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Pb and Sr isotopic compositions of snowpack from Québec, Canada: Inferences on the sources and deposition budgets of atmospheric heavy metals

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Abstract—Elemental concentrations of Al, Ba, Cd, Cu, Mg, Mn, Pb, Rb, Sr, and Zn, as well as Pb and Sr isotopic compositions were determined in samples of snowpack obtained along two main transects from the province of Quebec (Canada); one north-south (between 47°N and 55°N; 1994) and the other within the St. Lawrence Valley (1997). Median enrichment factors (relative to upper crustal abundances) for Cd, Cu, Mn, Pb and Zn for all samples range from ≈300 to ≈42,000 and are indicative of an anthropogenic origin. Pb isotope ratios for snow samples retrieved in 1994 are highly variable ($^{206}\text{Pb}/^{207}\text{Pb} = 1.148$ to 1.193) and are characterized by the most radiogenic Sr isotope values ($^{87}\text{Sr}/^{86}\text{Sr} \geq 0.710$). In contrast, the Pb and Sr isotope results for 1997 snow samples collected along the St. Lawrence Valley (below latitude 47°N), yield the most radiogenic Pb isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb} = 1.180$ to 1.190) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.708 and 0.710. The former indicate that the atmospheric pollution in this region of Quebec is dominated by a mixture of anthropogenic emissions from U.S. ($^{206}\text{Pb}/^{207}\text{Pb} \approx 1.20$) and Canadian ($^{206}\text{Pb}/^{207}\text{Pb} \approx 1.15$) sources. Pb isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb} = 1.160$ to 1.180) for 1997 samples collected north of latitude 47°N indicate input of an additional anthropogenic component, possibly that of Eurasian pollution being transported over the high Arctic during the winter season.

A comparison of the Pb isotope results between lichens and snow samples from identical sample locations indicate that these either overlap (along St. Lawrence Valley), or are significantly different (north-south transect). The latter discrepancy may be attributed to either: (1) different time scales for the integration of the atmospheric signal (months for snow vs. years for lichens); (2) recording of the atmospheric signal at substantially different altitudes; or (3) the presence of an important, local point source of atmospheric pollution.

Annual depositional budgets have been estimated for Pb, Cd, Zn, Cu, and Mn, and average values ($\text{g km}^{-2} \text{yr}^{-1}$) are 1500, 130, 196,000, 1900, and 6400, respectively. Compared to previous depositional fluxes (1993–1994) estimated from adjacent regions in North America, those reported here are slightly lower with the exception of Mn and Zn. The nondecrease in depositional fluxes of Mn may be attributed to combustion of Mn-bearing fossil fuels by automotive vehicles. The exact cause for the elevated annual depositional values for Zn, however, remains enigmatic. Copyright © 1999 Elsevier Science Ltd

1. INTRODUCTION

In the northern hemisphere, anthropogenic activities seriously affect the chemical composition of the atmosphere as these comprise >90% of worldwide emissions (Mart, 1983). Principal source areas include North America and Eurasia, which emit vast quantities of heavy metals, such as Pb, Cd, Cu, and Zn via industrial activities (e.g., heavy industry, coal burning, metallurgical smelters) and automotive traffic (Pacyna, 1986; Nriagu and Pacyna, 1988). For example, anthropogenic lead pollution is estimated to account for 96 to >99% of total atmospheric Pb deposition (Shirahata et al., 1980; Flegal et al., 1989; Nriagu, 1989). Deposition of such large quantities of heavy metals into the environment (e.g., 330,000 tons yr^{-1} of Pb worldwide in 1983; Nriagu and Pacyna, 1988) have become a major ecological and health problem (e.g., Patterson, 1980; Needelman, 1984; Friberg et al., 1985, 1986; Davis and Svendsgaard, 1987). The recent investigation of aquatic Pb concentration levels in both urban and suburban environments in the U.S. (Callender and Van Metre, 1997) shows, however,

that maximums occurred in the 1970s and have drastically declined thereafter in response to a reduction in emissions as a result of the Clean Air Act. Other studies that also indicate a concomitant decline in global concentrations of Pb since the 1970s include the study of corals from the western North Atlantic (e.g., Shen and Boyle, 1987), Pb in surface waters near Bermuda (e.g., Boyle et al., 1994) and Pb in Greenland ice (e.g., Boyle et al., 1994; Rosman et al., 1998a).

Atmospheric Pb is concentrated mainly in submicrometer aerosols that can be transported long distances and deposited over large areas of the earth. The composition of stable lead isotopes provides an effective method of monitoring long-range atmospheric transport of anthropogenic pollution. The latter is derived from nonferrous ore deposits and is released to the environment primarily by the combustion of alkyl-leaded gasoline and as a by-product of industrial activities. Sampling and subsequent Pb isotopic analysis of aerosols emitted from anthropogenic and natural sources (e.g., soil dust, sea salts, vegetation) may be determined directly with the use of high volume air samplers (e.g., Maring et al., 1987; Sturges and Barrie, 1987; Hopper et al., 1991). Indirect sampling methods of atmospheric constituents include the study of sediments (or soils), moss (e.g. Rosman et al., 1998b), peat bog (e.g., Shotyky

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et al., 1998), surface waters from lacustrine or marine environments (e.g., Véron et al., 1987; Hamelin et al., 1990, 1997; Erel et al., 1997), glacier ice (e.g., Rosman et al., 1993), and wet precipitations such as snow or rain. The latter are known to be effective scavengers of the chemical species present in the atmosphere; however, their “washout” ratios are not constant and can depend on meteorological conditions (Misra et al., 1985) and the type of precipitation (e.g., Raynor and Haynes, 1983). Isotopic studies of precipitations, however, are scarce as these require the use of a costly automated sample collection network equipped with appropriate low-blank sampling instruments.

