Mechanisms of Base-cation Depletion by Acid Deposition in Forest Soils of the Northeastern U.S.

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Abstract

Several studies have indicated a long-term decrease in exchangeable Ca in forest soils within the northeastern United States, but the regional extent of these decreases and the importance of acid deposition as a cause has not been fully resolved. Results, from two recently completed studies have provided the opportunity to further investigate the role of acid deposition in depletion of base cations in northeastern forest soils. These two studies entailed 1) a survey of soils in northeastern red spruce (*Picea rubens* Sarg.) stands, which were selected to encompass the range of environmental conditions to which this species is subjected, and 2) a study of base-cation leaching in soils of a hardwood watershed in the Catskill Mountains of New York.

Results from the survey of spruce stands indicated that exchangeable Ca concentrations varied considerably in the Northeast as a result of differences in parent material mineralogy. A stronger relationship between relative weathering potential of parent material and exchangeable Ca concentrations was observed in the Oa horizon than in the B horizon of soils at these sites. Concentrations of exchangeable Ca in the B horizon may have decreased to a level at which further decreases are buffered by high concentrations of exchangeable Al.

An upslope increase in atmospheric deposition of SO_4^{2-} corresponded to an upslope increase in the leaching of base cations, and an upslope decrease in acid-neutralizing capacity of stream water in the Catskill Mountain watershed. Upslope gradients in natural factors that could increase base-cation leaching were not detected. Decreases in concentrations of exchangeable base cations were approximately balanced by increases in concentrations of exchangeable Al. Greater Al mobilization in the mineral soil by acid deposition at upper elevations than at lower elevations was the most probable explanation for the upslope increase in leaching of base cations and stream water acidity.

Low Ca to Al ratios in mineral soil solution were found to be related to high levels of Al saturation in the forest floor in the survey of spruce stands. Mobilization of Al in the mineral soil tends to increase Al saturation in the forest floor by making Al available for upward transport by biocycling and water movement. Reversal of past decreases in exchangeable Ca concentrations will be hindered by 1) continued inputs of mobile anions that facilitate leaching, 2) high Al saturation in the mineral soil that will interfere with uptake of Ca by roots, 3) increasing Al saturation in the forest floor, and 4) decreasing trends of atmospheric deposition of Ca..

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Introduction

The possibility that acid deposition could deplete base cations in soils was acknowledged in the early stages of acid rain research in the 1970's (Cowling and Dochinger 1980). The effect of acid deposition on forest soils remained unresolved at the close of the National Acid Precipitation Program (NAPAP) in 1990, however, because (1) there was no historical soil data to show that changes in soil Ca concentrations had actually occurred, either through natural processes or acid deposition, 2) release of bases through weathering could possibly compensate for losses from leaching, and 3) the importance of natural sources of acidity relative to acid deposition was unknown. A comprehensive literature review by Shortle and Bondietti (1992) provided the first indication that exchangeable base concentrations may have decreased in the second half of the 20th century. This paper showed that, before 1950, concentrations of exchangeable Ca plus Mg in the soils of coniferous forests in the Northeast were generally about twice that of concentrations measured after 1970. The first study to directly compare Ca concentrations measured early in the century with those measured after the discovery of acid deposition in the 1970's showed that extractable Ca concentrations were significantly lower in 1984 than in 1930-32; a result attributed to forest aggradation in this study (Johnson et al. 1994a). Detailed Ca budgets developed on Whiteface Mountain, NY, indicated that the exchangeable Ca pool in the forest floor of this site declined from 1986 to 1990 (Johnson et al. 1994b) at a rate greater than that found in in the study of Johnson et al. (1994a). In this study, a long-term decreasing rate of atmospheric deposition of Ca, identified by Hedin et al. (1994), was cited as a possible cause for the decrease in the 80's (Johnson et al. (1994b). The development of ecosystem Ca budgets through the use of stable isotopes of Sr (a biogeochemical analog of Ca) at Whiteface Mountain, NY (Miller et al. 1993), and Cone Pond, NH (Bailey et al.1996) provided additional evidence of decreasing pools of exchangeable Ca in the Northeast.

The results of these studies indicate that decreases in exchangeable soil-base concentrations have occurred at several locations within the Northeast, but the regional extent of these changes, and the importance of acid deposition as their cause was not fully resolved. Results from two recently completed studies have provided the opportunity to further investigate the role of acid deposition in depletion of base cations in northeastern soils. In the first of these projects, soil and soil solution samples were collected from 12 red spruce stands (*Picea rubens* Sarg.) in New York, Vermont, New Hampshire and Maine (Figure 1), which were chosen to encompass the range of environmental conditions and stand health experienced by

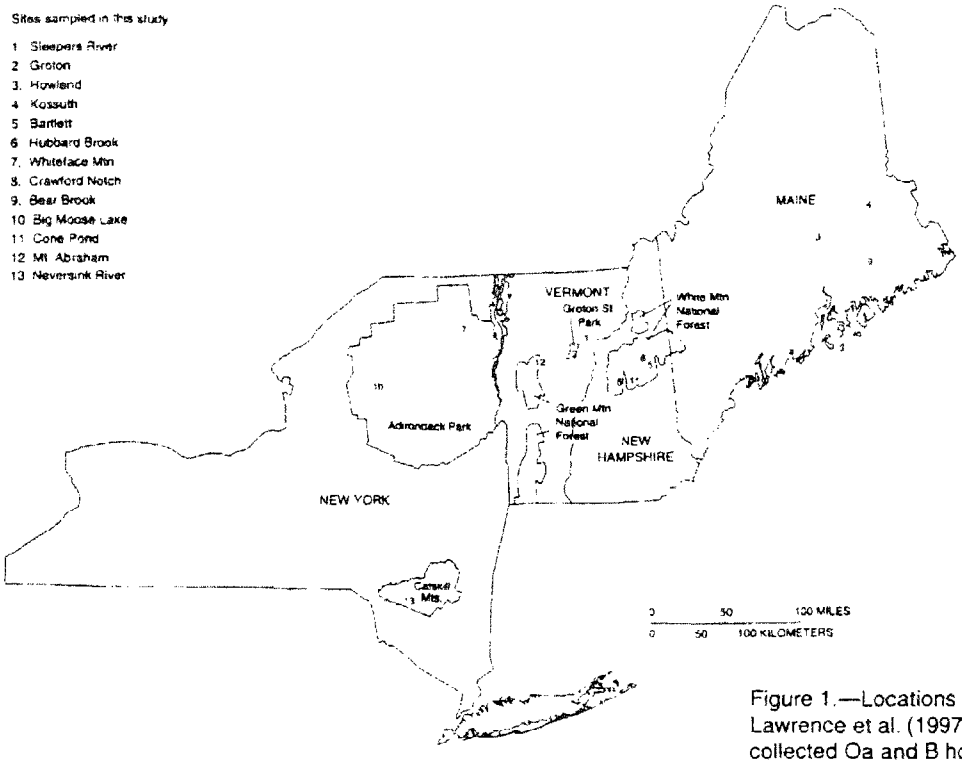


Figure 1.—Locations of red spruce stands where Lawrence et al. (1997) and Lawrence et al (in press) collected Oa and B horizon soil samples.

red spruce in this region. In the second project, soil-base leaching was studied over an elevational gradient in a hardwood forested watershed in the Catskill Mountains of southeastern New York (Figure 1). The purpose of this report is to integrate the published results of these two studies to summarize the mechanisms through which acid deposition affects the availability of base cations in the forest soils Northeast.

