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Tracing sources of atmospheric pollution in Western Canada using the Pb isotopic composition and heavy metal abundances of epiphytic lichens

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Abstract

The Pb isotopic composition and trace metal concentrations of epiphytic lichens collected from tree branches within northwestern North America are reported here, with a latitudinal coverage extending from the Beaufort Sea (Arctic circle) to the Canada–USA border. Overall, the trace metal concentrations and Pb isotope compositions correlate with latitudinal position, since lichens retrieved north of latitude 60°N are characterized by low enrichment factors (EF) (mainly between 10 and 30) for heavy metals (i.e. Pb, Zn) and radiogenic $^{206}Pb/^{207}Pb$ isotope values ($\sim$1.170–1.180). Samples collected further south are characterized by higher EF for heavy metals and much lower Pb isotopic compositions (i.e. $^{206}Pb/^{207}Pb \leqslant 1.150$). Lichens retrieved in the immediate vicinity of major urban centers (i.e. Calgary, Alberta and Victoria, British Columbia) record distinct Pb isotopic values compared to the regional signal measured in adjacent (remote) samples. The total variation defined by the Pb isotopic compositions of the lichens may be attributed to the mixing of atmospheric particulates and aerosols derived from at least four end-member components, three anthropogenic and one natural. The latter is the predominant signal recorded in lichens retrieved north of 60°N, and is similar in Pb isotopic composition to a natural component identified in aerosols collected during the autumn season of 1994 at Alert (Canadian High Arctic). In contrast, samples collected further south reflect in-part mixing between Canadian and USA anthropogenic sources of atmospheric Pb. The third (unradiogenic) anthropogenic end-member most probably represents atmospheric emissions originating from one of the world's major Zn/Pb smelters located at Trail, British Columbia.

Keywords: Air pollution; Anthropogenic; Heavy metals; Lead isotopes; Lichens

1. Introduction

During the past two decades, emissions and atmospheric dispersal of heavy metal (Pb, Cu, Zn, Cd, Ni) pollution has received much attention due to the toxicity of these inorganic pollutants deemed unsafe to both the environment and humans. Air pollution by heavy metals is predominantly associated with solid particulate material (Harrison, 1986), in general, with particles having a diameter in the range of 0.6–10 μm (e.g. Davidson, 1980; Nriagu, 1980). Thus, the residence time for lead-bearing aerosols in the atmosphere is $\sim$10 days (Settle and Patterson, 1991) resulting in their long-distance transport and deposition in regions remote from their source of emission. Recent investigations of metal concentrations in aerosols from urban environments, in particular the fine particle fraction, indicate a more complicated pattern of atmospheric transport characterized by shorter and highly variable residence times (e.g. Wróbel et al., 2000).

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Monitoring the major sources of airborne anthropogenic Pb has been achieved predominantly with the use of lead isotope compositions for aerosols scavenged directly (airflow-pumped; e.g. Bollhöfer and Rosman, 2000, 2001) and/or indirectly (precipitations; snowpack e.g. Simonetti et al., 2000a–c) from the troposphere. The Pb isotopic composition of atmospheric emissions originating from industrial activity reflects the composition of the ores (materials) used in their production, and these are not altered during combustion and other industrial processes. In the past decades, countries worldwide have used different sources of industrial Pb with distinct geological histories, thus making it possible to apportion the atmospheric matter based on their Pb isotopic composition (e.g. Chow et al., 1975; Sturges and Barrie, 1987; Church et al., 1990; Hopper et al., 1991; Véron et al., 1992). Moreover, the Pb isotopic composition of airborne particulates provides an effective method of monitoring long-range atmospheric transport of pollution since these are not modified by physical or chemical processes occurring in terrestrial environments (e.g. Sturges and Barrie, 1987; Maring et al., 1987; Sturges and Barrie, 1989). The Pb isotopic fingerprinting technique, mainly in terms of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios, of the anthropogenic component emitted from different regions of the globe has proved successful (e.g. Shirahata et al., 1980; Sturges and Barrie (1987, 1989); Véron et al., 1992, 1993; Rosman et al., 1994; Graney et al., 1995; Bollhöfer and Rosman, 2000, 2001). For example, it is well established that the Pb isotopic composition of atmospheric particulate matter in eastern Canada and eastern USA is radically different (Sturges and Barrie, 1987) with the $^{206}Pb/^{207}Pb$ values ranging from $\sim$1.15 for Canadian (Sturges and Barrie, 1987) and $\sim$1.20 for US (Véron et al., 1992; Rosman et al., 1994) sources.

Tracing sources of anthropogenic pollution have involved the use of vegetals (e.g. lichens—Carignan and Gariépy, 1995 and moss—Rosman et al., 1998) as proxies for the sampling (scavenging) of atmospheric aerosols. Recently, Carignan et al. (2002) report the Pb isotopic data of epiphytic lichens collected from trees within northeastern North America (ca. 500,000 km^2) as a proxy for the average isotopic composition of Pb pollution reaching ground levels. These vegetals derive their moisture and nutrients exclusively from ambient air (Déruelle and Lallemant, 1983), and have been effectively used to trace the dispersal of atmospheric pollutants reaching ground levels within North America (Carignan and Gariépy, 1995) and Europe (Monna et al., 1999; 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 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" to pollution (e.g. Galun and Ronen, 1988). Processes by which lichens develop resistance to pollution 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, several lichen species have been shown to be non-specific accumulators of metals (Chiarenzelli et al., 2001; Doucet and Carignan, 2001).

The results from Carignan et al. (2002) indicate that $^{206}Pb/^{207}Pb$ values for lichens from northeastern North America vary from 1.146 to 1.206, and these are interpreted as the result 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 $^{206}Pb/^{207}Pb$ values, typical of US industrial Pb, whereas lichens sampled in northern Québec have the lowest $^{206}Pb/^{207}Pb$, typical of Canadian industrial Pb. Lichens sampled along the St. Lawrence Valley yield intermediate isotopic composition, which is interpreted as the result of mixing between USA and Canadian sources. Thus, USA industrial Pb contributes 75–35% of the total atmospheric Pb in this area of North America, and the contribution decreases from Montréal towards the Gulf of St. Lawrence.

