Extractability of Elements in Sugar Maple Xylem along a Gradient of Soil Acidity

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Dendrochemistry has been used for the historical dating of pollution. Its reliability is questionable due primarily to the radial mobility of elements in sapwood. In the present study, the extractability of seven elements was characterized to assess their suitability for the monitoring of environmental conditions. Nine mature sugar maple trees (*Acer saccharum* Marsh.), a wide-ranging species in eastern North America that has suffered decline in past decades, were sampled in three Quebec watersheds along a soil acidity gradient. Five-year groups of annual tree rings were treated by sequential chemical extractions using extractants of varying strength (deionized H_2O, 0.05 M HCl, and concentrated HNO_3) to selectively solubilize the elements into three fractions (water-soluble, acid-soluble, and residual). Monovalent K; divalent Ba, Ca, Cd, Mg, Mn; and trivalent Al cations were found mostly in the water-soluble, acid-soluble, and residual fractions, respectively. Forms more likely to be mobile within the tree (water-soluble and acid-soluble) do not seem to be suitable for temporal monitoring because of potential lateral redistribution in sapwood rings. However, certain elements (Cd, Mn) were responsive to current soil acidity and could be used in spatial variation monitoring. Extractability of Al varied according to soil acidity; at less acidic sites, up to 90% of Al was contained in the residual form, whereas on very acidic soils, as much as 45% was found in the water-soluble and acid-soluble fractions. Sequential extractions can be useful for determining specific forms of metals as key indicators of soil acidification.

The impact of atmospheric acid deposition on forest ecosystems of North America and Europe has been reported since the 1960s (Likens and Bormann, 1974; Likens et al., 1996). Decline of sugar maple trees (*Acer saccharum* Marsh.) has been widely documented in numerous studies (Bernier et al., 1989; Duchesne et al., 2003; Kolb and McCormick, 1993; Ouimet et al., 1996; Payette et al., 1996), and it is frequently associated with soil acidification (Duchesne et al., 2002; McLaughlin et al., 1992; Ryan et al., 1994; Watmough, 2002). Sugar maple has also proven sensitive to Al-induced Ca deficiency (Côté and Camiré, 1995; Long et al., 1997; McLaughlin, 1998; Mohamed et al., 1997; Watmough, 2002).

Aluminum is potentially toxic (Kochian, 1995; Rengel, 2004) and is usually unavailable in soils until mobilized by acidification (Cronan and Schofield, 1990; McLaughlin, 1998; Ulrich et al., 1980). When soluble, it can interfere with absorption of base cations by roots (DeWalle et al., 1991; Shortle and Smith, 1988; Shortle et al., 1997) or can dislodge base cations from soil binding sites, thus inducing leaching (Johnson and Fernandez, 1992; Lawrence et al., 1995; Tomlinson, 1983). The negative impacts of Ca deficiency on tree growth and health are well documented (DeHayes et al., 1999; Likens et al., 1996; Long et al., 1997; Watmough, 2002). Several studies have reported the inhibition of Ca uptake by mobilized soil Al (Cronan, 1991; Lawrence et al., 1995; Ulrich et al., 1980), and the Ca/Al ratio in soil, wood, and leaves has often been used as an indicator of soil acidification (Berger et al., 2004; Bondietti et al., 1989; Rustad and Cronan, 1995) and of tree health (Cronan and Grigal, 1995; Matzner et al., 1986; Shortle and Smith, 1988).

Dendrochemical analyses have been used in many monitoring studies during the last three decades (Hagemeyer, 1993; Watmough, 1997). However, interpretation of element concentrations in wood as temporal witnesses of the tree's environment has been questioned because of radial translocation in the sap-conducting rings, where redistribution is common (Cutter and Guyette, 1993; Houle et al., 2002; Kennedy and Bergeron, 1991; Martin et al., 1998, 2003; Watmough,

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Table 1. Characteristics of the mineral soil horizon (first 15 cm of B) for the three sites.

	Site		
Soil variable†	Clair	Laurent	Duchesnay
pH	5.1 (0.4)‡	4.9 (0.5)	4.6 (0.1)
K, cmol$_c$ kg^{-1}	0.14 (0.03)	0.13 (0.04)	0.14 (0.03)
Ca, cmol$_c$ kg^{-1}	2 (3)	2 (1)	0.30 (0.09)
Mg, cmol$_c$ kg^{-1}	0.3 (0.1)	0.6 (0.8)	0.13 (0.03)
Mn, cmol$_c$ kg^{-1}	0.11 (0.07)	0.3 (0.4)	0.02 (0.02)
Al, cmol$_c$ kg^{-1}	1.6 (0.7)	2 (1)	5 (1)
Ca/Al	1.25	1	0.06
EA, cmol$_c$ kg^{-1}	1.8	2.0	5.6
CEC, cmol$_c$ kg^{-1}	5 (2)	5 (2)	6 (1)
BS, %	55 (21)	53 (23)	10 (2)

† BS, base saturation; CEC, cation exchange capacity; EA, exchangeable acidity. Ranking is based on soil BS, EA, and Ca/Al ratio, with least to most acid site from left to right. Ranking was similar when considering organic soil horizons.

‡ Values are averages (n = 10 for Clair; n = 8 for Laurent; n = 14 for Duchesnay) with SD in parentheses.

