

# The effect of organic acids on base cation leaching from the forest floor under six North American tree species

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## Summary

Organic acidity and its degree of neutralization in the forest floor can have large consequences for base cation leaching under different tree species. We investigated the effect of organic acids on base cation leaching from the forest floor under six common North American tree species. Forest floor samples were analysed for exchangeable cations and forest floor solutions for cations, anions, simple organic acids and acidic properties. Citric and lactic acid were the most common of the acids under all species. Malonic acid was found mainly under *Tsuga canadensis* (hemlock) and *Fagus grandifolia* (beech). The organic acids were positively correlated with dissolved organic carbon and contributed significantly to the organic acidity of the solution (up to 26%). Forest floor solutions under *Tsuga canadensis* contained the most dissolved C and the most weak acidity among the six tree species. Under *Tsuga canadensis* we also found significant amounts of strong acidity caused by deposition of sulphuric acid from the atmosphere and by strong organic acids. Base cation exchange was the most important mechanism by which acidity was neutralized. Organic acids in solution from *Tsuga canadensis*, *Fagus grandifolia*, *Acer rubrum* (red maple) and *Quercus rubra* (red oak) were hardly neutralized while much more organic acidity was neutralized for *Acer saccharum* (sugar maple) and *Fraxinus americana* (white ash). We conclude that quantity, nature and degree of neutralization of organic acids differ among the different tree species. While the potential for base cation leaching with organic acids from the forest floor is greatest under *Tsuga canadensis*, actual leaching with organic anions is greatest under *Acer saccharum* and *Fraxinus americana* under which the forest floor contains more exchangeable cations than does the strongly acidified forest floor under *Tsuga canadensis*.

## Introduction

Soil properties such as pH and the amount of base cations available in the soil may differ greatly under trees of different species. These differences can reflect differences in soil parent material, but can also be caused by differences among tree species (van Breemen *et al.*, 1997).

Trees affect the soil and its formation by producing organic acids in the soil solution. These organic acids are derived from the decomposition of litter and organic matter within the soil and from leaf leaching and leaf washing. Low molecular weight (LMW) organic acids are exuded by soil fungi (Cromack *et al.*, 1979; Malajczuk & Cromack, 1982) and plant roots (see review by Jones, 1998). Organic acidity can be neutralized by exchange with base cations on the cation exchange complex (CEC) and by mineral weathering (e.g.

Mulder *et al.*, 1987; Raulund-Rasmussen *et al.*, 1998). In return, the neutralized anions can enhance leaching of base cations from the surface soil (Mollitor & Raynal, 1982; Vance *et al.*, 1986). Evidently those tree species that produce more organic acidity will have a greater potential for base cation leaching. Actual leaching of base cations depends also on the presence of base cations in the surface soil, however.

The organic acidity produced in the forest floor is determined by the concentration and the degree of dissociation and strength of the organic acids. A large fraction of dissolved organic acids in soils are of high molecular weight and are usually referred to as fulvic acids. Little is known about their dissociation properties. Lundström (1993) could describe the organic acids from solutions of a coniferous stand in Sweden as one monoprotic acid. Bergelin *et al.* (2000) identified four groups of organic acids with specific  $pK_a$  values from forest soils in Sweden and Finland, and Tipping and co-workers described organic dissociation properties by a combination of intrinsic  $pK_a$  values and an electrostatic interaction factor

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(Tipping *et al.*, 1988; Tipping *et al.*, 1995). Van Hees *et al.* (2000) showed that the LMW organic acids, although small in concentration, played a significant part in the total acidity of soil solutions. Little is known about the organic acid properties and production in soils for different tree species, though Strobel *et al.* (1999) have found different LMW organic acid concentrations in soil solutions from different vegetation types.

To investigate the role of organic acids, we titrated solutions taken from the forest floor of six tree species and evaluated them by Gran plots (Gran, 1952). Low molecular weight organic acids were determined by the method of van Hees *et al.* (1999). Total dissolved organic carbon (DOC), pH, and ion concentrations were determined. The principal component analysis (PCA) was used to analyse all variables measured in the forest floor solution, together with data of exchangeable cations in the forest floor. In this way we attempted to relate properties of specific organic acids to certain tree species and their importance for base cation leaching.

## Materials and methods

### Site description

The 3000 ha Great Mountain Forest in northwestern Connecticut, USA, is on Canaan Mountain, at 300–500 m above sea level. The soils throughout are acidic, well-drained, sandy loams derived from glacial till over mica-schist bedrock. They are poorly developed without a clear eluvial horizon and at most a slightly developed illuvial horizon. Six tree species, namely *Acer saccharum* (sugar maple), *Tsuga canadensis* Carr. (eastern hemlock), *Fagus grandifolia* Ehrh. (American beech), *Acer rubrum* L. (red maple), *Fraxinus americana* (white ash) and *Quercus rubra* L. (red oak) are common there and we investigated the soil beneath them. The study site is in a second growth stand with a history of logging but no recent history of agriculture. The structure of the forest is simple, with no major shrub or sub-canopy tree species. We selected 36 fairly flat sites, six for each species. At each site 4–10 mature trees (approximately 80–130 years old) of one of the six tree species clustered together were dominating the vegetation.