In this study, we report the Pb isotopic compositions, and trace metal abundances for epiphytic lichens collected from northwestern North America, spanning a geographic area from the Yukon to the Canada–USA border (southern British Columbia and Alberta; Fig. 1). Of interest, the southern region of the study area is marked by the presence of the Sullivan Mine at Kimberley and associated zinc–lead smelter at Trail, British Columbia (Fig. 1). In particular, the Trail smelter (TeckCominco) produced 288,700 tonnes of zinc metal ($\sim$5% of world's refined zinc output) in 1999, and 3% of the primary lead production worldwide. Due to the rather large geographic extent covered by the more than 40 sample sites in this study, the data set has been arbitrarily sub-divided according to geographic

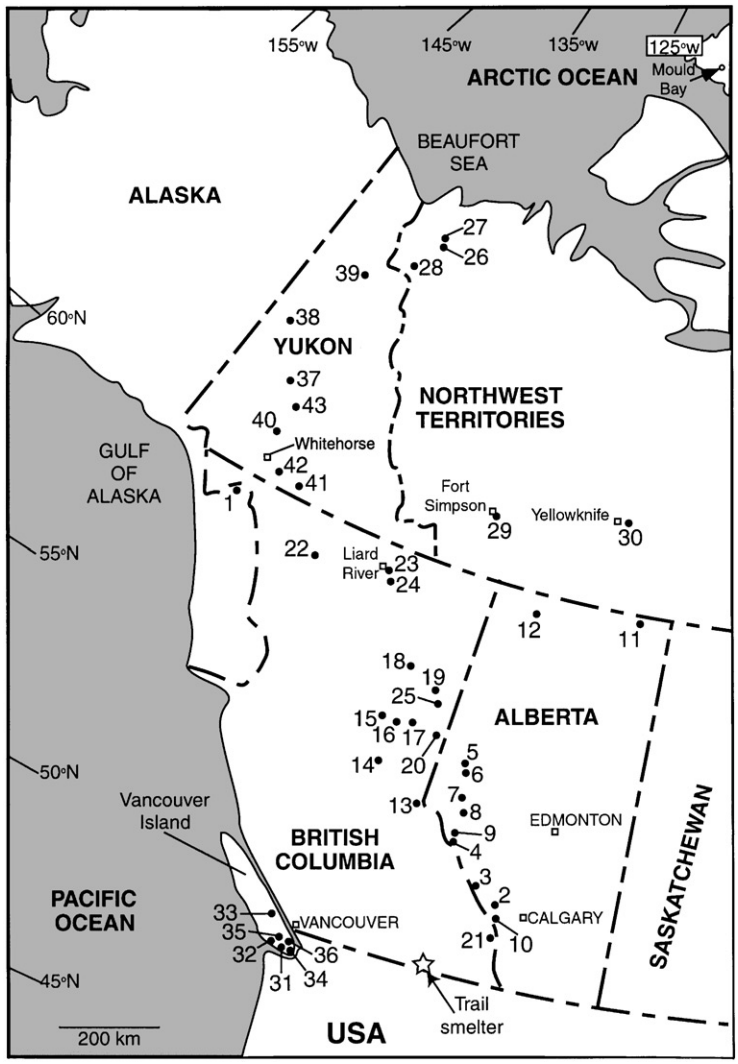

Fig. 1. Map of the northwestern region of North America showing the geographic distribution of lichen sampling sites investigated here, and location of the Zn–Pb smelter at Trail, British Columbia. The numbers of the sample sites correspond to those listed in Tables 1 and 3.

"domains". Thus, lichen samples from the Northwest Territories (NWT) and Yukon are considered representative of atmospheric conditions in the 'northern' (sub-Arctic) region, samples from Alberta and British Columbia represent that of atmospheric conditions in the 'southern' mountainous (Cordilleran) region, and lichens retrieved from Vancouver Island monitor atmospheric particulates present along the Pacific coast. Thus, the vast geographic extent covered by the sample sites permits to evaluate the impact of emissions from Canadian and USA anthropogenic sources (i.e. Alberta and British Columbia lichens), and possible influence of long-range atmospheric particulates emanating from both the northeastern Pacific (i.e. Vancouver Island lichens) and eastern Europe/Asia transported over the Arctic (NWT and Yukon lichens).

2. Sampling and analytical methods

The samples of lichen used herein were fruticose (form a beard-like growth) species of *Usnea* and *Bryoria*. These were collected between the summers of 1995 and 1997 mainly in uninhabited areas (e.g. hiking trails) remote from industries and major or secondary roads. The exceptions being certain samples from Vancouver Island such as 95-BC-1C, 2B, 2C (site nos. 31, 32) which were retrieved by the sea-side, 95-BC-4 (no. 33) was taken

from Lizard Lake campground, and 95-BC-5A collected from the campus grounds of the University of Victoria. The lichens were collected from trees, and all were taken near the tip of (young) branches less than a few millimeters in diameter. Thus, the lichens represent samples exposed to the atmospheric signal for a relatively short period of time (likely <5 years). Samples were taken with pre-cleaned gloves and plastic tools and sealed in hermetic plastic containers. In the laboratory, the samples were freeze-dried, placed in hermetic bags, and subsequently stored in a freezer.

For determination of Pb isotopic measurements, all laboratory treatments were conducted in a HEPA class 100 clean-room environment. Between 30 and 100 mg of lichen were weighed and placed in Teflon capsules and digested in ultrapure *aqua regia* using a hotplate at 100°C overnight. Separation of lead was achieved using anion-exchange chromatography (after Manhès et al., 1980). The total procedural blank is $\leqslant 30$ pg and is considered negligible. The isotopic composition for Pb was determined by thermal ionization mass spectrometry (TIMS) in single collector, peak-switching mode. Pb aliquots were loaded on a single Re filament using a silica gel-H_3PO_4 acid mixture. During the course of this study, repeated measurements ($n = 20$) of the NIST SRM 981 Pb isotope standard yielded an average external reproducibility (2σ) of $\pm 0.1\%$ amu^{-1} (i.e. 0.1%, 0.2%, 0.3%, and 0.4% for the $^{206}Pb/^{207}Pb$, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ values, respectively).

