Aluminum and calcium in fine root tips of red spruce collected from the forest floor

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Abstract: Root chemistry is being increasingly used as a marker of biologically relevant soil chemistry. To evaluate this marker, we determined the precision of measurement, the effect of organic soil horizon, and the effect of stand elevation on the chemistry of fine root tips of red spruce (*Picea rubens* Sarg.). Fine root tips were collected from the F and H horizons of the forest floor of nine locations. Six of the locations were selected as pairs that differed in elevation. The concentrations of Al, Ca, Mg, and Fe in fine root tip collections were determined by direct current plasma emission spectroscopy. Element concentrations were not well correlated between collections made from the F and H layers associated with individual trees. The concentration of Ca was significantly higher and the concentrations of Al and Fe were significantly lower in fine root tips collected from the F than in tips collected from the H horizons. Fine root tips collected from the higher elevation member of paired locations yielded a higher Al:Ca ratio than did those collected from the lower elevation member. These results indicated the need to stratify fine root collections by soil horizon within the forest floor.

Résumé : On a de plus en plus recours à la composition chimique des racines pour détecter les caractéristiques chimiques du sol qui ont une incidence biologique. Afin d'évaluer cette approche, nous avons déterminé la précision des mesures, l'effet de l'horizon organique du sol et l'effet de l'altitude du peuplement sur la composition chimique de l'apex des racines fines de l'épinette rouge (*Picea rubens* Sarg.). L'apex de racines fines fut prélevé dans les horizons F et H de la litière dans neuf sites. Six de ces sites étaient pairés en fonction de l'altitude. Les concentrations en Al, Ca, Mg et Fe dans l'apex des racines fines récoltées ont été mesurées par spectrométrie d'émission à plasma en courant direct. Il n'y avait pas une bonne corrélation dans la concentration d'éléments entre les échantillons des horizons F et H provenant d'un même arbre. La concentration de Ca était significativement plus élevée et celles de Al et Fe significativement plus faibles dans l'apex des racines fines récoltées dans l'horizon F que dans l'horizon H. L'apex des racines fines récoltées dans les sites pairés avait un ratio Al:Ca plus élevé à l'altitude la plus haute qu'à l'altitude la plus basse. Ces résultats mettent en évidence la nécessité de stratifier la récolte des racines fines en fonction des horizons dans la litière.

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Introduction

Red spruce (*Picea rubens* Sarg.) are especially sensitive to atmospheric deposition because of soil characteristics in the rooting zone. The rooting zone of red spruce is shallow, with much of the uptake of essential elements being from the naturally acidic forest floor, which is of low base saturation (Cronan 1991; Majdi and Persson 1993). The root chemistry of red spruce may be used as a marker of adverse changes in soil chemistry attributed to atmospheric deposition (Godbold et al. 1988; Joslin and Wolfe 1992; Schlegel et al. 1992; Shortle and Smith 1988).

The deposition of HNO_3 and H_2SO_4 pollutants shifts the equilibrium of base cations from a bound to a dissociated form in the forest floor (Gobran and Bosatta 1988; Richter et al. 1992). This shift in equilibrium results in increased mobilization and leaching of essential base cations such as Ca^{2+} and Mg^{2+} and increased mobilization of potential antagonists to uptake such as Al^{3+} (Cronan 1991; Joslin et al. 1988; Federer et al. 1989; Godbold et al. 1988; Johnson and Fernandez 1992). The underlying mechanism for this potential blockage rests in the soil–rhizosphere ion exchange system and is independent of further soil acidification (Kunin 1960; Haynes 1980). In this scenario, the proportion of Al to Ca interacting with the ion exchange system of the root is the critical factor, rather than the absolute concentration of the elements themselves (Johnson

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and Fernandez 1992; Schröder et al. 1988). Building on these facts established by various researchers, Shortle and Smith (1988) linked the atmospheric deposition of acid anions to cation mobilization in the soil, which caused a brief period of enhanced base availability followed by the prolonged impairment of essential base uptake (Bondietti et al. 1990), decreased wood production, increased canopy shedding, and premature tree mortality from pest, pathogens, and abiotic stresses.

