UNIVERSITÉ DU QUÉBEC À MONTRÉAL

COMPORTEMENT DES ÉLÉMENTS DANS LE XYLÈME DE L'ÉRABLE À SUCRE SELON UN GRADIENT D'ACIDITÉ DU SOL

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RÉSUMÉ

L’acidification des sols forestiers fut identifiée comme une des causes possibles du dépérissement des érablières dans le Sud du Québec et le Nord-Est des États-Unis. La dendrochimie – l’analyse des concentrations des éléments dans les anneaux de croissance des arbres – offre la possibilité de retracer l’historique des conditions environnementales du passé, sur la prémisse que les concentrations retrouvées dans un anneau donné sont représentatives des conditions environnementales de cette même année. Toutefois, la fiabilité de cette méthode est remise en question par la mobilité des éléments au sein de la partie conductrice du tronc (l’aubier). L’objectif de cette étude était de caractériser le comportement des éléments dans le bois de l’érable à sucre, afin d’évaluer leur mobilité et leur potentiel pour l’étude des conditions environnementales. Sept bassins versants du Sud du Québec ont été sélectionnés pour représenter un gradient de conditions d’acidité du sol. Les échantillons de bois de 21 érables à sucre ont été soumis à des extractions chimiques séquentielles basées sur la gradation du pouvoir d’extraction (eau déionisée, HCl 0,05 M, HNO_3 ultrapure), qui ont permis de discriminer trois fractions (soluble, échangeable, résiduelle) sous lesquelles se retrouvent les éléments étudiés (Al, Ca, Cd, K, Mg, Mn). Les arbres croissant en sols moins acides démontraient des concentrations d’aluminium à près de 90% sous forme résiduelle (immobile), alors que sur les sols plus acides les fractions mobiles (soluble et échangeable) atteignaient 40% de la concentration totale. L’aluminium s’est donc révélé être beaucoup plus mobile que l’avaient rapporté les études antérieures. Aucune relation ne put être fortement établie entre la fraction résiduelle de l’aluminium et les conditions d’acidité du sol, ce qui pose un doute quant à son utilité pour la surveillance à long terme des conditions environnementales. Les cations basiques (calcium, potassium, magnésium), nutriments majeurs pour les arbres et prétendument lessivés par l’acidification des sols forestiers, sont apparus peu influencés par les variations d’acidité des sites. Toutefois, d’autres éléments étudiés se sont avérés intéressants, nommément le cadmium et le manganèse. Les fractions mobiles de ces éléments pourraient être appelées à servir de traceurs environnementaux pour une comparaison spatiale entre sites. Leurs fractions résiduelles étant aussi sensibles à l’acidité, elles permettraient d’évaluer l’évolution temporelle des conditions des sols, une avenue qui mériterait néanmoins d’être approfondie.

Mots-clés : acidification, aluminium, dendrochimie, érable à sucre, sols forestiers.

INTRODUCTION

Les émissions de polluants atmosphériques, notamment de dioxydes de soufre (SO_2) et d'oxydes d'azote (NOx), ont engendré des dépositions acides (Likens et al. 1972) ayant infligé d'importants dommages aux écosystèmes aquatiques (Likens et Bormann 1974, Schindler et al. 1985, Turk 1983) et forestiers (Cogbill 1976, Johnson et Siccama 1983, Tomlinson II 1983, Whittaker et al. 1974) de l'Est de l'Amérique du Nord (Bormann 1982ab, 1985) et d'Europe (Andersson 1986). Le phénomène, mis à jour au cours des années 1950-60 (Gorham 1958, Gordon et Gorham 1963), avait nécessité l'adoption de politiques législatives, tels le « Clean Air Act » aux États-Unis (instauré en 1970, amendé en 1990), le Programme canadien de lutte contre les pluies acides (1985), et l'Accord Canada-États-Unis sur la Qualité de l'Air (1991). Ces initiatives permirent de réduire les émissions de particules de SO_2 et d'améliorer la situation en de nombreux endroits, notamment en diminuant la quantité de sulfates (SO_4^{2-}) dans les eaux de surface de l'Est de l'Amérique du Nord (Likens 1989, Likens et al. 1996, Newell 1993). Malgré les efforts déployés, de nombreux plans d'eau n'ont toujours pas récupéré des dommages causés par les dépositions acides (Dupont et al. 2005, Likens 1996, Stoddard et al. 1999). Au Québec, la situation ne s'améliore pas pour plusieurs lacs de la rive nord du bassin versant du fleuve Saint-Laurent, le sol étant incapable de neutraliser les apports acides (Houle et al. 1997). Cette incapacité de se rétablir semble reliée à un appauvrissement en cations basiques échangeables des sols des bassins versants (Houle et al. 2004, 2006).

Il a été suggéré que les pertes en cations basiques des sols jouent aussi un rôle dans le dépérissement des forêts (Federer et al. 1989, Morrison et al. 1992, Shortle et Bondietti 1992, van Oene 1992). En effet, les dépôts acides créent un apport important en ions H^+ dans le sol, ce qui résulte en une mobilisation des éléments, qui sont déplacés des sites de liaisons par l'incursion des H^+ (Binkley et al. 1989, Reuss et Johnson 1986). L’entrée en solution des éléments résulte donc en une biodisponibilité accrue, les rendant cependant vulnérable au lessivage hors de la zone racinaire, et par le fait même à une diminution des réserves du sol en nutriments (Bondietti et al. 1990, Likens et al. 1996). Cette situation est corroborée par une augmentation des concentrations de cations basiques dans le bois des arbres au début des années 1960 (alors que les taux d’émissions de particules acides étaient très élevés), suivie d’une soudaine diminution de ces concentrations dans les années subséquentes (Bondietti et al. 1990, Likens et al. 1996, Shortle et al. 1997). Finalement, la croissance et la santé des arbres sont fortement reliées aux réserves de nutriments du sol (Bernier et Brazeau 1988, Ouimet et Camiré 1995, Ouimet et al. 1996). La capacité du sol à neutraliser les apports acides dépend de ses réserves en cations basiques, qui agissent pour créer un effet tampon (Houle et al. 2006). Les sols faiblement tamponnés, comme ceux du Bouclier Canadien, sont particulièrement sensibles à l’acidification (McLaughlin 1998).

Le dépérissement des populations d’érable à sucre (*Acer saccharum* Marsh.) a été largement confirmé par de nombreuses études et attribué à des causes variées : conditions climatiques (Bauce et Allen 1991, Bernier et al. 1989, Payette et al. 1996), épidémies d’insectes (Bernier et al. 1989, Kolb et McCormick 1993, Payette et al. 1996), densité élevée du peuplement (Bauce et Allen 1991) ou acidification des sols forestiers (Duchesne et al. 2002, McLaughlin et al. 1992, Ryan et al. 1994, Watmough 2002). Une acidité élevée des sols interfère avec la croissance des racines, l'absorption des nutriments et la croissance de l'arbre (Ouimet et al. 1996). Duchesne et al. (2002) ont observé une réduction de la croissance radiale de l'érable à sucre en lien avec l'augmentation de l'acidité du sol, hypothèse corroborée par d'autres études rapportant une croissance plus élevée suite à un chaulage (Long et al. 1997, Moore et al. 2000). Le calcul du seuil critique de tolérance au soufre (S) et à l’azote (N) de l’érable à sucre (et de plusieurs autres types de peuplement) par Ouimet et al. (2001) a révélé un lien entre la réduction de la croissance des arbres et le dépassement de ce seuil critique. Par ailleurs, selon certains auteurs la croissance de l’arbre pourrait donner une bonne indication de sa santé générale (Bauce et Allen 1991, Duchesne et al. 2003, Kolb et McCormick 1993). Hutchinson et al. (1998) ont observé, suite à l’acidification du sol, une modification de la chimie des feuilles d’érable à sucre n’étant pas accompagnée de signes visuels de déficience nutritive, suggérant que les effets de l'acidification se feraient plutôt sentir à long terme.

Outre les cations basiques, des métaux potentiellement toxiques tels Al, Cd et Mn sont aussi rendus mobiles par l’acidification des sols. Le cadmium (Cd) ne remplit aucune fonction physiologique et est phytotoxique (Andersen et al. 2002). Une diminution du pH du sol accroît les concentrations de Cd en solution (Bergkvist 1987, Berggren 1992, Tyler et al. 1987).

Le manganèse (Mn) est un micronutriment essentiel, pouvant s’avérer toxique au-delà d’un certain seuil (Kogelmann et Sharpe 2006, McQuattie et Schier 2000). L’exposition à une forte intensité lumineuse peut en exacerber les effets toxiques, autant chez l’érable à sucre (St. Clair et Lynch 2004) que chez certaines plantes à usage agricole (Gonzales et al. 2000). Il est davantage mobilisé dans le sol suite à une diminution du pH (Driscoll et al. 2001, Reichman 2002). Kennedy et Bergeron (1991) soutiennent que les concentrations naturellement élevées de Mn dans les anneaux annuels de l'érable à sucre rendent difficile l’évaluation de l’effet de la pollution. Plusieurs études ont néanmoins remarqué, chez cette même espèce, une augmentation des concentrations de Mn dans le bois suite à la diminution du pH du sol (DeWalle et al. 1991, 1999, Guyette et al. 1992, Houle et al. 2002, Long et al. 1997, Martin et al. 1998, Matusiewicz et Barnes 1985, Smith et Shortle 2001). D'autre part, la ré-équilibration des concentrations de Mn entre les anneaux annuels de l'érable à sucre fait en sorte qu’il ne serait pas recommandable pour les analyses dendrochimiques à long terme (Houle et al. 2002, Martin et al. 2003, Watmough 2002). Guyette et al.

(1992) ont malgré tout fait appel au Mn dans les anneaux annuels pour reconstruire le pH du sol dans le passé.

Une attention particulière a été portée à l'aluminium (Al), puisque c'est un élément non essentiel (Borer et al. 2004) potentiellement toxique (Kochian 1995, Rengel 2004), retrouvé en grandes quantités dans les horizons minéraux (Hallet et Hornbeck 1997) où il est généralement non disponible sauf lorsque mobilisé suite à l'acidification du sol (Cronan et Schofield 1990, Driscoll et al. 2001, McLaughlin 1998, Ulrich et al. 1980). Les cations Al^{3+} ainsi libérés peuvent alors interférer avec l'absorption des cations basiques par les racines des arbres (DeWalle et al. 1991, Shortle et Smith 1988, Shortle et al. 1997) ou déloger les cations basiques des sites de liaisons du sol, en causant ainsi le lessivage (Johnson et Fernandez 1992, Lawrence et al. 1995, Tomlinson II 1983). L'érable à sucre s'est aussi révélé sensible à l'effet inhibiteur de Al sur l'absorption de Ca (Côté et Camiré 1995, Long et al. 1997, McLaughlin 1998, Mohamed et al. 1997, Watmough 2002). D'ailleurs, les impacts négatifs d'une insuffisance en calcium (Ca) sur la santé et la croissance des arbres sont bien documentés (DeHayes et al. 1999, Likens et al. 1996, Long et al. 1997, Watmough 2002). Conséquemment, le rapport de Ca sur Al dans le sol, le bois et les feuilles a fréquemment été présenté comme étant représentatif d'une acidification du sol (Berger et al. 2004, Bondietti et al. 1989, Cronan 1991, Lawrence et al. 1995, Rustad et Cronan 1995) et de l'état de santé des arbres (Cronan et Grigal 1995, Matzner et al. 1986, Shortle et Smith 1988).

