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Pb isotopic investigation of aircraft-sampled emissions from the Horne smelter (Rouyn, Québec): Implications for atmospheric pollution in northeastern North America

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Abstract—This study reports metal abundances and Pb isotope ratios of emissions from the Horne copper smelter, and ambient (ground level) atmosphere at Rouyn, Québec retrieved during 2-week field studies in the winter and summer seasons of 2000. Plume aerosols were sampled during horizontal and vertical passes using a DHC-6 Twin Otter aircraft, which typically tracked the plume up to 30 km from the stack. Samples of the ‘background’ atmospheric conditions were taken simultaneously from a ground site meteorological station located 2.5 km in the predominant upwind direction from the stack.

Overall, metal concentrations (ng/m³ of As, Cd, Cu, Pb, Se, Zn) for the in-plume samples are elevated by one or more orders of magnitude over those measured in the ground site samples. The Pb isotope compositions for the in-plume samples are extremely variable (²⁰⁶Pb/²⁰⁷Pb range from ~1.120 to ~1.170) but define well-constrained linear arrays in conventional Pb-Pb isotope plots. Correlations between metal concentrations (e.g. As/Pb, Cu/Pb, Zn/Pb) and the Pb isotope data are indicative of binary mixing between two anthropogenic end members; most probably imported industrial Pb found in recycled materials, and nonradiogenic Pb derived from Archean sulfide ore deposits. Pb isotope data from the winter ground site (‘background’) samples indicate that the ground level atmosphere at Rouyn contains a mixture of Pb emitted from the Horne smelter and long-range anthropogenic Pb transported from Eurasian pollution sources. Compared to the Pb isotope composition of epiphytic lichens, snowpack, and precipitations collected in 1990 to 1999 from adjacent geographic regions, the Pb isotope results obtained here suggest that aerosols emitted from the Horne smelter are dispersed into northeastern North America. However, future studies dealing with point source apportionment for this region of the globe will be rendered difficult due to the processing at the Horne smelter of recycled material containing industrial Pb from various sources. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

Industrial activity related to important point-source emitters of heavy metals and sulfur dioxide, such as smelters may cause severe damage to the surrounding ecosystems. For example, some of the world’s most important smelters are found within the Kola Peninsula (Russia), a region which was the focus of the most comprehensive environmental geochemical study on a regional scale (Reimann et al., 1998). However, detailed assessment of the microphysical and chemical properties of airborne particulates from industries such as smelters are lacking; yet these parameters are crucial in determining the depositional budgets of heavy metals and their direct impact on local or distant regions. The geographic area influenced by deposition of aerosols derived from important point sources of pollution may be evaluated via a comparative evaluation of the Pb isotope signatures of the industrial emissions versus that of ambient (background) atmosphere. The Pb isotopic composition of airborne particulates provides an effective method for monitoring long-range atmospheric transport of pollution (e.g., Maring et al., 1987; Sturges and Barrie, 1987; Sturges and Barrie, 1989) since it is not altered by physical or chemical processes occurring in terrestrial environments (Doe, 1970;

Flegal and Smith, 1995). The Pb isotopic fingerprinting technique has proved successful in assessing the anthropogenic component emitted from North America (e.g., Sturges and Barrie, 1987,1989; Véron et al., 1992,1993; Graney et al., 1995; Bollhöfer and Rosman, 2001).

Previous investigations have clearly shown that the Pb isotopic composition of atmospheric aerosols in eastern Canada and the eastern USA is radically different with ²⁰⁶Pb/²⁰⁷Pb values of ~1.15 for Canadian (Sturges and Barrie, 1987) and ~1.20 for USA (Véron et al., 1992; Rosman et al., 1994) anthropogenic sources. Tracing sources of anthropogenic pollution in Canada has involved the use of several proxies for sampling (scavenging) atmospheric aerosols; these include epiphytic lichens (Carignan and Gariépy, 1995; Carignan et al., 2002; Simonetti et al., 2003), snowpack (Simonetti et al., 2000a,b) or precipitations (Simonetti et al., 2000c). The Pb isotopic compositions of these proxies in northeastern North America define a coherent geographic gradient. Samples retrieved from northern Québec have the lowest ²⁰⁶Pb/²⁰⁷Pb values, typical of Canadian industrial Pb, whereas those from the USA yield the most radiogenic compositions, typical of US industrial Pb. Samples retrieved in the intermediate region of the St. Lawrence River valley yield intermediate Pb isotope compositions, which reflect a mixture of anthropogenic Pb from Canadian (40%) and USA (60%) sources (Carignan and Gariépy, 1995; Carignan et al., 2002). Of particular relevance to this study are the Pb isotope results for a series of lichens

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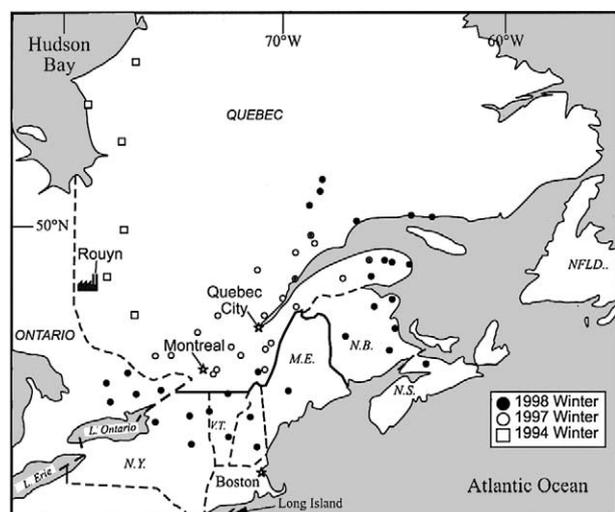


Fig. 1. Location of the Horne smelter at Rouyn, Québec within northeastern North America. Also shown are the snowpack sampling sites for the 1994, 1997 (both from Simonetti et al., 2000a), and 1998 (Simonetti et al., 2000b) winter seasons. The position of the 1994 snowpack samples represent the identical locations for the lichens investigated by Carignan and Gariépy (1995) along the north-south transect in northwestern Québec. N.B. = New Brunswick; NFLD. = Newfoundland; N.H. = New Hampshire; N.S. = Nova Scotia; N.Y. = New York State; M.E. = Maine; V.T. = Vermont. Figure modified after Simonetti et al. (2000b).

taken along a north-south transect in northwestern Québec (Fig. 1). Carignan and Gariépy (1995) concluded that the emissions from smelting activities at Rouyn are recorded in lichens located up to 500 km north of Rouyn (48°N), with the most polluted signal (i.e., lowest $^{206}\text{Pb}/^{207}\text{Pb} \approx 1.04$) measured in a sample taken approximately 100 km away (northeast direction). The Pb isotope compositions for snowpack samples retrieved at the same locations as the lichen samples, however, do not yield identical results (Simonetti et al., 2000a). This discrepancy was attributed to either: 1) different time scales for the integration of the atmospheric signal (months for snow versus years for lichens); 2) recording of the atmospheric signal at different altitudes (ground level versus lower troposphere); or 3) the presence of an important, local point source of atmospheric pollution.

The accurate characterization of the Pb isotopic composition of atmospheric emissions from singular point sources of pollution, however, remains essential for the valid use of any proxy (i.e., air samplers, lichens, snowpack) used to assess regional atmospheric dispersal patterns. Therefore, this study presents the results from two extensive aerosol sampling experiments using a Twin Otter aircraft (DHC-6) carried out within the plume of the Horne smelter stack (48.25°N ; 79.02°W ; Fig. 1) during the winter and summer seasons of 2000. Aerosols were also collected simultaneously from a meteorological station (ground level) located 2.5 km southwest (upwind) of the smelter. We report the Pb isotope composition, heavy metal and SO_2 abundances of aerosol samples taken within the pollution plume of the Horne smelter, and those at ground level retrieved with conventional air samplers. To our knowledge, this study constitutes the first detailed, aircraft-sampled investigation of the trace metal abundances and Pb

isotopic compositions of plume emissions from an industrial source. The results obtained here are compared to those reported for precipitations and epiphytic lichens from northeastern North America to evaluate the long range dispersal pattern of Horne smelter-related pollution in this region of the globe.

