

Combining tree-ring metal concentrations and lead, carbon and oxygen isotopes to reconstruct peri-urban atmospheric pollution

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ABSTRACT

In this study, we analysed the tree-ring metal concentrations and isotope ratios of five stands located in three contrasted settings to infer the diffuse air pollution history of the northern part of the Windsor–Québec City Corridor in eastern Canada. Tree-ring series show that the Cd and Zn accumulation rates were higher between 1960 and 1986 and that the long-term acidification of the soil (Ca/Al series) was likely induced by NO_x and SO_x deposition ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ trends as proxy). The Pb concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios indicate that the dominant source of lead from 1880 to the 1920s was the combustion of north-eastern American coal, which was succeeded by the combustion of leaded gasoline from the 1920s to the end of the 1980s. Our modelling approach allows separating the climatic and anthropogenic effects on the tree-ring $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ responses. Diffuse air pollution caused an enrichment in ^{13}C in all stands and a decrease of the $\delta^{18}\text{O}$ values only in three of the stands. This study indicates that dendrogeochemistry can show contrasted responses to environmental changes and that the combination of several independent indicators constitutes a powerful tool to reconstruct the air pollution history in the complex context of peri-urban regions.

Keywords: atmospheric pollution, tree rings, stable isotope ratios, metal concentrations, lead isotope ratios, multi-elemental analysis

1. Introduction

The reconstruction of atmospheric pollution is essential to infer past levels of contamination and to evaluate the impact of environmental regulations on forest ecosystem. In North America, the systematic long-term monitoring of air pollutants is generally limited to the last 20 yr and restricted to urban areas or rural point-source regions. Several natural archives can be used to palliate the lack of long-term past records. Some can infer only the contemporary pollution level such as moss (Weiss et al., 1999) or lichens (Carignan et al., 2002), or have a circumscribed geographical distribution such as glacier ice (e.g. Zheng et al., 2007) and non-remobilised lake sediments (e.g. Ouellet and Jones, 1983). Unlike those natural archives,

trees are widespread and can provide annual records of air pollution over several decades, even centuries. Trees are suitable to reconstruct the historical changes of environmental perturbations because the metal concentrations and isotopic ratios of their annual rings represent at least partly the chemistry of the environment (air and soil) at the time of their formation (Amato, 1988).

Previous applications of dendrogeochemistry have shown that the long-term modification of the tree-ring carbon ($\delta^{13}\text{C}$), oxygen ($\delta^{18}\text{O}$), nitrogen ($\delta^{15}\text{N}$) and hydrogen ($\delta^2\text{H}$) isotopic values is modulated by environmental conditions, such as climate, tree diseases, land use or air quality, because trees absorb natural and anthropogenic compounds through the same pathways (leaves, bark and roots). The cited dendrogeochemical indicators can also provide insights on the physiological adaptation of trees to those environmental changes. Several studies have been successful to infer long-term trends of point source air

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pollution (e.g. Freyer, 1979; Sakata and Suzuki, 2000; Savard et al., 2004; Savard et al., 2005, 2006; Wagner and Wagner, 2006; Novak et al., 2010; Mihaljevič et al., 2011), but few studies have addressed the question of diffuse atmospheric pollution as reconstructing environmental changes in such a context constitutes a real challenge (e.g. Bukata and Kyser, 2007; Savard et al., 2009a, b; Doucet, 2011). Among those studies, six have combined several dendrogeochemical indicators to reconstruct the past history of air pollution (Savard et al., 2006; Mihaljevič et al., 2008; Kwak et al., 2009; Novak et al., 2010; Doucet, 2011; Mihaljevič et al., 2011). However, only one study has combined multiple indicators to infer the diffuse air-pollution history and a new statistical approach with tree-ring carbon isotopic values to clearly model and separate the effect of climatic conditions from the impact of anthropogenic air pollution (Doucet, 2011). This last study has combined metal concentrations (As, Cd, Zn) and isotope ratios ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) of a single tree species and presented a temporal perspective on pollution for a site located at the north-east end of the Windsor–Québec City Corridor (Canada), one of the three most polluted regions in Canada (Reid et al., 1996). Other pieces of work presented spatial perspectives in this region, through the geochemical analyses of epiphytic lichens (Carignan et al., 2002) and surface lake sediments (Blais, 1996), but these investigations used only one indicator (lead) and covered a narrow time span.

In the present study, we document $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ values with metal concentrations (Ca/Al, Cd, Zn, Pb) of tree-ring series covering the 1880–2007 period. These analysed tree-ring indicators were selected for their complementarity and their links with air pollution. The Cd, Zn and Pb concentrations represent the particles commonly emitted by several pollutant industries, and the tree-ring Ca/Al ratios were analysed to understand the history of soil acidification. The Pb isotopes values were studied to identify the principal sources of Pb depositions, and the C and O isotope values were selected to verify the impacts of air pollution on the physiological mechanisms of trees. Those indicators were studied with four species (*Picea rubens* Sarg., *Fagus grandifolia* Ehrh., *Pinus strobus* L. and *Thuja Occidentalis* L.) from two distant sites along the Windsor–Québec Corridor, and integrate and interpret them along with the published multi-indicator dendrogeochemical data set obtained near Québec (Doucet, 2011). This interspecies investigation aiming at assessing if multiple tree-ring geochemical indicators can depict the distinct pollution history for three peri-urban areas located along the Windsor–Québec City Corridor, and increasing our understanding of the response of various tree species to air pollution.

2. Materials and methods

2.1. Selected sites

The three selected sites (Fig. 1) are located along the north-east section of the Windsor–Québec Corridor. This industrial axis is highly populated, industrialised and one of the most polluted regions of Canada partly due to its geographical location and population density (Reid et al., 1996). The selected study sites have to be located in the peri-urban areas of the three most important cities of the Corridor (Québec City, Montréal and Toronto), be part of protected areas where the anthropogenic perturbations of the last 100 yr are limited or not present, and where healthy trees of at least 100-years-old are present (Table 1). The site in the north-eastern end of the Windsor–Québec City Corridor (Qc site) is located 40 km northwest of Québec City at the Tantaré Ecological Reserve (47°04' N, 71°32' W; Fig. 1). The site corresponding to the centre of the Windsor–Québec City Corridor (Mtl site) is located 30 km west of downtown Montréal in the Morgan Arboretum (45°25' N, 73°57' W; Fig. 1). Finally, the site representing the western part of the Windsor–Québec City Corridor (GB site) is located at 110 km of Toronto on Beausoleil Island, in the protected area of the Georgian Bay Islands National Park (14 km², 44°52' N, 79°52' W; Fig. 1). The studied tree species and the environmental conditions differ between each site (Table 1).

2.2. Sampling and sample preparation

The soil horizon samples were collected along a typical vertical profile at every studied sector. Between 11 and 30 trees of each stand were carefully selected and sampled at breast height with a 5- and 12-mm diameter increment borer for dendrochronological purpose (Table 2). Those cores were sanded and measured using standard dendrochronological methods. The COFECHA program was used to verify dating (Holmes, 1992). Among those trees, three specimens of each stand were selected for isotopic and metal concentration analyses. They must have more than 100 years old, dominate the surrounding trees and show a good general health. From those trees, the rings of four cores per tree were manually separated at 2-yr resolution (ring-pair) with clean stainless blades from 1880 to 2007. Exceptionally, tree rings of the Qc site were separated from 1840, and those of the period from 1880 to 1915 and 1970 to 2007 were annually separated. For each tree, the corresponding tree rings of the four cores were pooled together for geochemical analyses. Tree-ring subsamples were split into two parts to make isotopic and elemental analyses on the same material. One part was ground with a Wiley mill at 40 mesh and used for analysis of tree-ring $\delta^{13}\text{C}$ and