Methods

Survey of Soil Chemistry in Northeastern Red Spruce Stands

Red spruce was the predominant species in each of the 12 stands, although other coniferous and deciduous species were common. Increment cores indicated that the average age of canopy spruce at each site ranged from 96 to 175 years. Apparent stand health varied from good to poor where extensive dieback had occurred. Stand elevations ranged from 80 m at Howland ME to 975 m on Whiteface Mountain, NY. Wet deposition of SO_4 at six of the sites, was determined from on-site monitoring; at the remaining six sites, wet deposition was estimated from the nearest monitored site. Details of how wet deposition estimates were derived are available in Lawrence et al. (1997). Wet-only atmospheric deposition of SO_4 ranged from 12.7 mmol m^{-2} yr^{-1} at 150 m elevation at Kossuth, ME to 28.8 mmol m^{-2} yr^{-1} at 810 m elevation in Crawford Notch, NH.

A relative value of calcium weathering potential was assigned on the basis of general mineralogy, determined from bedrock maps and a till-source model that identified rock types that could be present in non-local till (Bailey and Hornbeck, 1992). Relative weathering potential varied from 1 at sites underlain by metapelite and quartzite, to 3 at sites influenced by calcareous schist. Further details about these sites including ratings of relative Ca weathering potential are available in Lawrence et al. (1997). Soils at all sites were classified as Spodosols.

Soil samples were collected from the faces of nine individual soil pits at each site (grouped in three plots, each with three pits). Eight of the 12 sites were sampled in mid-June and late September or early October of 1992 and 1993; four of the 12 sites were only sampled once (early summer or early fall) in each of the two years. In each pit, a sample was collected from the middle of the Oa horizon and from the top 10 cm of the B horizon. This sampling design was chosen to compliment assessments of red spruce tree condition conducted in conjunction with the soils investigation. Sampling in the early summer and early fall was timed to coincide with the periods when nutrient concentrations in foliage were both high and low for purpose of biochemical studies of foliage processes. The three individual soil samples from each horizon, in each plot, were combined into one sample and thoroughly mixed before chemical analysis to yield one sample from each horizon in each plot. All samples were analyzed for exchangeable cations (Ca, Mg, Na and K) by extraction with 1 *M* NH_4Cl (Blume et al.

1990) and exchangeable acidity (Al, H) by extraction with 1*M* KCl (Thomas 1982). Samples from Oa horizons collected on two dates at each site were analyzed for acid-extractable-Ca concentrations (Friedland et al. 1984), and Oa-horizon samples collected on one date were analyzed for total Ca concentrations by neutron activation (Parry 1991). Mineral Ca concentrations were calculated by subtracting concentrations of acid-extractable Ca from concentrations of total Ca; reactive nonexchangeable Ca concentrations were calculated by subtracting concentrations of exchangeable Ca from acid-extractable Ca concentrations. Exchangeable Ca is probably the most representative form of plant-available Ca.

The study of Johnson et al. (1994a), in which Ca concentrations in Adirondack Mountain soils in 1930-32 were compared to values in 1984, followed the methods of Heimburger (1934), which were not directly comparable to the method of Friedland et al. (1984); a commonly used method for determination of extractable Ca concentrations in the 1980's and 1990's. Methods tests by Lawrence et al. (1997) showed that the data from the studies of Johnson et al. (1994a) and Heimburger (1934) yielded concentrations about 25% higher than the Friedland et al. (1984) method. This factor was applied to the data of Johnson et al. (1994a) and Heimburger (1934) to allow comparisons with data from other studies.

Soil solutions were collected from all soil samples by expulsion (described and evaluated in Lawrence and David 1996). The procedure entails 1) manually packing field moist soil in a PVC cylinder to reduce porosity, 2) adding simulated throughfall solution to saturate the soil column, 3), discarding solution that drains off by gravity, and 4) applying air pressure (172 kPa for Oa horizon samples; 138 kPa for B horizon samples) to force out the solution that is collected for analysis of total Al, total monomeric Al and organic monomeric Al by methods in Lawrence et al. (1995). Concentrations of polymeric Al were determined by subtracting total monomeric Al concentrations from total Al concentrations; inorganic monomeric Al concentrations were determined by subtracting organic monomeric Al concentrations from total monomeric Al concentrations.

As part of the regional survey of spruce stands, soil chemistry also was evaluated in spruce stands of two adjacent watersheds in eastern Maine. Through the EPA-sponsored Watershed Manipulation Project 1800 equiv ha^{-1} yr^{-1} of $(NH_4)_2SO_4$ was applied to one of these watersheds between 1989 and 1995 (Norton et al. 1994). This treatment resulted in significantly higher concentrations of NO_3 in stream water of the treated watershed than the reference watershed, in response to elevated nitrification rates in soil. The effects of increased nitrification rates and associated acidity on Al mobilization were evaluated by determining pH and concentrations of total Al, total monomeric Al and organic monomeric Al in soil solutions collected by expulsion, as described above. To further investigate possible changes in soil Al concentrations associated with changes in soil acidity, archived Oa horizon soil collected in spruce stands in the Hubbard Brook Experimental Forest, NH, in 1969-1970, 1987 and 1992, were analyzed for concentrations of exchangeable and acid-extractable Ca and Al, by the methods given above.

Soil-Base Leaching in Hardwood Forested Watershed

The effects of acid deposition on base leaching were studied over an elevational gradient (approximately 800 m to 1230 m) in Winnisook watershed, a subbasin of the Neversink River, in the Catskill Mountains of NY. Atmospheric deposition was measured along the gradient at 14 stations from 799 m to 1234 m near the summit of the watershed. At each station, four 20-cm diameter funnels collected throughfall solutions that were combined by station for analysis. During November through April, the funnels were replaced with galvanized cylinders lined with plastic bags, to collect frozen precipitation. Throughfall measurements have been shown to be a reliable method for estimating total atmospheric S deposition (Lindberg and Garten, 1988; Lindberg and Lovett, 1992, Lawrence and Fernandez, 1993). Throughfall collections also were used to estimate water input to the watershed.

This watershed is forested primarily by *Acer saccharum*, *Betula alleghaniensis*, and *Fagus grandifolia*, but stands of *Abies balsamea* are common along upper elevation ridges. Soils are classified as Inceptisols. Soil samples were collected from the B horizon at 48 locations along the elevational gradient, by taking equal volumes of soil from each 10 cm increment of the mineral profile, which were mixed before analysis to yield one B horizon sample from each location. Exchangeable cation concentrations were determined by methods used in the survey of northeastern spruce stands. Mineral soil was also collected from a single pit downslope of Winnisook watershed at 570 m elevation where soil-base saturation was higher than within Winnisook watershed. This soil (the 0-10 cm layer below the O horizon) was thoroughly mixed and put in nylon mesh bags, which were then placed beneath the Oa horizon at 35 locations along the elevational gradient. The approach followed the buried bag method described in David et al. (1990). Bags were removed and chemically analyzed after one year by the methods used in the survey of spruce stands.

Relations among acid deposition, soil base saturation and base leaching were further evaluated by leaching solutions of H_2SO_4, HNO_3, CaCl and NaCl through B horizon soil of three different base saturation values. Ionic strength (0.32 to 0.52 mM_c L^{-1}) and pH (3.7 to 4.8) of the added solutions were similar to mean values measured in Oa horizon soil solutions in the Neversink watershed (D.A. Burns, USGS, unpublished data). Soil samples used for the buried bag experiment were also used for the leaching study; samples with the highest base saturation (14.4%) had not been placed in the soil profile in Winnisook watershed, whereas the other samples (base saturation 9.6% and 4.5%) had been in the soil profile of Winnisook watershed for one year. Solutions were extracted from the soil samples with a mechanical vacuum extractor (Blume et al. 1990). Duplicate extractions were done for each treatment. Concentrations of base cations (Ca, Mg, Na and K) and acid anions (SO_4, Cl, and NO_3) were measured in leachates, as described in Lawrence et al. (1995).