Emissions from the Horne smelter were presumably recorded at approximately 400 km south of Rouyn, at Dorset (eastern Ontario), in 1984 and 1986 since very low $^{206}\text{Pb}/^{207}\text{Pb}$ values of 1.04 to 1.14 were measured in aerosols associated with air masses originating from the north (Sturges and Barrie, 1989). These low $^{206}\text{Pb}/^{207}\text{Pb}$ values approach those measured in Abitibi Cu sulfides (0.92 to 1.04; Delouie et al., 1989) and galena (0.92; Franklin et al., 1983) from the local ore deposits within the late Archean Superior craton, the predominant source of ore being then processed at the Noranda Horne smelter. However, within the last decade the Noranda Cu-smelting operations are no longer processing solely ores from Archean deposits. For example, in the year 2000, the Horne smelter processed 702 kilotons of ore from various geologic deposits (domestic and imported) and 86 kilotons of recyclable material (e. g., electronic components, etc.), both of which resulted in the emission of 85 metric tons of atmospheric Pb (Noranda Co. Web site, <http://www.norandaca.com>; Noranda Sustainable Development Report, 2000). Thus, a reevaluation of the apportionment in anthropogenic sources in northeastern North America is required due to the highly variable nature of materials (including recycled materials originally manufactured abroad) being processed at an important point source emitter such as the Horne smelter.

1. ANALYTICAL METHODS

2.1. Sampling and Airborne Measurements

The aircraft was flown into plumes from the Horne smelter on a total of twenty-two flights in February and July/August of 2000 (Fig. 2). Each flight lasted approximately 2 h, and plumes were sampled up to 40 km downwind of the stack (stack 2) for ageing times of ≤ 1 h in a variety of meteorological conditions. The tracking of plumes was conducted using wind measurement systems developed for the aircraft over the past two decades. In contrast, ambient air was characterized by measurements made outside the plume and in an upwind direction from the stack. Plume aerosols were collected using an isokinetic inlet located near the front of the aircraft. Ground site samples were collected at a meteorological station located 2.5 km southwest (predominant upwind direction) from the ~ 120 m tall stack 2. Particles were collected on 47 mm diameter polycarbonate filters. The volume of air sampled through each filter was monitored continuously and the information transferred to a data capture system. At the meteorological station filters were exposed in open-faced filter packs, facing down and mounted under a 30 cm diameter hood providing protection from the elements. Filters on the aircraft were exposed in the plume as indicated by the particle measurements described below.

Particle concentrations were measured during the airborne experiments using the PCASP (Passive Cavity Aerosol Spectrometer Probe), an optical particle counter which measures the concentration and size distribution of particles in the range of 0.13 to 3 μm . The TSI 7610 counts the number of condensation nuclei with a lower detection limit of ~ 0.018 μm . Concentrations of SO_2 (during the flights) were obtained using 47 mm diameter Whatman 41 filters impregnated with KCO_3 at 25% w/v. The filters were prepared and analyzed by the Canadian Air and Precipitation Monitoring Network (CAPMoN). Double or triple filter packs were used, with the polycarbonate filter to remove particles followed by one or two impregnated filters for the collection of SO_2 . The second impregnated filter was used to determine the breakthrough of SO_2 . Correction for breakthrough needed to be applied for two sampling periods. The analysis protocol began with

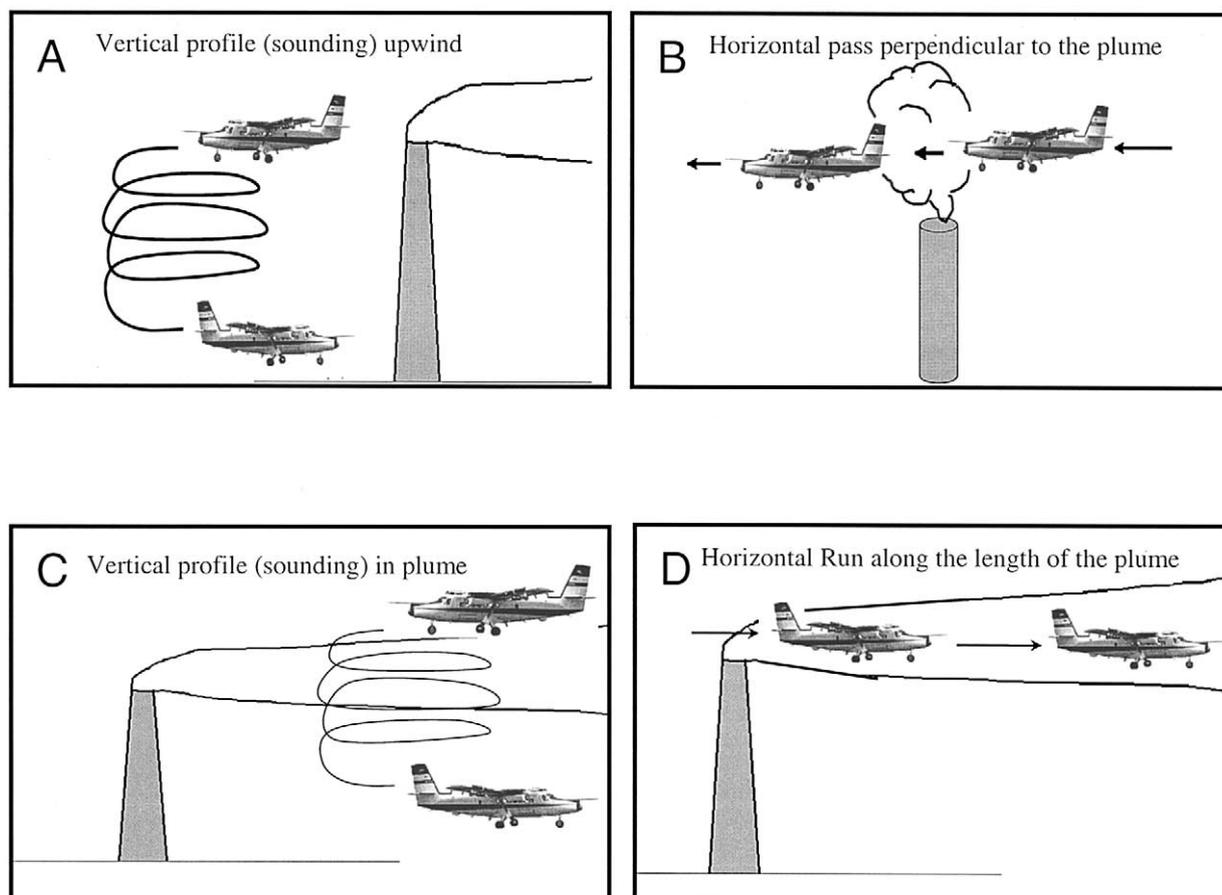


Fig. 2. Diagram illustrating the different types of plume passes conducted by the Twin Otter aircraft.

triple washing (using 18.2 mol/L Ω ultrapure water) the Whatman 41 filters, and subsequent saturation with an aqueous solution of 5% w/v glycerol and 20% w/v potassium carbonate. Each filter was then placed in a polystyrene centrifuge tube and extracted with 10 mL of 0.09% H_2O_2 solution in an ultrasonic bath for 1 h. The filter extract was diluted by a factor of five and analyzed for SO_4^{2-} by ion chromatography using a Dionex DX 500 system with an AS12A column (3.51 mM Na_2CO_3 and 0.39 mM NaHCO_3 eluent). All calibration standards were validated using certified quality control solutions.