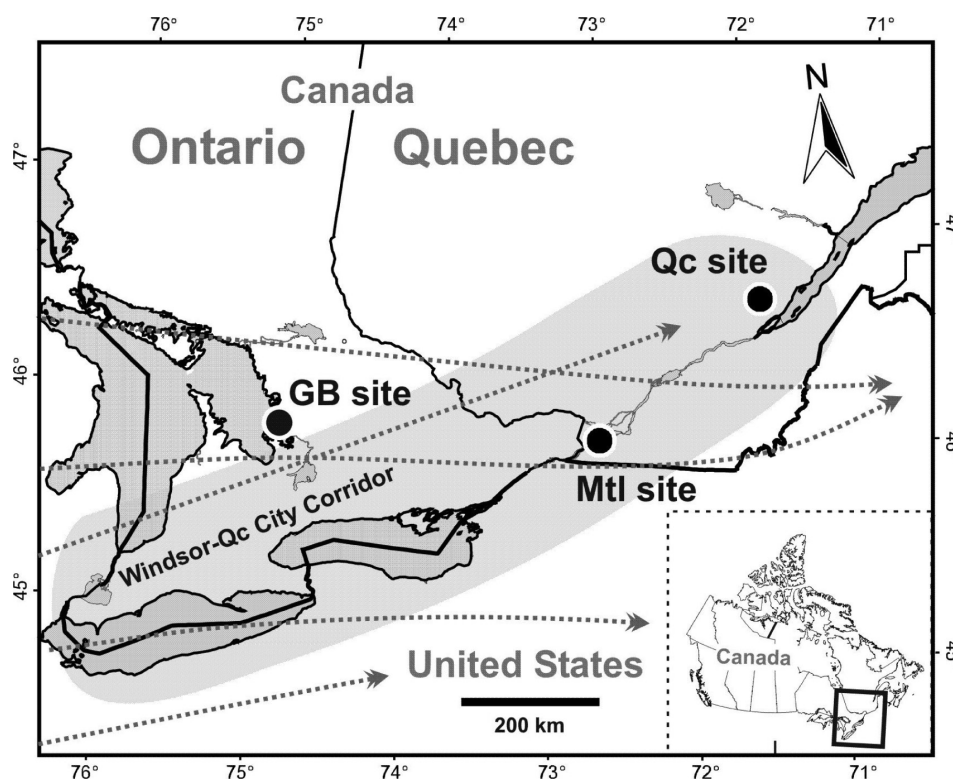


Fig. 1. Location of the Québec (Qc), Montréal (Mtl) and Georgian Bay (GB) study sites. Arrows indicate the main directions of cyclones over North America (Irving, 1990).

$\delta^{18}\text{O}$ values. The second part was cut into small pieces of wood and used for the analyses of metal concentrations and lead isotope ratios. Seven wood samples of each tree were first analysed to ensure that the studied metal concentrations and lead isotope ratios followed similar long-term patterns. If geochemical values follow similar trends, the ring-pairs of the three trees by stand were combined in order to provide sufficient amount of wood for the geochemical analyses.

2.3. Stable isotope analyses

To prevent inter-ring artificial $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ variations caused by fluctuating proportions of wood components, the ground samples were treated to extract cellulose (Savard et al., 2004, references therein). The treatment involves removal of soluble compounds using a mixture of benzene/methanol (1:1) and acetone. Those steps include bleaching the wood sample with sodium chloride (17%) and acetic acid (10%) for delignification and subsequent

Table 1. Study site description

Site (coordinate)	Tree species (cambial age)	Soil type (geological province)	Soil pH		Mean summer temperature (°C)	Total annual precipitation (mm)
			Organic horizon (L, F, H)	Mineral horizon (C)		
Qc (47°04' N, 71°32' W)	<i>Picea rubens</i> Sarg. (236–280)	Podzol derived from till (Canadian Shield)	3.80	4.48	18	1124
Mtl (45°25' N, 73°57' W)	<i>Fagus grandifolia</i> Ehrh. (130–138); <i>Pinus strobus</i> L. (111–143)	Brunisolic soils derived from sandy alluvial deposits (St. Lawrence Lowlands)	4.41	4.70	20	975
GB (44°52' N, 79°52' W)	<i>Fagus grandifolia</i> Ehrh. (140–149); <i>Thuja</i> <i>occidentalis</i> L. (160–180)	Brunisolic (beech – St. Lawrence Lowlands) and gleysolic (cedar – Canadian Shield) soils	5.11	6.05	21	1100

Table 2. Information summary for trees sampled for geochemical analyses

Site	Tree species	No. of trees for dendrochronology/dendrogeochemistry	$\delta^{13}\text{C}$ values		$\delta^{18}\text{O}$ values	
			EPS	Mean variability (‰)	EPS	Mean variability (‰)
Qc	Red spruce	30/3	0.9	0.3	0.9	0.7
Mtl	Beech	12/3	0.8	0.4	0.9	0.6
	Pine	20/3	0.8	0.3	0.7	0.4
GB	Beech	11/3	0.8	0.4	0.8	0.5
	Cedar	13/3	0.9	0.3	0.8	0.5

alkaline extraction removed hemicelluloses. Wood samples are then soaked in acetic acid, carefully rinsed with demineralized water and dried in oven. Wood samples were analysed at the Delta-Lab of Natural Resources Canada. In order to determine the $\delta^{13}\text{C}$ values of trees, cellulose (0.2 mg) was encapsulated in tin and combusted in an Elemental Analyzer (Carlo Erba, NC 2500) in Continuous Flow with an Isotope Ratio Mass Spectrometer (IRMS; Fisons Prism III). The $\delta^{13}\text{C}$ values were calibrated relative to the international standards NBS 19, LSVEC and IAEA-CH-6, and the accuracy of the method ($\pm 0.3\text{‰}$) was assessed using the internal standard vanillin. Cellulose samples (0.2 mg) were encapsulated in silver for the analysis of their $\delta^{18}\text{O}$ values and combusted in a pyrolysis-elemental analyser online with an IRMS (TC/EA-CF-IRMS; Thermo Finnigan Delta Plus XL). The $\delta^{18}\text{O}$ values are calibrated relative to the IAEA C3 reference material, and the accuracy of the method ($\pm 0.3\text{‰}$) was assessed using the internal standard sucrose and vanillin. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ results are reported in values relative to VPDB and VSMOW, respectively. For the three study sites, a total of 1131 wood samples were analysed for their $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, and the precision on duplicates was $\pm 0.1\text{‰}$ for $\delta^{13}\text{C}$ ($n = 209$) and $\delta^{18}\text{O}$ ($n = 101$).

The $\delta^{13}\text{C}$ results were corrected with a Matlab code to remove the long-term decline of the $\delta^{13}\text{C}$ values and the increase of ambient carbon dioxide (CO_2) concentrations caused by industrialisation (McCarroll and Loader, 2004; McCarroll et al., 2009; McCarroll, 2010). Also, a total of 17 ring pairs representing parts of the isotopic series showing juvenile effect, such as the assimilation of CO_2 with depleted isotopic values emitted by the surrounding plants and soil during the early stage of tree growth, had to be withdrawn (da Silveira Lobo Sternberg et al., 1989; Duquesnay et al., 1998). Then, each isotopic series was normalised relatively to its average value to minimise inter-tree and interspecies differences potentially induced by metabolic effects. The expressed population signal (EPS; Table 2) representing the short-term inter-tree correlation of results was applied to verify if tree results are representative of the site (Wigley et al., 1984). Finally, the Gleichlaufigkeit parallel agreement (GLK) was used to

measure the synchronicity of variations between the analysed parameters (Kaennel and Schweingruber, 1995), whereas the Pearson correlation coefficient (r) was used to measure the long-term agreement between the studied series.

2.4. Statistical approach for the treatment of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ results

Statistical models were built to verify if the variations of the tree-ring $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the entire studied period were fully explained by natural causes (climatic conditions). Artificial neural network (Guiot et al., 1995; Guiot and Nicault, 2010) was used to build non-linear regression between tree-ring isotopic values and their highest correlated (r) meteorological parameters for the oldest period (calibration period), which is assumed to be the least air polluted (1880–1881 to 1938–1939 for the Mtl and GB sites; 1880–1909 for the Qc site; $n = 30$). The model selection was mainly based on the highest coefficient of determination (r^2). The derived equation reproducing the isotopic values based on meteorological conditions for the calibration period is then applied to the recent period (1940–1941 to 2006–2007 for the Mtl and GB sites; 1910–2007 for the Qc site) to estimate the isotopic values. Deviation between the measured and modelled isotopic values will suggest that natural conditions cannot entirely explain the isotopic trends (given that ecological causes have been previously discarded), but that another factor, such as air pollution, may have influenced the absorption of carbon and oxygen by trees. The Student's t -test (for normally distributed series) and the Wilcoxon signed ranks test (for non-normally distributed series) have been used on moving windows of 7 data to identify the period where the deviation between the measured and the modelled series was significant.

2.5. Metal concentrations and Pb isotope analysis

The total digestion of wood samples (150–300 mg) involved succession of digestion with nitric and hydrofluoric acid in polytetrafluoroethylene containers (Aznar et al., 2008).

