ALUMINUM MOBILIZATION AND CALCIUM DEPLETION IN THE FOREST FLOOR OF RED SPRUCE FORESTS IN THE NORTHEASTERN UNITED STATES

Gregory B. Lawrence[1], Mark B. David[2] and Walter C. Shortle[3]

Abstract: Mechanisms of Ca depletion were investigated as part of a regional study of relations among acidic deposition, soil chemistry and red spruce decline. Comparison with results from studies in the Adirondack Mountains of New York and the White Mountains of New Hampshire indicates that current acid-extractable Ca concentrations in the Oa horizon are less than one-half the average measured in the 1930's. A statistically significant decrease of similar magnitude was also observed for both exchangeable and acid-extractable Ca, over the past two decades, in archived Oa horizon samples collected in red spruce stands at the Hubbard Brook Experimental Forest, N. H. The same samples indicated increases in exchangeable and acid-extractable Al concentrations over this period. Our results indicated no relation between concentrations of exchangeable Ca and exchangeable H in the forest floor, whereas a strong inverse relation was observed between concentrations of exchangeable Ca and exchangeable Al. We also found that exchangeable Al concentrations were related to the concentrations of acid-extractable Al (mostly organically complexed Al), but unrelated to mineral Al concentrations. Furthermore, the exchangeable Al content of the forest floor was positively correlated with the molar ratio of inorganic Al to Ca in the soil solution of the B horizon. We propose that Al mobilized within the mineral soil by acidic deposition is an important contributor to the pools of exchangeable and acid-extractable Al in the forest floor. Once mobilized in the mineral soil, Al is transported by water movement and root uptake into the forest floor, where it can replace Ca on exchange sites through its strong affinity for organic functional groups.

INTRODUCTION

Concern about the effects of acidic deposition on forest soils has led to numerous investigations in both Europe and North America, as summarized by Johnson et al. 1991. The underlying hypothesis of these studies is that acidic deposition enhances leaching of base cations, increases soil acidity and reduces soil fertility. Decline and dieback of red spruce forests (Shortle and Smith 1988), acidification of surface-water (van Breemen et al. 1984), and decreases in forest productivity (Federer et al. 1989) have all been linked to increased soil acidity resulting from acidic deposition.

Investigations of soil acidification have shown that measurable increases in soil acidity can occur in as little as two decades and that both acidic deposition and natural growth processes can cause significant soil acidification (Johnson et al. 1991). Despite the progress that has been made, however, no consensus has been reached on whether acidic deposition has significantly increased soil acidity in declining red spruce forests of the northeastern United States. Varying interpretations of the effects of acidic deposition on soil chemistry in red spruce forests result from difficulties in quantifying processes such as plant uptake, weathering and leaching by organic acids, and also from a lack of data that characterizes the regional variability of these processes.

---

[1]Research Hydrologist, US Geological Survey, 425 Jordan Rd., Troy, NY 12180.

[2]Associate Professor, Dept. of Natural Resources and Environmental Sciences, University of Illinois, W-503, Turner Hall, 1102 S. Goodwin Ave., Urbana, IL 61801.

[3]Supervisory Research Plant Pathologist, USDA Forest Service, Northeastern Forest Experiment Station, Durham, NH 03824.

With support from the Northern Global Change Research Program, a joint project was begun by the U.S. Geological Survey, the USDA Forest Service, the University of Illinois, and Yale University to investigate relations between acidic deposition and the health of northeastern red spruce forests. A primary goal of this project was to determine if acidic deposition has caused measurable changes in soil chemistry in these forests. This report summarizes data on Ca and Al concentrations in soil and soil-solution samples from 12 red spruce forests in the northeastern U.S., and compares these data to results reported by Heimburger, 1934 and Lunt, 1932 for the same region.

METHODS

Sites were selected to include the four physiographic regions in the Northeast where spruce forests are common; the Adirondack Mountains of New York, Green Mountains of Vermont, White Mountains of New Hampshire and low-to-mid elevation areas in Maine. The sites were selected to encompass the range of conditions found in red spruce forests in the Northeast with respect to elevation, climate, bedrock, mineral weathering characteristics, acidic deposition, and forest-stand condition. Each site was sampled either two or four times during 1992 and 1993.

