season, Ca budgets were influenced by the disturbance effects, and vertical flux of Ca within the soil profile greatly exceeded root uptake. During the 1990 season, strong acid loading appeared to have a significant impact on Ca cycling and root uptake, and Ca flux through the canopy and soil was accelerated in the high acid treatment.

Responses of the K budget were much different than for Ca. The K budget for the forest floor horizon changed markedly through the four-year study: in 1987 leaching and uptake greatly exceeded returns whereas in 1990 returns exceeded forest floor leaching. Potassium removal by root uptake and leaching was nearly in balance with returns in 1990 (Fig. 2b). Exchangeable K pools in the shallow mineral soil more than doubled between 1987 and 1990 whereas pools in the deep mineral soil did not change. In 1990 the pools of K in biomass were much greater than exchangeable pools in the soil indicating high plant demands for this nutrient relative to supplies. Root uptake of K was lower in 1990 than in 1987 even though biomass increment was greater in 1990; this paradox can be explained by lower foliar K and higher percent retranslocation in 1990 than in 1987. Apparently nutrient demands for new growth were largely met through increased internal recycling of K. Resorption of K from older and senescing tissues supplied approximately 25% of the tree requirements in 1987 and 48–59% in 1990, with greater retranslocation in the pH 5.1 treatment. Foliar leaching increased in 1990 primarily due to the increase in foliar biomass; however, no rain pH treatment effects were observed. Significantly more K was taken up by the trees in the pH 3.1 treatment during the 1990 season. In both years, root uptake flux was greater than leaching flux suggesting that, even under conditions of high acid loading, tree uptake was a more important mechanism of K removal from the system.

In 1987, N mineralization rates exceeded plant demands and high soil leaching fluxes were observed (Fig. 2c). In contrast, in 1990 leaching of N through the soil profile was very low illustrating that biological uptake immobilized nearly all of the mineralized and added N. Although nitrogen leaching was slightly elevated in the pH 3.1 treatment in 1990, this flux was small in comparison to plant uptake. The magnitude of N accumulation in biomass also was significantly greater in the pH 3.1 treatment during the 1990 season. Root N uptake and plant requirements for N decreased in 1990

