Leaching of nutrient cations from the forest floor: effects of nitrogen saturation in two long-term manipulations

William S. Currie, John D. Aber, and Charles T. Driscoll

Abstract: Nitrogen saturation results in greater mobility of nitrate, which in turn is often correlated with concentrations of nutrient cations in soil solution and streamwater. At the Harvard Forest, U.S.A., under long-term NH₄NO₃ inputs, a Pinus resinosa Ait. forest has exhibited signs of N saturation more rapidly than a mixed-Quercus forest. We test the hypothesis that increased nitrate leaching increased concentrations of nutrient cations in soil solution. Over 2 years (years 6 and 7 of treatment) we measured SO₄²⁻, NO₃⁻, Cl⁻, Ca²⁺, K⁺, Mg²⁺, Na⁺, H⁺, and NH₄⁺ in throughfall solution and in forest-floor (Oa) leachate. Concentrations of NO₃⁻ in forest-floor leachate increased with rates of N amendment and correlated positively with cation concentrations, with stronger overall correlations in the pine forest: r² values were 0.51 (pine forest) and 0.39 (oak forest) for Ca²⁺, 0.45 (pine) and 0.16 (oak) for K⁺, and 0.62 (pine) and 0.50 (oak) for Mg²⁺. In summer and fall, the oak forest showed some negative relationships between nutrient cation leaching and rate of N amendment. These contrasts showed retention of cations and N to occur together in an N-limited system, whereas increased nitrate mobility occurred with increased cation losses in an N-saturated system.

Résumé : La saturation en azote se traduit par une plus grande mobilité des nitrates, laquelle est alors corrélée aux concentrations des cations nutritifs dans la solution de sol et dans le cours d’eau. À la forêt de Harvard aux États-Unis, une forêt de Pinus resinosa Ait. soumise à des apports à long terme de NH₄NO₃ a présenté des signes de saturation en N plus rapidement qu’une forêt mélangée de Quercus. Nous avons vérifié l’hypothèse voulant qu’un accroissement du lessivage des nitrates causerait une augmentation des concentrations des cations nutritifs dans la solution de sol. Sur deux années (ans 6 et 7 du traitement), nous avons mesuré SO₄²⁻, NO₃⁻, Cl⁻, Ca²⁺, K⁺, Mg²⁺, Na⁺, H⁺ et NH₄⁺ dans la solution de pluviolessivage et dans le lessivat de la couverture morte (Oa). Les concentrations de NO₃⁻ dans le lessivat de la couverture morte ont augmenté avec les taux d’ajout de N et étaient positivement corrélées avec les concentrations des cations, les plus fortes corrélations étant observées dans la forêt de pin : les valeurs de r² étaient de 0,51 (forêt de pin) et 0,39 (forêt de chêne) pour Ca²⁺, de 0,45 (pin) et 0,16 (chêne) pour K⁺, et de 0,62 (pin) et 0,50 (chêne) pour Mg²⁺. Durant l’été et l’automne, la forêt de chêne a montré quelques relations négatives entre le lessivage de cations nutritifs et le taux d’ajout de N. Ces contrastes montrent que la rétention des cations et de N peut être observée simultanément dans un système pauvre en N tandis qu’une mobilité accrue des nitrates est survenue avec une augmentation des pertes de cations dans un système saturé en N.

[Intraduit par la rédaction]

Introduction

The dominant anions associated with cation leaching from forest soils may either be naturally occurring organic anions, bicarbonate, or the strong acid anions, sulfate and nitrate (Cronan et al. 1978). Increased production or input of any of these mobile anions could potentially accelerate cation losses from soils. Assessments of the role of SO₄²⁻ in cation leaching are more straightforward than NO₃⁻ because SO₄²⁻ leaching is generally thought to be controlled more by conservative transport or abiotic soil adsorption, while inputs of nitrogen (N) are generally strongly retained by biotic processes (Johnson et al. 1982; Johnson 1992; Mitchell et al. 1996). However, high levels of nitrate leaching have been observed in sites with N-fixing tree species (Johnson et al. 1988), high N inputs in atmospheric deposition (Gundersen et al. 1998), disturbance (Vitousek et al. 1979; Hornung and Reynolds 1995), or N inputs in experimental manipulations (Kahl et al. 1993). Concern over nitrate leaching in northeastern North America has been heightened by findings such as increasing nitrification across gradients in increasing N deposition (McNulty et al. 1990; Gundersen et al. 1998). The theory of N saturation in forest ecosystems predicts that nitrate leaching may increase seasonally or over the long term even under conditions when elevated N inputs are retained (Ågren and Bosatta 1988; Aber et al. 1989). Long-term N amendments at the Harvard Forest in central
Massachusetts, U.S.A., have exhibited this pattern (Aber et al. 1993).

