SPATIAL AND TEMPORAL VARIATION IN CALCIUM AND ALUMINUM IN NORTHERN HARDWOOD FOREST FLOORS

R. D. YANAI[1,*], R. P. PHILLIPS[2], M. A. ARTHUR[3], T. G. SICCAMA[4] and E. N. HANE[5]
[1] *SUNY College of Environmental Science and Forestry, 1 Forestry Drive, Syracuse, NY 13210, U.S.A.;* [2] *Cornell University, Ithaca, NY, U.S.A.;* [3] *University of Kentucky, Lexington, KY, U.S.A.;* [4] *Yale School of Forestry and Environmental Studies, New Haven, CT, U.S.A.;* [5] *Rochester Institute of Technology, Rochester, NY, U.S.A.*
*(*author for correspondence, e-mail: rdyanai@mailbox.syr.edu, Fax: 315 470-6954, Tel. 315 470-6955)*

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Abstract. Acid rain results in losses of exchangeable base cations from soils, but the mechanism of base cation displacement from the forest floor is not clear, and has been hypothesized to involve mobilization of aluminum from the mineral soil. We attempted to test the hypothesis that losses of calcium from the forest floor were balanced by increases in Al in New Hampshire northern hardwoods. We measured exchangeable (six stands) and acid extractable (13 stands) Ca and Al in horizons of the forest floor over an interval of 15 years. Our sampling scheme was quite intensive, involving 50 or 60 blocks per stand, composited in groups of 10 for chemical analysis. Even at this level of effort, few stands exhibited changes large enough to be significant. Because of high spatial variability, differences would have had to be greater than about 50% to be statistically detectable. Differences in Ca and Al concentrations between Oi, Oe, Oa, and A horizons, however, were readily detected. Acid-extractable Al increased with depth, while Ca concentrations decreased; Ca-to-Al ratios decreased from 8.3 (charge basis) in the Oi to 0.2 in the A horizon. Therefore, a small change in sampling depth, or the inclusion of more or less A horizon material in the forest floor, could cause large differences in measured Ca and Al concentrations. To detect small changes in exchangeable cations over time would require sampling very intensively with careful control for comparability of horizons.

Keywords: acid rain, Ca:Al, cation depletion, forest floor, soil

1. Introduction

Acid rain is thought to have accelerated the loss of base cations from soils (Likens *et al*., 1996), with adverse consequences for forest health and productivity. Calcium and magnesium depletion have been implicated in the decline of red spruce and sugar maple (Pitelka and Raynal, 1989). In addition to accelerating the loss of base cations, soil acidification increases the availability of aluminum, which affects plants directly by decreasing root growth and indirectly by interfering with base cation uptake (Cronan and Grigal, 1995). The ratio of Ca to Al in soil solutions has been proposed as an indicator of the risk of damage to trees (Cronan and Grigal, 1995).

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Soil acidification reflects an increase of acid cations (H^+ and Al^{3+}) at the expense of base cations on exchange sites. The low pH of the forest floor makes it difficult to base explanations of further acidification on the acidity of precipitation (Krug and Frink, 1983; Brandtberg and Simonsson, 2003). Alternatively, mobilization of Al by acid rain from the mineral soil below may provide the acid cation responsible for the loss of base cations in forest floors (Lawrence *et al.*, 1995). Although water moves down through well drained soils after a rain event, the water potential gradient maintained by soil evaporation and root uptake of water results in a net upward movement of water during rainless periods. Aboveground litterfall and roots and their associated mycorrhizal hyphae can also move Al into the forest floor (Giesler *et al.*, 2000).

The primary evidence for the hypothesis that Al, not H, is responsible for Ca loss from the forest floor during soil acidification is based not on observations of change over time but on an analysis of variation among samples from a single point in time. Exchangeable Ca concentrations in Oa horizons from red spruce stands showed little relationship to exchangeable H but a strong inverse relationship to exchangeable Al (Lawrence *et al.*, 1995; Shortle *et al.*, 1997). An alternate explanation for this result is a pattern in Ca and Al concentrations with depth in the forest floor, such that samples collected at different depths would display an inverse relationship of Ca to Al. A better test of the hypothesis that Al is displacing Ca from the forest floor would be a comparison of change over time in these two elements, rather than an analysis of spatial pattern.

