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Biogeochemical controls on aluminum chemistry in the O horizon of a red spruce (*Picea rubens* Sarg.) stand in central Maine, USA

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Abstract. This study examined the biotic and abiotic processes controlling solution chemistry and cycling of aluminum (Al) in the organic horizons of a northern coniferous forest ecosystem. A mass balance budget indicated that aboveground inputs of Al to the O horizon averaged 0.9 kg ha^{-1} yr^{-1}, with major inputs accounted for by litterfall (69%), followed by precipitation (21%), and net canopy throughfall plus stemflow (10%). Estimated leaching losses of Al from the O horizon averaged 2.1 kg Al ha^{-1} yr^{-1}. We hypothesize that the difference between measured Al inputs and outputs can be accounted for by Al release from weathering of soil minerals admixed into the O horizon. Variations in O horizon solution Al chemistry were influenced by a number of factors, including pH, Al equilibria with different solid-phase organic exchange sites, and Al complexation with humic ligands in soil solution.

Introduction

Because of its crustal abundance and important structural role in primary and secondary soil minerals, aluminum (Al) has long been recognized as an essential geochemical component of terrestrial ecosystems. However, in recent decades, interest in Al has increasingly focused on the biological interactions and toxicity of this "nonessential" element. Studies have shown that ionic Al can cause lethal and sublethal impacts on animals and plants through direct toxicity, nutrient imbalances, and interferences with osmoregulation (Ulrich et al. 1980; Baker and Scofield 1982; Johnson and Siccama 1983; Schier 1985; Shortle and Smith 1988; Cronan et al. 1989; Raynal et al. 1990). Such findings have stimulated renewed efforts to develop a mechanistic understanding of the factors controlling the biogeochemical cycling of Al in forest ecosystems.

The forest floor plays an important role in element cycling and energy flow in forest ecosystems and is the primary rooting zone for many species (Kimmins & Hawkes 1978; Vogt et al. 1981; Strong & la Roi 1983). Although the mobilization of Al is generally associated with the acid hydrolysis of Al hydroxides and Al silicates in upper mineral horizons (Johnson et al. 1981; Dahlgren et al. 1989; Reuss et al. 1990), studies have shown that significant amounts of Al are mobilized in and transported from surface organic horizons (Cronan 1980; David & Driscoll 1984; Driscoll et al. 1985; Turner et al. 1985; Bergkvist 1987; Cronan et al. 1990; Walker et al. 1990; Alvarez et al. 1992; Miller et al. 1992). However, as no detailed element budget of Al in the O horizon has been reported, the major sources of this soluble Al have not been identified. Potential sources include wet and dry atmospheric deposition, net canopy throughfall and stemflow, decomposition of above- and belowground detritus, translocation of Al from roots in mineral horizons to roots located in surface organic horizons, ion exchange from organic and/or inorganic exchange sites, and/or weathering of primary and secondary minerals admixed into the forest floor. Given the importance of the O horizon in forest ecosystem element cycling, the potential role of the O horizon as a source of mobile Al, and the risk of Al toxicity and antagonism for some tree species, a better understanding is needed of the biogeochemistry of Al in surface organic soil horizons.

The purpose of this investigation was to determine the major biotic and abiotic processes controlling solution Al chemistry and cycling in the O horizon of a northern coniferous ecosystem. The study was conducted in a mature red spruce (*Picea rubens* Sarg.) stand because this cover type is important in the landscape of northern New England and because of interest in the possible interactions between red spruce decline and Al stress (Johnson & Siccama 1983).

Experimental methods

Study site

The study was conducted in a 1/4-ha red spruce stand located on a level terrace on the southwestern slope of Tunk Mountain (elevation 120 m) in Hancock County, Maine (68°05′ W, 44°38′ N). The site was bordered to the east and to the west by two small ephemeral streams. The forest vegetation was dominated by mature red spruce (80–120 yr) with occasional codominant white pine (*Pinus strobus* L.) and an understory of mixed red maple (*Acer rubrum* L.), northern white cedar (*Thuja occidentalis* L.), white birch (*Betula papyrifera* Mill.), and balsam fir (*Abies balsamea* L. Mill.). Stand basal area was 46 m^{-2} ha^{-1}, density was 1960 stems ha^{-1}, and the average diameter breast high (DBH) was 17 cm. Soils at the site were formed in late Wisconsin granitic tills and are classified as loamy, mixed, frigid Lithic Haplorthods and coarse, loamy-skeletal, mixed, frigid Typic Haplorthods. The climate is characterized by mean annual precipitation of 111 cm, mean annual temperature of 6 °C, average snowfall of 203 cm, and mean frost-free season of 131 days (Lautzenheizer 1972).

Solution chemistry

The chemistry of bulk precipitation, canopy throughfall, O horizon leachate, and stream water was monitored from October 1984 through October 1986. Solution samples were collected biweekly during the snowfree months and approximately monthly during the winter.

During the snowfree months, bulk precipitation was collected from three 20-cm-diam funnel-type collectors (Likens et al. 1977) located on an open ridge ~200 m from the site and throughfall was collected from 20 funnel-type collectors located at random grid points within the spruce stand. Stemflow was collected with 1.3-cm Nalgene^r tubing collars fitted to the boles of five dominant spruce trees (after Likens & Eaton 1970). During the winter, two precipitation and four throughfall collectors were replaced with 61-cm-diam snow buckets lined with polyethylene bags for snow collection. Twenty 465-cm^2 zero-tension lysimeters (Jordan 1968), co-located with the throughfall collectors, were used to collect O horizon leachate. Stream samples were taken from points directly below the study site when flow permitted.

Hydrologic flux was determined directly from volume measurements for precipitation, throughfall, and stemflow. Soil moisture flux and stream hydrologic flux were estimated by using Cl as a conservative tracer, such that the total input of Cl in throughfall was assumed to be equal to the total export in O horizon leachate and streamflow. Chemical flux was calculated as volume-weighted mean concentration times total volume for precipitation, throughfall, and stemflow; and as mean concentration times estimated total volume for soil solutions and stream output.