Nitrate leaching represents a link between the N cycle and cation cycles in forest ecosystems. Among the potentially deleterious effects of N saturation in forests, cation leaching is often listed, including increased mobility of aluminum and losses of nutrient cations from the rooting zone. Nitrate concentrations have been correlated with Ca$_2^+$, Mg$_2^+$, and Al concentrations in soil solution and with Ca$_2^+$ and Al concentrations in streamwater, suggesting a strong control on cation movement (Driscoll and Schafran 1984; Foster et al. 1989; Driscoll et al. 1989; Morrison et al. 1992; Homann et al. 1994).

Here we focus on the forest floor (the O horizon), the organic layer that accumulates on the surface of mineral soil in temperate and boreal forests. Litter in the forest floor stores the nutrient cations Ca, K, and Mg, slowly releasing the nutrients through mineralization, after rapid initial leaching in some cases (Gosz et al. 1973; Berg 1986; Blair 1988). In the humus layer, organic matter carries a high cation exchange capacity, providing a mechanism of cation retention (Kalisz and Stone 1980). The O horizon may contain half of the fine roots in the soil profile (Fahey et al. 1988). Loss of nutrient cations from the forest floor raises the possibilities of nutrient depletion, although there are numerous factors involved, such as soil parent material, rates of biotic cycling, and methods of forest harvesting (Johnson et al. 1982, 1988; Federer et al. 1989).

Federer and Hornbeck (1985) wrote that "Empirical evidence for changes of behavior of forest soils in response to acid precipitation still lies in the future... quantitative proof of effect under natural conditions is difficult to obtain." Short-term manipulations at small scales have demonstrated that N additions can result in leaching of Ca and Mg from the forest floor (David et al. 1990). However, where N saturation occurs as a result of chronic N deposition it is likely to involve long-term and interconnected ecosystem responses. In the "chronic N" plots at the Harvard Forest, N amendments have been made continuously since 1988 to two forest stands in 30 × 30 m plots in an effort to observe the multifaceted ecosystem responses to continued N inputs. The reference and N-amended plots have continued to receive ambient inputs of sulfate, other anions, and nutrients. A red pine (Pinus resinosa Ait.) and a mixed oak forest have exhibited contrasting responses. Both forests began by retaining all of the added N, both forests eventually showed "breakthrough" of nitrate in deep lysimeters, and both have shown elevated nitrate leaching from the forest floors. The pine forest, however, has shown much greater loss of nitrate from the forest floor and solum (Aber et al. 1993; Currie et al. 1996a; Magill et al. 1997).

Our primary objective in the present study was to examine, in ecosystem-level manipulations, the effects of N saturation induced changes to the cation–anion chemistry of soil solution leaching from the forest floors. In particular we sought to test the hypothesis that increased nitrate leaching would cause increased concentrations of nutrient cations in solution draining the forest floors. To this end, we identified the dominant ions in forest-floor (Oa) leachate in reference plots. We then identified changes in cation chemistry of Oa leachate as nitrate became a more important factor in the anion chemistry in treated plots in the sixth and seventh years of N amendments. To provide a greater biogeochemical context for hypothesized changes in forest floor solution chemistry, we also studied the chemistry of throughfall solution and quantified the exchangeable base cations present in the forest floors of the two stands under reference (untreated) conditions.

Materials and methods

Site description

The Harvard Forest, in the Central Highlands of Massachusetts, is a site in the Long-Term Ecological Research (LTER) network sponsored by the U.S. National Science Foundation. Elevation ranges from 220 to 410 m; monthly mean temperatures are −7°C in January and 19°C in July. Average precipitation is approximately 110 cm-year$^{-1}$, distributed fairly evenly throughout the year (Van Cleve and Martin 1991).

The chronic N addition experiment includes two forest stands: an even-aged red pine stand planted in 1926, and a predominantly oak (Quercus velutina Lam. and Quercus borealis Michx. f.) stand approximately 45–50 years old in 1993, naturally regenerating from clear-cutting. Soils are rocky and well drained, formed from glacial till, and contain well-defined O horizons (mor type). Soils in the pine stand are Montauk variants, described as coarse-loamy, mixed, frigid Typic Dystrochrepts. An Ap horizon is present in the pine stand. Soils in the oak stand are Canton variants, coarse-loamy over sandy-skeletal, mixed, frigid Typic Dystrochrepts.

N amendments

Nitrogen amendments have been made since 1988 in six equal applications per year, approximately once per month from early May through late September. In each stand there is one reference (no N addition), one low N addition (5 g N·m$^{-2}$·year$^{-1}$) and one high N addition (15 g N·m$^{-2}$·year$^{-1}$) plot. Plots are each 0.09 ha in size (30 × 30 m). Backpack sprayers are used to apply fertilizer onto the forest floor as 1.3 mol·L$^{-1}$ NH$_4$NO$_3$ in the low N addition and 4.0 mol·L$^{-1}$ NH$_4$NO$_3$ in the high N addition treatments.

