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Dispersal of atmospheric lead in northeastern North America as recorded by epiphytic lichens

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Abstract

Epiphytic lichens collected from trees within northeastern North America (ca. 500,000 km²) have been used as natural filters of airborne lead in order to document the spatial distribution of this metal in the atmosphere and identify its principal sources. Lichens record an integrated signal over a few years of atmospheric fall-out and thus minimise any signals due to variable (seasonal) atmospheric circulation patterns, and biases related to discrete events focusing atmospheric pollution from a single point source. The Pb/Al ratios measured in lichens are 20–600 times higher than that of upper crustal rocks, indicating that most of their Pb is of anthropogenic origin. Hence, their Pb isotopic composition is directly related to that of the pollution sources. The ²⁰⁶Pb/²⁰⁷Pb values for the lichens vary from 1.146 to 1.206 and these are interpreted as results of mixing between Canadian and USA industrial lead. Pb isotope ratios of lichens define a coherent geographic distribution since samples from the US have high ²⁰⁶Pb/²⁰⁷Pb, typical of US industrial Pb, whereas lichens sampled in northern Québec have the lowest ²⁰⁶Pb/²⁰⁷Pb, typical of Canadian industrial Pb. Lichens sampled along the St. Lawrence Valley have intermediate isotopic composition, which is interpreted as a result of mixing between USA and Canadian sources. USA industrial Pb contributes 75–35% of the total atmospheric Pb in this area and the contribution decreases from Montréal towards the Gulf of St. Lawrence. Overall, geographic Pb isotope gradients may be sharp and indicate a strong control by both sources and prevailing meteorological conditions. From these results, it is possible to draw the first Pb isotopic distribution map of atmospheric Pb pollution over northeastern North America. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Atmosphere; Lead; Pollution; Lichens; North America

1. Introduction

Northeastern North America is densely populated and heavily industrialised and is one of the important regions of atmospheric emissions of heavy metal pollution in the Northern Hemisphere (Mart, 1983; Flegal et al., 1989). Sturges and Barrie (1987) reported a systematic difference in Pb isotopic composition between aerosols sampled in Canadian and US urban areas surrounding the Great Lakes. This is because the major industrial Pb suppliers in the two countries use ores from different mines, with contrasted geological

histories. Thus, the average Pb isotopic composition of the ores used in the US and Canada yield distinct isotopic ratios, and this difference was recorded in aerosols collected in the respective countries (Sturges and Barrie, 1987). This implies that the Pb isotopic composition of anthropogenic atmospheric matter emitted in northeastern North America can be used to distinguish between a Canadian and a US origin. This approach was efficiently used in the region of the Great Lakes (Flegal et al., 1989), across the USA–Canada border (Sturges and Barrie, 1987), and also in several other areas worldwide using either atmospheric aerosols (Sturges and Barrie, 1989), rainwater (Roy, 1996), recent sediments (Shirahata et al., 1980; Graney et al., 1995), corals (Shen and Boyle, 1987) or snow deposits (Rosman

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et al., 1994). Here, we use epiphytic lichens as a proxy for the average isotopic composition of Pb pollution reaching ground levels.