Within 12 hours of collection, solution pH was determined, and aliquots for dissolved organic carbon (DOC) were filtered through preashed GF-C glass fiber filters were ampulated. The remaining sample was passed though a Whatman 44 filter (3-um pore size) to remove coarse particulates and was subsampled for cations and anions. Cations were acidified to pH 1 with HNO_3 prior to analysis and anions were frozen. Solution concentrations of Al, Ca, Mg, Fe, Mn, and Si were determined by inductively coupled plasma emission spectrophotometry (Thermal Jarrel Ash Plasma Atomcomp model 975 ICP), K and Na by atomic absorption spectroscopy (Instrument Labs model Video-12 AAS), and SO_4, NO_3, and Cl by ion chromatography (Dionex model 2000I/SP IC). Dissolved organic carbon concentrations were determined by persulfate digestion and infrared analysis using an Oceanographics International model 525 carbon analyzer. Precision was within 5% for all parameters and accuracy was within 5% for Al, Ca, Mg, K, Na, SO_4, and NO_3, and 10% for Cl. Certified values were not available for Fe, Mn, Si, and DOC. Aluminum speciation was calculated using ALCHEMI (copyright 1987 William D. Schecher, version 3.10).

Litterfall

Litterfall (needles, twigs, and small branchlets <1 cm diam and <43 cm long) was collected monthly from twenty 30-cm-diam plastic buckets located adjacent to the throughfall funnels and lysimeters, and larger branches and bolewood were collected annually from five randomly located 10-m^2 ground plots (Rustad & Cronan 1988). Litter samples were oven-dried at 85 °C for 48 hours, weighed, ground to pass a 850-um mesh steel screen, and wet digested with a nitric-perchloric acid procedure (Thornton et al. 1985). Digests were analyzed for Al by ICP. Recovery rates for National Bureau of Standards Reference Material 1575 (pine needles) were within 5% of the certified value for Al.

Litter decomposition

Decomposition of red spruce, white pine, and red maple leaves was studied using a mesh bag technique (Rustad & Cronan 1988; Rustad 1994). Three to five grams of each of the three species as well as a mixture of the three and a dacron 'black' were weighed into 18×18-cm mesh bags and placed on the forest floor in each of five randomly located 5×5-m plots in November 1984. One bag of each litter type was collected from each of the five plots at 6, 9, 12, 18, 24, 41, 48, and 57 mo. Sample processing and analysis were identical to that described for litter samples. Data were corrected for mineral soil contamination following the method of Blair (1988).

Physical and chemical properties of the O horizon

At the end of the study, 38×15-cm forest floor cores were removed quantitatively from directly above ten of the twenty lysimeters (chosen to represent a range of solution Al values) and were separated into O1 (Oi and Oe) and O2 (Oa) horizons in the field on the basis of recognizable litter (O1) and unrecognizable litter (O2) (Brady 1974). The depth of each horizon was measured to the nearest 1 cm. Samples of the top 10 cm of the B horizon (Bh) were collected from below each organic horizon core for comparative purposes. The samples were weighed and subsamples were dried at 80 °C to determine moisture content for bulk density calculations. For forest floor samples, roots were removed, washed thoroughly with distilled water, hand sorted into four categories [fine roots (1 to 3 mm), slender roots (3 to 10 mm), large roots (>10

Table 1. Soil and analytical methods.

Parameter	Description	Reference
pH	0.01 $CaCl_2$	Robarge & Fernandez 1986
Exchangeable Al, H, Fe, Mn, Ca, Mg	1 N KCl extraction	Robarge & Fernandez 1986
Water-soluble Al, Fe, Mn, Ca, Mg	Distilled-deionized water extraction	Robarge & Fernandez 1986
Organically complexed Al	$CuCl_2$ extraction	Juo & Kamprath 1979
Total exchange capacity	$BaCl_2$-TEA procedure	Soil Conservation Service 1972
Total acid soluble element content	HF digest	Robarge & Fernandez 1986
Organic matter	Loss-on-ignition	Robarge & Fernandez 1986
Ash content	Loss-on-ignition	Robarge & Fernandez 1986

mm), and dead roots], weighed, and analyzed for Al by the nitric-perchloric method described for litter samples. After removal of root mass, the remaining organic material was sieved through a 2-mm mesh screen and stored field moist at 4 °C. Mineral soil samples were air-dried, homogenized, and sieved through a 2-mm screen. Organic soil samples were analyzed by the methods in Table 1. Mineral soil samples were analyzed for total acid-soluble element content as referenced in Table 1.

Bulk density was calculated for each core as the oven-dry mass divided by the core volume. Total mass for the O1 and O2 horizons was calculated at the mean bulk density times mean depth (n = 10); root-free forest floor mass was calculated by subtracting the root mass from the total horizon mass. Water-soluble, exchangeable, organically complexed, and total element masses were calculated as the product of the corresponding element concentration and root-free forest floor mass. To correct for overlap between the water and KCl extractions, the exchangeable element pool was calculated as the total exchangeable element mass less the water-soluble mass; to correct for overlap between the $CuCl^2$ and the water and KCl extractions, the reported organically complexed Al pool was calculated by subtracting both the water-soluble and the corrected exchangeable Al masses from the organically complexed mass. To correct for overlap between acid-soluble element content and the preceding extractions, the reported acid-soluble element pool was calculated by subtracting corrected organically complexed, exchangeable, and water soluble mass from the total acid-soluble mass. O horizon means were calculated from the O1 and O2 horizon values, weighted by horizon mass. The bound aluminum ratio (Cronan et al. 1986) was calculated by dividing the $CuCl^2$-extractable Al by the $BaCl^2$-TEA acidity.

Biomass

Aboveground biomass by species and tree part (i.e., foliage, branches, bark, stemwood) was calculated from regression equations based on DBH (Whittaker et al. 1974; Young et al. 1980). Samples of foliage, branches, bark, and stem wood were taken from ten dominant trees each of red spruce, white pine, and red maple, which together comprised ~95% of stand basal area at this site. Vegetation samples were analyzed for total nutrient content using the methods described for litter samples. Belowground biomass in the forest floor was calculated on an area basis from the roots collected in the forest floor cores. This underestimates total belowground biomass in the O horizon because it does not include the mass of the stump roots of the dominant trees. However, given the relatively low concentration of Al in large roots and stemwood, even if all the stump roots calculated from regression equations based on DBH (Young et al. 1980) were located in the forest floor, they would contribute less than 10% to the belowground Al budget. Total Al in each component of the aboveground and O horizon biomass was calculated as the product of total biomass (kg ha^{-1}) of each component and its respective Al concentration (mg kg^{-1}).