Then, the samples were slowly warmed to concentrate metals that were sometimes present in low concentration in the studied wood. Finally, ultrapure water and nitric acid were added to the digested samples. The metal concentrations and lead isotope ratios of tree rings were performed by inductively coupled plasma-atomic emission spectrometry (ICP-AES; Ca, Al, Zn) and ICP-mass spectrometry (ICP-MS; Cd, Pb, lead isotope ratios) at the INRS-ETE Geochemistry Laboratory. Blank solutions (ultrapure water) and internal standards (pine needles) were placed throughout each analysed batch of samples to assess the quality of the analyses. The detection limits were 0.04, 0.01 and 0.02 ppm for Ca, Al and Zn, respectively, and 0.4 and 0.01 ppb for Cd and Pb, respectively. The precision obtained for Ca, Al and Zn was 2.0, 6.3 and 7.5%, respectively, and 6.3% for Cd and Pb ($n = 10$). The precision of the lead isotope ratios was better than 0.4% ($n = 10$).

In order to analyse the portion of metal concentrations and lead isotope ratios bioavailable in soils, partial extraction of lyophilised soil samples was performed. These extractions involved a series of digestions in hydrogen chloride and heating in water bath. After being mixed, the residual solution of soil was analysed using an ICP-MS at the INRS-ETE laboratory.

Because of the unusually flat patterns of all metal concentrations in cedar trees, these indicators will not be used to reconstruct the atmospheric pollution history of the site. In addition, the red spruce-ring lead isotope concentrations of the Qc site for the period between 1840–1841 and 1878–1879 were below detection limit, therefore, these results will not be presented here.

3. Results

3.1. Metal concentrations and Pb isotope ratios of trees and soils

The tree-ring Cd and Zn concentration and Ca/Al series were smoothed with a moving average of 4 ring pairs in order to emphasise their mid- and long-term trends and to ease the inter-tree species comparison. The Cd and Zn concentrations of both beech stands (Mtl and GB sites) show different patterns from the coniferous species (Fig. 2A and B). The latter have Cd concentrations which are slowly increasing since 1880–1881, constantly decrease after 1952–1953 at the Mtl site and after 1950–1951 at the GB site, to reach lower concentrations than those of the 1880–1881 in 2006–2007. In beech trees of Mtl, the Zn concentrations are decreasing after 1916–1917, but in the GB site, they form a flattened pattern. Contrastingly, the Cd and Zn concentrations of red spruce trees (Qc site) began to increase in 1880–1881 and reach highest concentrations between 1958–1959 and 1984–1985, whereas in the

pine trees, they start to slowly increase during 1932–1933 and augment abruptly during 1968–1969 (Fig. 2B). Tree-ring Cd and Zn concentrations decrease rapidly since 1984–1985 in both tree species. Finally, soil samples of all sites reveal that Cd and Zn concentrations are more elevated in the first centimetres of soil than in the mineral horizon (Fig. 2C and D).

The Pb concentrations of the two beech stands show trends similar to those of the coniferous Cd and Zn values (Fig. 3A). Their Pb concentrations increase after 1934–1935, peak between 1970–1971 and 1984–1985 and then abruptly decrease during 2006–2007, where the concentrations become similar to those of the 1940s. The pine of the Mtl site and the red spruce trees of the Qc site reveal different patterns. The Mtl pine Pb concentrations show a gradual long-term increase from 1880–1881 to 1930–1931, then a rather flat long-term trend, with all along a high variations from 1 yr to the other (Fig. 4A). The Pb concentrations of the Qc trees start to increase from 1884–1885 to 1914–1915, and then they increase progressively from 1930–1931 until 2006–2007 and show an irregular up-and-down short-term pattern (Fig. 4B). Again, the soil Pb concentrations of each site are higher in the organic horizon than in the mineral horizon (Fig. 3B).

The long-term tree-ring $^{206}\text{Pb}/^{207}\text{Pb}$ trends of beech trees of the Mtl ($r = -0.81$; $P < 0.001$; $n = 62$) and the GB ($r = -0.55$; $P < 0.001$; $n = 64$) sites are opposite to their Pb concentration patterns (Fig. 3C). The general pattern of their tree-ring $^{206}\text{Pb}/^{207}\text{Pb}$ is characterised by higher lead ratios for the oldest portion of the studied period (1.19–1.22), followed by a decrease in 1924–1925 at the GB site and in 1930–1931 at the Mtl site. Although the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are almost the same between the two sites for the period between 1880–1881 and 1932–1933, the lead ratios of Mtl beech trees become distinctly more depleted (1.17) than trees of GB (1.19) during the subsequent years. In contrast to the beech trees, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the pine ($r = 0.56$; $P < 0.001$; $n = 64$) and red spruce ($r = 0.30$; $P < 0.02$; $n = 64$) trees follow a long-term trend similar to their Pb concentrations (Fig. 4). Finally, the soil $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the C horizon distinct for all sites gradually converge towards similar ratios near the surface (Fig. 3D).

Calcium concentrations are higher in soil samples of the GB site compared to the sites of Mtl and Qc, and in the organic horizon compared to the mineral horizon at all sites (Fig. 5A). The long-term trend of the Ca/Al ratios in red spruce trees of the Qc site increases from ~ 250 in 1840–1841 to ~ 350 in 1966–1967, and then diminishes to ~ 200 in 2006–2007 (Fig. 5C). The Ca/Al ratios of the beech trees of the Mtl site are characterised by three decreasing periods, each showing a decline of about 150 (Fig. 5D). The first period extends from 1882–1883 to

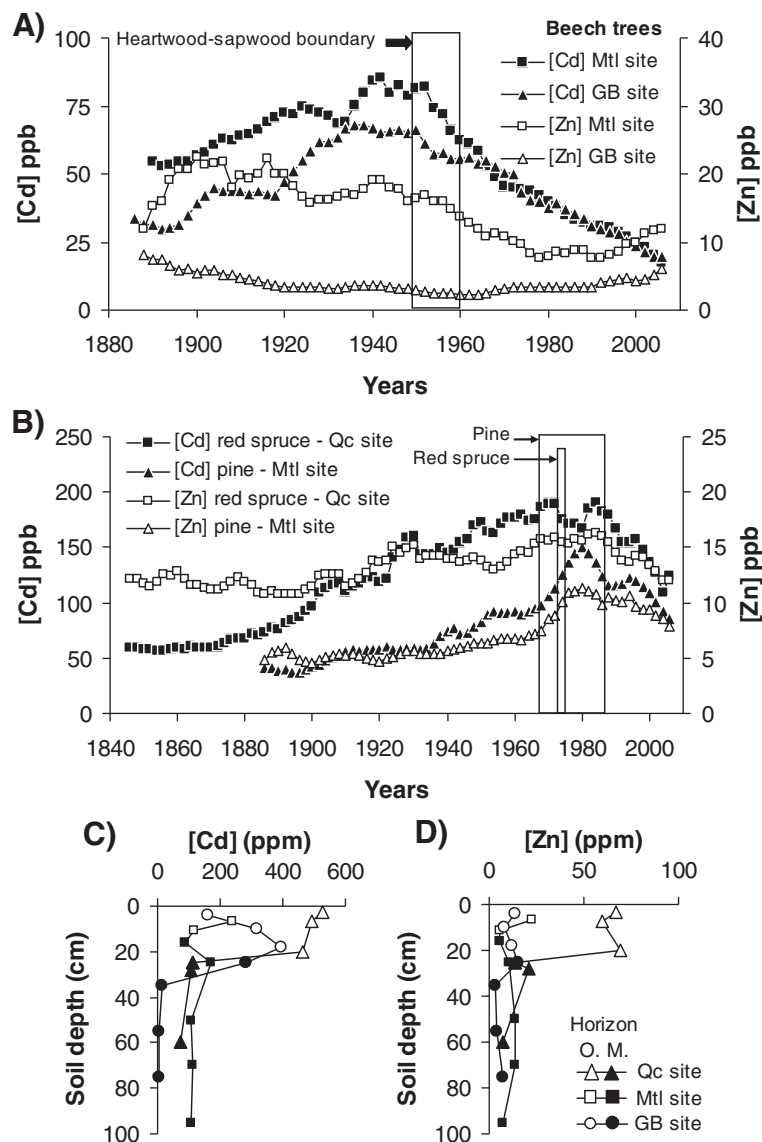


Fig. 2. Montréal (Mtl) and Georgian Bay (GB) patterns of Cd and Zn concentrations in beech trees influenced by physiological mechanisms (A); Cd and Zn series in the Québec (Qc) red spruce trees and the Mtl pine trees not influenced by internal mechanisms (B); and Cd (C) and Zn (D) concentrations in soil profiles of the study sites. The tree-ring concentration series are smoothed with a moving average of four ring pairs, and the rectangles indicate the heartwood-sapwood boundary.