2002). In addition, Momoshima and Bondietti (1990) and Herbauts et al. (2002) have demonstrated that the cation exchange capacity of tree wood, which decreases with trunk diameter, is also responsible for decreasing trends observed for divalent cations.

Balk and Hagemeyer (1994) and Hagemeyer and Shin (1995) used a sequence of different extractants to assess the mobility of Cd and Pb in stemwood of sessile oak (*Quercus petrea* [Matt.] Liebl.) and Scots pine (*Pinus sylvestris* L.), respectively. Herbauts et al. (2002) also used sequential extractions to characterize Ca, K, and Mg in pedunculate oak (*Quercus robur* L.) and European beech (*Fagus sylvatica* L.). These three studies defined fractions of different binding strength to predict the mobility of certain fractions of the investigated elements. Results suggest that sequential extractions allow the identification of immobile fractions of elements, which would better demonstrate the link between wood chemistry and soil chemistry. It further implies that some tree species usually not recommended for dendrochemical monitoring, such as sugar maple (Cutter and Guyette, 1993), might provide reliable information on past environmental conditions when properly characterized.

The reduced mobility of Al in tree rings has been established through observations that Al concentrations in wood closely corresponded to periods of industrial activities (Baes and McLaughlin, 1984, 1986; Zayed et al., 1991), increased with atmospheric concentrations of SO_2 (Bondietti et al., 1989), or exhibited increasing trends starting in the 1960s (Matusiewicz and Barnes, 1985; Mohamed et al., 1997; McLaughlin, 1998; McLaughlin et al., 1992). Thus, the demonstration of Al immobilization in wood is based on indirect evidence that does not preclude the existence of processes leading to Al mobility in wood. Usefulness of Al for dendrochemical monitoring of historical rates of increasing soil acidity depends on a clear demonstration of its very limited mobility in tree rings.

The purpose of this study was to assess, by means of sequential extractions, the extractability of Al and other cations (Ba, Ca, Cd, K, Mg, and Mn) in sugar maple. A detailed and thorough characterization of elemental speciation in wood has never been done for this species, despite its wide distribution in eastern North America and its ecological importance. Furthermore, it was hypothesized that the use of sequential chemical extractions would overcome the difficulties related to the physiological limitations inherent to sugar maple tree wood, such as its high number of rings in sapwood (Cutter and Guyette, 1993) and the lateral redistribution of divalent cations (Houle et al., 2002). On three sites contrasting in soil acidity, differences in fractionation driven by soil acidity were evaluated to verify whether the observed characteristics could be generally applied in different environmental settings.

Materials and Methods

Site Selection

Wood and soil samples were collected in three watersheds (Clair [45°36′N, 76°04′W], Laurent [46°28′N, 74°11′W], and Duchesnay [46°57′N, 71°40′W]) of the Quebec Lakes Network (Houle et al., 2004, 2006). The three sites provided a gradient of soil acidity (i.e., pH, base saturation, Ca/Al ratio, and exchangeable acidity; Table 1) and were characterized by the dominance of sugar maple trees. Soils at all sites were classified as Haplorthods or Placorthods (Soil Survey Staff, 1998) or as Podzols or Brunisols (Canada Soil Survey Committee, 1992). Soil pits were dug in the watersheds (n = 10 for Clair; n = 8 for Laurent; n = 14 for Duchesnay), and the first 15 cm of the B horizon were sampled. Samples were air-dried and sieved to 2 mm. Exchangeable cations (K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, and Al^{3+}) were extracted with an unbuffered NH_4Cl (1 M, 12 h, mass/volume ratio of 1:10) solution and measured using inductively coupled plasma emission. Exchangeable acidity was calculated as the sum of H^+ (measured with a pH probe) and Al^{3+} concentrations of the soil extract. Effective cation exchange capacity corresponded to the sum of base cations (Ca, K, and Mg) and exchangeable acidity. Soil pH was measured with water using a soil/solution ratio of 1:2.5 (wt/wt). Effective base saturation was determined as the ratio of base cations to cation exchange capacity. See Houle et al. (1997) for more details on soil sampling and chemical analysis.

Tree Sampling

Nine healthy dominant or codominant sugar maple trees (mean age = 94; SD = 21; range = 72–131) were cut from the three watersheds (three trees per watershed). In different areas around the lake, trees were selected to potentially encompass a range of distinct watershed microenvironments (e.g., differing in slope, drainage, rockiness, aspect, etc.). A transversal slice (disk) was taken from the trunk at breast height. Upon return to the laboratory, slices were dried at 40°C for 48 h or kept at –20°C until drying was possible. All wood samples were manipulated with plastic nitrile gloves, and care was taken to avoid contamination by cleaning instruments regularly.

