Aluminum solubility and mobility in relation to organic carbon in surface soils affected by six tree species of the northeastern United States

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Abstract

We compared Al solubility and mobility in surface soils among six tree species (sugar maple [*Acer saccharum*], white ash [*Fraxinus americana*], red maple [*Acer rubrum*, L.], American beech [*Fagus grandifolia*, Ehrh.], red oak [*Quercus rubra*, L.], and hemlock [*Tsuga canadensis*, Carr.]) in a mixed hardwood forest in northwestern Connecticut. We analyzed forest floors and mineral soils at 0–5- and 10–20-cm depths for exchangeable cations, pyrophosphate extractable Al (Al_{pyr}; presumably solid organically bound Al), and total carbon, and solutions (from tension lysimeters) at 0- and 20-cm depths for pH, total organic C (TOC), and Al fractions. Forest floors beneath red maple, beech, and red oak had the highest exchangeable and extractable Al contents (0.4–0.6 and 2.9–3.2 mol m^{-2}, respectively), and the forest floor beneath sugar maple the lowest (0.1 and 0.8 mol m^{-2}, respectively). High concentrations of exchangeable H (under hemlock) and exchangeable Ca (under sugar maple) appear to depress exchangeable Al in forest floors. For soil solutions at 20-cm depth during the spring season, we found a strong and significant relationship between dissolved organic Al complexes (Al_{org}) and TOC. The TOC under all species appeared to have a similar capacity to bind Al_{org}. The capacity to bind dissolved Al was not saturated at high TOC concentrations in the forest floors of hemlock and red oak. Particularly under hemlock, low pH (3.5–3.7) and high concentrations of TOC (40–70 mg l^{-1}) percolating from the forest floor helped to

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dissolve Al from soil minerals, and more Al_{org} moved to deeper soil layers under hemlock than under the hardwood species. Despite pronounced differences in dissolved Al among tree species, no significant differences were found in the pyrophosphate extractable Al pools in mineral soil among tree species at different depths. The intensity, with which these trees influence Al migration throughout their life span, was probably too small to have caused pronounced effects in Al redistribution in the soil.

1. Introduction

Tree species have been found to affect calcium (Ca) availability in surface soils in a temperate forest in northwestern Connecticut, USA (Finzi et al., 1998a). A mechanism that could affect the Ca availability in the soil is the displacement of Ca^{2+} on the exchange complex by Al^{3+} in soil solution (Lawrence et al., 1995). The displaced Ca^{2+} is then prone to leach out of the soil with drainage water. Low Ca^{2+} concentrations in soil solution may enhance the phytotoxicity of dissolved Al^{3+} (e.g. McCormick and Steiner, 1978; Schier, 1985; Asp et al., 1988; Parker et al., 1988; Ulrich, 1989; Cronan and Grigal, 1995).

Complexes of Al with organic compounds (both in solid and dissolved form) suppress Al toxicity (Bartlett and Riego, 1972; Hue et al., 1986) by reducing dissolved Al^{3+} activities in surface soils, especially at high concentrations of organic matter (Bloom et al., 1979; Mulder et al., 1989a; Walker et al., 1990; Berggren and Mulder, 1995; Wesselink et al., 1996). These strong Al complexes may also be less competitive for cation exchange with Ca^{2+} than Al^{3+} because of their less favorable charge properties.

Organic Al bound to organic C in solution that is resistant to (rapid) degradation is able to migrate to deeper soil layers where adsorption and coprecipitation of organic Al complexes may occur (Ugolini and Dahlgren, 1987). Tree species may influence the solid and dissolved organic binding of Al through their effect on soil C. Several studies have shown that tree species differ in their effect on soil organic matter pools and organic C concentrations in solution (e.g. David and Driscoll, 1984; Binkley, 1996; Finzi et al., 1998b). While the linkage between organic C and organic Al is well established, we are not aware of any studies investigating the influences of tree species on the chemistry of Al in relation to organic C concentrations in the soil. The objective of our study was to identify the effects of tree species on the solubility and mobility of Al in the soil through their effect on organic C. We compared cation exchangeable ($BaCl_2$ extraction), Al extractable (Na pyrophosphate extraction), and carbon pools in the soil and Al and total organic C (TOC) concentrations in soil solution, sampled intermittently from September 1997 until April 1999, among different tree species at different depths. Factors controlling the binding of Al to organic compounds were determined to estimate their importance on Al speciation and mobility for each tree species.

2. Materials and methods

2.1. Study site

The study area was the Camp Pond watershed (~ 25 km^2) at Great Mountain Forest (GMF), a mixed hardwood forest (elevation 300–500 m) located in the northwestern part of Connecticut (Canham et al., 1994). Mean annual precipitation is 1400 mm and mean annual temperature is 7 °C (-5 °C in January and 20 °C in July). The study site at GMF is in a second growth (~ 80–130 years old) stand with a history of logging but no recent history of agriculture. The most common tree species were sugar maple (*Acer saccharum*), hemlock (*Tsuga canadensis*, Carr.), American beech (*Fagus grandifolia*, Ehrh.), red maple (*Acer rubrum*, L.), white ash (*Fraxinus americana*), and red oak (*Quercus rubra*, L.), which were also the tree species used for this study. The soils throughout are acidic, well-drained, sandy loams, derived from Wisconsinian glacial till over mica–schist bedrock. Soils in the Camp Pond watershed are Dystrochrepts that do not show signs of podzolization with an A horizon not thicker than 5 cm. We selected 36 fairly flat sites (slope < 10%), six for each species. At each site, 4–10 mature trees of one of the six tree species clustered together dominated the vegetation. Soils of 18 of the sites (three replicates for each tree species) were similar in texture and XRF data showed that all 36 sites varied little in total Al content (Dijkstra, 2001).

2.2. Sampling

In the summer of 1997, tension lysimeters (Rhizon SMS, Eijkelkamp) were installed at 18 of the 36 sampling sites (three replicates for each tree species) at two depths, 0 cm (the boundary between the forest floor and mineral soil) and 20 cm deep (all in the B horizon). To improve the power of statistical analysis, we installed the same lysimeters at the other 18 sites in the summer of 1998, at both depths. The lysimeters consisted of a 10-cm-long hydrophilic porous polymer sheath (diameter: 0.5 cm) fitted around a stainless steel wire and connected to PVC tubing with a needle at the other end. At each site, a small pit was dug and, at each depth, six lysimeters were pushed into the sidewall (minimum horizontal distance between two lysimeters was 10 cm). The PVC tubing with needle was then led to the surface and the pit was backfilled. Soil solutions were sampled by sticking the needles from the lysimeters into vacuumed bottles (40 kPa) containing a septum. The six lysimeters at one depth were connected to two bottles (three to each bottle) to ensure enough solution for analysis, and so that solutions were sampled in duplicate at each depth. Soil solutions were obtained from the bottles after 24 h. Soil solution samples were collected on 4 September and 2 October 1997; 23 April, 6 May, and 20 October 1998; and 27 April 1999. During the summer period, we were unable to collect enough soil solution. Solutions were stored before analyses at 4 °C in the dark. All materials for solution sampling were cleaned in 15% hydrochloric acid and rinsed with nanopure water before use. In the summer of 1998 at each sampling site, after removing fresh litter, forest floor (Oe + Oa) and mineral soil from 0 to 5- and 10 to 20-cm depths were sampled with a soil core (diameter: 4.5 cm) at three locations in the vicinity of the lysimeters. We sampled mineral soil at specific depth increments rather than by soil horizon because this gave us a