### Sampling and processing

Solutions were sampled from the forest floor. At each site six PVC cylinders (diameter 4.6 cm, height 7 cm) were driven vertically into the forest floor and upper mineral soil. The cylinders were then removed and capped at top and bottom and brought back immediately to the laboratory where the samples were stored at 4°C for a maximum of 24 h. Before centrifuging, any mineral material was removed from the samples which were then centrifuged for 15 minutes at an acceleration of 16 500 g while maintaining the temperature at

5°C. Immediately after centrifuging, the samples were filtered through a 0.45- $\mu\text{m}$  filter (Millex-HV, Millipore). The solution was bulked for the six replicates from each site and then divided into two subsamples. One subsample for each site was measured for pH, dissolved organic C, ions and Al speciation as soon as possible. The other subsample was deep frozen and analysed later for LMW organic acids and used for titration. Deep freezing of soil solutions appeared to be able to preserve LMW organic acids in soil solutions better than sterile filtration or the use of chloroform (Karlsson *et al.*, 1999).

At 18 sites (three replicates for each tree species) forest floor samples were analysed for exchangeable cations. At each of the 18 sites three PVC cores (diameter 4.5 cm, height 15 cm) were driven into the forest floor and upper mineral soil after removing the fresh litter. In the laboratory the forest floor was separated from the upper mineral soil with a sharp knife, and forest floor samples were bulked for each site. Forest floor samples were sieved to pass 8 mm and dried for 48 h at 105°C.

### Analyses

The pH in the solution was measured with a glass electrode connected to a pH meter (Accumet). Dissolved organic C and inorganic C ( $\text{HCO}_3^-$ ) were determined with a total carbon analyser (Shimadzu TOC 5050). Concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in solution were determined with an inductively coupled plasma emission spectrometer (Perkin-Elmer) and  $\text{Na}^+$  and  $\text{K}^+$  with a graphite furnace autosampler (Perkin-Elmer). Total monomeric Al ( $\text{Al}_m$ ) and organic Al ( $\text{Al}_{org}$ ) were determined using the pyrocatechol violet and cation exchange method of McAvoy *et al.* (1992). Inorganic Al ( $\text{Al}_{in}$ ) was calculated as the difference between  $\text{Al}_m$  and  $\text{Al}_{org}$ . The concentrations of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  were determined by ion chromatography (Dionex LC-20) while  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were determined colorimetrically (Alpkem).

The low molecular weight organic acids were determined by HPLC by the method of van Hees *et al.* (1999). Samples were filtered twice through a 1000-D filter (Diaflo YM-1, Amicon), under pressure with  $\text{N}_2$  gas at 350 kPa, to remove interfering compounds. Cations were removed by running the sample through a cation exchange column (Bio-Rex 70, 200–400 mesh). A chromatograph (Shimadzu LC-10) with a Supelco C610-H ion exclusion column, with a mobile phase of 2%  $\text{H}_3\text{PO}_4$ , was used for separation. Oxalic, acetic, fumaric, malonic, formic and propionic acid were determined at 30°C, while citric, lactic and shikimic acid were determined at 70°C. These LMW organic acids were considered to be the most common acids in forest soil solutions (van Hees *et al.*, 2000).

For the titration, solutions were first acidified to  $\text{pH} < 2.85$  with M HCl and stabilized for 15 minutes at 25°C. By acidifying the sample, any  $\text{HCO}_3^-$  present was removed as  $\text{CO}_2$ . Samples were titrated at 25°C with 0.01 M NaOH to  $\text{pH} > 10.6$ . A constant flow of argon was supplied to the sample to remove any atmospheric  $\text{CO}_2$  during the titration. The

titrations were performed with an Autoburette system (Metrohm) and a DG 115-SC glass electrode (Mettler Toledo) connected to a HP 34401 A Multimeter. The Gran procedure was used to evaluate the amounts of strong and weak acids in the solutions (Molvaersmyr & Lund, 1983). In interpreting the titration results, we assumed that the organically bound Al recombined with the organic compounds during the titration (Lundström, 1993).

The exchangeable cations from the forest floor samples were measured by extracting 3 g of sample with 30 ml of 0.1 M BaCl<sub>2</sub> (Hendershot *et al.*, 1993). Samples were shaken for 2 h on a shaker table and then filtered through Whatman No 41 filter paper. Concentrations of exchangeable Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup> and Al<sup>3+</sup> were measured by atomic absorption spectrometry (Perkin-Elmer). For 10 samples exchangeable acidity (exchangeable Al<sup>3+</sup> and H<sup>+</sup>) was measured by titration with 0.01 M NaOH to pH 8.2. After subtraction of exchangeable Al<sup>3+</sup>, the calculated exchangeable H<sup>+</sup> concentrations were regressed on H<sup>+</sup> concentrations that were calculated from H<sup>+</sup> activities measured in the original BaCl<sub>2</sub> extracts with a glass electrode ( $R^2=0.988$ ). The exchangeable H<sup>+</sup> of the other samples was then calculated by using this regression on H<sup>+</sup> concentrations calculated from pH measured in the BaCl<sub>2</sub> extracts.