Preparation and handling of the sampling (aerosols) filters was carried out in a clean room (class 100) environment using a mobile laboratory. A series of filters were processed during the various aspects of the fieldwork to assess the “blank” level of Pb. Most of the field blank measurements ($n = 10$) yielded ≤ 1 ng of total Pb, and reflects the presence of minute amounts of Pb within the polycarbonate filter used to capture the aerosols. However, this level of Pb blank is negligible compared to the quantity of Pb processed for all of the samples studied here (Tables 1 to 3). Wong et al. (in press) describes the sampling and analytical protocol used for determining metal concentrations for samples listed in Table 1.

2.2. Ion Exchange Chromatography and Pb Isotope Measurements

All sample treatments, including metal separation and purification by ion-exchange chromatography, were conducted in class HEPA 100 clean laboratories at GEOTOP (Université du Québec à Montréal). Ground site and airborne filter samples were processed differently due to the significant difference in sampling techniques utilized, resulting in much higher particulate loading for ground site filters. The latter were handled with precleaned Teflon tweezers and two fractions were cut

with precleaned (blank-tested) scissors each representing approximately 25% of the entire filter. One fraction was taken as is, immersed in 0.8 N HBr and ultrasonicated for approximately 30 to 40 min. The other fraction of filter was spiked with an accurately measured amount of pure (99.997%) ^{206}Pb tracer to determine the Pb abundances. It is assumed in this procedure that the distribution of Pb on the filter is uniform (homogeneous). This assumption is supported since duplicate Pb concentration determinations for separate fractions of three ground site filters yield reproducibilities between 1 and 18% (Table 2). The soluble lead fraction from spiked and unspiked filter aliquots was then processed on anion-exchange columns (after Manhés et al., 1980). The filters representing airborne samples were entirely leached in 0.8 N HBr in an ultrasonic bath for 30–40 min. The aliquot was then split into two fractions, one to determine the Pb isotopic composition, the other the concentration of Pb.

The evaporated samples were taken into solution with ~ 0.6 mL of a 2% HNO_3 solution spiked with the NIST SRM 997 Thallium standard (2.5 ppb). Pb isotope compositions of the samples were measured on an IsoProbe multicollector-ICP-MS. Samples were aspirated (~ 50 $\mu\text{L}/\text{min}$) into the ICP source using an ARIDUS microconcentric nebulizer. Simultaneous measurement of all the Pb and Tl isotopes, and ^{202}Hg ion signal was achieved by using seven Faraday collectors. The $^{205}\text{Tl}/^{203}\text{Tl}$ ratio was measured to correct for instrumental mass bias (exponential law; $^{205}\text{Tl}/^{203}\text{Tl} = 2.3887$). Before sample introduction, collector baselines were measured with the line of sight valve closed (50 s) followed by an “on-peak-zero” baseline measurement (i.e., gas and acid blank) also for 50 s. Upon sample introduction, data acquisition consisted of 2 half-mass unit baseline measurements and 1 block of 50 scans (10 s integration each) for isotope ratio analysis. Hg interferences were monitored and corrected using ^{202}Hg , however, the latter is negligible in all cases. At the beginning of each analytical session, a 25 ppb

Table 1. Metal concentrations (ng/m³) of winter and summer 2000 aerosols at Rouyn.

Date	Inlet no.	Volume (m ³)	As	Cd	Cu	Ni	Pb	Se	Zn	As/Pb	Cd/Pb	Cu/Pb	Ni/Pb	Se/Pb	Zn/Pb
Ground—winter															
14, 15/02/00	3	55.8	1.3	0.4	6.0	1.3	5.6	0.5	21.1	0.23	0.08	1.05	0.22	0.10	3.7
16, 17/02/00	3	38.9	1.5	0.5	7.6	1.5	6.3	0.6	18.7	0.23	0.08	1.22	0.24	0.09	3.0
18, 19/02/00 ^a	3,4	25.4	0.8	0.8	6.7	3.2	4.6	0.6	15.4	0.17	0.18	1.46	0.70	0.12	3.4
20, 21/02/00	5	25.5	12.0	1.9	63.4	1.2	46.0	5.2	28.0	0.26	0.04	1.38	0.03	0.11	0.6
22/02/00	2	20.2	0.9	0.3	3.5	1.4	3.5	0.9	11.0	0.26	0.09	0.98	0.40	0.26	3.1
24/02/00	2	33.1	460	17.5	726	14.2	942	83.2	361	0.49	0.02	0.77	0.02	0.09	0.4
In-plume—winter															
15/02/00	2	1.5	63.8	13.6	65.1	—	174	5.9	49.9	0.37	0.08	0.37	—	0.03	0.3
17/02/00	1	0.6	116	14.6	52.6	—	167	11.7	92.3	0.70	0.09	0.31	—	0.07	0.6
18/02/00	1	0.4	422	14.7	139	—	409	15.3	135	1.03	0.04	0.34	—	0.04	0.3
19/02/00	1	0.8	103	4.5	54.6	—	109	28.6	52.3	0.94	0.04	0.50	—	0.26	0.5
21/02/00	1	1.1	210	19.4	94.4	—	554	45.8	111	0.38	0.04	0.17	—	0.08	0.2
21/02/00	1	0.1	247	161	120	—	747	247	350	0.33	0.22	0.16	—	0.33	0.5
23/02/00	1	0.1	407	29.2	249	—	762	143	129	0.53	0.04	0.33	—	0.19	0.2
24/02/00	2	2.2	1060	317	511	5.0	3388	434	601	0.31	0.09	0.15	0.001	0.13	0.2
Ground—summer															
25, 26/07/00	1	27.4	2.3	2.0	6.9	3.5	3.1	0.1	30.6	0.73	0.64	2.25	1.13	0.05	10.0
27/07/00	2	11.9	6.2	5.5	16.2	7.6	7.1	0.0	69.5	0.88	0.79	2.30	1.08	—	9.9
In-plume—summer															
25/07/00	1	0.1	1849	10.1	888	139	550	135	146	3.36	0.02	1.62	0.25	0.24	0.3
26/07/00	2	1	188	1.7	177	11.6	315	18.9	188	0.60	0.01	0.56	0.04	0.06	0.6
26/07/00	1	0.8	584	5.5	602	122	166	0.0	115	3.52	0.03	3.62	0.74	0.00	0.7
27/07/00	1	0.3	492	26.6	834	75.1	1329	41.2	303	0.37	0.02	0.63	0.06	0.03	0.2
28/07/00	2	1.3	915	2.8	301	20.7	341	108	88.1	2.68	0.01	0.88	0.06	0.32	0.3
29/07/00	2	1.3	116	2.2	130	5.2	122	2.6	39.8	0.96	0.02	1.07	0.04	0.02	0.3
29/07/00	2	0.9	1675	8.0	2344	20.3	1513	180	504	1.11	0.01	1.55	0.01	0.12	0.3
04/08/00	2	0.5	286	8.7	268	14.5	384	12.8	42.0	0.75	0.02	0.70	0.04	0.03	0.1
04/08/00	1	0.4	889	49.9	2249	88.0	1352	250	333	0.66	0.04	1.66	0.07	0.18	0.2

^a Average volume and concentrations for two samples taken on the same day.

solution of the NIST SRM 981 Pb standard, which was also spiked with the NIST SRM 997 Tl standard (1.25 ppb), was analyzed. Each analysis of the standard consumes approximately 12.5 ng of total Pb. Repeated measurement ($n = 44$) of this standard solution over the period of December 1999 to present yields the following mean values and associated (2σ) standard deviations: $^{206}\text{Pb}/^{204}\text{Pb} = 16.938 \pm 0.016$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.492 \pm 0.018$, $^{208}\text{Pb}/^{204}\text{Pb} = 36.702 \pm 0.051$, $^{207}\text{Pb}/^{206}\text{Pb} = 0.91461 \pm 0.00050$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.1668 \pm 0.0017$, $^{208}\text{Pb}/^{207}\text{Pb} = 2.3692 \pm 0.0009$. The associated standard deviations correspond to an external reproducibility of the order of $\pm 0.04\%$ amu⁻¹.

