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Assessment of sugar maple tree growth in relation to the partitioning of elements in xylem along a soil acidity gradient

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ABSTRACT

Partitioning of elements in tree xylem is being increasingly studied, as it suggests that elements are potentially mobile within the xylem long after their uptake. A recent study revealed that only the most mobile xylem fraction (water-soluble) of base cations (calcium [Ca], magnesium [Mg], and potassium [K]) increased at higher soil acidity, while the two mobile fractions (water- and acid-soluble) of acidic metals-potentially phytotoxic aluminium (Al), cadmium (Cd) and manganese (Mn)-were significantly enhanced on very acid soils. The current paper presents an investigation of soil-wood chemistry relationships with basal area tree growth. It was hypothesized that the growth of sugar maple would be reduced by low base cation and high acidic metal concentrations in the xylem mobile fractions. Sugar maple trees (n = 55) from six watersheds in southern Quebec, Canada were analysed by sequential chemical extractions for the water-soluble, acid-soluble and residual fractions of base cations (Ca, K, Mg) and acidic metals (Al, Cd, Mn) in xylem. Generally, tree growth was positively correlated to concentrations of base cations in wood (ρ = 0.27–0.50) and soil (ρ = 0.41–0.67), and negatively correlated to concentrations of acidic metals in wood ($\rho = -0.33$ to -0.52) and soil ($\rho = -0.67$). However, these relations differed depending on the element fraction considered. Water- and acid-soluble xylem concentrations of base cations and Al were among the best predictors of growth trends ($R^2 = 0.46 - 0.51$). The relationship between acidic metals and tree growth is further discussed.

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1. Introduction

Decline of sugar maple (*Acer saccharum* Marsh.) trees in Eastern North America has been linked to atmospheric acidic deposition (McLaughlin et al., 1992; Ryan et al., 1994; Ouimet et al., 1996; Duchesne et al., 2002; Watmough, 2002), among other factors (Horsley et al., 2002). This species was also shown to be sensitive to Al-induced Ca deficiency (Côté and Camiré, 1995; Long et al., 1997; Mohamed et al., 1997; McLaughlin, 1998; Watmough, 2002). Soil acidification is responsible for the mobilization of usually unavailable soil Al (Cronan and Schofield, 1990; McLaughlin, 1998). Mobilized Al can interfere with the uptake of base cations by roots (Shortle and Smith, 1988; DeWalle et al., 1991; Shortle et al., 1997) or displace base cations from soil binding sites, thus induc-

Abbreviations: BAI, basal area increment; BC, exchangeable base cations; BS, effective base saturation; CEC, effective cation exchange capacity; EA, exchangeable acidity; ICP-AES, inductively coupled plasma atomic emission spectroscopy.

^c Corresponding author. Tel.: +1 514 987 3000x3781; fax: +1 514 987 4647. *E-mail address*: simonbgauthier@yahoo.ca (S. Bilodeau-Gauthier). ing their leaching (Tomlinson, 1983; Johnson and Fernandez, 1992; Lawrence et al., 1995). Additionally, several studies reported inhibition of Ca uptake by mobilized soil Al (Ulrich et al., 1980; Cronan, 1991; Lawrence et al., 1995). The negative impact of Ca-deficiency on tree growth and health is also well documented (Likens et al., 1996; Long et al., 1997; DeHayes et al., 1999; Moore et al., 2000; Watmough, 2002). As a result, the ratio of Ca-to-Al in soil, wood and leaves was often used as an indicator of soil acidification (Bondietti et al., 1989; Rustad and Cronan, 1995; Berger et al., 2004) as well as of tree health (Matzner et al., 1986; Shortle and Smith, 1988). More precisely, a Ca/Al molar ratio under 1.0 in soil solution has been proposed as a sign of potential Al stress and nutrient imbalance to the ecosystem (Cronan and Grigal, 1995). Momoshima and Bondietti (1990) suggested that most of the Al could be immobilized in the trunk, as they observed for Fe, and thus not reach higher parts of the tree. It was later stated that roots discriminate against Al from soils during uptake (De Visser, 1992; Godbold, 1994; Kochian, 1995; Smith and Shortle, 1996), and that its translocation in plant parts is limited (Godbold, 1994; Kochian, 1995).

Availability of other potentially phytotoxic metals is also enhanced by soil acidification. Cadmium (Cd), a non-essential ele-

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ment, is among the most toxic heavy metals (Andersen et al., 2002; Benavides et al., 2005; Gratão et al., 2005b). A decrease in soil pH increases Cd concentrations in the soil solution (Bergkvist, 1987; Tyler et al., 1987; Berggren, 1992; Römkens and Salomons, 1998). It can induce oxidative stress (Schützendübel et al., 2001; Vitória et al., 2001) and cause serious damage on general plant metabolism (Benavides et al., 2005; Gratão et al., 2005a). Manganese (Mn) is an essential trace element for trees, which can be toxic at excess concentrations (McQuattie et al., 1999; McQuattie and Schier, 2000; Kogelmann and Sharpe, 2006; St. Clair et al., 2008), causing oxidative stress (Ducic and Polle, 2005). Exposition to high light intensity can exacerbate its toxic effects on sugar maple (St. Clair and Lynch, 2004) as well as certain crop plants (González et al., 2000). It is also mobilized in soils by low pH (Driscoll et al., 2001; Reichman, 2002) and can potentially accumulate in tree wood (Butkus et al., 2004).

Numerous studies have observed, for sugar maple trees, elevated Mn concentrations in wood and leaf tissues at low soil pH (Matusiewicz and Barnes, 1985; DeWalle et al., 1991, 1999; Guyette et al., 1992; Long et al., 1997; Martin et al., 1998; Smith, 2001; Houle et al., 2002). Due to this relationship, Guyette et al. (1992) used Mn to reconstruct past levels of soil pH from tree-rings of eastern redcedar (Juniperus virginiana L.) while Augustin et al. (2005) estimated past soil base saturation from wood Mn in Norway spruce stands (Picea abies L. Karst.). However, it should be noted that reliability of wood element concentrations to act as historical records of environmental conditions is challenged due to radial re-equilibration of elements in sap-conducting tree-rings, which is now commonly acknowledged (Kennedy and Bergeron, 1991; Cutter and Guyette, 1993; Martin et al., 1998; Herbauts et al., 2002; Houle et al., 2002; Watmough, 2002; Martin et al., 2003; Drouet et al., 2005). Wood element concentrations furthermore vary depending on soil acidic conditions, as shown by Bilodeau-Gauthier et al. (2008) in a study conducted at three sites along a soil acidity gradient. They reported for the first time that concentrations of the mobile (water- and acid-soluble) fractions of Al, Cd, and Mn in tree xylem increased significantly when soil acidity was higher, while only the most mobile fraction (water-soluble) of Ca and Mg responded in this way (Bilodeau-Gauthier et al., 2008).

Because of the various impacts that chemical elements have on tree health and considering the varying behaviours of those elements in response to environmental conditions, it is thus important to assess the relation between the growth of trees at acidic sites and their xylem elemental concentrations in the different fractions. This paper presents an in-depth examination of the link between wood chemistry, soil chemistry, and tree growth. These relationships are examined on an individual tree basis and its immediate soil environment for 55 sugar maple trees distributed among six sites, thus covering a wide range of soil conditions among typical forest soils of glacial origin in Québec, Canada. This represents a more robust statistical and ecological approach than using site means. Average sapwood concentrations in elemental fractions (water-soluble, acid-soluble, residual) of basic (Ca, Mg, K) and acidic (Al, Cd, Mn) cations are compared to various soil variables associated with soil acidity. Most importantly, and despite the fact that other authors have previously reported relationships between tree growth and total concentrations of some elements in xylem (Bondietti et al., 1989; Mohamed et al., 1997; Houle et al., 2002; Watmough, 2002; Berger et al., 2004), the present investigation is the first to define how tree growth is related to the concentrations of elements found in the water- and acid-soluble fractions of xylem and how it varies with soil acidity.