Statistical analyses

Significant differences between years, seasons, and ecosystem strata were investigated using analysis of variance followed by the Scheffe method for means separation (Berenson et al. 1983). The Scheffe method was chosen because it is robust to sample size differences. Correlation analysis was used to test for significant relationships between the elements (Berenson et al. 1983). All statistical tests were performed on the Statistical Analysis System (SAS 1985) using the 0.05 level of significance.

Results and Discussion

Aluminum fluxes

Inputs

Litterfall represented the major aboveground input of Al to the O horizon at the Tunk Mountain site, accounting for 69% of the total aboveground flux (Fig. 1). Precipitation accounted for an additional 21%, net canopy throughfall for 7%, and stemflow for 3%. The aboveground inputs of Al observed in this forest were moderate by comparison with those found at other study sties, particularly those in the heavily polluted forests of Germany and Scandinavia

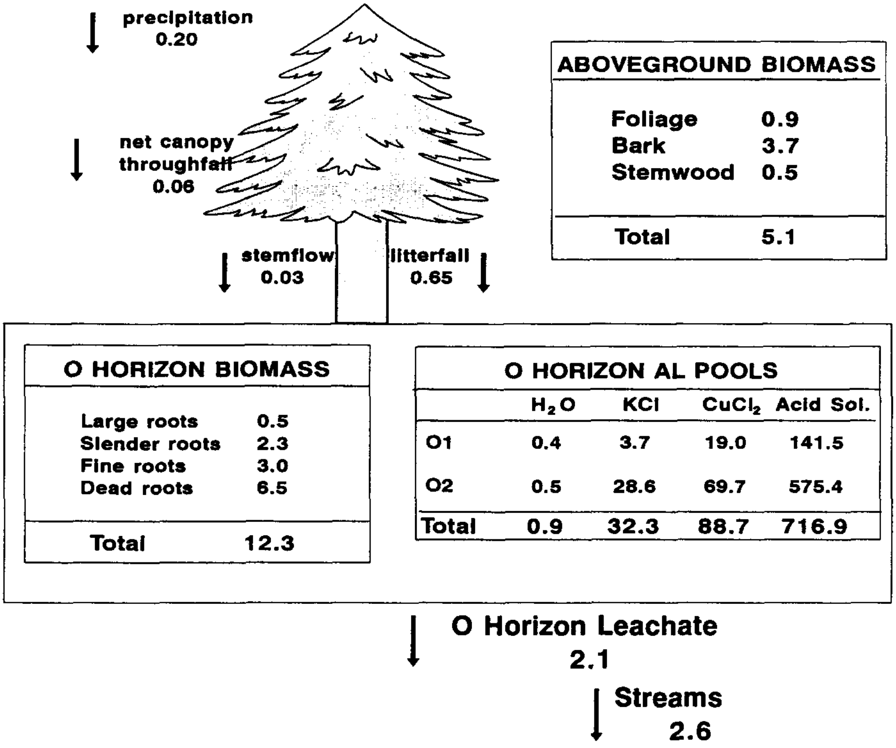

Fig. 1. Annual fluxes and storage of Al in a mature red spruce stand at Tunk Mountain, ME. Units are kg ha^{-1}.

(Table 2). The relatively small Al inputs in precipitation, throughfall, and stemflow may be typical of remote forested sites removed from sources of terrestrial 'dust' and fossil fuel industrial emissions.

Although litterfall represented a major aboveground input of Al to the O horizon, this input was not a source of readily available Al. Results from the litter decomposition study indicated that Al was not only immobilized in decaying litter but was actually accumulated during the first 57 months of litter decay (Fig. 2). These accumulations ranged from 260 ug Al g^{-1} original litter in the white pine litter to 800 ug Al g^{-1} original litter in the red maple litter. Given the annual litter input for this site of 2500 kg ha^{-1} yr^{-1} (Rustad & Cronan 1989) and a litterfall composition of 69% red spruce, 22% red maple, and 9% white pine (calculated from allometric relationships between DBH and leaf weight [Young et al. 1980] and foliar retention time), decomposing litter accumulated 0.8 kg Al ha^{-1} over the initial 57 months of litter decay at this site.

Table 2. Comparative aluminum chemistry in precipitation, throughfall, stemflow, O horizon leachate and stream water for a variety of forested stands in North America and Europe. Units are umol L^{-1}.

Study	Stand type	Precipitation	Throughfall	Stemflow	O horizon	Stream
This study	Red spruce	0.7	1.1	9.3	11.1	16.7
Turner et al. 1985, New Jersey Pine Barrens	Pitch pine	0.4	5.2		22.6	7.8
Cronan 1980, Mt. Mooselauke, NH	Subalpine balsam fir	0.7	1.9		18.5	7.8
Bergkvist 1987, Sweden	Norway spruce	0.7	1.5			
Ugolini et al. 1977, Findley Lake, WA	Pacific silver fir	1.1			29.6	
Stahr et al. 1980, Black Forest, FRG	Beech	0.4				
Brezinska-Paudyn et al. 1986, Canada	Urban	5.9				
Heinrichs & Mayer 1977, Solling Forest, FRG	Norway spruce	7.0	11.5–18.5		40.7	
David & Driscoll 1984, Adirondack Mtns, NY	Mixed hardwoods		4.1		17.4	
Cronan et al. 1989, ALBIOS	Mixed forest types of Spodosols			3.3–8.2		
Nilsson & Bergkvist 1983, Sweden	Norway spruce		1.5		7.4	
Driscoll et al. 1985, Hubbard Brook, NH	Northern hardwoods			19.6	8.9	
Litaor 1987, Front Range, CO	Subalpine forest				15.6–27.4	