Dendrochemical Analyses

Disks were sanded to reveal annual rings, which were separated into 5-yr segments (five annual rings) with a scroll saw (1-mm width), which was cleaned with ethanol between disks to avoid mixing of samples from different trees. Each segment was ground in a stainless steel Wiley mill with a 20-mesh filter. To check for contamination from sanding and grinding processes, five samples from a single tree disk were taken at different points along the same circumference, which included five sapwood rings. Each sample was separated into six subsamples: Even-numbered subsamples were ground and pooled, and odd-numbered subsamples (also pooled) were sawed into thin pieces comparable in size to the ground product. Five other samples were similarly divided, with three subsamples sanded and three left unsanded, and sawed into thin pieces. All 20 samples (five ground, five not ground, five sanded, and five unsanded) were digested in concentrated HNO_3, and the concentrations of elements of interest were determined by inductively coupled plasma atomic emission spectroscopy (Vista AX; Varian Australia, Melbourne, Australia). Matched-pair t tests made on log-transformed data showed that grinding was not a significant source of contamination. Sanding was found to be marginally significant for Al at $p < 0.1$; therefore, a few additional millimeters were sawed off each segment on the side that had been in contact with the sand paper.

Sequential dendrochemical extractions consisted of the following sequence: (i) deionized water (Milli-Q water > 18.2 $M\Omega$ cm) aiming for the water-soluble fraction, (ii) 0.05 M HCl (acid-soluble fraction), and (iii) digestion with concentrated HNO_3 (residual fraction). Before sample processing, reaction kinetics were tested to determine the efficiency of various agitation periods. Three tubes containing wood samples were agitated for designated periods of time (30 min and 1, 2, 5, and 12 h). Solutions were analyzed for concentrations of elements of interest (Fig. 1).

For the first extraction, the samples consisted of 3 g of ground wood, to which were added 30 mL of deionized water. Samples were agitated at 30 rpm for 2 h and centrifuged at 1500 $\times g$ for 10 min. The supernatant was removed as much as possible, transferred to a UV-sterilized polyethylene tube, and preserved with concentrated HNO_3 (final concentration 0.025 M) until analysis. In the second extraction, 30 mL of 0.05 M HCl was added to the remaining wood. The samples were agitated at 30 rpm for 2 h followed by centrifugation, and the supernatant was similarly acidified before analysis. The remaining wood was rinsed twice with approximately 25 mL of deionized water before being dried for 48 h at 70°C. For the third extraction, 300 mg of wood were taken from the 3 g remaining from the first two extractions. Wood samples were put in Teflon bombs (linear closed vessels; CEM Corp., Matthews, NC) in 3 mL of concentrated HNO_3 and digested in a high-performance microwave (MDS-2000; CEM Corp.). The digested solutions were transferred to polyethylene tubes, and the volumes were adjusted to 30 mL with deionized water before analysis by inductively coupled plasma atomic emission spectroscopy. Method detection limits were calculated from a series of 10 sample solutions composed of the extractant plus metal concentrations near the expected limit of detection. Values for detection limits were obtained by multiplying the SD of these samples with the Student's t value for a 99% confidence level with $n - 1$ degrees of freedom ($t = 2.82$ for 10 replicates; Table 2) (Martin et al., 1996). Replicability of the extraction method was verified with a series of 10 ground wood samples, which were obtained by subsampling from a homogenous combination of 20 annual rings from the sapwood of a single tree. These 10 replicate samples were treated with the previously described extraction method; an aberrant value for Al was found in one replicate, which was eliminated. The replicability was calculated as the SD divided by the mean value × 100 to be expressed as a percentage (Table 3).

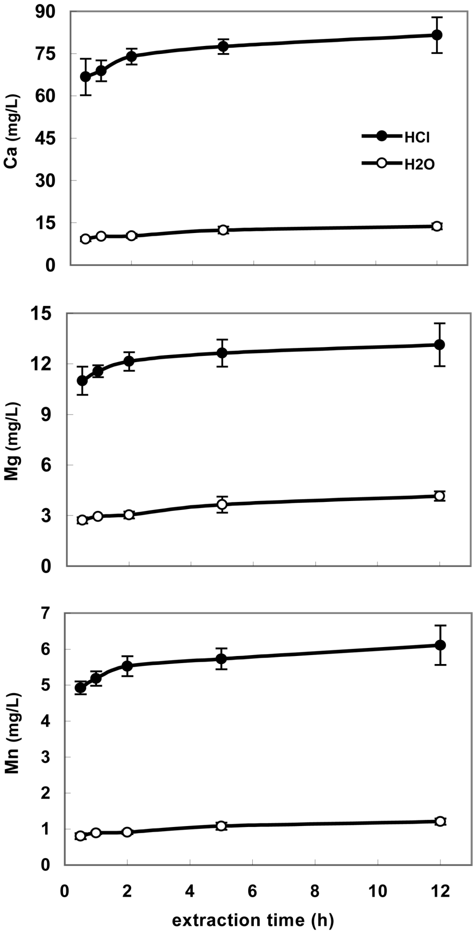

Fig. 1. Reaction kinetics from H_2O and HCl extractions for a few key elements. Values are means, and error bars are ranges (max minus min) from three replicates.

Similar to the works of Balk and Hagemeyer (1994), Hagemeyer and Shin (1995), Herbauts et al. (2002), and Houle et al. (2008), the present study defines three elemental fractions, herein designated as the water-soluble fraction, the acid-soluble fraction, and the residual fraction. The water-soluble fraction comprises organic and inorganic salts; it is the most mobile and is assumed to be displaced by the movement of sap in the trunk, thus being easily extracted by water. Cations comprising the acid-soluble fraction can be displaced by protons (Houle et al., 2008; Momoshima and Bondietti, 1990) when the extracting solution is at a pH lower than physiological cell pH. The 0.05 M HCl solution used in this study had a pH of 1.3, whereas pH measured on a series of solutions of water-extracted ground wood samples (thus similar to sap, just like the water-soluble fraction) was 5.6 on average (SD = 0.2; $n = 25$; data not shown). The acid-soluble fraction is assumed to be mobile in tree wood (although to a lesser extent than the water-soluble fraction) if sap acidity changes through time because of physiological processes or because of

Table 2. Average concentrations (per unit mass) of elements per fraction and their respective proportion in sapwood and heartwood ($n = 9$ trees for residual; $n = 8$ for water-soluble and acid-soluble from all three sites combined).

