DENDROCHEMISTRY AND GROWTH OF THREE HARDWOODS IN THREE GEOLOGICAL REGIONS OF SOUTHERN QUEBEC FROM 1940-1999

by

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ABSTRACT

This thesis used novel methodologies in dendrochemistry to observe past nutrient and Al change in relation to incremental stem xylem growth to predict current and future forest health. The methods included (1) sequential digestion of wood tissue to remove the elemental fraction that is mobile across tree rings leaving the structurally intrinsic, residual (or less mobile) ion fraction for analysis and (2) transformation of elemental concentrations into multivariate ratios (compositional nutrient diagnosis (CND)) over a time series. Sampling of trees represented a gradient in acidity resilience using three regions of southern Quebec (St.Lawrence Lowlands; Lower Laurentians; and Appalachian Highlands) and three species (red maple (*Acer rubrum* L.); sugar maple (*Acer sacharum* Marsh.); and American beech (*Fagus grandifolia* Ehrh.). The elemental residual fraction had differences from the mobile fraction over time for Ca, Mg and Mn, but not for K or Al. The base rich Saint-Lawrence region had the highest and slightly increasing incremental stem xylem Al of the regions yet had stable or increasing growth. By contrast the acid sensitive Appalachian region had the greatest increase in Al accompanied by a decrease in growth beyond 1970. The Appalachians also had the highest Mn, which had an adverse effect on growth of sugar maple. The acid-resilient species American beech had stable or decreasing Al while having stable or increasing growth in contrast to the less resilient sugar and red maple. The nutrient poor Laurentian region had a persistent deficiency of K over time but no relationships with Al. Aluminium had a general negative correlation with the other cations. Although Mn had the highest levels in red maple for each region, it appears to be limiting growth. The changes in wood chemistry and growth over time appear to be driven by the resilience of the region or species to increasing acidic load in the ecosystems.

RÉSUMÉ

Cette thèse utilise de nouvelles approches dendrochimiques pour observer les changements passés de la disponibilité des nutriments et de l'aluminium en relation avec les changements de la croissance radiale des arbres et ainsi permettre de prédire la croissanve/vigueur future de la forêt. Les méthodes incluent (1) une digestion séquentielle du bois pour enlever la fraction mobile des éléments et mesurer les concentrations des éléments faisant partie intrinsèque ou résiduel du bois et (2) l'utilisation dans les séries temporelles des composantes fractionnaires (compositional nutrient diagnosis ou CND). L'échantillonnage des arbres a été fait pour étudier un gradient de résistance à l'acidification en utilisant trois régions du sud du Québec (basses terres du Saint-Laurent); les Basses Laurentides; et les Appalaches) et trois espèces d'arbres (érable rouge (*Acer rubrum* L.); érable à sucre (*Acer saccharum* Marsh.); et le hêtre d'Amérique (*Fagus grandifolia* Ehrh.). Les changements temporels de la fraction résiduelle différaient de la fraction mobile pour le Ca, Mg et Mn mais pas pour le K et Al. Les basses terres du Saint-Laurent avec leurs sols riches en cations basiques avaient le xylème le plus élevé en Al avec des valeurs croissantes dans le temps mais une croissance stable ou croissante. Les Appalaches avec leurs sols sensibles à l'acidification avaient les plus grandes augmentations en Al, les valeurs les plus élevées en Mn et des croissances décroissantes pour l'érable à sucre après 1970. Le hêtre, une espèce bien adaptée aux conditions acides, avait des niveaux stables ou décroissants en Al et une croissance stable ou croissante. Les Laurentides avec leurs sols pauvres avaient des déficiences persistentes en K mais ne présentaient pas de relations significatives avec l'Al. Même si le Mn était le plus élevé chez l'érable rouge, il semble qu'il était déficient en cet élément. Les changements de la chimie du bois semblent être liés à la résilience du sol/substrat des régions et des espèces aux dépositions atmosphériques acides.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

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CHAPTER I
GENERAL INTRODUCTION

1. Overview

The forests of southern Quebec have been studied extensively in regard to acidic deposition and more specifically the forest decline of the 1980s (Côté and Ouimet 1996). Forests in southern Ontario and northeastern United States of America have also been studied with a similar regard (Drohan et al. 2002; McLaughlin 1998; Mohamed et al. 1997; Shortle et al. 1997). These forests are mostly hardwood or mixed-wood stands. Acidic deposition, with the consequence of soil acidification and base cation leaching, is seen as a likely predisposing cause to this decline, in combination with known decline initiators such as natural climatic events and insect epidemics (Côté and Ouimet 1996). Forest decline is typically diagnosed from noticeably diminished crown condition and increased incidence of mortality. An earlier indication, though, is a decrease in growth noted in the incremental tree rings (generally a retrospective discovery) prior to obvious crown effects (Duchesne et al. 2003). In Quebec, this forest decline event began visibly *circa* 1980, primarily affecting sugar and red maple, with other species such as American beech being less affected. By possible explanation, sugar and red maple are known to be more sensitive to acidity than American beech.

The decline continues and has varied temporally and spatially between regions. In southern Quebec, the Appalachian Highland region (being south of the Saint-Lawrence River) was more greatly impacted than the Lower Laurentians (north of the Saint-Lawrence River) while the Saint-Lawrence Lowland area (located between the two previously mentioned) has had minimal impact (Côté and Ouimet 1996). The primary difference between the regions is in the underlying substrates (Gagnon et al. 1994) which in conjunction with deposition load should predict susceptibility to acidification (Ouimet et al. 2001).

Various combinations of soil, foliar and tree ring elemental analyses (amongst other methods) have been used to examine environmental change while using various tree species, elements and time frames (Bailey et al. 2004; Bernier and Brazeau 1988; Bondietti et al. 1989; Cote and Camire 1995; Cronan and Grigal 1995; DeWalle et al.

1999; Drohan et al. 2002; Duchesne et al. 2002; Heisey 1995; Hendershot and Belanger 1999; Horsley et al. 2000; Kolb and McCormick 1993; Likens et al. 1996; Ouimet et al. 2001; Shortle et al. 1997; Timmer and Teng 1999; Watmough 2002). Amongst these studies, significant relationships between wood chemistry and forest health have been found. In particular the adverse relationship between forest health and increasing levels of available aluminium is reiterated throughout several of these studies. In a recent re-analysis of some previous studies, manganese toxicity was suggested as an additional factor contributing to reduced sugar maple growth and therefore should be further researched (Timmer and Teng 1999). Manganese, although a nutrient, may increase to toxic levels (for some plants) under acidic conditions similarly to aluminium. Mass flow of Mn, dependent on ambient soil concentrations predicts Mn concentration in xylem as opposed to Al concentration which depends on a tree species' ability to restrict Al uptake (Graham et al. 1988).

In regard to anthropogenically-driven environmental change, there is a need for long-term monitoring of forest stands and their soils (McLaughlin 1999). Dendrochemistry has been developing towards this goal and recent advancements help make it a possible monitoring method. Studies have shown wood chemistry in significant relationships with tree growth, soil and/or foliar chemistry, and environmental impacts (Abrams 1998; Hutchinson et al. 1998; McLaughlin 2002; Watmough 1997). An examination of a forest stand through extraction of increment cores and their elemental analysis can reveal long term trends and short term aberrations of climate, atmospheric composition, atmospheric deposition, soil acidity, base and acid cation availability, amongst other factors (Schweingruber 1996; Smith and Shortle 1996). A basic assumption of these results is that the ambient environment (i.e. soil and atmosphere) was recorded in the annual tree ring which grew at the time of impact and that this result remains intact in that ring. In the past, this assumption was managed by choosing species or elements with known minimal mobility (across rings) after impact (Cutter and Guyette 1993). Another coping strategy was to analyse whole cores or large time segments to dilute the possible effect of mobility (Côté and Camiré 1995; Watmough 2002). Only recently has a method been developed to give more reliable results and the potential to lessen or remove these constraints. This method is the sequential digestion of the wood such that the mobile (i.e. soluble and/or exchangeable) proportion of each element is separated from that which is immobile (or residual) (Herbauts et al. 2002). The residual fraction is assumed to be free of the influence of environmental change since the time of formation of each ring.

This thesis is inspired by the incidence of acidic deposition and also the recent forest decline in southern Quebec, as differences were noted in the degree of impact among regions as well as tree species. In this work I propose to identify long term trends of nutrient, base cations (calcium, magnesium, potassium, manganese) and the non-nutrient, acid cation, aluminium, and their relationships to growth in the incremental wood xylem. Manganese will be discussed from both basic and acidic viewpoints. Three tree species that were notably affected by forest decline will be studied: sugar maple, red maple and American beech. Three regions of southern Quebec, with differing resilience to soil acidification will be used. The time period of 1940-1999 will be considered as it encompasses the 'before and after' effect of the increase and decrease in acidic deposition. Individual trees will be chosen by physiologic age to form a cohort that is expected to be experiencing positive growth, in the maturation phase of growth. The novel methodology of sequential digestion in combination with the transformation of elemental concentrations to multivariate values with the Compositional Nutrient Diagnosis approach will be used and discussed.

2. Literature review

2.1 Atmospheric deposition, regional soil/geology and critical load

Acidic deposition is the result of various anthropogenic activities with the result of wet and dry deposition of nitrous and sulphurous materials affecting forests and their soils. The general result is leaching of base cations, with subsequent soil acidification. An increase in acidic deposition occurred after the Second World War, with even higher acidity loads into the 1970s (Cogbill 1976). Since legislation to reduce acidic emissions came into effect in the 1980s, sulphurous compounds have decreased, while nitrous compounds have remained stable or increased (Driscoll et al. 1989). Acidic deposition is of concern as some soils and lakes are prone to acidification which may adversely affect their biota.

The time of impact of both point source and regional air pollution have been solidly evidenced in the chemistry of tree rings (Watmough 1997). Recent studies have shown that soil acidification resulting from increased H_2SO_4 and HNO_3 deposition has greatly affected the chemical composition of some forest soils. The increase in soil acidity due to acidic deposition has led to significantly increased aluminium mobility and base cation depletion through leaching (Likens et al. 1996). McLaughlin (1998) found that since the mid-1970s, Al had doubled in sugar maple tree rings growing on acid sensitive soils in Ontario. On similar soils, declining maple trees had higher Al concentrations than healthy trees (Mohamed et al. 1997). No such relationship existed on acid tolerant soils. In similarly sensitive Quebec soils, sugar maples experiencing decline had an Al/K ratio in tree rings that had tripled since about the 1960s (Côté and Camiré 1995). Ouimet et al. (2001) measured the critical load of tolerance to acidic deposition of soils in various areas of Quebec and found some in danger of approaching or already experiencing exceedance.

2.2 Dendrochemistry

2.2.1 Retranslocation of elements

Radioactive isotopes of elements from nuclear explosions or volcanic eruptions have served as good specific time point sources in dendrochemical analyses. Kagawa et al (2002) used the 1945 nuclear bombing of Japan as the time origin of the introduction of ^{137}Cs and ^{90}Sr into the environment of Japanese cedar (*Cryptomeria japonica* (L. f.) D. Don) and Japanese persimmon (*Diospyros kaki* Thunb.). ^{137}Cs was detected in tree rings formed before 1945, indicating retranslocation of Cs. In contrast, the activity of ^{90}Sr in the Japanese cedar showed the highest level in 1945, due to the relatively immobile characteristics of Sr compared with Cs.

The chemistry of a tree ring is made up of elements fractioned between those relatively immobile within the structure of the wood and those mobile by being soluble or held on exchange sites. The concentration of the immobile fraction of a given year is dependent not only on that year's sap stream composition but also on the soluble and exchangeable fractions of older or younger conducting rings. The mobile fraction is in flux dependent on concentrations equilibrating throughout the conducting rings and also on the activity of the ray cells to transport specific elements (Brownridge 1984; Frelich et al. 1989). The changing contribution of the mobile fraction therefore has the ability to alter the total of the concentrations of the mobile and immobile fractions for any given year. This total is the reference value used in all but one study using tree ring chemistry.

Trees may develop heartwood rings in the oldest rings as compounds such as phenolics are transported and deposited to protect wood from potential pathologies by creating occlution to sap flow. This deposition affects the chemical signature of these rings as it occurs at a time other than that of ring formation. Radial retranslocation of elements along ray pathways may continue across the developing heartwood boundary. Many element trends in various species show a large difference in concentration at the transition of the heartwood rings into actively conducting outer rings known as sapwood (De Visser 1992; Momoshima et al. 1994; Momoshima et al. 1995).

2.2.2 Species choice

Cutter and Guyette (1993) conducted a survey of species previously studied in dendrochemistry to formulate guidelines for species choice and also to suggest specifically suitable species. They recommend that a tree species is suitable if it is long-lived; grows on a wide range of sites over a large geographic distribution; has distinct heartwood with a low number of rings in the sapwood; has low heartwood moisture content; and has low radial permeability. Only American beech (*Fagus grandifolia* Ehrh.) was recommended out of the three species of this master's thesis. With analysis in this study pertinent to only the residual fraction, the restrictions relating to heartwood and radial permeability have less pertinence. The autecology of sugar maple (*Acer saccharum* Marsh.) and red maple (*Acer rubrum* L.) agree with the guidelines of distribution and lifespan in the forests of southern Quebec (Farrar 1995).

2.2.3 Element choice

Macro- or micro- nutrients for trees of considerable concentration within the wood xylem are calcium, magnesium, potassium, manganese and iron although many others are detectable. Aluminium (and Mn as suggested by Timmer and Teng 1999) content is of interest as it acts antagonistically towards the uptake of base nutrient cations.

Al and Fe are less mobile than Ca, Mg, K and Mn across tree rings and give more reliable results but yet may be less sensitive indicators of subtle soil chemical changes than others such as Mn in regard to acidification (McClenahen et al. 1989). Again, with analysis based on the residual fraction of elements, the reliability of all elements to represent the year of impact should be improved. The six elements mentioned will be analysed in this thesis.

Relationships between base and acid cations have been linked to forest health. Cronan and Grigal (1995) found that the calcium/aluminium (Ca/Al) molar ratio of the soil solution provides a valuable ecological indicator of forest damage arising from Al stress accompanied by increases in nutrient imbalances. Heisey (1995) also found a significant relationship between the Ca/Al ratio and sugar maple growth. Hendershot and Bélanger (1999) included a review of this topic.

Timmer and Teng (1999) suggested that Mn toxicity may be adversely affecting sugar maple growth; perhaps even more importantly than Al. Through vector analysis of previously published works of other researchers on sugar maple growth and foliar chemistry from Pennsylvania forests and a greenhouse study, they suggested that soil Mn may be antagonistically limiting uptake of Ca and Mg. In addition, increased foliar Mn may be inhibiting internal transport of Ca and Mg. Mn availability in the rhizosphere depends on a multiplicity of factors. A change of Mn concentration in tree foliage or rings may reflect a change in various soil components/conditions such as: anaerobic conditions, nitrogen (N) source/form, Fe and Al availability, base cation availability, soil acidity; and mycorrhizal populations (Graham et al. 1988). Mn has been shown to be a sensitive indicator of soil pH (Guyette et al. 1992) and low soil pH has also been related to slow tree growth (Watmough 2002). Soil liming (Houle et al. 2002) and artificial acidification (DeWalle et al. 1999) trials have shown significant responses in tree ring Mn, with decreases in the former and increases in the latter. St.Clair and Lynch (2004) tested Mn toxicity in seedlings of sugar maple and red maple in conjunction with high light levels (as canopy or gap leaves would experience) and deduced that both species were sensitive to high Mn availability. The effect on American beech is unknown.

2.2.4 Time period choice

In numerous studies, a marked change in incremental growth and/or elemental composition was observed to coincide with increased acidic deposition rates around 1950 or 1960 in North America and to depend on site or regional characteristics (McLaughlin 1999). A study with red spruce showed mobilization of base cations followed by depletion, being generally concurrent with an increase in incremental growth followed by a decrease (Bondietti et al. 1992). Ouimet et al. (2001) noted that from 1972-1990 northern hardwood stands in southern Quebec on sites sensitive to acidification from atmospheric deposition experienced a growth rate 30% lower than less affected sites, perhaps indicating a response to decreased cation availability. In order to encompass these noted time frames, this thesis will include analysis from 1940 to 1999.

An effective division of this 60-year time period into incremental time segments has some precedents: Côté and Camiré (1995) used 15 year increments while others used one (Bondietti et al. 1989; Duchesne et al. 2002) two, five (Frelich et al. 1989) or ten (Shortle et al. 1995) year periods. A large grouping of years yielding few increments over a total time period may show an increasing or decreasing trend, but definition could be lost for short term trends within these large time increments. By contrast, an analysis based on every annual ring would have definition beyond the needs of this thesis. A grouping of five to ten years is a median between these ranges and a combination of them will be used here for both efficiency and economy of analysis.

2.2.5 Element extraction

Extractions of elements from wood have been accomplished primarily by complete digestions in acid (Bondietti et al. 1992; Côté and Camiré 1995; DeWalle et al. 1999; Watmough and Hutchinson 1996). Some studies have used nuclear analysis techniques (e.g. PIXE; XRAY; neutron activation) which extract and analyse simultaneously (Legge et al. 1984; McClenahen et al. 1989; Mohamed et al. 1997). With either method, a reading is made of the total element content (i.e. sum-total of mobile and residual proportions). Cutter and Guyette (1993) suggested an extraction methodology to remove deposits of heartwood compounds prior to a complete digestion through a series of preliminary washes. No reference to, or methodology similar to their suggestion has been noted in the literature until 2002 by Herbaut et al. (2002). They used sequential extractions of water then $SrCl_2$ to produce speciation of water soluble and exchangeable fractions. A replicate of the sample was totally digested. The residual fraction was calculated by subtracting the soluble and exchangeable fractions from the total digest. Their results generally showed significant differences over time between water-soluble cations, cations adsorbed on exchange sites, and non-exchangeable cations.

Most early dendrochemical studies used atomic absorption spectrometry (AAS) to detect elements in digests of tree rings. More recent studies have used inductively coupled plasma - mass spectrometry (ICP-MS) and inductively coupled plasma – atomic emission spectrometry (ICP-AES). The sample preparation for both ICPs is similar to AAS, but the number of elements that can be analysed per sample is greater, and detection levels are lower (Watmough 1997). ICP-AES will be used in this work.

2.2.6 Relationship to foliar and soil chemistry

Attempts have been made to correlate a static view of element concentrations within the soil and/or foliage to that of associated wood in order to model a historic view (Heisey 1995; Momoshima 1995; Shortle et al. 1997; Watmough et al. 1999). Mohamed et al. (1997) took sugar maple cores from sites with differing forest soil types and health status in Ontario and then analysed each whole core. These cores showed a significant relationship with Al concentrations in the soil and also an adverse relationship between health status and Al concentration (soil and xylem).

Soil pH has been related to wood elemental concentrations (Guyette et al. 1992) with low soil pH being generally related to low wood Ca (Watmough 2002) but higher levels of Al and Mn (DeWalle et al. 1991; Hutchinson et al. 1998).

2.3 Detecting nutrient change through elemental concentrations, ratios or composite ratios

Most research on tree ring chemistry has used simple concentrations of elements to infer diagnoses. The dilution effect on concentrations by differential growth between samples may be a problem. A more pertinent signal of elemental change is found in the use of element ratios as they are unitless (i.e. no dilution effect) and give a relative view of change of one element against another (e.g. Al/Ca). Multiple bivariate ratios give a broader, more comprehensive view of the relative significance of specific elements changing over time against each other (e.g. diagnosis and recommendation integrated system or DRIS) (Beaufils 1973.). In order to see elements changing within the composition of all given elements, each concentration must be presented as a changing component within the changing composition. This is possible with the method developed by Parent and Dafir (1992) for nutrient diagnosis of agricultural crops: Compositional Nutrient Diagnosis (CND). CND will be applied to concentrations in this thesis and further explained in chapter II.

3. Hypotheses and objectives

3.1 Hypotheses

- The pattern of change over time of mobile and residual elements is different.
- The pattern of change over time of elemental concentrations and CNDs is different.
- There are regional and interspecific differences in nutrient cations and Al levels of the residual fraction of stem xylem.
- The base cation rich Saint-Lawrence Lowlands has experienced smaller elemental change than the nutrient poor and acid-sensitive Appalachians or Laurentians; I expect a greater decrease in base cations with an associated increase in acid cations (Al and Mn) in the latter two regions relative to the first.
- The more acid tolerant American beech will have less elemental change than either of the acid-sensitive sugar maple and red maple. I expect an increase in Al and/or Mn in the acid sensitive species.
- Regions and/or species with larger acid cation increases will be characterized by decreasing tree growth.

3.2 Objectives

- To test alternative dendrochemical methodologies in order to decrease interference resulting from mobility of ions across rings and dilution of ion concentration by differential growth.

- To better enable regionally-based predictions of change in Quebec's hardwood forests in relation to nutrient status, health (as shown by growth) and therefore ultimately, species composition.