The first objective of this study was to test the hypothesis that displacement of Ca by Al is an important mechanism of Ca loss in forest floors over time. We applied this test by comparing exchangeable Ca and Al in the Oa horizon of six stands of New Hampshire northern hardwoods at a time interval of 15 years. If Al mobilized by acid rain were responsible for losses of Ca in the forest floor, then we should find gains in exchangeable Al coincident with losses in exchangeable Ca. The exchangeable Ca and Al pools are the most relevant to the hypothesis test; we also had values for acid-extractable Ca and Al in the forest floor as a whole for 13 stands, so we compared them as well. The second objective was to describe patterns of acid-extractable Ca and Al with depth within the forest floor. If Ca and Al concentrations vary systematically with depth, then measurements of Ca–Al relations will be sensitive to the depth of sampling.

2. Methods

We sampled forest floors in 13 stands of northern hardwoods in the central White Mountains of New Hampshire, all between 310 m and 550 m elevation. The older stands were dominated by yellow birch (*Betula alleghaniensis* Britton), beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh), red maple (*Acer rubrum*), and paper birch (*B. papyrifera*), while the younger stands had a high proportion of pin cherry (*Prunus pennsylvanica* L.f.) (Yanai *et al.*, 2000). Stands ranged in age from 1 year to over 120 years and originated following logging. These stands had been previously sampled by Federer (1984) in 1979 and 1980 and therefore provided an opportunity to assess changes in forest floor chemistry over time.

Six of the 13 stands, those located in the Bartlett Experimental Forest, were sampled in 1979 and 1994. On both occasions, samples were separated by horizon (Oi, Oe, Oa, and A). The other seven stands, located elsewhere in the White Mountain National Forest, were sampled in 1980 and 1995. The 1980 samples were not separated by horizon; the 1995 samples were separated into O and A horizons. In all stands, samples were taken using a plastic template holding stainless steel pins in a 10 × 10 cm square array to collect 0.01 m^2 forest floor blocks to the depth of the E or B horizon. Ten blocks were collected and composited from each transect. Transects ranged from 33–90 m in length, depending on the size of the stand. Five transects were sampled per stand each year except 1979, when six transects were sampled. More details of site descriptions and sample collection can be found in Federer (1984) and Yanai *et al.* (1999). Changes in base cation chemistry (Yanai *et al.*, 1999), organic matter (Yanai *et al.*, 2000), and lead chemistry (Yanai *et al.*, in press) are reported elsewhere as well.

In the laboratory, samples were air dried, sieved, weighed, and subsampled for air-dry moisture content. Samples from 1979–80 and 1994–95 were analyzed at the same time to prevent systematic differences in analytical methods. Exchangeable Ca and Al were measured in Oa horizon samples by extraction with 1 N NH_4Cl (Bertsch and Bloom, 1996). Exchangeable Al was also determined by extraction with 1 N KCl followed by titration to identify the portion of exchangeable acidity due to Al (Sims, 1996). Acid-extractable Ca and Al were measured in 5 N HNO_3 extracts of ashed soils.

We report concentrations on the basis of the organic mass of the forest floor, calculated from loss on ignition, rather than on the basis of the total mass. Most of the cation exchange capacity in the forest floor is provided by organic matter (Ross and Bartlett, 1995). None of the extractants used dissolves primary minerals, so this choice of units reduces variation in concentrations caused by variation in the mineral fraction of the forest floor (Federer *et al.*, 1993).

Statistical analyses were performed using SAS version 6.09 for UNIX. We log-transformed concentrations before performing *t*-tests or calculating detectable differences. We used Satterthwaite's approximation for degrees of freedom for the unequal variance two-sample *t*-tests (Snedecor and Cochran, 1989).

3. Results

The hypothesis that losses of Ca from the forest floor would be accompanied by increases in Al was not supported by our data. Of the six stands for which we measured exchangeable Ca and Al in the Oa horizon, only one falls in the lower right quadrant of Figure 1, corresponding to a loss of exchangeable Ca and gain of exchangeable Al. Similarly, in the thirteen stands for which we measured acid-extractable Ca and Al in the forest floor, there is no pattern of Al gains in stands with Ca losses (Figure 2).