Element	Fraction	Concentration		Highest in†	Detection limit	Proportion of total		Highest in†
		Sapwood	Heartwood			Sapwood	Heartwood	
		mg kg^{-1}			mg kg^{-1}	%		
	water-soluble	347	435	ns	0.02	48.3	53.4	ns
K	acid-soluble	312	326	ns	0.7	43.6	39.9	ns
	residual	58.1	54.4	ns	3.0	8.1	6.7	ns
	water-soluble	0.73	0.78	ns	0.0007	5.7	3.2	S
Ba	acid-soluble	7.41	15.3	H	0.03	57.4	63.4	ns
	residual	4.76	8.06	H	0.007	36.9	33.4	ns
	water-soluble	61.2	85.2	ns	0.07	8.7	5.8	ns
Ca	acid-soluble	460	1048	H	1.0	65.7	71.6	ns
	residual	179	330	H	1.0	25.6	22.5	ns
	water-soluble	0.007	0.006	ns	0.002	4.7	2.4	S
Cd	acid-soluble	0.103	0.190	ns	0.006	72.3	77.1	ns
	residual	0.0326	0.050	ns	0.02	23.0	20.4	ns
	water-soluble	23.1	25.3	ns	0.006	18.1	11.6	ns
Mg	acid-soluble	82.1	156	H	0.2	64.2	71.8	ns
	residual	22.6	36.1	ns	0.04	17.7	16.6	ns
	water-soluble	8.37	8.32	ns	0.002	16.8	7.8	S
Mn	acid-soluble	31.4	76.2	H	0.1	63.1	71.4	H
	residual	9.97	22.2	ns	0.0006	20.0	20.8	ns
	water-soluble	0.128	0.090	ns	0.02	7.5	5.1	ns
Al	acid-soluble	0.156	0.28	H	0.01	9.1	16.0	ns
	residual	1.43	1.40	ns	0.09	83.4	78.9	ns

† Results from van der Waerden rank scores at $p < 0.05$. H = highest value in heartwood; S = highest value in sapwood; NS = no significant difference between heartwood and sapwood.

variations in soil acidity. For example, the concentrations of Mn, a divalent cation found mostly in the acid-soluble fraction (see the discussion below), were reduced fourfold in the wood of sugar maple trees due to higher soil pH after liming (Houle et al., 2002). The residual fraction is the last to be extracted, by using a strong extractant such as HNO_3, and is composed of elements strongly retained in wood structure, incorporated in cell walls for instance, thus being potentially fixed shortly after absorption.

Data Analysis

Linear regressions of concentrations of elements extracted over time were tested among sites for equality of slopes using a one-way ANOVA; slopes were significantly different, which prevented the use of covariance analysis on these linear regressions. As a result, average concentrations in both stem sections (heartwood and sapwood) were calculated for each tree. Proportions (percentages of each fraction over the total) were calculated. Element concentrations in wood did not follow a normal distribution (Shapiro-Wilk test, $p < 0.05$), and variances were not equal (Brown-Forsythe test, $p < 0.005$). Logarithmic transformations were applied to concentrations to ensure normality of residuals, but some still did not follow normality, thus requiring the use of nonparametric tests. The Kruskall-Wallis ANOVA on ranks (followed by the Tukey-Kramer Honestly Significant Distance test) was performed on the average concentration (sapwood and heartwood separately) and proportions of each fraction, using site as a fixed effect. Sites were ranked by soil characteristics (pH, sum of base cations, base saturation; Table 1). Van der Waerden rank scores were calculated to compare average concentrations in heartwood and sapwood. A significance level of 0.05 was used in all analyses.

Table 3. Replicability of the extraction method, per extractant and for each element. Corresponding chemical fractions: water-soluble (H_2O), acid-soluble (HCl), and residual (HNO_3) fraction.

Element	Replicability		
	H_2O	HCl	HNO_3
	%		
Monovalent			
K	0.5	0.4	3.8
Divalent			
Ba	0.9	0.6	1.4
Ca	0.9	0.5	5.9
Cd	6.4	0.6	1.2
Mg	0.7	0.6	4.4
Mn	0.9	0.6	3.6
Trivalent			
Al	1.3	1.5	18.6

Temporal trends for each element and each tree were tested using linear regressions of concentrations over time to statistically verify the observed tendencies separately for heartwood and sapwood. Trends were significant if slopes were significantly different from zero ($p < 0.05$). To allow for easier characterization of the general radial distributions (Fig. 2), all trees were combined to build an average trend. According to Cutter and Guyette (1993), sugar maple trees often contain as much as 40 annual growth rings in sapwood; this value varied from 24 to 64 in our study (44 ± 10). Hence, for the sake of a straightforward presentation, the sapwood width was set at 44 rings when creating those average trends.