better quantitative estimate of tree species effects on Al and C contents in the soil. The 0–5-cm soil sample included the entire A horizon and some of the B horizon, while at 10–20-cm depth, soil was sampled in the B horizon only. Forest floor and mineral soil samples were separated with a sharp knife and forest floor depth was recorded from the hole. The samples from the three sampling locations at each site were then bulked.

2.3. Analyses

Soil solutions were analyzed for pH (glass electrode, Orion 610A), TOC (Total Carbon Analyzer, Shimadzu 5050), and total Al (AAS Perkin Elmer AA 300). Soil solutions sampled on 6 May 1998 and 27 April 1999 were taken to Syracuse University, New York, and analyzed colorimetrically for total monomeric Al (Al_m) and organic complexes of Al (Al_{org}) according to a technique utilizing pyrocatechol (McAvoy et al., 1992). The Al_{org} was separated from inorganic Al (Al_{in}) by cation exchange chromatography. Inorganic Al was calculated as the difference between Al_m and Al_{org}. All analyses were completed within 3 weeks of sampling, with pH being measured immediately after sampling. Forest floor and mineral soil samples were dried for 48 h at 105 °C and sieved (through 8- and 2-mm mesh, respectively) to remove roots and coarse fragments. Dry soil and large stones were weighed. Calculated soil bulk density was adjusted for the volume taken by stones (with stone bulk density of 2.61 g cm^{-3}; Finzi et al., 1998a). Exchangeable cations were extracted with 0.1 M $BaCl_2$ (Hendershot et al., 1993). A 0.5-g subsample of the homogenized forest floor and a 3-g subsample of the mineral soil were each mixed with 30 ml of 0.1 M $BaCl_2$ and placed on a shaker table at 45 rpm for 2 h. The suspensions were centrifuged at 2000 rpm for 15 min, extracts were filtered through Whatman 41 filter paper and Ca, Mg, K, Na, and Al were measured by AAS. For Ca and Mg, the extracts were diluted 10 times with 1.11% aqueous $LaCl_3$, and for K and Na, 10 times with 0.63% aqueous CsCl. Exchangeable acidity was measured for 10 samples, varying in pH, by titration with 0.01 M NaOH to pH 7.8 (Buurman et al., 1996). Exchangeable H was calculated by subtracting exchangeable Al and these concentrations were regressed with H^+ concentrations that were calculated from H^+ activities measured in the $BaCl_2$ extracts with a glass electrode ($P < 0.001$, $r^2 = 0.988$). For all other samples, exchangeable H was estimated from the pH of the $BaCl_2$ extract using this regression (Dijkstra et al., 2001). Pyrophosphate extractable Al (Al_{pyr}) was obtained by shaking 1 g of the forest floor or mineral soil sample overnight with 100 ml of 0.1 M Na pyrophosphate (Buurman et al., 1996). Superfloc was added before centrifuging at 2500 rpm for 15 min. Extracts were then filtered through Millipore filters (VSWP, 0.025 μm) before analyses of Al by AAS (Schuppli et al., 1983). Total C of ground samples was measured for the forest floor and mineral soil samples with the Elemental Analyzer (Fisons Instruments, EA 1108).

Repeated measures of analysis of variance (ANOVA) were performed on pH, TOC, and total Al in soil solution, and one-way ANOVA on Al_m, Al_{org}, and Al_{in} in soil solution and on measured soil properties, for each soil depth separately (SYSTAT, version 9). For the latter analyses, Tukey's post hoc test was used to separate the means of soil content and

Fig. 1. Temporal changes in pH, total organic C (TOC), and total Al in solution for six different tree species at 0 and 20 cm in the soil (error bars are standard error).
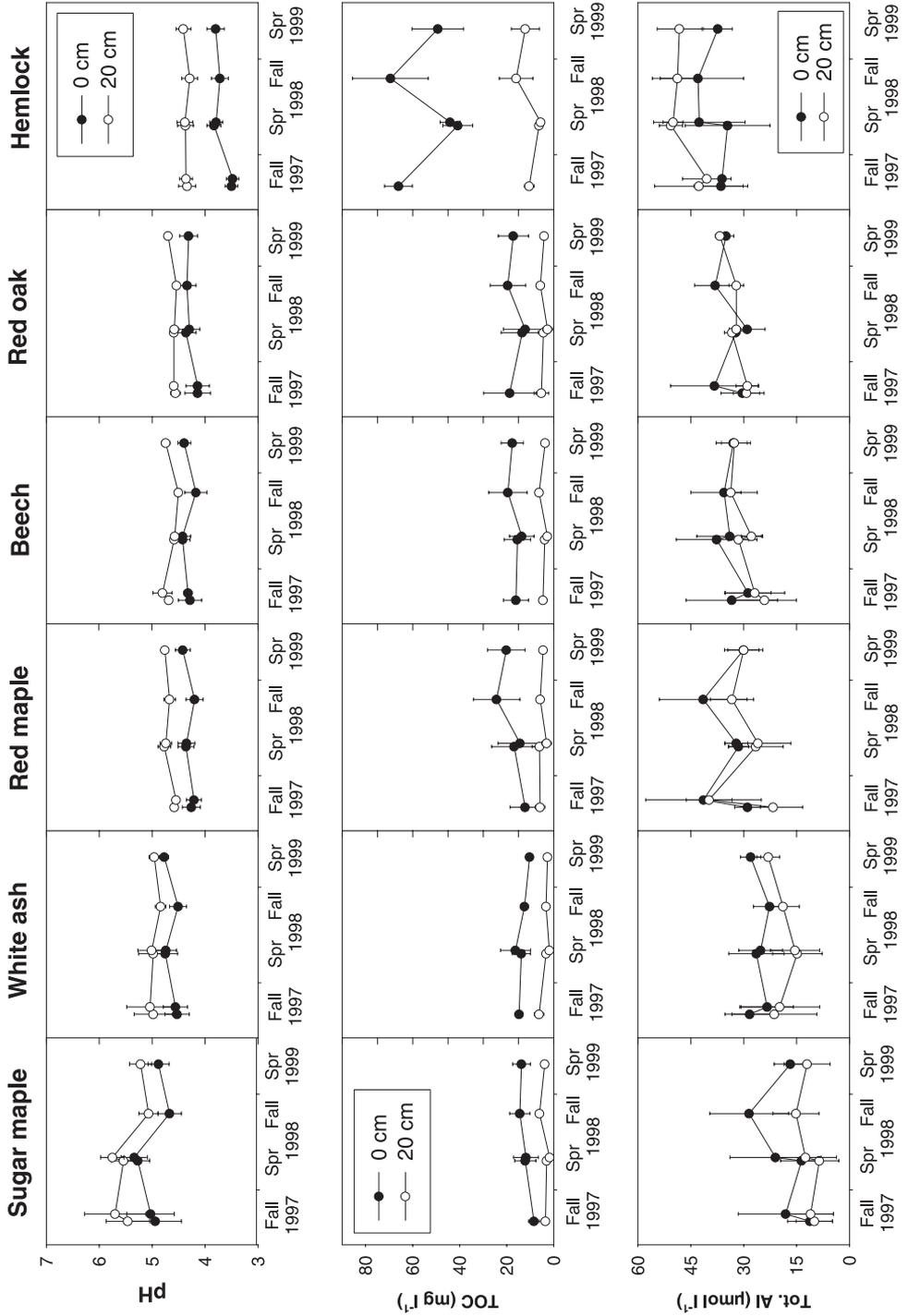
solution concentration among tree species. Significant differences were accepted at $P < 0.05$. For the solution data, the average concentrations from the two soil solution samples at each site and soil depth were taken. The variance of the solution concentrations from the two solution samples at a given depth and site did not differ significantly from that between tree species (nested ANOVA with tree species as a fixed factor and solution sample as a random factor).