CHAPTER III

MATERIALS AND METHODS

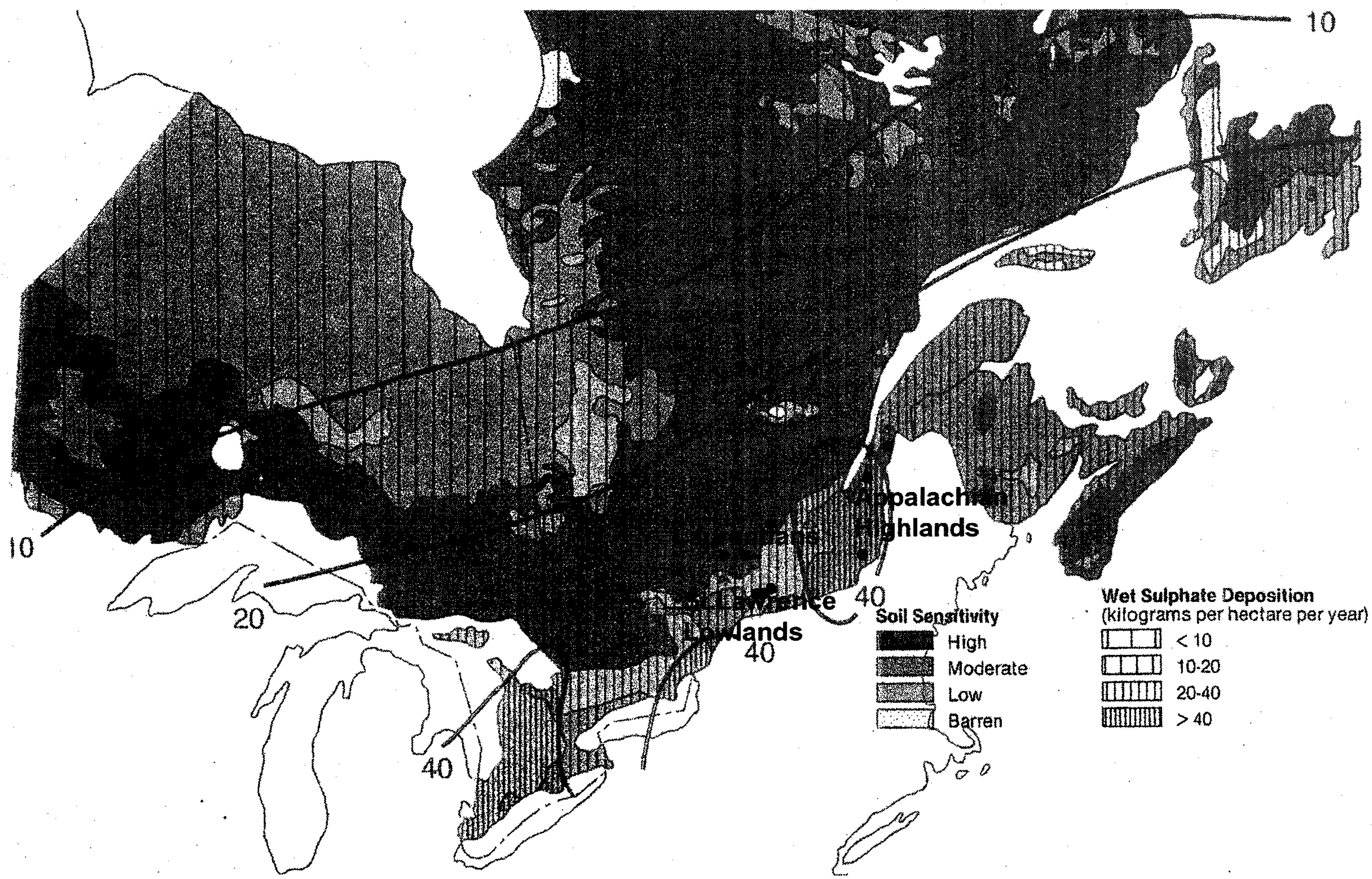
1. Study regions

Three distinct geological regions of southern Quebec were chosen for this research based on their inherent sensitivities to acidic deposition as predisposed by differing parent material. The chosen regions, with their associated parent materials are:

- Appalachian Highlands with ultra-basic, orogenic bedrock with a till of sedimentary, schist (shale) or acid granite
- Lower Laurentians on the Canadian Shield with an acid bedrock and till of gneiss (metamorphic – similar to granite) or schist
- Saint-Lawrence Lowlands with sedimentary marine deposits.

In the 1986 Environment Canada risk assessment map (Figure 1), the Saint-Lawrence region had the least sensitive soil to acidic deposition and received moderate amounts of wet sulphate deposition. Similarly, the Laurentians received moderate amounts of deposition, but on highly sensitive soil. The Appalachians received the highest level of deposition but had less sensitive soil than the Laurentians, but more sensitive than the Saint-Lawrence Lowlands (Bird and Rapport 1986). Although the difference between the sensitive regions cannot be quantified, they can be considered to differ qualitatively from the lesser impacted Saint-Lawrence. Ouimet et al. (2001) identified the Laurentian and Appalachian regions as exceeding their abilities to absorb acidic deposition while the Saint-Lawrence region was below its critical level.

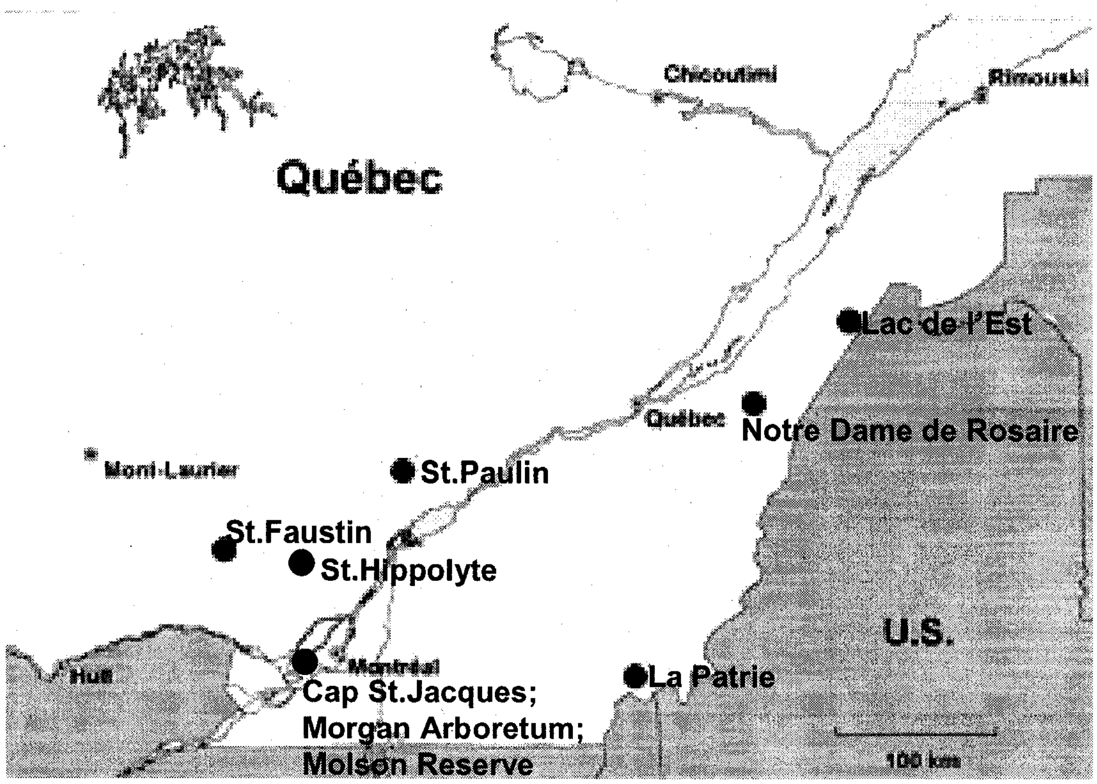
Figure 1: Regions/sites superimposed on wet sulphate deposition (snow and rain) and soil sensitivity to change in base cation nutrient status in Eastern Canada *circa* 1985 (after Bird and Rapport 1986).



2. Study sites

Three sites were selected within each region. Each site had no known or obvious forest management since at least 1940, and has sugar maple as the dominant species with American beech and red maple as secondary species (Figure 2). The Appalachian Highlands sites being on ultrabasic bedrock also had high manganese in the elemental composition of sugar maple foliage (Gagnon et al. 1994).

Figure 2: Study sites (adapted from Duchesne et al. 2002).



The majority of sites are on Crown lands protected by the Canadian province of Quebec under the Forest Ecosystem Research and Monitoring Network (RESEF) while the remaining sites are managed as research forests by McGill University, University of Montreal or as part of a public park by the Montreal Urban Community (MUC). Site characteristics are given in Table 1.

Table 1: Site characteristics.

Study sites	Main tree sps.	Stand age	Soil type	Parent material	Lithology	pH ~0-20cm	Prec. mm $year^{-1}$	Mean °C	Lat./Long
Saint-Lawrence									
Molson Reserve (McGill)	Acer sacch.	80	PHF.O	Fluvial sand	Unknown	neutral	930	6.2	45° 25'N/73° 57'W
Morgan Arboretum (McGill)	Acer sacch.	100	PHF.O	Fluvial sand	Unknown	4.1-5.5	930	6.2	45° 25'N/73° 57'W
Cap.Saint-Jacques Park (MUC)‡	Acer sacch.	100	PHF.O	Fluvial sand	Unknown	n/a	930	6.2	45° 25'N/73° 57'W
Laurentians									
Saint-Hippolyte	Acer sacch.	125	PFH.O	Shallow till	Anorthosite	3.8-4.8	1150	3.9	45° 59'N/74° 01'W
Saint-Paulin	Acer sacch.	110	PFH.O	Shallow till	Gneiss	3.8-4.9	840	3.9	46° 27'N/73° 04'W
Saint-Faustin‡	Acer sacch.	90	PFH.O	Shallow till	Anorthosite	4.6-4.9	900	3.9	46° 03'N/74° 28'W
Appalachians									
La Patrie	Acer sacch.	80	PHF.O	Till	Schist	3.2-3.5	1130	n/a	45° 22'N/71° 14''W
Notre Dame de Rosaire	Acer sacch.	130	PHF.O	Shallow till	Schist	3.3-4.2	990	n/a	46° 51'N/70° 27'W
Lac de l'Est‡	Acer sacch.	125	PHF.O	Shallow till	Shale	n/a-4.9	870	n/a	47° 14'N/69° 34'W

PHF: podzol ferro humic ortho
‡ Site not included in data analysis
After: Boucher and Côté 2002; Courchesne et al. 2005; Gagnon et al. 1994; Ouimet et al. 2001, and personal communication with G. Larocque.

3. Tree species

Species were chosen to represent a gradient in response to soil acidity. Red maple and sugar maple are both considered acid sensitive species while American beech is considered acid tolerant (Dewalle et al 1999) and is commonly intermixed with maples. Prior to European colonization, American beech was amongst the dominant species of southern Quebec (Duchesne et al. 2005). Since then the maples have increased to dominance in the composition of some stands through anthropogenic interactions such as selective tree cutting (Côté and Ouimet 1996). The maples prefer slightly acid soils but will establish on more acid soils (Burns and Honkala 1990) with sugar maple out-competing red maple for mesic conditions and leaving red maple to establish on wetter or drier areas (Abrams 1998; Burns and Honkala 1990). All three species have good ecological amplitude in southern Quebec (Gagnon et al. 1994).

4. Field sample collection

Within each site 20 trees of each species were chosen from co-dominant individuals with a live-crown ratio of at least 1:3. An additional requisite was no obvious signs of major stem, bark or limb damage, fungal infection or major change in a tree's surroundings for approximately the past 60 years (i.e. road; cut or fallen trees). Individuals with a diameter at breast height (DBH) between 25 cm and 65 cm were chosen to ideally reduce variance due to age. Tree measuring and sampling were in June and September of 2003.

Cores were extracted from each tree with a 5.1 mm diameter Suunto or a 4.3 mm diameter Haglof increment borer. The cores were taken at a height of approximately 1.3 m from ground level on the south side of each tree, if possible. Two cores were extracted 1-2 cm apart, vertically proximate to one another and bored to the pith of the tree in order to yield chronological age. Cores were transferred to plastic 'MacDonald's restaurant' straws directly upon extraction, put as soon as possible on ice in the field, and then to a freezer at -20° C until analysis. The borers were cleaned by brushing with methyl alcohol regularly during each field day. The diameter of each tree was measured where cores were extracted for transformation of ring width to basal area increment.

5. Increment core analysis

5.1 Growth measurements

Cores were visually assessed for physical damage and/or fungal invasion. Many cores were broken into numerous pieces by the coring process and were therefore excluded. One core from each pair per tree was analysed for growth. This core was secured in a wooden vice with its vessels aligned vertically and was sliced horizontally (i.e. lengthwise) with a stainless steel blade to reveal annual growth rings while preserving as much of the original core matter as possible. The sliced core was digitally scanned to record the image of the incremental rings. The ring widths from bark edge to central pith ring were measured digitally in WinDENDRO™ (Regent Instruments, 2003) to the nearest 0.001 mm.

In order to verify that any missing or double rings were accounted for in the chronology, each individual tree chronology was compared to its reference chronology based on the mean of its species and site combination. Crossdating in WinDENDRO™ is facilitated by the automatic calculation of a percentage of similarity between chronologies. No missing or double rings were found in any of the chronologies. According to Lorimer et al. (1999), in dominant sugar maple trees, ring anomalies are rare, with a mean percentage of 1.3. All the sugar maple trees in this thesis are dominant or co-dominant, as are the red maples and American beech trees, minimizing the occurrence of anomalies. In addition, a comparison of the sugar maple chronologies with the published chronologies of five RESEF sites in common with this thesis (Duchesne et al. 2002) yielded concurrence.

5.2 Growth and physiological age assessment

Individual trees will be chosen by physiologic age to form a cohort that is expected to be experiencing positive growth, in the maturation phase of growth.

To determine growth, the confounding effect of increasing DBH on ring was removed by transforming the ring width into basal-area increment by the formula:

$$BAI = 3.1416\,(R^2_n - R^2_{n-1})$$

where R is the tree radius (DBH*0.5) and n is the year of tree ring formation.

A distinct range of age-since-release was desired for the selected sample sets in order to minimize variation in age-growth relationships associated with suppression periods. A graphical analysis of BAI revealed the year of growth release for each tree in order to determine physiological age (i.e. age since release). For sugar maples, release was considered as the first year of the 20 year period with a BAI = 2 cm^2 or more for every year (Duchesne et al. 2003). A physiological age range of 63-99 years was chosen to constrain this parameter and yet leave a sufficiently large sample set of the various sites and species. The mean age since release was 73 for sugar maple and red maple and 74 for American beech. In the case that more than 10 trees were suitable by age selection (per species per site), then a comparison to the average BAI of that species on that site was used to exclude trees with greater short term growth aberrations, indicative of a subsequent release or suppression episode to the original release.

As a result of the application of this criterion, samples from Cap Saint-Jacques and Lac de l'Est were excluded from further analysis. The Saint Faustin site was excluded from further analysis because of poor condition of the majority of the cores. From the original sample set of 540 trees, only 150 met all the criteria to be included in the chemical analysis. One sample was subsequently destroyed. The breakdown of these trees by site (given region) and species is given in Table 2.

Table 2: Number of trees analysed by region, species and site.

	Sugar maple	American beech	Red maple	Total
Laurentians				
Saint-Paulin (RESEF)	10	10	9	29
Saint-Hippolyte (U of M)	10	7	8	25
Saint-Faustin (RESEF)‡	(6)	(2)	Ø	(8)
Sub-total	20	17	17	54
Appalachians				
La Patrie (RESEF)	10	10	11	31
Notre Dame du Rosaire (RESEF)	5	4	Ø	9
Lac de l'Est (RESEF)‡	(6)	Ø	Ø	(6)
Sub-total	15	14	11	40
Saint-Lawrence Lowlands				
Morgan Arboretum (McGill Univ.)	10	10	7	27
Molson Reserve (McGill Univ.)	10	10	8	28
Cap Saint-Jacques (MUC) ‡	(10)	(6)	Ø	(16)
Sub-total	20	20	15	55
Total	55	52	43	149

Ø: species not present on site; ‡: subsequently not included in analyses

6. Sample preparation and elemental analyses

6.1 Core segment preparation

A digital calliper (calibrated to 0.01 mm) mounted on a plastic vice was used to identify each time period and allow for separation into discrete time periods based upon the measurements made with WindDendro™2003b (Régent Instruments 2003). The chronosequences were separated into ten increments: 1940-49, 1950-59, 1960-64, 1965-

69, 1970-74, 1975-79, 1980-84, 1985-89, 1990-94, and 1995-99. Each incremental segment was then chopped into fine disks (i.e. < 0.5 mm) with a Teflon coated carbon steel microtome blade. The chopped segments were air dried before being weighed into 100 mg random samples. Some segments weighed less than 100 mg and the whole chopped segment was used.

6.2 Sequential digestion

In order to remove the soluble or exchangeable fraction of each element from a sample, it was placed in a 5 ml capped tube with 5 ml of 0.05 M hydrochloric acid (HCl) and shaken at 200 RPM for five hours. The extract was removed and preserved at 5° C. The remaining 'washed out' segment sample was air dried *in situ* for at least 24 hours and then transferred to 10 ml digestion tubes. Two ml of 16.7 N nitric acid (HNO_3) were added to the sample material and heated in blocks to 100° C. for six hours or until the digest was colourless. The resulting digest was diluted with double deionized water to a total volume of 10 ml for analysis. A preliminary trial was conducted to measure the mobility of each element and to compare the change in concentration over time of each fraction. The subsample used was made up of ten sugar maple from La Patrie, three from Saint-Paulin and three from the Molson Reserve (3), 11 red maple and 10 American beech from La Patrie.

Herbauts et al. (2002) used similar, yet different methods to reveal the various fractions and total concentration. They deduced the value of the residual (or non-exchangeable) fraction as the difference of the sum of the water soluble and exchangeable fractions from the total concentration. The residual values were noted graphically but not analysed for relevance to the hypothesis of an environmental influence on the decreasing radial trend of base cations: hence, the novelty in this thesis of the use of the residual fraction for that purpose.

6.3 Elemental analyses

The initial 410 samples had both the HCl (i.e. mobile element fraction) and HNO_3 (i.e. immobile fraction) extract analysed for elemental content. The initial interpretations of long term trends of both fractions were similar and therefore the balance of the samples (1,785) had only the HNO_3 digest analysed. Analysis was done by inductively coupled plasma emission spectrometry for Ca, Mg, K, Mn, Al and Fe or Sr.

Iron was analysed for only the first 39 increment cores as contamination was suspected from processing tools containing iron (e.g. increment borer and knives). See Appendix I for results and discussion of Fe.

7. Computation of multivariate element ratios

When elemental analysis is based on simple concentrations or bivariate ratios of concentrations (i.e. Diagnosis and Recommendation Integrated System (DRIS)), there is an inherent dilution effect due to differential growth. Compositional Nutrient Diagnosis (CND) removes this effect. CND has been used for numerous studies of field and greenhouse crops as well as a few perennial crops (Parent et al. 1995). Recently Vizcayno-Soto and Côté (2004) and Quesnel (2004) used CND to develop foliar nutrient standards and apply them to trees/forests for nutrient diagnoses. This thesis will not endeavour to develop stem xylem nutrient standards (although it may be possible) but will track relational change in elements over time.

In CND analysis, a unit mass of plant tissue (e.g. 1 gm) is considered to be made up of its component elements which sum to the equivalent mass of 1000 mg. A change in the contribution to the sum by any one element will cause a relative change in the concentration of all other elements. This is known as the "bounded sum constraint" (Aitchison 1986). Elements of interest are specified and the balance of unknown values (i.e. unspecified elements) is represented collectively by a filling value "R" to maintain the bounded sum constraint. The filling value is calculated as follows when concentrations of Ca, Mg, K, Mn and Al are expressed in mg/g:

$$R = 1000 - (Ca+Mg+K+Mn+Al)$$

Then, log-centered ratios (v scores) are calculated using a geometric mean (g):

$$g = (Ca*Mg*K*Mn*Al*R)^{1/6}$$

and the following formula is used to compute a V score (e.g. V_{Ca})

$$V_{Ca} = \ln([Ca]/g)$$

Where [Ca] is the concentration in Ca.

8. Data analysis

The effects of tree species, regions and time and their interactions were tested using ANOVAs with repeated measures over time for the dependent variables (BAI, elemental concentrations and CNDs). Significant effects of regions and species were further explored using the Least Significant Difference (LSD) test.

The rate of change in acid cations (Mn and Al) and the rate of change in tree growth of each species were used to assess the evolution of tree ring chemistry and growth at each site. To this end, the slopes of tree growth over time (1970-99) were plotted against the slopes of V_{Mn} and V_{Al}.

Within time period variation of tree ring chemistry and growth was analyzed through forward stepwise regressions to identify elemental CND values that were significant predictors of BAI for regions and species. Time periods from 1975-79 to 1995-99 were analyzed. Observations outside two standard deviations range around the mean were removed before analysis.

A mean of the time period of 1975-99 was used to analyze variation of tree ring chemistry and growth through forward stepwise regressions to identify elemental CND values that were significant predictors of BAI for regions, species and species by region.

A 5% probability level was set for significance. All statistics were computed with the statistical program Statistica 6.1 (StatSoft 2004).