Epiphytic lichens derive their moisture and nutrients exclusively from ambient air (Déruelle and Lallemand, 1983) and have been widely used to monitor air quality around urban areas, industrial sites and pollutants reaching ground levels (Carignan and Gariépy, 1995; Monna et al., 1999; Doucet and Carignan, 2001). The processes by which lichens intercept allogenic atmospheric matter include wet precipitation, occult precipitation (fog and dew), dry deposition and gaseous absorption (Nash, 1996). Lichens do not contain the waxy cuticles of vascular plant leaves, and elemental exchange occurs across their entire surface (Nash, 1996). Lichens also lack a vascular root system, thus have no means to cleanse non-beneficial metabolic substances. The relative sensitivity of lichens to airborne contaminants is related to their biology (Nash and Gries, 1995). Metallic ions may exist in different compartments within lichens, such as (i) intercellular and surface fractions, (ii) ion exchange site fraction, (iii) intracellular fraction, and (iv) residual fraction (Brown and Buck, 1979). Hence, some lichen species are “sensitive” and die because of air pollution, while others are “tolerant” and develop resistance to pollution (e.g. Galun and Ronen, 1988). Processes by which lichens develop resistance are various, but this occurs generally by complexation of heavy metals leading to the synthesis of insoluble oxalate or carboxylic groups (e.g. Sarret et al., 1998). In remote areas of northern Canada, but also in northeastern France, many lichen species have been shown to be non-specific accumulators of metals (Chiarenzelli et al., 2001; Doucet and Carignan, 2001). The advantages in using lichens to monitor the isotopic composition of atmospheric Pb include their: (1) ubiquity and ease of sampling; (2) high Pb contents (> 1 ppm) allowing for routine analysis; and (3) capacity to average the atmospheric signal over a period of a few years. The latter is critical to monitor the distribution in Pb isotopic compositions at the continental scale in order to minimise: (1) seasonal changes of atmospheric circulation patterns; and (2) biases due to discrete, short-lived events such as forest fires or exceptional wind conditions which focus atmospheric pollution from a single point source.

2. Samples and methods

The samples (51 out of 37 site location) of lichen used herein were fruticose (form a beard-like growth) species of *Usnea*, *Bryoria* and *Evernia*. They were collected during the summer seasons of 1994–1996 from the northeastern USA, along the St. Lawrence Valley, the Maritime Provinces of Canada and from the boreal

forest of Québec Province (Fig. 1). Samples were collected mostly from uninhabited areas, remote from industries, highways or national roads. They were taken with pre-cleaned plastic tweezers and transferred to sealed plastic bags. Lichens were only taken from the extremities of small tree branches in order to obtain samples that had been exposed to the atmospheric signal for a period of only a few years. Indeed, over the last 40 yr, the isotopic composition of atmospheric Pb has evolved in response to the continuous change in the nature of source emissions (e.g. Shirahata et al., 1980; Rosman et al., 1994; Graney et al., 1995). To document the distribution of the Pb signal for a given time interval, we need to analyse lichens that are not more than a few years old, in order not to compare 20 and 5 yr average compositions. In the laboratory, the lichen samples were immediately separated from their substratum, freeze-dried and stored in hermetic vessels. To avoid potential contamination, samples were not powdered but rather an aliquot of small lichen filaments was processed for analysis. Lead isotopic compositions were determined by thermal ionisation mass spectrometry (TIMS; e.g. Carignan and Gariépy, 1995), Al concentrations by ICP-MS (e.g. Doucet and Carignan, 2001), and Pb concentrations by isotope-dilution TIMS (Carignan and Gariépy, 1995; Simonetti et al., 2000a,b) and ICP-MS (Doucet and Carignan, 2001). Repeated measurements of the NIST SRM 981 Pb standard yielded external reproducibilities (2σ mean) better than 0.1% and 0.2% for the $^{206}\text{Pb}/^{207}\text{Pb}$ and the $^{208}\text{Pb}/^{206}\text{Pb}$ ratios, respectively. Total Pb blanks for isotopic analyses were between 50 and 100 pg and negligible in all cases. The reproducibility of Pb and Al concentrations measured by ICP-MS on the lichen standard BCR-CRM 482 were better than 3% and accurate according to the certified values (Doucet and Carignan, 2001). Although measured concentrations may vary from one aliquot to another for the same lichen sample, elemental ratios (Pb/Al) are reproducible at ca. $\pm 10\%$; in contrast the measured Pb isotopic compositions are essentially within the associated analytical uncertainties (Table 1). No systematic bias was determined between Pb concentrations measured by ID-TIMS and ICP-MS (Simonetti et al., 2000a).