3. Results

During the time period sampled, average pH in solution differed significantly among tree species at both depths ($P = 0.008$ and $P = 0.02$ for solutions at 0- and 20-cm depth, respectively), where average pH was always highest for sugar maple and lowest for hemlock, often up to 1.5 units (Fig. 1). We found significant differences in TOC concentrations in solution at 0 cm ($P = 0.01$) where hemlock had much higher TOC concentrations than the other species. At 20 cm, TOC concentrations were much smaller than at 0 cm, and again higher for hemlock than for the other tree species, but not significantly. The repeated ANOVA further showed significant temporal variations for TOC at both depths ($P = 0.01$ and 0.02 for 0- and 20-cm depths, respectively) with average highest concentrations during the fall. Total Al concentrations differed significantly among tree species at 20 cm ($P = 0.04$), but not at 0 cm. In general, total Al concentrations were at both depths highest for hemlock and lowest for sugar maple.

Table 1

The average monomeric Al (Al_m), organic Al (Al_{org}), and inorganic Al (Al_{in}) concentration in solutions from 0- and 20-cm depths, sampled on 6 May 1998 ($n = 3$) and 27 April 1999 ($n = 6$), for the different tree species (standard error in brackets)

Tree species	6 May 1998			27 April 1999		
	Al_m (μmol l^{-1})	Al_{org} (μmol l^{-1})	Al_{in} (μmol l^{-1})	Al_m (μmol l^{-1})	Al_{org} (μmol l^{-1})	Al_{in} (μmol l^{-1})
0 cm						
Sugar maple	11.4 (5.6) *a*	9.2 (4.4) *a*	2.3 (1.3) *a*	10.2 (2.5) *a*	6.6 (2.1) *a*	3.6 (0.9) *a*
White ash	14.4 (5.6) *a*	9.6 (3.0) *a*	4.8 (2.6) *a*	21.6 (4.1) *a*	11.3 (2.1) *a*	10.3 (2.1) *a*
Red maple	22.0 (4.1) *a*	7.6 (4.0) *a*	14.4 (2.4) *a*	20.4 (3.6) *a*	8.8 (2.8) *a*	11.6 (6.4) *a*
Beech	25.1 (4.6) *a*	11.7 (3.9) *a*	13.3 (5.8) *a*	23.1 (3.0) *a*	11.4 (3.0) *a*	11.7 (3.0) *a*
Red oak	19.9 (6.0) *a*	6.7 (1.2) *a*	13.2 (6.9) *a*	23.3 (3.4) *a*	9.0 (1.6) *a*	14.9 (3.8) *a*
Hemlock	25.4 (3.4) *a*	15.4 (5.3) *a*	10.0 (2.0) *a*	28.2 (7.3) *a*	15.3 (2.9) *a*	12.9 (5.5) *a*
20 cm						
Sugar maple	7.5 (0.6) *a*	2.7 (0.2) *a*	4.8 (0.4) *a*	10.1 (4.6) *a*	2.2 (0.9) *a*	7.9 (3.9) *a*
White ash	11.4 (4.8) *a*	3.5 (0.3) *a*	7.9 (4.5) *ab*	17.5 (3.6) *ab*	2.3 (0.2) *a*	15.2 (3.5) *ab*
Red maple	23.2 (4.1) *ab*	5.0 (2.6) *a*	18.2 (4.5) *ab*	28.9 (5.6) *ab*	2.6 (0.5) *a*	26.3 (5.3) *ab*
Beech	22.9 (6.1) *ab*	5.1 (1.3) *a*	17.8 (5.1) *ab*	28.2 (3.3) *b*	3.7 (0.6) *ab*	24.5 (3.7) *ab*
Red oak	25.5 (1.0) *ab*	4.7 (2.3) *a*	20.8 (1.5) *ab*	28.3 (1.1) *b*	4.2 (1.4) *ab*	24.1 (2.0) *ab*
Hemlock	37.2 (8.8) *b*	7.3 (1.5) *a*	29.9 (7.3) *b*	40.0 (5.7) *b*	8.4 (1.8) *b*	31.6 (6.8) *b*

Different letters in each column within a depth indicate significant differences between tree species ($P < 0.05$) with one-way ANOVA, post hoc Tukey's test.

The concentrations of Al_m, Al_{org}, and Al_{in} that were measured on 6 May 1998 and 27 April 1999 differed significantly at 20 cm among tree species (Table 1). Differences were in general more pronounced on 27 April 1999, where more replicates were taken. At 20-cm depth, concentrations of Al_m, Al_{org}, and Al_{in} were highest for hemlock and lowest for sugar maple. Similar trends were found at 0 cm, where average concentrations of Al_m, Al_{org}, and Al_{in} were often two to four times higher for hemlock than for sugar maple, although we could not detect significant differences at 0 cm between tree species for both sampling days. Concentrations of Al_m and Al_{in} were also high for red maple, beech, and red oak.