Trace element analyses were measured using a Perkin-Elmer ICP-MS SCIEX ELAN 5000 instrument located at the CRPG, Nancy (France). The analytical procedure is outlined in Doucet and Carignan (2001). The accuracy of the method was verified by calibration to lichen standard reference material (BCR-CRM 482). The fact that samples were not ground and homogenized prior to analysis resulted in some variability in concentration determinations (between 5% and 25% difference) for duplicate measurements of several lichens (Table 1); however, metal/metal ratios are similar (Table 2). Previous studies involving the determination of metal concentrations in different vegetals such as moss (e.g. *Hylocomium splendens*) also document a variation of 3–6% for reproducibility in duplicate analyses (e.g. Ross, 1990).

3. Results

3.1. Metal concentrations and enrichment factors

Tables 1 and 2 list the trace element concentrations (ppm) and heavy metal enrichment factors (EF) for the samples analyzed in this study. In general, concentrations for most elements are comparable in all of the lichens regardless of their geographic location. Table 1 also lists abundances for certain elements for different lichen species (i.e. *Cetraria cucullata* and *Cetraria nivalis*) retrieved from numerous sampling sites within the NWT (Puckett and Finegan, 1980), and these contents are similar to those determined herein. The trace metal concentrations are also expressed in terms of metal/metal ratios (Table 2; Fig. 2), and these are compared to those measured in lichens from the Vosges and the Alps (Haute Savoie) of northeastern and eastern France, respectively (Doucet and Carignan, 2001). The main reasons for this comparison are that the lichens studied here are of a similar species, they also grew in mountainous terrain, and the Doucet and Carignan (2001) study is one of the few previous investigations of a similar nature in which both accurate trace metal concentrations and Pb isotope ratios are reported. In general, it is clear from Fig. 2 that the lichens from western Canada contain higher Zn/Pb, Zn/Cd, and Cu/Pb but similar Cu/As values compared to those from northeastern and eastern France (Doucet and Carignan, 2001). The higher Zn/Pb and Zn/Cd values are primarily due to the higher absolute concentrations of Pb and Cd in the lichens from France.

The determination of EF, defined as $[metal/Al]_{sample}/[metal/Al]_{crust}$, is a commonly used method for identifying and quantifying the influence of anthropogenic activity with respect to global element cycles. However, Reimann and De Caritat (2000) demonstrate the important flaws in using a set of 'global' values for the Earth's continental crust (e.g. Taylor and McLennan, 1995) primarily due to the following reasons: (1) natural fractionation of elements during their transfer from the crust to the atmosphere, (2) differential solubility of minerals during their alteration in the environment, and (3) neglect of the assessment of the impact of biogeochemical processes. Discussion of the EF for the lichens examined here is therefore limited to 'regional' values (Table 2). With the exception of lichens from Vancouver Island, those from the remaining regions are characterized by rather low EF, in particular for Pb. The lowest regional heavy metal EF are for lichens from the NWT, whereas lichens from Vancouver Island record the highest values (Table 2). The latter may be attributed to the fact that several samples were retrieved from 'populated' areas, such as the Lizard Lake campground and the campus of the University of Victoria. In general, the EF listed in Table 2 are lower than those determined for similar lichen species from northeastern and eastern France (Doucet and Carignan, 2001). The latter simply reflects the greater proximity of these lichen samples to anthropogenic activities, which are numerous in this rather densely populated region of western Europe, compared to the population density (or degree of urbanization) in western Canada.