3. Results and discussion

Measured concentrations and isotopic compositions for Pb are listed in Table 1. Variations in Pb and Al contents in lichens are large between different and within individual sites (1–30 ppm Pb—median of 4 ppm; 50–3000 ppm Al—median of 175 ppm). Lichens also display a large range in Pb isotopic compositions between sites with $^{206}\text{Pb}/^{207}\text{Pb}$ ratios varying between 1.146 and 1.206, but have relatively homogeneous isotopic compositions

Table 1
Pb and Al concentrations and Pb isotopic composition of lichens

Sample	Lat. N	Long. W	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb	Pb (ppm)	Al (ppm)	Pb/Al	Pb EF ^a
Along St. Lawrence Valley											
<i>Mauricie (Rivière Croche)</i>			18.340	15.590	38.068	1.176	2.076	2.1	623	0.0034	21
<i>n = 3</i>	47°48'32"	72°43'49"	0.087	0.022	0.084	0.004	0.005				
<i>Lac à la Croix (Saguenay)</i>			18.459	15.624	38.157	1.181	2.067				
<i>n = 2</i>	48°17'59"	70°33'3"									
<i>Lac Decoigne (Parc)</i>			18.410	15.597	38.076	1.180	2.067	6.2	122	0.0514	216
<i>n = 2</i>	47°48'?	71°09'?	0.019	0.014	0.052	0.002	0.003				
<i>Lac Brome</i>			18.554	15.653	38.229	1.185	2.060	18.6			
<i>Lusignan</i>			18.577	15.643	38.267	1.188	2.060				
<i>n = 2</i>			0.004	0.016	0.045	0.001	0.001				
<i>Rougemont</i>			18.475	15.627	38.104	1.182	2.062	28.7	2995	0.0096	39
<i>NE Lac St-Jean (Lac Brochet)</i>			18.311	15.614	38.068	1.173	2.079	4.6	281	0.0164	76
<i>n = 2</i>	48°41'09"	71°12'05"	0.066	0.045	0.162	0.001	0.001				
<i>Arboretum de Labrieville</i>			18.466	15.647	38.281	1.180	2.073	6.5	304	0.0214	86
<i>n = 2</i>			0.065	0.008	0.079	0.004	0.003				
<i>Lac Doreen (Manic 5)</i>			18.179	15.574	37.901	1.167	2.085	7.8	142	0.0549	221
<i>KM-178 (Manic road)</i>			18.260	15.595	38.046	1.171	2.084	2.7	66	0.0409	166
<i>Chutes McDonald</i>			18.460	15.65	38.247	1.180	2.072	4.6	62	0.0742	302
<i>Pointe-aux-Outardes</i>			18.266	15.612	38.031	1.170	2.081	1.8	77	0.0234	93
<i>Rivière des Escoumins</i>			18.412	15.626	38.165	1.178	2.073	7.3	390	0.0187	75
<i>Havre St-Pierre (NE)</i>			18.472	15.666	38.28	1.179	2.072	3.1	80	0.0388	156
<i>Parc du Bic</i>			18.246	15.628	38.031	1.168	2.084				
<i>Laporte</i>			18.253	15.562	38.028	1.173	2.083	6.8	231	0.0294	118
Northern Québec											
<i>Chibougamau</i>			17.857	15.471	37.568	1.154	2.104	5.2	237	0.0219	116
<i>n = 3</i>			0.173	0.061	0.213	0.007	0.008				
<i>KM-199</i>			18.269	15.546	37.995	1.175	2.080	2.7	885	0.0031	12
<i>KM-300</i>			18.699	15.644	38.830	1.195	2.077	4.0	1524	0.0026	10
<i>LA 40 Sta, 8</i>			17.978	15.495	37.670	1.161	2.095	6.1	517	0.0118	47
<i>94C-145 Laforge2</i>			17.986	15.498	37.666	1.161	2.094	12.9	173	0.0746	300
<i>Chisasibi</i>			17.754	15.486	38.689	1.146	2.123	8.7	1614	0.0054	22
<i>Kouri</i>			17.680	15.433	37.348	1.146	2.113	6.2	121	0.0509	205
New Brunswick											
<i>Mt. Carleton Park</i>			18.628	15.669	38.330	1.189	2.058	2.6	814	0.0032	13
Nova Scotia											
<i>Liscomb Sanctuary</i>			18.381	15.620	38.211	1.177	2.079	1.7	260	0.0064	26
<i>n = 2</i>	45°13'16"	62°34'41"	0.062	0.000	0.082	0.004	0.003				
<i>King Cross</i>			18.308	15.611	38.092	1.173	2.081	3.1	82	0.0380	150
<i>n = 3</i>	46°27'54"	60°54'49"	0.037	0.013	0.034	0.001	0.004				
<i>Lac Bras D'or-Washabuck</i>			18.378	15.624	38.121	1.176	2.074	4.6	48	0.0951	397
<i>n = 4</i>	46°02'10"	60°47'32"	0.110	0.008	0.080	0.006	0.008				
<i>Debert</i>			18.366	15.633	38.192	1.175	2.080	3.0	130	0.0228	92
<i>n = 3</i>	45°28'50"	63°26'44"	0.052	0.007	0.065	0.003	0.007				
<i>Parc Kemijukujik</i>			18.606	15.637	38.179	1.190	2.052	2.4	141	0.0168	68
<i>n = 2</i>	44°23'08"	65°11'54"	0.008	0.004	0.167	0.0002	0.008				
<i>Peggy's Cove</i>			18.427	15.633	38.156	1.179	2.071	4.5	222	0.0205	82
	44°30'04"	63°55'20"									
USA											
<i>Maine (Topsfield)</i>			18.541	15.649	38.273	1.185	2.064	4.4	67	0.0657	264
<i>New York State (Titus Lake)</i>			18.805	15.649	38.348	1.202	2.039	5.3	357	0.0148	60
<i>Vermont (Brattleboro)</i>			18.904	15.679	38.616	1.206	2.043				
<i>New Jersey (Belle Plain)</i>			18.838	15.651	38.439	1.204	2.041	3.3	118	0.0280	112
<i>Maryland (Pocomoke)</i>			18.825	15.654	38.440	1.203	2.042	1.2	199	0.0060	25