CHAPTER III

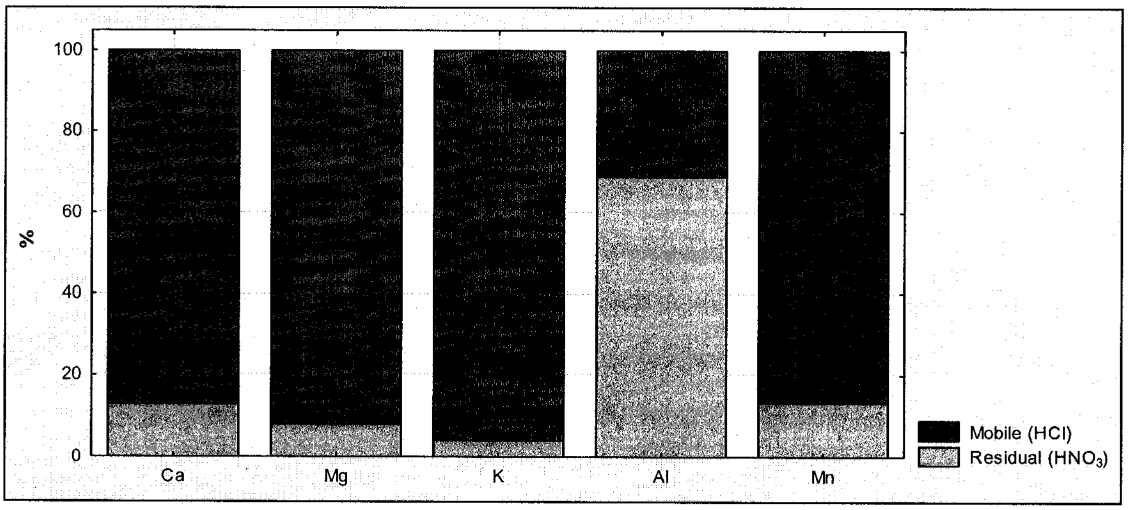
NOVEL METHODOLOGIES IN DENDROCHEMISTRY

1. Results and discussion

1.1 Sequential extraction

As expected, K was primarily in the exchangeable fraction (96%) (Fig. 3). Conversely Al concentration was primarily contained within the residual fraction (64 %) (Fig. 3). Similarly to K, the exchangeable (i.e.mobile) fraction of Ca, Mg and Mn was high with values of 89, 95 and 92%, respectively. These findings are similar to those of Herbauts et al. (2002) for the data given for Ca, Mg and K for European beech (*Fagus sylvatica* L.).

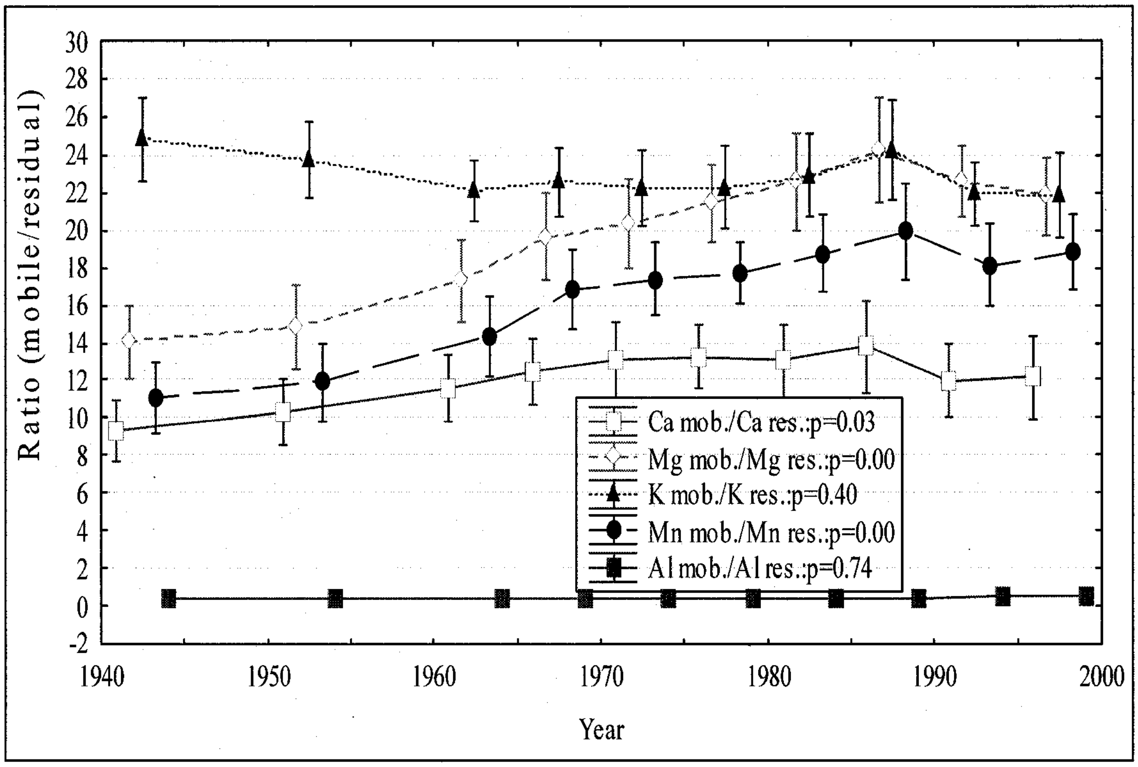
Figure 3: Fractionation of elements between mobile and residual fractions; N=410.



As a result of the higher proportion of the trace metal Al in the residual fraction compared with the nutrients, the difference in concentrations among all elements in the residual fraction is much smaller than for the total concentration or concentration of the mobile fraction. Computational difficulties may arise when the concentration of one element is much lower than that of another, such as Al versus Ca (Cronan and Grigal 1995). Considering that Al was lower by one order of magnitude relative to base cations for total concentration, the sequential digestion likely contributed to increasing the reliability of the results of the analyses to follow.

Long term trends of the relationships in the mobile to residual fraction of Ca, Mg and Mn changed over time (Figure 4). The concentrations of the separate fractions of Ca, Mg and Mn were all decreasing over time (data not shown), with the residual fraction decreasing at a greater rate, hence the increasing effect in ratio. Both fractions of K decreased at the same rate over time resulting in a relatively stable ratio. Al was stable over time in both fractions and, therefore, also had relatively stable ratios. The separation of the elements into their fractions did not affect the direction of long term trends, only the rate of change.

Figure 4: Change over time of the ratios of mobile to residual fractions of Ca, Mg, K, Mn and Al concentrations (N=37; error bars are 95% confidence intervals).



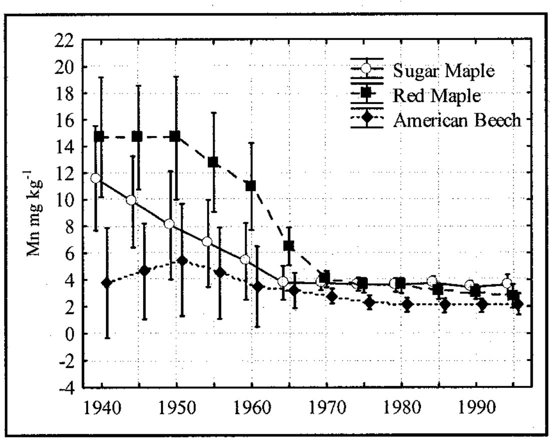
The species included in the analysis do not have a well defined heartwood/sapwood boundary (Cutter and Guyette 1993). The HCl extract should have removed elements on the sapwood side of the boundary that may have accrued from transport away from the pith along ray cells. Conversely, heartwood sequestration of exchangeable ions and extractive compounds, i.e. not an integral part of the woody plant cell wall, may not have been as effectively removed.

1.2 Conversion of concentrations to CND values

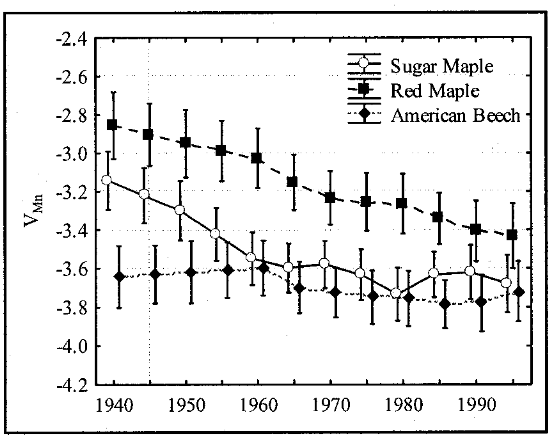
The variability of the concentrations decreased after 1960 (Fig. 5). Transformation to CND values resulted in homoscedasticity over time. The dilution effect of growth and the heterogeneity of soil chemistry on tree ring element concentrations were therefore minimized with CND, enabling a more reliable comparison of tree species and regional effects amongst trees in regards to elemental change over time and effect on growth.

Figure 5: Change over time in Mn concentrations and CND scores of the residual fraction of each tree species (bars are 95% confidence intervals; points representing 1945 and 1955 are interpolations).

a) Mn concentration



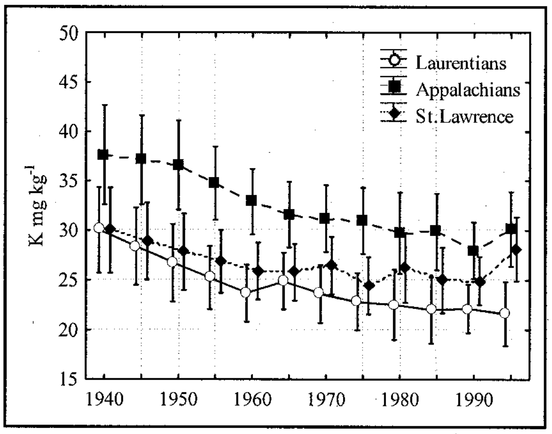
b)V_{Mn}



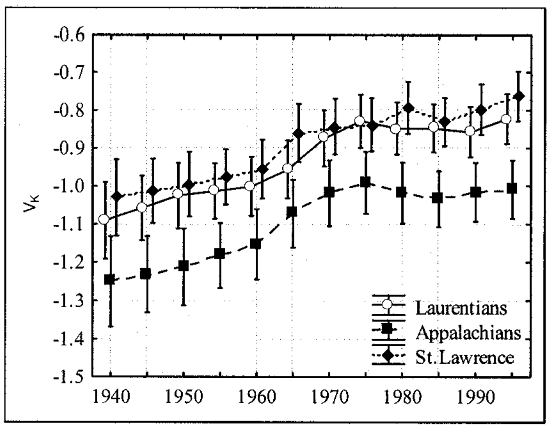
The use of CND resulted in a few cases in different ranking of tree species and regions in terms of average values and pattern of change over time. Figure 6 exemplifies the potential for differing ranking of factors as well as different direction of change over time with CND converted data. Whereas the use of concentrations may allow for comparisons of soil nutrient availability or species requirement, CND's constrained sum reveals relational composition of tree rings. Since most nutritional problems associated with soil acidification and decreased forest growth and health have been linked to nutrient imbalances (Côté and Ouimet 1996), the CND approach may provide more useful information about the evolution of nutritional changes in dendrochemical studies. Hence, results in the rest of the thesis will focus primarily on CND values rather than concentrations.

Figure 6: Change over time in K concentrations and CND scores of the residual fraction of each region (bars are 95% confidence intervals; points representing 1945 and 1955 are interpolations).

a) K concentration



b) V_K



Chapter IV

ELEMENTAL TRENDS

1. Results and Discussion

1.1 Overall effects

The effects of region, species, time and first- and second-order interactions were significant for most elements for concentrations and CND values (Table 3). Exceptions were noted for Mg concentration for effect of species and for Al for the effect of time.

1.1.1 Effect of region

The effect of region for element concentrations is that the Laurentians have low Ca and Mg compared to the Saint-Lawrence, but also the lowest Al (Table 4 a) whereas the Appalachians have the highest K and Mn. For CND values, the effect of region is that the Appalachians have the lowest V_{Ca}, V_{Mg} and V_K, but the highest V_{Mn}. The high Mn compared with Ca and Mg could infer various ecophysiological processes including uptake antagonism by Mn that limits the level of base cations in the tissues (Graham et al. 1988). This result could be expected in an acid sensitive region such as the Appalachians as acid cations are mobilized in response to acidic inputs (Bondietti et al. 1992). It is also notable that the Saint-Lawrence has the highest V_{Al}, but also the highest V_{Ca} and V_{Mg}. Considering that the Saint-Lawrence was not noted as having experienced forest decline, the high Ca should reflect good tree health (Hendershot and Bélanger 1999). It is likely that the high V_{Al} is not associated with toxicity or uptake antagonism. The ratio of Ca to Al in the wood is much higher than 10, a value usually considered to confirm Al toxicity.

1.1.2 Effect of species

The effect of species for element concentrations is that sugar maple is lowest in K but highest in Al, and American beech is highest in Ca but lowest in Mn (Table 4 b). For CND values, the effect of species is that American beech is highest in V_{Ca} and V_K but low in V_{Al}, reflecting its historically-established relationship with ectomycorrhiza of acidic soils (Brundrett et al. 1990), allowing a greater uptake of Ca. Red maple is highest in V_{Mn} which could indicate increased Mn activity from reducing conditions on which it typically thrives. However, Kogelmann and Sharpe (2006) found that higher levels of Mn were found even in red maple on mesic sites relative to sugar maple on similar sites. Our results are therefore consistent with their conclusion that there is an intrinsic species difference in Mn content with red maple having greater levels than sugar maple given similar edaphic conditions.

The fact that sugar maple was highest in V_{Al} was not expected as red maple was thought to be the most sensitive species to soil acidification. It has been hypothesized that sugar maple lacks the necessary mycorrhizal relationships to persist in acidic conditions (Brundrett et al. 1990). American beech leachate in a greenhouse study had adverse effects on sugar maple seedling physiology (Hane et al. 2003). A return to the pre-colonial dominance of American beech in forests of southern Quebec may be in process as sugar maple has been reduced significantly over the last few decades to the advantage of American beech (Duchesne et al. 2005). Such a rapid change implies a fundamental change in environmental conditions.

1.1.3 The general effect of time

Over the 60 year time period, each element had significant changes for both concentrations and CND values (Figure 7). Ca, Mg and Mn decreased, Al increased while K decreased in concentration but increased in CNDs.

Table 3: Summaries of repeated measure ANOVA of element concentrations (mg kg^{-1}) and CND values (V_n). Probabilities are significant at p=0.05.

		Ca		**Mg**		**K**		**Mn**		**Al**	
Effect	DF	F	p	F	p	F	p	F	p	F	p
Region	2	3.39	0.037	3.63	0.029	9.10	<0.001	93.76	<0.001	6.51	0.002
Species	2	3.19	0.044	2.20	0.114	5.49	0.005	9.87	<0.001	10.28	<0.001
Region*Species	4	1.67	0.160	2.46	0.048	5.01	<0.001	4.63	0.002	2.41	0.052
Error	140										
Year	9	19.18	<0.001	69.69	<0.001	10.37	<0.001	23.01	<0.001	5.12	<0.001
Year*region	18	1.07	0.379	0.90	0.583	1.02	0.434	14.72	<0.001	3.78	<0.001
Year*species	18	5.02	<0.001	6.02	<0.001	3.28	<0.001	4.23	<0.001	5.00	<0.001
Year*region*species	36	0.87	0.684	1.21	0.184	2.04	<0.001	2.78	<0.001	1.78	0.003
Error	1260										

		V_{Ca}		**V_{Mg}**		**V_K**		**V_{Mn}**		**V_{Al}**	
Effect	DF	F	p	F	P	F	P	F	p	F	P
Region	2	26.19	<0.001	61.28	<0.001	13.72	<0.001	232.9	<0.001	4.89	0.009
Species	2	10.62	<0.001	3.23	0.042	25.86	<0.001	16.48	<0.001	22.79	<0.001
Region*Species	4	5.15	<0.001	2.45	0.049	10.84	<0.001	6.74	<0.001	2.91	0.024
Error	140										
Year	9	13.55	<0.001	54.73	<0.001	26.89	<0.001	35.13	<0.001	20.60	<0.001
Year*region	18	1.51	0.078	1.35	0.148	0.37	0.993	5.20	<0.001	6.39	<0.001
Year*species	18	8.96	<0.001	7.58	<0.001	2.43	<0.001	5.26	<0.001	12.93	<0.001
Year*region*species	36	0.71	0.901	1.27	0.136	1.68	0.008	2.75	<0.001	1.66	0.009
Error	1260										

Table 4: Difference of means of region (a) and species (b) for concentrations (mg kg^{-1}) and CND values. A differing letter beside value within sub-group indicates significance at p=0.05. Nss indicates non-significance in ANOVA (Table 3).

a) Region

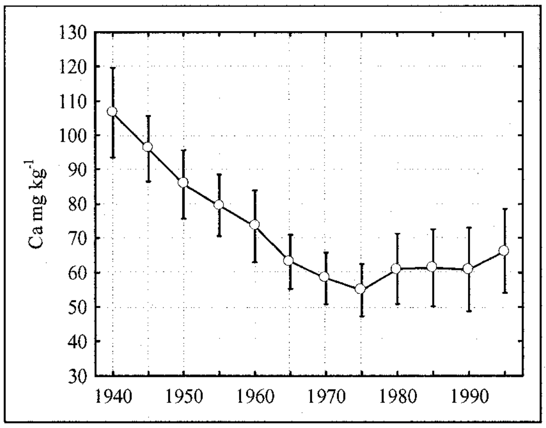
Concentration	**Ca**	**Mg**	**K**	**Mn**	**Al**
Laurentians	57.3b	8.3b	23.5b	1.5b	3.5b
Appalachians	67.1ab	8.8ab	31.5a	11.5a	5.4a
Saint-Lawrence	84.2a	9.9a	26.5b	1.3b	4.7a
CND values	V_{Ca}	V_{Mg}	V_K	V_{Mn}	V_{Al}
Laurentians	-0.13b	-2.04b	-0.93a	-3.84b	-2.89b
Appalachians	-0.53c	-2.44c	-1.08b	-2.36a	-2.95b
Saint-Lawrence	0.08a	-1.91a	-0.87a	-4.30c	-2.75a

b) Species

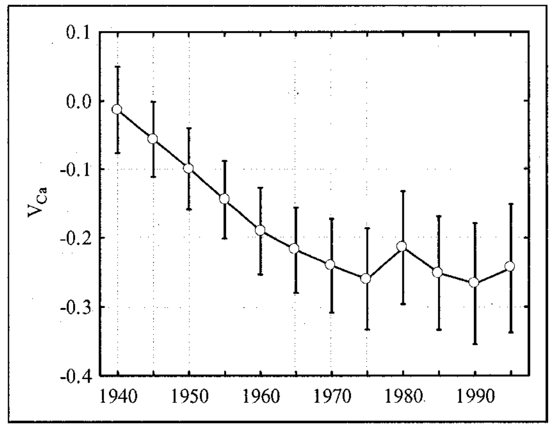
Concentration	**Ca**	**Mg**	**K**	**Mn**	**Al**
Sugar maple	66.2b	8.3nss	24.1b	5.1a	5.6a
Red maple	57.1b	9.1nss	29.0a	6.6a	4.1b
Am. beech	84.6a	9.5nss	29.1a	2.9b	3.6b
CND values	V_{Ca}	V_{Mg}	V_K	V_{Mn}	V_{Al}
Sugar maple	-0.19b	-2.17b	-1.10c	-3.66b	-2.60a
Red maple	-0.35c	-2.12ab	-0.93b	-3.31a	-2.93b
Am. beech	-0.03a	-2.03a	-0.81a	-3.81b	-3.07b

Figure 7: Concentration and CND values for the 1940-1999 period for all species and regions considered together: a) Ca; b) Mg; c) K; d) Mn; e) Al. Bars are 95% confidence intervals; points representing 1945 and 1955 are interpolations.