We found significant differences in exchangeable Ca content in the forest floor and mineral soil with highest contents for sugar maple and white ash and lowest for hemlock, beech, red maple, and oak (Table 2). Exchangeable Ca content in the forest floor of hemlock was fairly high, which was partly the result of a thicker forest floor under hemlock sites. Exchangeable Mg content showed similar trends, but differences among species were not always as significant (data not shown). Exchangeable K and Na occupied usually less than 5% of the effective cation exchange capacity (CEC_e, calculated as the sum of exchangeable Ca, Mg, K, Na, Al, and H) and differences among tree species were not significant (data not shown). Exchangeable Al content in the forest floor was highest

Table 2
Average forest floor depth, and exchangeable Ca, Al and H, extractable Al (Al_{pyr}), and total C content in the forest floor and mineral soil for the different tree species ($n = 6$, standard error in brackets)

Tree species	Forest floor depth (cm)	Exch. Ca (mmol m^{-2})	Exch. Al (mmol m^{-2})	Exch. H (mmol m^{-2})	Al_{pyr} (mol m^{-2})	Total C (kg m^{-2})
Forest floor						
Sugar maple	4.5 (0.7) *a*	597 (168) *b*	105 (35) *a*	404 (147) *a*	0.8 (0.2) *a*	2.3 (0.3) *ab*
White ash	3.9 (0.4) *a*	344 (103) *ab*	161 (20) *a*	219 (56) *a*	1.6 (0.3) *ab*	2.2 (0.2) *a*
Red maple	6.9 (0.8) *ab*	98 (38) *a*	564 (100) *b*	602 (126) *a*	3.2 (1.2) *b*	3.5 (0.3) *abc*
Beech	8.3 (0.4) *bc*	65 (18) *a*	592 (131) *b*	645 (157) *a*	2.9 (1.0) *b*	4.0 (0.3) *bc*
Red oak	6.6 (1.0) *abc*	49 (16) *a*	410 (81) *b*	539 (189) *a*	3.1 (1.3) *b*	3.3 (0.5) *abc*
Hemlock	10.4 (1.6) *c*	275 (40) *ab*	253 (128) *ab*	1707 (462) *b*	1.5 (1.1) *ab*	4.7 (0.8) *c*
0–5-cm mineral soil						
Sugar maple		540 (294) *b*	344 (88) *a*	282 (107) *ab*	5.7 (1.3) *a*	3.0 (0.2) *a*
White ash		194 (85) *ab*	460 (106) *a*	163 (46) *a*	7.2 (1.4) *a*	3.2 (0.1) *a*
Red maple		68 (51) *ab*	442 (73) *a*	360 (111) *ab*	5.3 (1.3) *a*	3.3 (0.1) *a*
Beech		24 (4) *a*	517 (40) *a*	367 (103) *ab*	5.5 (1.5) *a*	3.3 (0.3) *a*
Red oak		21 (4) *a*	368 (59) *a*	425 (170) *ab*	4.9 (1.8) *a*	3.0 (0.2) *a*
Hemlock		70 (16) *a*	557 (53) *a*	726 (228) *b*	4.0 (0.9) *a*	3.8 (0.4) *a*
10–20-cm mineral soil						
Sugar maple		362 (98) *b*	584 (73) *a*	336 (103) *ab*	20.9 (3.5) *a*	4.7 (0.4) *a*
White ash		187 (85) *ab*	550 (47) *a*	268 (32) *a*	25.6 (3.2) *a*	4.7 (0.6) *a*
Red maple		33 (18) *a*	842 (155) *ab*	423 (85) *ab*	21.2 (4.4) *a*	3.9 (0.5) *a*
Beech		27 (5) *a*	673 (64) *a*	300 (17) *ab*	25.7 (2.8) *a*	4.1 (0.3) *a*
Red oak		38 (13) *a*	975 (179) *ab*	550 (169) *b*	18.9 (4.9) *a*	3.8 (0.5) *a*
Hemlock		43 (16) *a*	1370 (227) *b*	608 (164) *b*	14.7 (2.4) *a*	4.1 (0.3) *a*

Different letters in each column within a depth indicate significant differences between tree species ($P < 0.05$) with one-way ANOVA, post hoc Tukey's test.

under red maple, beech, and red oak, and lowest under sugar maple and white ash. At 10–20-cm soil depth, exchangeable Al content was highest under hemlock and again lowest under sugar maple and white ash. We could not detect significant differences at 0–5-cm soil depth. Exchangeable H in the forest floor was much higher under hemlock than under the other tree species, and almost eight times higher than under white ash. At 0–5- and 10–20-cm soil depths, exchangeable H was still significantly higher for hemlock than for white ash, but differences were not as big as in the forest floor. Half of the CEC_e in the forest floor under hemlock was occupied by H, while Ca dominated the CEC_e under sugar maple and white ash, and Al dominated the CEC_e under red maple, beech, and red oak (Table 3). At 0–5- and 10–20-cm soil depths, Al became the dominant cation of the CEC_e for all species, while for sugar maple Ca still occupied a large fraction of the CEC_e. Pyrophosphate extractable Al (Al_{pyr}) in the forest floor was highest for red maple, beech, and red oak and lowest for sugar maple, while no significant differences were detected in the mineral soil. The Al_{pyr} contents at 10–20-cm soil depth were much higher than in the layers above. In the forest floor, total C was greater under hemlock than under sugar maple and white ash, due to differences in forest floor thickness (Table 2).

Using individual solution samples taken on 6 May 1998 and 27 April 1999, we found a significant linear positive relationship between dissolved Al_{org} and TOC at 20-cm depth

Table 3

Average cation exchange capacity (CEC_e), and the percentage of the CEC_e occupied by exchangeable Ca, Al, and H in the forest floor and mineral soil for the different tree species ($n = 6$, standard error in brackets)