Field studies have not yet established the critical proportion of available antagonists to essential divalent bases. Part of the difficulty in establishing thresholds is due to the formation of polymers that increase activity or organic complexes that decrease the activity of the antagonist (Asp and Berggren 1990; Parker et al. 1989; Shuman 1990). Previous reports used an Al:Ca molar ratio in fine root tips of ≥1 to mark the potential for blocked Ca uptake (Shortle and Smith 1988; Shortle and Stienen 1988). Estimates of the extent and severity of existing forest damage, if any, that are due to this shift in cation exchange equilibrium are controversial (Friedland et al. 1993; Johnson et al. 1992, 1994; Miller et al. 1992; Shortle and Bondietti 1992; Schlegel et al. 1992).

The fine root tip was selected for analysis in our previous and current research because the apoplastic uptake of Ca and Mg begins at the tip. As the translocation pathway of Ca is essentially apoplastic, it is especially sensitive to changes in the ion exchange environment (Haynes 1980). The chemistry of roots with a suberized endodermis is less likely to be a useful marker of impaired Ca uptake because of the dominance of the symplastic pathway for translocation of bases in larger, more developed roots.

The utility of fine root chemistry as a marker of environmental shifts depends, in part, on the inherent precision of analysis and the variability due to the soil layer and, in part, to the elevation of the forest to be sampled. The first objective of this experiment was to determine the inherent precision of the quantitative chemical analysis of Ca, Mg, Al, Fe, and the Al:Ca ratio in fine root tips. The second objective was to compare the concentration of elements in root tips collected from the F and H layers of the forest floor. The third objective was to compare the effect of elevation on the concentration of elements and the Al:Ca ratio.

Materials and methods

Fine roots from the F and H layers of the forest floor were collected from four canopy red spruce at each of nine forest locations in October and November of 1989 (Table 1). All locations contained red spruce (20–40 cm DBH) as the predominant tree with few or no broad-leaved trees in the canopy. All locations contained a well-developed mor forest floor (Pritchett and Fisher 1987) with a thickness of at least 10 cm for the combined F and H layers. Six of the locations (two each from Mount Mitchell, Mount Washington, and Whiteface Mountain) were chosen as pairs, with each member of the pair located at different elevations. As the layers of the forest floor were distinguished by subjective, qualitative features (Federer 1982), F and H nomenclature will be used in preference to the quantitative terms O_e and O_a of the Soil Conservation Service (1981). The F layer, located beneath the overlying litter at the surface of the forest floor, consisted of fragmented organic material. The organic material of the the F layer was partially decomposed, yet sufficiently unaltered to allow for the possible identification of the source of the material (branch wood, bark, root, foliage, etc.). The H layer, located beneath the F layer, consisted of organic matter that was sufficiently decomposed so as to appear amorphous and homogenous. The F and H layers varied in thickness within and between forest locations and within the rooting zone of individual trees. For consistency of application, the same two fieldworkers categorized the forest floors sampled.

Selected trees were representative of dominant or codominant red spruce, free of obvious physical defects. A major supporting root was followed away from the tree base by careful digging with a small trowel. Subdividing branches were followed by hand until a small woody root (0.5–1.5 cm) with an attached fine root mass was located in the F or H layer of the forest floor. Fine root masses from the F layer were collected from a depth of 3–6 cm, measured from the top of the forest floor, following removal of litter. Roots from the H layer were collected from a depth of 8–15 cm. Fine root masses were clipped off the root system and placed in plastic bags. Usually the same branch root would yield fine roots from both the F and H layers. The sampling was repeated for one or two additional supporting roots. The fine root masses from each supporting root were pooled into separate collections from the F and H layers associated with each tree and chilled on ice until returning to the laboratory. The bagged fine roots were frozen until dissection of the root tips.