Table 1.—Exchangeable Ca concentrations as $cmol_c kg^{-1}$ and as a percentage of cation exchange capacity (Ca saturation) for the Oa and B horizons of 12 red spruce stands and 2 hardwood stands in the Northeast. Samples were collected from the upper 10 cm of the B horizon in the spruce stands, from the Bh horizon at Hubbard Brook. In Winnisook Watershed equal volume samples were collected at 10 cm depth increments through the entire B horizon, then mixed before analysis.

	Oa Horizon		B Horizon	
SITE	($cmol_c kg^{-1}$)	(($cmol_c kg^{-1}$) CEC^{-1})100	($cmol_c kg^{-1}$)	(($cmol_c kg^{-1}$) CEC^{-1})100
SPRUCE STANDS				
Sleepers River, VT [1]	22	51	0.68	6.9
Groton, VT [1]	14	41	0.32	13
Howland, ME [1]	11	34	0.19	3.8
Kossuth, ME [1]	6.3	24	0.19	2.6
Bartlett, NH [1]	11	31	0.18	3.4
Hubbard Brook, NH [1]	7.9	25	not sampled	not sampled
Whiteface Mt., NY [1]	6.3	26	0.57	7.3
Crawford Notch, NH [1]	6.8	21	0.30	3.1
Bear Brook, ME [1]	5.3	21	0.32	4.1
Big Moose Lake, NY [1]	6.4	20	0.37	3.1
Cone Pond, NH [1]	3.5	10	0.11	1.6
Mt. Abraham, NY [1]	2.1	9.1	0.41	4.0
HARDWOOD STANDS				
Hubbard Brook, NH [2]	6.75	38.5	0.63	8.4
Winnisook Watershed, NY [3]	2.31	13.4	0.16	2.7

[1] From Lawrence et al. (1997)
[2] From Johnson et al. (1991)
[3] Previously unpublished data, G.B. Lawrence, U.S. Geological Survey

Stream water samples were collected weekly at the base of Winnisook watershed and approximately monthly at seven upstream sites from May 1991 through September 1994. These samples were analyzed for Ca, Mg, Na, K, SO_4, Cl, NO_3, total monomeric Al, and organic monomeric Al (methods described in Lawrence et al. 1995). To evaluate elevational trends in stream chemistry that were most influenced by soils (and least influenced by ground water), only samples collected on dates with the highest 20% of stream flows were included.

Results and Discussion

Current Status of Soil Calcium

Concentrations of exchangeable Ca, the predominant base cation in northeastern forest soils, varied by a factor of 10 in the Oa horizon of the 12 red spruce sites (Table 1). There were no geographical patterns other than high concentrations in eastern Vermont; the concentrations at the Big Moose Lake site were similar to those measured in Maine, and the concentration at the Bartlett, NH site, in the central White Mountains, was three times that of Cone Pond, in the southern White Mountains of New Hampshire. Exchangeable Ca concentrations expressed as Ca saturation (Ca as a percentage of total cation-exchange capacity) varied by a factor of 5. Exchangeable Ca concentrations in the upper 10 cm of the B horizon at these sites were less varied than in the Oa horizon, and 1 to 2 orders of magnitude lower (Table 1). Geographic patterns of B horizon concentrations also differed somewhat from the Oa horizon; Whiteface Mountain, NY and Mt. Abraham, VT had relatively high concentrations in the B horizon, but these sites had concentrations in the Oa horizon that were among the lowest. Although soils in hardwood stands are generally considered less acidic than soils in conifer stands, exchangeable Ca concentrations in the Oa and B horizons in Winnisook watershed were in the lower range of the spruce stands, and the average value reported for a hardwood watershed at Hubbard Brook was slightly less than that measured in the spruce stands at Hubbard Brook (Table 1).

Exchangeable Ca was the largest Ca fraction in the Oa horizon of all spruce sites except those with a mineral-matter content greater than 30 percent (Whiteface, NY, Bear Brook, ME, and Mt. Abraham, VT), where mineral-bound Ca was the largest fraction (Figure 2). Reactive-nonexchangeable Ca was generally a minor component. Averaged for the 12 sites, acid-extractable Ca was comprised of 92 percent exchangeable Ca and 8 percent reactive-nonexchangeable Ca.

Concentrations of acid-extractable Ca measured in the spruce survey ranged from 13.9 $mmol\ kg^{-1}$ to 103 $mmol\ kg^{-1}$ (Figure 3). This range encompassed values determined by McNulty et al. (1991) for 11 red spruce stands, also in New York, Vermont, New Hampshire and Maine. The average of samples collected in 59 red spruce stands throughout the Adirondack Mountains of New York by Johnson et al. (1994a) fell in the middle of the range of the spruce survey data of Lawrence et al. (1997), but the average value

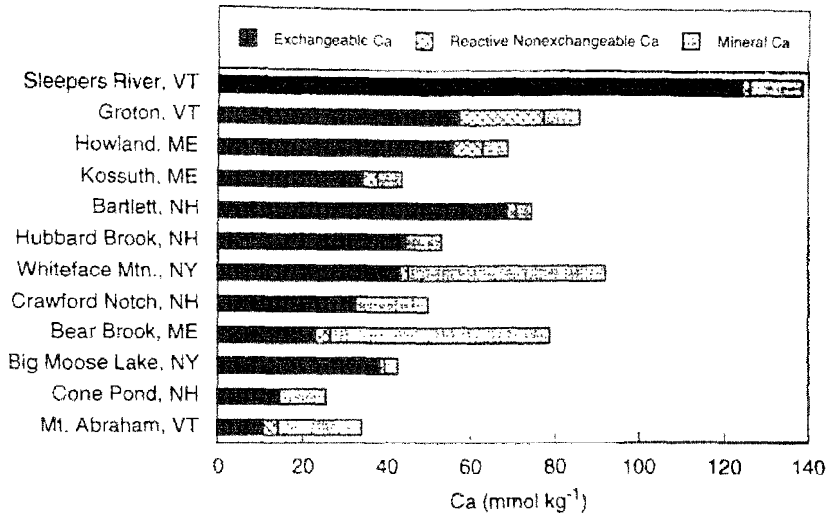


Figure 2.—Mean concentrations of exchangeable Ca, reactive nonexchangeable Ca (acid-extractable Ca concentrations minus exchangeable-Ca concentrations) and mineral Ca (total Ca concentrations minus acid-extractable Ca concentrations) in the Oa horizon of 12 northeastern red spruce stands. Reprinted with kind permission from Kluwer Academic Publishers (Biogeochemistry, vol. 38, 1997, Assessment of soil calcium in red srpuce forests in the northeastern United States, Lawrence, G.B., David, M.B., Bailey, S.W., and Shortle, W.C., figure 4, p. 30, copyright 1997).

obtained for the same sites by Heimburger in 1930-34 was approximately 30 mmol kg^{-1} higher, and in the upper quarter of the range determined in the spruce survey of Lawrence et al. (1997).