Tree species	CEC_e (cmol$_c$ kg^{-1})	Exch. Ca (%)	Exch. Al (%)	Exch. H (%)
Forest floor				
Sugar maple	46.6 (7.6) *b*	47.3 (6.8) *b*	15.1 (4.4) *a*	19.5 (7.2) *a*
White ash	34.3 (2.2) *ab*	36.1 (6.4) *b*	34.3 (8.5) *abc*	12.9 (2.3) *a*
Red maple	36.5 (2.0) *ab*	7.7 (3.2) *a*	62.2 (10.0) *c*	22.8 (5.3) *ab*
Beech	33.5 (1.4) *ab*	4.7 (1.0) *a*	59.9 (10.4) *bc*	27.3 (9.3) *ab*
Red oak	29.5 (2.9) *a*	4.9 (1.1) *a*	61.3 (9.9) *c*	27.8 (7.8) *ab*
Hemlock	37.1 (0.8) *ab*	16.4 (1.0) *a*	21.8 (10.1) *ab*	50.4 (8.6) *b*
0–5-cm mineral soil				
Sugar maple	15.4 (5.1) *a*	30.9 (10.2) *b*	44.4 (10.8) *a*	11.3 (3.7) *a*
White ash	12.0 (1.9) *a*	15.8 (2.7) *ab*	65.5 (1.6) *ab*	8.3 (1.9) *a*
Red maple	11.6 (1.5) *a*	6.2 (4.2) *a*	70.1 (9.1) *ab*	16.9 (4.5) *a*
Beech	9.4 (0.6) *a*	2.4 (0.4) *a*	75.5 (5.2) *b*	17.5 (4.6) *a*
Red oak	9.0 (1.1) *a*	2.9 (0.6) *a*	67.6 (6.9) *ab*	23.3 (6.5) *a*
Hemlock	16.6 (2.0) *a*	5.0 (0.8) *a*	65.4 (5.7) *ab*	22.9 (5.8) *a*
10–20-cm mineral soil				
Sugar maple	7.7 (1.0) *b*	20.1 (5.1) *b*	51.8 (4.8) *a*	9.3 (1.7) *a*
White ash	4.0 (0.4) *ab*	13.9 (5.0) *ab*	68.7 (5.9) *ab*	11.0 (1.2) *a*
Red maple	4.2 (0.8) *ab*	2.1 (0.9) *a*	82.8 (1.7) *bc*	14.1 (1.3) *a*
Beech	3.7 (0.4) *a*	2.2 (0.5) *a*	82.5 (1.3) *bc*	12.6 (0.8) *a*
Red oak	5.3 (1.0) *ab*	2.3 (0.6) *a*	81.6 (2.2) *bc*	14.1 (1.6) *a*
Hemlock	7.7 (1.4) *b*	1.6 (0.5) *a*	84.6 (1.5) *c*	12.3 (1.9) *a*

Different letters in each column within a depth indicate significant differences between tree-species ($P < 0.05$) with one-way ANOVA, post hoc Tukey's test.

($r^2 = 0.914$, $P < 0.001$; Fig. 2B). A significant linear positive relationship between Al_{pyr} and total C concentration was evident at 10–20-cm depth ($r^2 = 0.667$, $P < 0.001$; Fig. 3C). Both in solution and in the solid phase, less Al was organically bound per unit of carbon in the upper layers (Figs. 2A and 3A,B). At 0 cm, dissolved Al_{org} could be better described as a function of TOC, Al_{in} and pH than of TOC alone. The following regression was applied
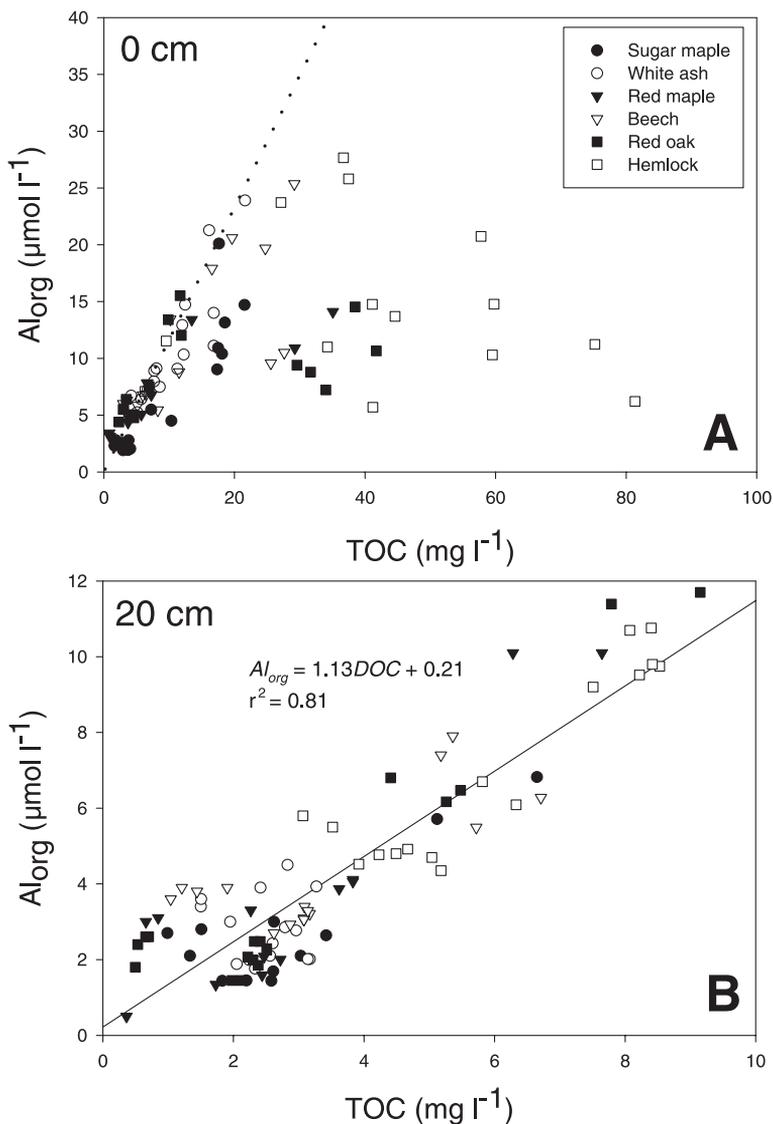
Fig. 2. Organic Al in solution (Al_{org}) as a function of total organic C (TOC) for six different tree species at two depths. Each data point represents a single solution sample, sampled on 6 May 1998 and 27 April 1999. (A) 0 cm; (B) 20 cm. The regression line in panel B ("saturation line") is drawn as a dotted line in panel A for comparison.
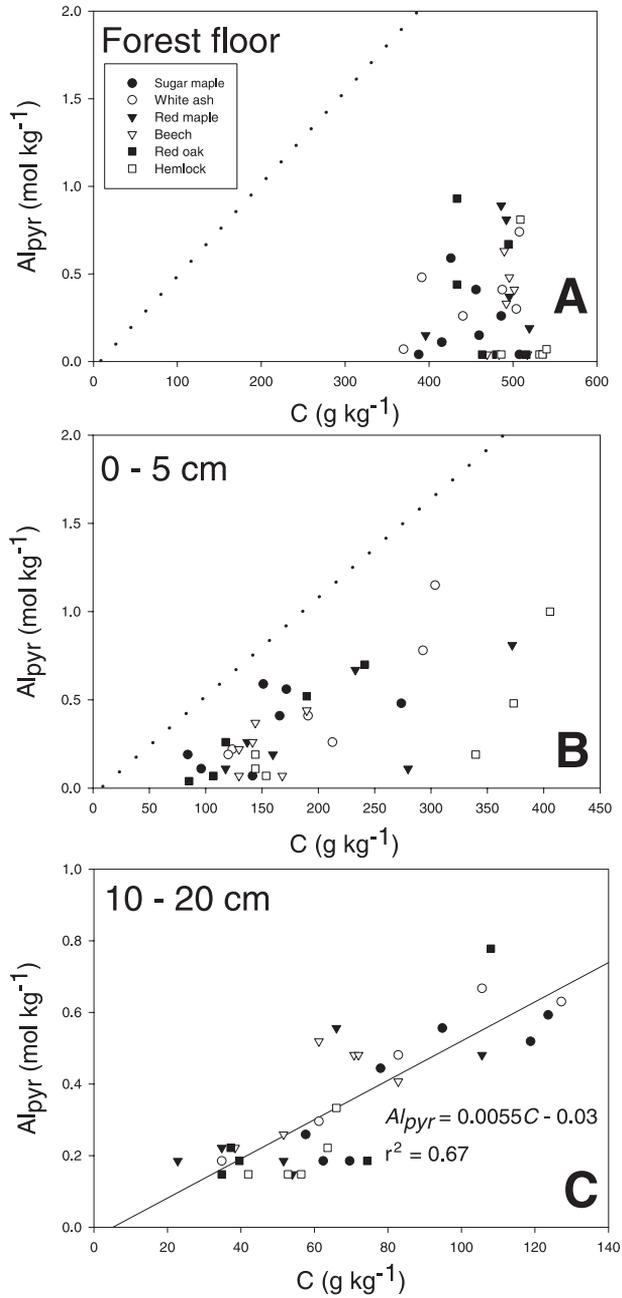
Fig. 3. Sodium pyrophosphate extractable Al (Al_{pyr}) as a function of the carbon content (C) in the soil for six different tree species at three depths. (A) Forest floor; (B) 0–5 cm; (C) 10–20 cm. The regression line in panel C ("saturation line") is drawn as a dotted line in panels A and B for comparison.