Spatial variation in forest floor chemistry was quite high, such that few of the changes were statistically significant within stands (Table I). We calculated the

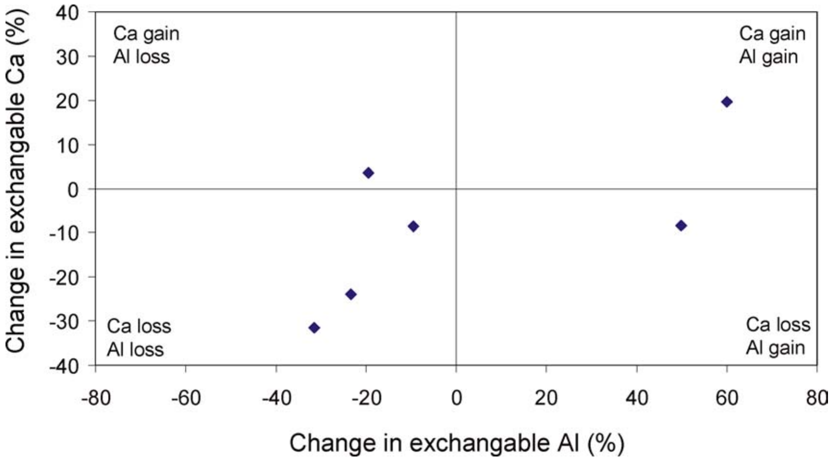

Figure 1. Changes over 15 years in exchangeable Ca and Al in the Oa horizon of six northern hardwood stands. The percentage change is based on the comparison of the mean of log-transformed concentrations (cmol/kg). Points in the lower right quadrant support the hypothesis that losses of Ca are accompanied by increases in Al concentrations.

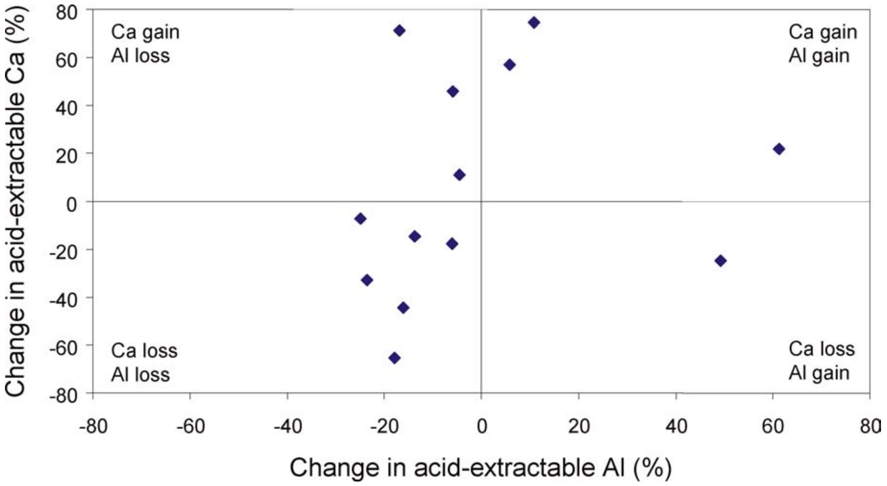

Figure 2. Changes over 15 years in acid-extractable Ca and Al in the forest floor (O + A horizons) of thirteen northern hardwood stands. The percentage change is based on the comparison of the mean of log-transformed concentrations (cmol/kg). Points in the lower right quadrant support the hypothesis that losses of Ca are accompanied by increases in Al concentrations.