It is hypothesized here that concentrations of base cations (Ca, K, Mg) in the most mobile wood fractions (water- and acid-soluble) should be positively correlated to growth since they take part in physiological processes for which mobility is required (Fromm, 2010). In addition, the residual fraction of Ca should be posi-

tively correlated to growth because this element is an important constituent of cell walls (Smith et al., 2009), where it is thus harder to extract and should appear in the residual fraction. On the other hand, the growth of sugar maples should be impeded by acidic metals mobilized at high soil acidity, which should also translate as greater xylem concentrations of those elements. Tree growth is expected to be negatively correlated to concentrations of acidic metals (Al, Cd, Mn) in the most mobile wood fractions (water- and acid-soluble), in part because it is hypothesized that these elemental fractions can potentially reach and harm the photosynthetically-active leaves (Mn-induced oxidative stress, for instance, is well-documented).

2. Methods

2.1. Site selection

Wood and soil samples were collected in six watersheds of the Quebec Lakes Network (Houle et al., 2004, 2006) during the years 2005 and 2006. The six sites provided a gradient of soil acidity (i.e., pH, base saturation, Ca/Al ratio, 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 Podzols or Brunisols (Canada Soil Survey, 1992).

2.2. Tree sampling

Eight to fourteen healthy dominant or co-dominant sugar maple trees (n = 55 trees) were selected per watershed, in different areas potentially representing distinct watershed microenvironments (e.g., differing in slope, drainage, aspect, rockiness, etc.). The tree stands from all watersheds were fairly comparable in term of tree age (mean age = 77; SD = 18) and width (mean diameter at breast height = 22 cm; SD = 6). Two tree cores were taken on opposite sides of the trunk at breast height. Upon return to the laboratory, cores were dried at 40 °C during 48 h. All wood samples were manipulated with plastic nitrile gloves and care was taken to avoid contamination by cleaning instruments regularly with 95% ethanol.

2.3. Dendrochronological measurements

Measurements of ring width were made on all cores, under a binocular, using a UniSlide device (Velmex Inc.) and the MeasureJ2X V3.1 software (Voortech Consulting, 2001). Rings were crossdated visually by way of the skeleton plot procedure (Fritts, 1976; Yamaguchi, 1991) before measurements to identify missing or absent rings. Series were statistically verified using the COFECHA program (Holmes, 1996), which identifies outliers to be excluded from the series. Measurements from both cores of the same tree were combined to produce an average trend for each tree. Growth was calculated using the basal area increment (BAI) with the following formula:

$BAI = \pi (R_n^2 - R_{n-1}^2)$

where, n is the year of ring formation and R is the distance from the pith to the other boundary of the ring formed in year n (Duchesne et al., 2003).

2.4. Dendrochemical analyses

The position of the heartwood-sapwood boundary on the tree cores was determined visually based on difference in wood color. Only the sapwood section (average number of annual rings = 45; SD = 13) was considered for analysis, because a previous study had shown that concentrations were relatively constant within the sap-

Table 1

Characteristics of the upper mineral soil horizon (first 15 cm of B) for the six sites.

| Soil variable ^a | | Site | | | | | | |
|---|--------------------------------------|---------------------------------|---------------------------------|-----------------------------------|---|--|-------------------------------------|--|
| | Coordinates Latitude Longitude | Blais 45° 56′ N 75° 10′ W | Clair 45° 36′ N 76° 04′ W | Laurent 46° 28′ N 74° 11′ W | General White 46° 21' N 74° 41' W | Truite Rouge 46° 09' N 74° 05' W | Duchesnay 46° 57' N 71° 40' W | |
| PH | | 5.1 ^b | 5.1 | 4.9 | 4.8 | 4.8 | 4.6 | |
| K (cmol _c kg ⁻¹) | | 0.10 (0.02) | 0.15 (0.03) | 0.13 (0.04) | 0.10 (0.04) | 0.07 (0.01) | 0.14 (0.02) | |
| Ca (cmol _c kg ⁻¹) | | 5(4) | 2(3) | 2(1) | 2(2) | 0.6 (0.3) | 0.3 (0.09) | |
| Mg (cmol _c kg ⁻¹) | | 0.4 (0.1) | 0.3 (0.1) | 0.6 (0.8) | 0.4 (0.3) | 0.09 (0.06) | 0.13 (0.03) | |
| Mn (cmol _c kg ⁻¹) | | 0.11 (0.07) | 0.11 (0.07) | 0.3 (0.4) | 0.04 (0.05) | 0.03 (0.02) | 0.02 (0.02) | |
| Al (cmol _c kg ⁻¹) | | 1.3 (0.9) | 1.6 (0.7) | 2(1) | 2.1 (1.6) | 3.0 (0.7) | 5(1) | |
| Ca/Al | | 3.76 | 1.52 | 1 | 1.15 | 0.21 | 0.05 | |
| EA (cmol _c kg ⁻¹) | | 1.6 | 1.8 | 2.0 | 2.2 | 3.1 | 5.6 | |
| CEC (cmol _c kg ⁻¹) | | 7(3) | 4(2) | 5(2) | 5(1) | 4(1) | 6(1) | |
| BS (%) | | 74 (21) | 55 (21) | 53 (23) | 52 (33) | 21 (10) | 10(2) | |

^a BS, base saturation; EA, effective acidity; CEC, cation exchange capacity. Ranking is based on soil base saturation (BS) and soil Ca/Al ratio, with least to most acidified site from left to right. Ranking was the same when considering organic soil horizons.

^b Values are averages (n = 8-14 per site, see soil sampling in the Methods section), with SD in parentheses.

wood because of radial re-equilibration (Bilodeau-Gauthier et al., 2008) and that any declining trend should rather be attributed to declining cation binding capacity of the wood (Momoshima and Bondietti, 1990). Moreover, it is the section that has been affected by recent or actual soil conditions (Berger et al., 2004; Bilodeau-Gauthier et al., 2008), and it is a coherent physiological stem section where sap flow occurs, therefore it was considered in its entirety. Sapwood was separated into very thin (1 mm) slices with a steel knife, which was cleaned with ethanol between cores to avoid contamination between different trees. Sapwood sections from cores of the same tree were pooled (mean mass = 1.2 g; SD = 0.4) and processed through a three-steps sequential extraction method (Bilodeau-Gauthier et al., 2008). The first step used deionised H₂O (to extract the water-soluble fraction), and the second one 0.05 M HCl (acid-soluble fraction). A ratio of 20 ml of solution to 1 g of wood was maintained. For the residual (immobile) fraction, a subsample (300 mg) from the whole sapwood was dissolved in 3 ml of concentrated HNO₃ in Teflon bombs (CEM linear closed-vessels, CEM corp.) put in a high-performance microwave (MDS-2000, CEM corp.). The sequential extraction method and the nature of the different fractions have been described in more details elsewhere (Bilodeau-Gauthier et al., 2008). Concentrations of Al, Ca, Cd, K, Mg and Mn were determined with an inductively coupled plasma atomic emission spectrometer (ICP-AES; model Vista AX from Varian, Australia, 1999).

2.5. Soil sampling

Four soil samples were taken around each tree, at cardinal points and at \sim 2.5 m from the base of the tree. For each tree, soil horizons (organic: FH; mineral: first 15 cm of B) were sampled separately and pooled accordingly. Soil samples were air-dried, ground (FH), and sieved to 2 mm. Exchangeable cations (Al, Ca, Mg, Mn, K) were extracted with an unbuffered NH₄Cl (1 M, 12 h, mass: volume ratio of 1:10) solution and measured using inductively coupled plasma emission. Exchangeable acidity (EA) was calculated as the sum of H⁺ (measured with a pH probe) and Al³⁺ concentrations of the soil extract. Effective cation exchange capacity (CEC) corresponded to the sum of the exchangeable base cations Ca, K, and Mg (BC), added to EA. Soil pH was measured in water using a soil/solution ratio of 1:2.5 (w:wt). Effective base saturation (BS) was determined as the ratio of base cations to CEC. See Houle et al. (1997) for more details on soil sampling and chemical analysis. Please note that in this text the term "soil acidity" refers to low values of soil pH, concentrations of exchangeable base cations (BC), and base saturation (BS), and to high values of soil Al and exchangeable acidity (EA).