on $-$ ^{10}log transformed data from individual solution samples, taken on 6 May 1998 and 27 April 1999:

$$pAl_{org} = 3.21 + 0.692\ pTOC + 0.245\ pAl_{in} - 0.169\ pH \quad r^2 = 0.74,\ P < 0.001$$

(1)

with Al_{org} and Al_{in} expressed in mol l^{-1} and TOC in g l^{-1}. Although pH contributed significantly to the regression ($P=0.001$), the r^2 improved only slightly from 0.700 to 0.740.

4. Discussion

The lysimeters were installed 4 months before sampling, and we expected minimal disturbance effects after this period on solution pH, TOC, and total Al concentrations. Since we only sampled solutions during spring and fall, seasonal patterns should be interpreted with caution. We found significantly higher TOC concentrations during the fall than during the spring, especially for hemlock at 0 cm. Low TOC concentration during the spring may be a result of a high hydrologic input into the soil due to snowmelt, while high TOC concentrations during the fall can be related to increased litter production and decomposition during this time of the year (e.g. Driscoll et al., 1984, 1989). Driscoll et al. (1989) further showed that dissolved organic C concentrations in the Oa and Bs horizon of a spodosol in the Adirondacks, NY, were relatively constant during the summer and winter months. The very high TOC concentrations in the forest floor that we found under hemlock may have been a result of organic matter quality characteristics of hemlock and of a thicker forest floor providing a greater opportunity for TOC supply.

Differences in inorganic and total Al concentrations in solution among species, especially at 20-cm depth, may partly be a result of species effects on solution pH. High solution pH beneath sugar maple may have resulted in less Al dissolution than beneath the other species. Modeling of Al speciation with MINEQL+ (version 2.2, Schecher, 1992) showed that Al^{3+} concentrations were always undersaturated in respect to gibbsite, especially at pH values below 4.5 (data not shown), probably because of Al binding with organic compounds (Bloom et al., 1979; Mulder et al., 1989a; Walker et al., 1990; Berggren and Mulder, 1995; Wesselink et al., 1996).

The fairly narrow linear relationship between Al_{org} and TOC at 20 cm for all sites, suggests that TOC was saturated with Al at this depth during spring and had the same complexation capacity for Al under all species. Dijkstra et al. (2001) found no differences in the density of functional groups of dissolved organic C from forest floor solutions among these tree species, which was on average 6.4 $mmol_c$ g^{-1} C. When this value is applied to TOC at 20-cm depth, then at this depth on average 18% of the functional groups were complexed with Al. At 0 cm, Al_{org}/TOC ratios had an upper limit similar to those at 20-cm depth, but tended to decrease with increasing TOC concentrations, most notably under red oak and hemlock. At 0 cm, especially, TOC and Al_{in} seemed to control the formation of Al_{org} (Eq. (1)). Although the range in pH was high (ranging between 3.59 for a hemlock sample and 6.04 for a sugar maple sample), the pH had only a slight influence

on Al complexation on TOC at 0-cm soil depth. LaZerte (1989) also found only a slight pH effect on Al_{org} at high dissolved organic C concentrations. The lower Al_{org}/TOC ratios at relatively high TOC values just below the forest floor might reflect a lack of available Al present to bind with TOC during spring. When moving downward through the soil profile, more Al becomes available to bind with TOC. In these young soils relatively high in weatherable minerals, this Al is presumably released from (aluminum silicate) minerals.

The higher TOC and Al_{org} concentrations suggest that migration of Al_{org} from the surface soil to deeper soil layers is more enhanced under hemlock than under the other tree species, at least during spring. Total organic C concentrations were much lower at 20 than at 0 cm, suggesting that TOC precipitated, adsorbed, or decomposed during downward migration (McDowell and Wood, 1984; McDowell and Likens, 1988; Jardine et al., 1989; Qualls and Haines, 1992). The fate of Al_{org} associated with such TOC is unclear, but possibly it will precipitate as secondary solid Al phases (organic or inorganic), remain in solution as inorganic Al, or enter the cation exchange complex.

The Al extracted with Na pyrophosphate (Al_{pyr}) was used to compare the distribution of organic Al in the soil affected by tree species. We assumed that the Na pyrophosphate extracted solid organically bound Al with only small amounts of amorphous Al hydroxides (McKeague, 1967). The Al_{pyr} content showed a large variation without significant differences among tree species in the different soil layers, except for the forest floor. In the forest floor, differences in Al_{pyr} concentrations (mol kg^{-1} soil) were not significant, and Al_{pyr} contents (mol m^{-2}) were significant because of large differences in forest floor thickness. Other studies used Al_{pyr} and other extraction methods to compare the effect of coniferous and deciduous tree species on the podzolization process and the distribution of organic Al complexes in the soil (De Kimpe and Martel, 1976; Herbauts and de Buyl, 1981). Organic Al in the spodic B horizon in soils in southeastern Quebec and Maine was higher under the coniferous forest (fir and spruce) than under sugar maple and beech (De Kimpe and Martel, 1976). Herbauts and de Buyl (1981) also observed incipient podzolization under an 80-year-old spruce and not under much older beech forest in the Belgian Ardennes, but without differences in Al_{pyr}. They conclude that the period of time that the spruce stands could have influenced the distribution of organic Al in the soil was probably too short to observe significant differences. At our study sites, trees were not older than 130 years and the identity of previous tree species grown on the sites are unknown. Therefore, the large variation in Al_{pyr} found at our sites may partly be related to differences in the vegetation history of each site and partly to mechanical disturbances, such as windthrows, and bioturbation by soil fauna.