Collection of throughfall and Oa-leachate

Five throughfall (TF) collectors were placed in each treatment and stand combination (30 total). Each collector consisted of a bottle, a funnel, and a thin plastic liner. Dark, opaque 1-L polyethylene bottles were used, staked firmly in place on the ground. Polyethylene funnels (14 cm diameter) were fitted with 2-mm nylon mesh to exclude debris. Funnels rested in bottle mouths and liners were placed inside bottles. Funnels were returned to the laboratory for cleaning at the start of the collection season each spring and approximately every 6 weeks thereafter. Throughfall funnels and bottles were either returned from the field or covered with plastic bags while plots were fertilized.

Zero-tension lysimeters (ZTLs) were installed beneath the forest floor (Oa horizon), five in each treatment and stand combination (30 total). Construction and installation were described by Currie et al. (1996a). During installation, four measurements were made of thickness of the Oa and Oi + Oe horizons at each ZTL (60 measurements per stand). Installation of ZTLs was completed in mid-August 1992.

We sampled TF and forest-floor (Oa horizon) leachate on an event basis where possible, with events defined as retrieval of samples within 36 h of the onset of rain. We installed new, deionized water rinsed and air-dried TF liners and acid-washed ZTL collection bottles for each sample collection. Two sets of ZTL collection bottles allowed for continuous sampling. The median length of time that ZTL samples remained in the field prior to collection was...
4.8 days, with a maximum of 24.5 days. No samples were collected from December to mid-April. We collected spring snowmelt in 1994 by placing clean collection bottles in ZTL wells underneath the 40 cm snowpack in late March and retrieving the samples 21 days later after the snowpack had completely melted.

The field collections spanned 25 months: two “litterfall years” (Qualls et al. 1991), from 1 October 1992 to 30 September 1993 (year 1), and from 1 October 1993 to 30 September 1994 (year 2). One final sample set was collected in October 1994. Overall, 33 ZTL sample sets were collected and 29 TF sample sets. Within each stand and N-amendment plot, the five pseudoreplicate samples of TF were bulked in all 29 sets, and the five pseudoreplicate ZTL samples were bulked in 30 of the 33 sets. In 3 of the 33 sets, ZTL sample sets were left unbulked for analysis. We analyze and summarize the data from these unbulked collections separately from those of the bulked collection sets.

Collection of forest floor slabs

We collected slabs of forest floor material, 15 × 15 cm in size, outside of the study plots (five from each forest stand) to characterize reference forest-floor material while avoiding destructive sampling of the study plots. Each slab included Oe and Oa material sampled to the bottom of the Oa horizon. Sampling took place on 13 June 1995.

Analysis of throughfall and Oa leachate

Throughfall and ZTL samples were transported on ice to the University of New Hampshire, where the amount of solution collected was measured gravimetrically and pH measured potentiometrically on each sample as it entered the laboratory. Samples were stored at 2°C until they were vacuum-filtered through ashed (1 h at 425°C) Whatman GF/F glass-fiber filters (0.7 μm); filtering was complete within 36 h of sample collection. Samples were frozen in high-density polyethylene storage bottles for 1–18 months. After thawing, NO₃⁻ and NH₄⁺ were measured immediately, while subsamples for cation analysis were acidified to pH < 2 by addition of 100 μL of 2.5 M H₂SO₄ and stored in tightly capped plastic vials at 25°C for up to 1 year prior to analysis (Greenberg et al. 1992). Subsamples for analysis of chloride and sulfate were refrozen in plastic vials for up to 1 year and refiltered (0.2 μm) before analysis.

Analyses for Ca, K, Mg, and Na were performed on a direct-coupled plasma (DCP) arc spectrophotometer at the U.S. Forest Service Northeast Experiment Station in Durham, N.H. A prepared stock solution (U.S. Department of Agriculture) was used for standardization, and standards were also measured as samples in each run. Blind duplicates were also included in each run. Independent check standards analyzed as samples measured within 11% of expected values. Since the DCP ionizes samples and measures total content for each element, our results should be considered total elemental concentrations.

Chloride and SO₄²⁻ were quantified through high-performance liquid chromatography using an IONPAC AS4A (10-32) Analytical Column from Dionex Corp., and a Waters 431 conductivity detector. Each analytical run included blind duplicates and standards run as samples. In repeated analyses of standards run as samples, mean chloride concentrations were within 2.5% (coefficient of variance, CV = 1.2%) of the standard, while mean sulfate concentrations measured within 1% (CV = 0.9%) of the standard. In an ULTRAcheck certified standard (ULTRA Scientific, North Kingston, R.I.), chloride concentrations measured within an average of 12% of the certified value and sulfate concentrations within an average of 3%. Measurement of NO₃⁻, Na, and NH₄⁺ were performed colorimetrically as described by Currie et al. (1996a).

Concentrations of H⁺ were calculated from pH with a slight correction for ionic strength (pHₜ = 0.98; Stumm and Morgan 1981). Anion charge deficit was calculated by subtracting the molar charge equivalents of SO₄²⁻, NO₃⁻, and Cl⁻ from the sum of those of Ca²⁺, K⁺, Mg²⁺, Na⁺, H⁺, and NH₄⁺. Amounts of solution collected were used to calculate mean solute concentrations (including anion deficit) on a volume-weighted basis within each combination of forest stand, N-amendment plot, and annual period.