Soil samples were collected from the Oa horizon and top 10 cm of the B horizon from the faces of nine soil pits during each sampling. Exchangeable-Ca concentrations were measured by NH_4Cl extraction, and mineral-matter concentrations were measured by loss-on-ignition, by the methods of Blume et al. (1990). Exchangeable-Al concentrations were measured by the method of Thomas (1982). Acid-extractable Ca concentrations were measured by the methods of Friedland et al. (1984), and total Ca concentrations were analyzed by neutron activation (Parry, 1991). Mineral Ca concentrations were calculated as the difference between total Ca concentrations and acid-extractable Ca concentrations.

Soil solutions were collected by a new method developed for this project, termed solution expulsion (Lawrence, et al. 1992). The solution-expulsion method was specifically designed to avoid the effort and expense required for lysimeter installations and to enable collection of soil solutions at a large number of sites regardless of soil moisture conditions before or at the time of sampling. In this method a soil sample is collected and then compressed in a PVC cylinder to increase bulk density by about 40 percent. A solution chemically similar to throughfall is then added to saturate the soil. Water not held by the soil is allowed to drain by gravity and is discarded. Positive air pressure is then applied to expel the remaining soil solution, which can then be chemically analyzed. Extensive experimentation has shown that the technique gives reproducible results that are insensitive to moderate changes in bulk density, duration of contact between soil and solution, and chemical concentrations of the added solution. Soil solutions were expelled from all Oa and B horizon samples and were chemically analyzed by the methods cited in Lawrence and Fernandez, (1991).

A literature search on the past and present status of available Ca in soils of northeastern red spruce forests, was also conducted to locate all data collected since 1980 that could be directly related to our study, plus any comparable data that was collected before the onset of acidic deposition in the region (assumed to be 1950).

RESULTS AND DISCUSSION

Samples from all 12 sites indicated that exchangeable Ca concentrations varied between 2.1 and 21.6 $cmol_c\ kg^{-1}$ in Oa horizons and 0.41 to 0.68 $cmol_c\ kg^{-1}$ in the upper B horizon. All comparable data on exchangeable Ca concentrations from other studies in northeastern red spruce stands were within these concentration ranges, except for the concentration reported for the O2 horizon by Mollitor and Raynal (1982), of 1.07 $cmol_c\ kg^{-1}$, which was about half the concentration we measured at Mt. Abraham, Vermont, our lowest value. At most sites, exchangeable Ca was the largest fraction of total Ca in the forest floor; exceptions were sites with the highest mineral matter concentrations, where mineral Ca was 55 to 70 percent of total Ca.

Concentrations of acid-extractable Ca measured in our study ranged from 13.9 $mmol\ kg^{-1}$ at Mt. Abraham, Vermont, to 102.6 $mmol\ kg^{-1}$ at Sleepers River, Vermont. Comparison of these values to those of Heimburger (1934) and Lunt (1932) for the White Mountains of New Hampshire and Adirondack Mountains of New York, indicates a highly

probable regional decrease in acid-extractable Ca concentrations since the 1930's (Fig. 1). Concentrations were less than the value we measured at Sleepers River (the site with the highest concentration in our study), at only nine of 38 sites sampled in the previous studies.