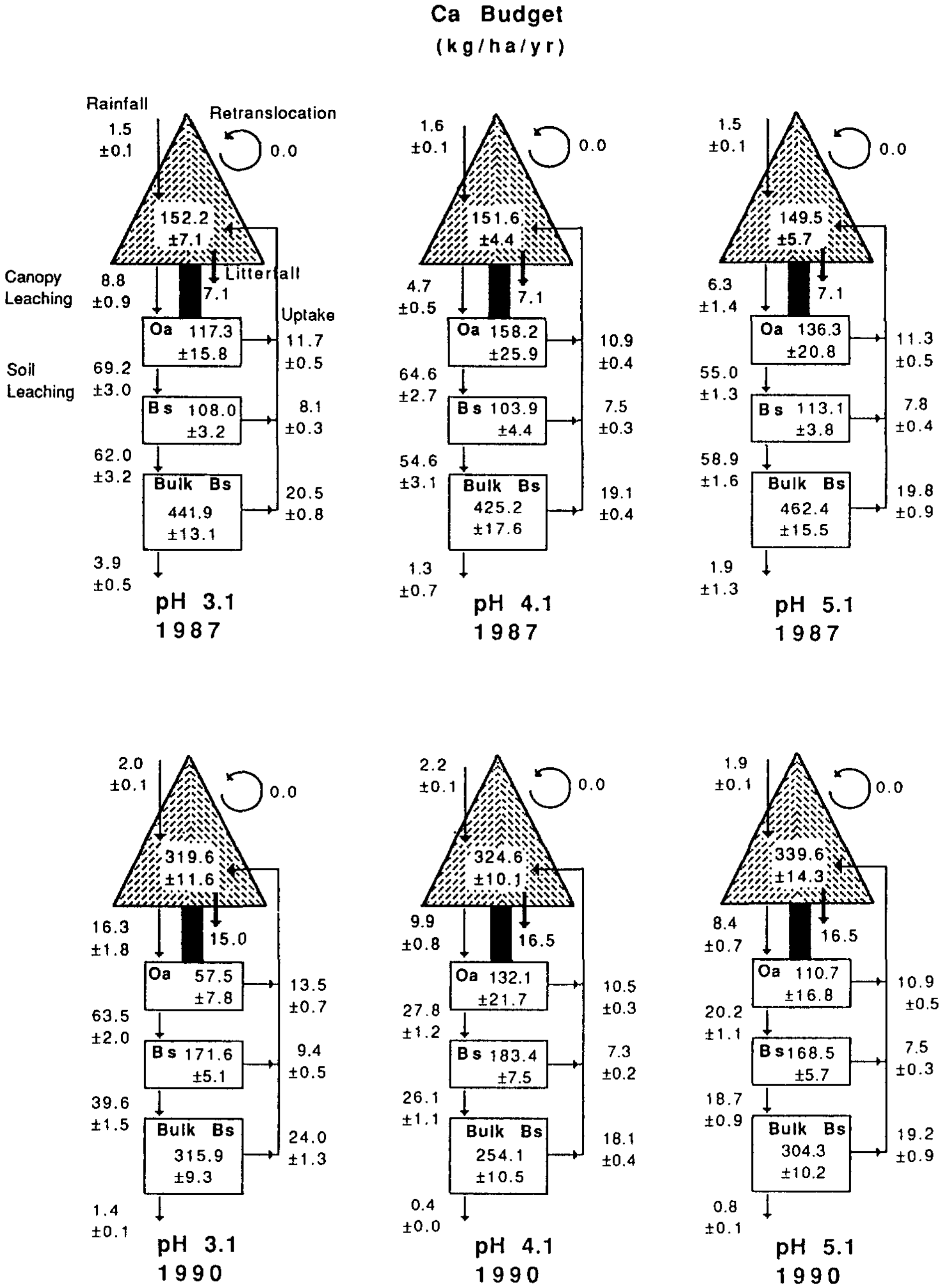

Fig. 2. Nutrient budgets of a) Ca, b) K, and c) N in miniature red spruce ecosystems exposed to acid precipitation of pH 3.1, 4.1, and 5.1 for 4 growing seasons. Budgets for the first and final year of treatments are presented. Values within the boxes represent total element pools and values outside the boxes are total element fluxes.

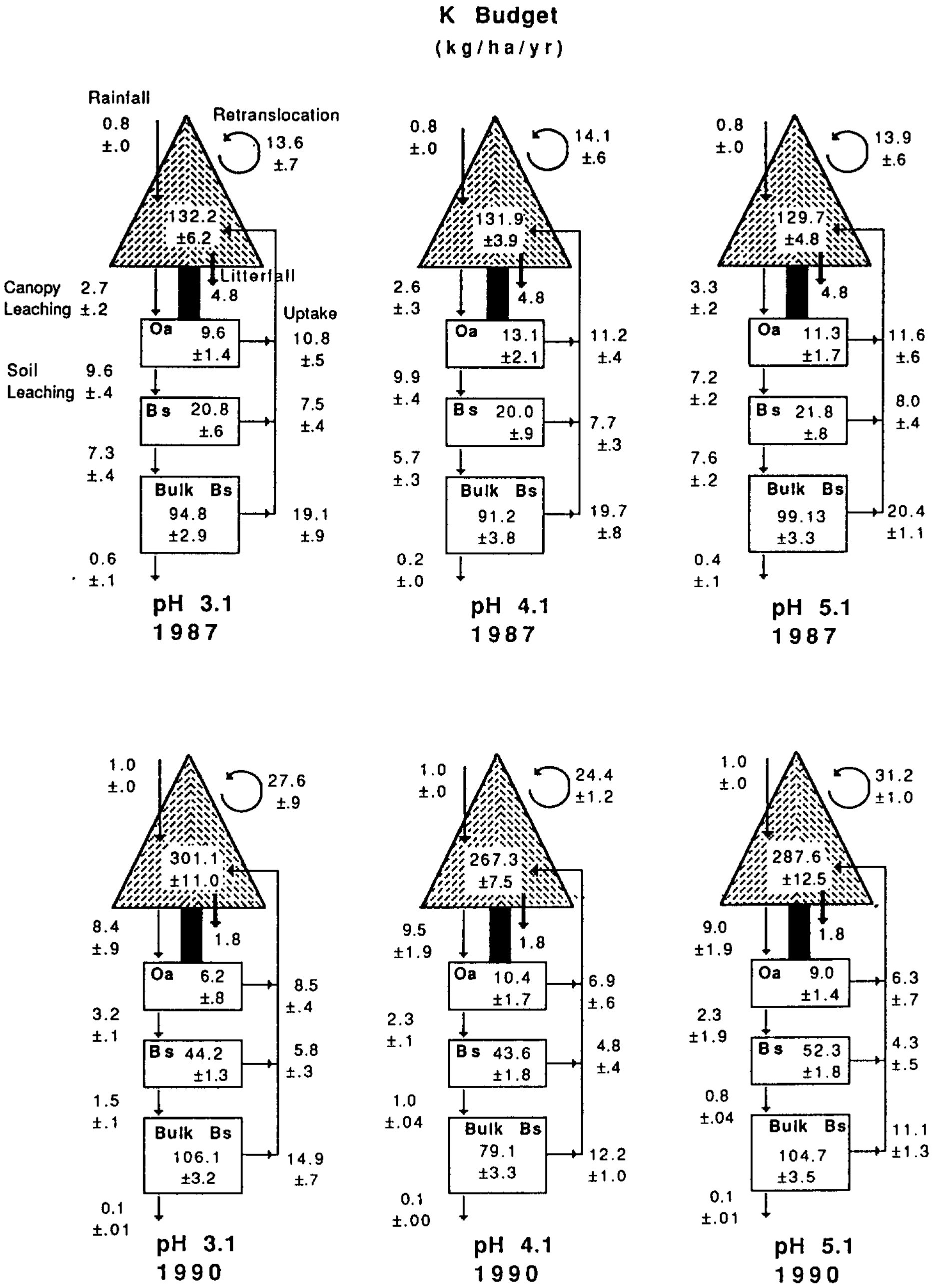

Fig. 2b. (Continued).