Table 1
Trace element concentrations (ppm) for western Canada lichens

Sample	As	Ba	Cd	Cr	Cu	Rb	Sr	Zn	Al	Pb
Alaska										
1. 95-AL-1[a] (*Usnea* sp.)										
Alberta										
2. 97.AB-1A (*Usnea* sp.)	0.60	17.8	0.17	3.95	4.58	3.22	8.2	28.6	745	23.9
3. 97-AB-2 (*Bryoria* sp.)	0.48	17.1	0.25	2.67	4.08	6.22	3.9	23.5	346	7.5
4. 97-AB-4A (*Usnea* sp.)	0.38	10.5	0.16	2.34	4.97	4.25	10.8	27.5	478	4.3
5. 97-AB-13 (*Usnea* sp.)										
6. 97-AB-14 (*Usnea* sp.)	0.25	67.2	0.28	1.94	4.15	3.44	10.4	51.3	112	1.0
7. 97-AB-15 (*Usnea* sp.)	0.34	19.8	0.18	1.98	4.73	3.04	6.8	19.1	466	1.7
8. 97-AB-16 (*Usnea* sp.)	0.48	43.7	0.06	1.72	2.87	5.62	17.2	23.6	509	3.1
9. 97-AB-18A (*Usnea* sp.)	0.52	6.6	0.39	0.36	4.52	5.33	2.8	38.6	201	2.2
10. 97-AB-21 (*Usnea* sp.)	0.64	13.5	0.23	2.61	3.09	2.24	43.6	25.5	565	15.2
11. Salt Lakes (*Usnea* sp.)	0.44	5.8	0.07	0.51	1.15	3.50	4.0	23.8	553	1.4
12. Louise Falls (*Usnea* sp.)	0.75	25.2	0.12	0.74	1.97	3.19	7.4	32.5	283	2.4
British Columbia										
13. 97-BC-5A (*Usnea* sp.)	0.18	6.8	0.06	0.97	2.65	2.04	14.8	41.7	39	3.3
14. 97-BC-6A (*Usnea* sp.)	0.39	22.4	0.19	2.18	4.50	3.31	5.9	23.6	263	0.8
15. 97-BC-7 (*Usnea* sp.)	0.26	13.0	0.14	2.46	3.74	1.49	11.4	17.1	446	1.1
16. 97-BC-8 (*Usnea* sp.)	0.39	15.7	0.15	2.59	2.69	5.53	4.0	23.0	259	3.3
17. 97-BC-9 (*Usnea* sp.)	0.70	50.2	0.35	2.67	2.60	2.81	21.8	32.4	1151	2.2
18. 97-BC-10 (*Usnea* sp.)	0.29	119	0.51	3.89	4.85	2.44	19.9	37.3	702	1.7
19. 97-BC-11 (*Usnea* sp.)	0.42	23.8	0.21	2.77	4.92	1.63	4.7	33.4	690	1.0
20. 97-BC-12A (*Usnea* sp.)	0.32	44.8	0.26	2.85	2.75	2.18	27.7	36.8	762	1.3
21. 97-BC-19B (*Usnea* sp.)	0.63	22.1	0.16	3.67	3.02	2.03	18.6	19.8	1015	5.6
22. 95-BC-11 (*Usnea* sp.)										
23. Liard River-hot spr.	1.78	53.1	0.10	2.15	2.35	3.82	167	83.2	167	1.3
24. Liard River (*Bryoria* sp.)	0.34	31.8	0.15	1.44	2.58	2.05	21.7	50.2	218	4.2
25. Fort St. John (*Usnea* sp.)	0.28	30.1	0.13	1.08	2.90	1.97	16.6	49.5	605	1.4
NW territories										
26. 96-NT-11A (*Bryoria* sp.)	0.66	29.8	0.04	1.48	2.61	3.00	7.2	21.8	877	3.1
27. 96-NT-12 (*Bryoria* sp.)	0.63	21.1	0.07	1.43	3.12	2.80	7.7	30.1	1112	17.6
28. 96-NT-13A (*Bryoria* sp.)	2.59	115	0.11	3.43	5.61	6.84	16.2	56.4	3240	4.3
29. Fort Simpson (*Usnea* sp.)	0.60	42.7	0.20	0.67	2.10	1.65	27.2	57.7	334	1.4
30. Yellowknife R. (*Usnea* sp.)	8.06	14.2	0.05	0.59	2.59	2.81	11.1	33.8	411	1.3
Vancouver Island										
31. 95-BC-1C (*Bryoria* sp.)	0.50	29.9	0.20	3.42	8.38	6.71	21.9	37.2	849	36.3
32. 95-BC-2B (*Usnea* sp.)	0.59	2.3	0.03	1.59	3.12	1.19	45.4	10.3	462	1.6
95-BC-2C (*Usnea* sp.)	0.37	2.0	0.04	1.28	2.57	1.27	26.7	21.7	237	1.6
33. 95-BC-4 (*Usnea* sp.)	0.20	3.9	0.11	0.75	3.21	3.51	9.3	31.7	31	2.1
34. 95-BC-5A (*Usnea* sp.)	0.38	20.6	1.42	1.65	3.23	4.47	37.0	21.5	66	12.1
35. 95-BC-7 (*Usnea* sp.)	0.33	10.1	0.17	2.34	4.20	1.04	35.5	56.0	297	7.6
36. 95-BC-9 (*Usnea* sp.)	0.49	9.5	0.11	1.39	2.60	5.04	22.6	15.5	268	4.9
Yukon										
37. 96-YK-8 (*Usnea* sp.)	0.48	116	0.21	1.53	3.04	2.46	31.3	90.2	554	4.6
38. 96-YK-9A *Bryoria* sp.	0.51	37.2	0.08	2.05	2.29	8.97	7.0	36.0	441	2.4
96-YK-9B (*Usnea* sp.)	0.47	88.2	0.06	2.29	1.83	6.95	25.2	77.2	289	1.9
96-YK-9C (*Usnea* sp.)	0.35	48.2	0.03	1.42	1.63	4.98	8.6	17.0	296	2.3
39. 96-YK-15 *Bryoria* sp.	0.63	27.0	0.04	2.63	2.30	3.88	20.9	35.6	756	1.6
40. 96-YK-16 (*Usnea* sp.)	0.54	48.8	0.11	1.78	3.01	1.91	34.9	33.2	1062	2.9
41. 96-YK-17A *Bryoria* sp.	0.35	36.0	0.11	0.50	2.66	1.71	7.0	50.8	270	3.5
96-YK-17B (*Usnea* sp.)	0.27	67.0	0.10	0.71	3.15	2.26	30.2	47.4	230	2.1

Table 1 (*continued*)

Sample	As	Ba	Cd	Cr	Cu	Rb	Sr	Zn	Al	Pb
42. 96-YK-18A *Bryoria* sp.	0.56	133	0.10	1.50	2.33	1.36	16.3	51.9	294	2.6
96-YK-18B (*Usnea* sp.)	0.28	96.2	0.18	1.57	1.33	2.57	17.0	35.4	325	1.4
43. 95-YK-1[a] (*Usnea* sp.)										
NW territories[b]										
Cetraria cucullata sp.	0.26			1.6	8.5			24.1	634	4.2
Cetraria nivalis sp.	0.28			1.5	6.2			25.0	370	5.6

[a] Not analyzed.
[b] Mean values from Puckett and Finegan (1980) based on a variable number of sampling sites ($n = 20$–38).

Table 2
Average and median values for enrichment factors and elemental ratios for heavy metals for western Canada lichens

Sample	EF-As	EF-Cd	EF-Cu	EF-Pb	EF-Zn	Zn/Cd	Cu/As	Zn/Pb	Cu/Pb
Alberta									
Average	75	592	38	52	125	191	8	13	1.4
Median	55	324	28	36	59	168	8	9	0.9
British Columbia									
Average	105	445	42	49	216	267	9	23	2.2
Median	33	377	25	11	76	147	10	19	2.0
NW territories									
Average	252	140	13	23	73	506	3	18	1.3
Median	43	51	10	14	31	524	3	13	1.3
Vancouver Island									
Average	142	3107	93	199	282	262	10	7.0	1.0
Median	84	346	35	103	104	278	9	6.5	0.6
Yukon									
Average	61	224	21	27	150	557	6	20	1.0
Median	62	226	18	29	154	481	5	20	1.0

3.2. Pb isotope compositions

The Pb isotopic data for the lichens studied here are listed in Table 3 and shown in Figs. 3–6. The geographic distribution of the Pb isotopic data ($^{206}Pb/^{207}Pb$ values) is shown in Fig. 3, and summarized along with the EF_{Pb} values for a north–south transect covering the entire study area in Fig. 4. Both EF_{Pb} and $^{206}Pb/^{207}Pb$ values correlate with geographic location, such that samples from the northern regions (Yukon) are characterized by lower EF_{Pb}'s and higher $^{206}Pb/^{207}Pb$ values (generally >1.170); these progressively increase and decrease, respectively, in a southern direction (Figs. 3 and 4). "Anomalous" peaks (and dips) are also noted for samples retrieved proximal to urban centers, such as Whitehorse in the north and Calgary in the south. In both instances, these lichens are characterized by lower $^{206}Pb/^{207}Pb$ values and higher EF_{Pb}'s compared to the surrounding samples (i.e. regional signal; Fig. 4).