Analyses of forest floor slabs

Forest floor slabs were shipped to Syracuse University for analysis. The procedures and methods used for forest floor analyses are summarized in Cappo et al. (1987). Samples were air-dried and sieved (2 mm) prior to analysis. Six subsamples from each forest floor slab collected (30 subsamples per forest stand) were measured for pH in 1:5 soil to solution ratios, including duplicate analysis of pH in distilled–deionized water, 0.01 M CaCl₂, and 0.002 M CaCl₂. Unbuffered exchangeable cations were analyzed on three subsamples of each forest floor slab collected. Samples were extracted in 1 M NH₄Cl, and the resulting solutions were measured for concentrations of basic cations with a Perkin Elmer atomic absorption spectrophotometer. Four subsamples from each forest floor slab collected were analyzed for C and N content using a Carlo Erba CN analyzer.

Statistical analyses

Differences in mean characteristics of forest floor slabs between pine and oak stands were tested with the student’s t test at the 95% confidence level.

We tested TF solute concentrations against rate of N amendment with ANOVA, within each forest stand over the 2-year period. In two of the 18 combinations (solute × stand) the patterns were statistically significant: NH₄⁺ concentration increased with N amendment in TF in the pine stand (p = 0.004, r² = 0.12), and Ca²⁺ concentration decreased with N amendment in the oak stand (p < 0.001, r² = 0.18). Because there were few significant effects and the fractions of variances explained (r² values) were small, we combined all aspects of TF chemistry among the three N treatments per forest stand. For Oa leachate, we tested the effects of N amendments on solute concentrations using data from three collections, in which samples were not bulked (5 replicate ZTL samples per treatment per stand). Since the experiment design was a single-factor treatment with multiple quantitative levels, we tested the significance of linear regressions of the rate of N amendment (0, 5, and 15 g N m⁻² year⁻¹) versus concentration for each solute (Mize and Schultz 1985). Each regression was thus performed on 15 data points.

Results

In TF of both stands, SO₄²⁻ concentrations and the anion deficits were approximately equal and dominated the anion chemistry (Fig. 1). The dominant cation in TF was H⁺ in both stands. In the pine stand, TF exhibited higher concentrations of NO₃⁻, SO₄²⁻, Cl⁻, H⁺, and Ca²⁺ than in the oak stand, but these were not tested statistically because of the experiment design of unreplicated, large experimental plots. Amounts of TF solution collected were similar between stands, averaging 1.6 cm per collection in each forest over the 2-year period. Values of the anion deficit and H⁺ concentration in TF exhibited striking contrasts between the 2 years.

Thickness of the forest floor was not significantly different on the treated plots of the two forests (Table 1). On reference slabs of forest floor (taken outside treated plots), pH, carbon, and nitrogen concentrations were not significantly different in the two stands (Table 1); exchangeable Ca was
greater per unit mass in the forest floor of the pine forest, while exchangeable K and Mg per unit mass were greater in the oak forest.

Chemistry of Oa leachate in reference plots

In reference plots, the anion deficit dominated the anion composition of Oa leachate in both stands, followed by $\text{SO}_4^{2-}$ (Fig. 1). Hydrogen ion was the major cation in both Oa horizon solutions of both stands during the first year, but during the second year, $\text{H}^+$ and $\text{Ca}^{2+}$ concentrations were approximately equal in the pine stand.

The most consistent contrast between TF and Oa solution chemistry was in the anion deficit, which was dramatically higher in Oa solution in all cases. Solute concentrations were consistently higher in TF compared with Oa leachate included $\text{Cl}^-$, $\text{Na}^+$, $\text{Ca}^{2+}$, and $\text{Mg}^{2+}$. Concentrations of $\text{H}^+$ in Oa leachate were similar to those in TF in the first year (when TF concentrations of $\text{H}^+$ were high) but increased markedly over those in TF in the second year. Concentrations of $\text{SO}_4^{2-}$ in Oa leachate were lower than TF values during the first year and higher than TF values during the second year, attaining similar values of annually
averaged concentrations in Oa leachate between years. Only NO$_3^-$ consistently decreased in solution concentration from TF to the forest floors.

Contrasts between forest types in exchangeable cations in untreated forest floors did not match contrasts between forests in cation concentrations in Oa leachate. Greater exchangeable Ca$^{2+}$ in forest-floor slabs in the pine forest did correspond to higher Ca$^{2+}$ concentrations in leachate. However, the greater quantities of exchangeable K$^+$ and Mg$^{2+}$ in the oak forest floors were not reflected as differences in chemistry of Oa leachate between stands.

Effects of N amendment

A clear shift in the mobility of NO$_3^-$ in Oa leachate occurred under N amendments. The anion deficit accounted for approximately 60% of the anion charge in the reference plots of both stands; in the high-N plots this value decreased to about 20% in pine stand and about 40% in the oak stand (Fig. 2). At the same time, NO$_3^-$ increased from less than 10% of the anion charge in reference plots to 30–70% in high-N plots. These shifts resulted from increases in concentrations of NO$_3^-$ associated with N amendments.