Fine root tips were excised from root masses in a shallow, glass baking dish. The baking dish was tilted approximately 30° above the horizontal plane. A root mass was placed on the upper, tilted surface of the dish. The root was thawed and rinsed with short bursts (<3 s per application) of distilled, deionized water dispensed from a squeeze bottle. The root mass was not permitted to soak in the rinse water. Individual fine root tips (0.1–0.2 mm in diameter × 2-3 mm in length) were excised from the root using dissecting needles. Care was taken to obtain bright, translucent-white root tips. Tips with heavy, obvious ectomycorrhizal sheaths were avoided, as were broken and discolored tips.

Excised tips were air dried on filter paper and then oven-dried at 104°C. Dried root tips (approximately 5 mg per sample, approximately 60–100 tips/mg) from each tree and layer of the forest floor were placed in glass crucibles and heated at 590°C for 12 h. Following cooling, the ash in each crucible was digested in 2 mL of 50% (v/v) HCl and diluted with 22 mL of deionized distilled water. Element analysis was performed by direct-coupled plasma emission spectroscopy using a Spectra-Span V ARL. Measured values of sample blanks were subtracted from sample values. The mean concentration of duplicate samples was taken as a single observation. Concentrations of Ca, Mg, Al, Fe, and Si were expressed as micromoles per gram of ovendried root tips. Molar ratios of Al:Ca were calculated for each sample. The precision of the total procedure was

Table 1. Stand locations of red spruce sampled for chemical analysis of fine root tips.

Stand code	Location	Elevation (m)
BED	Beddington, Maine	100
KOS	Kossuth, Maine	200
HOW	Howland, Maine	60
MMH	Mount Mitchell, North Carolina	1850
MML	Mount Mitchell, North Carolina	1500
MWH	Mount Washington, New Hampshire	790
MWL	Mount Washington, New Hampshire	680
WFH	Whiteface Mountain, New York	1010
WFL	Whiteface Mountain, New York	875

tested by repeated analysis of in-house reference material (a single, pooled collection of red spruce fine root tips) that was included in each sample set.

Variability in element concentration due to adhering soil minerals was assessed by comparison of Si concentrations. Any Si measured was presumed to be a mineral contaminant on the surface of the fine root tip. Concentrations of Si in root tip samples were compared by two-way ANOVA. Blocking factors consisted of forest location (8 df) and forest floor layer (1 df), with four observations per cell ($n = 72$).

To determine the relationship of element concentration in fine root tips associated with individual trees but differing in soil layer, correlation coefficients were calculated ($n = 36$). For each forest location, element concentrations for the F and H layers were compared by paired-sampled t-tests ($P \leq 0.05$, $n = 4$). The observations that composed each pair were from roots collected from a single tree. Within each layer of the forest floor (F and H), element concentrations in root tips were compared across all locations by one-way ANOVA ($P \leq 0.05$). Element concentrations were transformed to log values prior to ANOVA for increased stability of variance and normality of distribution. Fisher's protected LSD method ($P \leq 0.05$, df = 35) was used to separate mean values because of the power of the test, the reliability of the comparison-wise error rate, and because all pairs of comparison were of interest (Carmer and Walker 1982).

Results

Analysis of reference standard material indicated that the method was most precise for Ca, followed by Fe, Mg, Al, and Si (Table 2). Variation in element concentration in root samples was not due to adhering soil minerals, as indicated by Si concentration. Variation in Si concentration (overall mean = 23.3 $\mu mol \cdot g^{-1}$, SD = 4.88) was not attributable to forest location ($P = 0.16$) or forest floor layer ($P = 0.52$), as determined by ANOVA.

For individual trees, the correlation of element concentration in fine root tips from the F layer with tips collected from the H layer was significant ($P \leq 0.01$) for Fe ($r^2 = 0.50$), Ca ($r^2 = 0.31$), and Al ($r^2 = 0.26$). Concentrations of Mg in fine root tips of the F layer were not correlated with concentrations from the H layer ($r^2 = 0.04$, $P = 0.31$).

Table 2. Element concentrations ($\mu mol \cdot g^{-1}$) in fine root tip reference standard.