2.6. Data treatment

Average sapwood concentrations of Al, Ca, Cd, K, Mg, and Mn from individual trees (n=55) were related to soil chemical variables using non-parametric correlations (Spearman's ρ) – since a Shapiro-Wilk test revealed that normality of data was not respected -, with wood fractions (water-soluble, acid-soluble, residual, total) treated separately. Soil variables in the mineral and organic soil horizons were separately related to wood elements; however, only the results with mineral soil will be presented in following sections because organic soil variables showed the same trends, but weaker. Bilodeau-Gauthier et al. showed in a previous study (Bilodeau-Gauthier et al., 2008) that the total of all fractions of an element usually behaves similarly to its most abundant fraction, but that focusing only on total concentrations can obliterate the significant response of less abundant fractions. Therefore, it is suggested that sequential chemical extractions be preferably used when assessing changes in environmental conditions through dendrochemistry. Nonetheless, total concentrations will still be treated here, in order to allow comparisons with other studies that did not analyse wood elemental fractions separately. In addition, element ratios (e.g., Ca/Al, Ca/Mn) are often used in dendrochemical studies as a way to circumvent issues of varying cation binding capacity of tree wood. Correlations with these ratios were attempted in the course of the present analyses but will not be presented here as they did not provide any additional information compared to individual elements. Correlations with ratios often end up being very similar to the correlation with only one or the other element from the ratio, but weaker or with a reverse sign.

Tree growth trends (slope of the linear regression of annual BAI over time) from the years 1960 to 2005 were similarly correlated by non-parametric Spearman's rho to mineral soil variables and to sapwood concentrations. Trends of BAI over time are used because the effect of soil quality on tree growth is seen as a longterm effect rather than a punctual event (Phipps and Whiton, 1988). The year 1960 is used because impacts of atmospheric pollution on forests of eastern North America are typically considered to have become important during that decade (Turk, 1983; Duchesne et al., 2002). Duchesne et al. (2002) have previously used this very same date successfully to demonstrate relations between acid deposition and tree growth. Correlations between recent growth (BAI from 2000 to 2005) and soil variables were also attempted, but only revealed the same information that long-term growth did. Tree growth was further correlated to average sapwood concentrations, because mobile elements are translocated throughout the entire sapwood-probably no later than within a few years, according to

| Fabl | e | 2 |
|------|---|---|
| - | | |

Spearman's rank correlation coefficients (rho) between average element concentrations in sapwood and mineral soil chemistry, by elemental fraction.

| Soil variable ^a | Rho | P-value ^b | Rho | P-value | Rho | P-value | Rho | P-value |
|----------------------------|---------------------|----------------------|---------------|---------|----------|---------|---------|---------|
| Son variable | Ga | 1 Vulue | itilo | 1 Value | Kilo | 1 Vulue | iuio | 1 Vulue |
| | Ca Water-soluble | | Acid-soluble | | Residual | | Total | |
| FA | -0 5046 | ** | neid soluble | | -0 3873 | * | -0 5432 | ** |
| Al | -0.499 | ** | | | -0.3867 | * | -0.5374 | ** |
| CEC | 0.135 | | | | -0.303 | * | 0.557 1 | |
| nH | 0 5338 | ** | | | 0.505 | | 0 4738 | ** |
| BS | 0.4899 | ** | | | 0 3572 | * | 0 5365 | ** |
| BC | 0 3851 | * | | | 0.0072 | | 0.4558 | ** |
| 50 | K | | | | | | 011000 | |
| | Water-soluble | | Acid-soluble | | Residual | | Total | |
| EA | -0.4522 | ** | Tield Soluble | | neoradan | | -0.3172 | * |
| Al | -0.4532 | ** | | | | | -0.3146 | * |
| CEC | | | | | | | | |
| рH | | | | | | | | |
| BS | 0.4434 | ** | | | | | 0.2699 | * |
| BC | | | | | | | | |
| | Mg | | | | | | | |
| | Water-soluble | | Acid-soluble | | Residual | | Total | |
| EA | | | | | -0.4843 | ** | -0.3012 | * |
| Al | | | | | -0.4856 | ** | -0.2952 | * |
| CEC | | | | | | | | |
| pН | 0.4215 | * | 0.3121 | * | 0.3509 | * | 0.48 | ** |
| BS | | | | | 0.4777 | ** | | |
| BC | | | | | 0.3927 | * | | |
| | Al | | | | | | | |
| | Water-soluble | | Acid-soluble | | Residual | | Total | |
| EA | 0.6028 | ** | 0.4897 | ** | -0.4558 | ** | -0.4509 | ** |
| Al | 0.6035 | ** | 0.4791 | ** | -0.4613 | ** | -0.4567 | ** |
| CEC | | | 0.3735 | * | | | | |
| pH | -0.3705 | * | -0.435 | ** | 0.2964 | * | 0.3008 | * |
| BS | -0.599 | ** | -0.4559 | ** | 0.484 | ** | 0.4815 | ** |
| BC | -0.4765 | ** | -0.3443 | * | 0.3635 | * | 0.3597 | * |
| | Cd | | | | | | | |
| | Water-soluble | | Acid-soluble | | Residual | | Total | |
| EA | 0.4198 | * | 0.637 | ** | | | 0.6346 | ** |
| Al | 0.4293 | * | 0.6344 | ** | | | 0.6325 | ** |
| CEC | | | 0.4087 | * | | | 0.391 | * |
| pH | | | -0.5285 | ** | | | -0.5219 | ** |
| BS | -0.4507 | ** | -0.6077 | ** | -0.3854 | * | -0.611 | ** |
| BC | -0.4348 | ** | -0.5097 | ** | -0.3936 | * | -0.5168 | ** |
| | Mn | | | | | | | |
| | Water-soluble | | Acid-soluble | | Residual | | Total | |
| EA | 0.3591 | * | 0.4092 | * | | | 0.4281 | * |
| AI | 0.3607 | * | 0.4 | * | | | 0.4193 | * |
| CEC | -0.3277 | * | 0.3201 | * | | | | |
| pH | | | -0.3732 | * | | | -0.3688 | * |
| BS | -0.3633 | * | -0.3813 | * | 0.0070 | | -0.399 | * |
| BC | -0.3748 | * | -0.3327 | * | 0.2978 | * | -0.351 | * |

^a BC, sum of base cations; BS, base saturation; CEC, cation exchange capacity; EA, exchangeable acidity.

^b **P*<0.05; ***P*<0.001; non-significant correlations are not shown.

previous studies (DeWalle et al., 1999; Houle et al., 2002)—, which implies that concentrations in all sapwood rings could possibly influence growth. As an additional attempt to assess the determinants of tree growth, non-linear regressions were constructed for tree growth as the dependent variable, with every soil characteristics as the independent variable. Also, a multiple regression analysis (Stepwise Forward, with probability to enter the regression fixed at $\alpha = 0.05$) was performed in order to assess if variations in BAI slopes could be further explained by a combination of soil variables and tree age.

3. Results

3.1. Sapwood concentrations and soil chemistry

Significant (at P < 0.05) correlations were observed between chemical characteristics of the mineral soil horizon and average sapwood concentrations in the different chemical fractions (Table 2). Since cation exchange capacity (CEC) is a combined variable, correlations with soil CEC generally reflect one part of the combination or the other, being either similar to the correlation with EA or with BC (Table 2). When both EA and BC are significantly correlated to the xylem concentration, coefficient signs are reversed and consequently the correlation with CEC is often not significant.

Sapwood base cations (Ca, K, Mg) concentrations in the watersoluble fraction generally decreased at higher soil acidity (positive correlations with soil pH, BC and BS, and negative correlations with soil Al and EA; Table 2). However, the number of significant correlations and their strengths decreased in the order Ca > K > Mg, with water-soluble Mg being only related to soil pH. The acid-soluble fraction of base cations, on the other hand, showed no significant correlations with soil acid-base conditions, except for Mg with soil pH. The residual fraction of K was not correlated to any soil variables, but residual Ca and Mg decreased significantly at higher soil acidity. Total concentrations of base cations correlated to soil variables in proportions very similar to that of their water-soluble fraction (Table 2).