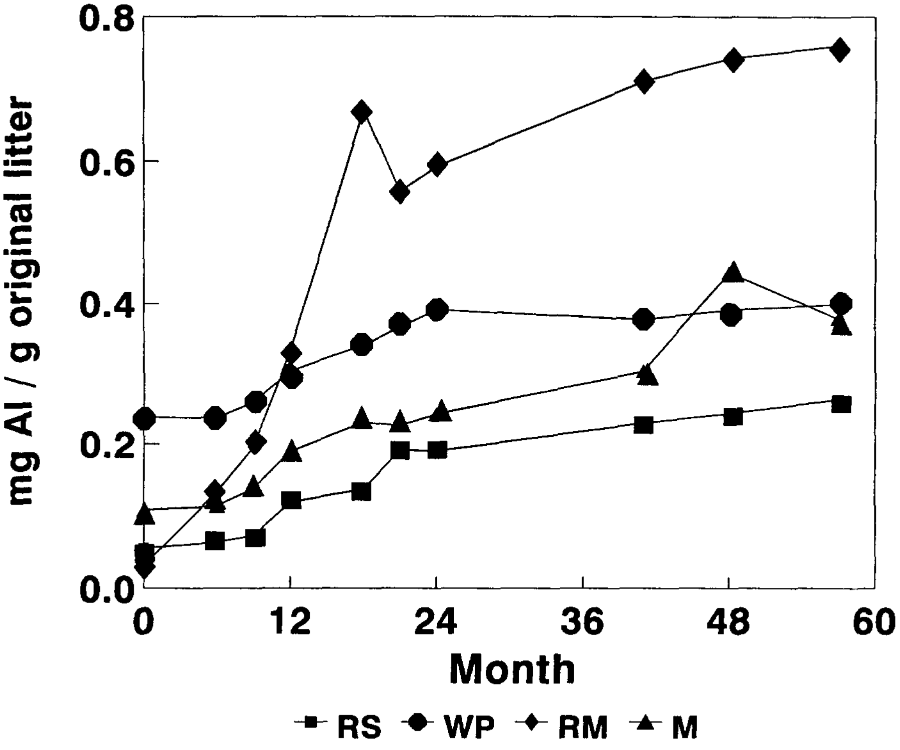

Fig. 2. Changes in absolute mass of Al during 57 months of litter decay at Tunk Mountain, Maine for red spruce (RS), white pine (WP), red maple (RM), and mixed-species (M) litter. Changes are standardized to 1 g original litter; sample number equals five for each species on each date; standard deviations (not shown) are generally less than 20% of the mean.

We hypothesized that the accumulation of Al observed in this study was due to the adsorption of Al onto humic carboxyl group exchange sites generated during humification of decaying litter and that, over time, as these exchange sites become more saturated with Al, the Al originally bound in the litter would be released (Rustad & Cronan 1988; Rustad 1994). The question remains as to when this release might occur. In the current study, Al concentrations in the red maple litter had exceeded the organically-complexed Al concentrations in the O2 by the end of the second year of litter decay (1005 ug Al g litter^{-1} vs 975 ug organically-complexed Al g O2^{-1}). Rather than beginning to release Al, the red maple litter continued to accumulate Al for the remaining 34 months of the study, reaching a peak concentration of 1370 ug Al g litter.$^{-1}$ Longer-term studies are, therefore, needed to determine at what point Al is finally mineralized from decaying litter, thereby completing the vegetation-to-soil mineral cycling pathway.

Although most litterfall studies are restricted to an analysis of aboveground detritus, belowground components may contribute as much or more litter to the total detrital pool. Vogt et al. (1987) have demonstrated that this is particularly true in the biological cycling of Al in a subalpine *Abies amabilis* stand, where >95% of the total detrital cycling of Al was accounted for by belowground components. At the Tunk Mountain site, O horizon fine roots (which represent the major belowground detrital input to this horizon) had an estimated mass of 4.4 Mg ha^{-1} and a total Al content of 3.0 kg ha^{-1} (Table 3). Estimates of fine root turnover and decay vary depending on size class distribution, species, and method. For example, Joslin & Henderson (1987) listed nine studies in which average fine root (<5 mm) residence times (calculated as size of live pool divided by turnover rate) ranged from 0.3 to 4.8 years. Even if we assume the conservative turnover rate of 20% per year, fine root turnover could contribute 0.6 kg Al ha^{-1} yr^{-1} to the forest floor detrital pool at this site, which is approximately equal to the amount returned to the forest floor from aboveground litterfall.

Although the production, death, and decay of roots (particularly fine roots) may affect the internal distribution of Al in the O horizon, root turnover cannot be considered an input of Al to the O horizon unless the Al is derived from lower mineral horizons. The possible translocation of Al from roots located in Al-rich mineral horizons to roots in the O horizon was investigated in a split-root study (Rustad 1988). Results suggested that Al could be translocated within the root systems of two-year-old *Abies balsamea* Mill. and *Pinus strobus* L. seedlings from older roots with high Al concentrations to new roots growing in an Al-free medium. Because there is no known physiological requirement for Al, we hypothesized that Al was passively translocated in the phloem as an Al-organic or Al-phosphate complex from older roots to growing root tips, where there would be strong requirements for both carbon and phosphorus. High concentrations of Al in phloem tissue have been observed by Vogt et al. (1987). Given the disparities between seedling and mature tree physiologies, we hesitate to extrapolate results from these greenhouse pot experiments beyond indicating that Al *could* be transferred from lower mineral horizons to surface organic horizons through this pathway.

The addition of mineral soil is another potential source of Al to the O horizon. Given the high concentrations of Al in mineral soil relative to organic materials (e.g., 67400 vs 194 mg kg^{-1} in Bh horizon soil vs litterfall [Rustad 1988]), even small contributions of mineral soil added to the O horizon by burrowing animals and insects, treethrow, anthropogenic disturbance, or aeolian inputs could dramatically alter the total Al content of the forest floor. The strong correlation between total acid-soluble Al in the O horizon and percent ash ($r = 0.95$; $P < 0.0001$) at this site supports the hypothesis that much

Table 3. Estimated mass, aluminum concentration and aluminum content of some components of aboveground and O horizon biomass at Tunk Mountain, ME. Standard error of the mean concentration given in parentheses.