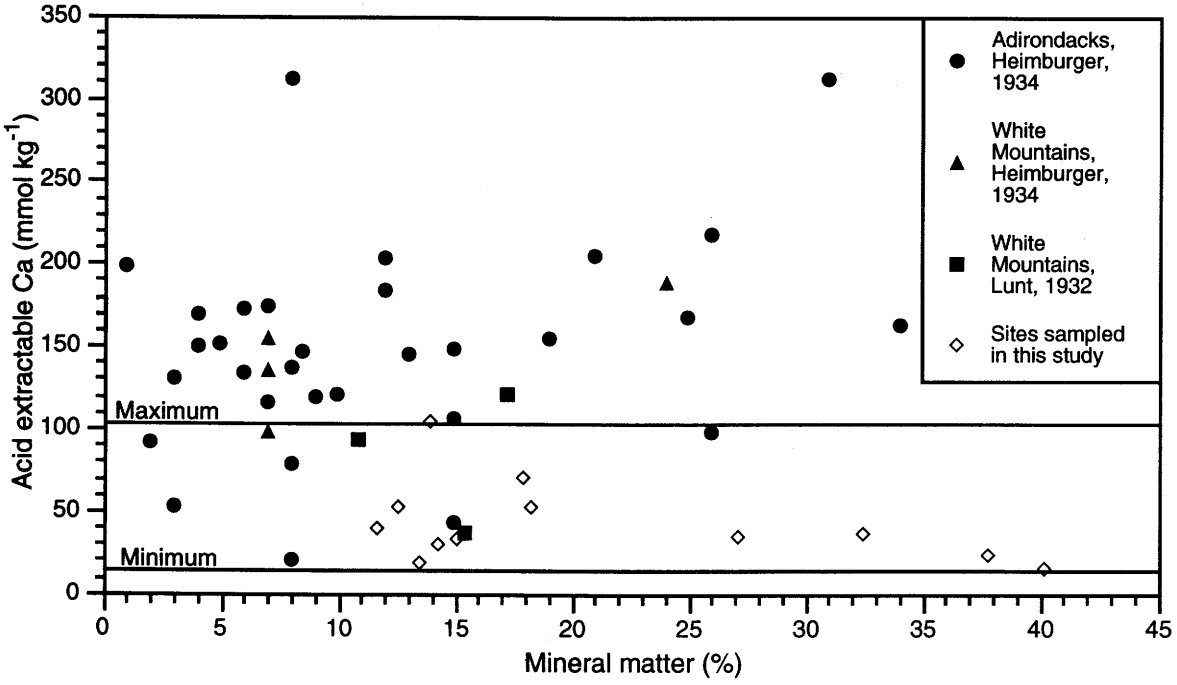

Figure 1. Acid-extractable Ca concentrations in Oa horizons of red spruce stands as a function of mineral matter concentrations (measured by loss-on-ignition), as determined by Heimburger (1934), Lunt (1932), and this study. Maximum and minimum lines represent the highest and lowest concentrations measured at the 12 sites we sampled.

Results of this study indicated, however, that concentrations of exchangeable Ca in the Oa horizon were correlated with neither exchangeable-H concentrations nor with soil pH ($p > 0.1$), but were inversely related to concentrations of exchangeable Al. Although an inverse relation between exchangeable Ca and Al concentrations in the mineral soil has been frequently observed (Johnson and Fernandez, 1992), this study is the first to identify the same relation in the forest floor, over a wide range of sites. This finding led to the hypothesis that the documented decreases of root-available Ca concentrations were associated with increases in concentrations of reactive forms of Al. No data from previous studies were available from which to evaluate temporal trends of forest-floor Al concentrations, but analysis of archived Oa-horizon soil samples collected from red spruce-balsam fir (*Abies balsamea* (L.) Mill) stands at the Hubbard Brook Experimental Forest (HBEF), New Hampshire suggested that, over the past two decades, concentrations of exchangeable and acid-extractable Al have increased, while concentrations of exchangeable and acid-extractable Ca have decreased, although the increase for exchangeable Al was not statistically significant.

The primary mechanism for incorporating Al into the forest floor has been hypothesized to be mixing of mineral soil with the forest floor through tree uprooting (Rustad, 1988), and a strong relation found between total Al and mineral content in this study ($p < 0.01$; $R^2 = 0.79$) supports this hypothesis. Once in the forest floor, mineral forms of Al can be mobilized by naturally derived organic acids, although dissolved Al is typically undersaturated with respect to mineral solubility in this horizon (Walker et al. 1990). Acidic deposition provides an additional source of H^+ that could possibly enhance Al mobilization and result in an increase in concentrations such as those observed at the HBEF. Results also showed, however, that in the forest floor, neither exchangeable- nor reactive-nonexchangeable Al (acid-extractable Al minus exchangeable Al) concentrations were related to mineral Al (total Al minus acid-extractable Al) concentrations, although exchangeable and reactive-nonexchangeable Al concentrations were positively correlated with each other ($p < 0.01$; $R^2=0.60$).