3. RESULTS

Metal abundances (Table 1) and Pb isotopic compositions of the winter and summer 2000 aerosols collected at ground level and within the plume are listed in Tables 2 and 3, and shown in Figures 3 to 7. It is clear that the metal concentrations for the in-plume samples are much higher (by several orders of magnitude) than their ground site counterparts. The exception being the ground site sample collected on February 24, 2000 (Table 1), which yields very high metal concentrations as the smelter emissions reached the ground site due mainly to a 40° to 50°N prevailing wind direction. This placed the ground site in a downwind position relative to the stack. Similar meteorological conditions also prevailed on February 21 (Table 1) and July 28 (Table 2) resulting in somewhat higher metal (and Pb) concentrations relative to the remaining ground site samples. Excluding the samples with extremely high Pb abundances, the average Pb content for the ground site samples is 30 ± 28 ng/m³ (1σ , standard deviation), which is higher compared to those typically recorded in several Canadian urban centers (range 1 to

15 ng/m³) but much less than that of large USA cities (e.g., New York City: 50–110 ng/m³; Bollhöfer and Rosman, 2001).

The concentration and size distribution of plume aerosols were investigated using a Passive Cavity Aerosol Spectrometer Probe (PCASP) and TSI 7610 instruments. The former is an optical particle counter designed to measure the number of particles in the 0.13 to 3 μm range, whereas the latter is a counter design to measure the number of particles constituting condensation nuclei with a lower detection limit of ~ 0.018 μm . Figure 3 indicates that the Pb contents for the in-plume winter samples seem to correlate with the PCASP average number but not the 7610 parameters (not shown). The implication is, therefore, that most of the Pb-bearing mass in aerosol particles collected in the plume during the winter experiment is present within the size distribution range of the PCASP instrument (i.e., 0.13 to 3 μm). The Pb abundances measured in plume samples obtained during the summer experiments do not exhibit significant correlations with either the PCASP or 7610 parameters. In addition, Figure 3b indicates that there is no simple correlation between Pb abundances and SO₂ contents for the in-plume winter samples.

The majority of in-plume samples taken on the same day from different inlets record similar Pb isotopic values despite the fact that each pair of analyses represents significantly different air volumes (Tables 2 and 3). The exceptions are flight numbers 35 and 36 both taken on August 4, 2000, which yield distinct Pb isotope compositions ($^{206}\text{Pb}/^{207}\text{Pb}$ values of 1.161 and 1.149, respectively; Table 3); with the lower air volume

Table 2. Pb concentrations and Pb isotopic compositions of winter 2000 aerosols at Rouyn.^a

Date	PCASP Avg. no.	SO ₂ (µg/m ³)	Pb (ng)	Volume (m ³)	Pb (ng/m ³)	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁷ Pb
Ground										
12, 13/02/00			1983 (2394)	43.0	46.1	17.711	15.412	37.441	1.1492	2.4293
12, 13/02/00			2087 (2049)	42.4	49.2	17.714	15.408	37.432	1.1497	2.4294
14, 15/02/00			81 (162)	58.8	3.1	17.730	15.474	37.556	1.1458	2.4270
14, 15/02/00			343	36.2	9.5	17.783	15.515	37.700	1.1462	2.4298
16, 17/02/00			286	47.0	6.1	17.471	15.462	37.410	1.1299	2.4195
16, 17/02/00 ^b						17.471	15.467	37.430	1.1296	2.4201
16, 17/02/00-dup			226	38.7	5.8	17.431	15.481	37.464	1.1260	2.4201
18, 19/02/00			108	41.1	2.6	17.737	15.540	37.778	1.1414	2.4311
20, 21/02/00			1212	17.2	70.5	17.400	15.347	37.096	1.1338	2.4171
20, 21/02/00 ^b						17.403	15.351	37.112	1.1337	2.4176
22/02/00		57.7	19.4	3.0	17.902	15.537	37.726	1.1522	2.4282	
23/02/00			1003	12.2	82.2	17.574	15.343	37.178	1.1454	2.4231
23/02/00 ^b						17.571	15.340	37.171	1.1454	2.4231
24/02/00			12880	21.9	588	17.616	15.356	37.224	1.1472	2.4241
In-plume										
14/02/00			165	0.48	345	17.989	15.413	37.546	1.1671	2.4360
15/02/00	59	148	100	0.53	189	17.700	15.398	37.377	1.1495	2.4274
16/02/00	81	36	16.3	0.36	45.3	17.447	15.316	37.028	1.1391	2.4175
17/02/00	109		106	0.80	133	17.201	15.286	36.906	1.1253	2.4144
18/02/00	285	86	203	0.55	368	17.181	15.273	36.860	1.1249	2.4135
19/02/00	48	172	86.3	0.85	102	17.118	15.264	36.799	1.1215	2.4108
21/02/00		309	398	0.92	433	17.441	15.352	37.158	1.1361	2.4204
21/02/00	910	1244	163	0.21	775	17.497	15.347	37.164	1.1401	2.4216
22/02/00	239	1619	117	0.16	729	17.310	15.283	36.939	1.1326	2.4170
23/02/00	658	218	119	0.19	627	17.704	15.371	37.307	1.1518	2.4271
24/02/00		8475	1206	0.42	2871	17.689	15.359	37.288	1.1517	2.4271

^a Pb concentrations determined by isotope dilution; values in parentheses determined on a separate filter aliquot.

^b MC-ICP-MS duplicate analysis using same solution aliquot.

sample (sample 35) recording the more radiogenic Pb isotopic value. Unlike their similar Pb isotope compositions, the in-plume samples taken on the same day record substantial differences in Pb abundances (ng/m³; Tables 2 and 3), and suggests a somewhat heterogeneous distribution of aerosols at the

sampling scale employed. Also of importance, the Pb isotope compositions of the in-plume samples indicate significant correlations with As/Pb, Cu/Pb, and Zn/Pb values (Fig. 4).

Figure 5 illustrates the temporal variation in the ²⁰⁶Pb/²⁰⁷Pb values for both the in-plume and ground samples during the

Table 3. Pb concentrations and Pb isotopic compositions of summer 2000 aerosols at Rouyn.^a

Date	PCASP Avg. no.	SO ₂ (µg/m ³)	Pb (ng)	Volume (m ³)	Pb (ng/m ³)	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁷ Pb
Ground										
25, 26/07/00			87.9	35.3	2.5	17.258	15.396	37.143	1.1210	2.4126
26, 27/07/00			48.5	13.5	3.6	17.856	15.458	37.478	1.1559	2.4239
27/07/00			142	12.7	11.2	16.981	15.289	36.673	1.1106	2.3986
28/07/00			3488	7.1	491	17.118	15.267	36.786	1.1212	2.4095
28/07/00			2643	10.0	264	17.547	15.360	37.209	1.1424	2.4225
29/07/00			120	20.0	6.0	17.590	15.391	37.249	1.1429	2.4202
In-plume										
25/07/00	2630	59	28.8	0.07	411	17.801	15.391	37.400	1.1567	2.4292
26/07/00	4308	547	110	0.37	297	17.734	15.376	37.349	1.1533	2.4289
26/07/00		79	16.3	0.08	204	17.749	15.387	37.345	1.1535	2.4271
27/07/00	6374	180	378	0.29	1303	17.624	15.353	37.238	1.1479	2.4255
28/07/00	2618	63	172	0.50	343	17.572	15.341	37.185	1.1454	2.4238
29/07/00		47	107	0.72	148	17.462	15.317	37.068	1.1400	2.4201
29/07/00	4398	118	106	0.48	221	17.446	15.314	37.058	1.1392	2.4199
03/08/00		74	285	0.22	1297	17.491	15.338	37.135	1.1404	2.4212
04/08/00	3822	33	14.3	0.04	358	17.968	15.475	37.975	1.1611	2.4424
04/08/00		1032	126	0.33	383	17.647	15.364	37.260	1.1486	2.4252
Forest fire										
31/07/00			4.0	0.89	4.5	18.698	15.724	38.569	1.1883	2.4525

^a Pb concentrations determined by isotope dilution.