1916–1917, the second from 1924–1925 to 1940–1941 and the last from 1946–1947 to 1972–1973. In contrast to the two first decreasing periods, the last one is not followed by positive peak but by a flattened trend. Finally, the beech Ca/Al ratios of the GB site are relatively stable from 1880–1881 to 1962–1963, then the ratios decrease to ~ 400 in 2006–2007 (Fig. 5E). The beech Ca/Al series of the GB site is characterised by elevated year-to-year variations with an average amplitude of 111, much higher than the Qc and Mtl sites, where the mean amplitude variations were 23 and 22, respectively.

3.2. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values

The strong inter-tree correlations between the $\delta^{13}\text{C}$ values at each of the studied sites confirm that the measured $\delta^{13}\text{C}$ trends are representative of the site (mean $\text{EPS} = 0.8$; Table 2). In addition, the $\delta^{13}\text{C}$ long-term patterns of the tree-ring series are similar for the three sites (mean $r = 0.75$). The mean amplitude of the $\delta^{13}\text{C}$ variations at the three sites is 0.3‰ (Table 2). At every site, the flat trend of the tree-ring $\delta^{13}\text{C}$ values of the first portion of the series is followed by an increase in the isotopic values; in ~ 1928 –1929 at the GB

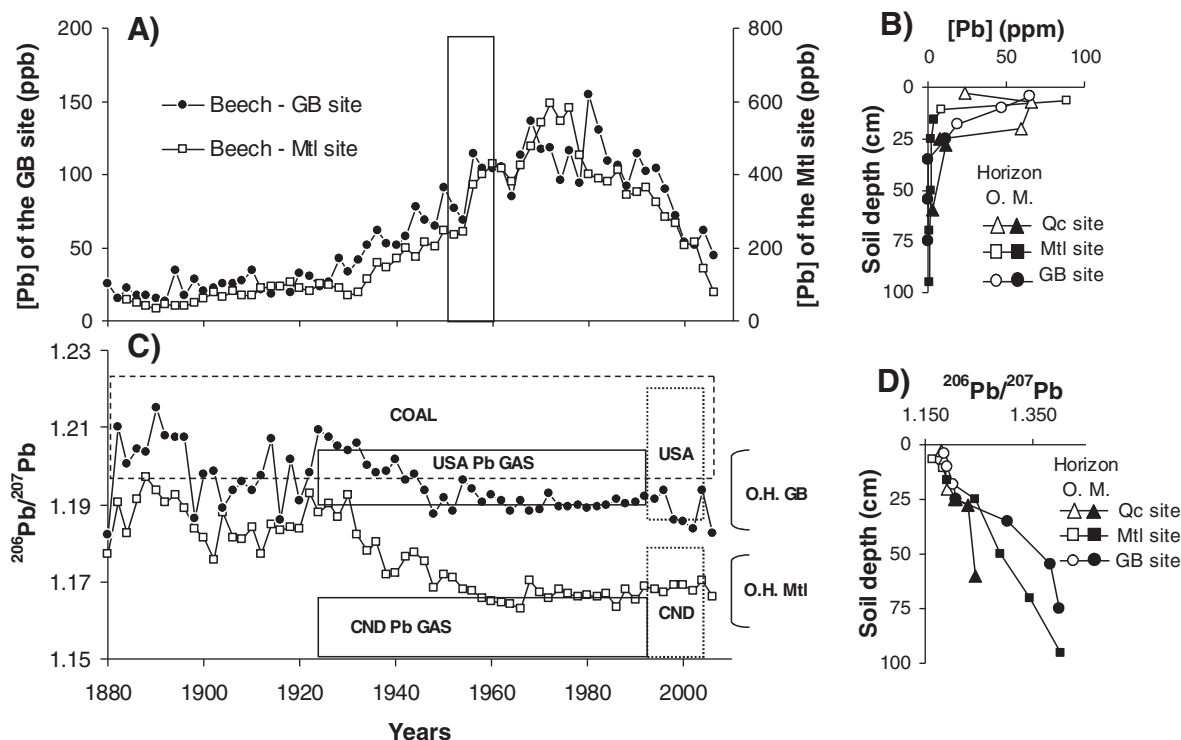


Fig. 3. Pb concentrations in the Montréal (Mtl) and Georgian Bay (GB) beech trees (A) and in the soil profile of the study sites (B); the rectangle indicates the heartwood-sapwood boundary. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the Mtl (open squares) and GB (solid circles) beech trees (C) are compared with the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of their respective mineral (M.H.) and organic (O.H.) horizons (D), the Canadian (CND) and United States (USA) urban air (Bollhöfer and Rosman, 2001), the American coal combustion (COAL) (Chow and Earl, 1972) and the leaded gasoline in Canada (CND Pb GAS) and in United States (USA Pb GAS) (Sturges and Barrie, 1987).

site, in 1938–1939 at the Mtl site and in 1944–1945 at the Qc site (Fig. 6).

There are also good inter-tree correlations between the $\delta^{18}\text{O}$ values at each site (mean EPS = 0.8; Table 2). But, in contrast to the $\delta^{13}\text{C}$ values, the tree-ring $\delta^{18}\text{O}$ values are similar among tree species of the same site, but not between sites. The mean amplitude of $\delta^{18}\text{O}$ variations for the three sites is 0.5‰ (Table 2). The $\delta^{18}\text{O}$ values of the two species growing at the Mtl site increase from 1880–1881 to 1914–1915 by 2.6‰, then the beech rings show a relatively stable trend, whereas the pine rings show a slight decrease from 1934–1935 to 1972–1973 (Fig. 7A and B). The $\delta^{18}\text{O}$ values of the beech and cedar trees of the GB site increase from 1880–1881 to 1912–1913 by 1.7‰, then slightly decrease until 2007 (Fig. 7C and D).

Modelling of the tree-ring $\delta^{13}\text{C}$ values based on their statistical link with meteorological parameters for the period of calibration (1880–1881 to 1938–1939) shows good estimation of the measured isotopic values for stands of the Mtl and GB sites (Table 3; Fig. 6A–D). These models reveal major deviation between the measured and the estimated isotopic values of all stands, where the $\delta^{13}\text{C}$

values entirely controlled by climatic conditions are lower than the measured values.

Modelling of the tree-ring $\delta^{18}\text{O}$ values with meteorological parameters resulted in high correspondence with measured isotopic values for the calibration period of the Mtl and GB stands (Table 3; Fig. 7A–D). The $\delta^{18}\text{O}$ values modelled on the basis of climatic parameters alone for the 1940–1941 to 2006–2007 period match the measured $\delta^{18}\text{O}$ values of the Mtl beech trees well. The same approach reveals departures between the measured and modelled $\delta^{18}\text{O}$ values for the Mtl pine trees and the GB beech and cedar trees. For these three sites, the modelled $\delta^{18}\text{O}$ values are higher than the measured values. Results and interpretation of the modelling of the red spruce $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are presented in the study of Doucet (2011).

4. Discussion

4.1. Spatiotemporal trends of metal concentrations

There are three common patterns of elements physiologically influenced by trees' internal processes: (1) a decrease of element concentrations towards the bark through the

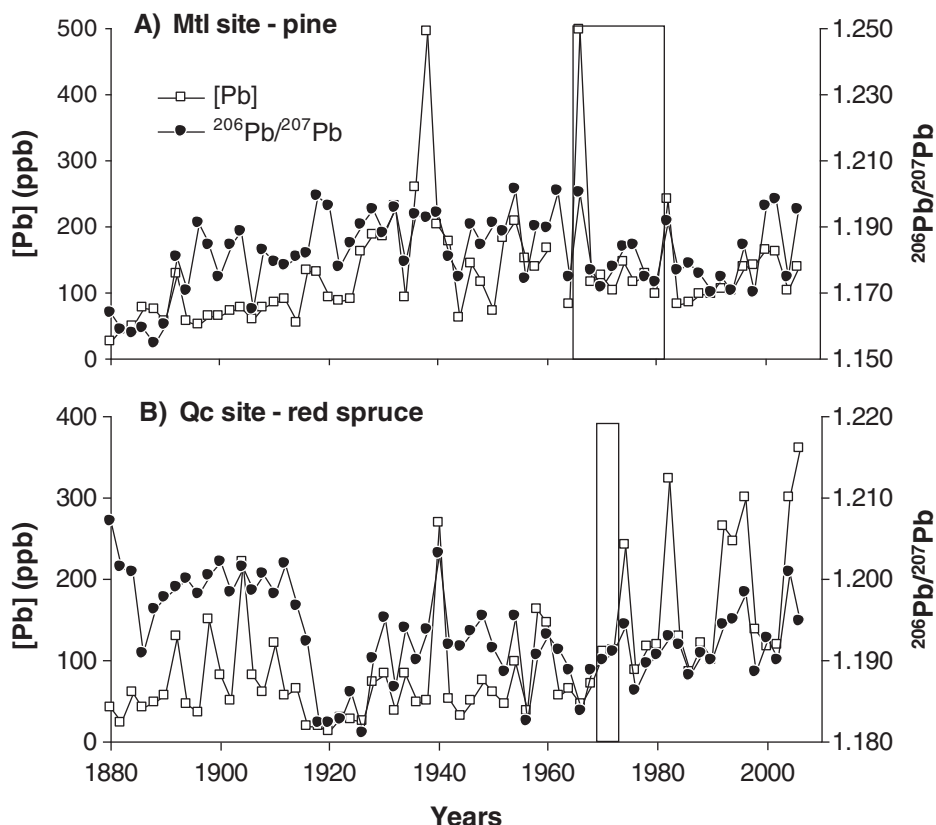


Fig. 4. Pb concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the pine trees of the Montréal site (A) and in the red spruce trees of the Québec site (B). Graphs show short- and long-term positive correlations between the two indicators in each stand. The rectangles indicate the heartwood–sapwood boundaries.