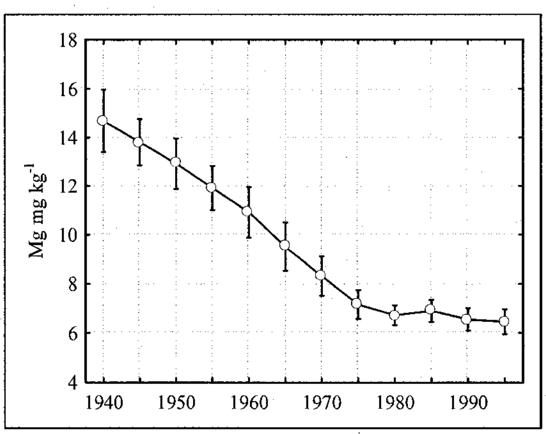
a) [Ca]



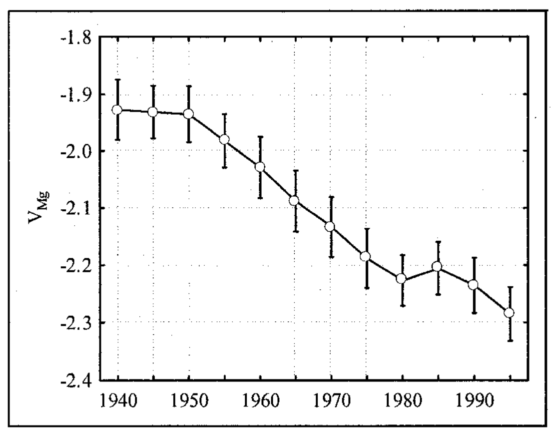
V_{Ca}



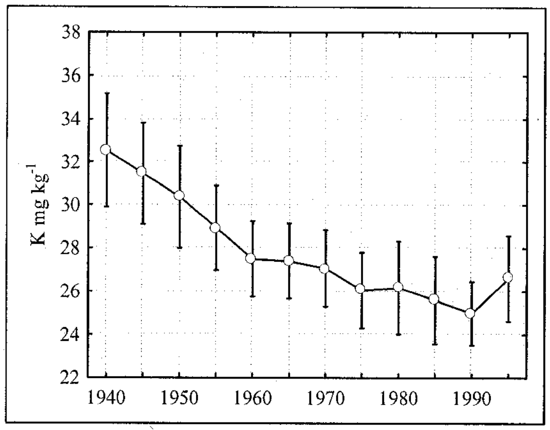
b) [Mg]

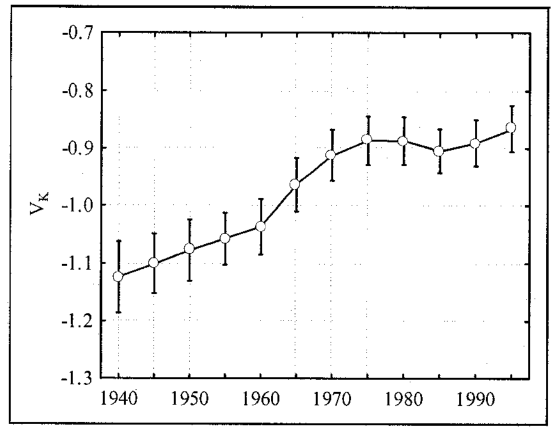


V_{Mg}

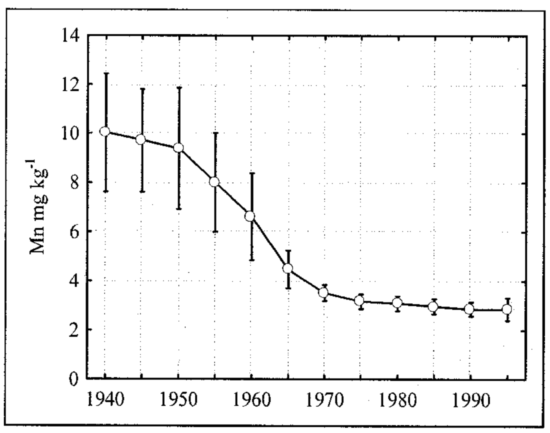


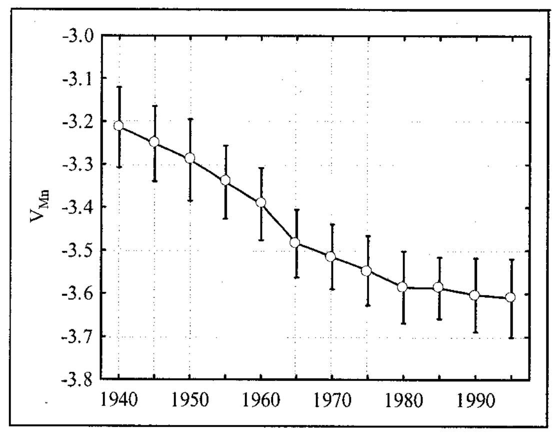
c) [K] V_K



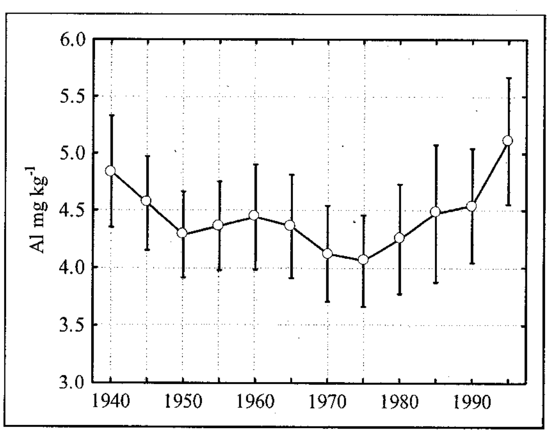


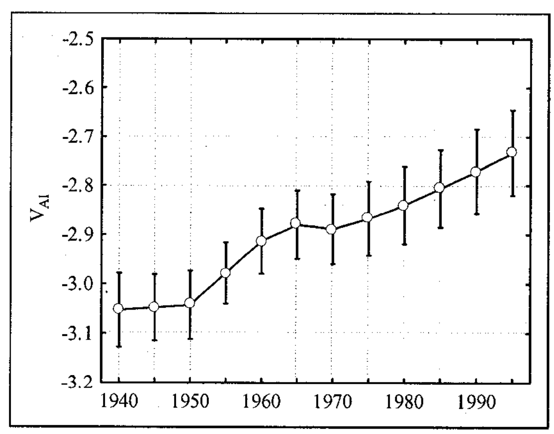
d) [Mn] V_{Mn}





e) [Al] V_{Al}





1.1.4. Discussion

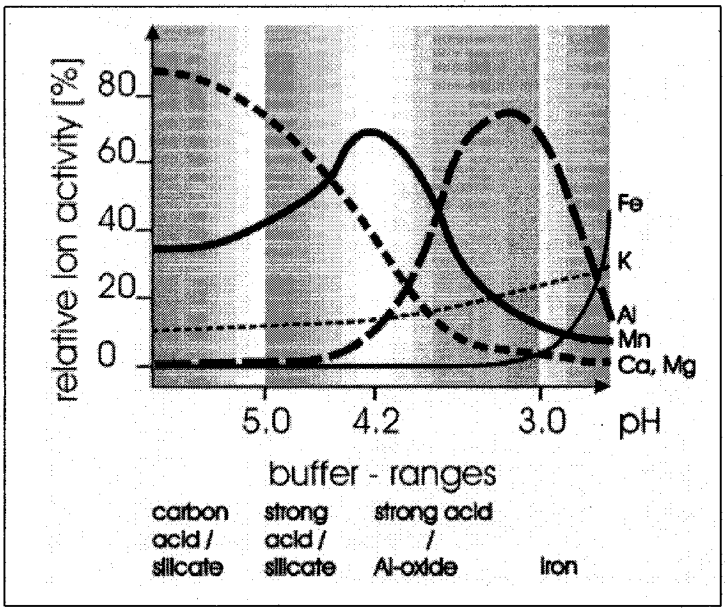
Over time, the residual fraction of elements in tree ring xylem is not expected to change or fluctuate given an environment without change. In aggrading hardwood forests, such as those in this work, environmental change is inevitable as soil acidity accrues from natural processes, with the consequence of an eventual decrease in pH (Knoepp and Swank 1994) with a concomitant shift in element bioavailability. Concurrently, the sequestration of nutrient elements in the forest biomass will deplete nutrient elements from exchangeable soil stores (Likens et al. 1998). As a corollary, if biomass is removed from a site, the effect would be a loss of recharge to soil nutrient stores (Joslin et al. 1992). In this work, the significant trends of all nutrient cation concentrations decreasing while aluminium is increasing (Figure 7) are as expected from these natural changes. The magnitude of change, though, and the interrelationships of elements infer an extrinsic influence, such as acidic atmospheric deposition. Critical load assessments of some of the studied sites suggest acidic input beyond those of natural processes (Ouimet et al. 2001) resulting in a deficiency of available base cation nutrients. In accordance with those findings the results in Table 3 show fundamental differences between the regions in nutrient and Al contents.

Watmough (2002) found that both Al and K in sugar maple xylem of southern Ontario increased with decreasing pH. Such a shift over time could indicate a drop in pH greater than expected from intrinsic, natural processes, for the time span considered. A 30 year study of a pine stand in South Carolina showed a drop in pH of one unit for the A horizons and 0.4 and 0.3 in the B and C horizons. Based on H^+ modelling, about one third of this acidification was from acidic deposition while the balance was from natural ecosystem processes (Markewitz et al. 1998). Similar findings were made over a 30 year period on the Allegheny Plateau in Pennsylvania (Bailey et al. 2005). In a review article of the state of health for eastern Canadian maple-dominated forests McLaughlin (1998) concluded that increases in decline symptoms coincide with decreases in pH and base saturation of the B horizon and with increases in exchangeable Al.

Another natural process or influence on the decreasing trends of base cations over time may be that of decreasing cation binding sites within xylem cell walls as stem radius increases (Momoshima and Bondietti 1990). These trends are based on the cation fraction held on exchange sites rather than the fraction within structural bonds such as implicitly represented by the residual fraction of cations. The application of these trends to this work is presumably less meaningful, if the methodology used here was successful in removing the majority of mobile cations across all rings regardless of radius, leaving only (or at least primarily) immobile (residual) cations. A basic premise of the theory of cation binding sites is based on the Donnan principle of ion selectivity, in that single valence cations (e.g. K) will consistently decrease at a greater rate than double valence cations (e.g. Ca, Mg) from pith to bark. The trends observed here do not follow this pattern. Rather than an overall, continuous decrease, all nutrient concentrations decreased and then stabilized by the time segment 1975-79 when Al concentration began increasing (Figure 6). In addition, the concentration of K (single valence) decreased from 1940 to 1975-79 at a lesser rate than that of any multiple valence base cation (i.e. Ca, Mg or Mn). This was shown by the slope of V_K showing a relative increase to the decrease in V_{Ca}, V_{Mg} and V_{Mn} (due to the lesser rate of decrease in the latter concentrations). V_{Al} also increased although Al concentration was stable. Other possibilities to explain the trend in V_K are: in adherence to the Donnan principle it is possible that the concentration of K was affected by different factors such as an incomplete washout of the exchangeable fraction, leaving intact some previously mobile ions trapped in heartwood compounds which then show as trends presumably increasing towards the pith (i.e. oldest rings); or an environmental influence pre-existing to the time period used here; or intrinsic species differences to red spruce which was the species used by Bondietti and Momoshima (1990). Similar results of K concentration change relative to divalent cations were also found by Herbauts et al. (2002) for European beech.

The unexpected shift in nutrient and Al concentrations around 1975 could be the result of an environmental influence that synergistically combined the increase in Al with the stabilizing of nutrient concentrations, perhaps from the soil reaching a different pH buffering equilibrium. Using CND values rather than concentrations, a stronger argument can be made for extrinsic influence, as V_{Mg} continues to decrease beyond 1975 while the other cations stabilize and V_{Al} rises. These changes may reflect a shift in the primary acid cations involved in buffering soil acidity, perhaps from Mn to Al (Ferretti et al. 2002) or some combination of the transition from silicate/base cation buffering to aluminium buffering or even iron involvement, with Mn bridging the change. Mg is easily leached and is additionally in competition with Mn for uptake (Graham et al. 1988). Perhaps this is why Mg and V_{Mg} have the greatest and most consistent loss over time. A conceptualized scheme of relative ionic shifts as pH decreases is shown in Figure 8. This graph is based on a compilation of numerous observations of forest soils in Europe (personal communication with K.von Wilpert, co-author of Ferretti et al. (2002)). The similarity to the element trends of this work is notable including V_K rising from the mid- to lower-pH range.

Figure 8: Conceptualized scheme of the relative ion activities in soil solution in relation to soil pH of European forest soils (Ferretti et al. 2002).



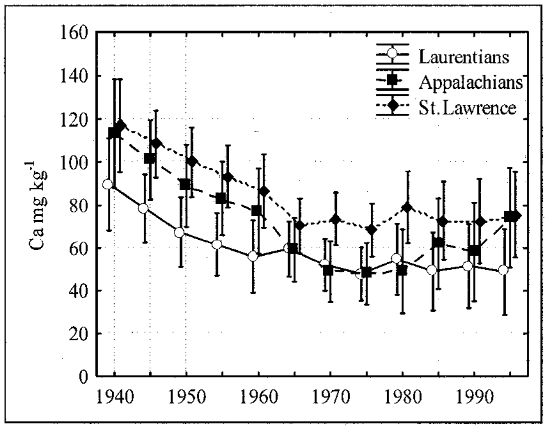
1.2 Effect of time by region

1.2.1 Results

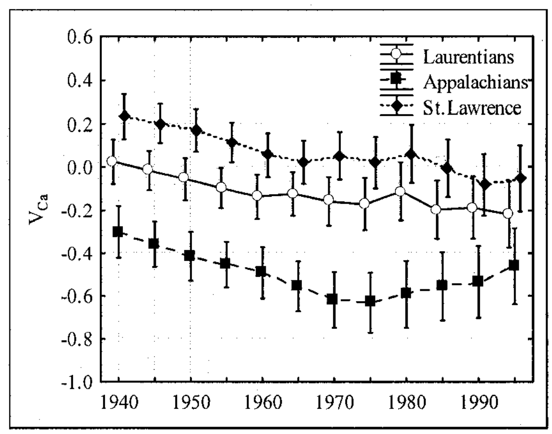
Differences in mean elemental concentrations were observed between regions. Larger regional differences were observed with CND values. Only the acid cations, Mn and Al (Figure 9 d and e; both conc. and CND) had a different trend over time between regions. The CND values for the base cations (Figure 9 a, b and c) appear to show a gradient in nutrient richness among regions with the Appalachians being consistently base poor. Mn in the Appalachians was higher and had a greater decrease over time than the other regions. The regional difference of Al is driven by its increase over time in the Appalachians.

Figure 9: Concentration and CND values for the effect of time by region: a) Ca b) Mg c) K d) Mn e) Al. Bars are 95% confidence intervals; points representing 1945 and 1955 are interpolations.

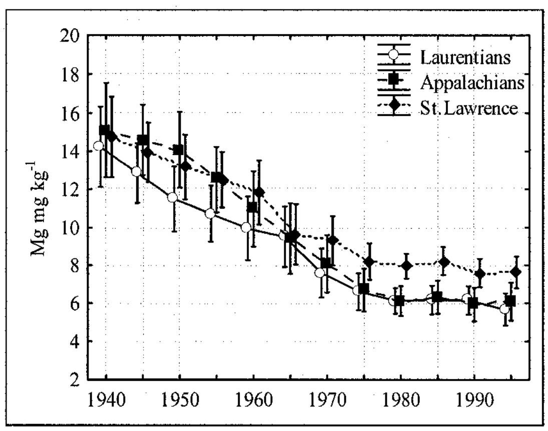
a) Ca concentration



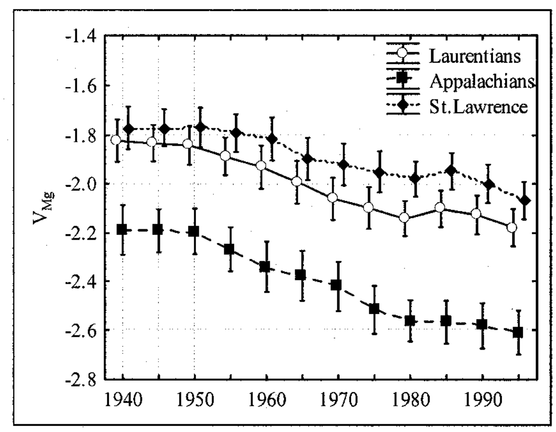
V_{Ca}



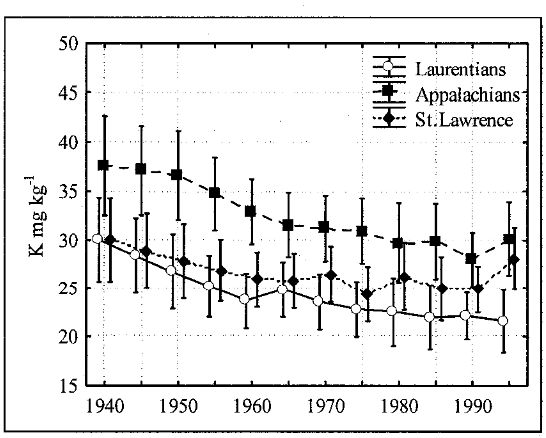
b) Mg concentration



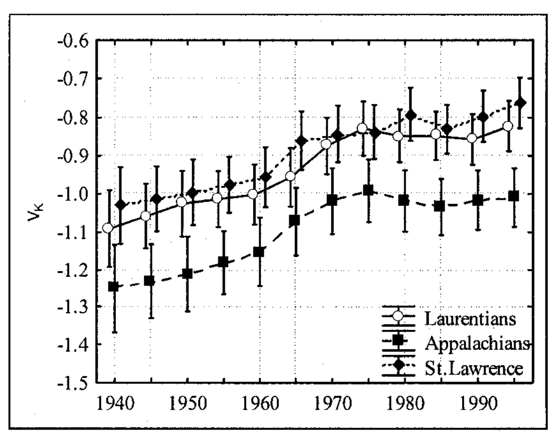
V_{Mg}



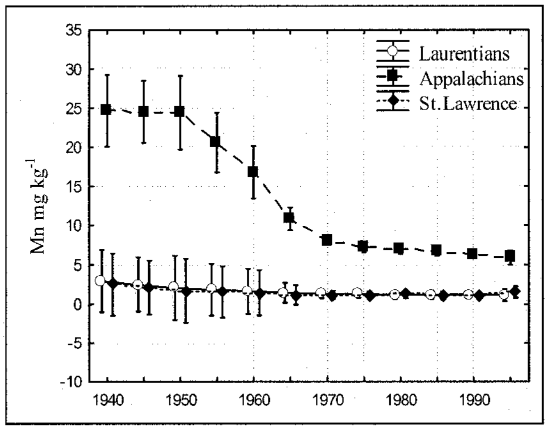
c) K concentration



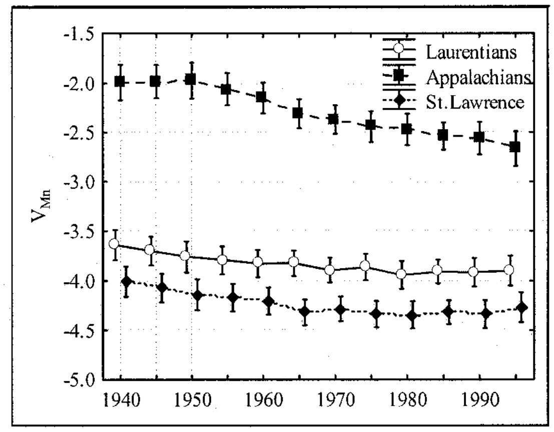
V_K



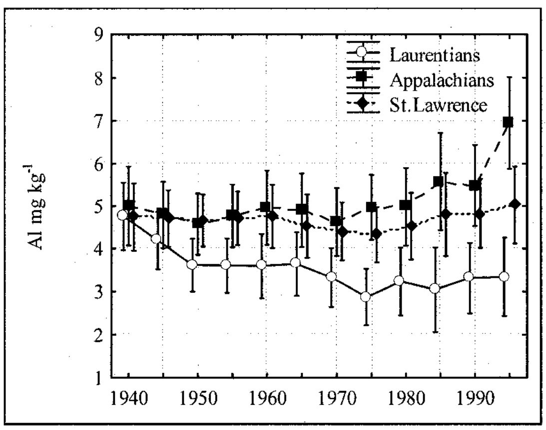
d) Mn concentration



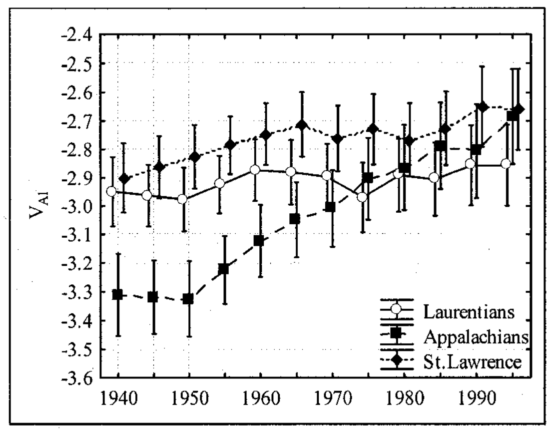
V_{Mn}



e) Al concentration



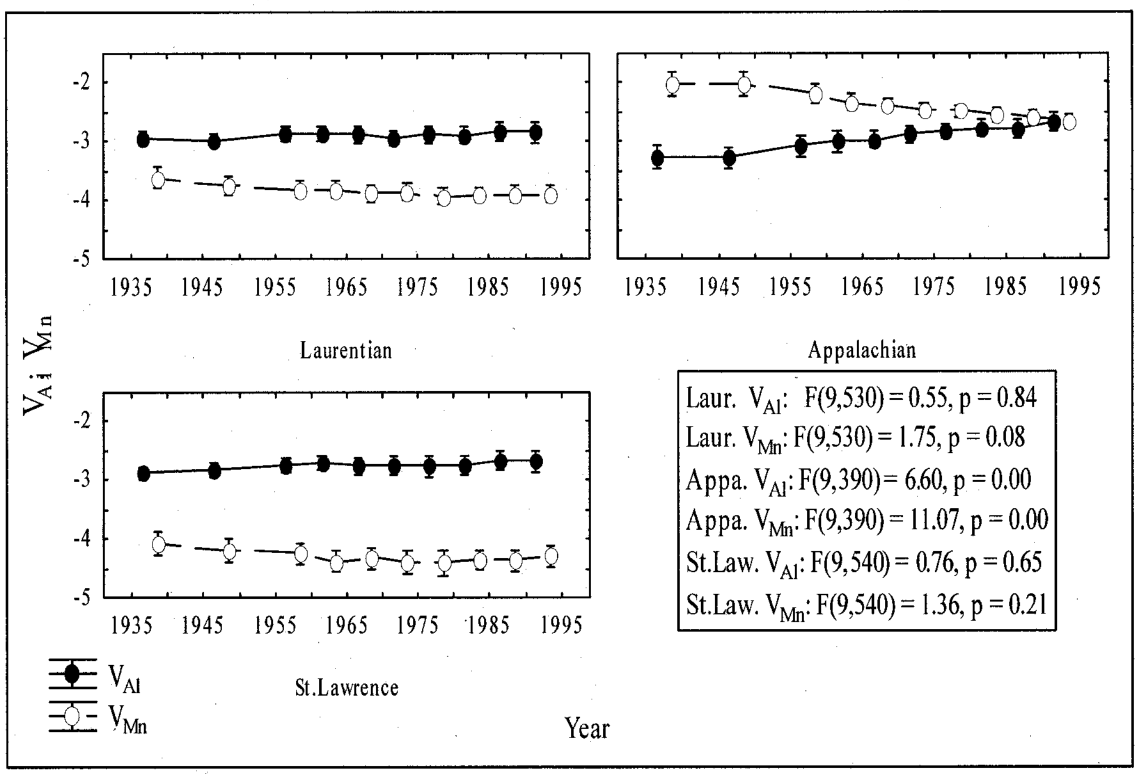
V_{Al}



1.2.2 Discussion

For both CND values and concentrations, the acid cations, Al and Mn were different between regions over time. Ca, Mg and K displayed decreasing trends and different average concentrations/CNDs that suggest the following ranking for regional nutrient availability: Saint-Lawrence > Laurentians >> Appalachians (Figure 9). The regional ranking in terms of Mn levels was the inverse of the base cations, with the Appalachians having much higher levels than the other regions implying Mn rich parent material and/or mobilization of Mn for buffering acidity. The metavolcanic, basic portion of its parent material may have high Mn (Gagnon et al. 1994). The high Mn level may yield a situation of saturation and therefore antagonism to base cations, particularly Mg (Graham et al. 1988). Where the other regions had V_{Mn} levels below V_{Al}, Appalachians V_{Mn} was greater than V_{Al} (Figure 10). Additionally, Appalachians V_{Al} increased while V_{Mn} decreased quickly, in contrast to the other regions. The Laurentians and Saint-Lawrence had similar although weaker trends of decreasing V_{Mn} (respectively, p=0.08 and p=0.2) without the concurrent increase in V_{Al}. This may infer a change in the Appalachians of the element which primarily buffers acidity: from Mn to Al.