Component	Estimated biomass (Mg ha^{-1})	Al (mg Kg^{-1})	Al (Kg ha^{-1})
Foliage			
Red spruce	16.6	40 (15)	0.66
White pine	0.7	230 (52)	0.17
Red maple	0.6	30 (7)	0.02
Stem and branch wood			
Red spruce	105.3	4 (3)	0.42
White spruce	17.2	3 (1)	0.05
Red maple	16.3	2 (1)	0.05
Stem and branch bark			
Red spruce	14.4	220 (60)	3.15
White pine	2.1	235 (50)	0.50
Red maple	2.0	15 (4)	0.03
Cones			
Red spruce	na	55 (20	na
Lichen	na	706 (129)	na
Moss	na	745 (38)	na
Litterfall			
Litterfall	2.5 (0.1)	180 (95)	0.50
Woody debris	2.7 (2.1)	55 (30	0.15
Fine roots (>3 mm)			
O1	1.2 (0.4)	565 (80)	0.69
O2	3.2 (0.3)	740 (105)	2.35
Slender roots (3–10 mm)			
O1	0.4 (0.1)	260 (30)	0.11
O2	5.7 (0.9)	390 (55)	2.23
Large roots (>10 mm)			
O1	0.8 (0.5)	45 (10)	0.04
O2	9.1 (4.0)	50 (15)	0.45
Dead roots			
O1	2.0 (0.8)	675 (200)	1.33
O2	3.7 (0.6)	1390 (210)	5.14

Estimated biomass of aboveground components is from regression equations on DBH and thus does not include an error term; na = not available.

of the Al in the O horizon is of mineral origin. Perhaps the most dramatic example of the incorporation of mineral soil into surface horizons is tree throw. Studies on the occurrence of treethrow in boreal and sub-boreal forests indicate that, on average, one large tree per hectare tips over every ten years, exposing a root area of 10 m^2 to a mineral soil depth of 25 cm (White 1979). Given a mean bulk density for the B horizon at this site of 0.9 g cc^{-1} and a mean Al concentration of 6.7% (Rustad 1988), we can estimate that treethrow could contribute 2250 kg mineral soil and 150 kg Al to the forest floor every ten years, or 22,500 kg mineral soil and 1510 kg Al every 100 years, which is the approximate age of this stand. Although treefall and the concomitant mixing of mineral soil into the O horizon is a stochastic event, it has a great potential for adding Al and other mineral elements to the O horizon.

Export

Aluminum can be exported from the O horizon either by leaching processes or by biological uptake. Estimated leaching losses of Al from the O horizon averaged 2.1 kg Al ha^{-1} yr^{-1} over the two year period. Plant uptake, on the other hand, is more difficult to quantify. Likens et al. (1977) defined uptake as:

uptake = litterfall + net throughfall and stemflow + root exudates + root litter + living biomass accumulation.

With the assumptions that (1) the uptake and return of Al during root growth and turnover in the O horizon is primarily a within system cycle, (2) Al in net throughfall and stemflow is derived from washoff of atmospheric dry deposition and not from biological uptake, (3) the stand is in a steady state and net biomass accumulation is approximately zero (as supported by increment core analysis), and (4) fifty percent of fine root mass and therefore fifty percent of plant uptake is in the O horizon (based on field observations and published conifer root distribution studies (e.g., Kimmins & Hawkes 1978; Strong & La Roi 1983]), then the above equation reduces to the following:

annual O horizon plant uptake = 1/2(annual litterfall) = 0.3 kg Al ha^{-1} yr^{-1}

Clearly, this is a rough estimate of plant uptake since we do not have precise data on biomass accumulation or root distribution in organic and mineral horizons. However, we believe that this is a reasonable order-of-magnitude estimate of an ecosystem flux which is typically difficult to quantify.

Even without estimates of plant uptake, the export of Al from the O horizon through leaching exceeds measured inputs by 1.2 kg Al ha^{-1} yr^{-1}. Similar net losses of Al from the O horizon compared to aboveground inputs have been observed by Cronan (1978), Nilsson & Bergkvist (1983), and David & Driscoll (1984). Results from this investigation, however, suggest that the apparent net loss may be balanced by belowground inputs either from root translocation of Al from mineral to organic horizons and/or from the dissolution of minerals admixed into the O horizon. Even without these additional inputs of Al, the net loss of Al from the O horizon relative to aboveground inputs is small when compared to the total reserves of Al in the O horizon (i.e., ~850 kg Al ha^{-1}; Fig. 1) and could continue for over 500 years before all such reserves were depleted.

For perspective, the export of Al in the streams draining the site was 2.6 kg Al ha^{-1} yr^{-1}, which represented a net gain of 0.5 kg Al ha^{-1} yr^{-1} over that exported in O horizon leachate. The mass of Al mobilized in O horizon leachate was, therefore, equivalent to ~80% of the total mass of Al exported from this forested stand. Turner et al. (1985), Cronan (1980), and Driscoll et al. (1985) all reported lower Al concentrations in streams than in O horizon leachate, i.e., the reverse of the pattern reported here (Table 2). Given that hydrologic flux is typically greater through the O horizon than in streams, this would result in a greater amount of Al being exported from O horizons than in streams at these other sites. Although it remains surprising that so much Al is mobilized *in* these O horizons, it is typical of the pedogenic process that Al mobilized from upper soil horizons is precipitated lower within the soil profile, thus limiting the amount generally exported to surface waters. At the Tunk Mountain site, however, soils were generally shallow (i.e., <50 cm to an impermeable layer) and it is likely that the acidic, highly organic solutions from the O horizon would mobilize additional Al from the upper B horizons, much of which would move laterally into these first-order streams through macropore flow.

Aluminum storage in O horizon soil and biomass

O horizon organic matter

O horizon organic matter represented a large pool of exchangeable, complexed and mineral Al (Fig. 1). The total mass of root-free forest floor Al was estimated at 840 kg Al ha^{-1}. Of this Al, 0.1% of the Al was water-soluble, 4% was exchangeable, and 11% was organically complexed. The remaining 85% of the Al in the O horizon was associated either with complex humic ring structures (and is thus virtually nonexchangeable [Jenny 1980]) or with the mineral component of this horizon. The strong correlation between total acid-soluble Al and percent ash ($r = 0.95$; $P < 0.0001$) implies that much of the Al in the O horizon is of mineral origin.