heartwood–sapwood boundary; (2) an outward increase of element concentrations from the heartwood–sapwood boundary; and (3) a peak of element concentrations at the heartwood–sapwood boundary (Okada et al., 1993). Long-term Cd and Zn concentrations of beech trees of the Mtl and GB sites are clear examples of trends caused by the physiological process of radial mobility (Okada et al., 1993) (Fig. 2A). The Cd concentrations of both beech stands and the Zn concentrations of the Mtl beech trees reveal a long-term decreasing trend with a more pronounced decline coinciding with their heartwood–sapwood boundary, whereas the Zn concentrations of the GB beech trees do not show any variation over the studied period. Consequently, those concentrations cannot be interpreted in terms of air pollution history. However, as patterns of the Cd concentrations in the Qc red spruce trees and the Mtl pine trees do not present signs of radial mobility or heartwood–sapwood boundary influence, those indicators can be used to reconstruct the metal deposition at the studied sites (Fig. 2B). Those trends indicate a progressive increase in anthropogenic Cd and Zn deposition from the beginning of the 20th-century that potentially came from

several sources developed during the economic expansion periods of the Québec province (Lacoursière et al., 2000; Lebel and Roy, 2000). The increase of the tree-ring Cd concentrations at the Qc site started in 1902–1903 coincides with the development of two important sources of Cd emissions located upwind of the Qc site (~100 km), specifically an aluminium plant and a petrochemical plant that began their production of non-ferrous metals and calcium carbide in 1902 and 1904, respectively. At the Mtl site, tree-ring Cd and Zn concentration increases are intense in the 1930s, the 1950s and in the 1970s. Each of these periods coincides with the establishment of a plant located less than 40 km around the Mtl site. These sources have been emitting important quantities of Cd and Zn in the air (Environment Canada, 2010) precisely since 1931 (one of the most important world refineries of copper and precious metals), 1955 (lead, zinc and tin smelter) and 1963 (zinc smelter). We therefore propose that the Cd and Zn concentrations in the organic horizon of the three sites are principally due to anthropogenic depositions of the 1930–1985 period. The simultaneous decrease of the tree-ring Cd and Zn at the Qc and the Mtl sites is likely associated with

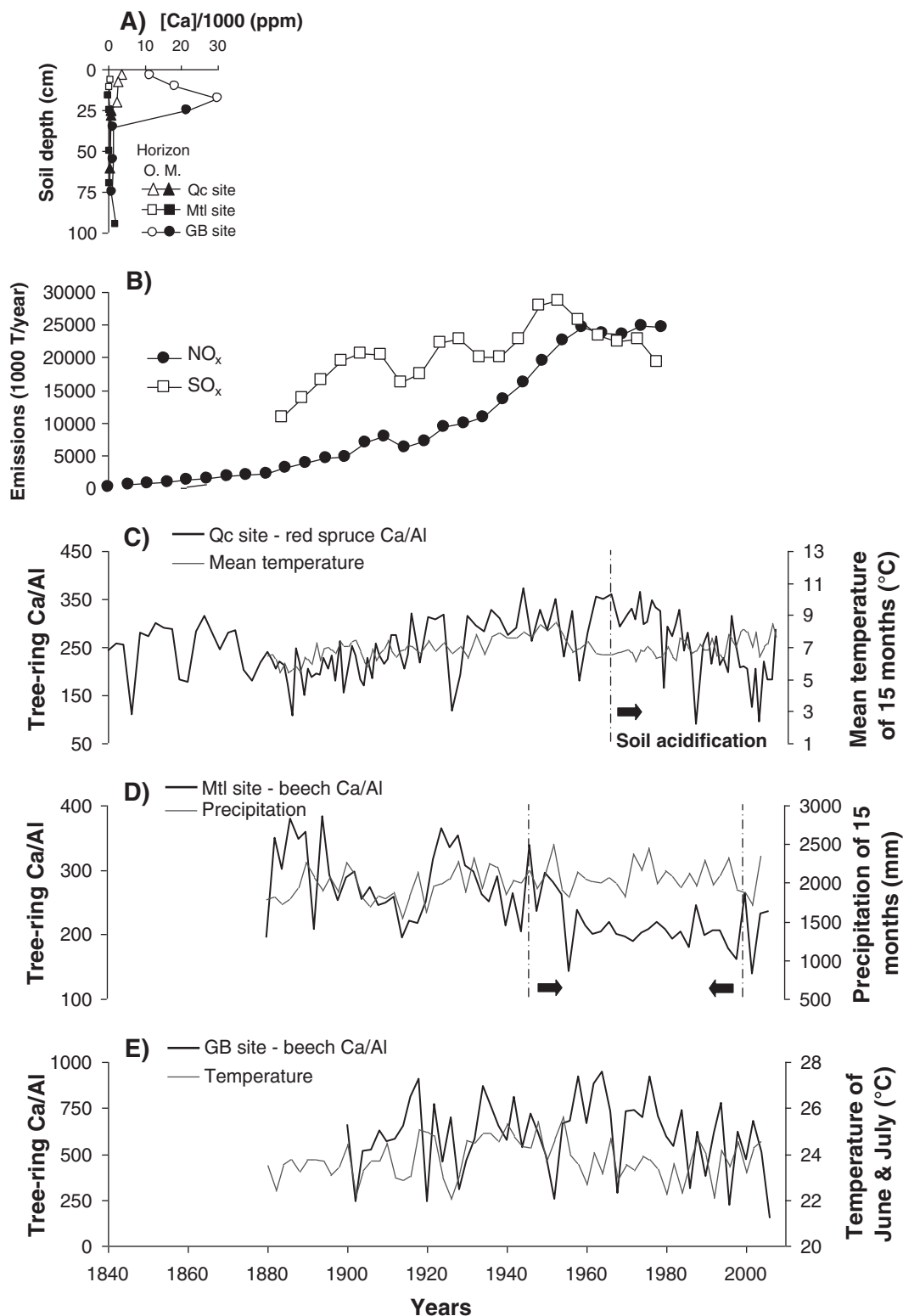


Fig. 5. Comparison between soil Ca concentrations of each sites (A), North American NO_x (Husar, 1994; Galloway, 1995; Bélanger, 2000) and SO_x (Husar, 1994; US EPA, 2000) emissions (B), tree-ring Ca/Al ratios of each studied site (C), and meteorological parameters (temperature and precipitation). The term '15 months' represents the data from June of the last year to August of the current year. The vertical dashed line indicates the inferred soil acidification period.