Les analyses dendrochimiques ont connu un usage grandissant au cours des trois dernières décennies dans le cadre d'études de surveillance écologique (Hagemeyer 1993, Watmough 1997). La principale prémisse de la dendrochimie repose sur l'hypothèse que les éléments absorbés par les racines de l'arbre au cours d'une certaine année se retrouvent dans l'anneau de croissance de cette même année. Cependant, la fiabilité des concentrations dans le bois en tant que témoin des conditions environnementales du passé est remise en question à cause de la translocation radiale des éléments, surtout dans les anneaux conducteurs de l’aubier, où la ré-équilibration est commune (Cutter et Guyette 1993, Houle et al. 2002, Kennedy et Bergeron 1991, Martin et al. 1998, 2003, Watmough 2002). Par ailleurs, Momoshima et Bondietti (1990) et Herbauts et al. (2002) ont démontré que la capacité d’échange cationique du bois diminue du centre vers l’écorce et est fonction du diamètre du tronc, ce qui résulte en d’apparentes diminutions dans le temps des concentrations de cations divalents et fausse donc les interprétations. Afin de palier à cette tendance des éléments à se déplacer radialement dans le bois de l'arbre, on utilise régulièrement en dendrochimie les rapports des concentrations des éléments, par exemple Ca/Mn (Houle et al. 2002), Ca/Mg (DeWalle et al. 1999), Ca/Al (Watmough 2002). Cette façon de faire permet de "normaliser" les valeurs et est plus utile que les concentrations absolues des éléments (Smith et Shortle 1996). Cutter et Guyette (1993) font toutefois remarquer qu'il pourrait être possible de détecter les éléments qui sont retenus fortement dans le bois, par une extraction faisant appel à un éventail de solvants organiques et inorganiques.

Balk et Hagemeyer (1994) et Hagemeyer et Shin (1995) ont utilisé une séquence de différents extractants pour évaluer la mobilité de Cd et Pb dans le bois de chênes sessiles (*Quercus petrea* [Matt.] Liebl.) et de pins sylvestres (*Pinus sylvestris* L.), respectivement. Herbauts et al. (2002) ont aussi utilisé des extractions séquentielles pour analyser Ca et K chez le chêne pédonculé (*Quercus robur* L.) et le hêtre commun (*Fagus sylvatica* L.). Ces équipes de recherche ont identifié trois fractions selon le degré de liaison au bois, et ont conclu que certaines fractions étaient mobiles pour les éléments étudiés. Par conséquent, l’extraction séquentielle, en discriminant entre les fractions, permet de cibler la fraction la plus immobile, qui pourrait conférer une meilleure vision du lien entre la chimie du bois et celle du sol.

L’immobilité de Al dans les anneaux annuels des arbres a été rarement (Dion et al. 1993) sujet de doute depuis que Baes et McLaughlin (1984) ont écarté la possibilité de translocation radiale, car divers auteurs ont observé une étroite concordance entre les concentrations de Al dans le bois et les périodes d’activité industrielle (Baes et McLaughlin 1984, 1986, Zayed et al. 1991), ainsi que les émissions de SO_2 (Bondietti et al. 1989), ou parce que les tendances temporelles allaient en augmentant à partir des années 1960 (Matusiewicz et Barnes 1985, Mohamed et al. 1997, McLaughlin 1998, McLaughlin et al. 1992). Ces présomptions sont basées sur des coïncidences, et pour cette raison ne constituent pas une preuve sans faille en faveur de l’immobilité de Al. L’utilité de cet élément à des fins de surveillance écologique et d’analyses dendrochimiques repose en grande partie sur sa force de liaison au bois.

L’objectif de cette étude était donc d’évaluer, par les moyens d’une extraction séquentielle, la mobilité dans le bois de l’érable à sucre de l’aluminium (Al), des cations basiques (Ca, K, Mg), de certains cations divalents potentiellement toxiques (Cd, Mn) et quelques autres éléments (Ba, Fe, Pb). Une description complète et sérieuse du comportement des éléments dans le bois de cette espèce n’avait jamais été entreprise. La proportion des diverses fractions pour chaque élément a été déterminée, ainsi que la différence de répartition selon l’acidité du sol. Les arbres échantillonnés provenaient de sept bassins versants du sud du Québec, choisis car représentant un fort gradient d’acidité du sol. Les tendances temporelles des fractions immobiles ont été comparées entre les sites pour tenter de découvrir un signal des conditions historiques du sol. Les concentrations moyennes dans l’aubier ont servi à relier chaque fraction à l’acidité du sol. La croissance a été mesurée puis comparée à la chimie du bois et du sol.

CHAPITRE 1

EXTRACTABILITY OF ELEMENTS IN SUGAR MAPLE XYLEM ALONG A GRADIENT OF SOIL ACIDITY

1.1 Abstract

Dendrochemistry has been used frequently for the historical dating of pollution. However, its reliability is questionable due primarily to the radial mobility of elements in sapwood. The extractability of 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 suffered from decline in past decades - were sampled in three Quebec watersheds along a soil acidity gradient. Annual tree-rings were treated by sequential chemical extractions, using extractants of varying strength (deionized H_2O, HCl 0.05 M, ultrapure HNO_3) to selectively displace the different element fractions (soluble, exchangeable, residual). Monovalent (K), divalent (Ba, Ca, Cd, Mg, Mn) and trivalent (Al, Fe, Pb) cations were respectively found mostly in the soluble, exchangeable and residual fraction. Mobile forms (soluble and exchangeable) do not appear suitable for temporal monitoring because of potential lateral re-equilibration in sapwood rings, but certain elements (Cd, Mn) were responsive to current soil acidity and could be used in spatial variation monitoring. Extractability of aluminium also varies according to soil acidity; at less acid sites up to 90% is contained in residual form, while on very acid soils as much as 45% can be found in mobile fractions. Sequential extractions are consequently very useful for determining specific forms of metals as key indicators of soil acidification.

Key words: Aluminium, base cations, sequential extractions, soil acidification, sugar maple

1.2 Introduction

The impact of atmospheric acid deposition on forest ecosystems of North America and Europe has been reported since the 1960’s (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 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 Aluminium-induced Calcium-deficiency (Côté and Camiré 1995, Long et al. 1997, McLaughlin 1998, Mohamed et al. 1997, Watmough 2002).

Aluminium (Al) 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). After being mobilized, it can interfere with absorption of base cations by roots (DeWalle et al. 1991, Shortle & 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 II 1983). The negative impact 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), while the Ca to Al ratio in soil, wood and leaves has often been presented as indicative of soil acidification (Berger et al. 2004, Bondietti et al. 1989, Rustad and Cronan 1995) as well as 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 their environment’s chemistry has been questioned because of radial translocation in the sap-conducing rings, where re-equilibration is common (Cutter and Guyette 1993, Houle et al. 2002, Kennedy and Bergeron 1991, Martin et al. 1998, 2003, Watmough 2002). In addition, Momoshima and Bondietti (1990) and Herbauts et al. (2002) have demonstrated that the cation exchange capacity (CEC) 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 analyse Ca, K and Mg in pedunculate oak (*Quercus robur* L.) and European beech (*Fagus sylvatica* L.). Both studies identified three fractions depending on binding strength, and characterized the mobility of certain fractions of the studied elements. Sequential extractions could therefore allow the targetting of immobile fractions of elements, which would better demonstrate the link between wood and soil chemistry.

The reduced mobility of Al in tree-rings has been established through observations that Al concentrations in wood either closely mimicked periods of industrial activities (Baes and McLaughlin 1984, 1986, Zayed et al. 1991), followed atmospheric emissions of sulphur dioxide (Bondietti et al. 1989) or exhibited increasing trends starting in the 1960’s (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 coincidences, and for that reason does not constitute hard proof in support of the immobility of Al in wood. Its utsefulness 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 mobility of Al and other cations (Ba, Ca, Cd, Fe, K, Mg, Mn, Pb) in sugar maple. A detailed and thorough characterization of elemental speciation in wood has never been done for this species. Differences in fractionation driven by soil acidity were also evaluated on three sites contrasting in soil acidity.

1.3 Methods

1.3.1 Site selection

Wood and soil samples were collected at 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). Sites were chosen based on the presence of sugar maple trees along a gradient of soil acidity (i.e., pH, base saturation, Ca/Al ratio; see Table 1.1). Soil piths were dug in different areas of the watersheds (n = 10 for Clair, n = 8 for Laurent, n = 14 for Duchesnay), and soil horizons were sampled and analysed separately (see Houle et al. 2006 for details on soil sampling).

1.3.2 Tree sampling

Nine healthy dominant or co-dominant sugar maple trees (age = 94 ± 21) were cut from the three watersheds. Trees were selected in vastly different areas around the lake, to potentially encompass a range of distinct watershed microenvironments. 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 hours, or kept at –20°C until drying was possible. Growth measurements (basal area increment [BAI]) were made according to Duchesne et al. (2002, 2003), and verified statistically with COFECHA (Holmes

1996). All wood samples were manipulated with plastic nitrile gloves and care was taken to avoid contamination by cleaning instruments regularly.

1.3.3 Dendrochemical analyses

Disks were sanded to reveal annual rings, which were separated into 5-year segments (5 annual rings) with a scroll saw (Mastercraft), which was cleaned with ethanol between disks to avoid mixing of samples from different trees. Each segment was ground in a Wiley mill (standard model n°3, Arthur H. Thomas Company, Philadelphia, USA). To check for contamination from both 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, and even-numbered subsamples were ground and pooled while uneven-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 then sanded and three left unsanded, and then sawed into thin pieces. All 20 samples (5 ground, 5 not ground, 5 sanded, 5 unsanded) were digested in ultrapure HNO_3 and the concentrations analysed by ICP-AES. Matched pairs t-tests made on log-transformed data showed that grinding was not a significant source of contamination, except for Fe (at $p<0.05$) with an average contamination of 1.20 mg/kg (58%) almost as important as inter-site variation (1.33 mg/kg). Sanding was found to be marginally significant for Al at $p<0.1$; therefore, a few additional millimetres 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: 1) deionised water *(Milli-Q water > 18.2 MΩ cm)* aiming for the soluble fraction; 2) HCl 0.05 M (exchangeable fraction); and 3) digestion with ultrapure HNO_3 (residual fraction). Prior to 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 minutes, 1, 2, 5 and 12 hours. Solutions were subsequently analysed for concentrations of elements (Figure 1.1).

For the first extraction, the samples consisted of 3 g of ground wood to which was added 30 ml of deionised water, agitated at 30 rpm for 2 hours, and then centrifuged at 3000 rpm for 10 minutes. The supernatant was removed as much as possible, transferred to a UV-sterilized polyethylene tube and fixed (acidification for preservation) with ultrapure HNO_3 (final concentration 0.2%) until analysis. In the second extraction, 30 ml of HCl 0.05 M was added to the remaining wood, agitated at 30 rpm for 2 hours, followed by centrifugation, with the supernatant similarly fixed until analysis. The remaining wood was rinsed with deionised water before being dried for 48 hours at 70^{o}C. For the third extraction, 300 mg of wood was taken from the 3 g remaining from the first two extractions. Wood samples were put in Teflon bombs (CEM linear closed-vessels) in 3 ml of ultrapure HNO_3, and digested in a high-performance microwave (MDS-2000, from CEM corp.). The digested solutions were transferred to polyethylene tubes and the volume adjusted to 30 ml with deionised water. Analyses of chemical elements were done on a charge coupled device simultaneous inductively-coupled plasma atomic emission spectrometer (CCD simultaneous ICP-AES) equipped with an axial torch (model Vista AX from Varian, Australia, 1999). Replicability of the extraction method was verified with a series of 10 grounded wood samples, obtained by subsampling from a homogenous combination of 20 annual rings from the sapwood of a single tree. These 10 samples were treated with the above-described extraction method. The replicability (expressed as a percentage) was calculated as the average value over standard error(Table 1.2).