The maximum yearly migration of Al by TOC between 0- and 20-cm depths was estimated by multiplying the decrease in TOC concentration between solutions from 0- and 20-cm depths, measured during the year, with the maximum Al complexation capacity of the TOC (regression line in Fig. 2B), and with water fluxes that were calculated with a hydrologic model (Federer, 1995). With these calculations, we assumed that the capacity of TOC to bind Al during the year does not change. The maximum Al migration was then calculated as 5.7 and 6.3 mmol m^{-2} $year^{-1}$ under sugar maple and white ash, respectively, while this was 26 mmol m^{-2} $year^{-1}$ under hemlock. The average pool of Al_{pyr} in the 10–20-cm soil layer alone ranged between 15 and 26 mol m^{-2} (Table 2). Although the capacity of TOC to bind Al during the year may vary, these rough

calculations suggest that actual migration of Al and precipitation as Al_{pyr} is a very slow process, contributing very little each year to the Al_{pyr} pool in the first 20 cm of the soil.

Significant differences were found among tree species in the exchangeable Al pools in the different soil layers. The soil under hemlock showed increased amounts of exchangeable Al at 10–20 cm in the mineral soil. Increased levels of exchangeable Al in the mineral soil may have originated from Al release after TOC decomposition, but also from increased Al dissolution induced by a low soil pH (Mulder et al., 1987, 1989b; Dahlgren et al., 1990; Van Grinsven et al., 1992). In the forest floor, exchangeable Al was especially high for red maple, beech, and red oak. This contrasts with other studies where Al pools in the forest floor under coniferous stands were higher than under hardwood stands (Messenger et al., 1978; David and Driscoll, 1984). High Al pools in the forest floor are ascribed to Al biocycling via plants and via ectomycorrhiza, capillary rise of dissolved Al, and incorporation of mineral grains by various processes (Messenger et al., 1978; David and Driscoll, 1984; Lawrence et al., 1995; Rustad and Cronan, 1995; Giesler et al., 2000; Van Breemen et al., 2000). In our study, protons occupied most of the CEC_e of the forest floor under hemlock. The source of exchangeable H is probably from organic acids that are constantly produced in the forest floor under hemlock (Dijkstra et al., 2001). In the absence of a significant Al supply in the forest floor, protons were then able to occupy most of the exchange sites.

5. Conclusions

The apparent capacity of TOC to bind dissolved Al was similar under the six tree species and TOC became more saturated with Al while moving deeper in the soil. Concentrations of TOC and Al_{org} were higher for hemlock than for the other tree species, causing higher Al migration to deeper soil layers for this tree species. However, no differences in the pyrophosphate extractable Al pools were detected among tree species in the mineral soil. Compared to other processes such as bioturbation and mechanical disturbances, Al migration with TOC appeared to be too small of a process to cause significant tree species effects. Because of limited supply of Al and high acid production in the forest floor, protons occupied a significant portion of the CEC_e under hemlock. Exchangeable Al was especially high in the forest floor under red maple, beech, and red oak while Ca was an important cation on the CEC_e of sugar maple and white ash. In the mineral soil, low pH may have caused increased mineral Al dissolution resulting in high exchangeable Al pools for hemlock.

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References

Asp, H., Bengtsson, B., Jensén, P., 1988. Growth and cation uptake in spruce (*Picea abies* Karst.) grown in sand culture with various aluminium contents. Plant Soil 111, 127–133.

Bartlett, R.J., Riego, D.C., 1972. Effect of chelation on the toxicity of aluminum. Plant Soil 37, 419–423.

Berggren, D., Mulder, J., 1995. The role of organic matter in controlling aluminum solubility in acidic mineral soil horizons. Geochim. Cosmochim. Acta 59, 4167–4180.

Binkley, D., 1996. The influence of tree species on forest soils: processes and patterns. In: Mead, D.J., Cornforth, I.S. (Eds.), Proceedings of the trees and soils workshop. Special Publication - Agronomy Society of New Zealand, vol. pp. 10, 1–33 (Canterbury).

Bloom, P.R., McBride, M.B., Weaver, R.M., 1979. Aluminum organic matter in acid soils: buffering and solution aluminum activity. Soil Sci. Soc. Am. J. 43, 488–493.

Buurman, P., van Lagen, B., Velthorst, E.J., 1996. Manual for Soil and Water Analysis. Backhuys Publishers, Leiden. 314 pp.

Canham, C.D., Finzi, A.C., Pacala, S.W., Burbank, D.H., 1994. Causes and consequences of resource heterogeneity in forests: interspecific variation in light transmission by canopy trees. Can. J. For. Res. 24, 337–349.

Cronan, C.S., Grigal, D.F., 1995. Use of calcium/aluminum ratios as indicators of stress in forest ecosystems. J. Environ. Qual. 24, 209–226.

Dahlgren, R.A., McAvoy, D.C., Driscoll, C.T., 1990. Acidification and recovery of a spodosol Bs horizon from acidic deposition. Environ. Sci. Technol. 24, 531–537.

David, M.B., Driscoll, C.T., 1984. Aluminum speciation and equilibria in soil solutions of a Haplorthod in the Adirondack Mountains (New York, U.S.A.). Geoderma 33, 297–318.

De Kimpe, C.R., Martel, Y.A., 1976. Effects of vegetation on the distribution of carbon, iron, and aluminum in the B horizons of northern Appalachian spodosols. Soil Sci. Soc. Am. J. 40, 77–80.

Dijkstra, F.A., 2001. Effects of tree species on soil properties in a forest of the northeastern United States. PhD dissertation. Wageningen University, Wageningen, The Netherlands. 120 pp.

Dijkstra, F.A., Geibe, C., Holmström, S., Lundström, U.S., van Breemen, N., 2001. The effect of organic acids on base cation leaching from the forest floor under six North American tree species. Eur. J. Soil Sci. 52, 205–214.

Driscoll, C.T., Baker, J.P., Bisogni, J.J., Schofield, C.L., 1984. Aluminum speciation and equilibria in dilute acidic surface waters of the Adirondack region of New York State. In: Bricker, O.P. (Ed.), Geological Aspects of Acid Deposition. Butterworth Publishers, Boston, pp. 55–75.

Driscoll, C.T., Wyskowski, B.J., DeStaffan, P., Newton, R.M., 1989. Chemistry and transfer of aluminum in a forested watershed in the Adirondack region of New York, USA. In: Lewis, T.E. (Ed.), Environmental Chemistry and Toxicology of Aluminum. Lewis Publishers, Chelsea, MI, pp. 83–105.