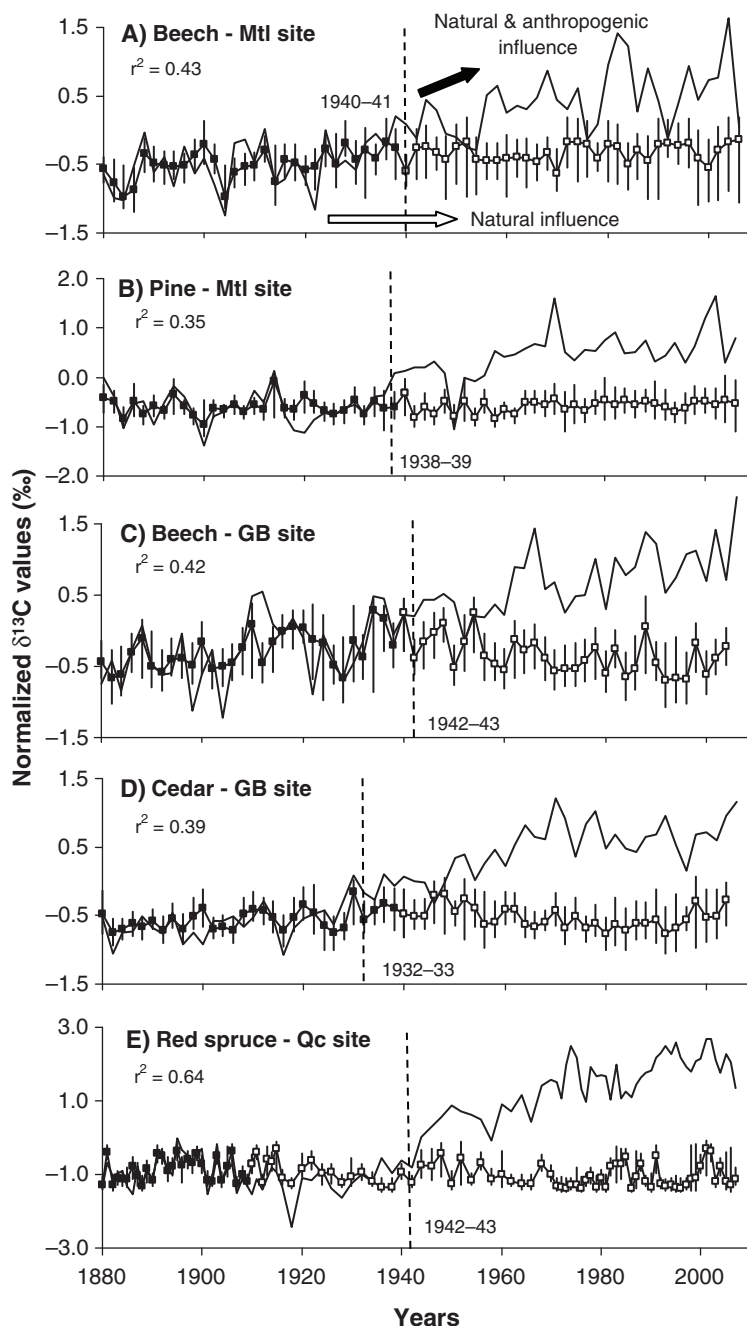


Fig. 6. Comparison between measured tree-ring $\delta^{13}\text{C}$ values (thin line) of beech (A) and pine (B) trees of the Mtl site, of beech (C) and cedar (D) trees of the GB site, and of red spruce trees of the Qc site (E), their $\delta^{13}\text{C}$ calibrated values based on a non-linear regression using meteorological parameters (black squares), and the modelled $\delta^{13}\text{C}$ values based on this equation (open squares). The estimation errors of the model are graphically represented and the starting point of the visible impact of air pollution on the isotopic values is indicated by the dashed lines.

the implementation of restrictive governmental regulations on emissions during the 1970–1980s, such as the Clean Air Act (1971), Air Quality Regulation (1979), Canadian Environmental Protection Act (1988) and Acid Rain Policy (1984) (Gouvernement du Québec, 1997).

The third metal investigated here is Pb, a non-essential element for trees that should consequently present limited effects of radial mobility (Watmough, 1999). This may be particularly true for conifers, which have frequently been suggested to be suitable for dendrogeochemical studies

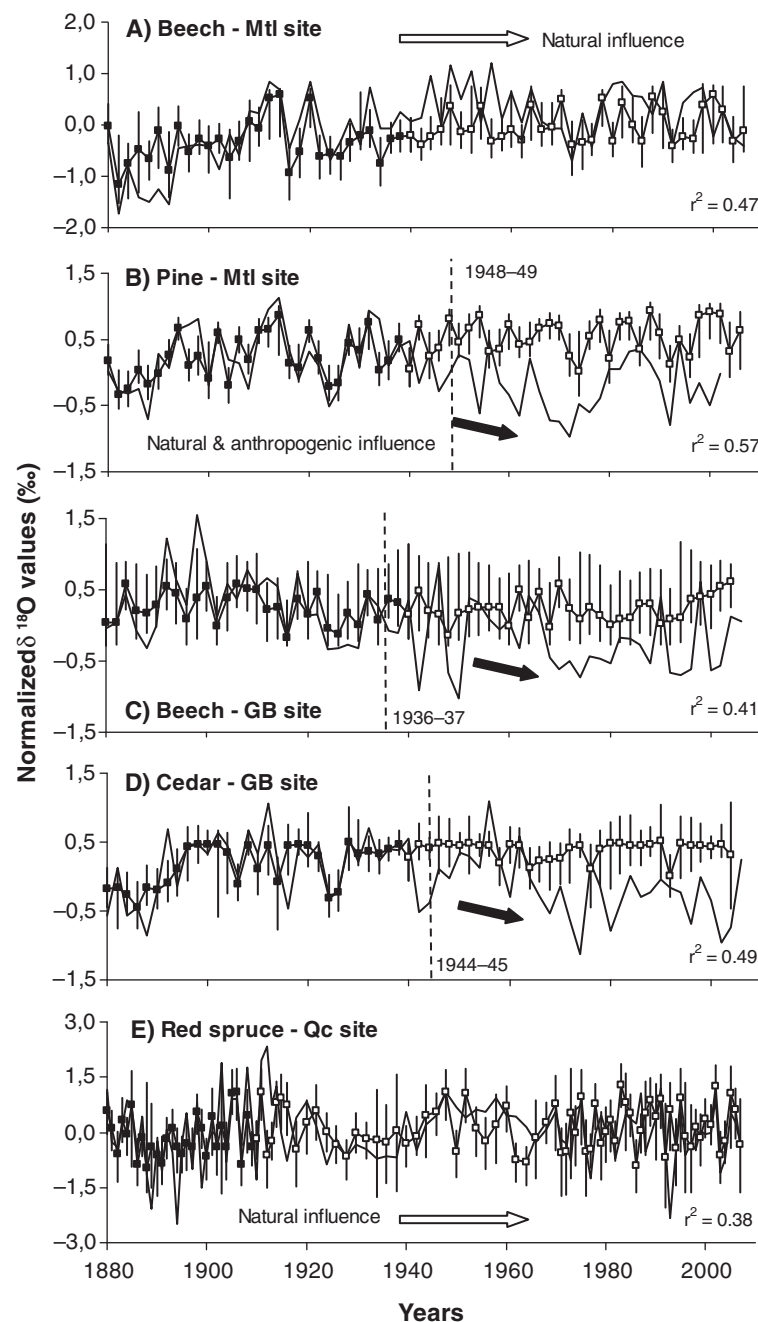


Fig. 7. Comparison between measured tree-ring $\delta^{18}\text{O}$ values (thin line) of beech (A) and pine (B) trees of the Mtl site, of beech (C) and cedar (D) trees of the GB site, and of red spruce trees of the Qc site (E), their $\delta^{18}\text{O}$ calibrated values based on a non-linear regression using meteorological parameters (black squares), and the modelled $\delta^{18}\text{O}$ values based on this equation (open squares). The estimation errors of the model are graphically represented and the starting point of the visible impact of air pollution on the isotopic values is indicated by the dashed lines.

because of their anatomical structure and the consistency of this latter in their tree rings (Lepp, 1975; Legge et al., 1984; Bégin et al., 1999). Several studies have shown the potential of tree-ring Pb concentrations and isotopic series to infer environmental perturbations caused by Pb deposi-

tion (Wu and Boyle, 1997; Watmough and Hutchinson, 1999; Bellis et al., 2002; Savard et al., 2002, 2006; Saint-Laurent et al., 2009; Saint-Laurent et al., 2011). Despite these previous observations made for coniferous trees, the comparison between the long-term Pb concentrations of

Table 3. Regression analysis of tree-ring $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the 1880–1881 to 1938–1939 period, with the significant climatic parameters for the Mtl and GB sites

	Sites	Tree species	r^2 of the model	Total precipitation (r)	Maximum temperature (r)
$\delta^{13}\text{C}$	Mtl	Beech	0.43	Annual ^a (rain) (0.41; $P < 0.01$)	15 months ^b (0.34; $P < 0.01$)
		Pine	0.35	Annual (–0.46; $P < 0.01$)	No correlated data
	GB	Beech	0.42	Annual (0.39; $P < 0.01$)	July (0.44; $P < 0.01$)
		Cedar	0.39	15 months (–0.34; $P < 0.1$)	May–December (0.51; $P < 0.01$)
$\delta^{18}\text{O}$	Mtl	Beech	0.47	June–July (rain) (–0.51; $P < 0.01$)	Annual 0.40; $P < 0.01$
		Pine	0.57	July (rain) (–0.49; $P < 0.01$)	15 months (0.49; $P < 0.01$)
	GB	Beech	0.41	April–September (–0.28; $P > 0.5$)	June (0.30; $P < 0.1$)
		Cedar	0.49	March–May (rain) (0.40; $P < 0.01$)	15 months (0.45; $P < 0.01$)

^aAnnual: meteorological data from January to December.