TABLE I

Exchangeable and extractable Ca and Al in forest floors of New Hampshire northern hardwoods

Horizon	Extraction	Concentration (g/kg_o) Ca	Concentration (g/kg_o) Al	Detectable difference (%) Ca	Detectable difference (%) Al
Oi	Acid extractable	10. 4	0.9	7	52
Oe	Acid extractable	7.7	3.5	12	49
Oa	Acid extractable	4.7	7.4	22	59
Oa	NH_4Cl exchangeable	4.3	0.7	46	173
A	Acid extractable	4.8	12.9	23	44
O+A	Acid extractable	7.7	8.3	30	92

Means are computed on untransformed data, providing values appropriate to scaling up to the stand. The minimum differences detectable at $\alpha = 0.05$ within stands are computed on log-transformed data. These results are the average for 6 stands, except for the O + A, which is an average for 13 stands. Each stand was sampled at two dates at 50 or 60 points composited for analysis into 5 or 6 transects.

magnitude of difference it would be possible to detect between stands or over time given the variation within stands in our measures of forest floor chemistry. The change in Oa horizon exchangeable Al required to be significant at $\alpha = 0.05$ ranged from 50 to 175%, depending on the stand. For exchangeable Ca, the range was 27 to 60%. For both elements, the acid extractable concentrations were less variable than the exchangeable concentrations, on average (Table I). For acid extractable concentrations, as for exchangeable concentrations, smaller differences would be statistically detectable for Ca than for Al, on average.

These estimates are specific to our sampling methods, which are rather intensive, involving five or six transects per stand, each of which combines ten 10 cm × 10 cm forest floor blocks. We also calculated the number of such transects that would provide the ability to detect a difference of 20%, using the variance we measured. The number of transects averaged 19 for exchangeable Ca and 55 for exchangeable Al in Oa horizons.

We also tested for a spatial relationship between Ca and Al concentrations with depth in the forest floor. In the six stands in which forest floors were separated into four horizons, acid-extractable Ca concentrations declined with depth, such that concentrations in the A horizon were only half that in the Oi (Table I, Figure 3). Acid-extractable Al concentrations increased by an order of magnitude from the Oi to the A (Table I, Figure 3). There is, therefore, a negative correlation of Ca with Al concentration when all horizons are combined ($p < 0.0001$ for linear regression over all samples, $n = 256$). Ca-to-Al ratios averaged 8.3, 1.6, 0.5, and 0.2 in the Oi, Oe, Oa, and A horizons. Within a horizon, in contrast, Ca and Al concentrations

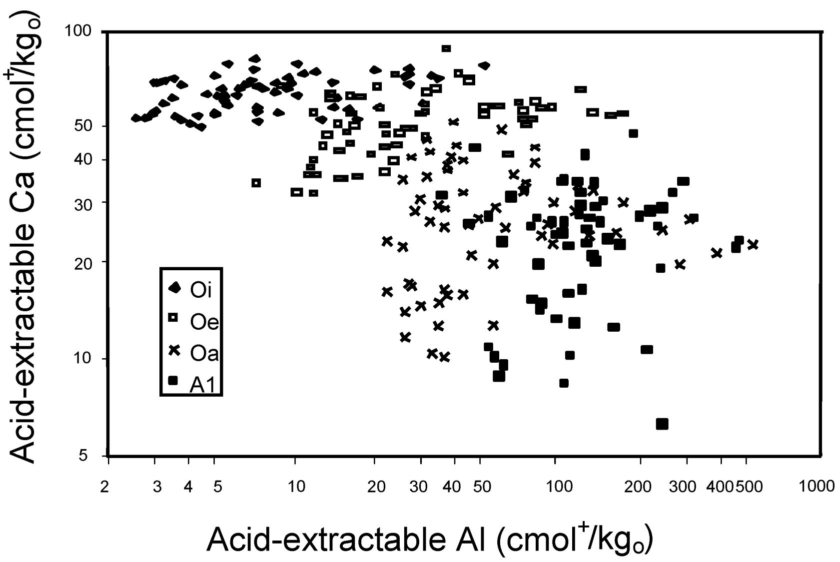

Figure 3. Acid-extractable Ca and Al concentrations in forest floor horizons of six northern hardwood stands are positively correlated within horizons, but negatively correlated across horizons. Each point represents one transect of 10 forest floor samples.

were positively correlated (Figure 3), significantly so in the Oi ($P < 0.04$) and Oe ($P < 0.001$) horizons.