The lichen samples from western Canada yield highly variable Pb isotopic values, and the entire distribution of the isotopic data define quasi-linear arrays in conventional Pb–Pb isotope plots (Figs. 5 and 6). Most of the Pb isotopic data for the western Canada lichens plot within a triangular area defined by the anthropogenic Pb compositions for Canada and USA airborne Pb (Carignan and Gariépy, 1995; Carignan et al., 2002), and a natural component. The latter may be represented by airborne particulates of Asian loess present over the adjacent region of the North Pacific (Jones et al., 2000), or local Cordilleran shales (Devonian–Mississippian–Silurian age) located in the Yukon (latitude $\sim 63^{\circ}$N, Godwin and Sinclair; Figs. 5 and 6). A fourth end-member component is required since several of the

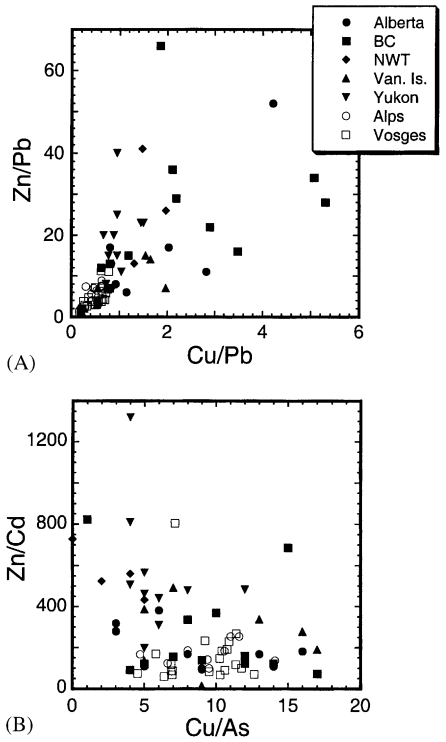

Fig. 2. Diagram illustrating (A) the variation between Zn/Pb versus Cu/Pb and (B) Zn/Cd versus Cu/As for lichens investigated here. For comparison, data for lichens of similar species from northeastern and eastern France are also shown (from Doucet and Carignan, 2001).

lichens contain less radiogenic values compared to that estimated for Canadian anthropogenic Pb (Fig. 6). Of interest, the Pb isotopic values for lichen samples retrieved from southern Alberta and Vancouver Island are remarkably similar to those obtained for atmospheric aerosols collected in nearby Calgary and Victoria in 1998–1999 (Bollhöfer and Rosman, 2001; see Fig. 3), 1–2 years subsequent the sampling of the lichens in this study.

4. Discussion—sources of atmospheric particulates

The concentrations of heavy metals for different lichen species collected at the same location (e.g. sample 96-YK-9; Table 1) are different for certain metals. These differences are much less than an order of magnitude and do not change the interpretations below.

In Fig. 2, lichens from western Canada are characterized by similar Cu/As values but much higher Cu/Pb, Zn/Cd and Zn/Pb values compared to similar species from northeastern and eastern France (Doucet and Carignan, 2001). This feature may be related to the higher concentrations of Cd and Pb in lichens from France or western Europe due to their greater proximity to both densely populated areas and industrial activities. Differences in metal/metal values may be the result of fractionation induced by bio-accumulation processes. The latter may be investigated by evaluating the abundances of Zn (relative to other heavy metals) since this element is an essential metabolic component in living organisms. The range in median Zn/Pb values (6.5–20) for the lichens investigated here is similar to that measured in precipitations (~ 6; $n = 54$ samples) collected in 1998–1999 from southwestern Québec (Simonetti et al., 2000b), which suggests negligible bio-accumulation-induced fractionation.

Most of the western Canada lichens are characterized by $EF_{Heavy\ metal}$ values that are >20 (Table 2), and thus most likely reflect an integrated atmospheric signal from anthropogenic emissions. One important source of anthropogenic atmospheric emissions in the study area is related to the smelting of Zn–Pb ore at Trail (southern British Columbia; Fig. 1). One way to evaluate the impact of this industrial activity is to examine the Zn/metal and EF_{Zn} values of lichens most proximal to the location of the smelter. These are lichen samples nos. 10 and 21 (Fig. 1), and they do not contain higher Zn/metal or EF_{Zn} values compared to the remaining lichens listed in Table 1. The Pb isotopic compositions of the lichens investigated here may therefore help to better evaluate the impact of the smelting activities at Trail, British Columbia. Ore from the Sullivan mine being characterized by a very unradiogenic isotopic composition ($^{206}Pb/^{207}Pb \sim 1.07$; Godwin and Sinclair, 1982).

In contrast to the variable metal abundances in the different lichen species from the same sample location (Table 1), their Pb isotopic compositions are essentially identical (Table 3). This result reinforces the notion of this isotope tracer as an effective tool for monitoring pathways and trajectories of atmospheric pollution. In conventional Pb–Pb isotope diagrams, data defining a linear array can only represent mixing between two end-members with different Pb isotopic compositions. The Pb isotopic data obtained in this study do not form linear arrays (Figs. 5 and 6), which suggests that more than two end-members are required to explain the total variation in the Pb isotopic data. Based on the distribution of the isotopic data, it is clear that lichens from western Canada record inputs from both the Canadian and USA anthropogenic Pb components. In particular, most of the lichens from Vancouver Island plot along the mixing line between Canada–USA anthropogenic components, which probably reflects atmospheric emissions from the proximal, major urban centers of Vancouver and Seattle. In particular, sample 95-BC-5A taken from the campus grounds of the University of Victoria yields an EF_{Pb} of 736 and $^{206}Pb/^{207}Pb = 1.154$, values indicative of Canadian