Within the O horizon, the O2 had significantly higher concentrations of exchangeable, organically complexed, and acid-soluble Al than the O1, and lower concentrations of exchangeable and acid-soluble Ca and Mn (Table 4). These patterns reflect both the relative mobility of elements in decomposing litter and the greater input of mineral soil to the O2 than the O1. It is clear from element:Al ratios in live vegetation, fresh litter, partially decomposed litter, and soil organic matter in the O1 and the O2 that there is a progressive loss of all elements examined in this study relative to Al during litter decay and humification (Table 5). The decreasing ratios from live vegetation to 57-mo litter is due both to the mineralization of the nutrient elements and to the actual accumulation of Al in the decaying litter. Iron, the only element whose ratio did not decrease during this period, was also accumulated in the decaying litter (Rustad 1994). The sharp drop in the element:Al ratios as litter is incorporated into the O1 and the O2 horizons may be attributed to the continued adsorption of Al onto organic exchange sites and concomitant mineralization of the nutrient elements, and to the addition of mineral soil to the litter, which has high Al concentrations relative to the nutrient elements (Table 4). The addition of mineral soil to the O1 and O2 horizons is reflected in the percent ash of these horizons, with a greater percent ash (and therefore amount of mineral soil) observed in the O2 than the O1 (Table 4). The influence of the incorporation of mineral soil into the O horizon is particularly evident in the Fe:Al and Mn:Al ratios in the O2, which was remarkably similar to that in the Bh soil (for Fe) and the parent material itself (for Fe and Mn; Table 5). These results reflect the role of mineral soil as a source of Al to the O horizon at this site.

Biomass

Aboveground biomass was estimated at 175 Mg ha^{-1}, which compares to 199 to 201 Mg ha^{-1} reported by Smith (1984) for a mature red spruce-balsam fir site at Weymouth Point, ME and to 207 Mg ha^{-1} reported by Johnson & Lindberg (1992) for a ~100 yr old low elevation red spruce stand at Howland, ME. Total O horizon root biomass was estimated from the soil cores as 26 Mg ha^{-1} (Table 3).

An estimated 5.1 kg Al ha^{-1} was stored in the aboveground biomass (Fig. 1; Table 3). This estimate represents a minimum value because Al content of species representing less than 5% of stand basal area, cones, and ground cover were not included. Note that the highest tissue Al concentrations measured at this site were found in moss taken from downed woody debris and lichen taken from boles of red spruce trees (Table 3). These high Al concentrations are consistent with the results of previous studies which have shown that mosses such as *Polytrichum* are Al accumulators (Chenery 1951) and that numerous lichens are metal accumulators (Nieboer et al. 1978). At this site, mosses and lichens grow profusely on tree stems, rocks, and decaying logs and may add significantly to the total Al in the aboveground biomass. An estimated 12.3 kg Al ha^{-1} was stored in belowground biomass within the O horizon (Fig. 1; Table 3). Again, this represents a minimum estimate because values for stump roots were not included.

Table 4. Physical and chemical properties of the O horizon at Tunk Mountain, ME. Standard error of the mean in parentheses. An '*' next to the O horizon mean indicates a significant differences between the O1 and O2 horizons at the 0.05 level, '**' at the 0.01 level, and '***' at the 0.001 level.

Property	O1	O2	O horizon	
Depth (cm)	4.2 (0.6)	8.8 (1.1)	13.0 (1.4)	**
Bulk density (g cc^{-1})	0.09 (0.01)	0.14 (0.01)	0.13 (0.01)	***
Ash content (%)	8.9 (0.8)	14.7 (2.1)	13.3 (2.2)	*
Total mass (Mg ha^{-1})	37.8 (5.1)	123.2 (18.3)	161.0 (21.3)	**
pH (CaCl$_2$)	3.11 (0.06)	2.74 (0.04)	2.80 (0.04)	***
		cmol$_c$ kg^{-1}		
Exchange acidity	7.16 (0.77)	12.23 (0.82)	11.04 (0.75)	**
BaCl$_2$ acidity	212 (10)	207 (10)	208 (7)	
Water-soluble				
Al	0.14 (0.03)	0.05 (0.01)	0.07 (0.01)	*
Fe	0.05 (0.01)	0.01 (0.01)	0.02 (0.01)	*
Mn	0.01 (0.01)	<0.01	<0.01	
Ca	0.15 (0.04)	0.01 (0.01)	0.04 (0.01)	**
Mg	0.07 (0.02)	0.02 (0.01)	0.03 (0.01)	*
Exchangeable				
Al	1.38 (0.24)	3.18 (0.30)	2.73 (0.28)	**
Fe	0.05 (0.01)	0.04 (0.01)	0.04 (0.01)	
Mn	0.38 (0.05)	0.10 (0.02)	0.17 (0.02)	****
Ca	13.93 (0.99)	7.79 (0.55)	9.31 (0.61)	***
Mg	3.75 (0.21)	4.64 (0.52)	4.42 (0.42)	
Organically complexed Al	7.70 (0.92)	10.82 (0.83)	10.05 (0.78)	*
Bound Al ratio (%)	4 (1)	5 (1)	5 (1)	
		mg kg^{-1}		
Total acid-soluble				
Al	4930 (515)	6640 (1100)	6216 (900)	
Fe	2540 (175)	2540 (305)	2540 (275)	
Mn	115 (10)	50 (5)	66 (5)	***
Ca	4095 (240)	2525 (195)	2915 (195)	***
Mg	835 (40)	890 (65)	876 (50)	
P	870 (25)	625 (15)	686 (15)	***

For the aboveground and O horizon components, the largest proportion of Al in biomass and necromass was in the dead roots (37%), followed by bark (21%), fine roots (17%), and slender roots (13%) (Table 3). Stem and branch

Table 5. Element ratios (mass:mass) in live vegetation, fresh and decomposing litter, O horizon, mineral soil, and parent material at Tunk Mountain, ME. Elements are normalized to Al.