	Ca	Mg	Al	Fe	Si
Mean	65	31	27	19	20
Standard deviation	3.9	5.2	4.9	2.7	5.1
Confidence interval (%)	4	10	11	9	15

Note: Confidence intervals for each mean ($n = 13$) were calculated as 2.18 ($t$critical value, $P \leq 0.05$, 12 df) multiplied by the standard error of the mean. Confidence intervals were expressed as a percentage of the mean value.

Certain patterns were consistent for all locations in comparison of fine root tips from the F and H layers. Concentrations of Ca were significantly higher in fine root tips collected from the F than from the H layer of the forest floor ($P \leq 0.05$). Concentrations of Al and Fe were significantly lower for fine root tips collected from the F than from the H layer. Concentrations of Mg were not significantly different in fine root tips from the F and H layers of the forest floor. The Al:Ca molar ratio was consistently higher in root tips from the H than from the F layer ($P \leq 0.05$). Between forest locations, the concentrations of Ca and Mg in fine root tips varied over a more narrow range than the concentrations of Fe and Al (Table 3).

For paired locations that differed in elevation, fine roots collected from the higher elevation contained greater Al:Ca ratios than tips collected from the lower elevation for both layers of the forest floor ($P \leq 0.05$, Table 3). The greater Al:Ca ratios in higher elevation locations were due to a higher concentration of Al at Mount Mitchell and Mount Washington and to lower Ca concentrations at Whiteface Mountain.

Discussion

The chemistry of fine root tips is a marker that integrates biologically relevant conditions of the rooting environment. In this experiment, the analytical precision of the fine root tip reference standard of red spruce ranged from approximately 5 to 10% (Table 2) and was adequate to compare element concentrations in root tips from sample collections. For all red spruce forest locations, fine root

Table 3. Stand means (and standard deviations) for element concentration ($\mu mol \cdot g^{-1}$) in fine root tips of red spruce collected from the forest floor.

Stand	Ca	Stand	Mg	Stand	Al	Stand	Fe	Stand	Al:Ca
				F layer					
MML	43(4)*a*	MMH	11(4)*a*	MWL	19(5)*a*	BED	6(2)*a*	MWL	0.3(0.1)*a*
MMH	43(7)*a*	WFH	11(2)*a*	MML	24(5)*ab*	MML	7(2)*a*	BED	0.4(0.1)*a*
WFH	45(6)*ab*	WFL	12(3)*a*	BED	24(5)*ab*	KOS	9(4)*ab*	MML	0.6(0.1)*b*
HOW	46(5)*ab*	MML	14(1)*ab*	WFL	31(3)*bcd*	MWL	10(3)*ab*	WFL	0.6(0.1)*b*
MWH	46(5)*ab*	MWL	14(1)*ab*	MWH	35(5)*bcd*	WFL	13(5)*b*	KOS	0.7(0.1)*bc*
WFL	51(5)*abc*	MWH	15(3)*ab*	KOS	38(7)*d*	MWH	14(4)*b*	MWH	0.8(0.1)*c*
KOS	55(5)*bc*	BED	18(3)*bc*	HOW	39(7)*d*	HOW	15(4)*b*	HOW	0.8(0.1)*c*
MWL	58(6)*c*	KOS	18(2)*bc*	WFH	59(11)*e*	WFH	34(10)*c*	WFH	1.3(0.1)*d*
BED	64(6)*c*	HOW	23(3)*c*	MMH	64(15)*e*	MMH	35(11)*c*	MMH	1.5(0.2)*d*
				H layer					
MMH	20(6)*a*	WFL	10(3)*a*	MWL	46(7)*a*	MWL	18(4)*a*	MWL	1.7(0.2)*a*
MML	21(2)*a*	MWH	12(3)*ab*	MML	58(15)*a*	MML	21(6)*ab*	MML	2.7(0.5)*b*
MWH	22(4)*a*	WFH	12(2)*ab*	HOW	110(20)*b*	WFL	36(8)*bc*	WFL	3.2(0.3)*bc*
WFH	23(3)*a*	MMH	12(3)*ab*	BED	112(22)*b*	MWH	39(17)*bc*	KOS	4.1(0.3)*cd*
BED	27(6)*ab*	BED	16(3)*ab*	MWH	113(17)*b*	BED	39(4)*bc*	BED	4.2(0.3)*cd*
HOW	28(5)*ab*	MWL	16(2)*ab*	KOS	118(21)*b*	HOW	46(8)*cd*	HOW	4.0(0.2)*cd*
MWL	28(6)*ab*	KOS	16(3)*ab*	WFL	118(15)*b*	KOS	47(19)*cd*	MWH	5.1(0.4)*de*
KOS	29(6)*ab*	MML	17(5)*b*	WFH	119(14)*b*	WFH	58(18)*d*	WFH	5.2(0.3)*de*
WFL	37(5)*b*	HOW	17(4)*b*	MMH	125(26)*b*	MMH	82(9)*d*	MMH	6.5(0.4)*e*