Table 1. Mean concentrations of exchangeable and acid-extractable Al and Ca in Oa-horizon soil samples collected in spruce-fir stands at the Hubbard Brook Experimental Forest, New Hampshire. Samples collected in 1969 and 1970 were averaged together, as were samples collected in 1987 and 1992. Means are based on nine to 14 samples. Statistically significant differences ($p < 0.05$) between sampling periods, determined from the Wilcoxon nonparametric test and the Tukey means separation test, are indicated by differing superscripts. Standard deviations are given in parentheses.

Sampling period	Exchangeable ($cmol_c \cdot kg^{-1}$)		Acid Extractable ($cmol_c \cdot kg^{-1}$)	
	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)

An alternate mechanism that could potentially increase exchangeable- and reactive- nonexchangeable Al concentrations in the forest floor is transport of mobile Al from the mineral soil through both biocycling (Rustad and Cronan, 1989) and movement of soil water (Mulder et al. 1991). Soil-solution data from our study indicated that inorganic Al was being mobilized in the B horizon at all sites. Soil-solution pH values were in the range in which Al is readily soluble (4.1 to 4.8), and the ratios of inorganic Al to Ca in mineral-soil solution (1.5 to 16.4) exceeded 1.0, above which numerous experiments indicate that Al can effectively compete with Ca for root exchange sites (Cronan and Grigal, 1995). The role of mineral-soil solution as a control of the size of the exchangeable-Al pool in the forest floor is corroborated by the strong positive relation between the Al-to-Ca ratio in mineral soil solution and the exchangeable-Al content in the forest floor (Fig. 2).

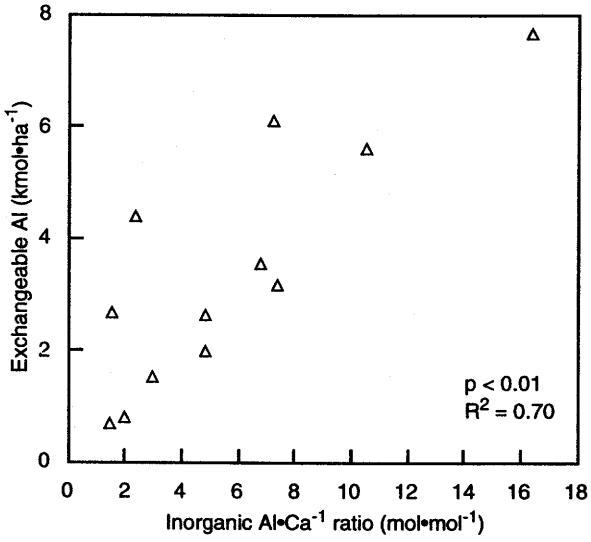

Figure 2. Exchangeable-Al content in Oa horizons of red spruce stands as a function of the molar inorganic Al-to-Ca ratio in B horizon soil solution. Exchangeable Al was expressed as content to normalize the data for varying forest-floor thicknesses. Each triangle represents the mean of 15 to 18 soil and soil-solution samples (combined into five to six samples before analysis) collected at each of 12 sites. One of the 13 sites was omitted because there was insufficient B horizon soil to sample.

We propose that Al mobilization in mineral-soil horizons, brought about by acid deposition, has significantly contributed to the documented decrease of root-available Ca in the forest floor of red spruce forests. Acidic deposition also might have enhanced Al mobilization from mineral matter within the forest floor, but the mechanisms of this process are currently unknown. In either case, mobile Al can exchange with Ca through its strong affinity for organic exchange sites (Deconink, 1980), increasing the susceptibility of Ca to leaching and also increasing the chemical similarity between the forest floor and the mineral soil.

LITERATURE CITED

Blume, L. J., B. A. Schumacher, P. W. Schaffer, K. A. Cappo, M. L. Papp, R. D. Van Remortel, D. S. Coffey, M. G. Johnson, and D. J. Chaloud. 1990. Handbook of methods for acid deposition studies: laboratory analyses for soil chemistry. U.S. Environmental Protection Agency, EPA/600/4-90/023. Environmental Monitoring Systems Laboratory, Las Vegas, Nevada.