In the studies of Balk and Hagemeyer (1994), Hagemeyer and Shin (1995) and Herbauts et al. (2002), three *fractions* were produced: the *soluble fraction*, the *exchangeable fraction*, and the *residual fraction*. The 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. The exchangeable fraction is also mobile, but less than the soluble fraction, and is extractable by a somewhat weak extractant with a low molarity, such as diluted HCl. The residual fraction is the last to be extracted, 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.

1.3.4 Data treatment

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 insure normality of residuals, but some still did not follow normality. Non-parametric test were thus used. Linear regressions of concentrations of elements over time were tested for equality of slopes using an analysis of variance; 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 also calculated. Analysis of variance (Tukey-Kramer’s Honestly Significant Distance) was performed on both the average concentration (each stem section separately) and proportions of each fraction, using site as a fixed effect. Sites were ranked based on soil characteristics (pH, sum of base cations, base saturation; see Table 1). An analysis of variance (Van der Waerden rank scores) was performed to compare average concentrations in heartwood and sapwood. A significance level of 0.05 was used in all analyses.

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, individual trees were combined to form an average trend, as there was in some cases a lot of variation from tree to tree and it was unwise to extrapolate a typical trend from the linear regression data. Besides, 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.

1.4 Results and discussion

1.4.1 Distribution of elements among fractions

Monovalent K was found mostly in the soluble and exchangeable fractions, which together represented more than 90% of the total concentration (Table 1.3). 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.

Divalent cations (Ba, Ca, Cd, Mg, Mn) were retrieved mostly (60-75%) by the HCl extraction. They can thus be described as being retained in major part in the exchangeable fraction. Furthermore, reaction kinetics previously presented for Ca, Mg and Mn (Figure 1.1) showed that H_2O and HCl extractions rapidly (within 1 hour) remove around 80% of what could be extracted after 12 hours of agitation, thus indicating that these fractions are very weakly retained in wood. All five divalent cations presented relatively the same distribution among fractions, suggesting that their repartition in tree wood is not dependent upon their function: for instance, one is not essential (Ba), one is phytotoxic (Cd), while 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 values of fractions were generally higher in heartwood (Table 1.3), particularly exchangeable and residual fractions. While concentrations of the soluble fraction of heartwood and sapwood were not significantly different, they were proportionally more abundant in sapwood. The pedunculate oaks analysed by Herbauts et al. (2002) exhibited higher concentrations of Mg (and K) in sapwood; Meerts (2002) had established from the literature that *Quercus* spp. were exceptions in this matter. Otherwise, observed behaviors of distribution 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 Ca, Mg and Mn found in the soluble and exchangeable extracts are in good agreement with the important lateral re-equilibration that followed soil liming of sugar maple reported by Houle et al. (2002). Such a high mobility raises serious doubt about the possible use of these elements in long-term dendrochemical monitoring, especially when focusing only on total concentrations.

Al, a trivalent cation, was found, on average, at 81% in the residual fraction. The exchangeable fraction was greater than the soluble fraction (12% vs 6%). Heartwood and sapwood contained similar concentrations of residual Al, while the exchangeable and soluble Al levels were higher in sapwood. Since the residual is the most abundant fraction, total Al was also in practically equal quantities in both heartwood and sapwood. Furthermore, this similarity in behavior between residual and total Al corroborates previous assumptions regarding its immobility in wood, and thus its suitability for temporal reconstruction. However, it remains to be seen whether the proportion occupied by mobile forms is constant in various conditions of soil acidity, as discussed below. Total concentrations of Al amounted to an average of nearly 2.0 mg/kg, ranging from 0.2 to 5.2 mg/kg and were comparable to values from other studies (Table 1.4).

Fe (92%) and Pb (99%) were found almost exclusively in the residual fraction. Very few samples contained detectable amounts of these elements in the exchangeable fraction, but they were present in the soluble fraction (Fe: 7.6%; Pb: 0.7%). The relatively high soluble Fe concentrations are likely the result of contamination from the grinding process. It should be noted that mean concentrations of metals such as Pb and Cd in tree wood were extremely low (< 1 mg/kg), while Al and Fe were slighlty more abundant (< 3 mg/kg).

1.4.2 Radial trends

Watmough (1997) noted that elements usually reported in dendrochemical studies either decrease steadily from pith to bark (Ca, K, Mg, Mn), increase sharply from the heartwood-sapwood boundary towards bark (Cu, Fe), or show a sudden peak right around the heartwood-sapwood boundary. Okada et al. (1993) suggested that alkaline earth elements were typical of the second pattern, while alkaline and halogens were associated to either the first or third. Our results show that total element concentrations indeed behave as is reported in those studies, but it is not true of each specific fraction (Figure 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 soluble, exchangeable and, by extension, total fractions of K decreased from the pith to the heartwood-sapwood boundary (Figure 1.2). Sharp increases of soluble K were observed in the outer sapwood; similar trends have been reported before (Herbauts et al. 2002, Watmough and Hutchinson 1996) and have been ascribed to K enrichment in live parenchyma cells (Momoshima and Bondietti 1990). The exchangeable fraction exhibited no significant trend in sapwood, being probably re-equilibrated among annual rings by sap flow. The residual fraction showed no significant trends in either trunk section. This absence of trends might indicate late fixation in a residual form after re-equilibration throughout sap-conducing tree-rings.

Divalent cations (Ba, Ca, Cd, Mg, Mn) showed a radial tendency for concentrations to decrease from pith to bark, usually more sharply in heartwood compared to sapwood (Figure 1.2). However, these tendencies mostly concern the exchangeable fraction and to a lesser extent the residual. Total concentrations follow the same decreasing trend, because divalent ions are mainly encountered in the exchangeable 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 (CEC) from pith to bark. The soluble fraction of these divalent cations was very low and exhibited no significant trend.

Concentrations of Fe in the residual and total fractions decreased slightly from the pith to the heartwood-sapwood boundary, remained more or less constant throughout the inner sapwood and increased radically in the inner sapwood towards the bark (Figure 1.2). The soluble and exchangeable fractions of Fe showed no significant trends. Pb showed a clear peak in the middle of the trunk slice, either in the inner sapwood or close to the heartwood-sapwood boundary. This peak is not sudden, but concentrations rather slowly but steadily increase from the pith to the inner sapwood, and decrease in the same manner from the inner sapwood to the bark. This peak pattern is only exhibited by the residual and total fractions, with the soluble and exchangeable fractions showing no significant trend whatsoever. The clear occurrence of this sharp peak was constant from tree to tree, but its position varied along the tree radius. These radial trends could be more than just the result of the element binding to wood structure following any remobilization processes, since the low mobility of this element (mobile fractions represent about 1% of total wood concentrations) suggests remobilization is a marginal phenomenon for Pb. Indeed, it seems to be in agreement with atmospheric emissions: a steady increase starting in the 1920’s and a decrease from the 1960’s onward coincidental with, respectively, the dates of addition and removal of lead from gasoline in North America (Ault et al. 1970, Baes and Ragsdale 1981). These results show for the first time the high immobility of Pb in xylem and further support its use as an accurate tracer of atmospheric pollution.

The radial tendency expressed by residual and total Al can best be described as erratic and fluctuating with wide variation between trees (note length of error bars in Figure 1.2). Soluble and exchangeable concentrations remain consistently low. Concentrations are generally higher in heartwood, except for the soluble fraction where sapwood concentrations are higher. Soluble Al could be transformed to a more tightly bound form upon creation of heartwood, or translocated into still-living sapwood rings through the apoplast (Meharg 1993, 2005).

1.4.3 Fractions and soil acidity

To verify whether the above-described behaviors could be generally applied in different environmental settings, the distribution of elements among fractions was compared in contrasting conditions of soil acidity.

Total concentrations of K and Ca in trees were significantly lower (Figure 1.3) at the most acid site (Duchesnay; Table 1.1). In contrast, the least acid site (Clair) had a significantly lower total Ba, Cd, Mg and Mn. Total Al and Mg were significantly higher in trees from the intermediate site (Laurent). Regarding Mg, it implies that the most acid site had intermediate total concentrations. Total concentrations of Pb differed significantly between sites, although not according to site ranking. Total Fe was significantly higher in the least acid site, and concentrations were ranked according to soil acidity. The only other element to apparently respond to soil acidity in its total concentration was Cd. However, individual fractions showed quite different patterns (Figure 1.3).

Soluble fractions of K were similar between sites. On the other hand, the most acid site had significantly lower concentrations in exchangeable and residual fractions. Only the residual fraction exhibited variations corresponding to site ranking.

The soluble fraction of divalent cations (Ba, Ca, Cd, Mg, Mn) was significantly lower in trees of the least acid site, and all sites ranked according to soil acidity. Ranking was not maintained in other fractions, except Cd for which all fractions were representative of soil characteristics. The least acid site consistently had significantly lower concentrations of Ba, Cd, Mg and Mn (except residual Mg where all sites were similar), whereas the most acid site had significantly lower concentrations of exchangeable and residual Ca (also observed in total concentrations). This could be due to the importance of Ca to tree nutrition, with steady supply warranted by selective absorption (Gerloff et al. 1976, Prenzel 1979). It could also be a sign of another stress particular to that site, such as soil Ca-depletion. Although concentrations of divalent cations varied between sites, respective percentages of individual fractions over the total remained steady: an increase or decrease in one fraction was mirrored by a proportional change in the other fractions (Table 1.3). This suggests that speciation of divalent cations is chiefly governed by wood physiology rather than environmental characteristics, especially when taking into consideration that the respective role of elements does not influence this phenomenon. However, it seems that soil acidity plays an important role in absorption of soluble forms of divalent cations, even if fluctuations of concentrations did not show up in the proportion of the soluble fraction over the total, possibly because this fraction represented a low percentage of total concentrations (Table 1.2). Soluble forms may enter roots by passive osmosis transport (Roy et al. 1988), facilitated at low pH (Cronan 1991), and may not be subject to the selective absorption theory. Considering that the most mobile fraction (soluble) exhibits the best concordance with site acidity ranking while the more strongly retained fractions display a weaker relation, then fractions could represent a temporal sequence of element fixation in wood: soluble, exchangeable, residual, in that order. Furthermore, these differences between sites apply only to sapwood, and are not evident in heartwood where there is more similarity between sites. It is usually thought that soil acidity and depletion of nutrient reservoirs have happened in the last few decades, which may explain why older wood (heartwood) would not show signs of recent soil depreciation.

Residual Fe was significantly higher in the least acid site. Differences between sites regarding residual Pb concentrations could not be linked to soil characteristics targeted in this study, either because Pb absorption is not related to these soil characteristics or because roots are not its main entry-pathway. Analysis could not be performed on exchangeable Fe, as well as soluble and exchangeable Pb, because too few trees contained quantities above detection limits (Table 1.3). Both Fe and Pb retained steadily constant relative proportion of each fraction over total. These elements thus seem to be strongly immobilized in tree wood.