Table 3

Spearman's rank correlation coefficients (rho) between tree growth (BAI, basal area increment) trends from 1960 to 2005 and mineral soil chemistry.

| Soil variable ^a | Rho | <i>P</i> -value ^b |
|----------------------------|---------|------------------------------|
| рН | 0.4067 | * |
| Al | -0.6689 | ** |
| Ca | 0.6017 | ** |
| Ca/Al | 0.6457 | ** |
| Mn | 0.567 | ** |
| EA | -0.6715 | ** |
| BC | 0.5672 | ** |
| CEC | | |
| BS | 0.6677 | ** |
| | | |

^a BC, sum of base cations; BS, base saturation; CEC, cation exchange capacity; EA, exchangeable acidity.

^b **P*<0.05; ***P*<0.001; non-significant correlations are not shown.

Acidic cation (Al, Cd, Mn) concentrations in the water- and acidsoluble fractions increased at high soil acidity (being, for instance, negatively correlated to soil pH, BC and BS, and positively correlated to soil Al concentrations). The residual fraction of Cd also increased with soil acidity, although the response was weaker since only BC and BS were significant correlated and only moderately. In contrast to Cd, xylem concentrations of residual Al and Mn decreased with soil acidity (Al: positive correlations with soil pH, BC and BS, negative correlation with soil Al and EA; Mn: positive correlation with BC and (marginally; P < 0.1) BS, and marginally negative correlation with EA). For Cd and Mn, total concentrations show the same trends as the acid-soluble fraction, while total Al behaves similarly to residual Al.

3.2. Tree growth, soil chemistry and sapwood chemistry

Average growth trends for each site are presented in Fig. 1. BAI trends (1960–2005) of all trees were submitted to correlation tests

Table 4

Spearman's rank correlation coefficients (rho) between tree growth (BAI, basal area increment) trends from 1960 to 2005 and sapwood chemistry.

| Element and fraction | Rho | P-value |
|----------------------|---------|---------|
| Ca | | |
| Water-soluble | 0.4701 | ** |
| Acid-soluble | 0.2676 | * |
| Residual | | |
| Total | 0.5008 | ** |
| К | | |
| Water-soluble | 0.435 | * |
| Acid-soluble | | |
| Residual | | |
| Total | | |
| Mg | | |
| Water-soluble | | |
| Acid-soluble | | |
| Residual | 0.2937 | * |
| Total | | |
| Al | | |
| Water-soluble | -0.4781 | ** |
| Acid-soluble | -0.4651 | ** |
| Residual | 0.3799 | * |
| Total | 0.384 | * |
| Cd | | |
| Water-soluble | -0.3329 | * |
| Acid-soluble | -0.4974 | ** |
| Residual | | |
| Total | -0.5155 | ** |
| Mn | | |
| Water-soluble | | |
| Acid-soluble | -0.3809 | * |
| Residual | | |
| Total | -0.365 | * |

^a **P*<0.05; ***P*<0.001; non-significant correlations are not shown.



Fig. 1. Growth trends (BAI, basal area increment; average of all trees per site, n=8-14; error bars are SE) for the years 1920–2005, from least to most acid site (top to bottom).

with several soil chemical variables from the trees' immediate environment (Table 3). Generally, growth was reduced on acid soils (positively correlated to soil pH, BS, and BC, and negatively correlated to soil AI and EA). Likewise, average BAI trends per site (Fig. 1) generally followed the gradient of soil acidity (Table 1), with trees at the least acid sites showing the highest increasing slopes. An investigation of every relationship between BAI and soil variables revealed that BS (%) was the best predictor of BAI through a non-linear relationship (although the relationship flattened for values of BS beyond 40%) with a variance explanation of 43%:

$$\mathsf{BAI} = -29.7 + 10.5 \times \ln(\mathsf{BS})$$

A multiple regression analysis (Stepwise Forward) showed that variations in BAI slopes were further explained by a model includ-



Fig. 2. Growth trends of sugar maple trees (n = 55) as a function of (A) water-soluble xylem concentrations of aluminium (Al), expressed as a linear regression, (B) residual Al, and (C) total Al, with the latter two expressed as logarithmic regressions. Equations and their R^2 are shown on the graphs. Growth trends refer to the slope of annual basal area increment (BAI) for the years 1960–2005.

ing tree age and Al-derived soil effective acidity, which yielded a variance explanation of 51%:

$BAI = (0.245 \times Al_{acid.}) - (0.26 \times tree\text{-}age) + 15.8$

Tree growth was generally slower when acid-soluble concentrations of acidic cations (Al, Cd, Mn) in xylem were higher (negative correlation; Table 4); total concentrations of Cd and Mn mirrored this pattern. Water-soluble Al also related negatively to tree growth, while the residual and total fractions of Al were positively correlated to tree growth. Fig. 2 presents graphically these three relations, where BAI was fitted to water-soluble Al as a linear regression ($R^2 = 0.23$), while to residual Al it was better fitted as a logarithmic regression ($R^2 = 0.23$; as a comparison, similarly fitting total Al yielded an R^2 of 0.18). The latter relationship notably includes an aggregation of data points at the lower end of the Al concentrations gradient (<2 mg kg⁻¹) where trees showed negative, or very low if positive, growth trends (Fig. 2). Trees showed faster growth when base cations (water-soluble, acid-soluble, and total Ca as well as water-soluble K, but not Mg in any fraction) were in high concentrations in the xylem (positive correlation). Multiple regression analyses showed that a model including the log ratio of the sum of base cation (Ca+Mg+K) to Al in the mobile fractions (water- and acid-soluble extracts) and tree age yielded the best explanation (46%) of the variation in BAI:

$$BAI = (30.1 \times \ln(Ca + Mg + K/AI)_{mob.}) - (0.22 \times tree-age) - 76.6$$

4. Discussion

4.1. Sapwood concentration and soil chemistry

4.1.1. Base cations

Previous studies have shown that soil reservoirs of exchangeable base cations have been depleted in the last decades by the input of acidic anions from atmospheric depositions (Lawrence et al., 1995; Likens et al., 1998; Johnson et al., 2008). Therefore, the uptake of base cations through tree roots should be reduced in acidic soil conditions, which should result in lower concentrations in tree xylem (Bondietti et al., 1990). In the present study, average concentrations of base cations (Ca, K, and Mg) in sugar maple xylem indeed decreased at higher soil acidity, notably for the water-soluble fraction of those elements. Although the acidsoluble fraction is the most abundant form of divalent cations in tree xylem (Bilodeau-Gauthier et al., 2008), for base cations it is the one that is the least related to soil acidity (Table 2). Even if residual Ca and Mg were well correlated to soil acidity, it is still not evident whether the assessment of xylem concentrations of base cations would provide a valuable method for the temporal monitoring of environmental events, because the processes of element fixation in tree wood, as well as its potential reversibility, remain poorly understood.

The observed decreasing trend in total concentrations of base cations in sapwood at higher soil acidity is in good agreement with those of previous studies that have linked total concentrations of base cations in wood with soil chemistry (Bondietti et al., 1989, 1990; DeWalle et al., 1991, 1999; Penninckx et al., 2001; Fisher et al., 2002; Houle et al., 2002, 2007; Watmough, 2002). Earlier studies had related decreasing radial trends of (total) base cation concentrations in tree-rings of recent decades (1960+) to the increased atmospheric acidic deposition on forest soils, although they had not directly measured soil acidity (Bondietti et al., 1989, 1990). Berger et al. (2004), on the contrary, observed higher wood Ca concentrations in Norway spruce on the most acid soils, which they ascribed to higher uptake following mobilization by acidification. This has been hypothesized by Bondietti et al. (1990) to happen only in the first few years of the 1960s, after the onset of increased atmospheric acid depositions in eastern North America, and that wood Ca would eventually decrease because of the depletion of soil reservoirs through leaching. Still, Herbauts et al. (2002) ascribed the observed decreasing radial trends to decreasing cation binding capacity in more recently formed tree-rings.