To examine differences between tree species, variables were analysed in a one-way analysis of variance (ANOVA). When there was a significant effect, the post hoc Tukey test was used to compare tree species means. A principal component analysis (PCA) was performed on all the variables measured in solution together with exchangeable pools. To run an ANOVA on the separate variables one at a time could create false impressions. This is because with a limited number of replicates, there is always a risk that a difference is no more than a sampling effect. The chance of judging significance wrongly increases with the number of variables. A better way is to look at all variables simultaneously. To run a PCA, data were first standardized to unit variance. Scores and variable correlations were then computed for the first eight principal components (PCs).

## Results

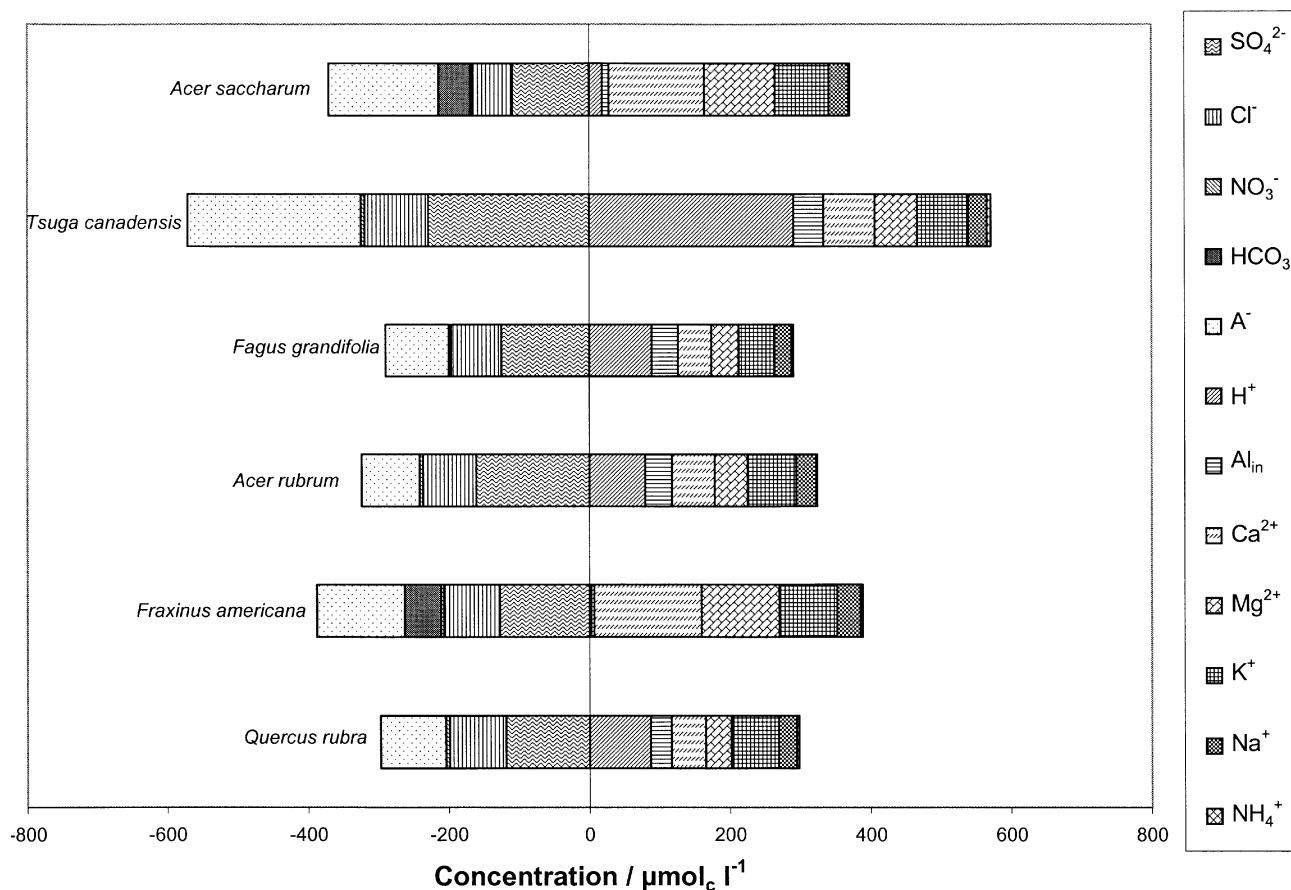
The average concentrations for ions in solution are shown in Figure 1. Sugar maple and white ash had significantly higher pH (1–2 units) and larger concentrations of Ca<sup>2+</sup> and Mg<sup>2+</sup> (2–3 times) than the other tree species ( $P<0.05$ ). Calcium and Mg<sup>2+</sup> were the dominant cations in solution under sugar maple and white ash, while protons were the most important cations in solution under hemlock. Because of the high pH, HCO<sub>3</sub><sup>-</sup> was found in most samples of sugar maple and white ash. Bicarbonate was not detected in the other samples. The forest floor under hemlock had significantly more SO<sub>4</sub><sup>2-</sup> (1.5–2 times) than that under sugar maple, beech, white ash and red oak ( $P<0.05$ ). Inorganic Al was significantly more concen-

trated (2–5 times) under hemlock, beech and red maple than under the other species ( $P<0.05$ ), while Al<sub>m</sub> and Al<sub>org</sub> were also rich in the forest floor under these species, although not significantly more so than for the other tree species.