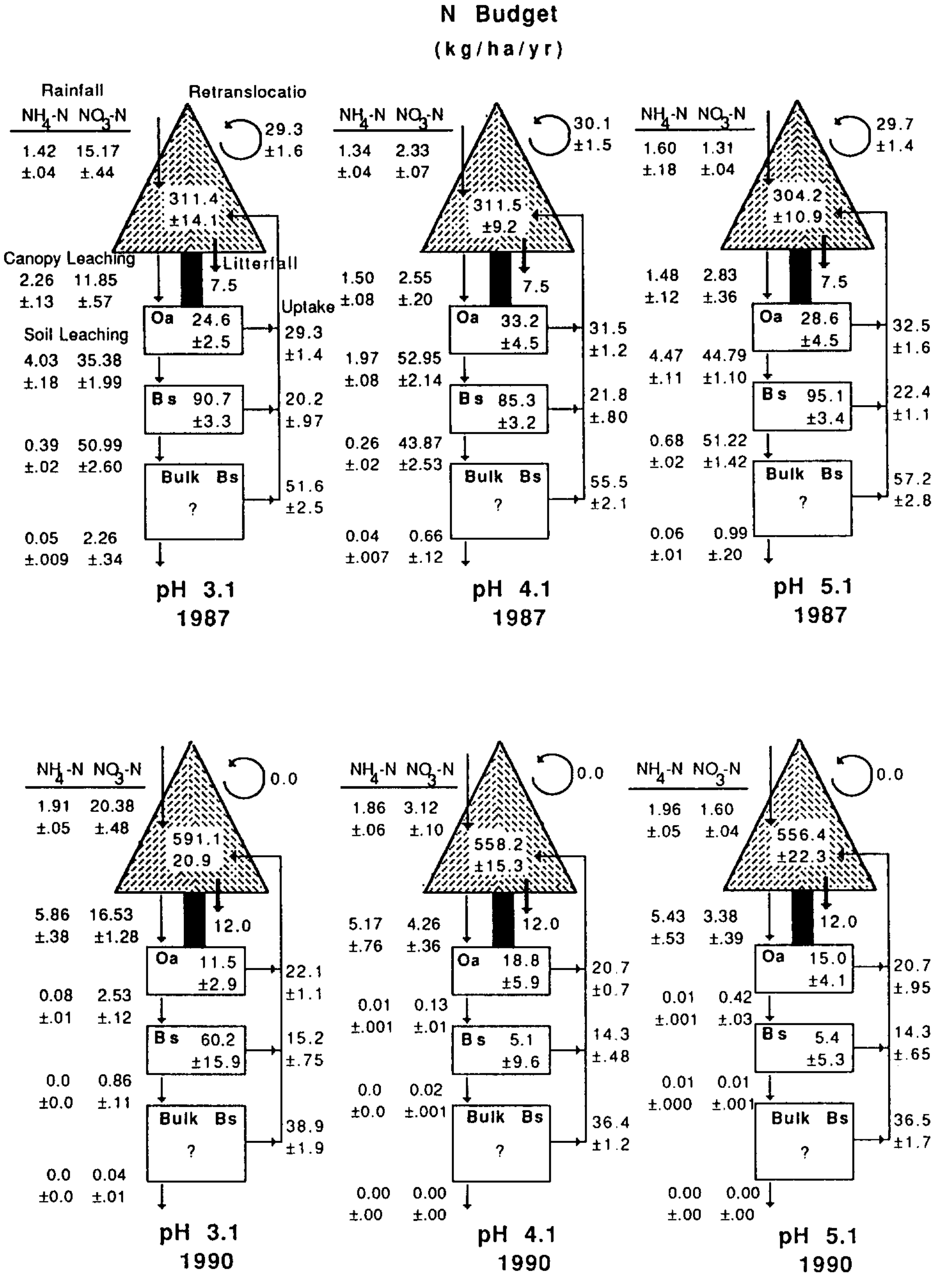

Fig. 2c. (Continued).

even though tree growth was greater than in 1987 mostly because foliar N concentrations declined. Resorption of N from senescing tissues provided approximately 22% of N requirements in 1987; however, in 1990 when N was most limiting, virtually no N was obtained through resorption. In the low pH (high N loading) treatment, some of the additional N required for new growth apparently was obtained through canopy absorption of NO_3^- from precipitation.

Proton budgets

Using the approach of Binkley (1992; see methods), we constructed proton budgets for each red spruce "ecosystem", and means and standard errors were calculated by pH treatment. The canopy neutralized a large portion of the acidity from precipitation (Table 5). Neutralization occurred primarily through the direct retention of H-ion in the foliage, although H-ion flux associated with canopy retention of both NO_3^- and SO_4^{2-} during the 1987 season and retention of NO_3^- and leaching of NH_4^+ from foliage in 1990 also neutralized a substantial portion of the acidity.

Net H-ion flux in the organic horizon was highly positive in all treatments and years indicating net retention of acidity in this soil horizon (Table 5). In 1987, net H-ion flux the organic horizon was significantly greater than in 1990 but there were no significant differences among treatments. In 1990, net H-ion flux in the forest floor of the pH 3.1 treatment was significantly greater than in the pH 4.1 and 5.1 treatments.