Federer, C.A., 1995. BROOK90: a simulation model for evaporation, soil water, and streamflow, Version 3.24. Computer Freeware and Documentation. USDA Forest Service, Durham, NH.

Finzi, A.C., Canham, C.D., van Breemen, N., 1998a. Canopy tree–soil interactions within temperate forests: species effects on pH and cations. Ecol. Appl. 8, 447–454.

Finzi, A.C., van Breemen, N., Canham, C.D., 1998b. Canopy tree–soil interactions within temperate forests: species effects on soil carbon and nitrogen. Ecol. Appl. 8, 440–446.

Giesler, R., Ilvesniemi, H., Nyberg, L., van Hees, P., Starr, M., Bishop, K., Kareinen, T., Lundström, U.S., 2000. Distribution and mobilization of Al, Fe and Si in three podzolic soil profiles in relation to the humus layer. Geoderma 94, 249–263.

Hendershot, W.H., Lalande, H., Duquette, M., 1993. Ion exchange and exchangeable cations. In: Carter, M. (Ed.), Soil Sampling and Methods of Analysis. Lewis Publishers, Boca Raton, FL, pp. 167–176.

Herbauts, J., de Buyl, E., 1981. The relation between spruce monoculture and incipient podzolisation in ochreous brown earths of the Belgian Ardennes. Plant Soil 59, 33–49.

Hue, N.V., Craddock, G.R., Adams, F., 1986. Effects of organic acids on aluminum toxicity in subsoils. Soil Sci. Soc. Am. J. 50, 28–34.

Jardine, P.M., Weber, N.L., McCarthy, J.F, 1989. Mechanisms of dissolved organic carbon adsorption on soil. Soil Sci. Soc. Am. J. 53, 1378–1385.

Lawrence, G.B., David, M.B., Shortle, W.C., 1995. A new mechanism for calcium loss in forest-floor soils. Nature 378, 162–164.

LaZerte, B.D., 1989. Aluminum speciation and organic carbon in waters of central Ontario. In: Lewis, T.E. (Ed.), Environmental Chemistry and Toxicology of Aluminum. Lewis Publishers, Chelsea, MI, pp. 195–207.

McAvoy, D.C., Santore, R.C., Shosa, J.D., Driscoll, C.T., 1992. Comparison between pyrocatechol violet and 8-hydroxyquinoline procedures for determining aluminum fractions. Soil Sci. Soc. Am. J. 56, 449–455.

McCormick, L.H., Steiner, K.C., 1978. Variation in aluminum tolerance among six genera of trees. For. Sci. 24, 565–568.

McDowell, W.H., Likens, G.E., 1988. Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook Valley, New Hampshire, USA. Ecol. Monogr. 58, 177–196.

McDowell, W.H., Wood, T., 1984. Podzolization: soil processes control dissolved organic carbon in streamwater. Soil Sci. 137, 23–32.

McKeague, J.A., 1967. An evaluation of 0.1 M pyrophosphate and pyrophosphate-dithionite in comparison with oxalate as extractants of the accumulation products in podzols and some other soils. Can. J. Soil Sci. 47, 95–99.

Messenger, A.S., Kline, J.R., Wilderotter, D., 1978. Aluminum biocycling as a factor in soil change. Plant Soil 49, 703–709.

Mulder, J., van Grinsven, J.J.M., van Breemen, N., 1987. Impacts of acid atmospheric deposition on woodland soils in the Netherlands: III. Aluminum chemistry. Soil Sci. Soc. Am. J. 51, 1640–1645.

Mulder, J., van Breemen, N., Eijck, H.C., 1989a. Depletion of soil aluminium by acid deposition and implications for acid neutralization. Nature 337, 247–249.

Mulder, J., van Breemen, N., Rasmussen, L., Driscoll, C.T., 1989b. Aluminum chemistry of acidic sandy soils with various inputs of acidic deposition in the Netherlands and in Denmark. In: Lewis, T.E. (Ed.), Environmental Chemistry and Toxicology of Aluminum. Lewis Publishers, Chelsea, MI, pp. 173–194.

Parker, D.R., Kinraide, T.B., Zelazny, L.W., 1988. Aluminum speciation and phytotoxicity in dilute hydroxy-aluminum solutions. Soil Sci. Soc. Am. J. 52, 438–444.

Qualls, R.G., Haines, B.L., 1992. Biodegradability of dissolved organic matter in forest throughfall, soil solution and streamwater. Soil Sci. Soc. Am. J. 56, 578–586.

Rustad, L.E., Cronan, C.S., 1995. Biogeochemical controls on aluminum chemistry in the O horizon of a red spruce (*Picea rubens* Sarg.) stand in central Maine, USA. Biogeochemistry 29, 107–129.

Schecher, W., 1992. MINEQL+, Version 2.2. Environment Research Software. Edgewater, Maryland.

Schier, G.A., 1985. Response of red spruce and balsam fir to aluminum toxicity in nutrient solutions. Can. J. For. Res. 15, 29–33.

Schuppli, P.A., Ross, G.J., McKeague, J.A., 1983. The effective removal of suspended materials from pyrophosphate extracts of soils from tropical and temperate regions. Soil Sci. Soc. Am. J. 47, 1026–1032.

Ugolini, F., Dahlgren, R., 1987. The mechanism of podzolization as revealed by soil solution studies. In: Righi, D., Chauvel, A. (Eds.), Podzols and podzolization. INRA, Assoc. Fr. Etude Sol, pp. 195–203 (Plaisir et Paris).

Ulrich, B., 1989. Effects of acidic precipitation on forest ecosystems in Europe. In: Adriano, D.C., Johnson, A.H. (Eds.), Acidic Precipitation. Biological and Ecological Effects, vol. 2. Springer-Verlag, New York, pp. 189–272.

Van Breemen, N., Finlay, R., Lundström, U., Jongmans, A.G., Giesler, R., Olsson, M., 2000. Mycorrhizal weathering: a true case of mineral plant nutrition? Biogeochemistry 49, 53–67.

Van Grinsven, H.J.M., van Riemsdijk, W.H., Otjes, R., van Breemen, N., 1992. Rates of aluminum dissolution in acid sandy soils observed in column experiments. J. Environ. Qual. 21, 439–447.

Walker, W.J., Cronan, C.S., Bloom, P.R., 1990. Aluminum solubility in organic soil horizons from northern and southern forested watersheds. Soil Sci. Soc. Am. J. 54, 369–374.

Wesselink, L.G., van Breemen, N., Mulder, J., Janssen, P.H., 1996. A simple model of soil organic matter complexation to predict the solubility of aluminum in acid forest soils. Eur. J. Soil Sci. 47, 373–384.