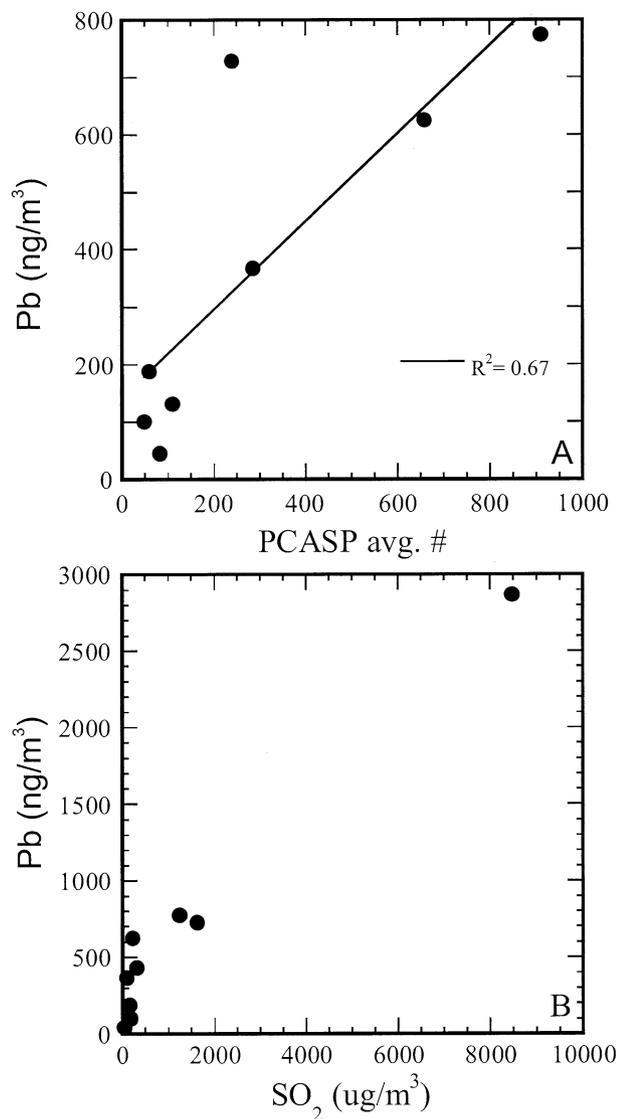


Fig. 3. Plots of concentrations of Pb (ng/m³) versus a) PCASP average number (Passive Cavity Aerosol Spectrometer Probe), and b) SO₂ (μg/m³) for in-plume samples collected during the winter 2000 experiments. The PCASP average number represents the net value (minus background values); note that the PCASP parameter in a) was not determined for flight 25 (Pb = 2871 ng/m³).

winter and summer experiments. For the winter 2000 experiment (Fig. 5a), the ²⁰⁶Pb/²⁰⁷Pb values for the in-plume aerosols range from ~1.120 to ~1.170, which is slightly larger than the range defined by the ground site winter samples. Of importance, the Pb isotope values for in-plume and ground site samples collected during the same period of time are significantly different since the external reproducibility (2σ) for the ²⁰⁶Pb/²⁰⁷Pb is ± 0.0005 , and thus within the size of the symbol. In addition, there does not seem to be a systematic bias in Pb isotope ratios between in-plume and ground site samples since these are either more or less radiogenic with respect to one another (Fig. 5a). The overall patterns for the winter experiment, however, are quite similar with the exception of the first 3 days (Fig. 5a). The similarity in the patterns is an interesting result given the (predominantly) upwind position of the ground

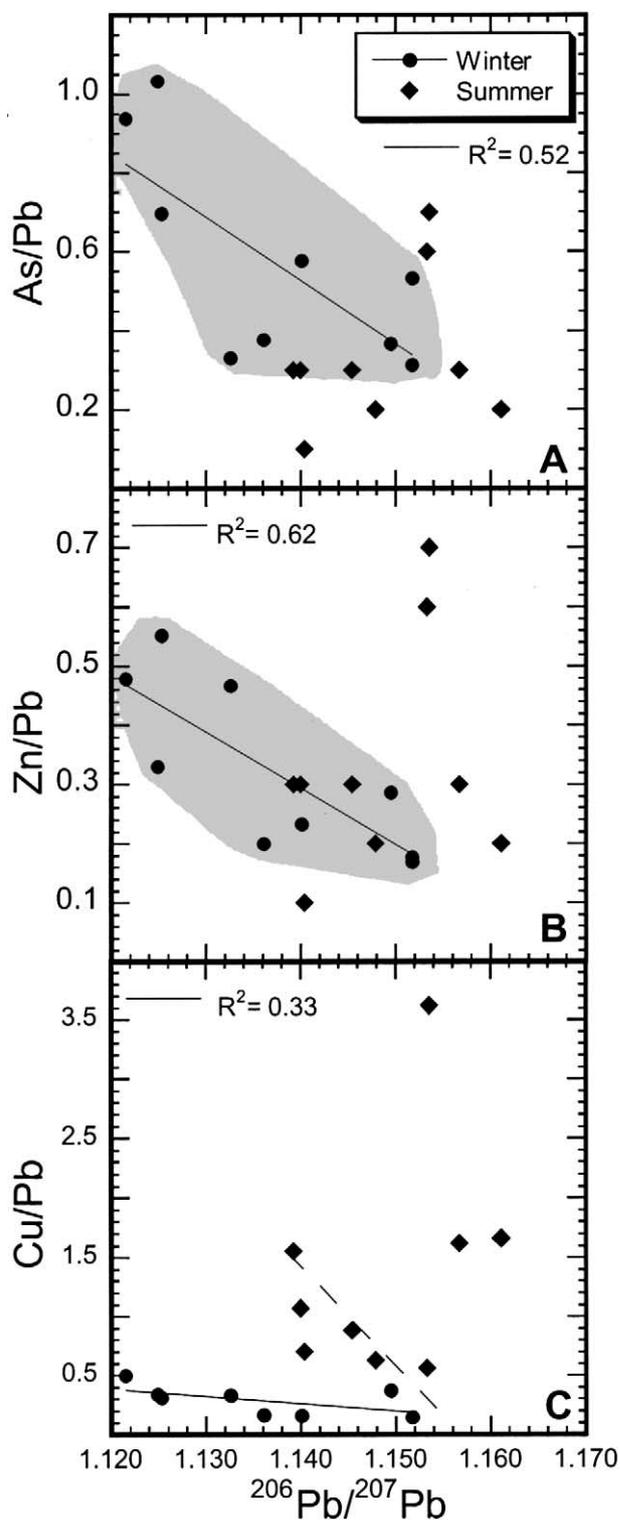


Fig. 4. (a) As/Pb, (b) Zn/Pb, and (c) Cu/Pb values versus ²⁰⁶Pb/²⁰⁷Pb for in-plume winter and summer 2000 samples. R^2 'best-fit' values correspond to linear regressions for the winter samples.