In 1987, H-ion flux associated with NO_3^- leaching constituted the largest source of acidity in the organic horizon in the pH 4.1 and 5.1 treatments, but in the pH 3.1 treatment, H-ion flux associated with strong acid loading was a larger source of acidity. Considerable acidity was generated in all treatments in 1987 as a result of high nitrification rates and consequent net NO_3^- losses; up to 3.6 kmol H^+ ha^{-1} yr^{-1} was generated in the organic soil horizon. In contrast, in 1990, NO_3^- was retained in the forest floor in all treatments, resulting in a net removal of H-ions from this soil horizon.

Accumulation of nutrient cations in biomass also was an important source of H-ion input to the soil, generating approximately 1.0 kmol H^+ ha^{-1} yr^{-1} in the forest floor in all treatments in both years. A significantly greater amount of acidity was generated in the pH 3.1 than the pH 4.1 and 5.1 treatments due to biomass accumulation in 1990 as compared to the pH 4. 1 and 5.1 treatments (Table 5).

During the 1990 season, cation accumulation in biomass represented the largest source of acidity in the pH 4.1 and 5.1 treatments. In the pH 3.1 treatment, cation exchange processes in the organic horizon accounted for 1.9 kmol H^+ ha^{-1} yr^{-1} of acidity, more than that associated with cation accumulation in biomass which generated 1.2 kmol H^+ ha^{-1} yr^{-1} in the organic soil horizon. Sulfate leaching was an important source of acidity (1.0 $kmol_c$ ha^{-1}) in the pH 3.1 treatment during 1990 but was largely offset by plant uptake of NO_3^-

which neutralized 0.95 kmol_c ha^{-1} yr^{-1}. Increased Al leaching in the pH 3.1 treatment neutralized another 1.38 kmol H^+ ha^{-1}.

Net proton flux in the mineral soil horizons was variable. Net H-ion balances that were both positive (acidifying) and negative (neutralizing) were observed among treatments and years. Cation accumulation in biomass usually generated more acidity than the element input-output balances. An exception was NO_3^- leaching in the shallow mineral soil in the pH 3.1 treatment during the 1987 season which contributed a greater amount of acidity than cation accumulation in biomass. In 1990, retention of H-ions and Al through cation exchange processes also contributed a substantial portion of the H-ion flux in the pH 3.1 treatment. Nitrogen retention in the deep mineral soil during 1987 was an important neutralizing mechanism in all treatments. Sulfate adsorption in the mineral soil neutralized a substantial amount of acidity in the pH 3.1 treatment both years and in the deep mineral soil of the pH 4.1 and 5.1 treatments during 1990.

Discussion

Hydrogen ion loading via precipitation in the pH 3.1 treatment averaged 4.95 kmol H^+ ha^{-1} yr^{-1}, 0.56 kmol H^+ ha^{-1} yr^{-1} in the pH 4.1 treatment, and 0.06 kmol H^+ ha^{-1} yr^{-1} in the pH 5.1 treatment. Hydrogen ion inputs at the Hubbard Brook Experimental Forest in New Hampshire, U.S., have been measured at 0.96–1.18 kmol_c ha^{-1} yr^{-1} (Driscoll and Likens 1982), and levels of acid loading at the different sites of the Integrated Forest Study ranged from 0.2–2.0 kmol_c H^+ ha^{-1} yr^{-1} (Schaefer et al. 1992a). Thus, our low pH treatment received higher hydrogen ion loading than even the most polluted sites in the US, whereas levels of H-ion loading in our pH 4.1 treatment were lower than most eastern US forests.

Soil and soil solution chemistry

We anticipated accelerated leaching of cations from the soils in response to strong acid loading as demonstrated previously (e.g., Cronan 1980; Stuanes et al. 1988; Kreutzer et al. 1989). The lack of a treatment effect on cation leaching during the first year of experimental applications can be explained by the high internal production of NO_3^- that resulted from the disturbance associated with the transplanting of the trees. Rapid mineralization of dead fine roots and decay of residual forest floor apparently fueled nitrification resulting in very high soil solution NO_3^- concentrations and consequent H-ion fluxes in the pots. Any treatment effects were masked by this large internal source of acidity (Table 4). Solution concentrations of NO_3^- and cations were highly correlated during the first year of experimental treatments ($r = 0.96$) suggesting that NO_3^- was the mobile anion regulating cation transport through the soil profile (Johnson & Cole 1980).

Table 5. Proton budgets of red spruce "ecosystems" exposed to acid precipitation of pH 3.1, 4.1, and 5.1 for four-consecutive growing seasons. Budgets are presented for the first and final years of experimental treatments (kmol$_c$ ha^{-1} yr^{-1} ± standard error). See text for a complete explanation of budgeting procedures.