Figure 10: Regional V_{Mn} and $V_{Al;}$ means with 95% confidence bars, F values and probabilities.



In a time series of tree chemistry, a 'bump' in Mn concentration may occur as a soil passes through the phase of acidity buffering from silicate to aluminium (Ferretti et.al., 2002). Guyette (1992) used Mn concentrations of red cedar xylem (whole cores, not time series), regressed on current soil pH, to enable inference of historic change in soil pH. He suggested that soils in transition from Ca to Al buffering had a greater decrease in pH during this non-stable buffering period relative to stable buffering decrease in pH. This could explain the greater rate of decrease in Mn, if its activity fell as that of Al rose. The 'bump' or evidence of mobilized Mn would have been already in progress in 1940. Undoubtedly, there was also Mn losses from leaching, similar to the decreasing trends of the other base cations. The results for the Appalachians imply environmental change associated with increasing soil acidity.

While the decrease in V_{Mn} in the other regions stabilized in the 1970's, Appalachian V_{Mn} continued to decrease, inferring a continuation of the transition between Ca and Al buffering phase, and/or loss from leaching. Many studies have relied on the ratio of Al to Ca as a predictor of accelerated environmental change on sensitive soils (Cronan and Grigal 1995). My results suggest that Mn can also be used effectively for that purpose as suggested by Guyette et al. (1992) and Augustin et al. (2005).

Ouimet et al. (2001) used mass-balance modelling with the program PROFILE to calculate acidity exceedance of forest soils of southern Quebec to acidic deposition. They identified the Laurentians to be in exceedance at current deposition rates. Results showed the Appalachian sites all having continued capacity to absorb acidity, but the authors noted an inherent problem with the PROFILE program: the antagonistic effect of some cations on others need to be considered as other research had noted negative health impacts from soil saturation of Mg on foliar Ca and K levels in sugar maple in this region. In this thesis, for the Appalachian region, Mn in synergy with Al seems to be driving change in base cations.

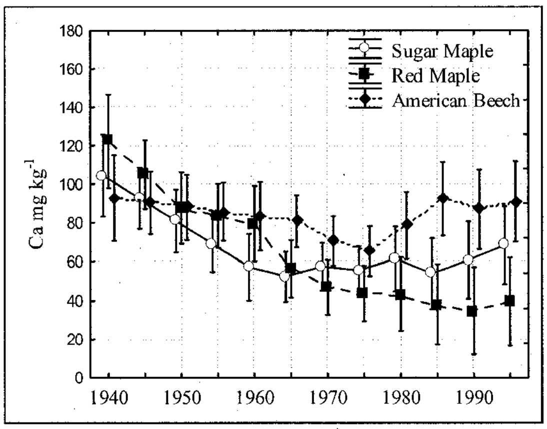
1.3 Effect of time by species

1.3.1 Results

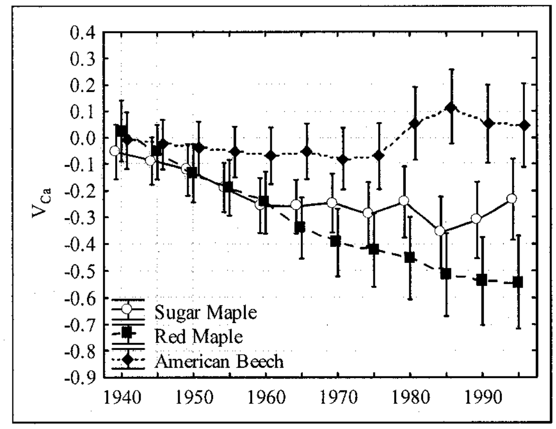
All elements have a significant time by species interaction for both concentrations and CND values (Figure 12 a-e). There was divergence amongst the species over time for Ca (a) and Al (e), while for Mg (b), K (c) and Mn (d) there was convergence. CND results showed a clearer divergence and larger interspecific differences in average values. In addition, American beech showed higher base cation and lower acid cation values than either sugar maple or red maple.

Figure 11: Concentration and CND values for the period of 1940-1999 for all three species: a) Ca b) Mg c) K d) Mn e) Al. Bars are 95% confidence intervals; points representing 1945 and 1955 are interpolations.

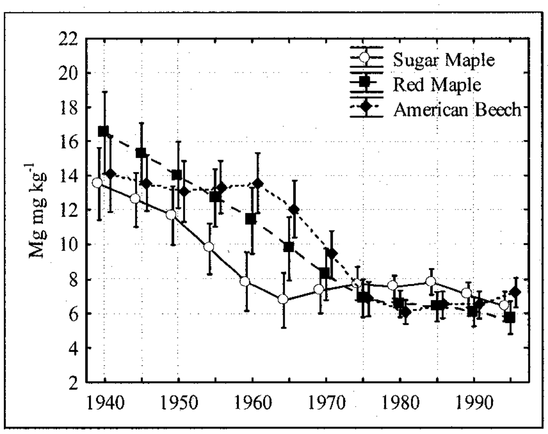
a) Ca concentration



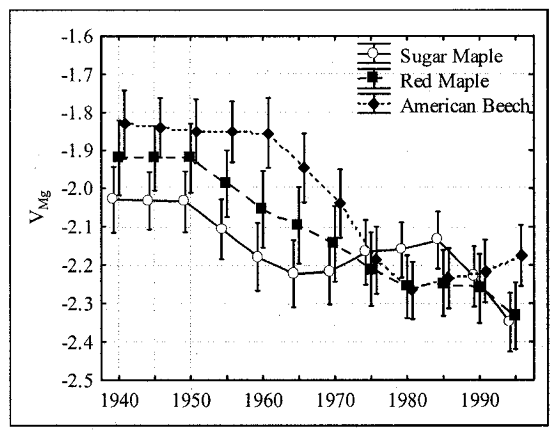
V_{Ca}



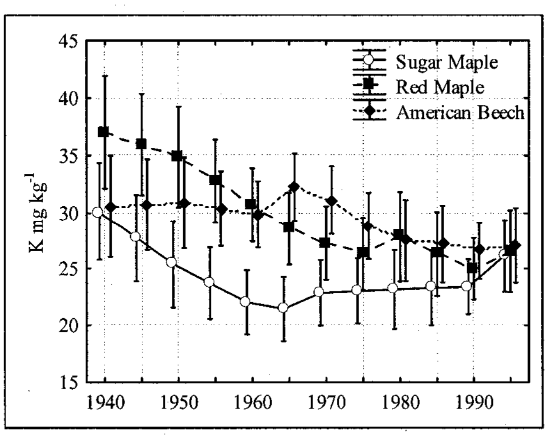
b) Mg concentration



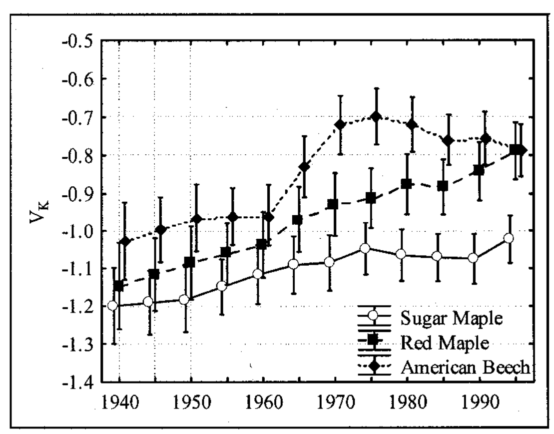
V_{Mg}



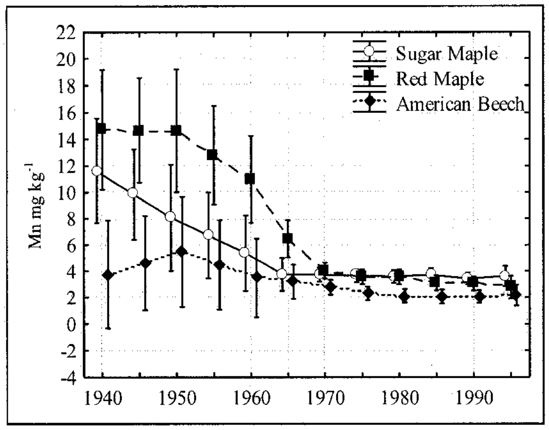
c) K concentration



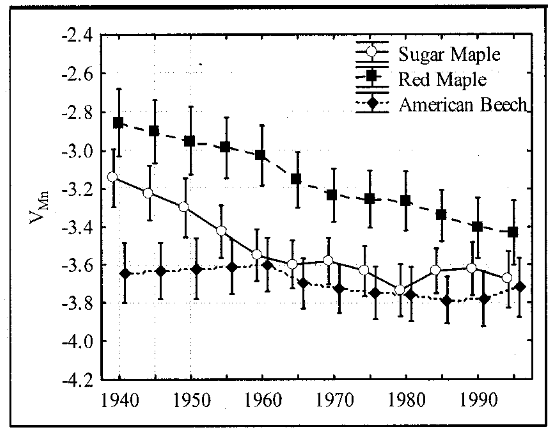
V_K



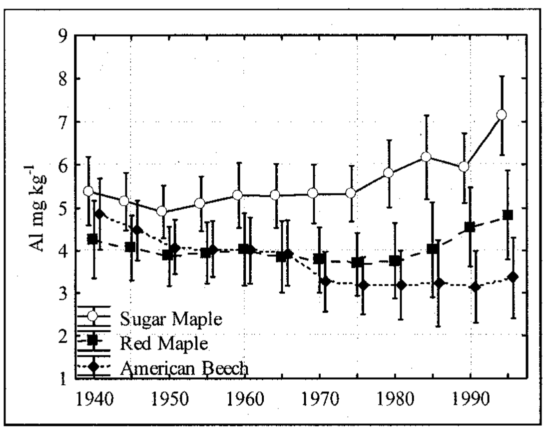
d) Mn concentration



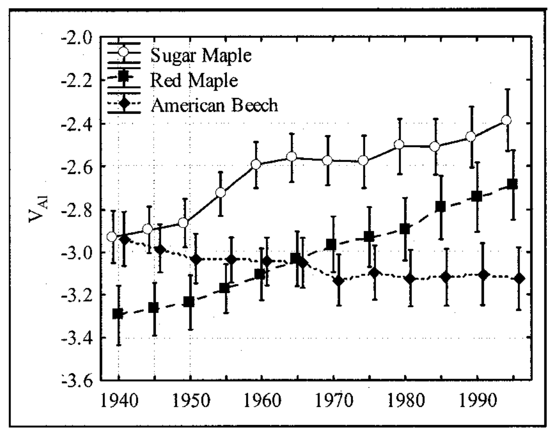
V_{Mn}



e) Al concentration



V_{Al}



1.3.2 Discussion

The effect of species on elemental trends was more diverse than the regional effect, with all elements having differences amongst species. A European study of a controlled planting of a group of various species on different sites (Hagen-Thorn et al. 2004) revealed that species differences were stronger than site differences in soil quality. Presumably each species is somewhat unique in how it competes for and exploits nutrients (e.g. rooting depth and mycorrhizal relationships).

The divergence over time of Ca and Al amongst species (Figure 11) is especially notable as American beech V_{Ca} increased over time while V_{Al} was stable in contrast to red maple which had the largest decrease in V_{Ca} and largest increase in V_{Al}. By comparison, it is notable that in concentration analysis, American beech decreased in Al and had stable Ca relative to sugar maple and red maple. Sugar maple was intermediate in V_{Ca}, with less of a change than red maple, and had the highest V_{Al}, although with less of an increase over time. Red maple had the highest V_{Mn}. DeWalle et al. (1999) noted species differences in response to artificial watershed acidification. Similar to the American beech in this study having an increase in V_{Ca} and stability of V_{Al}, they found American beech had a prolonged phase of cation mobilization in comparison to sugar maple and red maple: in other words, American beech has a unique mechanism/process to offset implications of increased soil acidity.

The health of a tree, including a balanced nutrient uptake has been related, in part, to symbiotic relationships with mycorrhizal fungi. Through greenhouse trials with sugar maple seedlings, Ouimet et al. (1995) suggested that soil chemical properties, particularly the soil composition in cations, regulates fine-root colonization by endomycorrhizal fungi and therefore sugar maple nutrition and health. The southern Quebec region was historically composed of ectomycorrhizal tree species and the shift to sugar maple dominated forests has had consequences of changes in nutrient cycling (Munzenberger 1999). In general terms, American beech has an association with ectomycorrhizae (Brundrett et al. 1990). Through this relationship, American beech can gain Ca that is otherwise not available to the maples as the ectomycorrhizae may directly weather apatite (i.e. this Ca never enters the soil available pool) (Hagen-Thorn et al. 2004). Apatite is present in parent materials of all origins (sedimentary, orogenic or metamorphic) (http://www.galleries.com/minerals/phosphat/apatite/apatite.htm 1995). This process could explain the increasing V_{Ca} in American beech as opposed to the decrease in the maples. Additionally, from agricultural testing, it has been found that some mycorrhizae ameliorate Al and/or Mn toxicity (Clark and Zeto 2000). Perhaps red maple lacks a mechanism/association to mitigate Mn, and sugar maple lacks one to control Al. Little is known of red maple mycorrhizal relationships, but sugar maple is known to have specific associations relative to the pH of acid, forest soils. The mycorrhizal population and its diversity increase with soil amendments to ameliorate acidity and also increase availability of base cations (i.e. beyond the level in the absence of mycorrhizae) (Coughlan et al. 2000). This implies that in soils of lower pH, the mycorrhizal associations are constrained and less benefit is gained by the host tree. Given the scenario of a continuing decrease in pH, American beech should have a greater advantage in element acquisition than either sugar maple or red maple. Even with stable, low pH, the maples will be at a disadvantage relative to American beech in nutrient acquisition.

Extreme moisture conditions affect the presence of mycorrhizae whether from flood or drought; chronic or acute. Red maple in comparison with sugar maple is found on wetter or dryer locations than sugar maple (Abrams 1998), and may be prone to mycorrhizal population fluctuations or near absence of a population. With the predicted increase in 'extreme' climate events, mycorrhizal relationships will play a greater role in tree health (Bernie 2002).

Aluminium antagonism and toxicity may affect rooting depth of sugar maple as roots concentrate in surface soil horizons which are less affected by Al. Most sugar maple fine roots are found in the organic layer which overlays the mineral layers in these mor type, soil profiles (Hendershot and Bélanger 1999) such as those of the Laurentians and Appalachians. In a calcareous, mull type soil like the Saint-Lawrence, sugar maple fine roots are distributed throughout the horizons (Badibanga et al. 1992). If the bulk of fine roots are in the surface horizon, the tree/soil may be more prone to drought and frost damage, due to loss of nutrients in leaching and lessened uptake.

Red maple had the most consistent elemental decreases (V_{Ca}, V_{Mg}, and V_{Mn}) and increases (V_K and V_{Al}) amongst the species: perhaps its edaphic specific traits are primarily in relation to water use efficiency rather than nutrient acquisition and balance. Considering the resilience of red maple to extremes of moisture, it may have greater survivorship in terms of increasing extreme weather events (Abrams 1998).

Herbauts et al. (2002) set out to determine if acidic deposition had an effect on radial trends in xylem of European beech and pedunculate oak. They followed the methods of Momoshima and Bondietti (1990) of assessing exchangeable (mobile) ions and cation binding capacity to determine base cation saturation but found no consistent radial change in either species. They could not verify an effect of acidic deposition from this method.

Some second-order interactions (i.e. time by species by region) can elucidate differences not easily seen within first-order interactions (i.e. species or region by time). American beech in the Appalachians is decreasing in V_{Mn} similarly to sugar maple and red maple, but unlike the maples it is not increasing in V_{Al} (Appendix I, Figure A1) suggesting an ecophysiologic adaptation to restrict Al uptake (as discussed above for American beech in general).

CHAPTER V
GROWTH AND CND VALUES

1.0 Results

1.1 Growth (BAI)

Except for the effect of species, all factors and interactions were significant for BAI (Table 5). The growth period of 1975-79 was the beginning of a generalized decrease in BAI, although some species recovered later on (Figure 12 d). During the period of 1970-1999 BAI in the Appalachians decreased in sugar maple (p=0.04) and increased in American beech (p=0.04) while red maple in the Laurentians had a decreasing trend.

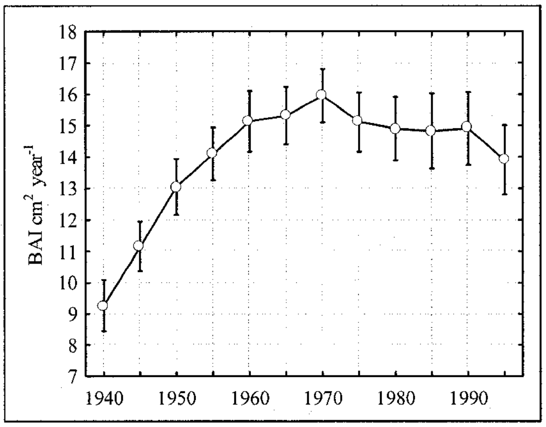
Table 5: ANOVA results of repeated measure (10 time periods) of BAI with region (3 levels) and species (3 levels) as dependent variables. Probability is significant at p=0.05.

BAI

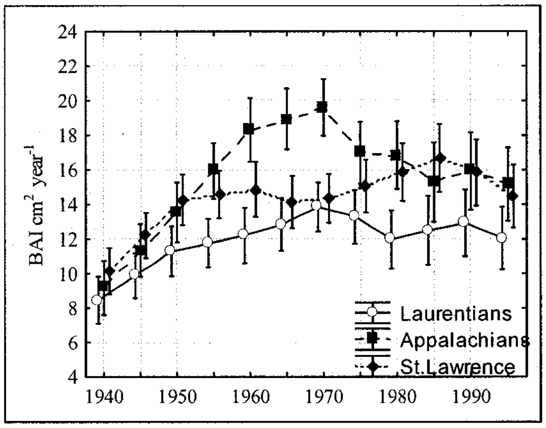
Effect	DF	F	p
Region	2	10.46	<0.001
Species	2	1.68	0.191
Region*Species	4	5.65	<0.001
Error	140		
Year	9	24.35	<0.001
Year*region	18	3.56	<0.001
Year*species	18	2.21	0.002
Year*region*species	36	2.86	<0.001
Error	1260		

Figure 12: Basal area increment (cm^2 year^{-1}) from 1940 to 1999 for a) all regions and species together; b) regions; c) species; and d) species by region. Bars are 95% confidence intervals; points representing 1945 and 1955 are interpolations.