^a EF: Enrichment factors were calculated as [Pb/Al(lichens)]/[Pb/Al(upper crust)]. Pb and Al concentrations used for upper crust are 20 and 80400 ppm, respectively, (Taylor and McLennan, 1995). When *n* is more than 1, the average EF may not correspond exactly to average Pb and Al concentrations.

n is the number of sample per site and italic numbers are standard deviation from the mean.

reported values on aerosols from the eastern USA (Sturges and Barrie, 1987; Rosman et al., 1994; Graney et al., 1995). Hence, the isotopic composition of these lichens probably represents that of atmospheric Pb in

the northeastern USA during the few years preceding sampling. Furthermore, these four lichens plot at one end of the linear array in Fig. 2, and most likely represent the composition of one end-member of the

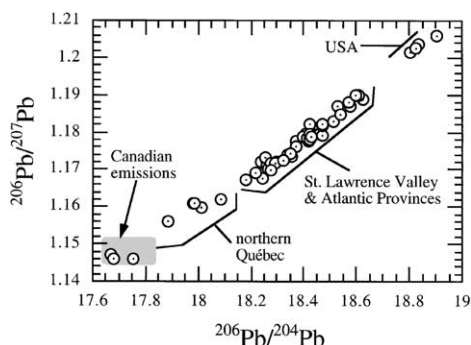


Fig. 2. All the data in a Pb isotope diagram define a linear array suggesting mixing between Canadian and USA Pb emissions. The Canadian emission field include data from