4.1.2. Acidic cations

Soil acidification has been recognized to enhance mobility of Cd (Römkens and Salomons, 1998; Andersen et al., 2002) and Mn (Guyette et al., 1992; St. Clair and Lynch, 2004; Kogelmann and Sharpe, 2006) in the soil. Therefore, the observed relations between sapwood and soil are in good agreement with the premise of increased absorption resulting from mobilization in soil. Moreover, the correlations with soil acidity were stronger for the water- and acid-soluble fractions of Cd and Mn than for their residual fraction. If Mn solubility in soils has been often assumed (Guyette et al., 1992; Kogelmann and Sharpe, 2006) to depend mostly on soil pH, results indicate that Mn uptake by tree roots is governed by

physicochemical mechanisms that depend not only on pH, but also on the soil acid-base status, notably base saturation (Houle et al., 2007).

The water- and acid-soluble fractions of Al in sugar maple xylem increased with soil acidity. Notably, these Al wood fractions increased at lower concentrations of soil base cations. Considering that soil base cation reservoirs were shown to contribute largely to the acid neutralizing capacity of forest soils (Houle et al., 2006), it is thus coherent that tree uptake of Al is lessened as base cations reduce the proportion of soil exchange sites being occupied by Al. The negative relation between wood Al and soil pH is consistent with the known enhanced solubility of Al following acidification of forest soils (Ulrich et al., 1980). Compared to total Al concentrations-which is the fraction most used in dendrochemical studies-, water- and acid-soluble fractions did not necessarily yield stronger correlations with soil variables but did provide different information, since total and residual wood Al decreased at higher soil acidity (Fig. 2). Together with results for Cd and Mn, these observations could indicate that soil acid-base conditions have an influence either on the uptake of these elements through roots or on their fixation, partitioning, and potential mobility in tree wood

Smith and Shortle (1996) argued that the mechanism of Al-exclusion from root surfaces would preclude the use of Al in dendrochemical studies. McLaughlin et al. (1992, see also McLaughlin, 1998) reported very high concentrations of Al in roots from declining sugar maple trees, but observed that very little Al was subsequently transferred to the stem. Other studies similarly indicated that Al is retained mostly in outer tissue of roots, not making its way to the inner root where it could be displaced along with sap flow (Arp and Ouimet, 1986; Hutchinson et al., 1986). On the other hand, Meharg (1993) suggested that non-essential elements (like Al) penetrate cells through passive diffusion or as analogues of essential ions. Results from the present study and from an earlier work (Bilodeau-Gauthier et al., 2008) confirmed that Al could in fact be found in the tree stem, since its more mobile wood fractions (water- and acid-soluble) are responsive to variations in soil acidity and their concentrations increase at lower pH. Similarly, Cronan (1991) had reported pH-dependant Al uptake by red spruce roots. Therefore, complete and effective Al exclusion from roots might not be valid for sugar maple, at least at the most acid sites.

4.2. Tree growth and soil chemistry

Results from this study indicated that soil acidity has a negative influence on the growth of sugar maple trees, as shown by the many significant correlations between BAI and the variables related to soil acidity, the non-linear relationship between BAI and BS, and the multiple regression model of BAI that included tree age and Alderived Effective Acidity. It is in accordance with Duchesne et al. (2002) who investigated sugar maple growth and similarly inferred that it was impaired by soil acidification, as well as with the various studies initially mentioned that related the decline of sugar maple forests with acidic depositions (McLaughlin et al., 1992; Ryan et al., 1994; Ouimet and Camiré, 1995; Ouimet et al., 1996; Watmough, 2002). It is also in agreement with the results from liming experiments (Long et al., 1997; Burke and Raynal, 1998; Moore et al., 2000; Wargo et al., 2002; Moore and Ouimet, 2006), or liming plus base cations fertilization (Wilmot et al., 1996), that resulted in improved maple growth and health.

Tree growth was higher in this study on soils with high Ca and low Al content. Similarly, by comparing soils naturally differing in nutrient levels, Schaberg et al. (2006) observed superior growth and foliar Ca content for sugar maples growing on Ca-rich soils with high Ca:Al ratio. As a matter of fact, the Ca to Al ratio in soil is regularly cited as indicative of soil acidity and of the potential stress to forest ecosystems (see Cronan and Grigal, 1995 for a review). Hence, the molar ratio of Ca:Al in soil solution was one of four measurable variables proposed by Cronan and Grigal (1995) to determine the risks inherent to Al stress in an ecosystem. Under a Ca:Al value of 0.2, these authors evaluated at 95–100% the risk of suffering from Al stress; the site with the most acidic soil in the present study (Duchesnay, soil Ca:Al=0.05) was under that threshold. The next most acid site (Truite Rouge) had a higher soil Ca:Al ratio (0.21), which barely places it in the bracket of 75% risk (Ca:Al under 0.5). The last bracket is for soil Ca:Al under 1.0 (50% risk), but Ca:Al ratios in soils of the other four sites were higher (>1.15; Table 1). On the other hand, Lange et al. (2006) have claimed that even under this value, Al concentrations in soil solution are rarely sufficient to harm forest vegetation. Another variable proposed by Cronan and Grigal (1995) was soil base saturation (BS), with possible Al stress for values of BS under 15% of effective CEC. In the present study, only the most acid site (Duchesnay) had such a low BS (10%). Overall, according to these variables from Cronan and Grigal (1995), two of the six sites in this study were thus at risk of Al-stress, which could partly explain their stronger declining growth trends (Fig. 1) and possibly the relationship between tree growth and wood residual (and total) Al (Fig. 2).

4.3. Tree growth and sapwood chemistry

In the present study, total xylem concentrations of Ca were positively correlated to growth (Table 4), in accordance to its important role in tree health often acknowledged in the literature (Likens et al., 1996; Long et al., 1997; DeHayes et al., 1999; Moore et al., 2000; Watmough, 2002; Moore and Ouimet, 2006). This relationship was mirrored by some base cation xylem fractions, namely the water-soluble fraction of Ca and K, the acid-soluble fraction of Ca, and the residual fraction of Mg. Among these, the strongest correlation to growth was obtained with the water-soluble fraction of Ca, although it was not different from total Ca. On the other hand, and contrary to the initial hypothesis, residual Ca showed no relation to tree growth. Nevertheless noteworthy is the fact that using sequential extractions to assess individual fractions allowed for supplementary information regarding K and Mg, since the total concentrations of these two elements did not correlate significantly to growth.

The negative correlation found between tree growth and the total xylem concentrations of Cd and Mn is consistent with most other studies concerning these metals (McQuattie and Schier, 2000; Reichman, 2002; Benavides et al., 2005; Kogelmann and Sharpe, 2006; Houle et al., 2007). The acid-soluble fraction of Cd and Mn was also significantly and negatively correlated to tree growth and consequently did not yield more information than the residual fraction. Berger et al. (2004), contrary to most studies, reported positive correlations between growth of Norway spruce and Mn concentrations in xylem (in certain situations of their study). However, the study of Berger et al. (2004) is also peculiar in reporting increased xylem concentrations of Ca on acid soils.

In trees from the sampled sites, total wood Al was positively correlated to tree growth. In contrast, Mohamed et al. (1997) observed higher total concentrations of Al in the xylem of declining trees on acidic soils, even though their calcareous site showed no difference in total xylem Al between healthy and declining trees. Similarly, Watmough (2002) reported poor growth associated to high xylem total Al concentrations for sugar maple growing on acidic Podzols, while Bondietti et al. (1989) observed an inverse relationship between radial growth and xylem Al:Ca ratios for spruce and hemlock trees. These studies show quite different results than the present one. However, there is one report of "immobile" Al being less abundant in leaves of declining red spruces (Borer et al., 2004). Such contradictions emphasize the need to discriminate between Al fractions. Indeed, sugar maples did not grow as well when xylem concentrations of water- and acid-soluble Al were high, while the residual fraction of Al was, on the contrary, related to faster growth (Fig. 2). Thus, assessing the behaviour of the individual fractions of Al conveyed additional information that was not available from the sole analysis of total concentrations and yielded more coherent observations, with both soil chemistry and tree growth, than did total Al concentrations. Also noteworthy was the numerous trees at the low end of the gradient of residual Al ($<2 \text{ mg kg}^{-1}$) that showed very poor growth (slopes below 10 or even negative)-hence the use of the logarithmic regression. Thus, while trees were relatively linearly distributed along the gradient of residual Al concentrations, under the threshold of 2 mg kg⁻¹ the relationship dropped abruptly and all trees were in struggling conditions for growth. This could also be important for future assessments of sugar maple health and its relations to soil conditions, which will be further discussed below.