Causes of Regional Variability

The considerable variability observed in exchangeable Ca concentrations in the spruce survey of Lawrence et al. (1997) could be a result of spatial variations in (1) net Ca uptake by trees, (2) atmospheric deposition of Ca, (3) acid deposition, or (4) mineralogy of parent material. Analysis of increment cores of 54-108 live trees at each site indicated that all of the red spruce stands averaged approximately 100 years in age or older and had been experiencing similar rates of declining growth since 1965. The extent of mortality was highly variable from site-to-site, however, which suggested that net uptake of Ca may also have varied from site-to-site. Variations in net Ca uptake could therefore not be ruled out as a factor in the observed spatial variability, although neither stand health nor stand age were related to exchangeable Ca concentrations. Atmospheric deposition of Ca was also unlikely to be the primary cause of variability in exchangeable Ca concentrations among the spruce sites because deposition of Ca decreases consistently from west to east (Table 2), whereas soil Ca concentrations did not show a spatial pattern.

Table 2.—Atmospheric wet deposition of Ca (kg ha^{-1} yr^{-1}) in the northeastern United States, measured by the NADP/NTN network (http://nadp.sws.uiuc.edu/).

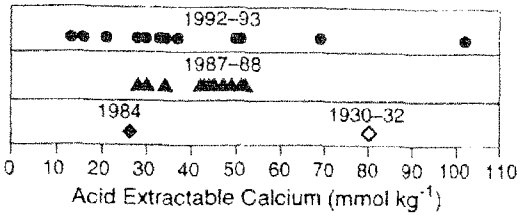
	1985	1995
Bennett Bridge, NY	1.95	1.60
Huntington Forest, NY	1.03	0.68
Underhill, VT	1.09	0.70
Hubbard Brook, NH	0.69	0.53
Greenville, ME	0.63	0.42

Calcium saturation was weakly related to wet deposition of SO_4 in the Oa horizon and unrelated to wet deposition of SO_4 in the B horizon (Figure 4), but was highly correlated with relative weathering potential in the Oa horizon. A weaker relation between Ca saturation and relative weathering potential was observed in the B horizon than the Oa horizon, despite the greater abundance of parent material in the mineral soil (Figure 4).

This relation suggests that acid deposition was unlikely to be the primary cause of variation in exchangeable Ca concentrations among sites, however enhanced leaching by acid deposition in the mineral soil can explain why Ca saturation is more strongly related to relative weathering potential in the Oa horizon than the B horizon. If base saturation is less than 20%, solute concentrations, and therefore cation leaching, are strongly controlled by exchangeable Al, which results in high rates of Al leaching and low rates of Ca leaching (Reuss, 1983). For example, in soil with a base saturation of 4.5%, only 0.11 meq L^{-1} of Ca are released per meq L^{-1} of added acid anion (Figure 5). The base saturation of the B horizon at all 12 spruce stands was less than 14% (Figure 6), whereas base saturation in the Oa horizon was greater than 20% at 10 stands, and greater than 16% at all 12 stands. Acidic deposition may have lowered base saturation in the B horizon to levels where further changes in base saturation were buffered by Al, which obscured the effect of differences in parent material Parent material was more clearly expressed in the Oa horizon where vegetative recycling reduces loss of Ca to leaching.

Acid Deposition and Ca Leaching

Additional information on leaching of Ca from soil was obtained in Winnisook watershed in the recent study by Lawrence et al. (in press). Within this watershed, atmospheric deposition of SO_4^{2-} increased by a factor of 2 from the lowest to the highest elevations in the watershed



EXPLANATION

- ● Mean concentrations of calcium in soils of individual sites in New York, Vermont, New Hampshire and Maine sampled by Lawrence and others (1997) in 1992–3.
- ▲ Mean concentrations of calcium in soils of individual sites in New York, Vermont, New Hampshire and Maine sampled by McNulty and others (1991) in 1987–88.
- ◇ Mean concentrations of calcium in soil of 38 samples collected by Heimburger (1934) throughout the Adirondack Mountains of New York in 1930–32.
- ◆ Mean concentrations of calcium in soil of 59 samples collected by Johnson and others (1994a) throughout the Adirondack Mountains of New York in 1984.

Figure 3.—Acid-extractable Ca concentrations in Oa horizons of red spruce stands in the northeastern US measured in this study and the studies of McNulty et al (1991), Johnson et al (1994a), and Heimburger (1934). Values from this study and the study of McNulty et al (1991) represent means of individual sites; the values from Johnson et al (1994a) represents the mean of 59 samples collected throughout the Adirondack Mountains of New York; the values from Heimburger (1934) represent the mean of 38 samples collected throughout the Adirondack Mountains of New York. Values reported by Johnson et al (1994a) and Heimburger (1934) have been adjusted for method bias. To express Ca concentrations on a soil mass basis loss-on ignition values of 0.90 were assumed for the data from the McNulty et al study and the Johnson et al study.

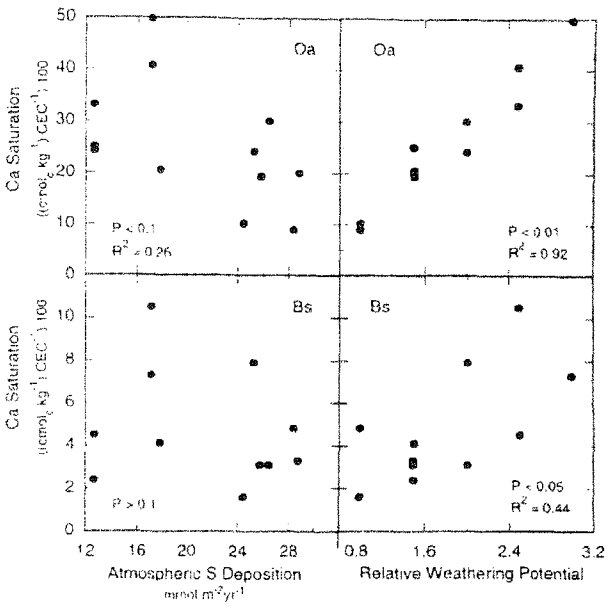


Figure 4.—Ca saturation as a function of atmospheric deposition and relative weathering potential in Oa and Bs horizons. Reprinted with kind permission from Kluwer Academic Publishers (Biogeochemistry, vol. 38, 1997, Assessment of soil calcium in red srpuce forests in the northeastern United States, Lawrence, G.B., David, M.B., Bailey, S.W., and Shortle, W.C., figure 5, p. 31, copyright 1997).

(fig. 7a), whereas the concentrations of exchangeable base cations in both undisturbed soil and soil bags, and the ratio of base cations to acid anions in stream water, decreased from the lowest to the highest elevations (fig. 7b,c,d). The decrease in exchangeable base cation concentrations in the soil bags was approximately balanced by an increase in exchangeable Al concentrations (Lawrence et al. in press).

Effects of the spatial trend in SO_4^{2-} deposition may be analogous to the effects of past temporal trends in acidic deposition through a space-for-time substitution. This approach assumes that the elevational gradient of SO_4^{2} deposition in Winnisook watershed has been maintained during past decades when acidic deposition rates both increased and decreased. Natural acidification processes may cause elevational gradients in the chemistry of soils and stream water, however (Lawrence et al., 1986). An elevational increase in net uptake of Ca by vegetation could contribute to an elevational trend in exchangeable base-cation concentrations in soil, as could decreased temperatures and increased abundance of conifers at upper elevations that would lead to a greater accumulation of organic acids and higher leaching rates than at lower elevations. Upslope increases in precipitation, decreases in evapotranspiration (ET), or decreases in soil depth would cause an elevational gradient in soil-water flux per volume of soil, which could also result in an elevational gradient in soil chemistry. Lastly, spatial variations in the mineral composition of parent material could result in an elevational gradient in base-cation concentrations in soil.