Budgetary component	1987			1990		
	pH 3.1	pH 4.1	pH 5.1	pH 3.1	pH 4.1	pH 5.1
Canopy						
$H^+_{(in)}-H^+_{(out)}$	+1.40 ± 0.25	+0.23 ± 0.04	+0.02 ± 0.01	+2.08 ± 0.29	+0.43 ± 0.05	+0.02 ± 0.02
$Al_{(in)}-Al_{(out)}$	+0.01 ± 0.00	+0.01 ± 0.00	+0.01 ± 0.01	+0.01 ± 0.00	+0.01 ± 0.00	+0.01 ± 0.00
$NH_{4(in)}-NH_{4(out)}$	–0.06 ± 0.03	–0.01 ± 0.02	+0.01 ± 0.02	–0.28 ± 0.11	–0.24 ± 0.22	–0.25 ± 0.56
$NO_{3(out)}-NO_{3(in)}$	–0.24 ± 0.08	+0.02 ± 0.05	+0.11 ± 0.09	–0.28 ± 0.22	+0.08 ± 0.11	+0.13 ± 0.11
$SO_{4(out)}-SO_{4(in)}$	–0.52 ± 0.19	–0.06 ± 0.03	+0.09 ± 0.06	+0.23 ± 0.34	+0.14 ± 0.06	+0.25 ± 0.13
Cation increment	–	–	–	–	–	–
Net H^+ flux	+0.59	+0.19	+0.24	+1.76	+0.42	+0.16
Organic soil						
$H^+_{(in)}-H^+_{(out)}$	+2.00 ± 0.36	+0.12 ± 0.04	–0.06 ± 0.01	+1.88 ± 0.22	–0.07 ± 0.03	+0.19 ± 0.04
$Al_{(in)}-Al_{(out)}$	–0.30 ± 0.17	–0.17 ± 0.06	–0.10 ± 0.04	–1.38 ± 0.20	–0.36 ± 0.07	–0.80 ± 0.06
$NH_{4(in)}-NH_{4(out)}$	+0.26 ± 0.04	+0.12 ± 0.02	+0.27 ± 0.03	+0.40 ± 0.10	+0.35 ± 0.21	+0.23 ± 0.09
$NO_{3(out)}-NO_{3(in)}$	+1.68 ± 0.29	+3.60 ± 0.58	+3.03 ± 0.29	–0.95 ± 0.22	–0.26 ± 0.08	–0.19 ± 0.11
$SO_{4(out)}-SO_{4(in)}$	–0.34 ± 0.08	+0.40 ± 0.03	+0.36 ± 0.05	+1.04 ± 0.36	+0.51 ± 0.16	+0.43 ± 0.22
Cation increment	+1.07 ± 0.05	+1.03 ± 0.04	+1.06 ± 0.05	+1.18 ± 0.06	+0.96 ± 0.02	+0.96 ± 0.05
Net H^+ flux	+4.37	+5.10	+4.56	+2.17	+1.13	+0.82
Shallow mineral						
$H^+_{(in)}-H^+_{(out)}$	+0.10 ± 0.02	+0.01 ± 0.01	+0.02 ± 0.01	+0.59 ± 0.10	+0.07 ± 0.02	+0.15 ± 0.02
$Al_{(in)}-Al_{(out)}$	+0.03 ± 0.03	+0.09 ± 0.03	+0.06 ± 0.03	+0.71 ± 0.11	+0.04 ± 0.07	+0.16 ± 0.03
$NH_{4(in)}-NH_{4(out)}$	+0.26 ± 0.04	+0.12 ± 0.02	+0.27 ± 0.03	+0.01 ± 0.03	–0.01 ± 0.01	–0.00 ± 0.00
$NO_{3(out)}-NO_{3(in)}$	+1.12 ± 0.35	–0.67 ± 0.31	–0.46 ± 0.28	–0.12 ± 0.03	–0.01 ± 0.00	–0.03 ± 0.01
$SO_{4(out)}-SO_{4(in)}$	–1.26 ± 0.21	–0.41 ± 0.07	–0.26 ± 0.04	–2.03 ± 0.32	–0.15 ± 0.16	+0.12 ± 0.04
Cation increment	+0.74 ± 0.03	+0.71 ± 0.03	+0.73 ± 0.04	+0.81 ± 0.04	+0.66 ± 0.02	+0.66 ± 0.04
Net H^+ flux	+0.99	–0.15	+1.28	–0.03	+0.96	+1.06
Deep mineral						
$H^+_{(in)}-H^+_{(out)}$	+0.06 ± 0.01	+0.05 ± 0.01	+0.05 ± 0.01	+0.09 ± 0.01	+0.13 ± 0.03	+0.07 ± 0.01
$Al_{(in)}-Al_{(out)}$	+0.34 ± 0.07	+0.31 ± 0.07	+0.31 ± 0.07	+0.46 ± 0.06	+0.31 ± 0.02	+0.23 ± 0.04
$NH_{4(in)}-NH_{4(out)}$	+0.02 ± 0.01	+0.02 ± 0.01	+0.04 ± 0.01	+0.00 ± 0.00	+0.00 ± 0.00	+0.00 ± 0.00
$NO_{3(out)}-NO_{3(in)}$	–3.48 ± 0.71	–3.09 ± 0.70	–3.59 ± 0.70	–0.58 ± 0.01	–0.01 ± 0.01	–0.00 ± 0.00
$SO_{4(out)}-SO_{4(in)}$	–0.52 ± 0.05	–0.34 ± 0.08	–0.33 ± 0.04	–2.62 ± 0.44	–1.04 ± 0.17	–0.95 ± 0.17
Cation increment	+1.88 ± 0.08	+1.81 ± 0.06	+1.87 ± 0.09	+2.07 ± 0.10	+1.69 ± 0.04	+1.69 ± 0.10
Net H^+ flux	–1.70	–1.24	–1.58	–0.58	+1.08	+1.04