mixing trend. Two samples in Northern Québec have low Pb enrichment factors of 10 and 12 (Fig. 1). Given the large uncertainty on the Pb/Al of mineral aerosols in this area, the high $^{206}\text{Pb}/^{207}\text{Pb}$ ratios measured in these samples, compared to those in nearby lichens with high Pb excess suggest that the total Pb in these two samples is a mixture of Pb between pollution and natural crustal sources (i.e. $^{206}\text{Pb}/^{207}\text{Pb}$ of ca. 1.20–1.22). With the exception of these two samples (Fig. 1), the remainder of the lichen samples from this region display a coherent isotopic composition with low $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$, ranging from 1.145 to 1.160 and 17.65 to 18.10, and high $^{208}\text{Pb}/^{206}\text{Pb}$, from 2.114 to 2.095, respectively. Average values obtained for lichens from this region are similar to those measured for aerosols in Canadian urban areas from the Great Lakes region (Sturges and Barrie, 1987), and likely represent the average isotopic composition of industrial Canadian Pb emissions during the years preceding sampling. Similar Pb isotope compositions were also reported by Carignan and Gariépy (1995) for lichens sampled in northern Québec in the early 1990s. Canadian anthropogenic Pb values plot at the other end of the linear array, and likely represent the other end-member of the mixing trend (Fig. 2). Samples from the St. Lawrence Valley and the Atlantic Provinces yield intermediate isotopic compositions, suggesting that the atmospheric Pb in these areas is a mixture of these two end-members

Simonetti et al. (2000a–c) analysed the Pb isotopic composition of snowpacks and individual precipitation events sampled in northeastern North America during the period December 1997–July 1999. In three different geographic regions, both lichen and snowpack were sampled (although not the identical years) and analysed. The results indicate that in the St. Lawrence valley, between Montréal and Québec City, snowpack and lichen yield a similar range of Pb isotopic compositions suggesting that, on average, there is no seasonal or other

punctual bias in this region. Contrarily, lichen and snowpack collected in the Gaspé–North Shore region (downstream along the St. Lawrence valley) and along a north–south transect between Montréal and Hudson Bay (lichen data from Carignan and Gariépy, 1995) indicate significant differences in their range of Pb isotopic compositions. Several of these snowpack samples contain Pb isotope ratios (Simonetti et al., 2000a) which deviate from the relatively well-defined linear trend in Pb–Pb diagrams based on lichen data (Fig. 2). This feature was interpreted by Simonetti et al. (2000a, b) as probably resulting from meteorological controls, namely the position of the polar front during winter. The latter is also dependent on other important meteorological conditions such as El Niño events. This suggests that lichens record an averaged and integrated signal, by smoothing any seasonal variations and related wind patterns, which is needed to document atmospheric dispersal of aerosols on both a large space and time scale.

Estimates of the relative proportions of atmospheric Pb derived from Canada and the USA may be calculated using the following end-member isotopic compositions: Canadian emissions— $^{206}\text{Pb}/^{207}\text{Pb} = 1.150$ (Carignan and Gariépy, 1995); USA emissions— $^{206}\text{Pb}/^{207}\text{Pb} = 1.203$ (average of four lichens sampled in the USA, this study). On the basis of the Pb isotope results for the different regions, the relative contributions of the two end-members are shown in Fig. 3, assuming that the $^{206}\text{Pb}/^{207}\text{Pb}$ measured in lichens represents mixing of USA and Canadian Pb. The proportions of the USA Pb decrease systematically from south to north. In northern Québec, the gradient of Pb proportions between USA and Canadian parallel the St. Lawrence Valley with a SW–NE orientation, whereas south of the valley this gradient has an approximately NW–SE distribution. The latter distribution is highlighted by the systematic decrease of the USA Pb contribution observed along a southwest–northeast transect in Nova Scotia (Fig. 3). Lichens retrieved from the southern part of the Gulf of St. Lawrence yield relatively homogeneous compositions, indicating an apparent contribution of USA Pb of approximately 35–40%. In terms of sources, the overall dispersal of atmospheric lead is in good agreement with the geography and regional atmospheric circulation patterns along the St. Lawrence Valley. The predominant wind direction in this region of North America is from the southwest (Great Lakes region/American mid-west) to the northeast (Gulf of St. Lawrence), as supported by meteorological observations (Koprivnjak et al., 1994; Mathieu et al., 1995; Poissant, 1999).