Concentrations of soluble and exchangeable fractions of the trivalent cation Al were significantly different between sites and were ranked in the same order as soil acidity (lower concentrations at higher soil pH). Neither residual nor total Al showed significant differences that could be related to soil characteristics; the intermediate site had the highest concentrations, while the most and least acid sites were similar. The most important distinction is to be made regarding the percentage of total concentration found in mobile forms: trees from the most acid site contained between 35% and 45% mobile Al, while the other two sites had only around 10% of mobile Al in sapwood. Absolute concentrations do not reach toxic levels observed in seedling shoots from laboratory experiments (sugar maple: Thornton et al. 1994, conifers: Hutchinson et al. 1986), but 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 cations uptake by roots. Some studies 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, since Al was detected in tree xylem on all sites. On the other hand, this mechanism could vary according to tree species, tree health or soil condition. Al might be pH-dependent given that Al concentrations in wood increased with lower soil pH, much as Cronan (1991) reported regarding root-affinity for Al, Ca and Mg that varied with soil pH.

1.5 Conclusion

To date, most research conducted in dendrochemistry has used complete digestion of wood samples with strong extractants (e.g., HNO_3, H_2SO_4, 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. For example, exchangeable Mn is indeed decreasing from pith to bark, but the soluble and residual forms are more or less constant through the whole tree radius. Moreover, behaviors differ in varying soil conditions. As a consequence, using only the total digestion of a wood sample alienates the distinctive response of individual fractions. Therefore, sequential extraction should be performed to ensure the immobility of a given element on a given site before undertaking any attempt at temporal reconstruction.

Monovalent and divalent cations are found mostly in mobile fractions, which have been shown to be radially translocated in sapwood. As a result, these mobile fractions, as well as the total concentration, would not be 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 still 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 soluble fraction of monovalent and divalent cations, which is responsive to varying soil acidity (especially for Cd), would constitute a valuable tool for spatial monitoring of acid deposition.

Fe and Pb are substantially immobile in sugar maple tree wood, since they are found in a considerable proportion in the residual fraction. Bondietti et al. (1990) found Fe to be retained in the lower part of the stem, a sign of its low mobility. Pb has been involved in numerous investigations because of its ability to bind strongly to tree wood and to adequately mirror atmospheric emissions (Watmough et al. 1999). Both elements appear to maintain the same capacity for immobility in sugar maple tree wood.

Only the mobile fractions of Al are influenced by soil acidity, and they generally do not constitute a substantial proportion of total Al, so that a total digestion masks all response from mobile fractions. This could probably explain the low or lack of response of wood Al concentrations to soil acidity reported in previous studies (DeWalle 1991, 1999, Hutchinson et al. 1998, Watmough 2002), which used the total digestion method. Furthermore, 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 mobile forms, either in the soluble or exchangeable fraction. Nonetheless, because Al is in general mainly found in residual form in tree wood, it could be considered to be largely immobile. Such a feature would make it a suitable candidate for dendrochemical assessments of historical pollution. However, its residual fraction did not vary according to soil acidity, and so is of no use for soil acidification studies.

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Table 1.1. Mineral soil characteristics. Values are averages (n = 10 for Clair, n = 8 for Laurent, n = 14 for Duchesnay), With standard deviations in brackets. EA = exchangeable acidity, CEC = cation exchange capacity. Ranking is based on soil base saturation (BS) and soil Ca/Al ratio, with least to most acid site from top to bottom. Ranking was similar when considering organic soil horizons.

Site	pH	K	Ca	Mg	Mn	Al	Ca/Al	EA	CEC	BS
		mg/kg						meq/100g		
Clair	5.1 (0.4)	57.4 (10.3)	478 (571)	31.9 (16.5)	28.8 (18.0)	142 (65.8)	3.37	1.80 (0.55)	4.44 (2.43)	55.0 (21.0)
Laurent	4.9 (0.5)	49.3 (13.8)	373 (295)	76.5 (95.5)	88.9 (104.5)	170 (87.8)	2.19	2.00 (0.97)	4.65 (2.00)	52.6 (23.0)
Duchesnay	4.6 (0.1)	54.4 (9.6)	59.2 (17.8)	16.0 (3.29)	6.54 (4.27)	491 (92.7)	0.12	5.64 (1.06)	6.24 (1.14)	9.73 (1.89)

Table 1.2. Replicability of the extraction method, per extractant and for each element .

	Replicability (%)		
Element	H_2O	HCl	HNO_3
Al	1.3	1.5	18.6
Ba	0.9	0.6	1.4
Ca	0.9	0.5	5.9
Cd	6.4	0.6	1.2
Fe	4.9	3.5	13.2
K	0.5	0.4	3.8
Mg	0.7	0.6	4.4
Mn	0.9	0.6	3.6
Pb	14.3	*	7.4

* These concentration values were under detection limit.

Table 1.3. Average concentrations (per unit mass) of elements per fraction and their respective proportion, in heartwood and sapwood (n = 9 trees for residual, n = 8 for soluble and exchangeable, from all three sites combined).

Element	**Fraction**	**concentration (mg/kg)**		**highest in ****	**detection limit**	**% of Total**		**highest in ****
		sapwood	**heartwood**		**(mg/kg)**	**sapwood**	**heartwood**	
Al	soluble	0.128	0.090	ns	0.02	7.5	5.1	ns
	exchangeable	0.156	0.284	H	0.01	9.1	16.0	ns
	residual	1.43	1.40	ns	0.09	83.4	78.9	ns
Ba	soluble	0.73	0.78	ns	0	5.7	3.2	S
	exchangeable	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
Ca	soluble	61.2	85.2	ns	0.07	8.7	5.8	ns
	exchangeable	460	1048	H	1.0	65.7	71.6	ns
	residual	179	330	H	1.0	25.6	22.5	ns
Cd	soluble	0.00673	0.00603	ns	0.002	4.7	2.4	S
	exchangeable	0.103	0.190	ns	0.006	72.3	77.1	ns
	residual	0.0326	0.0503	ns	0.02	23.0	20.4	ns
Fe	soluble *	0.155	0.170	ns	0.006	6.5	8.1	ns
	exchangeable	0.0091	0.0040	ns	0.01	0.4	0.2	ns
	residual	2.23	1.94	ns	0.03	93.1	91.7	ns
K	soluble	347	435	ns	0.02	48.3	53.4	ns
	exchangeable	312	326	ns	0.7	43.6	39.9	ns
	residual	58.1	54.4	ns	3.0	8.1	6.7	ns
Mg	soluble	23.1	25.3	ns	0.006	18.1	11.6	ns
	exchangeable	82.1	156	H	0.2	64.2	71.8	ns
	residual	22.6	36.1	ns	0.04	17.7	16.6	ns
Mn	soluble	8.37	8.32	ns	0.002	16.8	7.8	S
	exchangeable	31.4	76.2	H	0.1	63.1	71.4	H
	residual	9.97	22.2	ns	0	20.0	20.8	ns
Pb	soluble	0.00215	0.00119	ns	-	0.7	0.5	ns
	exchangeable	0	0	ns	0.04	0	0	ns
	residual	0.287	0.250	ns	0.1	99.3	99.5	ns

* Grinding of wood samples was a source of contamination for Fe, which probably explains these high values for the soluble fraction.

** Results from van der Waerden rank scores at $P < 0.05$; ns = no significant difference between sections; H = highest value in heartwood; S = highest value in sapwood.

Table 1.4. Comparison of Al concentrations reported by various authors.

Reference	Species	range of wood Al (mg/kg)
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

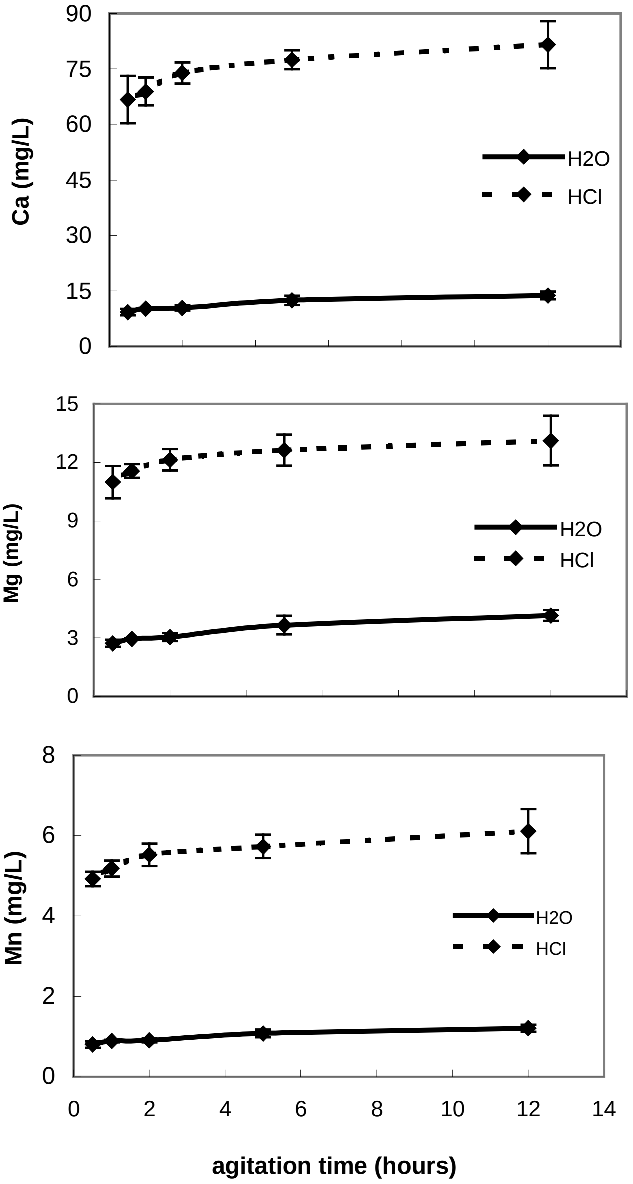

Figure 1.1. Reaction kinetics from H_2O and HCl extractions for a few key elements. Values are means and error bars are ranges (max minus min) from three replicates.

CHAPITRE 2

ASSESSMENT OF GROWTH AND XYLEM CHEMISTRY OF SUGAR MAPLE ALONG A SOIL ACIDITY GRADIENT

2.1 Abstract

Mobility of elements in tree xylem has been a growing concern for dendrochemists seeking to monitor long-term changes in soil chemistry, because it would contradict the basic premise that concentrations in tree-rings are representative of past environmental conditions. Although aluminium (Al) has been generally found in large part in a residual, immobilized form in sugar maple xylem, an earlier experiment confirmed that its mobile fractions were significantly enhanced on very acid soils. Cadmium (Cd) and manganese (Mn), other potentially phytotoxic metals, are known to be responsive to soil acidity. This paper presents an in-depth investigation of soil-wood relations, with a wider range of soil conditions, including data on soil acid-neutralizing capacity, and an assessment of tree growth. Sugar maple trees from seven watersheds in southern Quebec were analysed for base cations (Ca, K, Mg) and acidic metals (Al, Cd, Mn) in xylem. Annual tree-rings were treated by sequential chemical extraction, to selectively displace elements contained in the mobile and residual fractions. Mobile fractions of Al in wood were very responsive to soil acidity, but its residual form was not. Xylem concentrations of both mobile and residual Cd and Mn increased in acid soils. Ratios of Ca/Mg, Ca/Mn and Mg/Mn, in mobile and residual fractions, were good indicators of soil acidification, being related to soil pH and base saturation, as well as tree growth. The most acidified sites presented risks of Al stress, because of low soil Ca/Al and base saturation.