Winnisook watershed had been selectively cut up to about 900 m elevation before 1950, but we found no physical or historical evidence that the watershed was ever cleared or burned (Kudish, 1985). The cutting that had been done would most likely cause a decrease rather than an increase in exchangeable base-cation concentrations at low elevations by increasing aggradation rates. Spatial variations in tree species could not explain these spatial trends because all soil investigations (sampling and soil bag incubations) were done in similar stands of yellow birch (*Betula alleghaniensis* Britton), beech (*Fagus grandifolia* Ehrh.), and sugar maple (*Acer saccharum* Marsh). Vegetation uptake also did not explain the upslope decrease in exchangeable base-cation concentrations because decreased temperatures would tend to shorten the growing

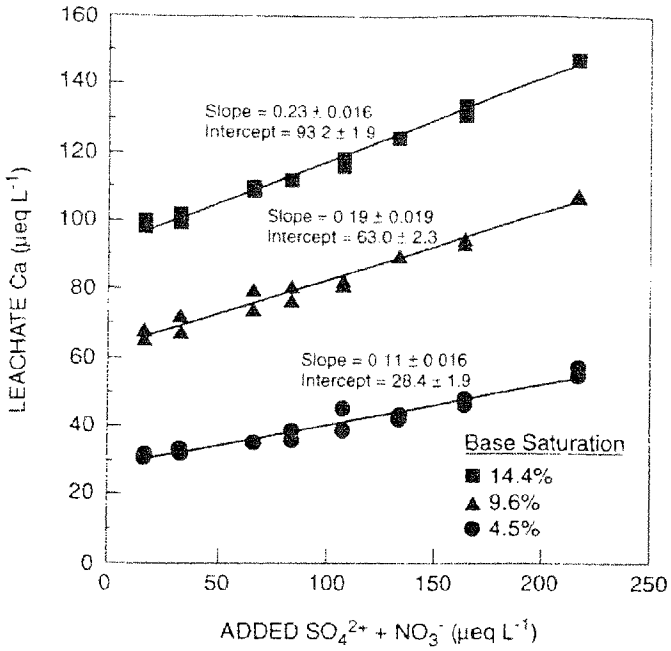


Figure 5. Concentrations of Ca in solutions leached through mineral soil with a vacuum extractor, as a function of SO_4 plus NO_3 concentrations in the added solution. Results of duplicate leachings are shown. Slope and intercepts of linear best-fit lines are given ± 95% confidence intervals (two-sided test). Soils with initial base saturations of 14.4%, 9.6% and 4.5 % were used in the experiment. Reprinted with permission from the Ecological Society of America (Ecological Applications, in press. Soil calcium status and the response of stream chemistry to changing acidic deposition rates in the Catskill Mountains, New York, Lawrence, G.B., David, M.B., Lovett, G. M., et al., figure 8, copyright 1999).

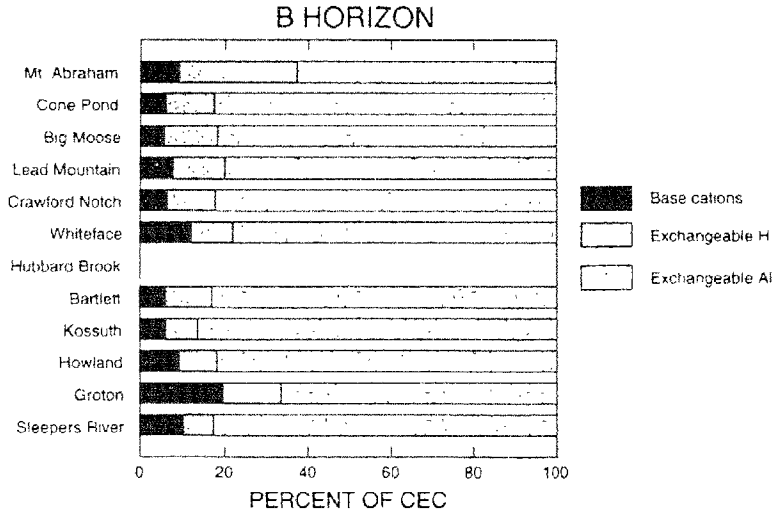


Figure 6.—Concentrations of exchangeable base cations, H and Al expressed as a percent of cation-exchange capacity for B horizons of the 12 northeastern red spruce stands. Reprinted with permission from Williams & Wilkins, (Soil Science, vol. 161, 1996, Soil and soil solution chemistry under red spruce stands across the northeastern United States, David, M.B., Lawrence, G.B., modified from figure 2, p. 320), copyright 1996).

season and decrease net uptake of Ca at upper elevations. A spatial trend in the intensity of podzolization from greater accumulation of organic acids at upper elevations than lower elevations was ruled out as a cause of the gradient in exchangeable base-cation concentrations because no spatial trends were observed in 1) organic carbon concentration in mineral soil, 2) cation exchange capacity of the mineral soil, or 3) pH of the Oa horizon.

Evidence of substantially higher soil water flux at upper elevations was also not apparent. Two years of throughfall measurements did not indicate an increase in precipitation with increasing elevation within the watershed, and no trend in soil depth was detected from the 48 soil pits. Annual ET, estimated by application of the adiabatic lapse rate (Anthes et al. 1975), resulted in an increase in soil-water flux of 14.5% from base to summit. The upslope increase in soil-water flux over the elevation range where soil bags were incubated was less than half this value, but nevertheless, a distinct gradient in base-cation concentrations developed within 1 year in soil of uniform parent material. Futher details of the gradient analysis in this watershed are given in Lawrence et al. (in press).