Table 3
Pb isotopic compositions of lichens

Sample	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
Alaska					
1. 95-AL-1	18.42	15.63	38.14	1.179	2.441
Alberta					
2. 97-AB-1A	17.96	15.59	37.70	1.152	2.417
3. 97-AB-2	17.69	15.55	37.42	1.137	2.406
4. 97-AB-4A	17.93	15.59	37.67	1.150	2.417
5. 97-AB-13	18.36	15.59	38.00	1.178	2.438
6. 97-AB-14	18.07	15.55	37.78	1.162	2.431
7. 97-AB-15	18.08	15.61	37.85	1.159	2.435
8. 97-AB-16	18.08	15.60	37.83	1.157	2.421
9. 97-AB-18A	17.82	15.47	37.45	1.152	2.418
10. 97-AB-21	17.94	15.56	37.64	1.149	2.417
11. Salt Lakes-Ft. Smith	18.17	15.59	37.92	1.165	2.432
12. Louise Falls	18.06	15.59	37.92	1.158	2.431
British Columbia					
13. 97-BC-5A	17.82	15.58	37.58	1.144	2.412
14. 97-BC-6A	17.99	15.56	37.70	1.157	2.423
15. 97-BC-7	18.33	15.59	38.11	1.176	2.445
16. 97-BC-8	18.19	15.66	38.07	1.162	2.433
17. 97-BC-9	18.18	15.55	37.78	1.169	2.430
18. 97-BC-10	18.42	15.61	38.17	1.180	2.447
19. 97-BC-11	18.55	15.67	38.52	1.183	2.457
20. 97-BC-12A	18.48	15.61	38.21	1.184	2.457
21. 97-BC-19B	18.38	15.65	38.17	1.174	2.439
22. 95-BC-11	18.37	15.63	38.05	1.176	2.435
23. Liard River-hot spr.	18.30	15.63	38.10	1.171	2.437
24. Liard River	17.92	15.57	37.63	1.151	2.417
25. Fort St. John	18.12	15.61	37.89	1.161	2.428
NW territories					
26. 96-NT-11A	18.10	15.61	37.88	1.160	2.426
27. 96-NT-12	17.89	15.60	37.63	1.147	2.413
28. 96-NT-13A	18.61	15.65	38.45	1.189	2.456
29. Fort Simpson	18.51	15.60	37.93	1.163	2.433
30. Yellowknife River	17.72	15.51	37.22	1.142	2.399
Vancouver Island					
31. 95-BC-1C	18.14	15.60	37.81	1.162	2.423
32. 95-BC-2B	18.28	15.63	38.14	1.170	2.439
95-BC-2C	18.31	15.66	38.13	1.170	2.435
33. 95-BC-4	18.61	15.64	38.16	1.190	2.441
34. 95-BC-5A	18.01	15.61	37.75	1.154	2.419
35. 95-BC-7	18.27	15.64	37.95	1.168	2.428
36. 95-BC-9	18.03	15.61	37.76	1.155	2.419
Yukon					
37. 96-YK-8	18.32	15.62	38.15	1.173	2.442
38. 96-YK-9A	18.30	15.64	38.13	1.170	2.437
96-YK-9B	18.23	15.62	38.06	1.167	2.436
96-YK-9C	18.42	15.64	38.17	1.177	2.440
39. 96-YK-15	18.43	15.65	38.29	1.178	2.446
40. 96-YK-16	18.31	15.64	38.08	1.170	2.435
41. 96-YK-17A	18.18	15.63	37.98	1.163	2.429
96-YK-17B	18.16	15.62	37.98	1.163	2.432
42. 96-YK-18A	18.19	15.61	37.96	1.165	2.431
96-YK-18B	18.17	15.63	37.96	1.160	2.428
43. 95-YK-1	18.42	15.63	38.25	1.178	2.447

Note: Numbers in bold face correspond to sample locations in Fig. 1. Mass fractionation corrections of 0.09% amu^{-1} and 0.24% amu^{-1} were applied to Pb isotope ratios (based on repeated measurements of NIST SRM 981 Pb standard) using Faraday and Daly analog detectors, respectively.

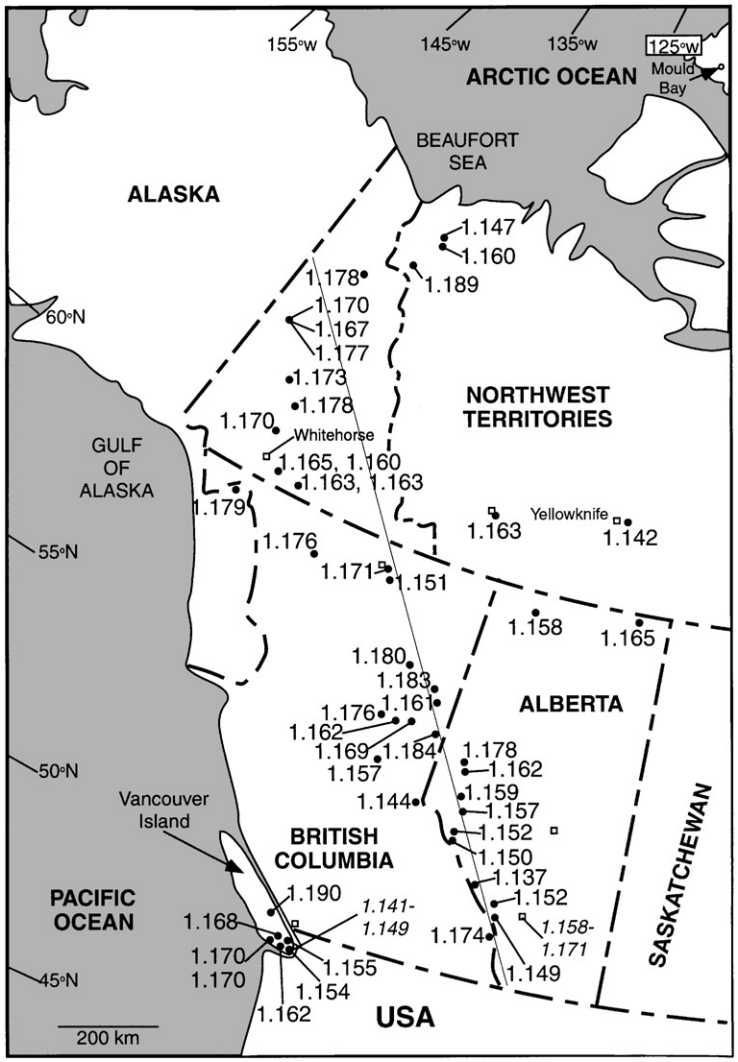

Fig. 3. Map illustrating the geographic distribution of $^{206}Pb/^{207}Pb$ values for lichen samples within the study area. In general, the Pb isotopic compositions of lichens decrease from north to south. The diagonal line represents the trace of the 'north–south' transect used in Fig. 4. Range of Pb isotopic values displayed in italicized font type represent results (1998–1999) for the cities of Victoria (British Columbia) and Calgary (Alberta) from Bollhöfer and Rosman (2001).