Note: Comparisons of log-transformed values were made between forest stands for collections made from a single layer (Fishers's protected LSD test, $P \leq 0.05$). Values were retransformed to the original scale for tabulation.

tips collected from the F layer contained higher concentrations of Ca and lower concentrations of Al and Fe than collections made from the H layer. On the basis of ion chemistry, the F layer was comparatively more favorable for root activity than the H layer. The similarity in Mg concentration in fine roots from the F and H layers may reflect the symplastic requirement for Mg. Unlike Ca and Al, Mg is actively concentrated within the cytoplasm and is not governed primarily by ion exchange with the cell walls.

Early in the decay process of needle litter and woody debris on the surface of the forest floor, concentrations of Ca, Mg, Al, and Fe fluctuate because of microbial immobilization and abiotic adsorption (Rustad 1994; Rustad and Cronan 1988, 1989). The weak or absent correlation of element concentration in root tips from the F and H layers suggests that markedly different input or mobilization processes may be occurring in the two layers even though the layers are immediately adjacent to one another. The different processes could be due to inherent differences in the F and H environments or to temporal shifts in the external environment during the formation of the forest floor.

Previous research on root chemistry has generally bulked together the roots collected from the different layers of the forest floor (e.g., Joslin et al. 1988; Majdi and Persson 1993). Unfortunately, such bulking obscures real differences in root chemistry within the forest floor. Chemical analysis of the floor of western hemlock (*Tsuga heterophylla* (Raf.) Sarg.) forests indicated that the F and H layers could be differentiated on the basis of cation exchange capacity, cation concentration, and other factors (Quesnel and Lavkulich 1981).

The greater Al:Ca ratios at higher elevation locations compared with lower elevation locations at Mount Mitchell, Whiteface Mountain, and Mount Washington may be due to the greater deposition of pollutants from cloud water at the high-elevation locations (Joslin and Wolfe 1992; Mohnen 1992). The increased deposition of pollutants at higher elevations resulted in significant increases in the Al:Ca ratio in the soil solution (Joslin and Wolfe 1992).

The use of markers of environmental change that threaten red spruce and other forests requires a multifaceted approach. Soil analysis is most convenient and can indicate which locations may be sensitive to change due to low cation exchange capacity, base saturation, and pH (Cronan 1991; Majdi and Persson 1993; Shortle and Bondietti 1992). Frequent collection and analysis of soil solutions can indicate the temporal patterns of ion mobilization and the ionic species involved. Fine root tip chemical analysis can be interpreted as a record of peak exposure to exchangeable ions. Peak mobilization events may be diluted or missed in soil solution analysis and not evident at all in traditional soil analysis. The importance of "occasional" periods of high Al:Ca ratios in soil solutions may be discounted because of their episodic occurrence (Johnson et al. 1991). However, a brief period of exposure can result in the essentially irreversible binding of Al and exclusion of Ca on the ion exchange site of fine root tips.

The chief drawback of analysis of fine root tips is that the acquisition and preparation of samples for analysis is laborious. This sample preparation and analysis procedure has the advantage of using a composite sample of many individual tips collected from a strictly defined layer of the forest floor. Consequently, this method should be less subject to variability between individual tips than highly localized techniques such as the laser microprobe (Schlegel et al. 1992; Schröder et al. 1988). Contamination of samples with soil minerals may also be reduced in that the tips are free of an irregular periderm that could trap adhering soil particles.