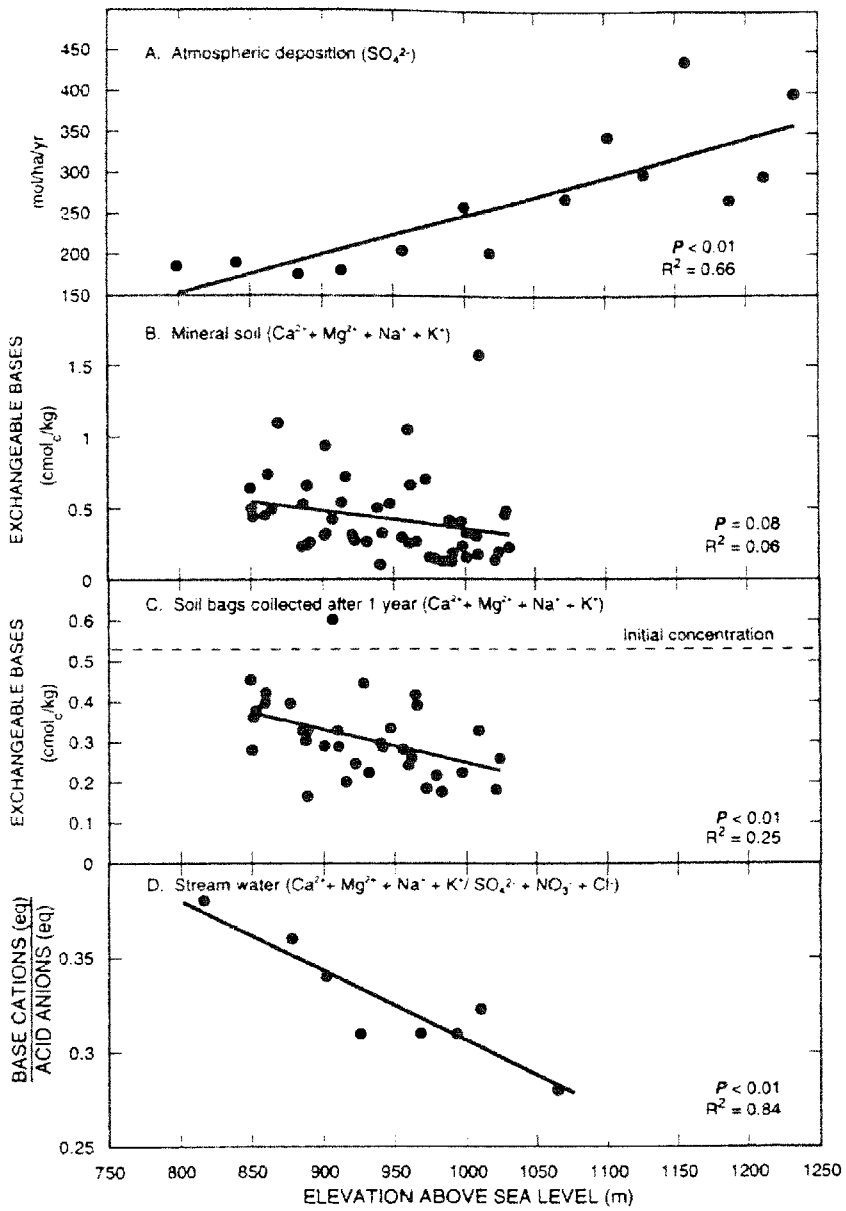


Figure 7.—Elevational gradients of selected chemical constituents in Winnisook watershed: A) annual mean SO_4 deposition measured in throughfall, June 1993 through May 1995, B) exchangeable base-cation concentrations (Ca, Mg, Na and K) in mineral soil samples collected in 1994, C) exchangeable base-cation concentrations in mineral soil samples buried in the mineral profile in mesh bags for one year, and D) the ratio of base-cation concentrations to acid-anion concentrations (SO_4, NO_3 and Cl) in stream-water samples collected during the highest 20% of stream flows from during May 1991 through April 1997. Reprinted with permission from EOS, Transactions, American Geophysical Union, v. 79, No. 16, 1998, p. 200.

In the absence of acidic deposition it is possible that natural acidification processes would cause elevational gradients in soil-base saturation and stream chemistry in Winnisook watershed, but an inability to detect significant gradients in any acidifying factors other than acidic deposition suggests that the effects of these factors were subtle relative to the gradient in atmospheric deposition of SO_4^{2-}, which doubled from the base to the summit of the watershed.

Aluminum Mobilization

B Horizon

Further indication that acid deposition has altered soil chemistry is evident from investigations of episodic acidification of streams in western Pennsylvania, in the Adirondack Mountains, and in Biscuit Brook, a tributary of the Neversink River, approximately 10 km from Winnisook watershed (Wigington et al., 1996). As streamflow increases during episodic periods of precipitation or melting snow, concentrations of inorganic monomeric Al can increase to levels that are toxic to fish (Baker et al. 1996). Concentrations of Al increase with increasing flow because a greater amount of water discharges directly from the soil into the stream channel than during baseflow (Chen et al. 1984; Lawrence et al., 1988; Potter, 1988). Water that has passed through the subsoil before discharging to the stream channel has had a greater opportunity for neutralization and immobilization of Al. Analysis of ionic controls of inorganic

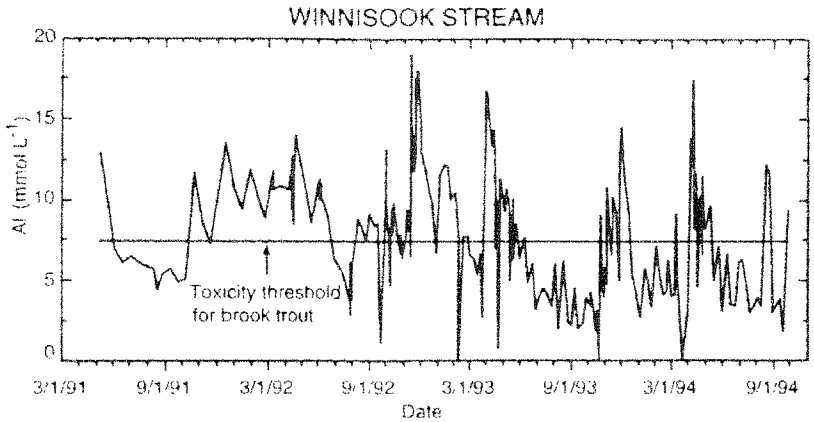


Figure 8.—Concentrations of inorganic monomeric Al in stream water at the base of Winnisook watershed from May 1991 through September 1994.

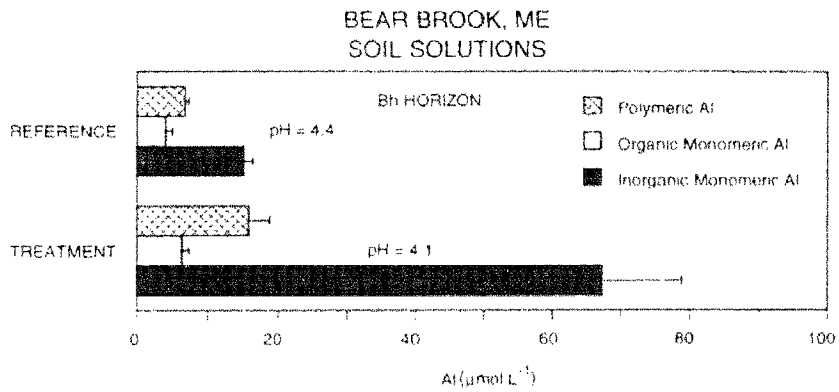


Figure 9.—Concentrations of inorganic monomeric Al (total monomeric Al minus organic monomeric Al), organic monomeric Al and polymeric Al (total Al minus total monomeric Al), in soil solutions of B horizons in treated (additions of $((NH4)_2)SO_4$) and reference stands of Bear Brook watershed, Maine. Each bar represents the mean of 45 samples that were combined into 15 samples for analysis, except for poylmeric Al, which represents 33 samples combined into 11 samples. Standard errors are indicated by horizontal lines. Mean pH for reference and treatment stands is also given. Reprinted with permission from the American Chemical Society (Environmental Science and Technology, vol. 31, 1997, Response of aluminum solubility to elevated nitrification in soil of a red spruce stand in eastern Maine, Lawrence, G.B., David, M. B., modified from figure 1, p. 827, copyright 1997).

monomeric Al concentrations in stream water showed that increased concentrations during high flows were associated with increased concentrations of SO_4^{2-} and NO_3 (Wigington et al., 1996). Naturally occurring organic acids can also mobilize Al and increase concentrations in stream water, but this process forms organically complexed Al, which is not toxic to fish (Driscoll et al., 1980). Concentrations of inorganic monomeric Al measured in the stream of Winnisook watershed from 1991-93 frequently exceeded the toxicity threshold for brook trout (Figure 8), and recent fish surveys indicated that the stream in Winnisook watershed does not support fish because of toxic concentrations of inorganic monomeric Al (Barry Baldigo and Lawrence, in press). Landowners of Winnisook watershed have reported, however, that a population of brook trout (*Salvelinus fontinalis*) previously existed in the stream (Royal Whiting, personal communication). High inorganic Al concentrations and the loss of a previously existing fish population suggests that an increase in inorganic monomeric Al concentrations occurred in this stream sometime in the past. An increase such as this would not occur without an increase of inorganic acidity in the mineral soil. An example of the effect of increased inorganic acidity on Al mobility is shown in Figure 9. Addition of $(NH_4)_2SO_4$ to the treated watershed at Bear Brook Maine increased nitrification rates, lowered pH, and increased concentrations of inorganic monomeric Al in the mineral soil solution (Lawrence and David 1997).