industrial Pb. In addition, sample 95-BC-4 retrieved from Lizard Lake campground is also characterized by a high EF_{Pb} (268), and a much more radiogenic $^{206}Pb/^{207}Pb$ value of 1.190 compared to the remaining samples from Vancouver Island. Both values may be attributed to atmospheric emissions related to campground fires, which would be characterized by a mixture of radiogenic (natural) Pb from the tree bark and labile Pb from anthropogenic sources (as described in Carignan and Gariépy, 1995). Also of interest, lichens 95-BC-1C, 2B, and 2C, which were sampled along the southwestern coast (hundreds of meters from the sea) of Vancouver Island, yield $^{206}Pb/^{207}Pb$ values of 1.160, 1.170, and 1.170, respectively (Table 3, Fig. 3). These values fall into the range of $^{206}Pb/^{207}Pb$ values (1.150–1.170) reported for anthropogenic emissions related to major urban centers of southeastern Asia (Bollhöfer and Rosman, 2001). It is possible therefore that the Pacific coast of western North America records industrial emissions from southeastern Asia, a phenomenon that has been documented to occur particularly during the spring (e.g. Berntsen et al., 1999; Jaffe et al., 1999)

Pb isotopic data for lichens from northeastern North America (Carignan et al., 2002) are plotted for comparison in Figs. 5 and 6. The data for the western Canada lichens do not completely superimpose the latter

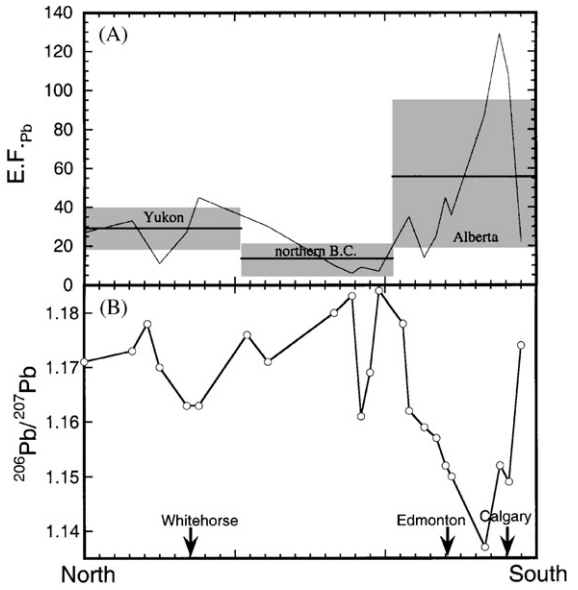

Fig. 4. Variation in (A) EF_{Pb} and (B) $^{206}Pb/^{207}Pb$ values transposed along the transect shown in Fig. 4. In (A) the individual data points are not shown due to the limitations when dealing with EF (see text for discussion); horizontal lines represent the average EF_{Pb} value for the different regions, and the associated shaded boxes represent the 1σ standard deviation. The arrows represent the orthogonal locations of principal urban centers along the transect.

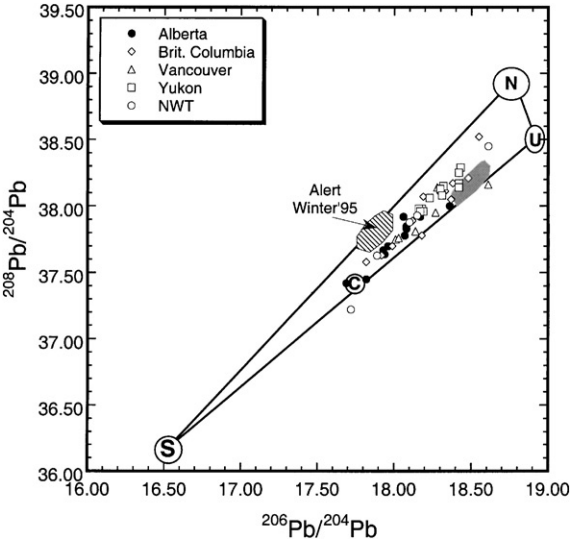

Fig. 5. Conventional Pb–Pb isotope plot illustrating the variation between $^{208}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ values for the lichens investigated here. Most of the data falls within the area encompassed by the Canadian (C) and USA (U) anthropogenic components, and aerosols derived from a 'natural' component (N), such as loess from China present over the north Pacific (from Jones et al., 2000), and local Devonian–Mississippian–Silurian shales (Yukon, Godwin and Sinclair, 1982). Data for Canadian and USA anthropogenic components are from Carignan and Gariépy (1995) and Carignan et al. (2002). (S) Represents Pb isotopic composition of ore from the Sullivan mine, southern British Columbia (Godwin and Sinclair, 1982). For comparison, shaded field represents the extent of Pb isotopic data for epiphytic lichens retrieved along the St. Lawrence valley, Québec (Carignan et al., 2002). Data for winter aerosol samples from the Alert meteorological station are from Mercier (2000).

field, thus additional end-members are required to explain the total variation of the values. One component must have a Pb isotopic composition less radiogenic than that estimated for Canadian anthropogenic emissions, whereas the other component is more radiogenic.