This research does not establish an "unsafe" or "unhealthy" benchmark concentration or ratio of essential elements or potentially antagonistic soil bases. The form or complexation of ions in the soil solution, especially for Al, greatly affects their biological activity, well beyond simple measures of total, extractable, or exchangeable concentrations (Parker et al. 1989; Shuman 1990). The ion exchange and complexation processes are themselves dynamic and change in response to changes in the physical and biological environment. The tree can partially compensate, at a metabolic cost, through the production of new fine root tips. The dynamic and episodic nature of these potentially harmful conditions in the rooting zone enhances the value of fine root tip analysis as a record of peak exposure to antagonistic conditions. Further research to link episodes of peak levels of antagonists to rates of fine root turnover and altered allometric patterns may help to resolve the effects of perturbations of dynamic soil processes and forest health.

The value of fine root analysis will increase with a better understanding of the biology and chemistry of fine root shedding and turnover (Majdi and Persson 1993; Vogt et al. 1986).

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References

Asp, H., and Berggren, D. 1990. Phosphate and calcium uptake in beech (*Fagus sylvatica*) in the presence of aluminum and natural fulvic acids. Physiol. Plant. **80**: 307–314.

Bondietti, E.A., Momoshima, N., Shortle, W.C., and Smith, K.T. 1990. A historical perspective on divalent cation trends in red spruce stemwood and the hypothetical relationship to acidic deposition. Can. J. For. Res. **20**: 1850–1858.

Carmer, S.G., and Walker, W.M. 1982. Baby bear's dilemma: a statistical tale. Agron. J. **74**: 122–124.

Clarkson, D.T., and Sanderson, J. 1971. Inhibition of the uptake and long-distance transport of calcium by aluminum and other polyvalent cations. J. Exp. Bot. **22**: 837–851.

Cronan, C.S. 1991. Differential adsorption of Al, Ca, and Mg by roots of red spruce (*Picea rubens* Sarg.). Tree Physiol. **8**: 227–237.

Federer, C.A. 1982. Subjectivity in the separation of organic horizons of the forest floor. Soil Sci. Soc. Am. J. **46**: 1090–1093.

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

Friedland, A.J., Miller, E.K., and Boyce, R.L. 1993. Element distribution in red spruce (*Picea rubens*) fine roots; evidence for aluminum toxicity at Whiteface Mountain: Discussion. Can. J. For. Res. **23**: 1732–1733.

Gobran, G.R., and Bosatta, E. 1988. Cation depletion rate as a measure of soil sensitivity to acidic deposition: theory. Ecol. Modell. **40**: 25–36.

Godbold, D.L., Fritz, E., and Hütterman, A. 1988. Aluminum toxicity and forest decline. Proc. Natl. Acad. Sci. U.S.A. **85**: 3888–3892.

Haynes, R.J. 1980. Ion exchange properties of roots and ionic interactions within the root apoplasm: their role in ion accumulation by plants. Bot. Rev. **46**: 75–99.

Johnson, A.H., Friedland, A.J., Miller, E.K., Battles, J.J., Huntington, T.G., Vann, D.R., and Strimbeck, G.R. 1992. Eastern spruce–fir. *In* Atmospheric deposition and forest nutrient cycling. *Edited by* D.W. Johnson and S.E. Lindberg. Springer-Verlag, New York. pp. 496–525.

Johnson, A.H., Andersen, S.B., and Siccama, T.G. 1994. Acid rain and soils of the Adirondacks. I. Changes in pH and available calcium, 1930–1984. Can. J. For. Res. **24**: 39–45.

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

Johnson, D.W., Van Miegroet, H., Lindberg, S.E., Todd, D.E., and Harrison, R.B. 1991. Nutrient cycling in red spruce forests of the Great Smoky Mountains. Can. J. For. Res. **21**: 769–787.

Joslin, J.D., and Wolfe, M.J. 1992. Red spruce soil solution chemistry and root distribution across a cloud water deposition gradient. Can J. For. Res. **22**: 893–904.