^b15 months: meteorological data from June of the precedent year to August of the current year.

the Mtl pine trees (Fig. 4A) and the Qc red spruce trees (Fig. 4B) highlights some features in those two conifer species that may be related to radial translocation. First, the gradual increase of the Pb concentrations in red spruce trees reflects a typical pattern of radial mobility in tree (Okada et al., 1993; Watmough, 1997). Second, the absence of major long-term variations in the pine-rings' Pb concentrations could also be associated with a pattern of radial mobility. Then, the disagreement between the red spruce tree-rings' Pb concentration trends and what was observed in the paleolimnological profiles from lake Tantaré (Gallon et al., 2005), located in the immediate vicinity of the Qc site, points towards the fact that the tree-ring Pb concentrations do not reflect the historical pollution of the region. Besides, the beech-ring Pb series (Fig. 3A) agree with the paleolimnological profile and make these temporal trends plausible (see further). Moreover, it has been observed that the positive short-term correlation between the Pb concentrations and the $^{206}\text{Pb}/^{207}\text{Pb}$ series of pine (GLK = 63%; $P < 0.05$; $n = 63$) and red spruce (GLK = 78%; $P < 0.001$; $n = 64$) trees is opposite to what is seen for the beech trees in the GB and Mtl sites. These three observations suggest that the Pb concentrations in the investigated conifer species exert an outward movement of Pb, carrying high $^{206}\text{Pb}/^{207}\text{Pb}$ ratios from the older rings towards the bark (Hagemeyer and Weinand, 1996; Bégin et al., 2010). Consequently, the long-term lead composition of the pine and red spruce trees is interpreted to be influenced by internal physiological mechanisms and, therefore, cannot be used to infer the air pollution history of their respective sites.

4.2. Spatiotemporal trends of lead isotope ratios

We consider that the beech trees of the Mtl and GB sites are useful to infer the Pb deposition history because their heartwood–sapwood boundary is not coinciding with a rupture in their Pb concentrations and isotopic series

(Fig. 3A–C). Between 1880–1881 and 1920s, the increase of tree-ring Pb concentrations and the highest beech-ring $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the Mtl and GB sites correspond to the accumulation of a mixture of anthropogenic lead from wood and north-eastern American coal combustion (Chow and Earl, 1972; Lima et al., 2005) with natural lead from the mineral soil horizon. Effectively, during these decades, the combustion of coal became the main source of energy in north-eastern America (US Energy Information Administration, 2008). We can state that lead deposition of this period did not only come from coal combustion because the air masses of USA ($^{206}\text{Pb}/^{207}\text{Pb} = \sim 1.22$) and Canada ($^{206}\text{Pb}/^{207}\text{Pb} = \sim 1.15$; Sturges and Barrie, 1987; Bollhöfer and Rosman, 2001) have distinct lead isotope signals, which necessarily had to contribute to the local lead load to produce the measured ratios in trees (Fig. 3C). Air masses from United States have likely reached the studied areas because the dominant winds transport the US air masses towards the north-east (CEC, 1997). The subsequent drastic increase of the tree-ring Pb concentrations in the 1930s coincides with lower $^{206}\text{Pb}/^{207}\text{Pb}$ ratios. These trends reflect the increasing use of leaded gasoline that was introduced in 1923 and prohibited in 1992 in North America (Pacyna et al., 1995). Because the leaded gasoline used in Canada mainly came from Canadian ores, its $^{206}\text{Pb}/^{207}\text{Pb}$ ratios were lower than those of leaded gasoline from USA, itself having lower isotopic ratios than those of American coal combustion (Fig. 3C) (Sturges and Barrie, 1987; Sturges and Barrie, 1989). Consequently, the increasing use of leaded gasoline was gradually echoed in the tree rings with lower $^{206}\text{Pb}/^{207}\text{Pb}$ ratios dominating until the end of the 1980s. The years corresponding to the beginning of the decreasing trend of the tree-ring $^{206}\text{Pb}/^{207}\text{Pb}$ ratios reveal that the impact of leaded gasoline combustion was first visible at the GB site (1924–1925) and then at the Mtl site (1930–1931). The fact that the beech $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the Mtl site are lower than those of the GB site since 1932–1933 (Fig. 3C) suggests that the proportion of Pb

from USA is higher at the GB site. It has been shown that Pb transported by the dominant winds from USA towards the north-east represents about 72% of the Pb deposited in the southern Ontario, relatively to 60% in the Montréal area (Blais, 1996). Also, the lower beech $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the Mtl site can reflect the emissions of Canadian lead by local industries and transportation, namely the international refinery of copper and precious metals (1931) and the two highways 20 and 40 built between 1858 and 1966. Then, the decreasing tree-ring Pb concentrations at the end of the 1970s and in 1980s at the Mtl and GB sites, respectively, represent the progressive phase-out of the leaded gasoline in Canada and the implementation of more restrictive regulations on air emissions by the industrial sector (Gouvernement du Québec, 1997). For the period between 1996–1997 and 2006–2007, the higher interannual variations of the tree-ring $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the GB site relatively to the last 50 yr may represent the change in the main sources of Pb. Those variations can reflect a mixture of several Pb sources such as the combustion of north-eastern American coal, the average lead isotope composition from the increasing use of recycled lead-containing material (Hurst, 2002) or the natural lead from mineral horizon. For the same period, the flat trend of the tree-ring $^{206}\text{Pb}/^{207}\text{Pb}$ ratios at the Mtl site proposes a more constant and potentially nearest sources of Pb from Canadian sources relative to the GB site. Lead sources in the nearby Mtl area, in addition to the previously cited industrial sources, include a smelter recycling lead batteries which was developed in 1984 at ~ 27 km from the study site. According to our data, there are no industries emitting as much lead as the one present near the Mtl trees in the vicinity of the GB site. Moreover, the increase of Pb concentrations accompanied by a decrease of the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and the convergence to similar ratios in the upper layers of the soil profile of the three sites are other features suggesting the anthropogenic deposition of Pb at the studied sites (Fig. 3B–D).

In this study, we have inferred the history of soil acidification by using the tree-ring Ca/Al series of the investigated sites. In general, a decrease in soil pH promotes the leaching of Ca and mobilises inorganic Al in soils, and indirectly in trees (Bondietti et al., 1990; DeWalle et al., 1999; Kuang et al., 2008). In addition, the absorption of Ca and Al by the root system depends on several factors such as soil temperature and moisture, tree physiological behaviour, root conditions, etc. (Vanguelova et al., 2007). The interpretation of each tree-ring Ca/Al series was made by comparing those dendrogeochemical series with the North American NO_x (Husar, 1994; Galloway, 1995; Bélanger, 2000) and SO_x (Husar, 1994; US EPA, 2000) emission series, and the meteorological data (temperature and precipitation) (Fig. 5B). This comparison shows that, for

Qc and Mtl studied stands, the portion of the tree-ring Ca/Al series that does not vary with climatic conditions corresponds to a decrease of the Ca/Al results and for all the studied stands to a period of high air pollution (Fig. 5). This decreasing Ca/Al trend observed in the studied trees of Qc and Mtl stands reflects an acidification of soils that occurs during the 1966–2007 period at the Qc site (Fig. 5C) and 1946–1999 at the Mtl (Fig. 5D). The dendrogeochemical series suggest that the soil acidification was caused by the long-term SO_x deposition, mainly emitted from fuel combustion (modelling of the $\delta^{13}\text{C}$ values; Doucet, 2011), and the long-term NO_x deposition, mainly emitted by car exhausts (decreasing $\delta^{15}\text{N}$ values; Doucet, 2011). Note that it is possible that acidification of soil has occurred at the GB site, but did not modify the concentrations of Ca in the beech trees because of the high buffering capacity of the naturally less acidic soils (Giasson and Jaouich, 2008) and its abundance of calcium (DeWalle et al., 1999).