Results of the soil survey of spruce stands showed that Al dominated exchange chemistry in all samples of mineral soil; a factor that is also reflected in Ca to Al ratios in these soils that are well below 1.0 in both soil solution and on exchange sites (Figure 10). Inorganic acids (H_2SO_4 and HNO_3) introduced by acid deposition are the most probable

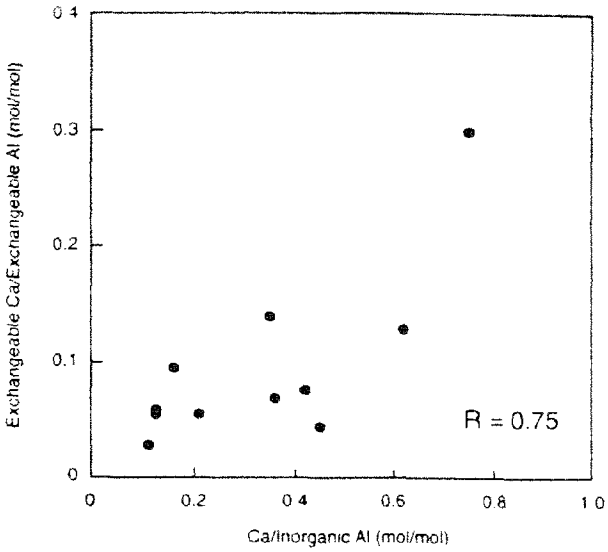


Figure 10.—Ratios of exchangeable Ca to exchangeable Al as a function of ratios of Ca to inorganic Al in soil solution of B horizons in the 12 northeastern red spruce stands. Insufficient mineral soil was available for sampling in the spruce stand at Hubbard Brook. Reprinted with permission from Williams & Wilkins, (Soil Science, vol. 161, 1996, Soil and soil solution chemistry under red spruce stands across the northeastern United States, David, M.B., Lawrence, G.B., modified from figure 6, p. 326), copyright 1996).

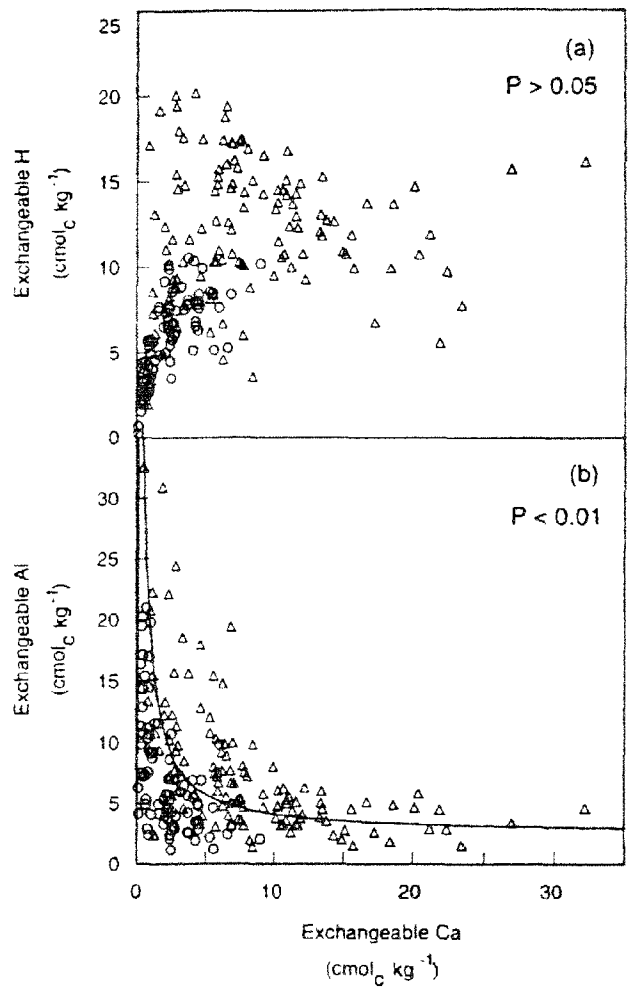


Figure 11.—Concentrations of (a) exchangeable H, and (b) exchangeable Al, as a function of exchangeable-Ca concentrations in the Oa horizon of stands of the 12 northeastern red spruce sites (triangles) and mixed hardwoods in Winnisook watershed (circles). Each triangle represents the value of three samples that were combined before analysis. Hardwood data are based on 68 individual samples. Reprinted by permission from Nature (vol. 378, 9 November 1995, p.163), copyright 1995, MacMillan Magazines Ltd.

cause of high concentrations of inorganic Al in solution and on exchange sites in the mineral soil. Organic acids that are leached from the forest floor also acidify the mineral soil and mobilize Al, but this process is limited by the tendency of organic acids to be removed from solution by adsorption to mineral particle surfaces (DeConinck, 1980). As a result, the mineral soil generally has a higher pH than the forest floor where the organic acidity originates. The high mobility of H_2SO_4 and HNO_3 in the mineral soil, however, makes these acids more effective than organic acids at decreasing the solution pH, leaching cations and increasing inorganic monomeric Al concentrations in soil solutions and stream waters.

Oa Horizon

Although acid deposition is likely to have decreased solution pH (and increased Al mobility) in the mineral soil, acid deposition is unlikely to have caused a decrease in pH in the naturally acidic forest floor. Production of organic acids through decomposition caused soil solution pH values to range from 3.3 to 3.8 in the Oa horizon of the 12 spruce stands (Lawrence et al. 1995). These values are below the pH of precipitation in this region, which averages about 4.4 and is seldom less than 4.0 (NADP/NTN, 1993). There is no established mechanism to explain how addition of precipitation above pH 4.0 could increase mobilization of Al within forest floors that have solution pH values normally less than 4.0. Although the low pH of these Oa horizons suggests that Ca availability is controlled by H, concentrations of exchangeable Ca in the Oa horizon were unrelated to exchangeable H concentrations in the 12 spruce stands and in Winnisook watershed, but inversely related to exchangeable Al concentrations (Figure 11).

The lack of a mechanism to explain mobilization of Al within the forest floor suggests that there is an outside source of Al

to this horizon. Mixing with the mineral soil when trees become uprooted provides a mechanism for introducing mineral forms of Al into the forest floor. Analysis of Al chemistry in the forest floor indicate that mineral content was not a strong controlling factor of exchangeable Al concentrations, however; dissolved Al concentrations in the Oa horizon were highly undersaturated with respect to Al bearing minerals, exchangeable Al concentrations were uncorrelated with mineral Al concentrations, and dissolved Al concentrations were unrelated to pH (Lawrence et al., 1995).

TABLE 3.—Concentrations in the Oa horizon of spruce-fir stands at the Hubbard Brook Experimental Forest, New Hampshire, USA. Samples collected in 1969 and 1970 were averaged together, as were those collected in 1987 and 1992. Values are means based on 9-14 samples. Statistically significant differences ($P<0.05$) between sampling periods, determined by the Wilcoxon nonparametric test, are indicated by superscripts with different letters. Standard deviations are given in parentheses.