Key words: Aluminium, base cations, cadmium, manganese, sequential extractions, soil acidification, sugar maple, tree growth

2.2 Introduction

Atmospheric acidic deposition seriously impacted European and North American forests in the last four decades (Likens and Bormann 1974, Likens et al. 1996). It has been often cited as one of the various causes contributing to the decline of sugar maple trees (*Acer saccharum* Marsh.) (Duchesne et al. 2002, McLaughlin et al. 1992, Ouimet et al. 1996, 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).

Aluminium (Al) is a non-essential element for plant nutrition (Borer et al. 2004), is potentially toxic (Kochian 1995, Rengel 2004), and is usually unavailable in soils until mobilized by acidification (Cronan and Schofield 1990, McLaughlin 1998). Following this, it can interfere with absorption of base cations by roots (DeWalle et al. 1991, Shortle & Smith 1988, Shortle et al. 1997), or dislodge base cations from soil binding sites, thus inducing their leaching (Johnson and Fernandez 1992, Lawrence et al. 1995, Tomlinson II 1983). Additionally, several studies reported inhibition of Ca-uptake by mobilized soil Al (Cronan 1991, Lawrence et al. 1995, Ulrich et al. 1980). The negative impact of Ca-deficiency on tree growth and health is also well documented (DeHayes et al. 1999, Likens et al. 1996, Long et al. 1997, Moore et al. 2000, Watmough 2002). As a result, the ratio of Ca to Al in soil, wood and leaves was often presented as indicative of soil acidification (Berger et al. 2004, Bondietti et al. 1989, Rustad and Cronan 1995) as well as 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 to the ecosystem (Cronan and Grigal 1995).

Availability of other potentially phytotoxic metals is enhanced by soil acidification. Cadmium (Cd), a non-essential element, is among the most toxic heavy metals

(Andersen et al. 2002, Gratão et al. 2005a). 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. 2005b). A decrease in pH increases Cd concentrations in the soil solution (Bergkvist 1987, Berggren 1992, Römkens and Salomons 1998, Tyler et al. 1987).

Manganese (Mn) is an essential trace element for trees, which can be toxic at excess concentrations (Kogelmann and Sharpe 2006, McQuattie and Schier 2000, McQuattie et al. 1999), 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 (Gonzáles et al. 2000). It is further mobilized in soils by low pH (Driscoll et al. 2001, Reichman 2002). Kennedy and Bergeron (1991) hypothesized that naturally high levels of Mn in sugar maple tree-rings render difficult the evaluation of pollution impact. Nonetheless, numerous studies have observed, for that same species, elevated Mn concentrations following a decrease in soil pH (DeWalle et al. 1991, 1999, Guyette et al. 1992, Houle et al. 2002, Long et al. 1997, Martin et al. 1998, Matusiewicz and Barnes 1985, Smith and Shortle 2001). Furthermore, there is re-equilibration of Mn concentrations between annual rings in tree xylem, which makes it not recommendable for long-term dendrochemical studies (Houle et al. 2002, Martin et al. 2003, Watmough 2002, see also Chap. 1). It has nevertheless been used by Guyette et al. (1992) to reconstruct past levels of soil pH.

Radial re-equilibration of elements in sap-conducing tree-rings is now commonly acknowledged (Cutter and Guyette 1993, Drouet et al. 2005, Houle et al. 2002, Herbauts et al. 2002, Kennedy and Bergeron 1991, Martin et al. 1998, 2003, Watmough 2002). In addition, decreasing cation exchange capacity (CEC) of tree wood from pith to bark has been deemed responsible for similarly decreasing trends of divalent cations (Momoshima and Bondietti 1990, Herbauts et al. 2002). As a result, reliability of wood concentrations to act as historical records of environmental conditions is challenged.

Sequential extractions, using a series of extractants of increasing strength, have been shown to discriminate between fractions of elements, according to their respective mobility in tree wood (Balk and Hagemeyer 1994, Hagemeyer and Shin 1995, Herbauts et al. 2002). This procedure has the advantage of allowing precise enquiry of the residual fraction, considered the most immobile elemental form present in wood, and thus the one most likely to be representative of the past.

For quite some time, there had been an assumption about the immobility of Al in tree-rings (Baes and McLaughlin 1984). This belief was mostly based on wood concentrations of Al coinciding with periods of industrial activities (Baes and McLaughlin 1984, 1986, Zayed et al. 1991) and atmospheric emissions of sulphur dioxide (Bondietti et al. 1989), or exhibiting increasing trends starting in the 1960's (Matusiewicz and Barnes 1985, Mohamed et al. 1997, McLaughlin 1998, McLaughlin et al. 1992).

However, a previous investigation (see Chap. 1), by means of sequential extractions, confirmed enhanced mobility of Al in the wood of sugar maple trees growing on very acidified soils (pH ~ 3). Hence, it was concluded that caution must be taken when performing dendrochemical monitoring with this element, as high mobility makes dubious its utility for long-term environmental assessment. Nevertheless, in cases where Al is retained in large part (>80%) in a residual - and thus immobile - form, it might confidently be used for such purposes.

This paper presents further examination of the link between wood, soil chemistry and tree growth, along a wider range of soil conditions. Sapwood concentrations in elemental fractions (soluble, exchangeable, residual) were related to soil acidity.

Temporal trends of elements (Al, Ca, Cd, K, Mg, Mn) in sapwood (44 ± 10 annual rings) were compared between sites, with the objective of defining whether slopes would vary according to soil acidity: the hypothesis was that an element whose concentration is lower in high pH should present a decreasing slope on acidified sites and an increasing (or flat) slope on non-acidified sites. In addition, investigation of sugar maple growth led to define how it is related to soil conditions and wood element concentrations.

2.3 Methods

2.3.1 Site selection

Wood and soil samples have been collected at seven watersheds of the Quebec Lakes Network (Houle et al. 2004, 2006). Sites were chosen for the presence of sugar maple trees along a soil acidity gradient. Soil samples were taken in different areas of the watersheds, and soil horizons were sub-sampled and analysed separately (see Houle et al. 2006 for details on soil sampling). Site characteristics are given in Table 2.1.

2.3.2 Tree sampling

Three healthy dominant or co-dominant sugar maple trees per watershed were cut down (except for one site, where two trees were cut). Trees were selected in vastly different areas around the lake, thus representing distinct watershed microenvironments. A transversal slice was taken from the trunk at breast height. Upon return to the laboratory, slices were dried at 40°C during 48 hours, or frozen at –20°C until drying was possible. Tree cores (two per tree) were also sampled on 12 trees per watersheds (84 trees overall). During fieldwork, cores were inserted in a piece of thick cardboard, which was dried upon return to the laboratory. All wood samples were manipulated with plastic nitrile gloves and care was taken to avoid contamination by cleaning instruments regularly.

2.3.3 Dendrochronological measurements

84 cored trees and 20 trunk slices sum up to 104 trees available for growth measurement. To reveal annual growth rings, a thin layer of wood was peeled off from the cores using a steel scalpel, while slices were sanded on one side. Two virtual radiuses were placed on the sanded side of a slice, one across the longest radius and the other across the shortest, and a straight line was then traced between the two to cover the whole diameter. Measurements of ring width were made from pith to bark on each side of the diameter, under a binocular, using a UniSlide device (Velmex) 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 and add some when necessary. Series were statistically verified using the COFECHA program (Holmes 1996), which identified outliers to be excluded from the series. Averaging measurements from both disk radiuses (or both cores of the same tree) produced a general trend for each tree. Growth was calculated for the whole lifetime using the basal area increment (BAI) with the following formula:

$$\mathrm{BAI} = \pi\,(R^{2}_{\mathrm{n}} - R^{2}_{\mathrm{n-1}})$$

Where R is the tree radius and n is the year of ring formation (Duchesne et al. 2003). This thus represents annual increase in surface instead of just radial growth.

2.3.4 Dendrochemical analyses

Disks were sanded to reveal annual rings, which were separated into 5-year segments (5 annual rings) with a scroll saw (Mastercraft), which was cleaned with ethanol between disks to avoid mixing of samples from different trees. Each segment was ground in a Wiley mill (standard model n°3, Arthur H. Thomas Company, Philadelphia, USA). To check for contamination from both 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, and even-numbered subsamples were ground and pooled while uneven-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 then sanded and three left unsanded, and then sawed into thin pieces. All 20 samples (5 ground, 5 not ground, 5 sanded, 5 unsanded) were digested in ultrapure HNO_3 and the concentrations analysed by ICP-AES. Matched pairs t-tests made on log-transformed data showed that grinding was not a significant source of contamination, except for Fe (at $p<0.05$) with an average contamination of 1.20 mg/kg (58%) almost as important as inter-site variation (1.33 mg/kg). Sanding was found to be marginally significant for Al at $p<0.1$; therefore, a few additional millimetres were sawed off each segment on the side that had been in contact with the sand paper.

A previous investigation (see Chap. 1) presented a sequential extraction procedure using three different solutions (H_2O, HCl, HNO_3). A similar method was used here, although the first two steps – H_2O and HCl – were combined in a single HCl 0.05 N extraction, which would extract both the soluble and exchangeable fractions, which will be referred to as “mobile fractions” thereafter. This way, separation of mobile and residual fractions was still feasible while manipulation time was reduced. For the residual (immobile) fraction, wood samples were subsequently dissolved by ultrapure HNO_3 in tightly shut Teflon bombs (CEM linear closed-vessels) put in a high-performance microwave (MDS-2000, from CEM corp.). Analyses of concentrations were processed on a charge coupled device simultaneous inductively-coupled plasma atomic emission spectrometer (CCD simultaneous ICP-AES) equipped with an axial torch (model Vista AX from Varian, Australia, 1999). Elements targeted were Al, Ca, Cd, K, Mg and Mn.

2.3.5 Data treatment

The different mineral horizons in a given soil sample were proportionally combined (according to horizon thickness) to provide a global value. Samples from the same site were averaged to obtain a site value. In following sections, the expression “organic soil layers” refers to the combination of litter and humus horizons, while “mineral soil layers” refers to the B-horizon (varying depth). There was some variation between soil samples, but soil heterogeneity is known to occur frequently and naturally (Jackson and Caldwell 1993), and thus site averages are considered more useful when working at a regional scale (Lechowicz and Bell 1991). Soil variables included pH, exchangeable acidity, exchangeable base cations, cation exchange capacity, and base saturation (except pH, units were meq/100g). Exchangeable acidity (EA) was calculated as the sum of H^+ and Al in soil extracts, while exchangeable base cations (exchBC) were the sum of the soil content of Ca, K and Mg. Cation exchange capacity (CEC) was considered as EA added to the sum of exchBC. Base saturation (BS) corresponded to the ratio of exchBC over CEC in soil. Formulas for soil chemical variables were adapted from Houle et al. (2002).

The position of the heartwood-sapwood boundary was determined visually based on difference in color. Only sapwood was considered for analysis, because it is the section that has been in contact with actual soil conditions for the longest period of time (Berger et al. 2004). Differences in temporal trends of concentrations in sapwood were compared by testing for parallelism of slopes, in which regressions of concentrations as a function of time (years) were discriminated using site as a categorical variable, and taking into account the interaction of time and site. Parallelism of temporal concentration trends was tested only on the residual fraction, as it is the most promising for long-term monitoring of soil conditions, due to its immobility (See Chap. 1). The objective was to define whether slopes would vary according to soil acidity: an element whose concentration is low in high pH should present a decreasing slope on acidified sites and an increasing (or flat) slope on non-acidified sites. In situations where parallelism was not confirmed, individual site trends were verified with simple linear regressions. Data were log-transformed to insure homogeneity of variance (Brown-Forsythe test) and normality of residuals (Shapiro-Wilk test), to which end it did not systematically succeed; although the F-test is relatively robust to deviation from its basic assumptions (Lindman 1974), caution was taken when interpreting results.