4.3. Carbon and oxygen isotope ratios

The long-term increase of the $\delta^{13}\text{C}$ patterns of the Mtl and GB trees is similar to patterns observed in the tree-ring $\delta^{13}\text{C}$ of the Qc site (Fig. 6). The modelling of the isotopic values with meteorological parameters reveals that the enrichment of the tree-ring $\delta^{13}\text{C}$ values was not caused by climatic conditions. The similar long-term $\delta^{13}\text{C}$ patterns in trees of all stands, even if they belong to different tree species and environmental conditions, suggest that the enrichment of the $\delta^{13}\text{C}$ values is mainly the result of a common external factor. Previous modelling of the red spruce $\delta^{13}\text{C}$ values of the Qc site has demonstrated that the increase of the isotopic values has been caused by phytotoxic air pollution, mainly the combustion of Canadian fossil fuels (Doucet, 2011). Here, modelling allows identifying the 1938–1939 to 1942–1943 period as the one during which atmospheric pollution first affected the absorption of carbon by trees of all studied stands over the Windsor–Québec Corridor (Fig. 6). However, a bias is included in the natural models of the Mtl and GB sites because their calibration period (1880–1881 to 1938–1939) likely involves results affected by pollution, as suggested by the tree-ring metal concentrations. We had to use those years because, to be statistically valuable, the calibration period should be based on a minimum of 30 points and the climatic series do not go further in the past. Therefore, if anything, it is possible that the tree rings could have responded to atmospheric emissions at the Mtl and GB sites earlier than the model allows us to deduce.

The modelling of the tree-ring $\delta^{18}\text{O}$ values by meteorological parameter reveals that climatic conditions are the main drivers of the Mtl beech trees for the entire studied

period (Fig. 7A). The same conclusion was drawn for the red spruce $\delta^{18}\text{O}$ values of the Qc site (Fig. 7E) (Doucet, 2011). However, modelling of the $\delta^{18}\text{O}$ values in pine trees suggests that this species of trees at the Mtl site recorded a $\delta^{18}\text{O}$ decrease related to air pollution after 1947 (Fig. 7B). Those contrasting results between two tree species of the same location suggest that pine trees are more sensitive to pollution stress than beech trees. This sensitivity could be related to the persistence of the foliage in coniferous trees compared to the foliage of deciduous trees which is renewed each year (Savard et al., 2009a). A similar decrease is visible on the modelled $\delta^{18}\text{O}$ values of GB beech and cedar trees (Fig. 7C and D). For both tree species, the measured isotopic values are lower than the modelled values for a short period after 1942–1943 and for a longer interval after 1968–1969 in beech trees, and after 1966–1967 in cedar trees. Again, the models show the minimal impact that air pollution could have induced on those stands, because the period of calibration possibly includes some tree rings formed during the years of exposure to pollutants. The fact that the beech-ring $\delta^{18}\text{O}$ series of the GB could not entirely be explained by climatic conditions relative to the Mtl beech trees could have been caused by higher atmospheric pollution at the GB site or by meteorological data not exactly reflecting the true climatic

conditions of the site, as a noticeable distance separates the trees from the meteorological stations, or by different site conditions that made the GB beech trees more sensitive to air pollution than the Mtl beech trees.

The year-to-year correlation between meteorological parameters and tree-ring $\delta^{18}\text{O}$ values of the Qc site suggests that this conifer species is less sensitive to atmospheric contaminants than the Mtl pine trees or that the Qc trees are affected by less atmospheric diffuse pollution than trees of other study sites. This last suggestion is based on the fact that the red spruce trees of the Qc site were the only trees showing interannual correlations between $\delta^{18}\text{O}$ values and meteorological data that remained significant for several climatic parameters during the entire studied period (Table 4). For the other stands, the high correlations of the calibration interval (1880–1881 to 1938–1939) were lost during the most intense pollution period (1940–1941 to 2006–2007) (Table 4).

In this project, no experiment has been conducted to identify the mechanisms responsible for the tree-ring $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ changes, but we have shown that part of the long-term isotopic pattern is induced by air pollution (modelling of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values). According to McLaughlin et al. (1990) and Elvir et al. (2006), the increase of the photosynthetic rate in red spruce and beech trees subjected

Table 4. Year-to-year correlation between tree-ring $\delta^{18}\text{O}$ values and meteorological parameters for the calibration (1880–1881 to 1938–1939) and the modelled (1940–1941 to 2006–2007) periods based on the GLK coefficient (%)

Site	Tree species	Meteorological parameter	Calibration period	Estimated values
Qc	Red spruce	max T^{a} July–Aug.	64*	62*
		max T June–Aug.	64*	67*
		max T May–Aug.	63*	63*
		mean T^{b} April–Sept.	68*	66*
Mtl	Beech	max T July–Aug.	–66*	61
		Prec. ^c June–Aug.	–72**	–55
		Prec. June–Aug.	–69*	–55
		Prec. July	79**	–39
GB	Pine	Prec. April–Sept.	–69*	–39
		Prec. Aug.	69*	33
		Prec. July–Aug.	69*	39
		Prec. April–Sept.	69*	48
	Beech	Prec. June–July	–66*	–58
		Prec. Aug.	76**	48
		Prec. Annual ^d	76**	55
		Prec. June–Aug.	72**	55
		Prec. April–Sept.	69*	45
	Cedar	Prec. 15 months ^e	72**	–24**

The negative sign indicates a negative correlation. The GLK coefficients were significant at * $P < 0.05$ and ** $P < 0.01$.

^a max T refers to maximum temperature.

^b mean T refers to mean temperature.

^cPrec. refers to precipitation.

^dAnnual refers to data from January to December.

^e15 months refers to data from June of the precedent year to August of the year of interest (Weiss et al., 1999).

to elevated N deposition occurs only if an adequate amount of Ca and Mg is supplied to the foliar system. Our dendrogeochemical results show that concentration of Ca in the red spruce and the beech trees declined in the last decades because of the soil acidification induced by elevated NO_x and SO_x deposition. In addition, the amount of SO_x emissions was higher than NO_x emissions in North America before the 1980s (Fig. 5B; US EPA, 2000). Consequently, during the pre-1980 period, the fertilising role of N in trees may have been counterbalanced by the reduced foliar Ca and the negative effect of SO_x (Guerrieri et al., 2011), thereby reducing the assimilation of CO_2 by trees through lowered stomatal conductance (Martin et al., 1988; Matyssek et al., 1992; Savard et al., 2006; Rinne et al., 2010). SO_x emissions can also increase the tree-ring $\delta^{13}\text{C}$ values by augmenting dark respiration and changing photosynthate allocation and partitioning (Wagner and Wagner, 2006). These response mechanisms to air pollution may have caused the increasing $\delta^{13}\text{C}$ and the unchanged $\delta^{18}\text{O}$ values of the Qc red spruce trees and the Mtl beech trees. Possible physiological mechanisms controlling the $\delta^{18}\text{O}$ values in trees are discussed in the work of Rinne et al. (2010), and reasons why these isotopic ratios may change under stress due to pollution are summarised in the study of Savard (2010). Unfortunately, the mechanisms involved in the decrease of the tree-ring $\delta^{18}\text{O}$ values of three of the five studied stands could not be clearly identified here. However, our observations and modelling confirm that the physiological responses were modified as a function of the type of pollutants emitted and the sensitivity of the tree species.

5. Conclusions

In this study, we have demonstrated that the complementarity of several geochemical indicators analysed in various tree species and soil samples allows to provide key information on past diffuse air pollution coherent with the industrial history of a broad region. Surprisingly, we have observed that the lead concentrations were influenced by some physiological mechanisms (radial mobility) in red spruce and pine trees, whereas their cadmium and zinc concentrations were useful to infer air pollution chronology. Opposite patterns, integrity for lead concentrations but translocation for cadmium and zinc, were observed in the two studied beech stands. The results obtained clearly show that all analysed indicators cannot be used together in any of the investigated tree species. For that reason we recommend combining several tree species to study past air pollution history, as this approach can provide complementary information to reconstruct the environmental perturbations.

An important highlight of this research is that we have come up with and assessed a new approach to separate the portion of the tree-ring $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values induced by climatic (natural) conditions from the portion caused by the influence of air pollution. The statistical approach allows inferring when the impact of air pollution on trees is significant and, at the different sites, what is the relative sensitivity of trees to air pollutant. The sensitivity seems to vary as a function of tree species, i.e., as a response controlled by physiological mechanisms. In terms of perspective, it is important to mention that the statistical approach could not be applied to metals in tree rings because these indicators harbour complex short-term variations not explainable by climatic conditions (e.g. soil pH). Consequently, the separation of the natural and anthropogenic trends for these indicators is based on comparison with the early portions of the measured series which are theoretically the least affected by air pollution (background concentrations). Future research on reconstruction of environmental changes should address the specific question of identifying the mechanisms controlling the short-term changes in metal concentration and isotope ratios. Indubitably, the different and complex physiological response of tree species to stress induced by changes in air quality and soil chemistry must be taken into account when reconstructing atmospheric pollution history.

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