Concentrations of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> were small for all tree species. The anion deficit in solution was calculated as the difference between cations and anions where the speciation of inorganic Al was calculated with the program MINEQL+ (version 2.2, Environmental Research Software, Edgewater, MD, USA), while organic Al was considered without charge. We expected to attribute the anion deficit to organic anions (Lundström, 1993). The forest floor under all tree species had significant amounts of organic anions (A<sup>-</sup>, Figure 1), ranging between 25 and 43% of the total sum of negative charge. Together with SO<sub>4</sub><sup>2-</sup>, organic anions were the most important anions in solution. Our estimation of organic anions was subject to large errors due to summation of many different components and the uncertainty about the Al speciation.

The concentrations of LMW organic acids in solution are shown in Table 1. All samples contained citric and lactic acid, which were also the dominant ones. In most samples also oxalic and shikimic acid were detected. Oxalic and shikimic acid can be detected at very small concentrations because of their UV absorbance, which explains why these acids were so often found in solution (van Hees *et al.*, 2000). The forest floor under hemlock and beech in particular contained malonic acid in the solution. Propionic acid was not found in any of the samples.

From titration curves of all solutions, the strong acidity (SA, strong acids minus free bases) and weak acidity (WA, sum of weak acids and free bases) were determined using Gran plots (after Molvaersmyr & Lund, 1983). The average strong acidity and weak acidity in the forest floor solutions under the six tree species together with concentrations of dissolved organic C are shown in Table 2. Sugar maple, white ash and red oak gave negative values for strong acidity. This indicated that a corresponding amount of free bases (weak acids neutralized by strong base cations) was present in solution. Solutions under sugar maple and white ash contained the most free bases and therefore neutralized the most weak acid. Hemlock was the only tree species with significant amounts of strong acids in solution. Hemlock was also associated with significantly larger concentrations of weak acidity and dissolved organic C than the other species. A significant correlation was found between weak acidity and total dissolved organic C (Figure 2). The density of weak acid functional groups of the organic C was estimated as the slope of the regression line, being 6.39 mmol<sub>c</sub> g<sup>-1</sup> C, while the intercept of 0.15 mmol<sub>c</sub> l<sup>-1</sup> indicates that some other weak acids were present in solution (e.g. inorganic aluminium). No differences in the density of functional groups of the dissolved organic C were found between tree species. We assumed that the weak acidity contained all the organic acidity in solution, except the first dissociating group of oxalic



**Figure 1** Average ion concentrations of forest floor solutions for the six tree species ( $A^-$  stands for organic anions).

and citric acid, which were considered as strong acids (van Hees *et al.*, 2000). Total acidity (i.e. mainly organic acidity) was then calculated by adding the oxalic and citric acid concentrations to the weak acidity. The contribution of LMW organic acids to the total dissolved organic C and the total acidity are shown in Table 2. Sugar maple and white ash contained the most LMW organic acids. The contribution of the LMW organic acids to the total acidity was considerably greater than their contribution to dissolved organic C. The largest fraction was under hemlock (26.2%). On average fractions ranged between 5.6% for red oak and 13.7% for white ash.

The average concentrations of exchangeable cations from the forest floor are presented in Figure 3. Significant differences were found between tree species for exchangeable  $Ca^{2+}$  and  $Mg^{2+}$  ( $P < 0.05$ ) with sugar maple and white ash having the largest concentrations (2–8 times larger than for the other species). This accords with the results of Finzi *et al.* (1998). The forest floor under hemlock had considerable amounts of exchangeable  $H^+$ , while that under beech, red maple and red oak contained the most exchangeable  $Al^{3+}$ . We had too few replicates (three) to establish significant differences in exchangeable  $H^+$  and  $Al^{3+}$  between tree species.

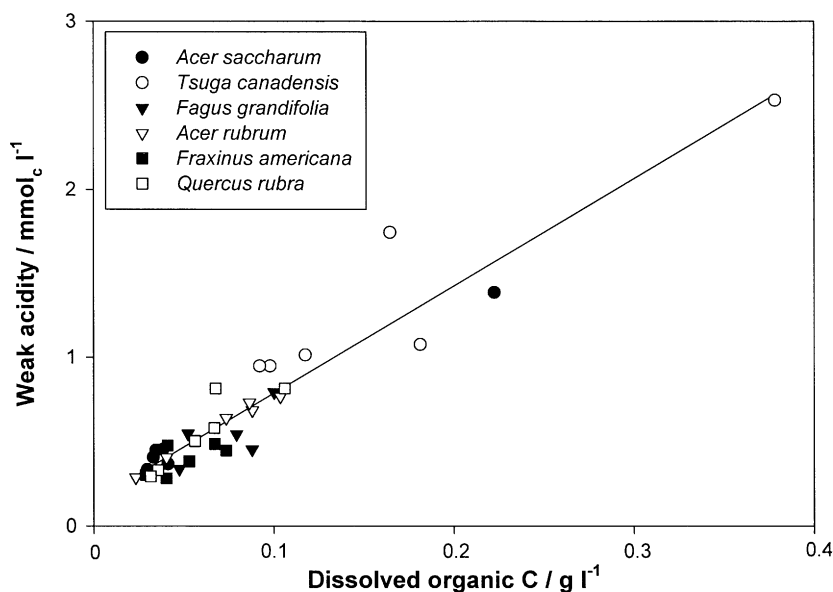
The principal component analysis was done on all the variables measured in the forest floor. The eigenvalues of the first eight components and their percentage of variance explained are shown in Table 3. The first two components explained most of the variance (37% for the first and 57% with the second) and so contain the main aspects of differences between sites. The scores of the first two components are shown in Figure 4, and their correlations with the original variables are shown in Figure 5. From Figure 4 it can be seen that the first component divides white ash and most of the sugar maple samples from the other tree species. The second component separates hemlock from beech, red maple and red oak. Concentrations of  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $HCO_3^-$  and pH and exchangeable  $Ca^{2+}$  and  $Mg^{2+}$  showed a strong negative correlation and concentrations of dissolved organic C, weak and strong acidity, Al species,  $SO_4^{2-}$ , most of the LMW organic acids and exchangeable  $H^+$  showed a strong positive correlation with the first component (Figure 5). Therefore, all these variables had a large influence on the separation of samples by the first component. Exchangeable  $Al^{3+}$  showed especially a strong negative correlation with the second component, causing a large influence on the separation of samples by this component.