site relative to the position of stack 2. With regards to the summer 2000 experiment (Fig. 5b), the Pb isotope values for the in-plume aerosols vary from ~1.140 to ~1.160 and thus

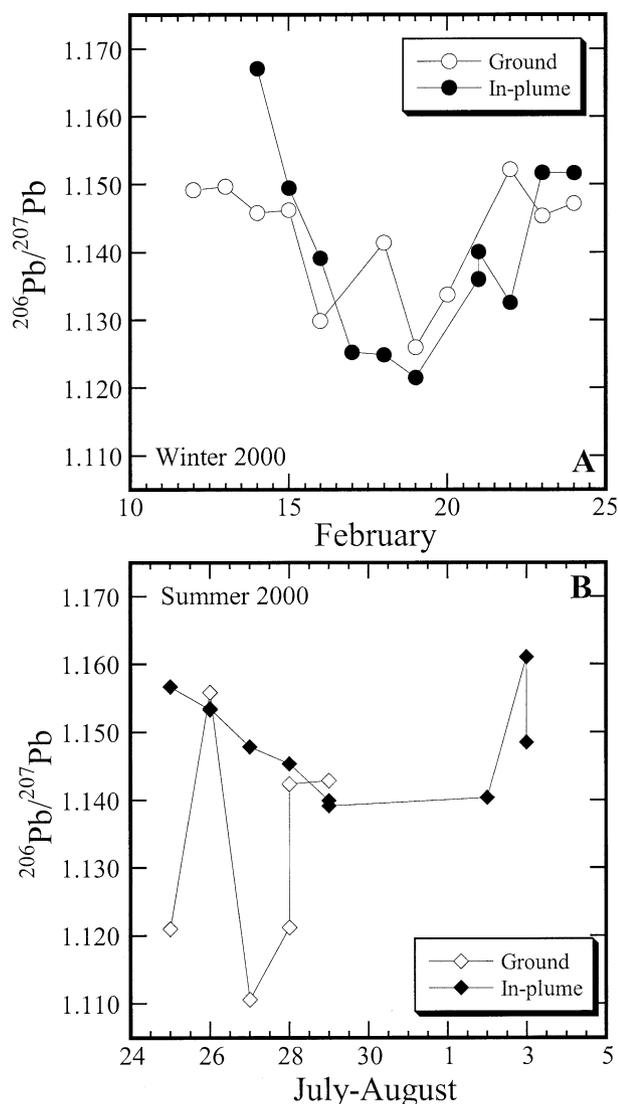


Fig. 5. Diagrams illustrating the temporal variation in $^{206}\text{Pb}/^{207}\text{Pb}$ values for both in-plume and ground site samples during the (a) winter and (b) summer 2000 experiments. Two flights were conducted on several days, and correspondingly two samples were collected (e.g., flights 21 and 22, Table 1).

record a slightly more restricted range of compositions compared to their winter counterparts (Fig. 5a). These steadily decline from July 25 to July 29, whereas within the same four consecutive days the ground site samples yield extremely variable results with $^{206}\text{Pb}/^{207}\text{Pb}$ values ranging from ~ 1.110 to ~ 1.155 . However, in-plume and ground site samples yield almost identical values on July 26 (Fig. 5b).

The Pb isotope composition of aerosols collected from a small forest fire occurring on July 31, 2000, near Hearst, Ontario (located at 49.22N, 83.93W, ~ 400 km NW of Rouyn; Friedli et al., 2003) is also shown for comparison in Figures 6 and 7. This isotopic composition most probably represents a weighted, mean value of the Pb, mainly of 'natural' origin, incorporated in trees and canopy. It is clear from Figures 6 and 7 that the forest fire aerosols are isotopically distinct and much more radiogenic compared to those sampled at the ground site

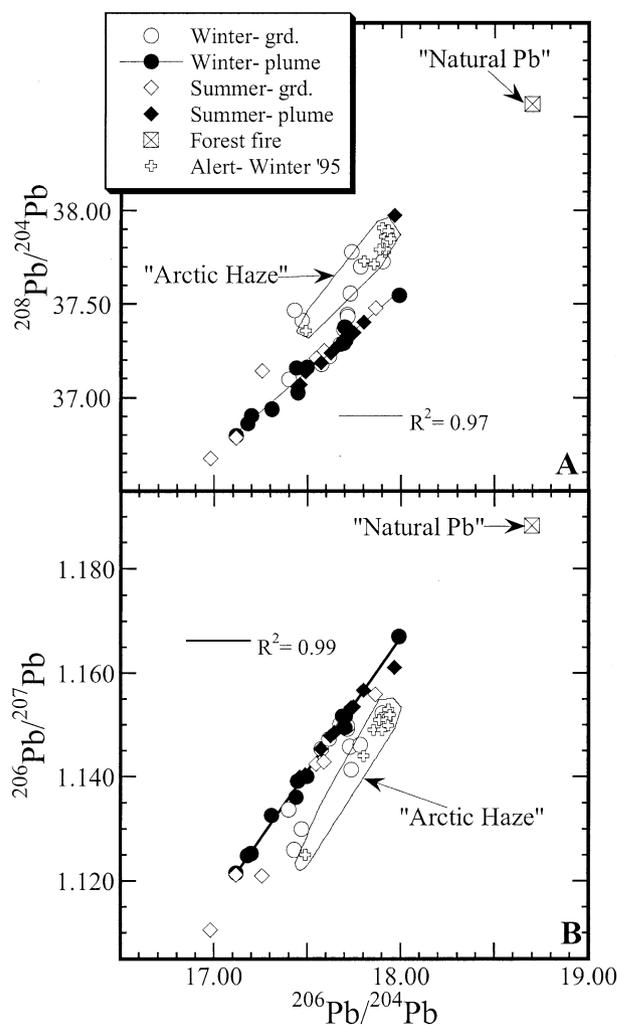


Fig. 6. a) $^{208}\text{Pb}/^{204}\text{Pb}$ and b) $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ plots illustrating the Pb isotope data obtained in this study. The correlation coefficients for the linear regressions are calculated using all the data minus the winter ground samples. Also shown for comparison are the Pb isotope compositions for weekly aerosol samples collected during the 1995 winter (period of 'Arctic Haze'; Mercier, 2000), and the forest fire aerosols collected on July 31, 2000, near Hearst, Ontario (Friedli et al., 2003).

and in-plume during the winter and summer 2000 experiments at Rouyn. However, the Pb concentration for the forest fire sample ($4.5 \text{ ng}/\text{m}^3$) is similar to that recorded by several ground site samples from both winter and summer experiments (Tables 1 to 3).