Average sapwood concentrations of Al, Ca, Cd, K, Mg and Mn from individual trees (n=20) were related to soil chemical variables using Spearman's non-parametric correlation coefficient. Fractions (mobile, residual, total) were treated separately. Ratios of concentrations (Ca/Al, Ca/Cd, Ca/Mn, Ca/Mg, K/Al, K/Cd, K/Mn, Mg/Al, Mg/Cd, Mg/Mn) were also calculated from average sapwood concentrations, coupling base cations (Ca, K, Mg) with the metals (Al, Cd, Mn) that best reacted to soil acidity in previous results (See Chap. 1), as well as Ca and Mg because of the previously reported antagonism between these two elements (Berger et al. 2004, Glatzel et al. 2000). Ratios are often used in dendrochemistry to "normalize" the fluctuating concentrations and thus minimize the problem of the generally decreasing trends from pith to bark (Berger et al. 2004, Bondietti et al. 1989).

By graphical analysis of BAI time series, the onset of growth decline in sampled trees was determined to be around the year 1970, so only the data from that year onward were used. It is a later, but still coherent date than what had been previously established as the moment when atmospheric pollution started impacting on forests of eastern North America (Duchesne et al. 2002, Turk 1983). Trends of BAI over time were calculated for each tree between 1970 and the felling year (2001-2005).

Spearman's coefficient assessed potential correlations between individual BAI trends (n = 20) and sapwood concentrations (absolute concentrations, ratios of elements, and ratios of mobile to residual fractions). Although sapwood did not necessarily contain the same number of annual rings used for trend calculation (sapwood width varied between trees from 24 to 64 annual rings [years]; average 44 ± 10), it is a coherent physiological stem section, and thus should be considered in its entirety. Furthermore, mobile elements are translocated throughout the entire section - probably no later than within a few years, according to previous studies (DeWalle et al. 1999, Houle et al. 2002) -, which implies that concentrations in all sapwood rings could possibly influence growth. Correlations were also tested between individual BAI trends and soil chemical variables, for which all slices and cores were used to produce site averages.

2.4 Results and discussion

2.4.1 Temporal concentrations trends in wood and Soil chemistry

In the present section, the residual fraction is the only one considered because it contains mostly immobile elements and thus offers more possibilities for long-term monitoring. Slopes of residual K differed between sites, but not in agreement with soil conditions. Residual fractions of divalent cations (Ca, Cd, Mg, Mn) exhibited generally decreasing radial trends from pith to bark (see Chap. 1). Slopes of Cd did not vary between sites, thus indicating that binding of this element along the tree radius is chiefly ruled by physiological characteristics of the wood structure, like CEC (Momoshima and Bondietti 1990, Herbauts et al. 2002). Slopes of Ca, Mg and Mn varied between sites, although it could not be ascribed to soil conditions. Even Al, which is mostly immobile in sugar maple xylem (See Chap. 1), had similar slopes among the sites. Overall, despite the strong acidity gradient found between the seven sites, radial trends of elements were similar between sites or not related to the soil acid-base status. Hence, it appears that linking temporal trends of sapwood concentrations to recent soil conditions is a doubtful endeavour.

Temporal trends of concentration ratios were also compared among sites. There was no significant difference in slopes regarding Ca/Cd, Ca/Mg, K/Cd, and Mg/Cd. Residual Ca/Al and Mg/Al decreased over time, but did not decrease more in acidified sites; in fact, two of the most acidified sites (Boisvert and Truite rouge) had increasing trends (these sites had increasing Ca trends), while the trend for the Laurent site was decreasing more than average (similarly to Ca). Slopes of K/Al significantly differed between sites, but not in a manner readily compatible with the gradient of soil acidity. In the case of Ca/Mn, K/Mn and Mg/Mn, all sites had generally increasing trends, except the least acidified site (Clair), for which it decreased significantly (as it did for Mn taken individually). Therefore, it seems to indicate that ratios mainly reflect the behavior of only one element, and that they are not more informative of long-term changes than are individual elements.

2.4.2 Average sapwood concentrations and Soil chemistry

It had been observed by a previous investigation (see Chap. 1) that the total of all fractions of an element usually behaves similarly to its most abundant fraction (Table 2.2). Therefore, total concentrations will be treated here only if their behavior differs from the main fraction. Various significant correlations were discerned between average sapwood concentrations and soil chemical variables (Table 2.3). Mobile fractions of K were negatively correlated to exchangeable base cations (exchBC) from mineral soil layers, while both mobile Ca and K exhibited negative relations to Mg in mineral soil layers. Mobile wood content of all three base cations displayed a negative relation to mineral soil K. Mobile Mg was negatively correlated to pH of organic soil layers. K was the only base cation to be related to its soil content (in mineral horizons, and negatively), and no base cations content from the organic horizons were related to wood concentrations of these elements. Residual fractions of Ca, K and Mg were not related in any way to soil conditions. Although soil reservoirs of base cations are presumably depleted by the lowering of soil pH (Likens et al. 1996), their wood content do not show any relation to soil pH. It had been previously suggested that trees selectively absorb base cations (Gerloff et al. 1966, Hagen-Thorn and Stjernquist. 2005, Prenzel 1979), which could account for equal wood concentrations from acidified and non-acidified sites. Furthermore, in a liming experiment on Ca-deficient sugar maple stands, Houle et al. (2002) observed a slight increase in wood Ca that was in no way proportional to the massive amounts of $CaMg(CO_3)_2$ added to the forest floor. Jandl et al. (2004) reported that a depletion of soil Ca was not necessarily related to wood content or even to tree growth, suggesting the existence of alternative sources of Ca not evident from soil chemical data. Smith and Shortle (2001) have put forward a different explanation for lack of wood-soil correlation, presenting xylem sap as a dynamic homeostasis tool for trees to maintain relatively constant concentrations of elements. In addition, other authors (Safford et al. 1974, Shortle and Smith 1988) observed equivalent molar Ca concentrations in slow- and fast-growing trees, and thus suggested that Ca is incorporated at a constant rate per unit volume of wood, independent of growth rate. Dijkstra and Smits (2002) proposed that sugar maple trees were capable of maintaining high content of exchangeable Ca in forest floor by rapid root-uptake (before leaching) and by pumping from deeper soil horizons, followed by recycling through litter fall. This would counterbalance the leaching induced by the production of organic acids that results from organic matter decomposition of leaf litter (Dijkstra et al 2001).

Both mobile and residual fractions of Cd and Mn were negatively correlated to the Ca/Al ratio and base saturation (BS) in mineral layers. Mobile Cd and Mn also showed a negative relation to exchBC in organic layers. Furthermore, there were marginally significant relation between mobile Cd and pH (negative) and exchangeable Al (positive) in mineral layers, which became significant in total Cd.

Soil acidification has been recognized to enhance mobility of Cd (Andersen et al. 2002, Römkens and Salomons 1998) and Mn (Guyette et al. 1992, Kogelmann and Sharpe 2006, St. Clair and Lynch 2004). Therefore, the observed relations between sapwood and soil are in good agreement with the premise of increased absorption resulting from mobilization in soil. If Mn solubility has been often assumed (Kogelmann and Sharpe 2006) to depend mostly on soil pH (there was indeed a strong correlation between soil pH and soil Mn in mineral layers among sites from the present study, but only marginal between wood Mn and mineral soil Mn), it appears that Mn uptake by tree roots is principally governed by soil base saturation (and Ca/Al). Interestingly, both mobile and residual fractions of Cd and Mn were responsive to soil conditions, whereas only mobile forms of other divalent (and monovalent) cations did relate to soil chemistry. Perhaps it is an indication that fixation of macronutrients (Ca, Mg and K) in tree wood occurs late after absorption, possibly because of their high demand and essential function in physiological processes. Mn is not needed in such great quantities for nutritional purposes (Kogelmann and Sharpe 2006, McQuattie and Schier 2000), and Cd does not fill any nutritional role (Andersen et al. 2002, Gratão et al. 2005a), which might explain a rapid immobilization.

Mobile Al was negatively correlated to BS and Ca/Al of mineral layers, as well as exchBC of organic layers. This could be a reflection of the large contribution of soil reservoirs of base cations to the acid-neutralizing capacity of forest soils (Houle et al. 2006), resulting in lower proportions of soil exchange sites being occupied by Al, and consequently in reduced tree uptake. In mineral layers, soil Al was strongly and inversely ($rho = -0.82$, $P < 0.05$) related to soil pH, which is consequent with assertions of enhanced solubility following acidification of forest soils. Both organic and mineral soil pH were negatively related to wood mobile Al, which was not, however, directly related to soil Al (only to soil Ca/Al). Residual wood Al was not related to any soil variable. 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). Meharg (1993) indicated 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 (See Chap. 1) confirmed that mobile fractions of wood Al are responsive to variations in soil acidity, with higher uptake occurring in lower pH. Therefore, Al exclusion from roots might not be valid for sugar maple, at least in these site conditions, but Cronan (1991) had reported pH-dependant Al uptake by red spruce roots.

2.4.3 Concentration ratios and Soil chemistry

The ratio of Ca to Al in wood responded inversely to soil chemical variables than did Al separately: wood mobile Ca/Al correlated positively to BS, Ca/Al and pH of mineral layers, as well as exchBC and pH of organic layers, while it was negative for Al (strengths of correlation were relatively equal). Former significant correlations of Ca to soil were not significant in ratio to Al. Therefore, the Ca/Al ratio in wood is not any more useful than are Ca and Al taken individually. Similarly, Borer et al. (2004) had found Ca/Al in red spruce needles to be less responsive than other variables (mobile foliar Ca, and residual/mobile foliar Al, in their case). A review by Cronan and Grigal (1995) detailed obstacles inherent to the use of Ca/Al ratios. For instance, the discrepancy between the very high quantities of wood Ca and very low wood Al content can be a source of misinterpretation of the Ca to Al ratio. This could be extended to any ratio where concentrations of elements are found in vastly different orders of magnitude (e.g., Ca/Cd).

Nevertheless, this same ratio in soil is regularly cited as indicative of potential stress to forest ecosystems (see Cronan and Grigal 1995 for a review). Indeed, 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. The first was soil base saturation, with possible Al stress for values under <15% of effective CEC. In the present study, only the most acidified site (Duchesnay) had such a low BS (11.5), but the next two (Boisvert, Truite Rouge) were also close (15.1 and 15.5). The second variable is the molar ratio of Ca to Al in soil. Under a value of 0.2, there is a 95-100% risk of suffering Al stress; again, the most acidified site (0.19) was under the threshold. The next two most acidified had higher Ca/Al ratios (0.26 and 0.33), which places them in the bracket of 75% risk (Ca/Al under 0.5). The last bracket is for Ca/Al ratio under 1.0 (50% risk), but Ca/Al ratios were higher than 1.0 in soil of the four other sites. The third and fourth variables from Cronan and Grigal (1995) consisted in fine root and foliage Ca/Al molar ratio. Unfortunately, to this day there is no established threshold for either Al or Ca/Al content in tree wood that would indicate potential Al-related stress.