In an analysis of only the unbulked sample sets of Oa leachate, concentrations of Ca$^{2+}$, K$^+$, and Mg$^{2+}$ in forest-floor leachate increased significantly with rates of N amendment in the pine forest but not in the oak forest. In two of the three unbulked sample sets, linear regressions of concentrations of these cations as a function of the rate of N amendment were significant in the pine stand (Table 2). No such consistent pattern was evident in the oak stand; in fact, Ca$^{2+}$ and Mg$^{2+}$ concentrations significantly decreased with N amendment on one of the three dates.

A somewhat different pattern emerged when cation concentrations were tested against nitrate concentrations in Oa leachate over the entire 2-year period. Calcium, K$^+$, and Mg$^{2+}$ concentrations were all significantly correlated with NO$_3^-$ concentrations in each stand (Fig. 3). The slopes and intercepts of a linear regression analysis of cation concentrations as a function of NO$_3^-$ were invariably greater for the pine stand, while the $r^2$ values of the linear curve fits were also higher for the pine stand for all three nutrient cations.

Peaks in NO$_3^-$ and SO$_4^{2-}$ concentrations were evident on particular sample dates (Figs. 4 and 5). Correlations were

© 1999 NRC Canada
not significant between NO$_3^-$ and amount of solution collected in either stand. Correlations were significant between solution amounts collected and concentrations of SO$_4^{2-}$ in each stand, although this explained little of the variance in SO$_4^{2-}$ (8% in pine, 5% in oak). Sulfate concentrations appeared to behave similarly among all treated plots within each stand (Figs. 4b and 5b), whereas NO$_3^-$ varied strongly with treatment as expected. Peaks in Ca$^{2+}$ concentration corresponded to peaks in NO$_3^-$ in the N-amended plots of both stands; however, in the oak stand the pattern was less consistent.

In the oak forest, concentrations of Ca$^{2+}$ and Mg$^{2+}$ in N-amended plots often decreased below reference values in the fall. Similarly, concentrations of K$^+$ in the high-N plots of amended plots often decreased below reference values in the oak stand declined below those in reference and low-N plots in most sample sets collected from August onward in both years.

**Discussion**

**Throughfall chemistry**

The higher concentrations of some solutes in TF from the pine stand in comparison to the oak stand could have resulted either from evaporative loss of the canopy, or from higher rates of dry deposition (Lovett et al. 1996). Solution may be channeled to stemflow to a greater degree in hardwood forest canopies than in coniferous canopies because of the differences in branching patterns; thus, TF from the oak stand may have experienced less evaporative water loss even though we saw no differences in TF quantities between stands. Dry deposition of NO$_3^-$, SO$_4^{2-}$, Cl$^-$, H$^+$, and Ca$^{2+}$ also occurs in forest canopies, at rates usually related to leaf area index. Leaf area index measured by projection was estimated as 5.0 m$^2$ m$^{-2}$ in the red pine stand and 3.6 m$^2$ m$^{-2}$ in the oak stand at Harvard Forest (M. Martin, unpublished data). If rates of dry deposition were similar between years, then interannual differences in TF chemistry may have been controlled in part by differences in quantity of precipitation: 118 cm during our first litterfall year and 142 cm during the second (Harvard Forest weather station data). Overall, significant correlations were evident between solute concentrations and quantity of TF collected in each stand (data not shown).

**Organic acid anions**

Calculations of anion deficit did not include measurements of HCO$_3^-$ but the contribution of this solute in both TF and Oa leachate should have been negligible. Over the 2-year study, pH in TF averaged 4.1 in the pine stand and 4.3 in the oak stand, while in Oa leachate, pH averaged 3.7 in the pine stand and 3.8 in the oak stand (data not shown). Concentrations of HCO$_3^-$ are very low (< 1 µmol·L$^{-1}$) in TF or Oa horizon leachate below pH 4.5 (Galloway et al. 1976; Cronan et al. 1978).