In addition to these correlations, multiple regressions offered further insights in the relationship between tree growth and sapwood chemistry. The log ratio of the sum of base cations (Ca + Mg + K) to Al in the mobile fractions (water- and acid-soluble) was—when combined with tree age—the best predictor of BAI, yielding a variance explanation of 46%. This model is consistent with many of the relationships found above between BAI and individual cation taken separately. As expected, tree growth is improved when the sum of nutrient cations on Al in the mobile fractions of wood is higher.

From the present results, it might be inferred, for instance, that Al in the soil can be toxic to trees (Hutchinson et al., 1986; Andersson, 1988; Shortle et al., 1997) or that soil acidity reduces the tree's capacity to immobilize Al in the stem–as previously mentioned, such Al immobilization was suggested by Momoshima and Bondietti (1990). Alternatively, it might mean that declining trees are less efficient at partitioning Al to an immobile form, or that the uptake of mobilized Al on acid soils increases the proportion of wood Al that is found in the water- and acid-soluble rather than in the residual form.

Immobilization of toxic metals in plant tissues as a defence mechanism against toxicity was proposed by Borer et al. (2004) following the observation that higher ratios of mobile to residual Al in red spruce needles were more frequent in declining trees. Schaberg et al. (2006) similarly reported higher Al and lower Ca concentrations in leaves of declining sugar maple trees. This phenomenon is not restricted to Al, though, since higher foliar Mn levels were similarly observed in declining sugar maple stands (Horsley et al., 2000). Such reports might indicate that these elements can move upwards in the tree stem, presumably when they are present in a mobile form; hence, when bound in a residual form in the lower xylem, they would be prevented from reaching and damaging the leaves.

5. Conclusion

This study consists in a first report on the relationship between tree growth and individual xylem elemental fractions on glaciated forest soils of northeastern North America. Sugar maple growth was enhanced when the xylem water- and acid-soluble fractions of the essential macronutrient Ca were high and that of the acidic, potentially phytotoxic Al, Cd, and Mn were low. Elevated residual (or total) Al concentrations coincided with better growth while Al in the xylem water- and acid-soluble fractions showed an inverse relationship with growth. An explanation was proposed to conciliate these contrasting results but remains to be tested. Although slower tree growth was linked to higher concentrations of more mobile (water- and acid-soluble) forms of acidic cations found in wood tissues of trees growing on acidic soils, it is currently not known what impact this has on tree health.

In addition, the present results confirmed and expanded on previous ones regarding relationships between wood and soil chemistry. Soil acidity showed the best relations to average sapwood concentrations of water-soluble Al and Ca, and acid-soluble Cd. Sapwood Mn was also related to many soil acid-base variables, but provided less information for each of them than did the above three elements. Xylem concentrations of the residual fraction of Al, Ca, Cd, Mg, and Mn were also responsive to soil acidity (with Al and Mg being the most responsive), albeit not as strongly as the more mobile fractions.

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References

- Andersen, M.K., Refsgaard, A., Raulund-Rasmussen, K., Strobel, B.W., Hansen, H.C.B., 2002. Content, distribution, and solubility of cadmium in arable and forest soils. Soil Science Society of America Journal 66, 1829–1835.
- Andersson, M., 1988. Toxicity and tolerance of aluminium in vascular plants. Water, Air, and Soil Pollution 39, 439–462.
- Arp, P.A., Ouimet, R., 1986. Uptake of Al, Ca, and P in black spruce seedlings: effect of organic versus inorganic Al in nutrient solutions. Water, Air, and Soil Pollution 31, 367–375.
- Augustin, S., Stephanowitz, H., Wolff, B., Schröder, J., Hoffmann, E., 2005. Manganese in tree rings of Norway spruce as an indicator for soil chemical changes in the past. European Journal of Forest Research 124. 313–318.
- Benavides, M.P., Gallego, S.M., Tomaro, M.L., 2005. Cadmium toxicity in plants. Brazilian Journal of Plant Physiology 17, 21–34.
- Berger, T.W., Köllensperger, G., Wimmer, R., 2004. Plant-soil feedback in spruce (*Picea abies*) and mixed spruce-beech (*Fagus sylvatica*) stands as indicated by dendrochemistry. Plant and Soil 264, 69–83.
- Berggren, D., 1992. Speciation and mobilization of aluminium and cadmium in Podzols and Cambisols of S. Sweden. Water, Air, and Soil Pollution 62, 125–156.
- Bergkvist, B., 1987. Soil solution chemistry and metal budgets of spruce forest ecosystems in S. Sweden. Water, Air, and Soil Pollution 33, 131–154.
- Bilodeau-Gauthier, S., Houle, D., Gagnon, C., Côté, B., Messier, C., 2008. Extractability of elements in sugar maple xylem along a gradient of soil acidity. Journal of Environmental Quality 37, 871–879.
- Bondietti, E.A., Baes III, C.F., McLaughlin, S.B., 1989. Radial trends in cation ratios in tree rings as indicators of the impact of atmospheric deposition on forests. Canadian Journal of Forest Research 19, 586–594.
- Bondietti, E.A., Momoshima, N., Shortle, W.C., Smith, K.T., 1990. A historical perspective on divalent cation trends in red spruce stemwood and the hypothetical relationship to acidic deposition. Canadian Journal of Forest Research 20, 1850–1858.
- Borer, C.H., Schaberg, P.G., DeHayes, D.H., Hawley, G.J., 2004. Accretion, partitioning and sequestration of calcium and aluminium in red spruce foliage: implications for tree health. Tree Physiology 24, 929–939.
- Burke, M.K., Raynal, D.J., 1998. Liming influences growth and nutrient balances in sugar maple (*Acer saccharum*) seedlings on an acidic forest soil. Environmental and Experimental Botany 39, 105–116.
- Butkus, D., Paliulis, D., Baltrenaite, E., 2004. Sorption of heavy metals from polluted water and their migration in the system soil-tree. Journal of Environmental Engineering and Landscape Management 12, 120–125.
- Canada Soil Survey, 1992. The Canadian System of Soil Classification. Agriculture Canada, Ottawa, ON, Canada.
- Côté, B., Camiré, C., 1995. Application of leaf, soil, and tree ring chemistry to determine the nutritional status of sugar maple on sites of different levels of decline. Water, Air, and Soil Pollution 83, 363–373.