In the present study, it was observed that: 1) elements in xylem were more frequently related to mineral soil Ca/Al than to mineral soil exchangeable Al (exchAl); 2) most of soil EA was produced by soil exchAl (Table 2.1; see also Coleman and Thomas 1967); 3) and soil Ca represented the majority of soil base cations (Table 2.1). Hence, it might seem that soil Ca/Al is perfectly adequate to assess potential stress. However, considering that: 1) soil pH also influences wood concentrations of certain elements (Tables 2.3 and 2.4); 2) all base cations, and not just Ca, can neutralize acidic inputs to forest soil (Bailey et al. 1992, Houle et al. 2006); and 3) exchBC (of organic layers) were also correlated to wood element concentrations (Al, Cd, Mn; see Table 2.3), soil base saturation could be a more accurate representation of soil conditions. In addition, given that correlations of wood element concentrations to soil Ca/Al and BS in the present study produced exactly equal coefficients (Tables 2.3 and 2.4), the use of soil BS would present a definite advantage for sites where exchangeable acidity and exchangeable base cations are not respectively composed in majority of Al and Ca.

Existing correlations of wood Ca and Cd with soil conditions became stronger by using the Ca/Cd ratio, while mineral soil CEC, which was not significantly correlated to either Ca or Cd, did correlate to wood Ca/Cd. Therefore, this ratio could be a good indicator of soil acidification. However, among the studied trees, wood content of Cd was very low and just above detection limit, especially for residual Cd (see Table 2.2). It would thus be hazardous to rely too much on that ratio.

Although mobile Mg was already correlated to organic soil pH, the relation was slightly stronger (reversed sign) when used in the Ca/Mg ratio; moreover, the correlation became significant (and positive) between residual Ca/Mg and organic soil pH. When they are not dislodged from soil binding sites by acidic cations at low pH, Ca and Mg could also compete for those binding sites, with Ca showing more affinity for organic matter (Bohn et al. 1985). Consequently, as pH increases, more Ca than Mg could be absorbed by roots. This antagonism had been previously reported (Berger et al. 2004), and proposed as a key indicator of nutrient cycling, due to the relative Ca enrichment of the O-horizon, a consequence of tree transpiration and water uptake from lower-depths horizons (Glatzel et al. 2000).

Previous relations for Ca and Mn were improved by combining them in a ratio, and soil pH (mobile Ca/Mn with mineral layers, residual Ca/Mn with organic layers, total Ca/Mn with both) was rendered significant (and positive). This relation to soil pH is in accord with a recent work by Kogelmann and Sharpe (2006), and is worthy of note because soil pH was not related to concentrations of either individual element. It could thus be indicative of a particular imbalance resulting from a low pH-induced mobilization of Mn in soil. Being similar in charge and mass, Mn would afterwards compete with Ca for soil exchange sites and absorption by roots. There has been suggestion of Mn-induced nutrient deficiency for sugar maple (McQuattie and Shier 2000, McQuattie et al. 1999).

Ratios of K to Al dulled the response of Al to soil chemistry; only the relation to organic soil pH remained significant, although not as strong (Al: rho = -0.63; K/Al: rho = 0.52). On the other hand, K/Cd improved correlations of mobile Cd to EA and pH in mineral soil, and to organic soil pH, and residual Cd to mineral soil pH, while worsening correlations of mobile and residual Cd to mineral soil BS and Ca/Al, and mobile Cd to organic exchBC. Ratios of K to Al, Cd and Mn completely obscured the significant relation of K to exchBC in mineral layers. Otherwise, Mn-soil relations are improved when combined with K, or rendered newly significant (mobile Mn to EA and pH of mineral layers, and to organic soil pH). Like Ca mentioned above, K is possibly outcompeted by Mn for root absorption in acid soils.

The previously significant relation of mobile Mg to organic soil pH did not appear when Mg was combined with Al, Cd or Mn. Relations between wood Al and soil variables were diminished in Mg/Al ratios. Mg/Cd and Mg/Mn improved already significant Cd- and Mn-soil relations, and conferred significance to others (residual Cd to mineral soil pH, mobile Mn to exchBC and pH of mineral layers), although it attenuated relations of mobile Cd and Mn to exchBC in organic layers. Because of low wood content of Cd, it would be more advisable to use ratios of Mg to Mn.

2.4.4 Tree growth and Soil chemistry

BAI trends from all cored trees and trunk slices are compared to soil chemical variables (Table 2.5). Relations are significant with mineral soil CEC and organic soil K. Soil CEC, calculated as the sum of EA and exchBC, was mainly related to soil EA (rho = 0.86, P = 0.014) rather than to soil exchBC (rho = 0.5, P = 0.25) in mineral layers. K content in organic layers, on the other hand, is significantly correlated to soil exchAl (rho = -0.79) and soil pH (rho = 0.86) of mineral layers. Overall, these relations indicate that soil acidity (e.g, high soil EA and exchAl, and low soil pH) has a negative influence on tree growth. Duchesne et al. (2002) had previously investigated sugar maple growth and inferred that it was impaired by soil acidification.

2.4.5 Tree growth and Wood chemistry

The only element in sapwood to be related (positively) to growth was mobile K (Table 2.5). It is probably indicative of higher K content in highly active tree rings (Houle et al. 2002, McClenahen et al. 1989). Mobile K/Al ratio in wood showed a slightly weaker relation with growth than did K alone, but it was still significant. Because Al alone is not related to growth, and that neither K/Cd nor K/Mn are, there might be some competitive processes for Al and K. The cause of the moderate, but significant, negative relation between growth and wood residual (and total) Mg/Mn is not clear, since both individual elements exhibited no relation to growth.

2.5 Conclusion

2.5.1 Assessment of forest health through tree growth and Al stress

Assessing tree growth through dendrochronology and chemistry revealed that growth was positively correlated to wood content of mobile K, which in turn was negatively related to K, Mg and exchBC in mineral layers, possibly meaning that fast growth demands high uptake of K from the soil, causing a diminution in soil content. The mobile K/Al ratio was also correlated to tree growth, as well as to organic soil pH. Another valid option is the residual (and total) Mg/Mn ratio, related to tree growth and soil base saturation.

According to the four variables proposed by Cronan and Grigal (1995) to assess Al stress, the three most acidified sites of this study (Duchesnay, Boisvert, Truite Rouge) are under potential threat, because of their low soil base saturation and soil Ca/Al. However, while trees from the Duchesnay site were indeed strongly declining, the Boisvert and Truite Rouge sites had some of the best growth rates (Table 2.1). It suggests that those soil variables are not always suitable assessment tools, or that other site characteristics could compensate for Al stress.

2.5.2 Assessment of soil acidification

Soil acidification was best assessed through sapwood means of mobile Al, mobile and residual Cd and Mn, as well as ratios of mobile and residual Ca/Mg, Ca/Mn and Mg/Mn. Although the wood Ca/Al ratio was also responsive to soil conditions, its response was systematically weaker than Al alone. The Ca/Al ratio in soil appears to be a pertinent indication of soil acidity, but the wood Ca/Al ratio does not seem to be an informative variable.

Ca/Mg, Ca/Mn and Mg/Mn in wood were particularly responsive to soil chemistry and brought to light relations with soil variables that were not significant for either individual element. This particular feature suggests some noteworthy interaction or antagonism between the elements, either in soil, in wood or both. Their similar charge and mass could instigate competition for both uptake by roots and binding in xylem. While only mobile Al responded to soil acidity, the residual fraction of these three ratios was also significantly related to soil chemistry, albeit not as strongly as the mobile fractions. Nevertheless, it suggests that these ratios could potentially be useful to long-term monitoring, although more investigation is needed, especially because their high proportion of mobile forms implies important lateral re-equilibration. Until element fixation in tree wood is better understood, variations in temporal trends of concentrations will remain hard to interpret.

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Table 2.1. Site characteristics. Selected soil variables are for upper B-horizon. 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 top to bottom. Ranking was similar when considering organic soil horizons. Tree growth is the slope of BAI trends for 1970-2005 (n = 3 for disks and n = 15 for cores).

Site	Latitude	Longitude	pH	K	Ca	Mg	Al	Ca/Al	EA	CEC	BS	Tree growth	
				----------------------		mg/kg		----------------------	--- meq/100g ---		(%)	cores	disks
Blais	45° 56' N	75° 10' W	5.1	39.5	947	47.4	113	8.36	1.61	6.52	74.4	-0.152	1.77
Clair	45° 36' N	76° 04' W	5.1	57.4	478	31.9	142	3.37	1.80	4.44	55.0	-0.309	-8.10
Laurent	46° 28' N	74° 11' W	4.9	49.3	373	76.5	170	2.19	2.00	4.65	52.6	-9.16	-11.1
General White	46° 21' N	74° 41' W	4.8	40.0	476	44.8	186	2.56	2.24	5.10	52.1	18.5	17.2
Truite Rouge	46° 09' N	74° 05' W	4.8	28.5	125	10.6	274	0.456	3.11	3.91	20.8	-6.51	15.9
Boisvert	46° 45' N	74° 02' W	5.1	12.6	33.1	3.96	126	0.262	1.40	1.63	15.1	58.5	24.4
Duchesnay	46° 57’ N	71° 40’ W	4.6	54.4	59.2	16.0	491	0.121	5.64	6.24	9.73	-17.4	-16.0

Table 2.2. Average sapwood concentrations (n = 20) of elements per fraction, and their respective proportion.

Element	Fraction	Concentration (mg/kg)	SE	% of Total	Detection limit (mg/kg)
Al	residual	1.05	0.2	80.5	0.09
	mobile	0.25	0.02	19.5	0.02
Ca	residual	147	19	19.5	1.0
	mobile	751	37	80.5	1.0
Cd	residual	0.022	0.003	15.8	0.02
	mobile	0.12	0.01	84.2	0.006
K	residual	51.5	4.7	9.0	3.0
	mobile	519	46.3	91.0	0.7
Mg	residual	16.3	2.2	11.9	0.04
	mobile	121	9.0	88.1	0.2
Mn	residual	7.4	1.2	13.0	0.1
	mobile	49.4	6.3	87.0	< 0.0001

Table 2.3. Correlation coefficients of element concentrations in sapwood to soil chemistry, by elemental fraction. Only significant (at $\rho > 0.05$) relations are shown.

Element	**Soil Variable**	**Soil Layers**	**Mobile Fraction**		**Residual Fraction**		**Total Fractions**	
			Spearman's ρ	*Prob*>$\lvert\rho\rvert$	*Spearman's* ρ	*Prob*>$\lvert\rho\rvert$	*Spearman's* ρ	*Prob*>$\lvert\rho\rvert$
Al	BS	mineral	-0.60	< 0.01				
	Ca/Al		-0.60	< 0.01				
	pH		-0.49	< 0.05				
	exchBC	organic	-0.68	< 0.001				
	pH		-0.63	< 0.01				
	Ca		-0.68	< 0.001				
	Mg		-0.78	< 0.0001				
Ca	K		-0.65	< 0.01			-0.60	< 0.01
	Mg		-0.48	< 0.05				
Cd	EA B	mineral	0.40	< 0.1			0.49	< 0.05
	BS		-0.56	< 0.01	-0.56	< 0.05	-0.63	< 0.01
	Ca/Al		-0.56	< 0.01	-0.56	< 0.05	-0.63	< 0.01
	Ca				-0.49	< 0.05		
	pH						-0.53	< 0.05
	exchBC	organic	-0.62	< 0.01			-0.62	< 0.01
	Ca		-0.62	< 0.01			-0.62	< 0.01
	Mg		-0.71	< 0.001			-0.71	< 0.001
K	exchBC	mineral	-0.48	< 0.05			-0.49	< 0.05
	K		-0.56	< 0.05			-0.55	< 0.05
	Mg		-0.49	< 0.05			-0.49	< 0.05
Mg	K	mineral	-0.47	< 0.05				
	pH	organic	-0.67	< 0.01			-0.64	> 0.01
Mn	BS	mineral	-0.56	< 0.05	-0.61	< 0.01	-0.56	< 0.05
	Ca/Al		-0.56	< 0.05	-0.61	< 0.01	-0.56	< 0.05
	exchBC	organic	-0.57	< 0.01			-0.54	< 0.05
	Ca		-0.57	< 0.01			-0.54	< 0.05
	Mg		-0.68	< 0.01	-0.48	< 0.05	-0.64	< 0.01

Table 2.4. Correlation coefficients of concentrations ratios in sapwood to soil chemistry, by elemental fraction. Only significant (at $\rho > 0.05$) relations are shown.