Material	Al	Fe	Mn	Ca	Mg	P
Green foliage	1.00	0.53	5.66	74.25	14.04	3.86
Fresh litter	1.00	0.83	9.54	52.47	15.94	22.92
57-mo litter	1.00	0.87	0.62	6.35	0.76	1.14
01	1.00	0.52	0.02	0.83	0.17	0.18
02	1.00	0.38	0.01	0.38	0.13	0.19
Bh	1.00	0.40	na	0.06	0.01	na
Tunk granite	1.00	0.27	0.01	0.09	0.02	<0.01

Element ratios in green foliage and litter were based on an estimated foliage composition of 69% red spruce, 22% red maple, and 9% white pine, which was calculated from regression equations of foliage on DBH (Young et al. 1980) and foliar retention times. Tunk granite values from Karner (1968).
na = not available.

wood, although accounting for 61% of the total estimated stand biomass, contained less than 5% of the total Al in the biomass. The distribution of Al in aboveground and O horizon biomass and necromass generally reflected the relative concentration of Al in these components, which decreased in the order: dead roots > fine roots > slender roots > bark > cones = foliage = large roots > stem and branch wood (Table 3). The greater concentration of Al in dead roots than in live roots may be attributed to the preferential retention of Al in decaying litter (Rustad 1994), whereas the greater concentration of Al in fine roots compared to larger roots and aboveground biomass reflects the general tendency for plants to localize Al at root surfaces and/or in free spaces within roots near the point of uptake (McCormack & Borden 1972).

Within the O horizon, root Al concentrations increased with depth (Table 3), which was the same pattern as that observed for the soil Al pools (Table 4). Fine root Al concentrations were significantly correlated to the concentration of exchangeable (r = 0.56; $P < 0.05$) and organically complexed Al (r = 0.63; $P < 0.01$), as well as to the bound Al ratio (r = 0.73; $P < 0.01$), which suggests that (a) exchangeable and organically complexed Al may be biologically available to the roots of higher plants, and (b) the Al saturation of the exchange sites may influence this availability.

Although few stand level Al data are available, comparison between this study and a study by Turner et al. (1985) for a *Pinus rigida* Mill. stand in New Jersey and Vogt et al. (1987) for an *Abies amabilis* Dougl. stand in Washington demonstrate variable patterns in aboveground Al distribution (Fig. 3). These patterns reflect differences in the relative concentrations of

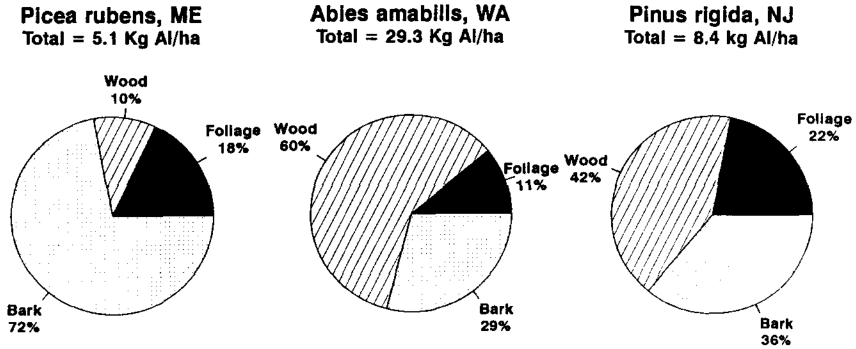

Fig. 3. Relative proportion of Al in aboveground biomass in three forested stands. Data for *Picea rubens* from this study; data for *Abies amabilis* from Vogt et al. (1987); data for *Pinus rigida* from Turner et al. (1985).

Al in the biomass components, with the Maine site characterized by the lowest tissue Al concentrations. These lower concentrations may be due to the shallow rooting patterns characteristic of red spruce, in which most of the roots are concentrated in the O horizon which contains comparatively low levels of plant-available Al (Joslin et al. 1988).

Biogeochemical controls on solution aluminum in the O horizon

Results from this study suggest that solution Al concentrations in the O horizon are regulated by several solution and solid phase properties of the O horizon. In solution, the significant correlations between Al and Si ($r = 0.61$; $P < 0.01$),and Al and Fe ($r = 0.74$; $P < 0.01$) suggest that mineral weathering is an important source of Al to O horizon leachate. Numerous studies have shown that the organic acids found in the O horizon are highly efficient at dissolving alumino-silicate minerals (Wright & Schnitzer 1963; Malcolm & McCracken 1969; Huang & Keller 1972). Weathering rates of primary and secondary minerals admixed into the O horizon would presumably be rapid.

Although mineral weathering may have been an important source of Al to the organic horizon, Al concentrations in O horizon leachates were largely undersaturated with respect to common Al hydroxide minerals. This phenomenon has been commonly observed in other studies of organic-rich systems (Cronan 1978; Nilsson & Bergkvist 1983; Dricsoll et al. 1985; Cronan et al. 1986; Alvarez et al. 1992) and can be attributed to two factors: Al hydroxide minerals, such as gibbsite, are unstable in the forest floor micro-environment and the dominant processes controlling Al chemistry are adsorption and complexation of Al by solid phase organic matter (Mortensen 1963; Bloom et al. 1979). Although reliable thermodynamic constants are not available for organo-aluminum equilibria (because of the highly variable nature of soil organic matter), both field and laboratory studies have shown that such ion exchange equilibria maintain lower Al activities and concentrations than those associated with aluminum hydroxides (Bloom et al. 1979; Cronan et al. 1986; Walker et al. 1990). This strong affinity of organic matter for Al is dependent on several factors, including: (a) the degree of humification, (b) the saturation of the exchange sites with Al, and (c) soil and solution pH.

Humic materials encompass a wide variety of structures, including humic acids, fulvic acids, and humin. Their ability to adsorb Al may be attributed to their high content of carboxyl, phenolic-alcoholic, and C = O groups (Stevenson 1985). The stability of the resulting metal-humic complexes decreases in the order $Fe^{3+} > Al^{+3} > Pb^{2+} > Zn^{2+} > Fe^{2+} > Mn^{2+} > Ca^{2+} > K^{+}$ (Schnitzer & Kahn 1975; Jenny 1980), indicating that humic exchange sites have a high selectivity for both Al^{3+} and Fe^{3+}.