4. DISCUSSION

Figures 6 and 7 are conventional Pb-Pb isotope diagrams illustrating the data contained in Tables 2 and 3. Overall, the summer in-plume aerosols were slightly more radiogenic in Pb isotopic composition compared to their winter counterparts (Fig. 6). With the exception of several of the winter ground site samples, the Pb isotopic composition for the remaining samples plot along significant regression lines ($R^2 \geq 0.97$). A "line" in such a plot can only represent two-component mixing between

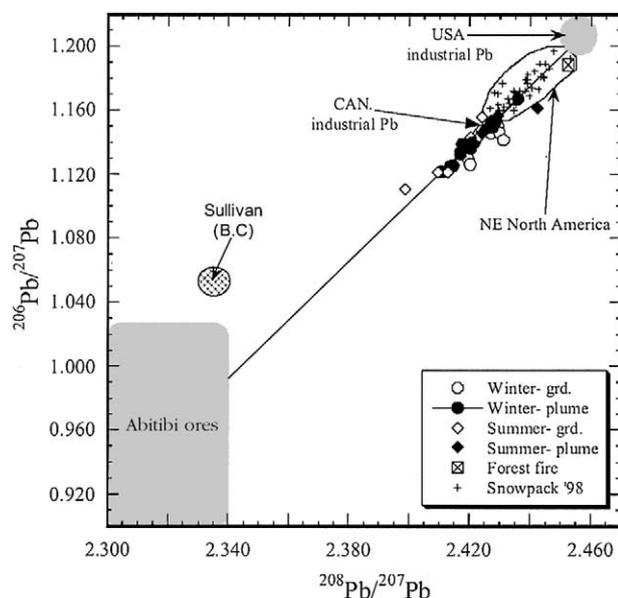


Fig. 7. Plot of $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ which illustrates the Pb isotope data presented here. In addition, fields representing the Pb isotopic composition of several well-established sources of industrial Pb in North America, USA (Carignan et al., 2002); Canada (Carignan and Gariépy, 1995); and Sullivan, British Columbia (Godwin and Sinclair, 1982). Abitibi ores (Franklin et al., 1983; Deloule et al., 1989) are shown for comparison.

end members with different isotopic compositions. Both the winter and summer in-plume aerosols plot along the same linear regression, which indicates that the two end members were present in both seasons (Fig. 6). For each experiment (flight), the proportions of the two components relative to one another control the final Pb isotopic composition of the aerosol sample, thus its position along the linear regression. Figure 7 illustrates the range in Pb isotope values for possible anthropogenic end members including sulfide ores from the local Archean Abitibi greenstone belt; this was the dominant material processed at the Horne smelter before the last decade. Their low $^{206}\text{Pb}/^{207}\text{Pb}$ values are consistent with the Pb isotopic composition of certain aerosols collected at Dorset in the mid-1980s (Sturges and Barrie, 1987), and for lichens collected in 1994 within a ~100 km radius from the Horne smelter (Carignan and Gariépy, 1995). The Pb isotope data obtained for the ground site and in-plume aerosols in this study, however, are isotopically distinct and much more radiogenic compared to those for the Abitibi ores (Figs. 6 and 7). This reflects that the Noranda mining company has significantly changed its smelting operation from processing predominantly Archean ores to a variety of source materials, such as recycled materials (i.e., electronic components), and ores from abroad of differing geologic age.

Figure 7 also illustrates the Pb isotope compositions for the well-established fields of Canadian and USA industrial Pb, and that for the ore (from Sullivan mine) processed at an important Pb-Zn smelter located at Trail, southern British Columbia. It is obvious that neither the Pb isotope composition of Canadian industrial Pb, nor that for smelter emissions (Sullivan mine) originating from British Columbia is appropriate to represent the nonradiogenic end member of the mixing array (Fig. 7). In

contrast, the isotopic composition for USA industrial Pb plots at the radiogenic end of the linear array defined by the in-plume and some ground site aerosols, thus rendering it a possible end member to the mixing array. One possibility for the nonradiogenic end member of the linear array remains the Archean sulfides and galena from the local greenstone belt (Fig. 7). This interpretation is consistent with the significant correlations shown in Figure 4, which indicates that the less radiogenic Pb isotope signatures are associated with samples characterized by higher As/Pb, Cu/Pb, and Zn/Pb values, in particular for the in-plume winter samples. As, Cu, and Zn are chalcophile elements that are hosted by ore minerals (arsenopyrite, chalcopyrite, and sphalerite, respectively) commonly found within Archean massive sulfide deposits. Also shown in Figure 7 are the Pb isotope results for snowpack collected in 1998 within northeastern North America (Simonetti et al., 2000b; Fig. 1). Pb isotope data for lichen samples retrieved from this region (Carignan and Gariépy, 1995; Carignan et al., 2002) are not included in Figure 7 since these overlap with the field outlined by the snowpack samples. The isotope data for the snowpack samples fall between the fields of USA industrial Pb and the in-plume (smelter emissions) and ground site (meteorological station) samples, respectively. Thus, emissions from the Horne smelter may be present in the atmosphere over northeastern (regional-scale) North America. This is supported by the observation that a substantial amount (between 30–70%) of particulates released from the Horne Cu smelter are deposited away from its immediate vicinity (>100 km radius; Bonham-Carter et al., 2002). Apportionment of industrial sources of pollution (e.g., Canada vs. U.S.) will be rendered more difficult in the future due to the processing of recycled material (at possibly increasing levels) over time. For example, atmospheric emissions from the Horne smelter impacting on northeastern North America can artificially increase the calculated component of U.S. industrial Pb affecting northeastern Canada. Thus, the results from this study clearly indicate the need in the future for similar studies of major industries to obtain a better understanding of long-range transport of atmospheric pollution.

Several of the winter ground site samples do not plot along the linear arrays shown in Figure 6, and thus indicate the presence of an additional anthropogenic component of distinct Pb isotopic composition. Also shown for comparison in Figures 6 and 7 are the Pb isotope compositions of aerosols sampled at the Alert meteorological station in the Canadian High Arctic during the winter of 1995 (Mercier, 2000). These aerosols represent atmospheric conditions during the most polluted season in the High Arctic, which give rise to the phenomenon of 'Arctic Haze' (Barrie and Hoff, 1985). During the months of December to April, meteorological conditions favor the transport of polluted air masses into the Arctic from Eurasia, however, most (between 85–90%) of this pollution does not deposit into the Arctic but travels out of this region (Iversen, 1984; Raatz and Shaw, 1984). The winter ground site samples which plot within the Arctic Haze Pb isotope compositional field yield the lowest Pb concentrations (~3 to 9 ng/m³; Table 2). The remaining winter ground site samples with much higher Pb abundances (~46 to 588 ng/m³; Table 2) plot either closer to or directly on the regression line defined by the in-plume samples. The latter are clearly influenced by airborne Pb derived from the Horne smelter emissions, whereas the former must repre-

sent the Pb isotopic composition of ambient (background) atmospheric conditions.

One possibility is that the ambient air at Rouyn contains anthropogenic pollution from Eurasian sources transported over the Arctic region during the winter season. The deposition of Eurasian pollution in northeastern North America was recorded in snowpack samples collected during the 1997 winter at similar latitudes in northeastern Québec (Fig. 1; Simonetti et al., 2000a). Moreover, this interpretation is also supported by a recent Pb isotopic investigation of sediment profiles in lakes within the Hudson Bay region, in particular Imitavik Lake located on the southeastern coast (Outridge et al., 2002). The results indicate a three-to-five-fold increase in Pb concentrations and corresponding decrease in the Pb isotope ratios for the most recent sediments from Imitavik Lake (Outridge et al., 2002). These features were attributed to the progressive input of anthropogenic Pb derived predominantly from Canadian and USA, but also required minor inputs from Eurasian sources.

To test this hypothesis, air mass back trajectories were calculated by the Canadian Meteorological Centre using archived meteorological data for the winter intensive time period. The path of the air for the previous 5 days was mapped, with the 900 and 925 millibar levels, over Rouyn as the end points. The back trajectories indicate that the air masses sampled at Rouyn during the winter experiments were transported from the western and northern regions of North America, mainly unpopulated areas. Based on the back trajectory analysis, there is no evidence for the influence of anthropogenic Pb derived from the major industrialized areas of eastern North America. It is also clear from the similar temporal patterns recorded by the winter samples (Fig. 5a) that a significant portion of the Pb recorded at the ground site (background location) is derived from the Horne smelter emissions.