Cronan, C. S. and D. F. Grigal. 1995. Use of calcium/aluminum ratios as indicators of stress in forest ecosystems. Journal of Environmental Quality 24:209-226.

Deconink, F. 1980. Major mechanisms in formation of spodic horizons. Geoderma 24:101-128.

Federer, C. A., J. W. Hornbeck, L. M. Tritton, R. S. Pierce, and C. T. Smith. 1989. Long-term depletion of calcium and other nutrients in eastern US forests. Environment Management 13:593-601.

Friedland, A. J., A. H. Johnson, T. G. Siccama, and D. L. Mader. 1984. Trace metal profiles in the forest floor of New England. Soil Science Society of America Journal 48:422-425.

Heimburger, C. C. 1934. Forest-type studies in the Adirondack Region. Cornell University Agriculture Experiment Station Memoir 165. Cornell University, Ithaca, New York.

Johnson, D. W. and I. J. Fernandez. 1992. Soil mediated effects of atmospheric deposition on eastern U.S. spruce-fir forests. Pages 235-270 *in* C. Eager and M. B. Adams, editors. Ecology and decline of red spruce in the eastern United States. Springer-Verlag, New York.

Johnson, D. W., M. S. Cresser, S. I. Nilsson, J. Turner, B. Ulrich, D. Binkley, and D.W. Cole. 1991. Soil changes in forest ecosystems: evidence for and probable causes. Pages 81-116 *in* F. T. Last and R. Watling, editors. Acidic deposition: its nature and impacts. Royal Society of Edinburgh, Edinburgh, Scotland.

Lawrence, G. B. and I. J. Fernandez. 1991. Biogeochemical interactions between acidic deposition and a low-elevation spruce-fir stand in Howland Maine. Canadian Journal of Forest Research 21:867-875.

Lawrence, G. B., W. C. Shortle, M. B. David, P. M. Wargo, K. Vogt. 1992. Forest floor aluminum and calcium chemistry: Relationships with acid deposition, root vitality, stand dynamics, and red spruce -- Study Plan for the Northeastern Station Global Change Research Program. U.S. Forest Service Internal Report, Radnor, Pa.

Lunt, H.A. 1932. Profile characteristics of New England forest soils. Connecticut Agricultural Experiment Station Bulletin 342. New Haven, Connecticut.

Mollitor, A. V., and D. J. Raynal. 1982. Acid Precipitation and ionic movements in Adirondack Forest Soils. Soil Science Society of America Journal 46:137-141.

Mulder, J., M. Pijpers, and N. Christophersen. 1991. Water flow paths and the spatial distribution of soils and exchangeable cations in an acid rain-impacted and a pristine catchment in Norway. Water Resources Research 27:2919-2928.

Parry, S. J. 1991. Activation Spectrometry in chemical analysis. in J. D. Winefordner and I. M. Kolthoff, editors. Chemical analysis volume 119. John Wiley and Sons, New York.

Rustad, L. E. 1988. The biogeochemistry of aluminum in a red spruce (Picea rubens Sarg.) forest floor in Maine. Ph.D. Thesis, University of Maine.

Rustad, L. E. and C. S. Cronan. 1989. Cycling of aluminum and nutrients in litterfall of a red spruce (Picea rubens Sarg.) stand in Maine. Canadian Journal of Forest Research 19:18-23.

Shortle, W. C. and K. T. Smith. 1988. Aluminum-induced calcium deficiency syndrome in declining red spruce. Science 240:1017-1018.

Thomas, G. W. 1982. Exchangeable cations. Pages 161-164, *in* A. L. Page, editor, Methods of soil analysis, part 2. 2nd edition. Agronomy Monographs, American Society of Agronomy, Madison, Wisconsin.

van Breemen, N., C. T. Driscoll, and J. Mulder. 1984. Acidic deposition and internal proton sources in acidification of soils and waters. Nature 307:599-604.

Walker, W.J., C. S. Cronan and P.R. Bloom. 1990. Aluminum Solubility in organic soil horizons from northern and southern forested watersheds. Soil Science Society of America Journal 54:369-374.