Results and Discussion

Distribution of Elements among Fractions

Monovalent K was found mostly in the water-soluble and acid-soluble fractions, which together represented more than 90% of the total concentration (Table 2). As such, K can be considered very mobile, which confirms previous observations (Brownridge, 1984; Herbauts et al., 2002). The residual fraction was consequently very low (7–8%), and its respective proportion of total concentration did not vary between heartwood and sapwood. Total K concentrations did not differ significantly between heartwood and sapwood.

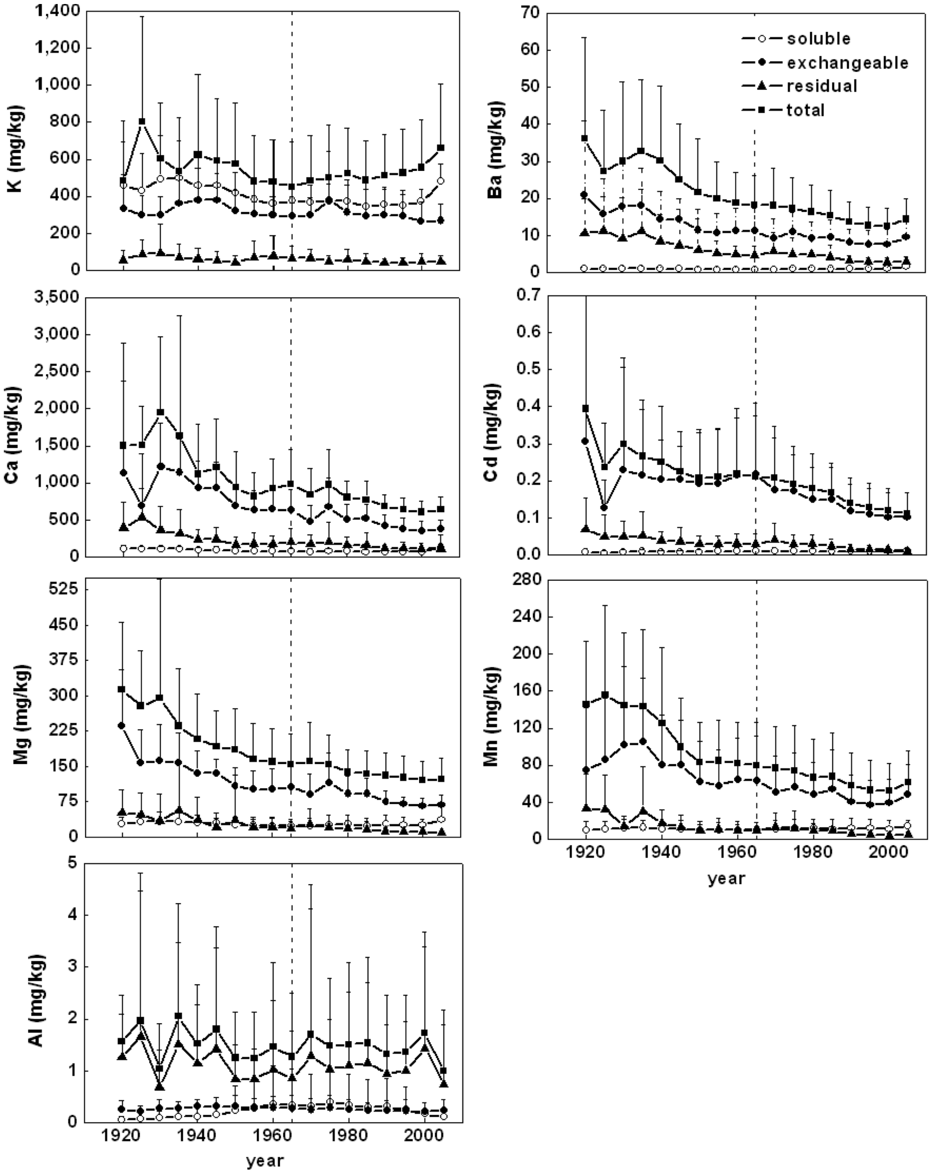

Fig. 2. Radial (temporal) trends of element concentrations in tree wood and distribution among fractions. Values are means, and error bars are SE (*n* = 9 trees for residual; *n* = 8 for water-soluble and acid-soluble from all three sites combined). The "total fraction" refers to the sum of the three distinct fractions. The vertical broken line is the heartwood–sapwood boundary.