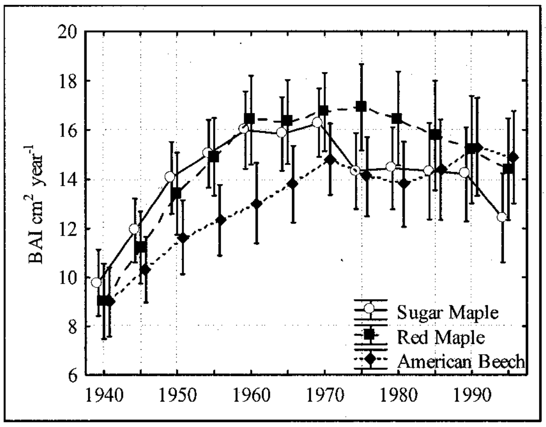
a) All regions and species together



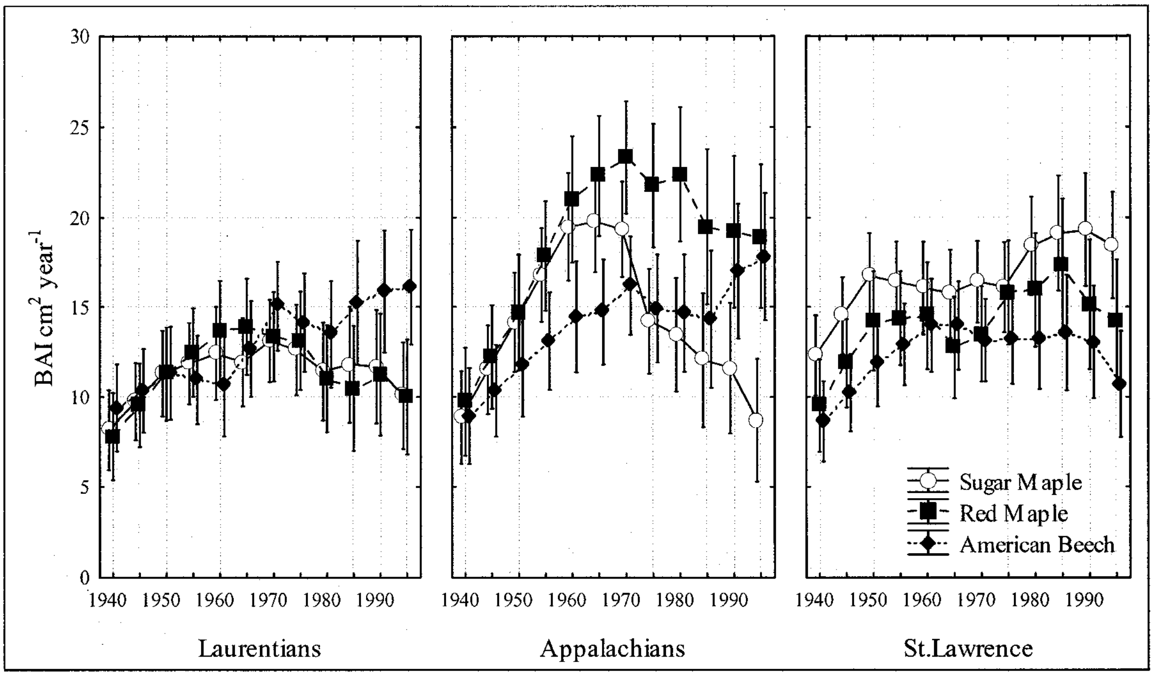
b) Regions



c) Species



d) Species by region: (i) Laurentians; (ii) Appalachians (note that red maple is represented by only one site, La Patrie); (iii) Saint-Lawrence.



1.2 Linking trend in BAI with trend in V_{Mn} and V_{Al}

In order to explore a possible antagonistic effect of the acid cations (Al and Mn) on growth, the time period noted previously of 1970 to 1999 (where growth changed from positive or stable growth to a general decrease) was used to calculate slope values for BAI and contrast these to those of V_{Mn} and V_{Al} (by species within sites given region). Figures 13, 14 and 15 represent sugar maple, red maple and American beech respectively with points being the co-ordinate of the slope of BAI with that of V_{Mn} (a) and V_{Al} (b) within each figure.

The points representing the slopes of BAI with those of V_{Mn} or V_{Al} may be seen as occupying quadrants which relate change in growth to change in element toxicity or nutrient availability such as:

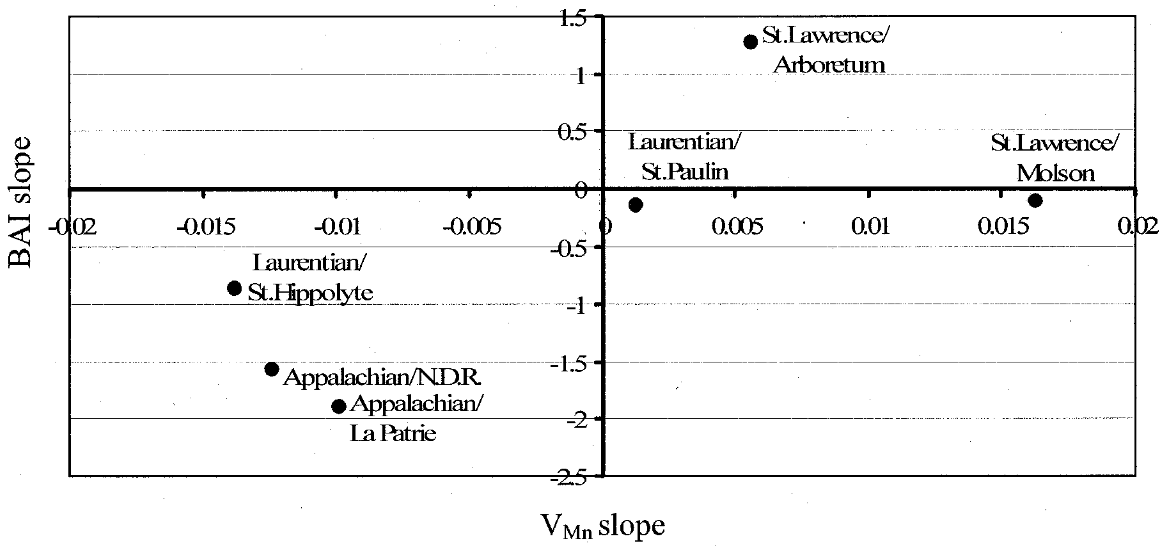
BAI slope

improving toxicity	improving nutrient
worsening deficiency	worsening toxicity

V_{Al} or V_{Mn} slope

Figure 13: BAI slopes with V_{Mn} (a) and V_{Al} (b) slopes of sugar maple for site (given region) for 1970-1999.

a)



b)

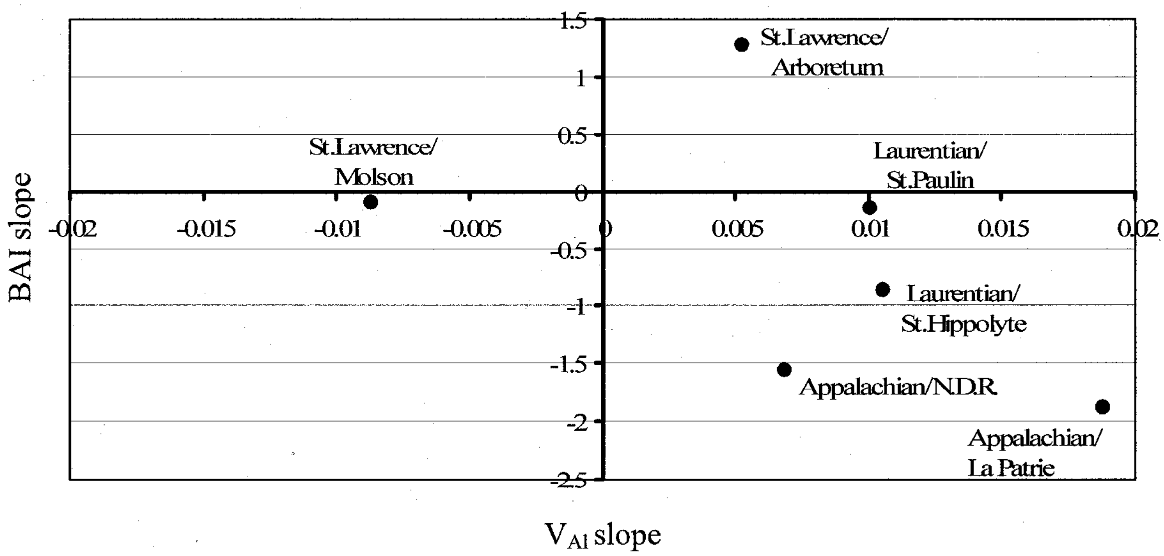
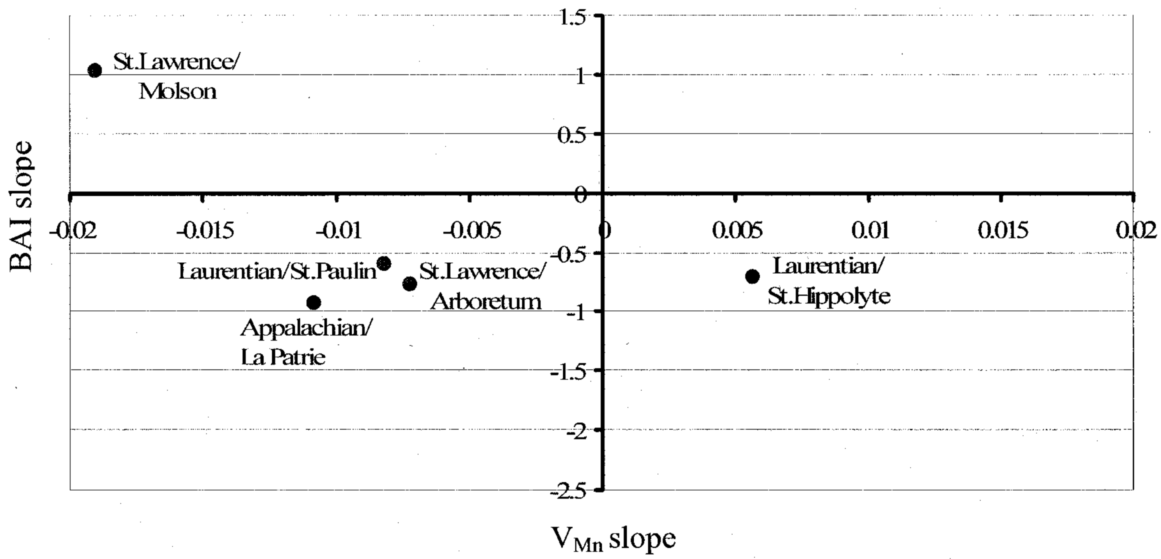


Figure 14: BAI slopes with V_{Mn} (a) and V_{Al} (b) slopes of red maple for by site (given region) 1970-1999.

a)



b)

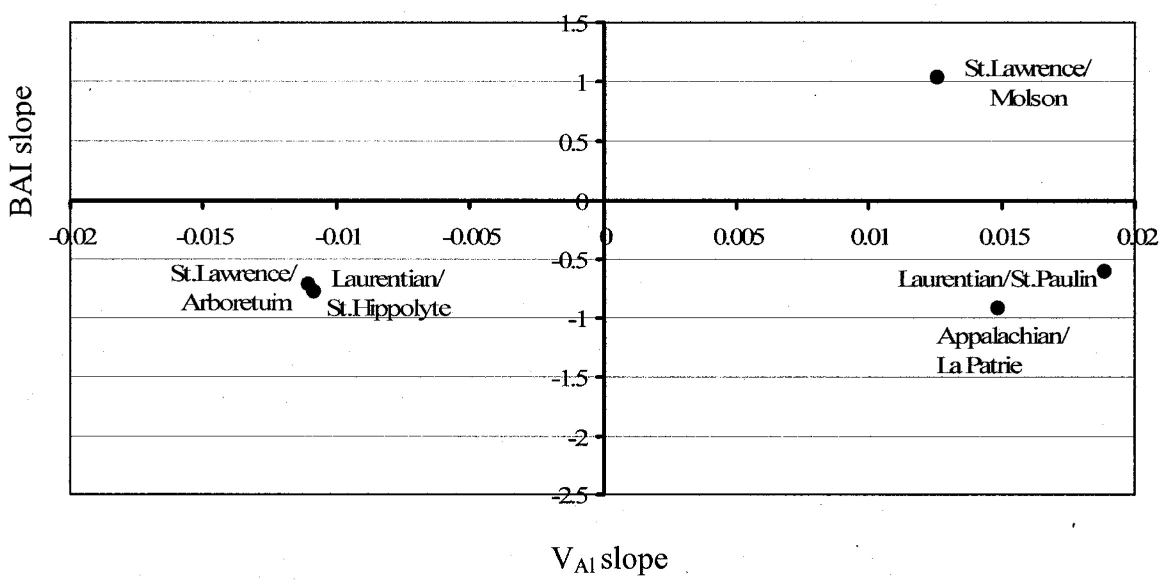
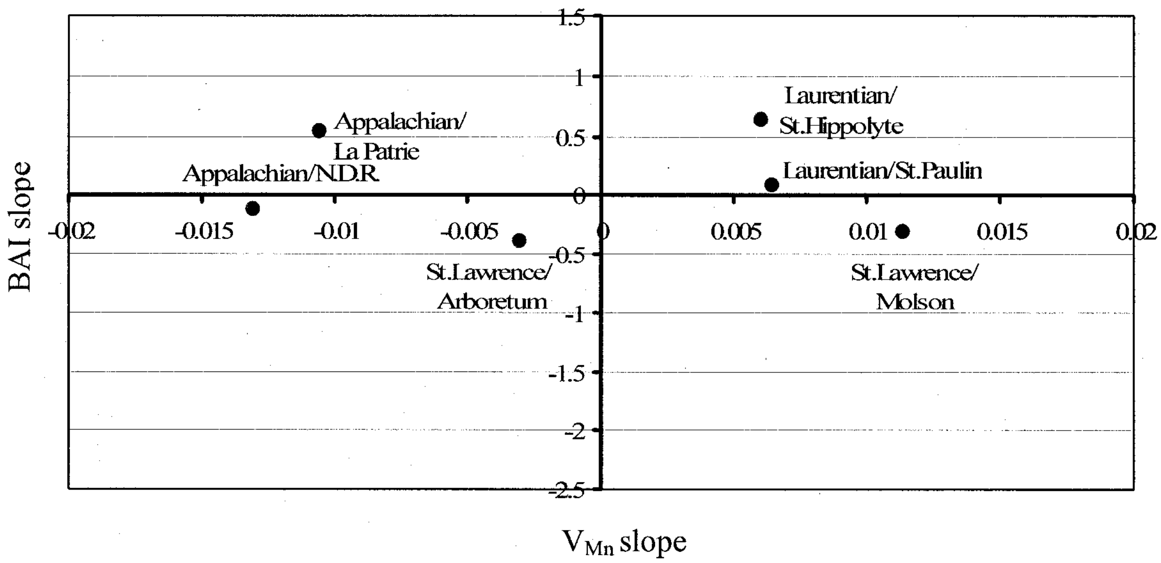
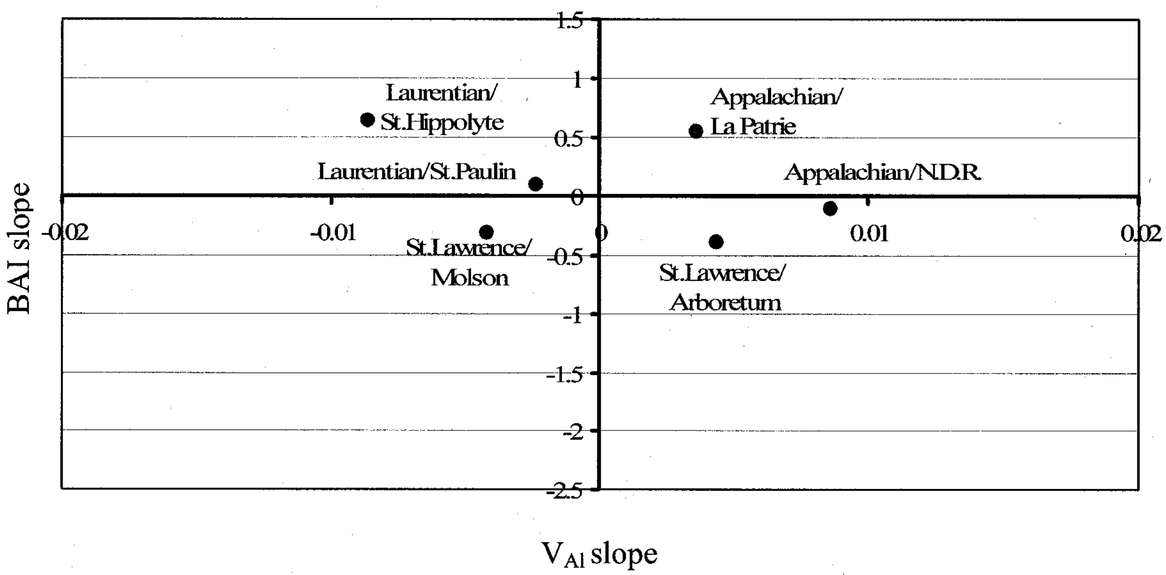


Figure 15: BAI slopes with V_{Mn} (a) and V_{Al} (b) slopes of American beech by site (given region) for 1970-1999.

a)



b)



There is a general mirror effect of sites about the axis when contrasting V_{Mn} and V_{Al} within each species regardless of growth. This result is expected as an increasing, toxic element such as Al would cause a decrease in a base cation such as Mn. As hypothesized for the sensitive regions and species, a worsening deficiency of Mn in conjunction with a worsening toxicity of Al is most apparent in sugar maple at Laurentian/St.Hippolyte, Appalachian/NDR and La Patrie and red maple at Laurentian/St.Paulin and Appalachian/La Patrie. By contrast, for the less sensitive region, sugar maple at St.Lawrence/Arboretum has increasing BAI, V_{Mn} and V_{Al} implying that Mn (being a nutrient) is improving in availability and is controlling BAI while Al is incidental. Indicative of this base rich region is the red maple at St.Lawrence/Molson having increasing BAI while incurring increasing V_{Al} and decreasing V_{Mn}. Similarly, red maple at St.Lawrence/Arboretum has decreasing BAI, V_{Mn} and V_{Al} which indicates a worsening deficiency of Mn controlling growth incidental to decreasing Al. Manganese may also have a toxic effect: a worsening toxicity of Mn in red maple at Laurentian/St.Hippolyte exists despite decreasing V_{Al}. American beech had less change in BAI than the other species yet with the notable difference that Laurentian/St.Hippolyte and Appalachian/La Patrie had increasing growth where their maple species had decreasing growth.

1.3 Regression of CND values of Ca, Mg, K, Mn and Al on BAI by time period

The total time period used for this analysis is for the period of decreased growth (1975-1999) and differs from the time period used to obtain slopes of decreasing growth in Figures 13 to 15 (1970-1999) as the time period 1970-1974 was pivotal and does not represent a decreasing period. The individual trees within this analysis cannot be considered completely independent as various groupings of species or regions are inherent. The forward stepwise regression of all element concentrations as CND values against BAI for each time period from 1975-79 through 1995-99 showed some distinct associations. Regionally, the Laurentians had a clear, positive relationship with K while the other regions had a generalized negative relationship with Al. Sugar maple had K and/or Ca in a positive relationship in each time period. Red maple generally had a positive relationship with Mn. American beech began the time period with a general negative relationship with Al which over time included a positive relationship with K and then with Mn. The regressions for species within regions had many time periods where no elements were entered into regression equation, therefore this data is not presented.

1.4 Regression of CND values of Ca, Mg, K, Mn and Al on BAI by mean of 1975-1999

Similar to the previous regression (Table 6) this analysis includes all elements as independent variables in relation to BAI in a forward stepwise regression but the time span is transformed into a mean (Table 7). Also, like the previous regression analysis, the individual trees within this analysis cannot be considered completely independent as various groupings of species or regions are inherent. The results for regions and species (Table 7 a and b) concur with Table 6 but further definition is gained from the more defined grouping of species by region (Table 7 c). These results were predicted from a combination of region (Table 6) and species (Table 6). Laurentian sugar maple (r^2=0.43) added Mn (Table 7 c) to the predicted Ca and K from Table 6 and Laurentian red maple (r^2=0.62) did not have K as predicted by Table 6, but did have Mn with the addition of Ca, Mg and Al (Table 7 c): the Laurentian maples reflect the nutrient poor status of their substrate. Laurentian Am.beech (r^2=0.27) did not retain relationships with K or Al (negative) as predicted by Table 6, but had a negative relationship with Mn (Table 7 c). Figure 15 (Am.beech) had shown increasing BAI with increasing Mn for Laurentian sites for Am.beech, but this regression analysis (Table 7 c) suggests that growth is yet being constrained by an excess of Mn. Of the Appalachian species, only sugar maple (r^2=0.24) had a significant regression: Al (negative), Ca and K were predicted from Table 6, but relationships existed for Mn (negative) and a trend in Al (negative p=0.06) (Table 7 c). This negative relationship with Mn was predictable given the Mn rich substrate of the Appalachians and that sugar maple is an acid sensitive species in an acid sensitive region. St.Lawrence sugar maple (r^2=0.15) had a trend in Al (negative; p=0.07) as predicted by Table 6 but did not retain Ca and K in this analysis. St.Lawrence red maple (r^2=0.54) had a relationship with Al (negative) as predicted from Table 6, but not one with Mn. St.Lawrence Am.beech (r^2=0.33) had a negative relationship with Al similar to Am.beech in the other regions and also to the other species of the St.Lawrence.