The anion deficits thus may be attributed largely to deprotonated organic acids (Cronan et al. 1978; De Walle et al. 1985). Mollitor and Raynal (1982) attributed similar anion deficits to organic acids in forest O horizons in Huntington Forest, New York, 327 µequiv·L$^{-1}$ in a coniferous forest and 210 µequiv·L$^{-1}$ in a mixed hardwood forest. It is likely that our results represent low estimates of the charge contributions of organic acids. In this study dissolved Al, Fe, and Mn were not measured, and these species would increase our values for anion deficits (Cronan et al. 1978). We found broad agreement in relative concentrations of dissolved organic carbon (DOC) and anion deficits in comparisons of Oa leachate between forest types. Over the 2-year period, mean volume-weighted DOC concentrations were 65% higher in the pine reference plots relative to oak (unpublished data), while anion deficits were about 50% higher in the pine versus the oak reference plots in the first year and about 30% higher in the second year (Fig. 1). To further assess whether measurements of DOC in our samples (Currie et al. 1996a) were consistent with the present results for organic charge, we performed regressions of anion charge deficits against DOC concentrations within each stand. Regression lines had intercepts close to zero, providing additional evidence that the charge deficits correspond to organic anions, with $r^2$ values of 0.71 in the pine stand and 0.34 in the oak stand. Slopes were 3.7 mequiv·g$^{-1}$ C in the pine stand and 4.9 mequiv·g$^{-1}$ C in the oak stand. These values compare well with the estimated values of 4.7 mequiv·COOH·g$^{-1}$ C for contributions to DOC charge from carboxylic acids in soil solution from Adirondack Park, New York, and Bear Brooks.
Fig. 3. Scatter diagrams of concentrations of nutrient cations and nitrate across all samples of Oa leachate collected over the 2-year period. Data from reference and treated plots are shown. Regressions are shown for data within each forest stand. (a) Calcium: pine regression: \( y = 0.097x + 107 \ (r^2 = 0.51) \); oak regression: \( y = 0.046x + 45 \ (r^2 = 0.39) \). (b) Potassium: pine: \( y = 0.044x + 59 \ (r^2 = 0.45) \); oak: \( y = 0.031x + 49 \ (r^2 = 0.16) \). (c) Magnesium: pine: \( y = 0.048x + 38 \ (r^2 = 0.62) \); oak: \( y = 0.037x + 28 \ (r^2 = 0.50) \). For each regression shown, \( p < 0.001 \).

Watersheds, Maine (Cronan and Aiken 1985; Cronan et al. 1992).

Nitrate leaching

Amendments of NH\textsubscript{4}NO\textsubscript{3} could accelerate cation leaching through two primary mechanisms: (i) preferential retention or uptake of NH\textsubscript{4}\textsuperscript{+} over NO\textsubscript{3}\textsuperscript{−} in the forest floor, in exchange for acidic or basic cations that leach from the O horizon with the NO\textsubscript{3}\textsuperscript{−} anion; and (ii) nitrification of the added NH\textsubscript{4} in the forest floor, followed by leaching of the NO\textsubscript{3}\textsuperscript{−} produced. In the first case, one H\textsuperscript{+} charge equivalent would be leached from the forest floor. In the second, two H\textsuperscript{+} ions would be produced in the forest floor in the oxidation process, with one H\textsuperscript{+} charge equivalent able to leach with the produced NO\textsubscript{3}\textsuperscript{−} anion, either as an acidic or basic cation. If both types of processes occurred, i.e., if the original NO\textsubscript{3}\textsuperscript{−} anion were leached, and NH\textsubscript{4}\textsuperscript{+} initially retained and then nitrified, with subsequent leaching loss of the new NO\textsubscript{3}\textsuperscript{−}, then two H\textsuperscript{+} charge equivalents would be leached (Reuss and Johnson 1986). Nutrient cations would be leached from the O horizon in the first case if NH\textsubscript{4}\textsuperscript{+} displaced Ca\textsuperscript{2+}, K\textsuperscript{+}, or Mg\textsuperscript{2+} on the cation exchange complex or if vegetative uptake of NH\textsubscript{4}\textsuperscript{+} resulted in production of H\textsuperscript{+} in the soil (Galloway 1995), which then displaced Ca\textsuperscript{2+}, K\textsuperscript{+}, or Mg\textsuperscript{2+}. Nutrient cations would be leached in the second case if either of the two H\textsuperscript{+} ions produced by nitrification displaced Ca\textsuperscript{2+}, K\textsuperscript{+}, or Mg\textsuperscript{2+} on the cation exchange complex. In both cases, immobilization or uptake of NO\textsubscript{3}\textsuperscript{−} in the forest floor would mitigate cation leaching. Under NH\textsubscript{4}NO\textsubscript{3} amendments, the leaching of NO\textsubscript{3}\textsuperscript{−} is necessary for direct increases in cation movements (whether H\textsuperscript{+}, inorganic aluminum, or nutrient cations) from the forest floor.

In the chronic N plots at the Harvard Forest, NH\textsubscript{4}\textsuperscript{+} has been preferentially retained over NO\textsubscript{3}\textsuperscript{−} in the forest floors (including biotic uptake), causing higher fluxes of NO\textsubscript{3}\textsuperscript{−} over NH\textsubscript{4}\textsuperscript{+} in the Oa leachate of both stands (Currie et al. 1996a). In the high-N plots during the seventh year of N amendments, the forest floor in the pine stand provided a sink for approximately 0.84 g NH\textsubscript{4}-N·m\textsuperscript{−2}·year\textsuperscript{−1}, while in the oak stand the forest-floor sink accounted for 5.4 g NH\textsubscript{4}-N·m\textsuperscript{−2}·year\textsuperscript{−1} (out of amendments of 7.5 g NH\textsubscript{4}-N·m\textsuperscript{−2}·year\textsuperscript{−1} in each stand). Some of the NH\textsubscript{4}\textsuperscript{+} inputs appear to have been retained by cation exchange in the forest floor, at least in the short term, because KCl-extractable NH\textsubscript{4}\textsuperscript{+} was elevated (about 0.7 g NH\textsubscript{4}-N·m\textsuperscript{−2} over reference plots in each stand) during the sixth year of amendments (Magill et al. 1997). Increased extractable NH\textsubscript{4}\textsuperscript{+} over the entire 6-year period could thus have accounted for about 1 year of the NH\textsubscript{4}\textsuperscript{+} retained in the forest floor in the pine stand but only about 15% of the NH\textsubscript{4}\textsuperscript{+} retained per year in the oak stand. Most of the N retained was in non-extractable form, including plant and microbial biomass and soil humus; in particular, plant uptake and incorporation into plant biomass increased much more significantly in the oak forest (Magill et al. 1997).