As the disturbance effects subsided, NO_3^- concentrations decreased and SO_4^{2-} became the predominant anion in soil solutions, supplying approximately 80% of the electrical charge balance in the pH 3.1 treatment in 1989 and 1990. Sulfate was highly correlated with cations in soil solution for these years ($r = 0.87$). In the pH 4.1 and 5.1 treatments, organic acids also were an important leaching agent providing up to 40% of the anionic charge balance, as estimated by difference of the sum of measured cations and anions. The soils used in the present study had the low SO_4^{2-} adsorption capacity typical of coarse textured Spodosols (Johnson & Cole 1980), and thus the flux of SO_4^{2-} and associated cations through the soil profile was not much affected by this process.

Sulfate leaching from the organic horizon in the pH 3.1 treatment exceeded inputs via precipitation and increased over time indicating a gradual release of SO_4^{2-} from an internal S pool. Coincident declines in organic matter concentration of the forest floor in the low pH treatment suggested that decomposition rates were stimulated in this treatment and release of SO_4^{2-} to solution may have been stimulated as well. At Whiteface Mountain, New York, substantial release of SO_4^{2-} from the forest floor was attributed to mineralization from organic S pools (Johnson et al. in press). Increased mineralization rates may have resulted from a fertilization effect on microbial biomass associated with the high N loading in the pH 3.1 treatment.

Calcium was the dominant cation in soil solutions, as would be expected from its high concentration on the soil exchange complex (Reuss & Johnson 1986; Binkley et al. 1989; Johnson 1992a). Several studies have demonstrated that leaching of the divalent cations, Ca^{2+} and Mg^{2+}, is highly responsive to additions of acid inputs, and these two cations will dominate soil solutions as long as they also dominate the soil exchange complex (Cronan 1980; Kreutzer et al. 1989; Stuanes et al. 1988). In this study, the very high atmospheric loading in the pH 3.1 treatment resulted in expected leaching responses of Ca^{2+} and Mg^{2+}.

More surprising was the significantly higher Ca^{2+} and Mg^{2+} leaching observed in the pH 4.1 than the pH 5.1 treatment. Previous studies have reported accelerated cation leaching associated with the most intensive levels of acid loading only ($pH \leq 3$) with little effect at higher pH treatments (Abrahamsen 1983; Fernandez & Rustad 1990). The long-term nature of our study combined with a large sample size and highly replicated design allowed us to detect a difference in cation leaching at more moderate levels of H-ion loading. Because levels of H-ion loading in our pH 4.1 treatment were lower than in most eastern U.S. forests, these results suggest that some eastern forests may be experiencing significantly higher losses of cations because of acid deposition.

Although Al was the dominant cation on the exchange complex in the mineral soil, Al concentrations were relatively low. Soil chemical responses to the high acid treatment were most prevalent in the organic soil horizon and proton budgets demonstrated that almost the entire H-ion load (up to 5.0

kmol H^+ ha^{-1} yr^{-1}) was neutralized in the upper soil profile with little acidity released to the mineral soil. Thus, the buffering effect of the organic soil horizon limited the amount of Al mobilized in the mineral soil. Long-term acid irrigation studies in forests of Norway and Germany also showed that acid effects were limited mostly to the organic horizon as soil pH, base saturation, and exchangeable pools of Ca^{2+} and Mg^{2+} decreased in the upper soil profile in response to the most intensive acid treatments but the mineral soil was not effected (Kreutzer et al. 1989; Stuanes et al. 1988).

Exchangeable Ca concentrations measured in organic soil horizons in northeastern U.S. spruce forests range from about 20–70 mmol kg^{-1} Ca (extracted with 1 M KCL or 1 M NH_4Cl; Joslin et al. 1992) and in Germany are reported to be as low as 1 mmol kg^{-1} (1 M NH_4Cl; Hantschel et al. 1988). Exchangeable Ca concentrations of the organic horizon in the present study ranged from 20–55 mmol kg^{-1} (Fig. 1), but the soils were extracted with a less concentrated extractant (0.1 M NH_4Cl) and thus relatively high in Ca. Nevertheless, labile Al increased significantly in the low pH treatment, exceeding 1.0 mg L^{-1} in both the Oa and upper Bs (Table 3); however, Al^{3+} did not appear to pose any threat to the health of the trees because concentrations of Ca^{2+} were high in comparison to Al, and the ratio of Al:Ca and Al:Mg may be more critical to root function than the absolute concentration of Al^{3+} (Tomlinson 1990). Root damage and reduced foliar concentrations of Ca^{2+} and Mg^{2+} were observed in red spruce when the molar ratio of Al:Ca exceeded 1:1 (Thornton et al. 1987; Shortle & Smith 1988). In our study, molar ratios of Al:Ca never exceeded 0.3 and no reductions in foliar Ca^{2+} and Mg^{2+} were observed in the low pH treatment.