4. Discussion

4.1. CHANGES IN EXCHANGEABLE Ca AND Al OVER TIME

Our study was conducted in northern hardwoods with an average pH of 3.5 in the forest floor (Taylor, 1996) and unknown rates of soil acidification. Sites with higher rates of acidic deposition and soil acidification, such as high-elevation red spruce, might provide a better test of the hypothesis that increases in exchangeable Al accompany decreases in exchangeable Ca in the forest floor. It is also possible that greater losses in exchangeable cations took place before our earliest collection date. Atmospheric deposition of acids was highest in the 1970s (Driscoll *et al.*, 2001) and reductions in exchangeable base cations result in reduced rates of loss (Kirchner and Lyderson, 1995). Studies conducted before 1950 reported higher exchangeable Ca and Mg in forest floors of red spruce stands than did studies conducted after 1970 (Shortle and Bondietti, 1992).

Changes in Ca and Al concentrations in the forest floor over the period from 1979 to 1995 were mostly too small to be statistically significant (Table I), even though our sampling intensity was relatively high (Yanai *et al.*, 2003). This limitation is common to the study of forest soils; high spatial variability results in low power to detect change over time (Yanai *et al.*, 2003). The magnitude of differences detectable with a *t*-test in other forest floor studies has ranged from 5–104% for Ca and 40–97% for Al (David *et al.*, 1990; Johnson, 1990; Johnson *et al.*, 1994; Wilson and Grigal, 1995; David and Lawrence, 1996; Lawrence *et al.*, 1997; Dijkstra and Fitzhugh, 2003). The same is true in mineral soils where detectable differences range from 22–145% (average by study) for Ca and 17–173% for Al (Johnson *et al.*, 1988, 1994; Johnson, 1990; David *et al.*, 1990; Kirchner and Lyderson, 1995; Wilson and Grigal,1995; David and Lawrence, 1996; Markewitz *et al.*, 1998).

4.2. PATTERNS OF Ca AND Al CONCENTRATIONS WITH DEPTH

It is attractive to measure variation in Ca and Al in space rather than over time, but this substitution has risks, due to the systematic variation in these elements with depth. A dramatic decline in Ca-Al ratios with depth makes it important to ensure that like horizons are compared in studies of Ca-Al relationships. Forest floor horizons are difficult to distinguish repeatably and accurately in the field, so this problem is not a trivial one (Federer, 1982). The definition of the Oi, Oe, and Oa is based on rubbed fiber content (Soil Survey Staff, 1975), which can be felt between the fingers but not precisely quantified in the field. The boundary between the O and A is defined at 20% organic carbon or 40% organic matter (Federer, 1982), which can be readily measured in the lab but only estimated in the field. In this study, for example, of the 101 cases in which O and A horizons were distinguished, there were 18 in which loss on ignition proved the division to be incorrect (Yanai *et al.*, 2000).

Differences in sampling technique can introduce differences in sampling depth that are important to the measured chemistry of the forest floor. In other forest floor studies, significant differences in Pb (Friedland *et al.*, 1984a,b) and Ca (Yanai *et al.*, 1999) between sampling dates were attributed to variation in measurement techniques rather than to change over time. Both decreased Ca and increased Al in the forest floor of the spruce-fir zone at Hubbard Brook between 1969–70 and 1987–92 (Lawrence *et al.*, 1995) could be due to greater inclusion of A horizon material at the latter date (Yanai *et al.*, 2000). The magnitude of error in Ca-to-Al ratios caused by differences in sampling depth could be quite large. Compared to the Oa horizon, the Ca-to-Al ratio of the Oe just above it was three times higher, and that of the A below it was more than 50% lower. Variation in sampling depth contributes to the high variance that makes it difficult to detect small changes in forest floor properties over time or between treatments (Yanai *et al.*, 2003).

5. Conclusions

Changes in exchangeable Ca and Al in forest floors of northern hardwoods since about 1980 generally averaged less than the 50–75% that would have been detectable statistically. We could not reject the hypothesis that losses in exchangeable Ca are mediated by increases in exchangeable Al, because most of the changes we observed were below these detection limits. High spatial variation in forest floor mass and chemistry makes it difficult to detect smaller changes over time. Both Ca and Al concentrations are sensitive to variation in the depth of samples collected from the forest floor, with Ca/Al ratios changing more than sevenfold between the Oe and A horizons. Comparing forest floor samples for Ca or Al chemistry requires careful control over sampling depths, because the changes introduced by differences in sampling methods could easily exceed the differences expected between stands or over time.

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