**Table 1** Concentrations of low molecular weight (LMW) organic acids in soil solution for all sites (bdl means below detection limit; detection limits for oxalic, citric, shikimic, lactic, acetic, fumaric, malonic and formic acid are 0.1, 2, 0.1, 5, 3.5, 0.1, 1.5 and 3.5  $\mu\text{mol l}^{-1}$ , respectively)

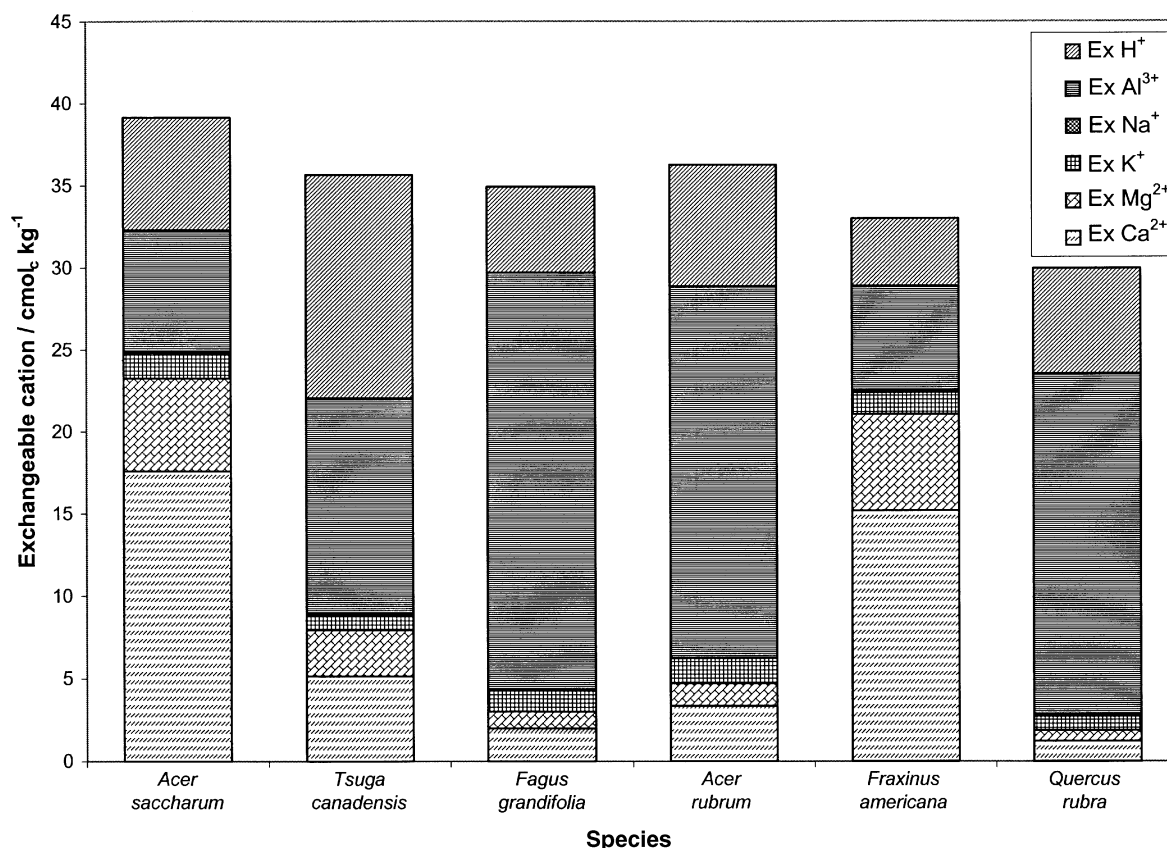
Species	Oxalic	Citric	Shikimic	Lactic	Acetic	Fumaric	Malonic	Formic	Sum LMW
	$/\mu\text{mol l}^{-1}$								
<i>Acer saccharum</i> (sugar maple)	0.1	4.9	0.4	25.3	bdl	0.1	bdl	bdl	30.9
	0.5	8.4	0.4	13.8	bdl	bdl	bdl	bdl	23.1
	0.5	11.0	1.1	13.8	bdl	0.2	3.2	bdl	29.8
	0.4	33.8	2.7	58.8	50.4	0.4	5.2	bdl	151.6
	0.1	9.7	0.2	15.1	4.4	bdl	bdl	bdl	29.5
	0.1	8.7	0.3	10.1	4.1	bdl	bdl	bdl	23.4
<i>Tsuga canadensis</i> (hemlock)	bdl	10.4	3.2	27.2	4.7	0.1	10.9	4.2	60.8
	0.5	4.7	0.7	19.8	bdl	bdl	5.2	bdl	31.0
	1.1	8.9	2.6	17.8	12.4	0.2	bdl	bdl	43.0
	bdl	11.7	18.5	7.0	bdl	0.1	39.4	7.2	84.0
	bdl	7.8	2.7	5.9	bdl	0.1	7.0	bdl	23.5
<i>Fagus grandifolia</i> (beech)	1.5	182.1	4.1	57.9	bdl	0.1	52.6	9.2	307.5
	0.3	13.9	0.5	8.4	bdl	0.1	2.7	bdl	25.9
	0.2	10.6	0.2	13.8	bdl	0.1	2.9	bdl	27.7
	0.1	8.2	0.6	14.4	9.8	0.1	9.8	bdl	43.1
	0.2	4.7	0.1	5.9	bdl	bdl	bdl	bdl	10.9
	0.2	8.7	0.2	17.5	bdl	bdl	5.0	bdl	31.6
	0.5	6.9	0.2	28.7	bdl	bdl	1.7	bdl	38.1
<i>Acer rubrum</i> (red maple)	0.2	3.0	0.5	7.0	bdl	bdl	bdl	bdl	10.7
	0.1	3.5	0.4	12.4	bdl	bdl	bdl	bdl	16.4
	0.3	29.8	0.3	7.5	bdl	0.1	bdl	3.7	41.6
	0.1	10.3	0.4	8.6	bdl	bdl	bdl	bdl	19.4
	0.4	6.1	0.3	6.4	bdl	bdl	bdl	bdl	13.2
<i>Fraxinus americana</i> (white ash)	0.2	5.8	0.3	16.9	bdl	0.1	10.1	bdl	33.3
	0.2	9.5	0.3	27.3	bdl	bdl	bdl	bdl	37.4
	0.4	20.4	0.5	35.6	bdl	bdl	bdl	bdl	56.9
	0.3	9.9	0.4	22.7	bdl	bdl	bdl	bdl	33.3
	0.5	2.2	0.1	23.1	bdl	bdl	bdl	bdl	25.9
	1.1	2.9	0.1	44.6	bdl	bdl	bdl	bdl	48.8
<i>Quercus rubra</i> (red oak)	0.2	4.9	0.1	17.7	bdl	bdl	bdl	bdl	22.9
	0.2	2.9	bdl	18.9	bdl	bdl	bdl	bdl	22.0
	0.2	3.3	bdl	6.1	bdl	bdl	bdl	bdl	9.7
	0.1	4.3	bdl	11.8	bdl	0.1	bdl	bdl	16.8
	0.2	4.3	0.3	23.4	3.8	0.1	bdl	bdl	32.1
	0.2	3.5	1.2	12.5	bdl	bdl	bdl	8.8	26.2
	0.1	3.3	0.1	20.0	bdl	bdl	bdl	bdl	23.6