5. CONCLUSIONS

The Pb isotope data for the in-plume aerosols from the Horne smelter collected during both the winter and summer experiments of 2000 indicate that the source materials processed were isotopically similar but these varied in their relative proportions to one another. The Pb isotope data define linear arrays indicative of binary mixing between two anthropogenic end members. These are most likely industrial Pb from USA sources present within materials such as computer soldering metals or wiring. The second, nonradiogenic component most probably represents Pb derived from ores recovered from Archean greenstone belts. The slightly more radiogenic compositions of the summer in-plume aerosols compared to their winter counterparts suggest that more recycled materials were processed during the summer (i.e., more local ores in the winter). Compared to the Pb isotope composition of lichens, snowpack, and precipitations collected during the last 5 yr from northeastern North America, it is highly probable that this region is influenced by emissions from the Horne smelter. In addition, results for the winter 2000 ground site aerosols indicate that a portion of these sampled at ground level contained smelter emissions despite its (predominant) upwind direction from the stack. Based on the Pb isotope ratios for the winter ground site samples, the 'background' atmosphere also contains anthropo-

genic Pb from Eurasian sources via the long-range transport over the Arctic region.

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REFERENCES

- Barrie L. A. and Hoff R. M. (1985) Five years of air chemistry observations in the Canadian Arctic. *Atmos. Environ.* **19**, 1995–2010.
- Bollhöfer A. and Rosman K. J. R. (2001) Isotopic source signatures for atmospheric lead: The Northern Hemisphere. *Geochim. Cosmochim. Acta* **65**, 1727–1740.
- Bonham-Carter G. F., Kettles I. M., and Kliza D. (2002) An empirical model for atmospheric metal deposition round Rouyn-Noranda, based on snow and peat surveys (abstract). *Geol. Assoc. Can.* **27**, 12.
- Carignan J. and Gariépy C. (1995) Isotopic composition of epiphytic lichens as a tracer of sources of atmospheric lead emissions in southern Québec, Canada. *Geochim. Cosmochim. Acta* **59**, 4427–4433.
- Carignan J., Simonetti A., and Gariépy C. (2002) Dispersal of atmospheric lead in northeastern North America as recorded by epiphytic lichens. *Atmos. Environ.* **36**, 3759–3766.
- Delouie E., Gariépy C., and Dupré B. (1989) Metallogenesis of the Abitibi greenstone belt of Canada: A contribution from the analysis of trace lead in sulfide minerals. *Can. J. Earth Sci.* **26**, 2529–2540.
- Doe B. R. (1970) *Lead Isotopes*. Springer-Verlag.
- Flegal A. R. and Smith D. R. (1995) Measurements of environmental lead contamination and human exposure. *Rev. Environ. Contam. Toxic.* **143**, 1–45.
- Franklin J.M., Roscoe S.M., Loveridge W.D., and Sangster D.F. (1983) Lead isotope studies in Southern and Superior provinces: Canada. Paper 351. Geological Survey of Canada.
- Friedli H. R., Radke L. F., Lu J. Y., Banic C. M., Leaitch W. R., and MacPherson J. I. (2003) Mercury emissions from burning of biomass from temperate North American forests: Laboratory and airborne measurements. *Atmos. Environ.* **37**, 253–267.
- Godwin C. I. and Sinclair A. J. (1982) Average lead isotope growth curves for shale-hosted zinc-lead deposits, Canadian Cordillera. *Econ. Geol.* **77**, 675–690.
- Graney J. R., Halliday A. N., Keeler G. J., Nriagu J. O., Robbins J. A., and Norton S. A. (1995) Isotopic record of lead pollution in lake sediments from the northeastern United States. *Geochim. Cosmochim. Acta* **59**, 1715–1728.
- Iversen T. (1984) On the atmospheric transport of pollution to the Arctic. *Geophys. Res. Lett.* **11**, 457–460.
- Manhés G., Allègre C. J., Dupré B., and Hamelin B. (1980) Lead isotopic study of basic-ultrabasic layered complexes: Speculations about the age of the Earth and primitive mantle characteristics. *Earth Planet. Sci. Lett.* **47**, 370–382.
- Maring H., Settle D. M., Buat-Ménard P., Dulac F., and Patterson C. C. (1987) Stable lead isotope tracers of air mass trajectories in the Mediterranean region. *Nature* **330**, 154–156.
- Mercier G. (2000) Composition isotopique du plomb et teneurs élémentaires des aerosols atmosphériques prélevés à la station d'Alert (Arctique Canadien) en 1994–1995: Sources et trajectoires. M.Sc. thesis, Université du Québec à Montréal.
- Outridge P. M., Hermanson M. H., and Lockhart W. L. (2002) Regional variations in atmospheric deposition and sources of anthro-

- ogenic lead in lake sediments across the Canadian Arctic. *Geochim. Cosmochim. Acta* **66**, 3521–3531.
- Raatz W. E. and Shaw G. E. (1984) Long-range tropospheric transport of pollution aerosols into the Alaskan Arctic. *J. Clim. Appl. Met.* **23**, 1052–1064.
- Reimann C., Äyräs M., Chekushin V., Bogatyrev I., Boyd R., de Caritat P., Dutter R., Finne T. E., Halleraker J. H., Jaeger Ø., Kashulina G., Lehto O., Niskavaara H., Pavlov V., Räsänen M. L., Strand T., and Volden T. (1998) *Environmental Geochemical Atlas of the Central Barents Region*. NGU-GTK-CKE special publication.
- Rosman K. J. R., Chilsom W., Boutron C. F., Candelone J. P., and Hong S. (1994) Isotopic evidence to account in changes in the concentration of lead in Greenland snow between 1960 and 1988. *Geochim. Cosmochim. Acta* **59**, 3265–3269.
- Simonetti A., Gariépy C., and Carignan J. (2000a) Pb and Sr isotopic compositions of snowpack from Québec, Canada: Inferences on the sources and deposition budgets of atmospheric heavy metals. *Geochim. Cosmochim. Acta* **64**, 5–20.
- Simonetti A., Gariépy C., and Carignan J. (2000b) Pb and Sr isotopic evidence for sources of atmospheric heavy metals and their deposition budgets in northeastern North America. *Geochim. Cosmochim. Acta* **64**, 3439–3452.
- Simonetti A., Gariépy C., Carignan J., and Poissant L. (2000c) Isotopic evidence of trace metal sources and transport in eastern Canada as recorded from wet deposition. *J. Geophys. Res. Atmos.* **105**, 12263–12279.
- Simonetti A., Gariépy C., and Carignan J. (2003) Tracing sources of atmospheric pollution in Western Canada using the Pb isotopic composition and heavy metal abundances of epiphytic lichens. *Atmos. Environ.* **37**, 2853–2865.
- Sturges W. T. and Barrie L. A. (1987) Lead 206/207 isotope ratios in the atmosphere of North America as tracer of U.S. and Canadian emissions. *Nature* **329**, 144–146.
- Sturges W. T. and Barrie L. A. (1989) The use of stable lead 206/207 isotope ratios and elemental composition to discriminate the origins of lead in aerosols at a rural site in Eastern Canada. *Atmos. Environ.* **28**, 1645–1657.
- Véron A., Church T. M., Patterson C. C., Erel Y., and Merrill J. T. (1992) Continental origin and industrial sources of trace metals in the northwest Atlantic troposphere. *J. Atmos. Chem.* **14**, 339–351.
- Véron A., Church T. M., Flegal A. R., Patterson C. C., and Erel Y. (1993) Response of lead cycling in the surface Sargasso Sea to changes in tropospheric input. *J. Geophys. Res.* **98**, 18269–18276.
- Wong H. K. T., Banic C. M., Robert S., Nejedly Z., and Campbell J. L. (in press) In-stack and in-plume characterization of particulate metals emitted from a copper smelter. *Geochem. Explor. Environ. Anal.*