Although the isotopic compositions of lichens represent a time-integrated signal, they may define sharp isotopic contrasts at a scale of <100 km. This is illustrated by the variation of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios along a north–south cross-section extending from Hudson Bay

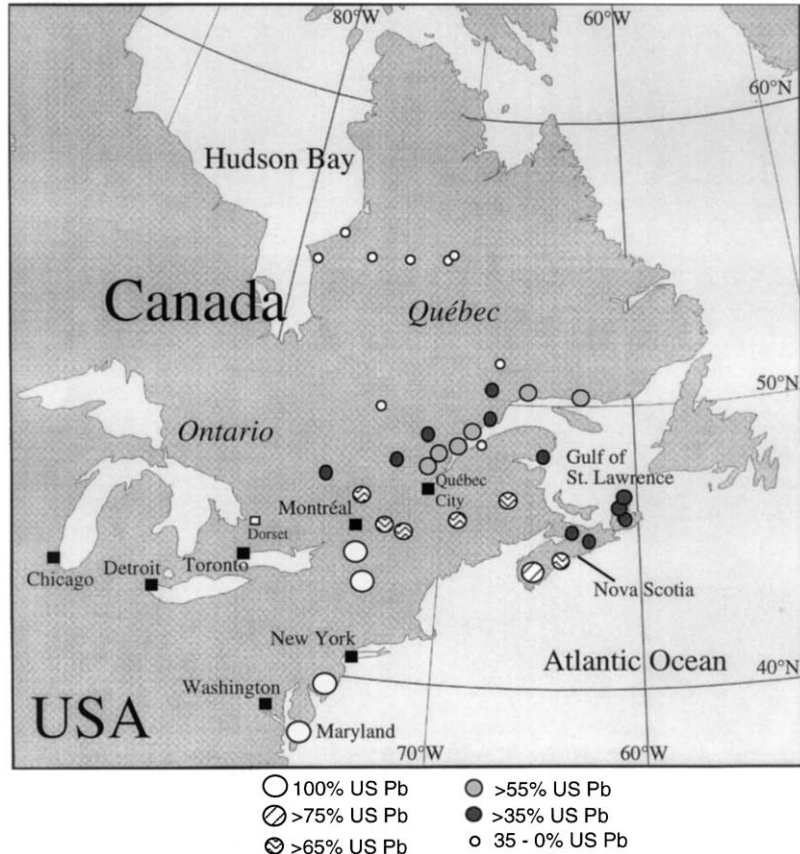


Fig. 3. Schematic map showing the distribution of the relative contribution of US industrial Pb assuming that the $^{206}\text{Pb}/^{207}\text{Pb}$ values measured in lichens result from a mixture of typical US and Canadian atmospheric emissions. This distribution reflects the role of geography and wind patterns along the St. Lawrence Valley, predominantly from the Southwest (Great Lakes region) towards the Gulf of St. Lawrence.