**Table 2** Averages and standard errors (in parentheses) of organic and acidic properties of the soil solutions for the different tree species. DOC, dissolved organic carbon; SA, strong acidity; WA, weak acidity; LMW, low molecular weight organic acids. Different letters in each column indicate significant differences between tree species ( $P < 0.05$ ) with one-way ANOVA, post hoc Tukey test

Species	DOC $/\text{mg l}^{-1}$		SA $/\mu\text{mol}_c \text{l}^{-1}$		WA $/\mu\text{mol}_c \text{l}^{-1}$		% LMW of DOC		% LMW of total acidity	
<i>Acer saccharum</i>	67	(31) a	-157	(17) a	565	(165) a	3.5	(0.2) bc	12.0	(1.0) ab
<i>Tsuga canadensis</i>	172	(44) b	236	(70) c	1377	(262) b	2.1	(0.5) abc	10.2	(3.6) ab
<i>Fagus grandifolia</i>	71	(9) a	46	(35) bc	531	(61) a	2.0	(0.2) abc	9.4	(0.8) ab
<i>Acer rubrum</i>	69	(13) a	21	(46) ab	585	(79) a	1.7	(0.2) ab	7.0	(1.3) ab
<i>Fraxinus americana</i>	51	(7) a	-174	(52) a	395	(36) a	3.6	(0.8) c	13.7	(2.1) b
<i>Quercus rubra</i>	61	(11) a	-40	(29) ab	555	(93) a	1.6	(0.2) a	5.6	(0.7) a



**Figure 2** Weak acidity as a function of dissolved organic C in forest floor solutions for the 36 sites. The regression of weak acidity ( $y$ ) on dissolved organic C ( $x$ ) is shown by the line through the data with equation  $y = 6.39x + 0.146$ .