Nutrient budgets

Several recent studies have addressed the acid deposition-soil acidification question from a nutrient cycling perspective (Johnson et al. 1985; Foster et al. 1991; Johnson et al. 1991; Johnson & Lindberg 1992; Johnson et al. in press). The Integrated Forest Study (IFS) provided a comprehensive analysis of the effects of atmospheric deposition on nutrient cycling by comparing several forested ecosystems (Johnson & Lindberg 1992). The authors concluded that the biogeochemical cycling patterns of base cations at most of the sites had been altered by strong acid deposition as accelerated cation flux through the soil and foliage and enriched levels of Al^{3+} in soil solutions were observed (Johnson 1992b). However, the degree to which internal nutrient transfer processes such as root uptake, retranslocation, and litterfall were altered could not be adequately addressed.

It has been suggested that root uptake of nutrients should increase in response to increased concentrations of cations in soil solutions and thereby partially offset foliar cation leaching that may be accelerated by acid deposition (Johnson et al. 1985; Reuss & Johnson 1986). Johnson et al. (1985) speculated that rates of uptake and return increased by as much as two-fold in response to high acid loading in a deciduous forest in Tennessee. In the present study, the behavior of Ca^{2+} was highly responsive to acid rain inputs, but foliar concentrations of this nutrient did not differ among treatments. Thus, the trees were able to replace the foliar Ca^{2+} lost as a result of high canopy leaching in the low pH treatment. This was accomplished through accelerated root uptake because litterfall patterns and retranslocation patterns did not differ among treatments.

The response of K cycling to acid deposition differed from that of Ca partly as a result of differences in patterns of internal cycling and storage pools. Potassium cycling was relatively insensitive to additions of strong acids. Greater amounts of K were stored in tree biomass than in soil exchangeable pools, and root uptake and internal cycling processes dominated K dynamics. Biological demands for K are generally higher than for other cations and the biota can exert strong control over this nutrient (Vitousek 1977). For example, Cronan (1980) demonstrated that K^+ leaching from a soil was enhanced by additions of strong acids in the absence of plants, but when plants were present, no appreciable increase in K^+ leaching was observed. Soil leaching of K^+ was not influenced to a great extent by acid deposition in ecosystems of the IFS study but rather biological uptake and recycling exerted primary control (Johnson 1992a). The only impact of acid deposition on K^+ cycling in the present study was an indirect effect on root uptake rates which were comparatively higher in the pH 3.1 treatment in response to the N-stimulated tree growth.

Patterns of K cycling differed markedly among years. Uptake rates and nutrient concentrations were higher in the first year of study, when the disturbance effect predominated, than in later years. In 1990, the amount of K retranslocated almost doubled, uptake rates declined, and tissue concentrations decreased as compared to the 1987 season. Tissue concentrations were still in the range of values reported for healthy red spruce trees (Joslin et al. 1992), suggesting that sufficient levels of K^+ were probably secured throughout the experiment. The trees may have responded to the elevated levels of K^+ in soil solutions in the first year with luxury uptake of K^+, but no pretreatment foliage collections are available to investigate this hypothesis.

Patterns of N cycling differ from the base cation nutrients in part because plants are largely dependent upon the continuous supply of N from atmospheric and organic matter transformations rather than exchangeable stored pools (Binkley & Richter 1987; Johnson 1992c). The growth-stimulating effect of N in the present study coincided with greater uptake rates of other nutrient elements because no nutrient imbalances were evident. Thus, despite accelerated leaching losses of Ca^{2+} in the high acid treatment, and a general decline in soil base status, no impairment of plant nutrition was detected. Tissue concentrations of Ca^{2+}, and K^+ all remained within the range of values reported for healthy red spruce (Joslin et al. 1992).

Although trees in the high acid (and high N deposition) treatment showed significantly higher foliar N concentrations in 1989, by the final year of the study foliar N levels had decreased far below those reported for healthy red spruce trees in all treatments (Joslin et al. 1992). The potential for N limitation in our experimental system was anticipated as a result of the rapid growth rate of these trees and the confinement of the roots to the limited soil volume of the pots. Apparently, N levels were so low that foliar N retranslocation was not possible and little or no N for new growth was supplied internally. Thus, tree growth was probably partly constrained by N limitation in all the treatments.

Proton budgets

Consumption of H-ions in the canopy was an important neutralizing mechanism in our experimental system and can be an important process in many forested ecosystems (Schaefer et al. 1992b). In the present study, retention of H-ions coincided with cation enrichment of throughfall solutions and cation exchange was a prominent buffering mechanism reducing external H-ion inputs to the forest floor. However, to compensate for foliar cation losses, root uptake was accelerated and the internal generation of H-ions subsequently increased. Neutralization in the canopy also resulted from protonation of organic acids leached from the canopy surface and retention of the principal strong acid anions, NO_3^- and SO_4^{2-}, in the canopy (Sayre & Fahey, in preparation). We were not able to determine the fate of the inorganic N and S in the canopy but it is possible that some of the apparently retained NO_3^- and SO_4^{2-} was converted to organic forms and subsequently lost to the forest floor (Lovett 1992). Unfortunately, organic N and S concentrations were not measured in rainfall and throughfall solutions of the present study.