In North America, $^{206}Pb/^{207}Pb$ values lower than 1.150, which represents the composition of the Canadian anthropogenic end-member (Carignan and Gariépy, 1995), have been recorded in the plume aerosols emitted from the Horne smelter at Rouyn-Noranda during the winter of 2000 (Québec; Simonetti and Gariépy, 2002), and in summer precipitations $\sim$100 km west of Montréal (Québec; Simonetti et al., 2000b). The latter suggested that such unradiogenic Pb isotopic signatures reflect atmospheric emissions from steel-making industries located within the Great Lakes region, since Montréal lies within the predominant down-wind (southwest) direction from this important industrial area. However, it would be quasi-impossible for anthropogenic, atmospheric pollution generated at either Rouyn-Noranda or within the Great Lakes region to attain the western region of North America due to the prevailing meteorological conditions (i.e. prevailing westerly winds in the Northern Hemisphere).

Another possible explanation is that the lichen samples from southern British Columbia and Alberta with $^{206}Pb/^{207}Pb$ values <1.150 reflect atmospheric emissions from smelting activities at Trail, British Columbia (Figs. 5 and 6). Lichen samples recording atmospheric emissions from one of the world's major Zn–Pb smelters should be enriched in both Zn and Pb. However, only one (97-BC-5A) of two samples with the least radiogenic Pb isotopic compositions in the southern region of the study area contains extremely high EF for both Zn (1205) and Pb (339).

Alternatively, the unradiogenic Pb isotopic component may represent long-range transport of emissions from western Europe over the Arctic region and into the study area. However, atmospheric aerosols retrieved on a weekly basis for 1 year (1994–1995) at the Alert meteorological station in the Canadian high Arctic indicate that winter samples, which are by far the most polluted (i.e. winter—'Arctic haze' phenomenon), yield an average $^{206}Pb/^{207}Pb$ value of 1.150 ± 0.006

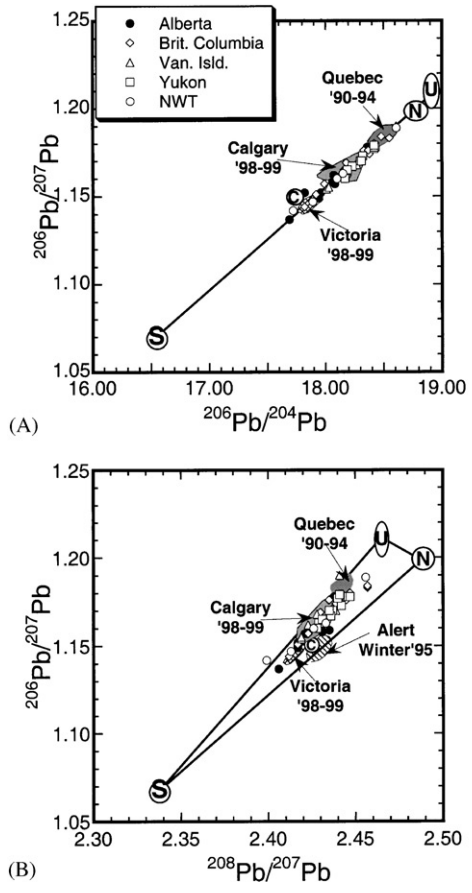

Fig. 6. Plot of (A) $^{206}Pb/^{207}Pb$ versus $^{206}Pb/^{204}Pb$ and (B) $^{206}Pb/^{207}Pb$ versus $^{208}Pb/^{207}Pb$ for isotopic data listed in Table 3. Anthropogenic and natural atmospheric components are those described in Fig. 5. Also shown for comparison are the fields for atmospheric aerosols sampled in major urban centers from western Canada during the period 1998–1999 (Bollhöfer and Rosman, 2001).

(2σ; $n = 20$ samples; Mercier, 2000). The Pb isotopic data for the Alert winter aerosol samples are shown in Figs. 5 and 6B, and these do not overlap with the values obtained for the western Canada lichens. In addition, the Alert aerosol samples taken during 'Arctic Haze' are characterized by high EF_{Pb}'s (range from 30 to 800; median = 121). Thus, there is a lack of chemical and isotopic evidence in lichens from the NWT and Yukon to confirm a large contribution of the anthropogenic (winter) component present in Arctic haze.

In contrast, the autumn 1994 aerosol samples from Alert yield radiogenic Pb isotope ratios ($^{206}Pb/^{207}Pb \sim 1.180$) and low EF_{Pb}'s, which likely reflects a natural atmospheric component. The Pb isotopic composition of this component is similar to certain lichens (with low EF_{Pb}'s) from British Columbia, NWT, and Yukon. Thus, it is possible that the 'natural' component is common to both the Arctic and northwestern regions of Canada. Mercier (2000) suggests that this natural component represents dust particles derived from local crustal rocks exposed during the summer and autumn seasons where snow/ice cover is at a minimum level. This interpretation is supported by a recent Pb isotopic investigation of sediment profiles in four High Arctic lakes (i.e. north of 66°N), including YaYa Lake (Yukon) along the margin of the Beaufort Sea (Outridge et al., 2002). The results indicate that the maximum possible contribution of anthropogenic Pb (acid-leachable) in sediment depths corresponding to the 1980s to 1990s is 0–19%. Thus, the contribution of Pb from anthropogenic emissions is small compared to inputs from local geological sources in these northern lakes (Outridge et al., 2002).

5. Conclusions

The elemental abundances and Pb isotopic compositions reported in this study indicate the effective use of lichens as tracers of the integrated signal of atmospheric pollution at a regional scale. Compared to the results obtained from analogous, large-scale regional studies of lichens from northeastern North America (Carignan and Gariépy, 1995; Carignan et al., 2002) and central Europe (Doucet and Carignan, 2001), those presented here indicate that much of western Canada is less affected by industrial atmospheric emissions (in particular the NWT and Yukon). The most 'polluted' lichen samples are found in the southern regions of the study area, namely those from Vancouver Island on the Pacific coast and both southern Alberta and British Columbia. The trace metal abundances and Pb isotopic compositions for the latter record inputs from three principal sources of atmospheric anthropogenic emissions, these are the Canadian and USA sources. The exact nature of the third anthropogenic component remains somewhat inconclusive. However, given the results from previous studies of a similar nature from the High Arctic and eastern North America, the third anthropogenic component most probably represents atmospheric emissions from the proximal Zn–Pb smelter at Trail in southern British Columbia.

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