- Cronan, C.S., 1991. Differential adsorption of Al, Ca, and Mg by roots of red spruce (*Picea rubens* Sarg.). Tree Physiology 8, 227–237.
- Cronan, C.S., Grigal, D.F., 1995. Use of calcium/aluminum ratios as indicators of stress in forest ecosystems. Journal of Environmental Quality 24, 209–226.
- Cronan, C.S., Schofield, C.L., 1990. Relationships between aqueous aluminum and acidic deposition in forested watersheds of North America and Northern Europe. Environmental Science and Technology 24, 1100–1105.
- Cutter, B.E., Guyette, R.P., 1993. Anatomical, chemical, and ecological factors affecting tree species choice in dendrochemistry studies. Journal of Environironmental Quality 22, 611–619.
- De Visser, P.H.B, 1992. The relation between chemical composition of oak tree rings, leaf, bark, and soil solution in a partly mixed stand. Canadian Journal of Forest Research 22, 1824–1831.
- DeHayes, D.H., Schaberg, P.G., Hawley, G.J., Strimbeck, G.R., 1999. Acid rain impacts on calcium nutrition and forest health. Bioscience 49, 789–800.
- DeWalle, D.R., Swistock, B.R., Sayre, R.G., Sharpe, W.E., 1991. Spatial variations in sapwood chemistry with soil acidity in Appalachian forests. Journal of Environmental Quality 20, 486–491.
- DeWalle, D.R., Tepp, J.S., Swistock, B.R., Sharpe, W.E., Edwards, P.J., 1999. Tree-ring cation response to experimental watershed acidification in West Virginia and Maine. Journal of Environmental Quality 28, 299–309.
- Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., Lambert, K.F., Likens, G.E., Stoddard, J.L., Weathers, K.C., 2001. Acidic deposition in the northeastern United States: Source and inputs, ecosystem effects, and management scenarios. BioScience 51, 180–198.
- Drouet, T., Herbauts, J., Demaiffe, D., 2005. Long-term records of strontium isotopic composition in tree rings suggest changes in forest calcium sources in the early 20th century. Global Change Biology 11, 1926–1940.
- Duchesne, L., Ouimet, R., Houle, D., 2002. Basal area growth of sugar maple in relations to acid deposition, stand health, and soil nutrients. Journal of Environironmental Quality 31, 1676–1683.
- Duchesne, L., Ouimet, R., Morneau, C., 2003. Assessment of sugar maple health based on basal area growth pattern. Canadian Journal of Forest Research 33, 2074–2080.
- Ducic, T., Polle, A., 2005. Transport and detoxification of manganese and copper in plants. Brazilian Journal of Plant Physiology 17, 103–112.
- Fisher, S., Nicholas, N.S., Scheuerman, P.R., 2002. Dendrochemical analysis of lead and calcium in southern Appalachian American beech. Journal of Environmental Quality 31, 1137–1145.
- Fritts, H.C., 1976. Tree Rings and Climate. Academic Press, New York, NY, USA.
- Fromm, J., 2010. Wood formation of trees in relation to potassium and calcium nutrition. Tree Physiology 30, 1140–1147.
- Godbold, D.L., 1994. Aluminium and heavy metal stress: from the rhizosphere to the whole plant. In: Godbold, D.L., Hüttermann, A. (Eds.), Effects of Acid Rain on Forest Processes. Wiley-Liss, New York, pp. 231–264.
- González, A., Steffen, K.L., Lynch, J.P., 2000. Light and excess manganese: implications for oxidative stress in common bean. Plant Physiology 118, 493–504.
- Gratão, P.L., Polle, A., Lea, P.J., Azevedo, R.A., 2005a. Making the life of heavy metalstressed plants a little easier. Functional Plant Biology 32, 481–494.
- Gratão, P.L., Prasad, M.N.V., Cardoso, P.F., Lea, P.J., Azevedo, R.A., 2005b. Phytoremediation: Green technology for the clean up of toxic metals in the environment. Brazilian Journal of Plant Physiology 17, 53–64.
- Guyette, R.P., Henderson, G.S., Cutter, B.E., 1992. Reconstructing soil pH from manganese concentrations in tree-rings. Forest Science 38, 727–737.
- Herbauts, J., Penninckx, V., Gruber, W., Meerts, P., 2002. Radial variations in cation exchange capacity and base saturation in the wood of pedunculate oak and European beech. Canadian Journal of Forest Research 32, 1829–1837.
- Holmes, R.L., 1996. Dendrochronology program library. Version 2.0. Lab. of Tree-Ring Res., Univ. of Arizona, Tucson, AZ, USA.
- Horsley, S.B., Long, R.P., Bailey, S.W., Hallett, R.A., Hall, T.J., 2000. Factors associated with the decline disease of sugar maple on the allegheny plateau. Canadian Journal of Forest Research 30, 1365–1378.
- Horsley, S.B., Long, R.P., Bailey, S.W., Hallett, R.A., Wargo, P.M., 2002. Health of Eastern North American sugar maple forests and factors affecting decline. Northern Journal of Applied Forestry 19, 34–44.
- Houle, D., Duchesne, L., Moore, J.-D., Richer Laflèche, M., Ouimet, R., 2002. Soil and tree-ring chemistry response to liming in a sugar maple stand. Journal of Environmental Quality 31, 1993–2000.
- Houle, D., Gagnon, C., Couture, S., Kemp, A., 2004. Recent recovery of lake water quality in Southern Québec following reductions in sulphur emissions. Water, Air, and Soil Pollution Focus 4, 247–261.
- Houle, D., Ouimet, R., Couture, S., Gagnon, C., 2006. Base cation reservoirs in soil control the buffering capacity of lakes in forested catchments. Canadian Journal of Fisheries and Aquatic Sciences 63, 471–474.
- Houle, D., Camiré, Paquin.R., Ouimet, C., Duchesne, R.L., 1997. Response of the Lake Clair Watershed (Duchesnay, Quebec) to changes in precipitation chemistry (1988–1994). Canadian Journal of Forest Research 27, 1813–1821.
- Houle, D., Tremblay, S., Ouimet, R., 2007. Foliar and wood chemistry of sugar maple along a gradient of soil acidity and stand health. Plant and Soil 300, 173–183.
- Hutchinson, T.C., Bozic, L., Munoz-Vegas, G., 1986. Responses of five species of conifer seedlings to aluminum stress. Water, Air, and Soil Pollution 31, 283–294.
- Johnson, A.H., Moyer, A., Bedison, J.E., Richter, S.L., Willig, S.A., 2008. Seven decades of calcium depletion in organic horizons of Adirondack forest soils. Soil Science Society of America Journal 72, 1824–1830.
- Johnson, D.W., Fernandez, I.J., 1992. Soil mediated effects of atmospheric deposition on eastern U.S. spruce-fir forests. In: Eagar, C., Adams, M.B. (Eds.), Ecology and

Decline of Red Spruce in the Eastern United States. Springer-Verlag, New York, Berlin, Heidelberg, pp. 235–270.