Table 6: Summaries of regressions of CND values of Ca, Mg, K, Mn and Al on BAI by time period (1975-1999) showing positive or negative relationship and significance at p=0.05 (those in parentheses have significance at p=0.10)

	1975-79			**1980-84**			**1985-89**			**1990-94**			**1995-99**		
	Elements	N*	R^2 ‡	Elements	N	R^2	Elements	N	R^2	Elements	N	R^2	Elements	N	R^2
Regions															
Laurentian	K	53	0.08	(K)	53	0.05	K	50	0.26	K	49	0.16	K	51	0.08
Appalachian	-Al	40	0.22	(-Al)	40	0.10	none sig.			(-Al)	40	0.09	Mg; -Al	40	0.31
St.Lawrence	-Al; -K	55	0.08	Ca; Mg; (Mn)	54	0.19	-Al	53	0.10	Mg; -Al	51	0.27	(Ca)	52	0.08
Species															
Sugar maple	K	53	0.09	K; Ca	54	0.24	Ca; K	52	0.16	Ca; -Al; K	49	0.39	Ca; (Mg)	53	0.31
Red maple	-Al; -K	42	0.22	Mn; Mg	39	0.50	Mn; Ca	40	0.26	-Al	40	0.19	Mn; (Mg)	41	0.19
Am.Beech	-Al	51	0.05	-Al	51	0.09	K; (-Al)	48	0.22	K	49	0.10	Mn; K	48	0.30

N* is number of trees in sample
‡ Adjusted R^2

Table 7: Summary of forward stepwise regressions for mean of 1975 -1999 time period of CND values of Ca, Mg, K, Mn and Al regressed on BAI of a) regions; b) species; and c) region by species. Beta values are the partial correlation of each element with BAI as all other elements are held constant. Probability levels are statistically significant at p=0.05.

a) Regions

Laurentian (N=54 and R^2 ‡= 0.03)			Appalachian (N=40 and R^2= 0.12)			St.Lawrence (N=55 and R^2= 0.11)		
	Beta	p-level		Beta	p-level		Beta	p-level
K	0.226	0.100	Al	-0.375	0.017	Al	-0.352	0.019
						Mg	0.223	0.093
						K	-0.221	0.134

b) Species

Sugar maple (N=55 and R^2= 0.31)			Red maple (N=43 and R^2= 0.30)			American beech (N=51 and R^2= 0.10)		
	Beta	p-level		Beta	p-level		Beta	p-level
Ca	0.368	0.002	Mn	0.960	0.001	K	0.356	0.020
K	0.411	0.001	Ca	0.302	0.050	Mn	0.330	0.030
Al	-0.196	0.098	Mg	0.491	0.078			

‡ Adjusted R^2

c) Species by region

(i) Laurentian species

	Laurentian sugar maple (N=20 and R^2= 0.43)			Laurentian red maple (N=17 and R^2= 0.62)			Laurentian American beech (N=17 and R^2= 0.27)	
	Beta	p-level		Beta	p-level		Beta	p-level
K	0.837	0.002	Mn	1.955	<0.001	Mn	-0.559	0.020
Mn	0.941	0.003	Ca	1.180	0.002			
Ca	0.868	0.005	Mg	0.944	0.004			
			Al	0.481	0.037			

(ii) Appalachian species (Regressions for red maple and Am.beech had no elements which could enter the regression equation)

	Appalachian sugar maple (N=15 and R^2= 0.24)	
	Beta	p-level
Al	-0.706	0.033
Mn	-0.618	0.057

(iii) St.Lawrence species

	St.Lawrence sugar maple (N=20 and R^2= 0.15)			St.Lawrence red maple (N=15 and R^2=0.54)			St.Lawrence American beech (N=20 and R^2=0.33)	
	Beta	p-level		Beta	p-level		Beta	p-level
Al	-0.406	0.072	Al	-0.777	0.001	Al	-0.604	0.005

2. Discussion

Previous attempts to relate growth and dendrochemical properties have used the assessment of tree health (i.e. declining or not) versus xylem chemical content of whole cores (Mohamed et al. 1997) or the graphical time series of growth and xylem chemistry which display synchronous aberrations (Bondietti et al. 1990). Neither of these gives a view of changing element composition in relation to growth.

A unique model, particular to the growth of northern hardwoods was developed by Ryan et al. 1994 and applied by McLaughlin (1998) where the effect of known variables (age, climate and stand dynamics) were removed. The model residuals had variability attributed to: between trees within a stand (13%); between stands within a sampling region (7%); and within tree (79%). The latter percentage was of unknown regional, environmental influence, implying ambient pollution. An inflection point in growth curves of northeastern species around the mid-1960s has been noted to be coincident with pollution increases (Bondietti et al. 1990; Duchesne et al. 2002). A critical load model was developed by Sverdrup et.al. (1994) based on Swedish soils and acidic deposition at 1990 levels which showed a large percentage of the forests affected by growth reductions. This assessment is similar to southern Quebec in terms of soils, deposition and noted growth reductions of sugar maple.

In this thesis, growth was not standardized as this process would remove long-term trends on growth and instead express punctual variability of environmental factors (Duchesne et al. 2002) when long term trends were of more interest. The expected growth trends of the three species should approximate a positive linear trend for the years/ages given (Duchesne et al. 2003). The trees used in this study have a constrained range of physiological age-since-release in order to reduce variability from chronological and physiological age. Although the expected growth rates between the species differ, with red maple having a faster growth rate and earlier senescence, and American beech a slower growth rate and later senescence in comparison to sugar maple (Burns and Honkala 1990), the linear trends should all be consistent and positive for this phase (maturation) of the species' life histories. During the time frame under consideration, all trees should be post-suppression, pre-senescence, and therefore in the maturation phase of growth rate or BAI. The Saint-Lawrence was hypothesized to represent a baseline for growth considering its nutrient rich soil with good buffering capacity. As well, amongst species, American beech was predicted to best fit the expected growth trends despite influences of acidity changes. From Figure 12 it is apparent that some of this expectation was true. Sugar maple of the Saint-Lawrence and American beech of the Laurentians and Appalachians have an approximation of the expected growth trend under constant or naturally occurring change. In the other combinations of regions and species, there may have been a fertilization effect due to increases of deposition of anthropogenic N which maintained or increased growth trends (Falkengren-Grerup and Eriksson 1990) to reach observed peaks in growth in 1960 to 1970. Most of these growth trends eventually had either a *nil* or negative slope. This pattern is similar to the findings of Nellemann and Thomsen (2001) of Norway spruce on acid sensitive soils exposed to acidic deposition in southern Norway. They found a decline in growth through the 1980s and 1990s: a change from peak growth in a relatively short time scale. A negative trend of BAI is a strong indicator of decline (i.e. adverse health not necessarily related to age) (LeBlanc 1990). Of primary interest is the effect of Al and Mn on BAI as noted and/or suggested throughout numerous previous studies (Bondietti et al. 1989; Timmer and Teng 1999; Watmough 2002) for the time period beyond the generalized peak/plateau of assumed N enrichment: 1975.

Figures 13, 14 and 15 show the linking trends of the slopes of BAI with V_{Mn} and V_{Al} for sugar maple, red maple and American beech respectively. As predicted, the change in BAI over time was negatively associated with Al and positively associated with Mn for the sensitive regions and species. This situation of implied Mn deficiency is in contrast to the suggestion by Timmer and Teng (1999) that an increase in Mn is adversely affecting growth in sugar maple (although BAI of red maple at Laurentian/St.Hippolyte appears to suffer from increasingly toxic Mn levels). In numerous studies of watersheds with soils sensitive to acidity, there have been relationships of lower growth rates in conjunction with base cation loss and increased acidity (Duchesne et al. 2002; Kolb and McCormick 1993; Ouimet et al. 2001). The dual adverse effects of Mn on BAI of saturation/antagonism and decreasing Mn levels may occur simultaneously. In this thesis V_{Mn} is consistently negatively correlated with the other base cations regardless of region or species (data not shown), which implies antagonism. Manganese, like the other base cations, is decreasing over time perhaps from the negative correlation (indicative of antagonism) generally shared with Al (data not shown).

A regression of growth against plant tissue nutrient concentration should yield a quadratic relationship when boundary points are used. Vizcayno-Soto and Côté (2004) devised methods to gain an accurate regression for diagnosing optimum foliar nutrient concentrations. A sample size of at least 50 individuals per species per site is suggested. These methods were beyond the scope of this thesis and the next best methods were applied given the more modest sample sizes (although in terms of dendrochemistry the sample is large). As a consequence, the ability to explain variation in growth dependant on nutrients and Al is diminished. The forward stepwise regression of BAI and all elements discerned by individual time periods (Table 6) clarifies the previous analysis (Figures 13 to 15) and allows a view of the change of primary element(s) controlling growth over this 25 year time period. Al and Mn were shown to primarily control growth but Mn was in positive relationships and K was of paramount importance to Laurentian growth while sugar maple had an evolution of change from K to Ca. The subsequent and similar regression using a mean of the decreased period of growth (Table 7) revealed relationships that weren't expected from the previous, more generalized groupings (Table 6: species or region). Intuitively, a more definitive grouping should reveal more defined relationships although sample size may be compromised with the possible consequence of a stepwise regression with no admissible elements (i.e. Appalachian red maple and Am. beech). Also, the more comprehensive, changing relationships over time were exchanged for the mean of the complete time period. Manganese was noted in positive (i.e. deficiency) and negative (i.e. excess) relationships at this scale. Most notable was the trend of an adverse effect of Mn ($p=0.06$) for Appalachian sugar maple which occurred secondarily to the adverse relationship with Al (Table 7 c). This situation is expected given that Mn levels are high across the species of this region and that both the region and species are sensitive to acidity. This result of an adverse effect on growth combined with the result from Figure 13 of decreasing Mn imply that this situation will persist as long as there are high Mn concentrations relative to the other nutrient cations. As Al is increasing (Figure 13 b) and is the primary adverse influence on BAI (Table 7 c), the role of Mn may diminish as pH drops and less Mn is mobilized. The suggestions of Timmer and Teng (1999) of Mn toxicity in sugar maple are therefore justified for the Appalachians. This nutrient imbalance may be better termed 'an excess of Mn'. Additionally, although sugar and red maple of the Laurentians show a deficiency in Mn, Am.beech has growth constrained by excess Mn (given the result of increasing growth in Figure 15).

Why would American beech in sensitive soil regions such as the Laurentians and Appalachians have increasing growth rates while sugar maple and red maple do not (Figure 12 d and Figures 13-15) In addition to the differences in relationships with mycorrhizae, could American beech be benefiting from the void in nutrient acquisition of the other species? A study of forest composition of some stands affected by maple decline predicts a change in forest composition with American beech taking over dominance from sugar maple (Duchesne et al. 2005). American beech leaf litter leachates are known to adversely affect sugar maple seedling growth (Hane et al. 2003) but the effect of mature trees of American beech on red maple and sugar maple is unknown.

A study of red spruce, a species known to be susceptible to acid precipitation, highlighted the problem of oversimplifying the relationship between Al and health. It showed that although Al levels could be at established toxic foliar levels, if sufficient Ca was present in the needle membrane, the toxic effect of Al was reduced yielding better resilience to freezing damage (Borer et al. 2004). This effect was found by using sequential digestions, similar to this thesis, in order to reveal differences in each fraction's relationships to various parameters. This is another example of relative quantities of elements rather than simple concentrations being deterministic.

CHAPTER VI
SUMMARY/CONCLUSION

The base rich Saint-Lawrence region had the highest and slightly increasing incremental stem xylem Al (CND) of the regions yet had stable or positive growth. By contrast the acid sensitive Appalachian region had the greatest increase in Al (CND) accompanied by a loss of growth since 1970. The acid resilient species American beech had stable or decreasing Al (CND) while having stable or positive growth in contrast to the less resilient sugar and red maple. The nutrient poor Laurentian region had a consistently positive relationship over time between growth and K (CND) without a relationship with Al other than the general negative correlation with the other cations noted amongst all regions and species. Although Mn had the highest levels in red maple (for each region) it had a positive relationship with growth.

Manganese in the Appalachians prior to 1970 may have been a more sensitive indicator of soil acidification than Al as an increase followed by a decrease was noted during this time. Mn was generally decreasing amongst regions and species but nonetheless an excess ($p=0.06$) was adversely affecting growth of sugar maple in the Appalachians. This region has high Mn and has received high levels of acidic deposition and is moderately sensitive to acidification. The suggestion by Timmer and Teng (1999) of Mn toxicity of sugar maples from increased acidification on sensitive soils may be requalified in this instance as an imbalance of excess Mn. Additionally, Mn appeared to be consistently antagonistic to other cations in uptake.

Compositional Nutrient Diagnosis for data analysis in a time series yielded information about ranking of species and region in elemental content and direction of change of elements over time that simple concentrations or bivariate ratios would not necessarily reveal. The CND transformation of nutrient concentrations decreases the variation in tree ring chemistry. This aspect is very useful as xylem rate of growth has many influences creating extensive variability within and between trees that can exceed differences between stands. For comparison purposes between studies, CND holds value not seen before in dendroecological studies and should be encouraged into usage by researchers.

The optimum balance or composition of elements in tree foliage is known for only a few tree species (Vizcayno-Soto and Côté 2004). No standards exist for xylem wood of any species, although past studies hold comparable data for total xylem concentrations (as compared to the fractions in this work). Species' standards would aid monitoring efforts of hardwood forest nutrition and health. However, the ongoing problem of re-equilibration of exchangeable ions within xylem needs to be examined and a verification of the efficiency of the methodology to wash-out extractive compounds of the heartwood rings (Cutter and Guyette 1993) is necessary before any standards can be established. Also, the small sample sizes typically used in dendrochemistry would need to increase substantially to gain definitive results.

As mass balance modelling has been suggested to be 'a best guess at cation loss from watersheds' (Watmough et al. 2005), tree ring chemistry as an *in vivo* expression of cation change over time may have advantageous potential if the pertinent signals can be discerned amongst the noise generated by the numerous dendroecological variables. Through the use of novel methodologies in dendrochemistry, such as sequential digestion and Compositional Nutrient Diagnosis, this study was able to identify regions and species at risk from increases in acidification which may affect growth and ultimately species composition. The challenge remains to remove the problems of traditional dendrochemistry to enable future predictions of ecophysiological changes.

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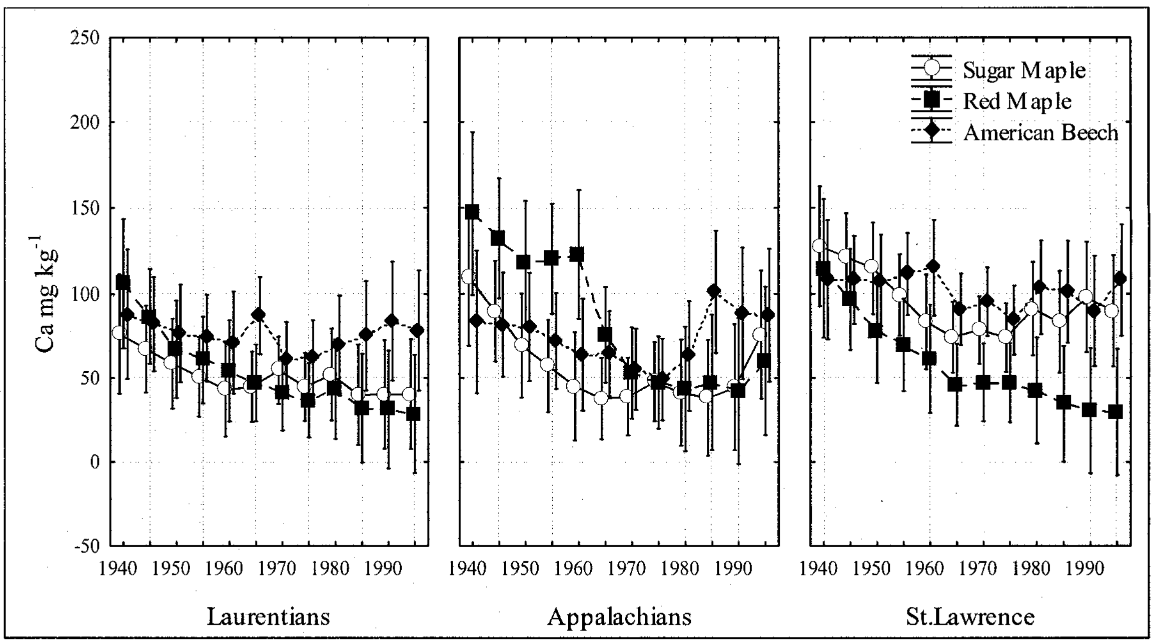
APPENDICES
SUPPLEMENTAL FIGURES AND TABLES

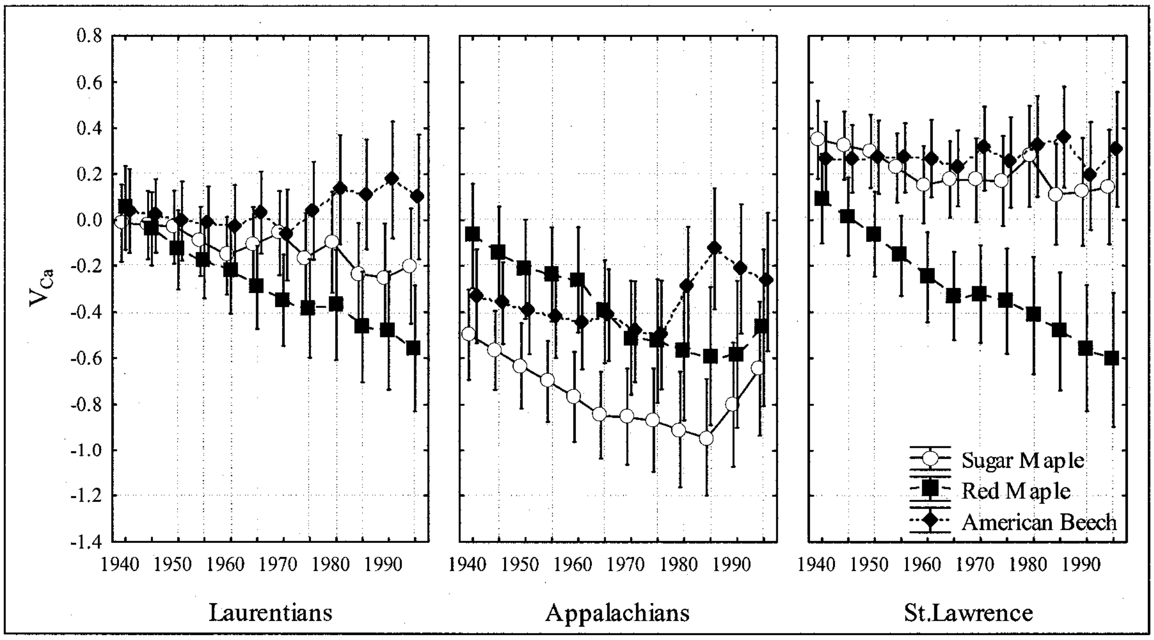
APPENDIX I

Figure A 1: Elemental concentrations and CND values for each combination of species and sites. Bars are 95% confidence interval; points representing 1945 and 1955 are interpolations.

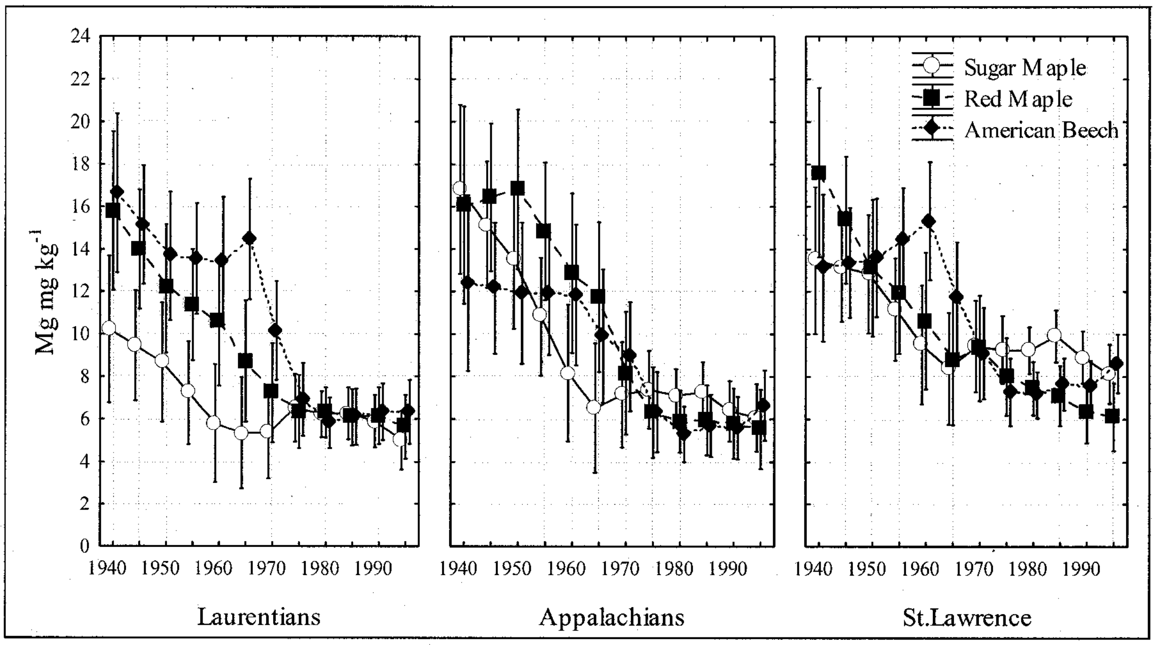
a) [Ca]