Divalent cations (Ba, Ca, Cd, Mg, and Mn) were retrieved mostly (60–75%) by the HCl extraction, which means that they are retained in major part in the acid-soluble fraction. Reaction kinetics previously presented for Ca, Mg, and Mn (Fig. 1) showed that H_2O and HCl extractions rapidly (within 1 h) remove around 80% of what could be extracted after 12 h of agitation, thus indicating that these fractions are very weakly retained in wood. All five divalent cations presented the same relative distribution among fractions, suggesting that their partitioning in tree wood is not dependent on their function. For instance, one is not essential to plants (Ba), one is phytotoxic (Cd), and another is an essential macronutrient (Ca). They were bound in a residual form in the following increasing order: Mg (17%) < Mn (20%) < Cd (22%) < Ca (24%) < Ba (35%). Average concentrations of fractions were generally higher in heartwood (Table 2), particularly the acid-soluble and residual fractions. Although average concentrations of the water-soluble fraction of heartwood and sapwood were not significantly different, they were proportionally more abundant in sapwood. The pedunculate oaks analyzed by Herbauts et al. (2002) exhibited higher concentrations of Mg (and K) in sapwood; Meerts (2002) established from the literature that *Quercus* spp. were exceptions in this matter. Otherwise, observed distributions among fractions and radial trends of Mg and K in the present study were similar to results from Herbauts et al. (2002). The large amounts of divalent cations found in the water-soluble and acid-soluble extracts are in good agreement with the important radial redistribution of Mg and Mn (Houle et al., 2002) and Sr (Drouet et al., 2005) due to increased soil pH after liming. This potential mobility raises serious doubt about the possible use of these elements in long-term dendrochemical monitoring, especially when focusing only on total concentrations.

Aluminum, a trivalent cation, was found on average at 81% in the residual fraction. The acid-soluble fraction was greater than the water-soluble fraction (12% vs. 6%). Heartwood and sapwood contained similar concentrations of residual Al, whereas the water-soluble and acid-soluble Al levels were higher in sapwood. Because residual Al was the most abundant fraction, total Al was also in practically equal quantities in heartwood and sapwood. This similarity in behavior between residual and total Al corroborates previous assumptions regarding its immobility in wood and thus its suitability for temporal reconstruction.

Table 4. Comparison of Al concentrations reported by various authors.

Reference	Species	Range of wood Al ($mg\ kg^{-1}$)
Berger et al. (2004)	white spruce	1–7
Bondietti et al. (1989)	red spruce	2–4
Zayed et al. (1991)	black spruce	5–100
Matusiewicz and Barnes (1985)	sugar maple	8–30
Mohamed et al. (1997)	sugar maple	3–9
Watmough et al. (1999)	sugar maple	2–9
Watmough (2002)	sugar maple	1–4
This study	sugar maple	0.2–5.2

It remains to be seen whether the proportion occupied by the water-soluble and acid-soluble fractions is constant in various conditions of soil acidity. Total concentrations of Al amounted to an average of nearly 2.0 mg kg^{-1} (range, 0.2–5.2 mg kg^{-1}) and were comparable to values from other studies (Table 4).

Radial Trends

Watmough (1997) noted that elements usually reported in dendrochemical studies decrease steadily from pith to bark (Ca, K, Mg, and Mn), increase sharply from the heartwood–sapwood boundary toward bark (Cu and Fe), or show a sudden peak right around the heartwood–sapwood boundary. Okada et al. (1993) suggested that alkaline earth metals were typical of the second pattern, whereas alkali metals and halogens were associated with either the first or third pattern. Our results for sugar maple show that total element concentrations behave as reported in those studies, but it is not true of each specific fraction (Fig. 2). The generally accepted radial tendencies reflect the behavior of the main fraction of an element, which, depending on the element, may or may not be suitable for temporal biomonitoring.

Concentrations in the water-soluble, acid-soluble, and, by extension, total fractions of K decreased from the pith to the heartwood–sapwood boundary (Fig. 2). An increase of water-soluble K was observed in the outer sapwood; similar trends have been reported elsewhere (Herbauts et al., 2002; Watmough and Hutchinson, 1996) and have been ascribed to K enrichment in live parenchyma cells (Momoshima and Bondietti, 1990). The acid-soluble fraction exhibited no significant trend in sapwood, being probably redistributed among annual rings by sap flow. The residual fraction showed no significant trends in either stem section. This absence of trends might indicate late fixation in a residual form after redistribution throughout sap-conducting tree rings.

Divalent cations (Ba, Ca, Cd, Mg, and Mn) showed a radial tendency for concentrations to decrease from pith to bark, usually more sharply in heartwood than in sapwood (Fig. 2). However, these trends were observed primarily for the acid-soluble fraction and to a lesser extent for the residual fraction. Total concentrations follow these same decreasing trends because divalent ions were mainly encountered in the acid-soluble fraction. This is in accordance with observations by Bondietti et al. (1989) and Herbauts et al. (2002), which they ascribed to decreasing wood cation exchange capacity from pith to bark. The water-soluble fraction of these divalent cations was very low and exhibited no significant trend.

The radial tendency expressed by residual and total Al can best be described as erratic and fluctuating, with wide variation among trees (Fig. 2). Water-soluble and acid-soluble concentrations remain consistently low. Concentrations are generally higher in heartwood, except for the water-soluble fraction where sapwood concentrations are higher. Water-soluble Al could be transformed to a more tightly bound form on creation of heartwood, or it may be translocated into still-living sapwood rings through the apoplast (Meharg, 1993, 2005).

Fractions and Soil Acidity

Total concentrations of elements generally did not correspond well to soil acidity ranking. Total K and Ca levels in trees were significantly lower (Fig. 3) at the most acidic site (Duchesnay; Table 1). In contrast, the least acidic site (Clair) had significantly lower concentrations of total Ba, Cd, Mg, and Mn. Total Al and Mg were significantly higher in trees from the intermediate site (Laurent). Trees at the most acidic site had intermediate total concentrations of Mg. The only element to respond to soil acidity in its total concentration was Cd. Individual fractions of the studied elements showed different patterns compared with the total concentration (Fig. 3).