to southern Maryland (Fig. 4a). At both ends of the section, the Pb isotopic compositions are relatively homogeneous over long distances. Lichens within the St. Lawrence Valley, proximal to Montréal, also display relatively homogeneous isotopic composition. This composition is very similar to that of excess Pb found in surface sediments of the Great Lakes (Graney et al., 1995), aerosols sampled at Dorset (Sturges and Barrie, 1989) north of Toronto (Fig. 1), and of precipitation collected in the Montréal area over several weeks or months (Simonetti et al., 2000c). Sturges and Barrie (1989) analysed aerosols collected at Dorset on a weekly basis for a period of 2 months during fall 1984 and spring 1986. The Pb isotopic composition coupled with the concentration of heavy metals such as Pb, Zn, Cu, In, As, and Se were used to identify the mining areas of northern Ontario and Québec as a source accounting for 2–9% of atmospheric metals measured at Dorset in southern Ontario (Fig. 1). Although some Pb may originate from the Abitibi/Sudbury mining areas, most

of the atmospheric Pb (>90%) entering the St. Lawrence Valley originates from USA and Canadian industries found within the area of the Great Lakes (Ouellet and Jones, 1983; Sturges and Barrie, 1989; Simonetti et al., 2000c). As with the results from Nova Scotia, a gradient in isotopic ratios is observed along the valley with $^{206}\text{Pb}/^{207}\text{Pb}$ ratios decreasing from Montréal (1.185–1.180) to the Gulf of St. Lawrence (1.180–1.170; Fig. 4b). The systematic decrease in a northeasterly direction of the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for these lichens most probably results from the fading out of Pb from USA sources combined with the addition of Canadian anthropogenic Pb. The relative contribution from the USA Pb drops from 75% in the Montréal area to about 35% near the Gulf of St. Lawrence. The isotopic distribution of atmospheric Pb along these two sections is certainly governed by the location of anthropogenic source emissions but also by prevailing meteorological patterns present in this region.

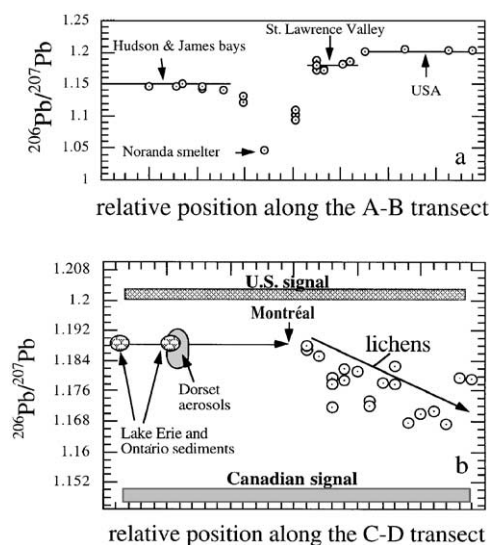


Fig. 4. (a) Composite ~2000 km north-south cross-section (A-B; Fig. 1) illustrating the variation in $^{206}\text{Pb}/^{207}\text{Pb}$ measured in lichens from Hudson Bay to Maryland. The Noranda smelter point source signal (Carignan and Gariépy, 1995) strongly overprint that of industries located more south. (b) Composite ~2000 km southwest-northeast cross-section (C-D; Fig. 1) illustrating the variation in $^{206}\text{Pb}/^{207}\text{Pb}$ measured in lichens along the St. Lawrence Valley in comparison to the isotopic composition of excess Pb found in the Great Lakes sediments for the late 1990s (Flegal et al., 1989; Graney et al., 1995) and aerosols collected at Dorset, southern Ontario, during the mid 1980s (Sturges and Barrie, 1989). The compositions for typical US and Canadian emission sources are shown for comparison.

4. Conclusions

The results from this study clearly demonstrate and confirm the effective use of lichen as a biomonitor of atmospheric pollution. Lichens from northeastern North America present large Pb excess relative to crustal compositions, suggesting that most of the Pb is anthropogenic. The Pb isotopic composition of lichens varies according to their geographic distribution, the major topography and prevailing meteorological conditions. Isotopic variations are interpreted as resulting from the mixing between Canadian and USA industrial sources. Along the Great Lakes and the St. Lawrence Valley corridor, USA Pb contributes 75–35% of the total atmospheric Pb and the contribution decreases towards the Gulf of St. Lawrence. The data allowed us to draw the first isotopic distribution map of atmospheric Pb over northeastern North America.

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