We do not expect NH\textsubscript{4}\textsuperscript{+} to accumulate on the cation exchange complex. In most forests the demand for NH\textsubscript{4}\textsuperscript{+} is high. When NH\textsubscript{4}\textsuperscript{+} availability exceeds demand by plant and microbial biomass it should be oxidized to NO\textsubscript{3}\textsuperscript{−} by nitrifying bacteria (Vitousek et al. 1982; Reuss and Johnson 1986; Tietema et al. 1992). At the Harvard Forest, net nitrification
in the O horizon increased significantly at both levels of N amendment in the pine stand but little if at all in the oak stand (Magill et al. 1997).

**Patterns in cation chemistry of Oa leachate**

Differences in relationships between nutrient–cation concentrations and NO$_3^-$ concentrations were not consistent with differences in exchangeable cation concentrations in the forest floors. Slopes and intercepts in the regressions for the pine stand were greater for all three nutrient cations (Fig. 3), while only concentration of exchangeable Ca$^{2+}$ was greater in the pine stand than the oak stand. We see two potential explanations. First, net nitrification was much greater in the pine stand. Its importance as an acidifying process appears to be highlighted by significant effects in the rate of N amendment on soil solution H$^+$ concentration in the pine stand in all three unbulked sample sets (Table 2). The second potential explanation could lie in greater demand for nutrient cations by the growing vegetation in the oak stand. Cole and Rapp (1981) summarized data from 28 of

---

*Fig. 4. (a–e) Concentrations of selected cations and anions in Oa leachate from the pine stand, covering the full 2-year study period. (○) Reference; (▲) low-N addition; (■) high-N addition. Nitrate concentrations in (a) are shown on a separate scale. Arrows below (e) indicate unbulked sample collections. (f) Average amount of solution collected in zero-tension lysimeters (cm) on each sample date.*
the International Biosphere Program study sites. Temperate deciduous forests had higher average concentrations of Ca, K, and Mg in biomass and shorter residence times for all three cations in the forest floor than did temperate coniferous forests. Currie et al. (1996) estimated growth requirements of Ca, K, and Mg to be greater than mineralization fluxes throughout the period of regrowth of an oak forest in Virginia, U.S.A. At the Harvard Forest, because increased forest growth under N amendments has been greater in the oak than in the pine stand, cation demand should also be expected to show greater increases in the oak stand. Such an increased demand may explain the decreases in Ca and Mg concentrations with N amendment that we observed in one unbulked sample set collected at the height of the growing season (Table 2).

It was surprising that nutrient cations in N-amended plots dropped below reference values in the fall. This seasonal pattern in cation leaching was decoupled from NO₃⁻ leaching, because the latter increased with N amendment. Concentrations of Ca²⁺, K⁺, and Mg²⁺ appeared to increase with

---

**Fig. 5.** (a–e) Concentrations of selected cations and anions in Oa leachate from the oak stand, covering the full 2-year study period. (○) Reference; (▲) low-N addition; (■) high-N addition. Nitrate concentrations in (a) are shown on a separate scale. Arrows below (e) indicate unbulked sample collections. (f) Average amount of solution collected in zero-tension lysimeters (cm) on each sample date.
N amendments early in the growing season, and then decreased with N amendments late in the growing season (Fig. 5). Further study could focus on understanding the interplay between forest growth requirements, litterfall and mineralization fluxes of cations, and seasonal patterns in nitrification and cation leaching.

Broader interpretations

Although TF and ZTL samples were collected at multiple points within each large-scale plot, the overall experimental design exhibits pseudoreplication because, for each forest type, there is only one control plot and one plot for each level of treatment. This design was chosen to maximize plot size. Large plots were considered necessary to study integrated, large-scale, ecosystem-level effects while minimizing edge effects. A reason for maximizing the size of manipulated areas is, as Schindler (1998) wrote concerning aquatic ecosystems, “smaller-scale experiments often give highly replicable, but spurious, answers.” It is our contention that the dramatic contrasts in NO3 leaching with treatment (Fig. 2) were due to treatment differences and not to pre-existing differences among plot locations; this contention is supported by the fact that NO3 leaching fluxes are strongly related to N amendment rates in both forests, and that NO3 concentrations in mineral soils of treated plots have increased over time (Aber et al. 1993, Magill et al. 1997).