**Figure 3** Average exchangeable cation concentrations in the forest floor for the six tree species.

### Discussion

Lactic and citric acid were the most common LMW organic acids in all solutions. Both have frequently been detected in

solutions and extracts of forest soils (e.g. Fox & Comerford, 1990; Krzyszowska *et al.*, 1996; Strobel *et al.*, 1999; van Hees *et al.*, 2000). Apart from malonic acid, which was specific to hemlock and beech, the organic acids could not be attributed to certain tree species. In general the concentrations of the

different LMW organic acids varied much between samples. In the PCA the correlation coefficients of the LMW organic acids were all in the same quadrant as the dissolved organic C (Figure 5), suggesting a positive correlation with dissolved organic C. When dissolved organic C was correlated with each individual LMW organic acid, correlations were all significant ( $P < 0.05$ , Table 4).

White ash had significantly larger LMW organic acid fractions of the total dissolved organic C and of the total acidity than red oak (Table 2). This could mean that under white ash relatively more LMW organic acids are produced from decomposition than under red oak, but could also indicate that other sources (e.g. root exudation) are responsible for the larger fractions found for white ash. For all samples the LMW organic acid fraction of the total acidity was much larger than the LMW fraction of the dissolved organic C. This is caused by the greater density of carboxyl groups of the LMW organic

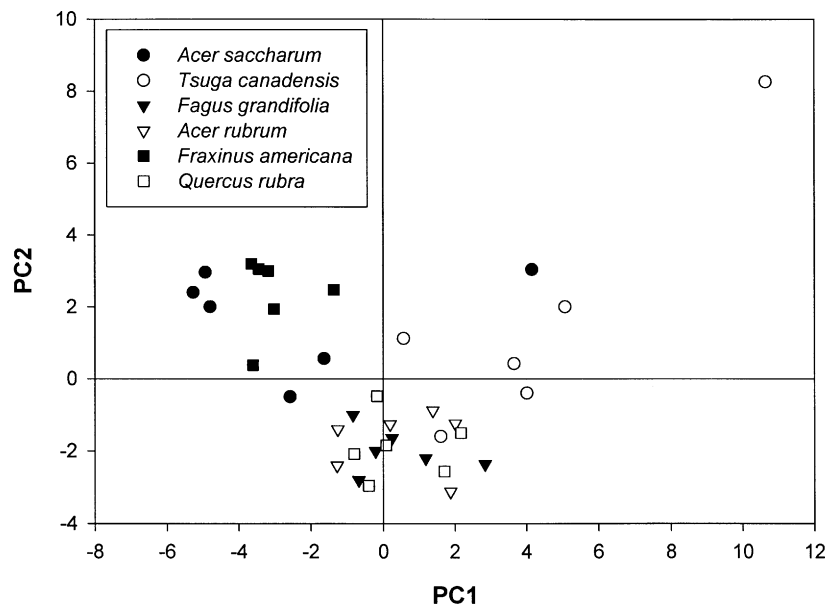
acids than in the remainder of the dissolved organic C (van Hees *et al.*, 2000).

Samples from hemlock contained significant amounts of strong acids in solution. Their presence implies that the forest floor of these samples has little capacity to neutralize incoming acidity. It could also mean that hemlock received more strong acid from the atmosphere than the other species. This accords with the significantly larger amount of  $\text{SO}_4^{2-}$  that we found under hemlock and with the results of Miller *et al.* (1991) who showed that coniferous tree species capture acidic compounds (e.g. sulphuric acid) from the atmosphere more efficiently than deciduous trees do. However, because there was a considerable amount of organic anions in solution under hemlock (see Figure 1), a substantial part of the strong acidity must be attributed to strong organic acids such as citric and oxalic acid and perhaps other unidentified organic acids. The forest floor under hemlock showed some unidentified peaks in the chromatogram of the HPLC that could be related to aromatic compounds that could not be clearly separated by the method we used. Aromatic compounds have often been found in forest litters from coniferous trees (Vance *et al.*, 1986; Pohlman & McColl, 1988). Bergelin *et al.* (2000) found in some soil solutions from coniferous stands in Sweden and Finland strong organic acids with  $\text{pK}_a$  values as little as 2.6.

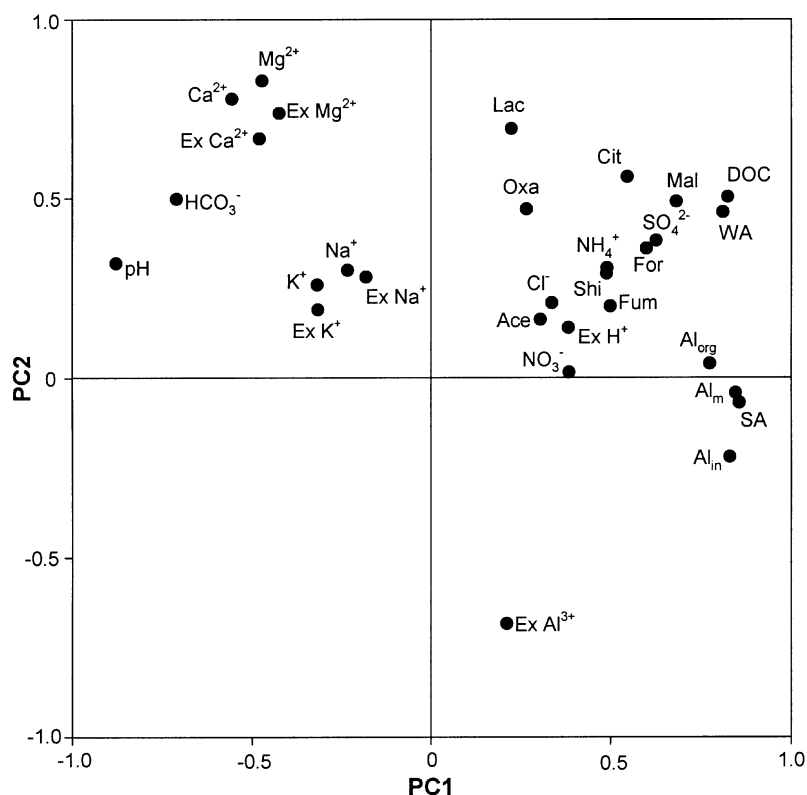
A strong correlation was found between weak acidity and concentration of dissolved organic C (Figure 2). However, no significant differences were found between tree species in the density of functional groups of the dissolved organic C. The average density of  $6.39 \text{ mmol}_c \text{ g}^{-1} \text{ C}$  accords with results of measurements from soil and surface waters by Oliver *et al.* (1983), Cronan & Aiken (1985), Lundström (1993) and Bergelin *et al.* (2000). Henriksen & Seip (1980) concluded that inorganic Al contributed significantly to the weak acid