- Kennedy, G., Bergeron, S., 1991. Tree-rings as monitors of heavy metal air pollution histories. Journal of Radioanalytical and Nuclear Chemistry 151, 337– 343.
- Kochian, L.V., 1995. Cellular mechanisms of aluminum toxicity and resistance in plants. Annual Review in Plant Physiology and Plant Molecular Biology 46, 237–260.
- Kogelmann, W.J., Sharpe, W.E., 2006. Soil acidity and manganese in declining and nondeclining sugar maple stands in Pennsylvania. Journal of Environironmental Quality 35, 433–441.
- Lange, H., Solberg, S., Clarke, N., 2006. Aluminum dynamics in forest soil waters in Norway. Science of the Total Environment 367, 942–957.
- Lawrence, G.B., David, M.B., Shortle, W.C., 1995. A new mechanism for calcium loss in forest-floor soils. Nature 378, 162–165.
- Likens, G.E., Driscoll, C.T., Buso, D.C., Siccama, T.G., Johnson, C.E., Lovett, G.M., Fahey, T.J., Reiners, W.A., Ryan, D.F., Martin, C.W., Bailey, S.W., 1998. The biogeochemistry of calcium at Hubbard Brook. Biogeochemistry 41, 89–173.
- Likens, G.E., Driscoll, C.T., Buso, D.C., 1996. Long-term effects of acid rain: response and recovery of a forest ecosystem. Science 272, 244–246.
- Long, R.P., Horsley, S.B., Lilja, P.R., 1997. Impact of forest liming on growth and crown vigor of sugar maple and associated hardwoods. Canadian Journal of Forest Research 27, 1560–1573.
- Martin, R.R., Naftel, S.J., Skinner, W., Jones, K.W., Feng, H., 2003. Micro-synchrotron X-ray fluorescence of the metal distribution in a black spruce tree stem: evidence for radial mobility. X-Ray Spectrometry 32, 402–407.
- Martin, R.R., Sham, T.K., Won Won, G., van der Heide, P., Jones, K.W., Song, S.-R., Protz, R., 1998. Secondary ion mass spectroscopy and synchrotron X-ray fluorescence in the study of the qualitative variation in metal content with time in tree rings. Canadian Journal of Forest Research 28, 1464–1470.
- Matusiewicz, H., Barnes, R., 1985. Tree ring wood analysis after hydrogen peroxide pressure decomposition with inductively coupled plasma atomic emission spectrometry and electrothermal vaporization. Analytical Chemistry 57, 406– 411.
- Matzner, E., Murach, D., Fortmann, H., 1986. Soil acidity and its relationship to root growth in declining forest stands in Germany. Water, Air, and Soil Pollution 31, 273–282.
- McLaughlin, D., 1998. A decade of forest tree monitoring in Canada: evidence of air pollution effects. Environmental Review 6, 151–171.
- McLaughlin, D.L., Corrigan, D.E., McIlveen, W.D., 1992. Etiology of sugar maple decline at selected sites in Ontario (1984–1990). Ontario Ministry of the Environment, Toronto, ON, Canada.
- McQuattie, C.J., Long, R.P., Hall, T., 1999. Sugar maple seedling anatomy and element localization at forest sites with differing nutrient levels. In: Horsley, S.B., Long, R.P. (Eds.), Sugar Maple Ecology and Health: Proceedings of an International Symposium. USDA Forest Service, Northeastern Research Station, Warren, PA, USA, p. 59.
- McQuattie, C.J., Schier, G.A., 2000. Response of sugar maple (*Acer saccharum*) seedlings to manganese. Canadian Journal of Forest Research 30, 456–467.
- Meharg, A.A., 1993. The role of the plasmalemma in metal tolerance in angiosperms. Physiologia Plantarum 88, 191–198.
- Mohamed, H.K., Pathak, S., Roy, D.N., Hutchinson, T.C., McLaughlin, D.L., Kinch, J.C., 1997. Relationship between sugar maple decline and corresponding chemical changes in the stem tissue. Water, Air, and Soil Pollution 96, 321–327.
- Momoshima, N., Bondietti, E.A., 1990. Cation binding in wood: applications to understanding historical changes in divalent cation availability to red spruce. Canadian Journal of Forest Research 20, 1840–1849.
- Moore, J.-D., Camiré, C., Ouimet, R., 2000. Effects of liming on the nutrition, vigor, and growth of sugar maple at the Lake Clair Watershed, Québec, Canada. Canadian Journal of Forest Research 30, 725–732.
- Moore, J.D., Ouimet, R., 2006. Ten-year effect of dolomitic lime on the nutrition, crown vigor, and growth of sugar maple. Canadian Journal of Forest Research 36, 1834–1841.
- Ouimet, R., Camiré, C., 1995. Foliar deficiencies of sugar maple stands associated with soil cation imbalances in the Québec Appalachians. Canadian Journal of Soil Science 75, 169–175.
- Ouimet, R., Camiré, C., Furlan, V., 1996. Effect of soil base saturation and endomychorrization on growth and nutrient uptake of sugar maple seedlings. Canadian Journal of Soil Science 76, 109–115.
- Penninckx, V., Glineur, S., Gruber, W., Herbauts, J., Meerts, P., 2001. Radial variations in wood mineral element concentrations: a comparison of beech and pedunculate oak from the Belgian Ardennes. Annals of Forest Science 58, 253–260.
- Phipps, R.L., Whiton, J.C., 1988. Decline in long-term growth trends of white oak. Canadian Journal of Forest Research 18, 24–32.
- Reichman, S.M., 2002. The Responses of Plants to Metal Toxicity: A Review Focusing on Copper, Manganese and Zinc. Australian Minerals & Energy Foundation, Melbourne, Australia, p. 54.
- Römkens, P.F.A.M., Salomons, W., 1998. Cd, Cu and Zn solubility in arable and forest soils: consequences of land use changes for metal mobility and risk assessment. Soil Science Society of America Journal 163, 859–871.
- 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.
- Ryan, D., Allen, O., McLaughlin, D., Gordon, A., 1994. Interpretation of sugar maple (Acer saccharum) ring chronologies from central and southern Ontario using a mixed linear model. Canadian Journal of Forest Research 24, 568–575.

- Schaberg, P.G., Tilley, J.W., Hawley, G.J., DeHayes, D.H., Bailey, S.W., 2006. Associations of calcium and aluminum with the growth and health of sugar maple trees in Vermont. Forest Ecology and Management 223, 159–169.
- Schützendübel, A., Schwanz, P., Teichmann, T., Gross, K., Langenfled-Heyser, R., Godbold, D.L., Polle, A., 2001. Cadmium-induced changes in antioxidant systems hydrogen peroxide content and differentiation in Scots pine roots. Plant Physiology 127, 887–898.
- Shortle, W.C., Smith, K.T., 1988. Aluminium-induced calcium deficiency syndrome in declining red spruce. Science 240, 239–240.
- Shortle, W.C., Smith, K.T., Minocha, R., Lawrence, G.B., David, M.B., 1997. Acidic deposition, cation mobilization, and biochemical indicators of stress in healthy red spruce. Journal of Environmental Quality 26, 871–876.
- Smith, K.T., Shortle, W.C., 1996. Tree biology and dendrochemistry, in: Dean, J.S., Meko, D.M., Swetnam, T.W. (Eds.), Tree Rings, Environment and Humanity, Proceedings of an International Conference, Tucson, AZ, USA. Radiocarbon, pp. 629–635.
- Smith, K.T., Shortle, W.C., Connolly, J.H., Minocha, R., Jellison, J., 2009. Calcium fertilization increases the concentration of calcium in sapwood and calcium oxalate in foliage of red spruce. Environmental and Experimental Botany 67, 277– 283.
- Smith, K.T.a.W.C.S., 2001. Conservation of element concentration in xylem sap of red spruce. Trees 15, 148–153.
- Soil Survey Staff, 1998. Keys to Soil Taxonomy, 8th ed. USDA Natural Resources Conservation Service, Washington, DC, USA.
- St. Clair, S.B., Lynch, J.P., 2004. Photosynthetic and antioxidant enzyme responses of sugar maple and red maple seedlings to excess manganese in contrasting light environments. Functional Plant Biology 31, pp. 1105–1014.
- St. Clair, S.B., Sharpe, W.E., Lynch, J.P., 2008. Key interactions between nutrient limitation and climatic factors in temperate forests: a synthesis of the sugar maple literature. Canadian Journal of Forest Research 38, 401–414.

- Tomlinson II., G.H., 1983. Air pollutants and forest decline. Environmental Science and Technology 17, 246A–256A.
- Turk, J.T., 1983. Evaluation of Trends in the Acidity of Precipitation and the Related Acidification of Surface Water in North America. U.S. Geol. Survey, Reston, VA, USA.
- Tyler, G., Berggren, D., Bergkvist, B., Falkengren-Grerup, U., Folkeson, L., Rühling, A., 1987. Soil acidification and metal solubility in forests of southern Sweden. In: Hutchinson, T.C., Meema, K.M. (Eds.), Effects of Atmospheric Pollutants on Forests, Wetlands and Agricultural Ecosystems. Springer-Verlag, Berlin-Heidelberg, pp. 347–359.
- Ulrich, B., Mayer, R., Khanna, P.K., 1980. Chemical changes due to acid precipitation in a loess-derived soil in central Europe. Soil Science Society of America Journal 130, 193–199.
- Vitória, A.P., Lea, P.J., Azevedo, R.A., 2001. Antioxidant enzymes responses to cadmium in radish tissues. Photochemistry 57, 701–710.
- Voortech Consulting, 2001. ProjectJ2X, MeasureJ2X. Holderness, NH, USA
- Wargo, P.M., Minocha, R., Wong, B.L., Long, R.P., Horsley, S.B., Hall, T.J., 2002. Measuring changes in stress and vitality indicators in limed sugar maple on the Allegheny Plateau in north-central Pennsylvania. Canadian Journal of Forest Research 32, 629–641.
- Watmough, S.A., 2002. A dendrochemical survey of sugar maple (Acer saccharum Marsh) in south-central Ontario, Canada. Water, Air, and Soil Pollution 136, 165–187.
- Wilmot, T.R., Ellsworth, D.S., Tyree, M.T., 1996. Base cation fertilization and liming effects on nutrition and growth of Vermont sugar maple stands. Forest Ecology and Management 84, 123–134.
- Yamaguchi, D.K., 1991. A simple method for cross-dating increment cores from living trees. Canadian Journal of Forest Research 21, 414–416.