Water-soluble fractions of K were similar among sites. On the other hand, the most acidic site had significantly lower concentrations of K in acid-soluble and residual fractions. Only the residual fraction of K exhibited variations corresponding to site acidity ranking. The water-soluble concentration of each divalent cation (Ba, Ca, Cd, Mg, and Mn) was significantly less at the least acid site than at the other two sites. Furthermore, concentrations in the water-soluble fraction of divalent cations increased from the least acidic to the most acidic sites. However, this ranking by soil acidity was not maintained in other fractions. Divalent cations were in large part found in the acid-soluble fraction, which was consequently similar in rank to the total concentration and did not match the soil acidity ranking. The least acid site consistently had significantly lower concentrations of acid-soluble and residual Ba, Cd, Mg, and Mn (except residual Mg, for which all sites were similar), whereas the significantly lowest concentrations of acid-soluble and residual Ca were found at the most acid site. This could indicate a stress particular to that site, such as soil Ca depletion. Various studies have reported leaching of cations and loss of soil fertility in watersheds of northeastern North America; these phenomena have been associated with soil acidification occurring in the last decades (Houle et al., 1997; Likens et al., 1994, 1998). Results for water-soluble Mn are in agreement with a study by Kogelmann and Sharpe (2006), who observed high sap Mn concentrations in sugar maple growing on acid soils. The only divalent cation for which all fractions were related to soil characteristics was Cd. This suggests that residual Cd could be a potential indicator of variations in soil acid conditions. However, a more extensive research on a greater number of trees at additional sites would be needed before concluding that it could be used for long-term temporal monitoring.

Although concentrations of divalent cations varied among sites, respective percentages of individual fractions over the total remained steady; an increase or decrease in absolute concentrations of one fraction was mirrored by a proportional change in absolute concentrations of the other fractions, so that proportions were maintained (data not shown, but see Fig. 3). This suggests that speciation of divalent cations is chiefly governed by wood physiology rather than by environmental characteristics, especially when taking into consideration that the respective role of elements does not influence this phenomenon. However, soil acidity is known to play an important role in the uptake of soluble forms of divalent cations, even if fluctuations of concentrations did not show up in the proportion of the water-soluble fraction over the total, possibly because this fraction represented a low percentage of total concentrations (Table 3). Soluble forms may enter roots by passive osmotic transport (Roy et al., 1988), facilitated at low pH (Cronan, 1991), and might not fall under the concept of the selective absorption theory. The most mobile fraction (water-soluble) exhibits the best concordance with site acidity ranking, whereas the more strongly retained fractions display a weaker relationship; therefore, fractions could represent a temporal sequence of element fixation in wood: water-soluble, acid-soluble, and residual, in that order. Furthermore, these differences among sites apply only to sapwood; they are not evident in heartwood, where there is more similarity among sites. It is usually thought that soil acidification and depletion of nutrient reservoirs have happened in the last few decades in sugar maple stands of eastern Canada (Houle et al., 1997; Likens et al., 1994, 1998), which may explain why older wood (heartwood) would not show signs of recent loss of soil fertility.