Because humic substances are synthesized over time in decaying litter, older, more highly decomposed organic matter (e.g., O2 material) should have a higher affinity for Al than newer, less humified litter (e.g., O1 material). The fact that the easily leached water-soluble Al was significantly lower in the O2 than in the O1 (Table 4) supports this hypothesis, as did a laboratory study showing that leaf litter samples aged in the forest floor for 12 and 24 months released significantly less Al when equilibrated with distilled water and absorbed significantly more Al when equilibrated with 5 mg Al l^{-1} solution than fresh litter (Rustad 1994).

The influence of the Al saturation of organic exchange sites,or the bound Al ratio (BAR), and solution pH on aluminum activity in organic horizons has been demonstrated by Cronan et al. (1986) and Walker et al. (1990). In general, they found that (a) as solution pH decreased, soluble Al increased, and (b) that for a given pH, the greater the surface bound Al, the lower the affinity of the exchange sites for Al, and thus the greater the soluble Al. Sanchez (1977) described a similar relationship in tropical soils, where mineral soils characterized by high Al saturation (i.e., >60% of the effective cation exchange capacity) had significantly greater soil solution Al concentrations than soils with low Al saturation. At Tunk Mountain, mean O horizon solution Al concentrations generally increased as a function of increasing BAR and decreasing solution pH.

Other studies have shown that temperature and moisture flux significantly influence aqueous Al chemistry. Turner et al. (1985), for example, noted high Al concentrations in forest floor leachate in the late winter and early spring, which they attributed to greater moisture flux during these periods. Nilsson & Bergkvist (1983), on the other hand, reported maximum soil solution Al concentrations in the late summer and early fall, presumably due to both high moisture flux and increased production of organic products resulting from favorable temperature regimes. Although there was a significant correlation between solution Al and DOC at the Tunk Mountain site (r 0.52; $P < 0.01$), no correlations were observed between Al and either throughfall volume or lysimeter volume (either actual volume collected or volume calculated using Cl as a conservative tracer), nor were any seasonal patterns in solution Al chemistry observed in any of the ecosystem strata. This is in contrast to H, Mg, Na, SO_4, which were all positively correlated to actual sample volume ($r = 0.35$ to 0.43; $P < 0.01$), and showed distinct seasonal trends (Rustad 1988). Therefore, fluctuations in temperature and moisture were not key factors regulating solution Al chemistry at this site.

The influence of aboveground litter on solution Al concentrations was also minor. No relationships were observed between solution Al concentrations and aboveground litter input, and results from the litter decomposition study clearly indicate that Al is only slowly released from decaying litter, if at all.

These results suggest the following model of the biogeochemical controls on solution Al chemistry in the O horizon at this site. Solution Al is derived primarily from the dissolution of primary and secondary minerals admixed into the O horizon and secondarily from the decomposition of organic matter. Aluminum from either of these two sources can be (a) leached directly into the soil solution, probably as a mobile organo-Al complex; (b) taken up by plant roots and/or soil microorganisms; and/or (c) adsorbed onto organic exchange sites. The affinity of these sites for Al depends on the type of exchange site (i.e., more complex multidentate exchange sites have a higher affinity for Al than single carboxyl group sites), the bound Al ratio (i.e., the greater the bound Al ratio, the lower the affinity of the exchange sites for Al and vise versa), and the soil and solution pH (i.e., the lower the pH, the greater the protonation of the exchange sites, and the lower the affinity of the exchange sites for Al). Within a given range of bound Al ratio and solution pH, Al will be more tightly bound to organic matter in the O2 than the O1 due to the presence of more complex, multidentate exchange sites.

Aluminum toxicity

Solution chemistry conditions were below reported thresholds for Al toxicity and divalent cation antagonism. Total Al in O horizon leachates ranged from below detection to 58 umol L^{-1}. Although we did not directly determine the speciation of solution Al at this site, results from the chemical equilibrium model ALCHEMI indicated that 98% of the observed O horizon solution Al was theoretically complexed to organic ligands. The significant correlation between Al and DOC supports this model. Numerous other studies have shown that organically complexed Al is the dominant form of dissolved Al in forest floor solutions (David & Driscoll 1984; Driscoll et al. 1985; Cronan et al. 1990; Lawrence & Fernandez 1991). Although inorganic Al^{3+} competes effectively with the divalent cations for the binding sites in the cortical apoplast of fine roots, organic Al complexes are considered much less effective competitors for these exchange sites (Meiwes et al. 1986). At the Tunk Mountain site, molar Ca:Al ratios were 2.00 and 0.73 for O horizon leachate and stream water, respectively; molar Mg:Al ratios were 1.62 and 0.77 for O horizon leachate and stream water, respectively. Even if all of the Al was an Al^{3+}, these ratios are below values that are thought to threaten spruce trees (Meiwes et al. 1986).

Conclusions

Although intra- and intersite variability is likely important in the biogeochemistry of Al, results from this study indicate that the cycling of Al through the O horizon at this site is dominated by belowground pools and fluxes. Aluminum in aboveground biomass was small compared to that in the O horizon roots, and Al inputs in precipitation, throughfall, stemflow, and aboveground detritus were modest relative to estimated belowground detrital and mineral inputs to the O horizon.

Within the O horizon, solid-phase Al concentrations increased with depth, which is attributed to (a) the greater affinity of humic exchange sites for Al with depth; (b) the preferential retention of Al relative to carbon and other elements in decaying litter; and (c) the greater incorporation of mineral soil into the O2 than the O1. Overall, solid-phase Al chemistry in the O horizon was dominated by Al associated with the acid-soluble mineral component of this horizon.

Although solution Al reflected a mineral origin (i.e., solution Al concentrations were positively correlated to solution Si and Fe concentrations), mineral equilibria did not control solution Al concentrations. Instead, results from this study suggest that the type of organic exchange site, the bound Al ratio, and soil and solution pH were important factors determining solution Al concentrations. The significant relationship between Al and DOC indicated that Al is transported through the O horizon predominantly as an organo-aluminum complex. Although often overlooked as a source of Al, dissolved Al exported from the O horizon at this site was equivalent to 80% of the total Al exported from this stand in stream water.

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