Internal H-ion production associated with cation accumulation in biomass was large in comparison to other reported values and was an important source of acidity in all treatments of the present study. Net H-ion flux associated with tree growth in an aggrading northern hardwood forest in New Hampshire was 0.51 $kmol_c\ ha^{-1}\ yr^{-1}$ (Driscoll & Likens 1982), in a lodgepole pine forest, 2.50 $kmol_c\ ha^{-1}\ yr^{-1}$ (Fahey & Knight 1986), and for the various IFS sites, 0.2 to 2.0 kmol $H^+\ ha^{-1}\ yr^{-1}$ (Binkley 1992), which are all less than the 3.2–4.1 kmol $H^+\ ha^{-1}\ yr^{-1}$ in the present study. The four-year average annual rate of biomass accumulation in our experimental systems (1,420 $g/m^2\ yr^{-1}$) was higher than would be expected in natural stands in our region at any time during stand development. For example, the most rapid biomass accumulation during the first 6 years of recovery following whole-tree harvest at Hubbard Brook, NH, was 1,180 g/m^2 (in year 5; Pu et al. 1993). Thus, the acidity generated by tree growth in this study probably exceeds that for most natural forests in the northeastern U.S.

Our estimates of H-ion flux associated with root uptake may be too high if a substantial amount of absorbed cations originated from decomposition because the H-ion release in root uptake would be balanced by an equivalent uptake of H-ion in the oxidation of the organic matter (Binkley 1992). For example, in an Engelmann spruce-subapline fir forest in Colorado, plant uptake generated 2.04 kmol H^+ ha^{-1} yr^{-1}, but net cation accumulation only accounted for 0.25 kmol ha^{-1} yr^{-1} because of neutralization during decomposition of fine roots and litter (Arthur 1990). We do not have an accurate measure of decomposition and our values represent the maximum rates of H-ion production.

During the first year of treatments, the disturbance of the soils resulted in a large pulse of acidity associated with nitrification, particularly in the organic horizon (1.7–3.6 kmol H^+ ha^{-1} yr^{-1}). High rates of acid production attributable to nitrification have been measured in many forested ecosystems. For example, following deforestation of a watershed at the Hubbard Brook Experimental Forest, N.H., 10.4 $kmol_c$ ha^{-1} yr^{-1} of acidity was produced as a result of nitrification (Nodvin et al. 1988). Net H-ion flux associated with NO_3^- leaching from a N-fixing red alder stand generated 2.5 $kmol_c$ ha^{-1} yr^{-1}, which exceeded all other sources of acidity, and subsequently acidified the soil (Binkley 1992). Atmospherically deposited NH_4^+ induced a net H-ion production rate of 2.4 $kmol_c$ ha^{-1} yr^{-1} through subsequent nitrification and leaching in an oak-beech forest in the Netherlands (Tietema & Verstraten 1991).

Root uptake of NO_3^- in the deep mineral soil was an important neutralizing mechanism during the first year of treatments (Table 5). The root systems of the trees, confined by the limited growing space in the pots, were able to utilize most of the NO_3^- in solution following the disturbance. In the final year of treatments, retention of SO_4^{2-} in the deep mineral soil was a more important process, neutralizing 1.0 kmol H^+ ha^{-1} yr^{-1} in the low acid treatments and 2.6 kmol H^+ ha^{-1} yr^{-1} in the high acid treatment. The adsorption of SO_4^{2-} is highly dependent upon soil pH (Nodvin et al. 1986), and acidity associated with both nitrification and acid precipitation inputs in our experimental system could have enhanced the SO_4^{2-} retention capacity of these soils. Depression of soil pH induced by nitrification following vegetation disturbance at Hubbard Brook, N.H., enhanced SO_4^{2-} adsorption and decreased SO_4^{2-} flux from the soil (Nodvin et al. 1986; Mitchell et al. 1989), and retention of SO_4^{2-} was an important acid consuming process in the mineral soil in a red-spruce stand at Whiteface Mt., NY (Johnson et. al. in press). Unfortunately, comparative measures of pre- and post-treatment soil pools of SO_4^{2-} were not available to rigorously investigate this hypothesis.

Conclusions

The role of acidic deposition in soil acidification and forest decline has proven difficult to quantify because of the complex set of mechanisms involved in acid processing, and the high spatial and temporal variation in these processes. The combination of an ecosystem approach, high level of replication, and relatively long duration of this experiment allowed us to evaluate quantitatively the role of acidic deposition in miniature red spruce ecosystems.

In the moderately acidic soils of our experimental systems, high acid loading (about twice as high as the highest eastern U.S. values) and rapid tree biomass accumulation resulted in significant responses of soil and solution chemistry; however, despite the major redistribution of acidity within the soil profile and the significantly more rapid cycling of basic cations through the vegetation, no measurable effects on tree nutrition or health was observed. Thus, while moderately well-buffered soils are sensitive to acidification from forest growth and acid deposition, trees on such sites seem unlikely to be adversely affected in the short run. Nevertheless, because base cation depletion was significantly accelerated by acid deposition-induced leaching, even under acid loadings near and below the range observed in eastern forests, continuing concern about the combined effects on soil base status of acid deposition and biomass removals in forest harvest is warranted.

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