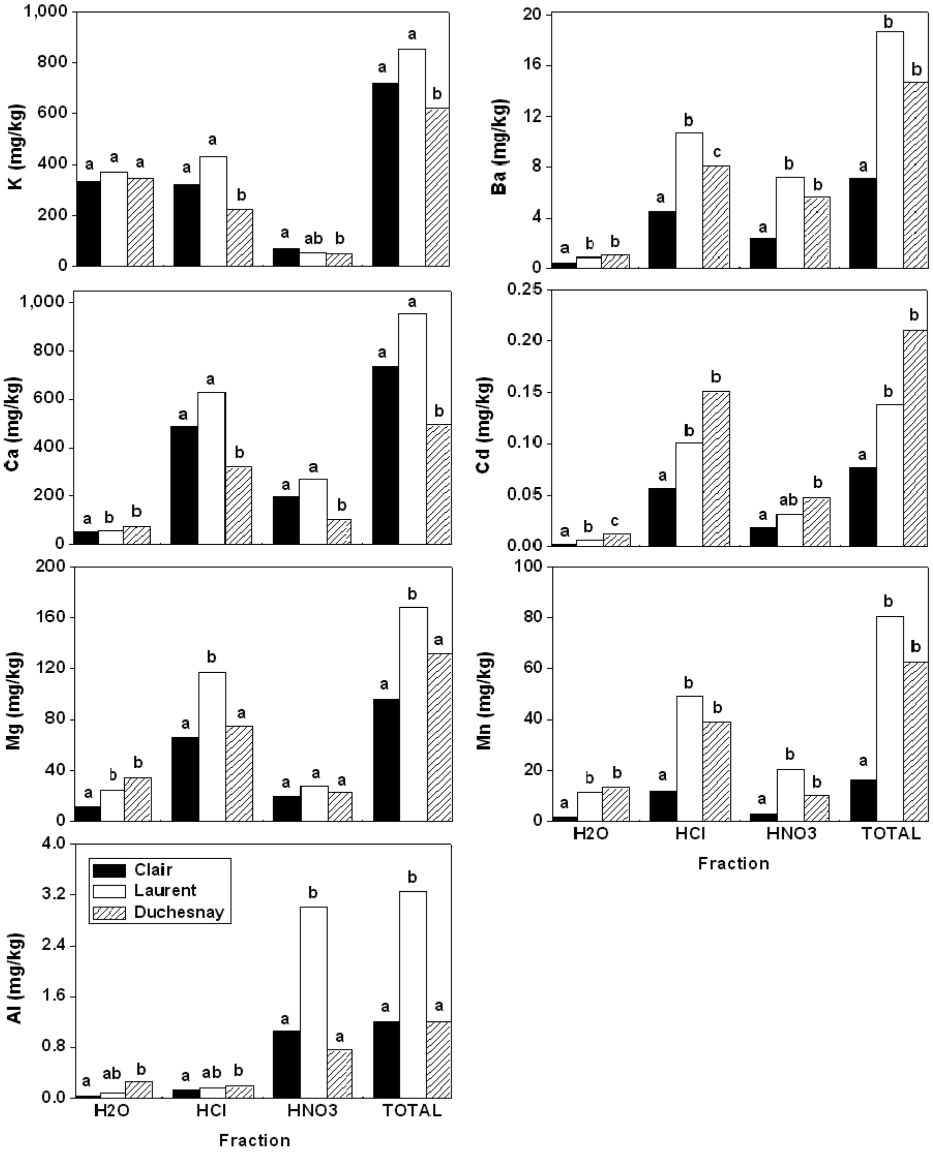

Fig. 3. Comparison of average sapwood concentrations between sites ($n = 3$ for Clair and Duchesnay; $n = 2$ for Laurent) and for each fraction (H_2O = water-soluble, HCl = acid-soluble, HNO_3 = residual, TOTAL = sum of all fractions). Sites are ranked (left to right) from least to most acid. Bars with different letters indicate that means were significantly different ($p < 0.05$) according to Tukey-Kramer's honest significant difference.

Neither residual nor total concentrations of the trivalent cation Al showed significant differences that could be related to soil characteristics; the intermediate site had the highest concentrations, whereas the most and least acid sites were similar. However, water-soluble and acid-soluble fractions of Al were significantly different among sites and were ranked in the same order as soil acidity (lower concentrations at higher soil pH). Another important distinction is to be made regarding the percentage of total Al concentration found in the water-soluble and acid-soluble fractions: These two fractions represented between 35 and 45% of Al in sapwood of trees from the most acid site but only around 10% of Al at the other two sites. Absolute concentrations did not reach levels that have been observed to be toxic to seedling shoots in laboratory experiments (sugar maple: Thornton et al., 19864; conifers: Hutchinson et al., 1986), but they could signal some other source of stress to tree health, such as soil acidity, depletion of soil base cations, or Al-induced blockage of base cation uptake by roots. Some studies have suggested that Al is excluded from absorption by roots (De Visser, 1992; Smith and Shortle, 1996). Sugar maple trees from the present study did not seem capable of such exclusion because Al was detected in tree xylem at all sites. On the other hand, this mechanism could vary according to tree species, tree health, or soil condition. Al uptake might be pH dependent, given that Al concentrations in wood increased with lower soil pH, as Cronan (1991) reported regarding root affinity for Al, Ca, and Mg that varied with soil pH.

Conclusions

Monovalent and divalent cations were found mostly in the water-soluble and acid-soluble fractions, which have been shown to be radially translocated in sapwood. As a result, these two fractions, as well as the total concentration, are not suitable for long-term dendrochemical monitoring, at least with sugar maple trees (Houle et al., 2002) or other species (Balk and Hagemeyer, 1994; Hagemeyer and Shin, 1995; Herbauts et al., 2002). However, the residual fraction could be suitable for such an investigation depending on the time necessary for an element to be fixed in a residual form in tree wood. Nevertheless, the water-soluble fraction of monovalent and divalent cations, when responsive to varying soil acidity (e.g., Cd and Mn), would constitute a valuable tool for spatial monitoring of soil acidity.

Aluminum is mainly found in the residual form (~80% of the total Al) in tree wood, and as such it could be considered to be largely immobile. Such a feature would make it a suitable candidate for dendrochemical assessments of historical pollution. However, results from the present study show that, in sugar maple tree wood, Al is more mobile than previously thought; on very acid soils, as much as 45% of the total concentration can be found in the water-soluble or acid-soluble fractions. Furthermore, the residual fraction does not vary according to soil acidity. Only the water-soluble and acid-soluble fractions of Al are influenced by soil acidity, and they generally do not constitute a substantial proportion of total Al. A total digestion masks all response from these two fractions. This could probably explain the low or lack of response of wood Al concentrations to soil acidity reported in previous studies (DeWalle et al., 1991, 1999; Hutchinson et al., 1998; Watmough, 2002), which used the total digestion method.

Most research in dendrochemistry has been done using complete digestion of wood samples with strong extractants (e.g., HNO_3, H_2SO_4, and HF). Consequently, previously reported radial tendencies of elements concerned mainly the total concentration, whose response generally resembles that of the largest fraction. However, the different fractions do not all behave similarly. As a consequence, using only the total digestion of a wood sample eliminates the distinctive response of individual fractions. Therefore, sequential extraction should be performed to determine the immobility of a given element within the xylem of trees at a given site before undertaking any attempt at temporal reconstruction.

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