How well should we expect these results for soil solution chemistry in the “chronic N” experiment to mimic the effects of longer term, lower-level N inputs in the region? A 15N tracer study in these plots showed that soils, including the forest floor, were responsible for larger fractions of N inputs at lower levels of N inputs (Nadelhofer et al. 1999; Currie et al. 1999). Over time, with the narrowing of the C/N ratio in the forest floor under accumulated N retention, we would expect increased nitrification and NO3 leaching (Gundersen et al. 1998). Emmett et al. (1998) concluded that the forest floor C/N ratio may control nitrification rates, and calculated that in temperate forests, the change from a C/N ratio of 30 to 24 could occur within several decades. Thus, the contrasts in net nitrification (Magill et al. 1997) and NO3 leaching (Fig. 2) between forest types and rates of N amendment in our experiment may well represent the effects of longer term, lower level N inputs. If so, then relationships that we observed between concentrations of NO3 and nutrient cations may also be expected to occur under lower level, longer term N inputs.

Our results agree with the theory of N saturation that nutrient cation concentrations and losses should not necessarily be expected to correlate with levels of N amendment (Table 2) but should be more closely linked to N saturation (a result of N saturation as opposed to a treatment, the rate of N amendment) (Fig. 3). In regressions against the level of treatment, linear responses are tested at the ecosystem level. Forest N cycles were predicted, however, to show nonlinear responses to chronic, elevated N inputs (Aber et al. 1989). The significant regressions between concentrations of nutrient cations and NO3 in both stands (Fig. 3) show that, when NO3 is mobile, it exerts some control over cation leaching. The linear effects on cation leaching with N amendment in the pine stand (Table 2) suggest that when N saturation has progressed to stage 2 (Aber et al. 1998), cation leaching may increase linearly with N inputs.

Summary and conclusions

The acidic soil O horizons at the Harvard Forest were representative of New England soils (Kalisz and Stone 1980; De Walle et al. 1985; David et al. 1990). Where N inputs in atmospheric deposition are retained, such highly acid soils are usually not expected to suffer acidification or nutrient depletion unless they are poorly buffered or unless cations are removed with biomass during forest harvest (Johnson et al. 1982; Federer et al. 1989). Under ambient levels of atmospheric deposition in these two forests, the anion deficit, which we consider to be due to organic acid anions, dominated the anion-leaching regime.

In the study of accelerated leaching of cations in forests subject to acidic deposition, controls on SO42– and NO3– retention or mobility have been emphasized (Johnson et al. 1982; Reuss and Johnson 1986; Mitchell et al. 1996). Nitrogen saturation of forest ecosystems, including nitrification and nitrate leaching even in regions where NH4 may be the dominant form of N in deposition, can increase the total leaching of strong-acid anions from the forest floor (Galloway 1995). Although accelerated loss of cations from the forest floor does not necessarily result in a loss from the ecosystem, it does imply a shift in the biogeochemistry of a major ecosystem component. The forest floor is central to the biogeochemistry of the forest ecosystem through nutrient inputs and storage in detritus, mineralization, ion exchange, and nutrient uptake, in addition to throughfall inputs and soil solution leaching.

In a red pine stand exhibiting nitrification and other characteristics of N saturation under continuing NH4NO3 amendments, the forest-floor leaching regime shifted dramatically to dominance by the strong-acid nitrate anion. In an oak stand that retained nearly all of the added N over the first 6 years of treatment, the anion leaching regime shifted to approximately equal contributions by nitrate and organic anions. In both forests, Ca2+, K+, and Mg2+ concentrations were significantly correlated with NO3– concentrations in Oa leachate (though greater fractions of the variances in cation concentrations were accounted for by these correlations in the pine stand). Comparisons between the two forests suggest that nitrification in the pine stand, or greater uptake requirement of nutrient cations in the oak stand, or both, exerted control on the relationships between nitrate and cation concentrations in Oa leachate. Differences in the biogeochemistry of the two forests highlights the need to study biogeochemical changes where ecosystems can integrate responses at appropriately large scales and levels of organization.

Acknowledgments

This work was supported primarily by the National Science Foundation through the Long-Term Ecological Research (LTER) program and by a NASA Graduate Training Grant Fellowship award. We appreciate the technical expertise of J. Mark Riddell, Bill Berger, Jeff Merriam, Rich Hallett, Gloria Quigley, Amy Simoneau, Jim Muckenhoupt, Pat Micks, Sansheng Mo, and Talley Lent. We thank the folks at
Currie et al.

the Complex Systems Research Center and at the Harvard Forest for valuable assistance, and folks at the U.S. Forest Service in Durham for the use of analytical equipment and the expertise provided by Jane Hislop and Dr. Jim Hornbeck. We thank Dr. Bill McDowell for the use of analytical equipment, project planning, and manuscript review. We also extend thanks to Dr. Rich Boone and Dr. Mark Hines for help in project planning and manuscript review, and to Dr. Gary Lovett, Dr. Per Gundersen, and Dr. Jana Compton for helpful points regarding data interpretation.

References


© 1999 NRC Canada