Element	**Soil Variable**	**Soil Layers**	**Mobile Fraction**		**Residual Fraction**		**Total Fractions**	
			Spearman's ρ	*Prob>|ρ|*	*Spearman's ρ*	*Prob>|ρ|*	*Spearman's ρ*	*Prob>|ρ|*
Ca/Al	BS	mineral	0.61	< 0.01				
	Ca/Al		0.61	< 0.01				
	pH		0.46	< 0.05				
	exchBC	organic	0.63	< 0.01				
	pH		0.57	< 0.01				
Ca/Cd	exchAl	mineral	-0.45	< 0.05				
	EA		-0.59	< 0.01			-0.56	< 0.01
	CEC		-0.45	< 0.05				
	BS		0.70	< 0.001	0.58	< 0.01	0.68	< 0.001
	Ca/Al		0.70	< 0.001	0.58	< 0.01	0.68	< 0.001
	pH		0.61	< 0.01	0.59	< 0.01	0.60	< 0.01
	exchBC	organic	0.70	< 0.001			0.66	< 0.01
Ca/Mg	exchBC	organic	0.56	< 0.05			0.54	< 0.05
	pH		0.73	< 0.001	0.58	< 0.01	0.76	< 0.0001
Ca/Mn	EA	mineral	-0.49	< 0.05			-0.49	< 0.001
	BS		0.72	< 0.001	0.59	< 0.01	0.73	< 0.05
	Ca/Al		0.72	< 0.001	0.59	< 0.01	0.73	< 0.001
	pH		0.49	< 0.05			0.53	< 0.05
	exchBC	organic	0.68	< 0.001			0.69	< 0.001
	pH				0.52	< 0.05	0.45	< 0.05
K/Al	pH	organic	0.52	< 0.05				
K/Cd	EA	mineral	-0.53	< 0.05			-0.49	< 0.05
	BS		0.50	< 0.05	0.61	< 0.01	0.53	< 0.01
	Ca/Al		0.50	< 0.05	0.61	< 0.01	0.53	< 0.05
	pH		0.60	< 0.01	0.45	< 0.05	0.56	< 0.01
	exchBC	organic	0.58	< 0.01			0.54	< 0.05
	pH		0.46	< 0.05				
K/Mn	EA	mineral	-0.55	< 0.05			-0.50	< 0.001
	BS		0.66	< 0.01	0.58	< 0.01	0.69	< 0.01
	Ca/Al		0.66	< 0.01	0.58	< 0.01	0.69	< 0.001
	pH		0.65	< 0.01			0.58	< 0.01
	exchBC	organic	0.71	< 0.001	0.49	< 0.05	0.72	< 0.001
	pH		0.57	< 0.01			0.59	< 0.01
Mg/Al	EA	mineral	-0.46	< 0.05				
	BS		0.56	< 0.05				
	Ca/Al		0.56	< 0.05				
Mg/Cd	EA	mineral	-0.48	< 0.05			-0.46	< 0.05
	BS		0.60	< 0.01	0.55	< 0.05	0.62	< 0.01
	Ca/Al		0.60	< 0.01	0.55	< 0.05	0.61	< 0.01
	pH		0.50	< 0.05	0.49	< 0.05	0.48	< 0.05
Mg/Mn	exchBC	mineral	0.49	< 0.05	0.52	< 0.05	0.55	< 0.05
	BS		0.68	< 0.001	0.61	< 0.01	0.69	< 0.001
	Ca/Al		0.68	< 0.001	0.61	< 0.01	0.69	< 0.001
	pH		0.46	< 0.05				
	exchBC	organic	0.48	< 0.05				

Table 2.5. Correlation coefficient of tree growth (BAI = basal area increment) to sapwood and soil chemistry. Relations to soil variables used all tree cores and trunk disks (n = 84), while relations to elements in wood are restricted to disks (n = 20). Only significant (at $\rho > 0.05$) relations are shown.

Soil chemistry			
Soil Variable	Soil Layer	Spearman's ρ	Prob>$\vert\rho\vert$
CEC	mineral	-0.79	< 0.05
K	organic	0.79	< 0.05

Wood chemistry			
Element	Fraction	Spearman's ρ	Prob>$\vert\rho\vert$
K	mobile	0.62	< 0.01
	residual		
	total	0.61	< 0.01
K/Al	mobile	0.50	< 0.05
	residual		
	total		
Mg/Mn	mobile		
	residual	-0.46	< 0.05
	total	-0.48	< 0.05

CONCLUSION

Cette étude a permis de caractériser le comportement de plusieurs éléments chimiques dans le bois de l'érable à sucre et d'éclaircir leur potentiel pour la surveillance écologique de l'acidification des sols forestiers.

L'approche méthodologique utilisée dans ce cadre constitue une rareté dans le domaine. En effet, on ne retrouve dans la littérature scientifique que trois autres mentions antérieures (Balk et Hagemeyer 1994, Hagemeyer et Shin 1995, Herbauts et al. 2002) de ce type d'extractions séquentielles appliquées au bois d'un arbre, bien que le procédé ait été exploité pour l'analyse des sols (Allan et Roulet 1994, Berggren 1992) et des feuilles (Borer et al. 2004). Par contre, ces tentatives avaient été effectuées sur des espèces européennes. La présente recherche s'en démarque donc puisqu'il s'agit du tout premier essai concernant un arbre d'Amérique du Nord, nommément l'érable à sucre. De plus, la présence d'aluminium (Al) dans le bois des arbres, un élément indicateur d'acidification, n'avait pas été évaluée par les précédents auteurs.

La particularité de la procédure utilisée ici réside dans la gradation de la force des produits utilisés pour extraire les éléments du bois. L'échantillon de bois a d'abord été soumis à une solution au faible pouvoir extractant (ici, l'eau déionisée), ce qui a permis de retirer les éléments les plus mobiles et les plus faiblement retenus (fraction soluble). Ce même échantillon a ensuite subi une extraction à l'acide chlorhydrique pour extraire les éléments encore assez mobiles, mais moins que les précédents (fraction échangeable). L'ultime étape a consisté en une digestion totale du bois à l'acide nitrique, les derniers éléments ainsi extraits étant considérés comme fortement liés à la structure du bois et à toutes fins pratiques immobiles (fraction résiduelle).

Ainsi, en faisant appel à cette séquence d'agents extracteurs successivement plus puissants, la spéciation des éléments a pu être déterminée. Des distinctions importantes apparaissent à prime abord entre les éléments, résultant notamment de leur valence, et donc de leur capacité à se lier à la structure du bois. Les cations monovalents, divalents et trivalents se retrouvaient, respectivement, en majorité dans la fraction soluble, échangeable et résiduelle.

La répartition entre les trois fractions n'est toutefois pas constante, puisque pour certains éléments elle varie selon l'acidité du sol. L'aluminium (Al), le cadmium (Cd) et le manganèse (Mn) sont tous sensibles à cette variable environnementale. Il était déjà reconnu que le Mn était sensible au pH (Kogelmann et Sharpe 2006), Guyette et al. (1992) l'ayant notamment mis à profit pour déterminer le pH du sol dans le passé. Le Cd avait également montré une mobilisation et une absorption accrues suite à l'acidification du sol (Hutchinson et al. 1998). De même manière, les résultats de la présente étude révèlent que les concentrations de Cd et Mn dans le bois augmentent avec l'acidification du sol, à la fois dans les fractions mobiles et résiduelles.

La mobilisation de l'Al dans les sols acides avait été mentionnée il y a déjà un certain temps (Ulrich et al. 1980). Les concentrations d'aluminium dans le bois avaient alternativement été présentées comme réagissant aux variations d'acidité (Bondietti et al. 1989) ou comme y étant insensibles (DeWalle et al. 1991, 1999). Les présents résultats éclaircissent cette controverse, en démontrant que les concentrations d'aluminium mobile augmentent dans le bois de l'érable à sucre à mesure que le sol s'acidifie, alors que la fraction résiduelle ne varie pas selon l'acidité du sol. L'Al étant en général majoritairement retrouvé sous forme résiduelle, sauf en sol très acide, il n'est donc pas étonnant qu'il ait été fréquemment décrit comme un élément ne répondant pas aux variations de son environnement chimique, puisque ces études faisaient appel à des extractions totales qui masquent la réponse de l'Al dans le bois face aux variations de la chimie du sol. En ne s'attardant pas aux différentes fractions dans le bois, les précédentes études se privaient possiblement d’informations importantes.

En effet, la concentration totale d’un élément dans le bois suit de près la tendance de sa fraction majoritaire. Ainsi, le comportement du calcium échangeable est à toute fin pratique identique à celui de la concentration totale, tout comme le potassium soluble est une image fidèle du total de cet élément. Pour les cations monovalents et divalents, une extraction totale pourrait donc être appropriée à des fins de comparaison spatiale (e.g., entre sites, entre traitements), puisque les concentrations totales reflètent la fraction mobile, celle-là même qui réagit aux variations de la chimie du sol. Pour ces éléments, l’extraction totale ne pourrait cependant pas répondre aux questions concernant les conditions environnementales antérieures.

La croissance des arbres est inférieure en sol acide. Par ailleurs, une relation significative a été observée entre les concentrations de K dans le bois et la croissance des arbres, possiblement à cause d’un enrichissement en K dans les anneaux les plus actifs. Les concentrations des cations basiques (Ca^{2+}, K^{+}, Mg^{2+}) dans le bois des arbres étudiés ici n’étaient pas modifiées par les variations de l’acidité du sol. Pourtant, de nombreux travaux précédents ont fait état du lessivage hors de la zone racinaire causé par une baisse importante du pH du sol (Bondietti et al. 1990, Likens et al. 1996).

L’étude des fractions résiduelles (immobiles) des éléments dans le bois visait à retracer l’historique des dépôts atmosphériques acides ayant affecté les forêts. Ceci aurait eu le mérite de contourner le problème maintes fois mentionné de la mobilité des éléments due à la circulation de la sève dans l’aubier (Cutter et Guyette 1993, Hagemeyer 1993, Houle et al. 2002, Watmough 1997). En évaluant les tendances temporelles des concentrations dans le xylème des éléments étudiés, il appert que les pentes des droites des fractions résiduelles ne varient pas d’une manière pouvant être clairement attribuée aux conditions d’acidité du sol.

Étant donné le manque de relation entre la fraction résiduelle et la chimie du sol, la fixation dans le bois de l’érable à sucre serait possiblement un phénomène ultérieur à l’absorption des éléments. Toutefois, l’intervalle de temps nécessaire à ce processus demeure pour l’instant inconnu. L’éventualité d’une fixation survenant uniquement après ré-équilibration des éléments dans l’aubier, masquant ainsi tout signal temporel, oblitère forcément l’utilité de la fraction résiduelle. Néanmoins, une fixation rapide sous une forme immobile demeurerait un indice pertinent de l’environnement chimique historique pour certains éléments.

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