**Table 3** Eigenvalues, percentage of variance explained and their cumulants (in parentheses) for the first eight components of the PCA from 30 original variables

Component	Eigenvalues		% of variance explained	
1	11.1	(11.1)	37.1	(37.1)
2	6.0	(17.1)	19.9	(57.0)
3	2.7	(19.8)	9.0	(66.0)
4	2.0	(21.8)	6.5	(72.5)
5	1.5	(23.2)	4.9	(77.4)
6	1.3	(24.5)	4.4	(81.8)
7	0.7	(25.2)	2.3	(84.1)
8	0.6	(25.9)	2.1	(86.2)



**Figure 4** Scores plot of the first two principal components from the PCA of forest floor exchangeable and solution concentration data.



**Figure 5** Variable correlation coefficients for the first two principal components from the PCA of forest floor exchangeable and solution concentration data.

concentrations in lake waters. However, the strong correlation of weak acidity with dissolved organic C that we found suggests that the amount of weak acidity coming from inorganic Al was small compared with the weak acidity from dissolved organic C.

Large amounts of strong and weak acidity under hemlock were not neutralized in the forest floor. Also under beech, red maple and red oak little of the weak acidity was neutralized (positive or slightly negative strong acidity). Small concentrations of exchangeable base cations under these tree species (Figure 3) prevented much organic acid neutralization through base cation exchange. The large exchangeable  $H^+$  under hemlock may have been caused by accumulated inputs of inorganic and strong organic acids in the forest floor.

In the forest floor solutions under sugar maple and white ash the organic anions were mainly compensated with base cations (Figure 1), and solutions contained significant amounts of free bases (negative strong acidity, Table 2). Most of these bases were considered to be organic anions, because  $HCO_3^-$  was removed before the titration started, and  $Al(OH)_x$  species were negligible for these samples (according to the MINEQL+ model, data not shown). With large amounts of exchangeable base cations in the forest floor (Figure 3) sugar maple and white ash sites neutralize more organic acidity and consequently leach more base cations from the forest floor than the other sites. Base cations in the forest floor under these species can be re-supplied through uptake from deeper soil layers, followed by mineralization in the forest floor. Unpublished

**Table 4** Pearson correlation coefficients between dissolved organic carbon and low molecular weight organic acids in forest floor solutions for the 36 sites

LMW organic acid	Correlation coefficient
Oxalic acid	0.44
Citric acid	0.81
Shikimic acid	0.49
Lactic acid	0.57
Acetic acid	0.37
Fumaric acid	0.53
Malonic acid	0.83
Formic acid	0.70

results show that the root density in the subsoil (30–60 cm) is significantly greater under sugar maple than under hemlock, suggesting that the former is better able to explore for base cations that are leached into the subsoil.

## Conclusions

Organic acids significantly influenced solution chemistry in the forest floor under six common tree species in the Great Mountain Forest of Connecticut. Between 25 and 43% of the negative charge could be attributed to organic anions. For *Acer saccharum* and *Fraxinus americana* these organic anions were



balanced mainly by base cations, while for hemlock protons were the most important cation.

The forest floor under *Tsuga canadensis* contained the most dissolved organic C and organic acidity in solution, and organic acids with the greatest strength. Exchange with base cations was most important in neutralizing organic acidity in the forest floor under *A. saccharum* and *F. americana*. The mobility of base cations caused by organic anions to move to deeper soil layers was greater for these two species than for the others. Under *Tsuga canadensis*, *Fagus grandifolia*, *Acer rubrum* and *Quercus rubra* much of the organic acidity remained un-neutralized in the forest floor. Exchangeable bases are also present in small concentrations in the upper mineral soil under these species (Finzi *et al.*, 1998), and so other mechanisms such as weathering under release of Al (e.g. Mulder *et al.*, 1987), decomposition (Lundström *et al.*, 1995) and adsorption and precipitation of organic acids with or without Al (Ugolini *et al.*, 1977; Driscoll *et al.*, 1985) are probably involved in neutralizing organic acids under these species.

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