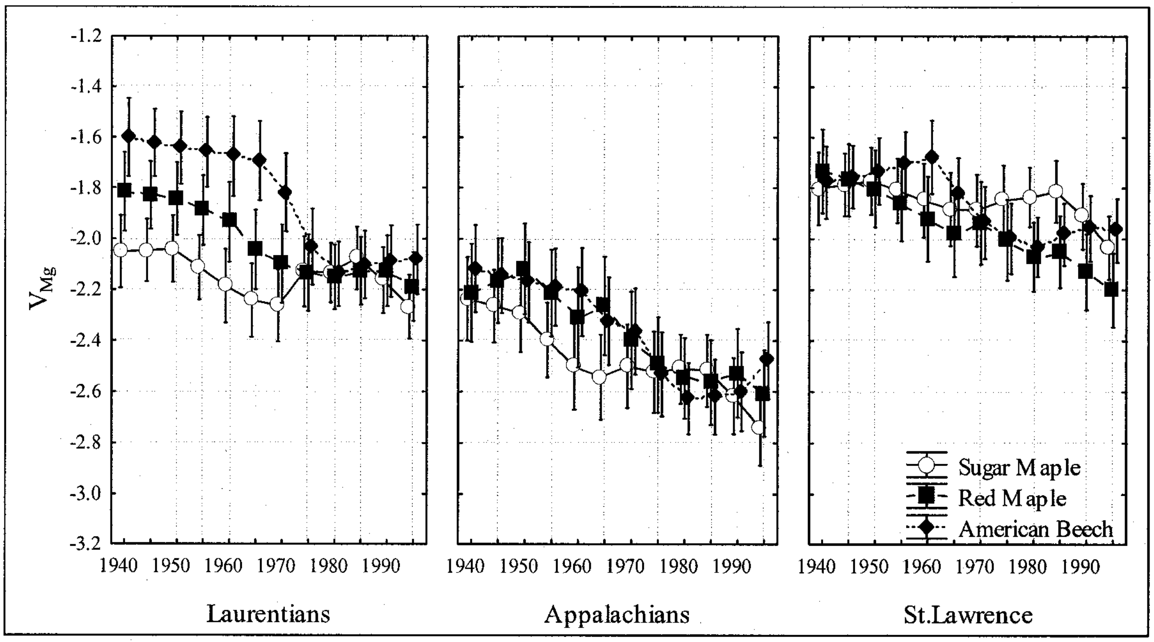
V_{Ca}



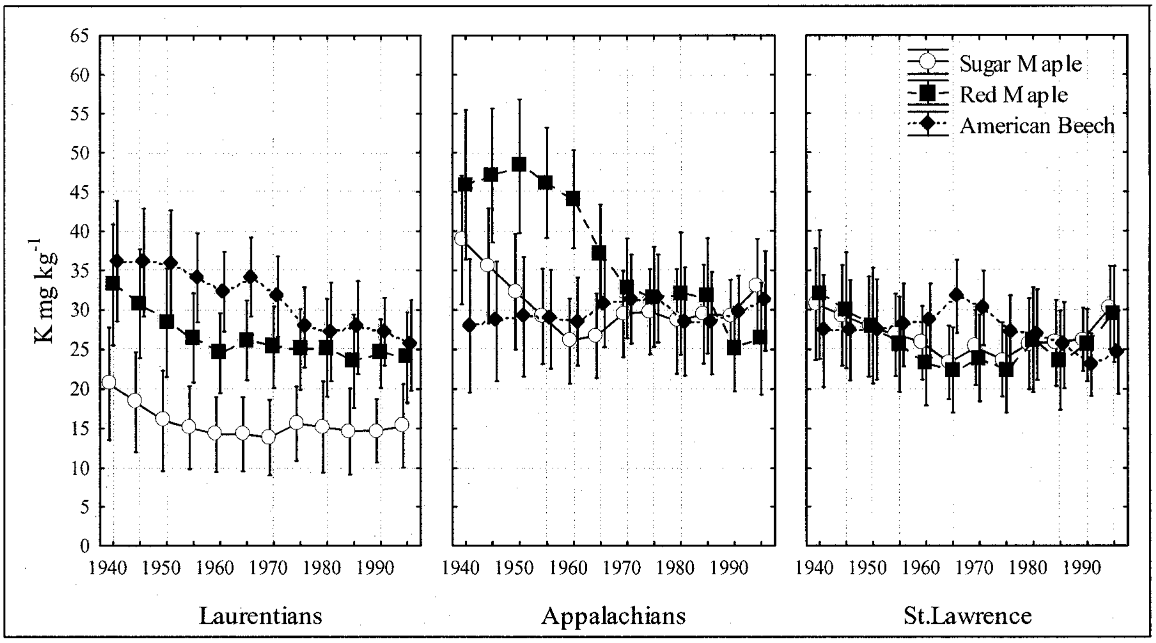
b) [Mg]


Mg mg kg^{-1}
Sugar Maple
Red Maple
American Beech
Laurentians
Appalachians
St.Lawrence

V_{Mg}

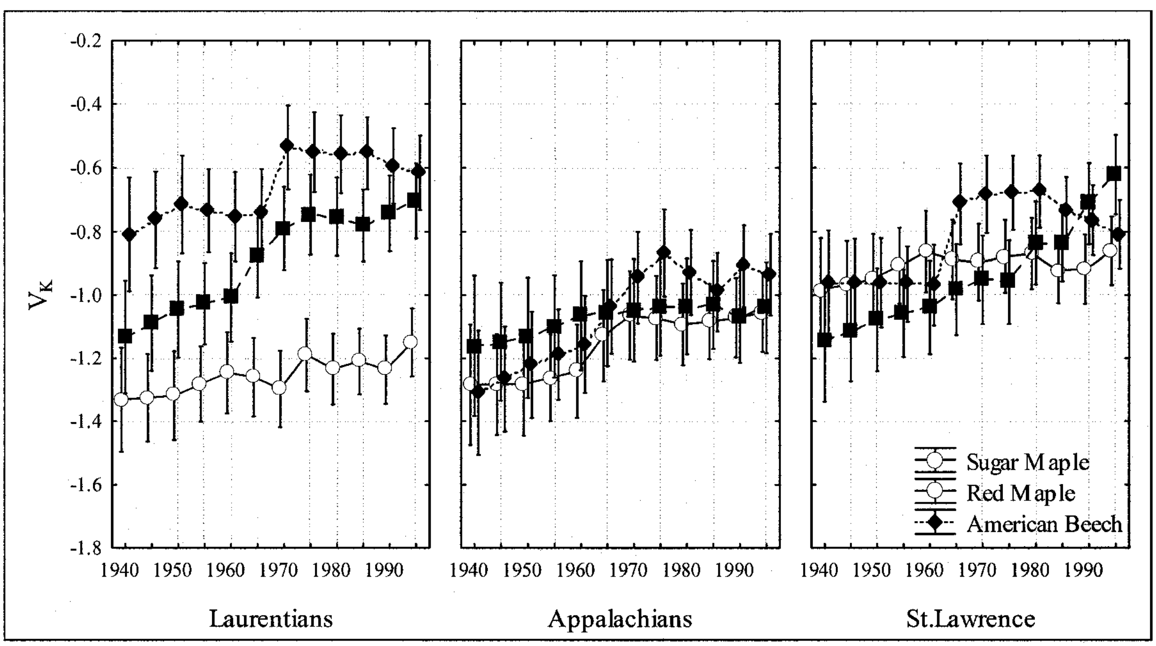

V_{Mg}
Sugar Maple
Red Maple
American Beech
Laurentians
Appalachians
St.Lawrence

c) [K]



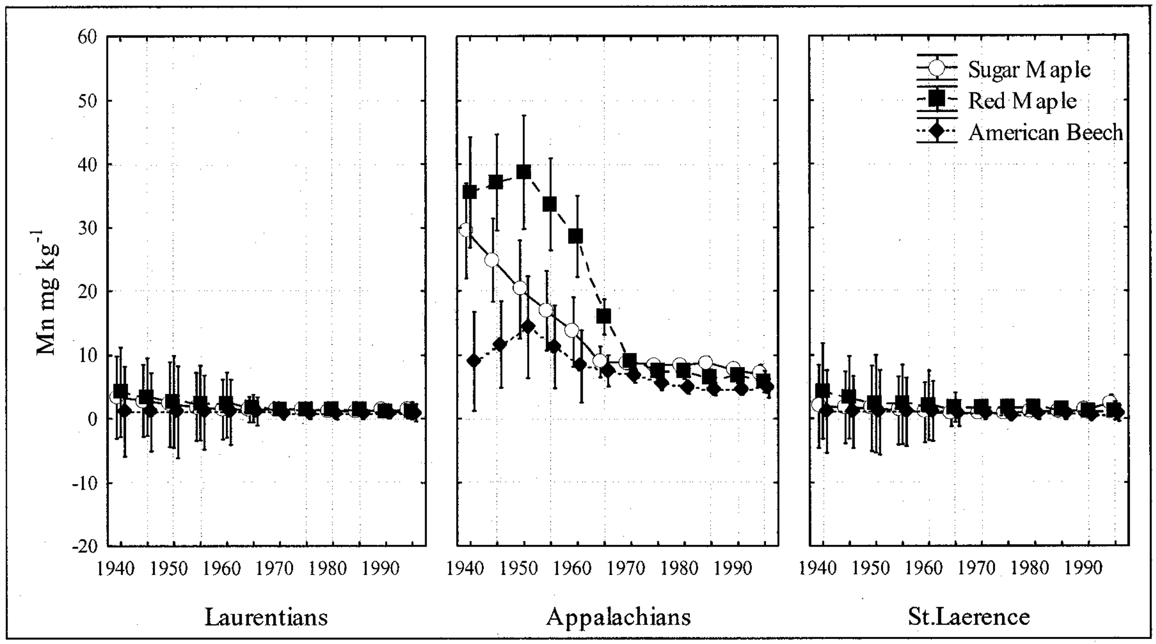
K mg kg-1
Sugar Maple
Red Maple
American Beech
1940 1950 1960 1970 1980 1990
Laurentians
Appalachians
St.Lawrence

V_K

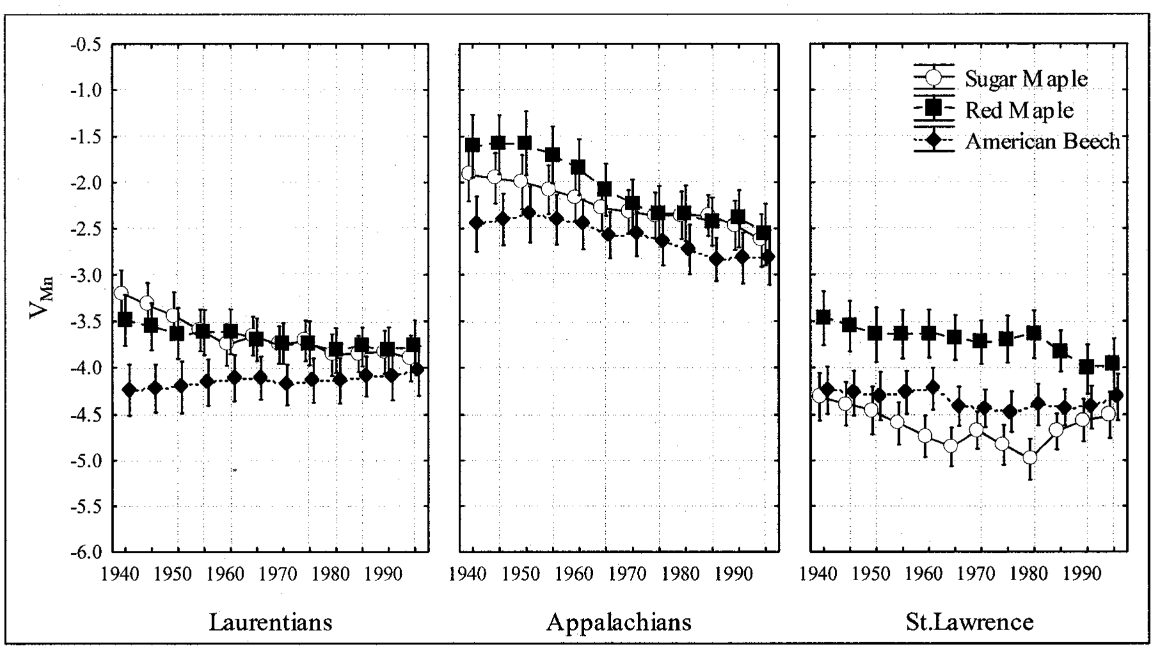


V_K
Sugar Maple
Red Maple
American Beech
1940 1950 1960 1970 1980 1990
Laurentians
Appalachians
St.Lawrence

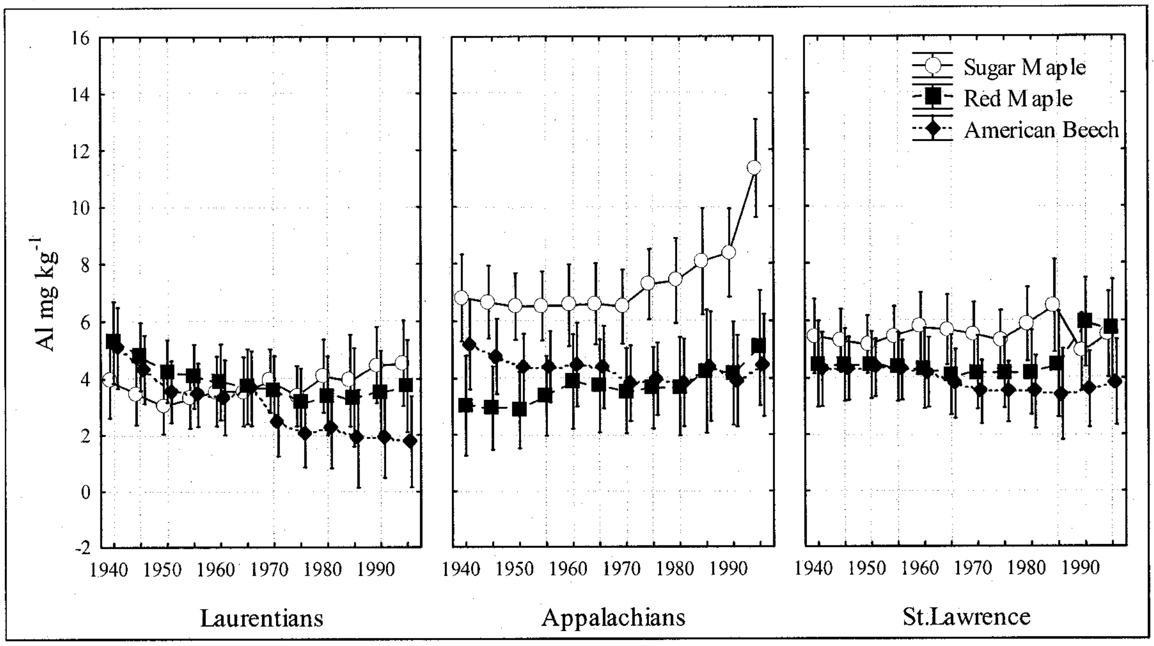
d) [Mn]


Sugar Maple
Red Maple
American Beech
Mn mg kg-1
60
50
40
30
20
10
0
-10
-20
1940 1950 1960 1970 1980 1990
Laurentians
Appalachians
St.Laerence

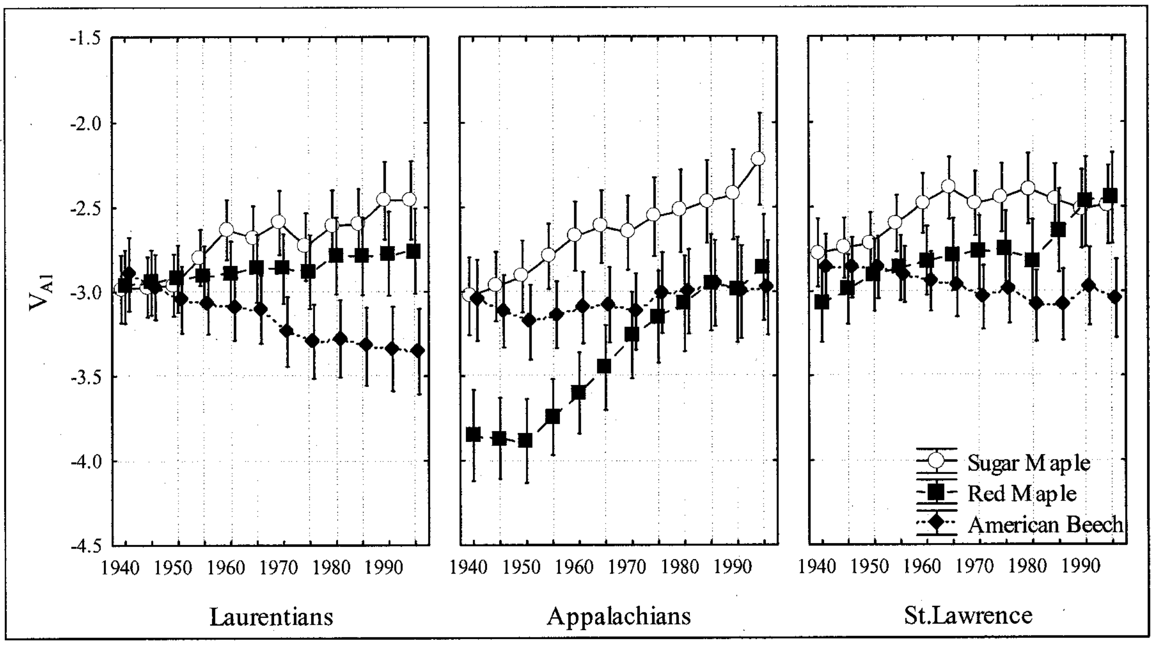
V_{Mn}


Sugar Maple
Red Maple
American Beech
VMn
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
-4.5
-5.0
-5.5
-6.0
1940 1950 1960 1970 1980 1990
Laurentians
Appalachians
St.Lawrence

e) [Al]


Al mg kg^{-1}
16
14
12
10
8
6
4
2
0
-2
1940 1950 1960 1970 1980 1990
Laurentians
Appalachians
St.Lawrence
Sugar Maple
Red Maple
American Beech

V_{Al}


V_{Al}
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
-4.5
1940 1950 1960 1970 1980 1990
Laurentians
Appalachians
St.Lawrence
Sugar Maple
Red Maple
American Beech

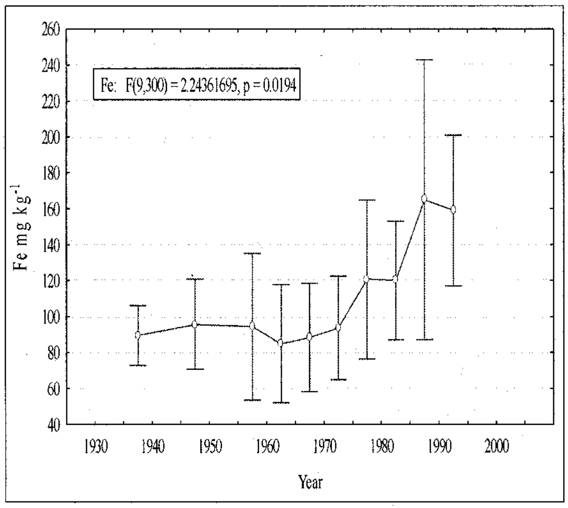
APPENDIX: II

IRON CONCENTRATIONS AND CND VALUES

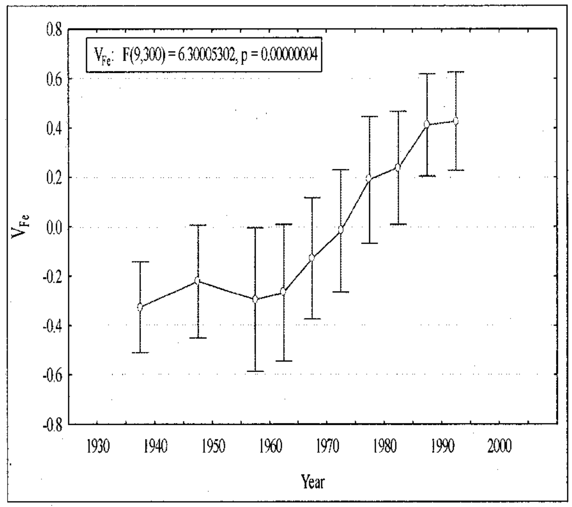
Iron (Fe) was analysed for only the first 37 trees, representing primarily the Appalachian site of La Patrie (10 sugar maple; 11 red maple; and 10 American beech) and three sugar maples from each of Laurentian/Saint-Paulin and Saint-Lawrence/Molson Reserve. Large variances were noted in a preview of the Fe concentrations. These differences are not unusual as iron is highly variable amongst trees (personal communication with S.Watmough) but some of the variability was suspected to be at least partially influenced by contamination from instruments as the concentrations within trees fluctuated, although such fluctuations have been noted in the literature (Vimmerstedt and McClenahen 1995). Retrospectively though, the variability was similar to those of other elements as were the trends. Figure A 2 shows Fe and Al concentrations and associated CND values (for all species considered together) of La Patrie. [Fe] increased in La Patrie from the 1980 time period, although [Al] only increased in the last time period (1995-1999). More importantly, V_{Fe} increased from the 1970 time period, whereas V_{Al} began to increase earlier, after 1960). This could be indicative of increasing acidity as Al is mobilized before Fe (refer to Figure 8).

Figure A 2: La Patrie (all species) (a) [Fe] and V_{Fe}. and b) [Al] and V_{Al}. Bars are 95% confidence intervals.

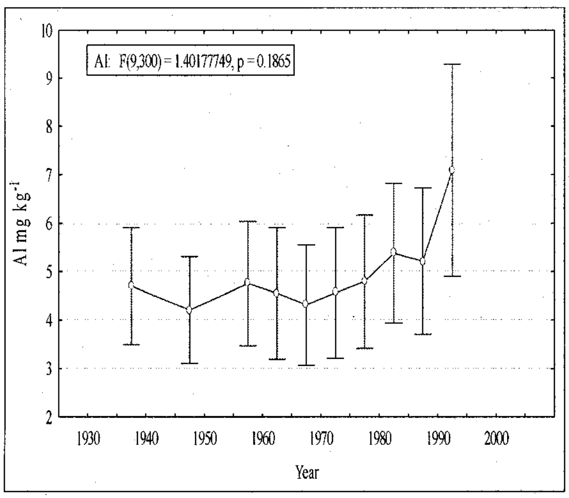
a) [Fe]



V_{Fe}



b) [Al]



V_{Al}