Joslin, J.D., Kelley, J.M., Wolfe, M.H., and Rustad, L.E. 1988. Elemental patterns in roots and foliage of mature spruce across a gradient of soil aluminum. Water Air Soil Pollut. **40**: 375–390.

Kunin, R. 1960. Elements of ion exchange. Reinhold Publ. Co., New York.

Majdi, H., and Persson, H. 1993. Spatial distribution of fine roots, rhizosphere and bulk-soil chemistry in an acidified *Picea abies* stand. Scand. J. For. Res. **8**: 147–155.

Miller, E.K., Huntington, T.G., Johnson, A.H., and Friedland, A.J. 1992. Aluminum in soil solutions from a subalpine spruce–fir forest at Whiteface Mountain, New York. J. Environ. Qual. **21**: 345–352.

Mohnen, V.A. 1992. Atmospheric deposition and pollutant exposure of eastern U.S. forests. *In* Ecology and decline of red spruce in the eastern United States. *Edited by* C. Eagar and M.B. Adams. Springer-Verlag, New York. pp. 64–124.

Parker, D.R., Kinraide, T.B., and Zelazny, L.W. 1989. On the phytotoxicity of polynuclear hydroxy-aluminum complexes. Soil Sci. Soc. Am. J. **53**: 789–796.

Pritchett, W.L., and Fisher, R.F. 1987. Properties and management of forest soils. 2nd ed. John Wiley & Sons, New York.

Quesnel, H.J., and Lavkulich, L.M. 1981. Distinguishing the forest floors of three ecosystems. Soil Sci. Soc. Am. J. **45**: 624–629.

Richter, D.D., Johnson, D.W., and Dai, K.H. 1992. Cation exchange reactions in acid forested soils: effects of atmospheric pollutant deposition. *In* Atmospheric deposition and forest nutrient cycling. *Edited by* D.W. Johnson and S.E. Lindberg. Springer-Verlag, New York. pp. 341–358.

Rustad, L.E. 1994. Element dynamics along a decay continuum in a red spruce ecosystem in Maine, USA. Ecology, **75**: 867–879.

Rustad, L.E., and Cronan, C.S. 1988. Element loss and retention during litter decay in a red spruce stand in Maine. Can. J. For. Res. **18**: 947–953.

Rustad, L.E., and Cronan, C.S. 1989. Cycling of aluminum and nutrients in litterfall of a red spruce (*Picea rubens* Sarg.) stand in Maine. Can. J. For. Res. **19**: 18–23.

Schlegel, H., Amundson, R.G., and Hüttermann, A. 1992. Element distribution in red spruce (*Picea rubens*) fine roots; evidence for aluminum toxicity at Whiteface Mountain. Can. J. For. Res. **22**: 1132–1138.

Schröder, W.H., Bauch, J., and Endeward, R. 1988. Microbeam analysis of Ca exchange and uptake in the fine roots of spruce: influence of pH and aluminum. Trees, **2**: 96–103.

Shortle, W.C., and Bondietti, E.A. 1992. Timing, magnitude, and impact of acidic deposition on sensitive forest sites. Water Air Soil Pollut. **61**: 253–267.

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

Shortle, W.C., and Stienen, H. 1988. Role of ions in the etiology of spruce decline. *In* Effects of atmospheric pollution on the spruce–fir forests of the eastern United States and the Federal Republic of Germany. *Edited by* G.D. Hertel. USDA For. Serv. Gen. Tech. Rep. NE-120. pp. 519–525.

Shuman, L.M. 1990. Comparison of exchangeable Al, extractable Al, and Al in soil fractions. Can. J. Soil Sci. **70**: 263–275.

Soil Conservation Service. 1981. Examination and description of soils in the field. Chap. 4 [revised]. Soil survey manual, SCS directive 430-V. Soil Conservation Service, Washington, D.C.

Vogt, K.A., Grier, C.C., and Vogt, D.J. 1986. Production, turnover, and nutrient dynamics of above- and belowground detritus of world forests. Adv. Ecol. Res. **15**: 303–377.