Sampling period	Exchangeable ($cmol_c kg^{-1}$)		Acid-extractable ($cmol_c kg^{-1}$)	
	Al	Ca	Al	Ca
1969-70	2.5^a (1.1)	8.3^a (4.4)	19.3^a (10.2)	9.9^a (6.4)
1987, 1992	3.7^a (2.9)	3.5^b (2.1)	37.0^b (21.6)	4.6^b (2.9)

Alternatively, inorganic Al mobilized in the mineral soil by acidic deposition may be transported into the forest floor, where it outcompetes Ca (and other base cations) for exchange sites due to the high affinity of Al for the functional groups of organic matter (DeConinck 1980). Rustad and Cronan (1995) found that biocycling (uptake of Al by roots that is transported upward through the tree then returned to the soil in leaves and branches) plus atmospheric deposition of Al, was roughly 60% of forest-floor leaching losses in a red spruce stand in Maine. Biocycling of Al in the mineral soil is likely at all of the northeastern red spruce stands because ratios of Ca to inorganic Al in soil solutions are considerably less than 1.0, the value defined by Cronan and Grigal (1995) below which Al competes effectively with Ca for uptake by roots. Ratios of exchangeable Ca to Al in Winnisook watershed (0.04 mol mol^{-1}) suggest that ratios in soil solution would also be less than 1.0 (Figure 10).

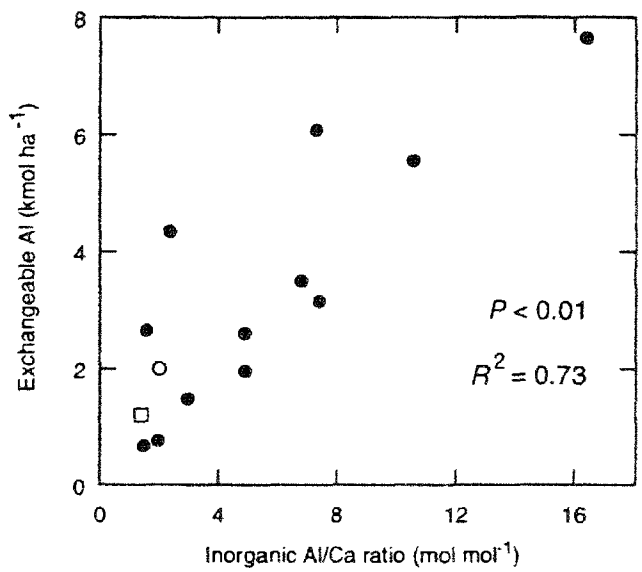


Figure 12.—Exchangeable Al content of Oa horizons of the 12 red spruce stands as a function of the molar concentration ratio of inorganic Al to Ca in B-horizon soil solution. Exchangeable Al was expressed as content to normalize the data for varying forest-floor thicknesses. Each filled circle represents the mean of 18-36 soil and soil solution samples (combined into 6-12 samples for analysis) collected at each of the 12 sites. Data from both the reference and treatment watersheds at Bear Brook Maine are included. The open circle represents the mean of 68 soil samples and 31 seep-water samples, collected in Winnisook watershed. The open square represents soil and seep-water concentrations measured at Tunk Mountain, ME, by Rustad (1988). Reprinted by permission from Nature (vol. 378, 9 November 1995, p.163), copyright 1995, MacMillan Magazines Ltd.

A rising water table provides an additional way to increase the reactive Al concentrations in organic surface horizons, as does upward movement of water through capillary action from drying of the forest floor by evapotranspiration (Lawrence et al., 1995). When mineral-soil solution, enriched in Al relative to Ca, moves into the forest floor, Al is more effectively retained so that the Ca to Al ratio in solution draining back into the mineral soil has increased, but the ratio of exchangeable Ca to exchangeable Al in the Oa horizon has decreased. A positive correlation between exchangeable Al content of the forest floor and the ratio of inorganic Al concentrations to Ca concentrations in the mineral soil solution supports this interpretation (Figure 12). Analysis of a limited number of archived soil samples collected in 1969-1970, 1987 and 1992, also show an increase in exchangeable and extractable forms of Al and a decrease in these forms of Ca (Table 3).

Potential decreases in the availability of Ca in the forest floor are particularly significant in light of the low Ca to Al ratios measured in the mineral soil. Although the forest floor is the primary horizon for nutrient uptake, the original source of mineral nutrients has generally been considered to be weathering in the mineral soil. Two recent studies have indicated, however, that 30 to 50% of available Ca in the forest floor originates from atmospheric deposition (Miller et al. 1993, Bailey et al. 1996), a source of Ca which has been steadily declining in recent decades (Hedin et al., 1994). Decreasing levels of atmospheric Ca deposition and low Ca to Al ratios in the mineral soil will both tend to impede the reversal of Al accumulation in the forest floor.

Summary and Conclusion

Significant progress has been made during the 1990's towards establishing the past and current status of base cation concentrations in forest soils of the Northeast. The studies of Shortle and Bondietti (1992), Johnson et al. (1994a), and Lawrence et al. (1995) presented historical data that indicated long-term decreases at sites in the Adirondack Mountains and northern New England. The survey of soils in northeastern red spruce forests by Lawrence et al. (1997) identified considerable variability in exchangeable Ca concentrations, but an analysis of the methodological bias of the previous studies showed that these data did not alter the conclusion that long-term decreases are common in this region.

Elevated concentrations of inorganic Al in surface waters, also common in this region, suggest that acid deposition has contributed to the decrease in base-cation concentrations in soils. Elevated concentrations of inorganic Al in surface waters is the result of mobilization of inorganic Al in the mineral soil, which, in turn, is the probable result of decreased pH from inorganic acids deposited from the atmosphere. Naturally derived organic acids also mobilize Al, but the high affinity of Al for organic functional groups favors the formation of dissolved organic Al over dissolved inorganic Al. The mobilization of Al in the mineral soil increases concentrations of exchangeable Al by displacing adsorbed Ca, which is then free to be leached with mobile inorganic anions.

The importance of acid deposition as a cause in the decrease of base-cation concentrations in forest soils has been further suggested by results of the survey of soils in northeastern spruce stands (Lawrence et al. 1995, Lawrence et al. 1997), and the analysis of base-cation leaching in the Catskill Mountains (Lawrence et al. in press). The strong relation between relative weathering potential and Ca saturation in the Oa horizon but not in the B horizon, observed in the survey of spruce stands, indicates that base saturation in the mineral soil has been reduced to levels at which Al dominates exchange chemistry and inorganic Al concentrations in soil solution become much greater than Ca concentrations. Data from the survey of spruce stands also indicate that exchangeable Al concentrations are likely to be increasing in the forest floor as a result of Al mobilization in the mineral soil. Lastly, an elevational gradient in base-cation leaching in a Catskill Mountain watershed that could not be explained with any factors, other than an elevational gradient in acid deposition, demonstrates the effect that acid deposition can have on base-cation leaching.

The information summarized in this paper suggests that reversal of past decreases in exchangeable Ca concentrations will be hindered by 1) continued inputs of mobile anions that facilitate leaching, 2) high Al saturation in the mineral soil that will interfere with uptake of Ca by roots, 3) increasing Al saturation in the forest floor, and 4) continued decreasing trends of atmospheric deposition of Ca.

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