Investigations on the Pb isotopic composition of the atmosphere have delineated, mainly in terms of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios, the anthropogenic component emitted from different regions of the globe (e.g., Mediterranean and Europe: Elbaz-Poulichet et al., 1984, 1986; Petit et al., 1984; Flament, 1985; Maring et al., 1987; Hopper et al., 1991; Grousset et al., 1995; Erel et al., 1997; North America: Sturges and Barrie, 1987, 1989a; Véron et al., 1992, 1993; Rosman et al., 1994; Graney et al., 1995). Overall, the $^{206}\text{Pb}/^{207}\text{Pb}$ values range from ≈ 1.10 to ≈ 1.15 for Europe and the Mediterranean region, and ≈ 1.15 and ≈ 1.20 for Canadian (Sturges and Barrie, 1987) and U.S. (Véron et al., 1992, 1993; Rosman et al., 1994) sources, respectively.

The tracing of atmospheric pollution has also included the use of epiphytic lichens. Their role as biomonitors (i.e., providing quantitative information) of trace-element air pollution is now widely acknowledged (e.g., Lawrey and Hale, 1988; Rope and Pearson, 1990; Sloof and Wolterbeek, 1991; Lawrey, 1993, and references therein). In a Pb isotope study of epiphytic lichens from southern Quebec ($^{206}\text{Pb}/^{207}\text{Pb}$ range from 1.179 to 1.188), Carignan and Gariépy (1995) concluded that the atmospheric Pb present within the St. Lawrence Valley represents a mixture of 40% from Canadian and 60% from U.S. anthropogenic sources. Carignan and Gariépy (1995) state, however, that two shortfalls associated with the use of epiphytic lichens as biomonitors include their slow metabolic rate and unknown age, both of which detract from recording signals of atmospheric Pb on short and precise time scales. Moreover, given the seasonality of the Quebec climate it is likely that these vegetals are biologically much more active during the summer months compared with the winter season. This is an important consideration as dominant air mass circulation patterns over North America are not the same year-round (Barrie, 1986); most notable is the southward migration during the winter season of the polar front, the boundary between tropical and polar air masses, to latitudes between 40 and 50°N from its summer position at 60 to 70°N (Raatz, 1991).

To quantify heavy metal deposition on a relatively short time scale and investigate possible variations in the sources of pollution over eastern Canada, we obtained core samples of snowpacks along two main transects (Fig. 1): (1) a N–S transect between 47 and 56°N from Noranda to the James Bay region; and (2) a SW–NE transect oriented primarily along the St. Lawrence Valley. Sample collection along these two transects was conducted during the 1994 and 1997 winter seasons, respectively. Of importance, the area covered by both transects will provide indirect monitoring of atmospheric emissions from two important emitters of atmospheric pollution in eastern

Canada. One being a Cu-smelting operation at Noranda, Québec (Fig. 1), which recent atmospheric emissions (yr^{-1}) have been approximated to 3.9, 133, and 355 tons of Cd, Cu, and Pb, respectively (Environment Canada, 1997); the other being a major Zn refining plant located in Valleyfield, Québec (≈ 40 km south of Montréal), which releases the highest amount of atmospheric Zn in Canada at 106 tons yr^{-1} (Environment Canada, 1997).

Elemental concentrations and Pb and Sr isotopic compositions are presented for snow samples retrieved from 30 sites. It is acknowledged that, in general, variations in the chemical composition of snowfalls reflect chemical differences within the air masses from which they are derived (Jones and Stein, 1990). Thus, the chemical and isotopic compositions of snow cores should represent a “naturally” weighted sample of the wet and dry atmospheric aerosols deposited over a period of 3 to 5 months. In addition, the existence of a snowpack for several months should curtail the quantity of locally derived, natural aerosols such as soil dust. The aims of this study are to (1) compare the Pb isotope results obtained from snow samples to those for lichens from proximal areas and document any variability in the sources of atmospheric pollution; (2) with the use of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, determine the relative contributions of Sr-rich aerosols such as sea salts and those of crustal origin (soil derived); and (3) quantify the annual deposition budget of several heavy metals over northeastern North America.

2. SAMPLING AND ANALYTICAL METHODS

Samples were collected during the months of March 1994 (N–S transect) and March–April 1997 (St. Lawrence Valley transect). All samples were retrieved kilometers away from cities, industries, highways, main roads, and railways to obtain a regional atmospheric signal rather than that of a local point source. A strict set of criteria were used in the selection of sampling sites, which included sampling in uninhabited areas at least 1 km away from villages, summer resorts, and secondary roads. In all cases, the immediate sampling site was reached by means of snowshoes. Most samples were obtained in “clear” areas of the snowpack so as to reduce the contribution from any overlying vegetation canopy. Nevertheless, the samples occasionally contained millimeter-sized vegetation debris, such as fragments of spruce/fir needles, deciduous tree leaves, or bark.

The corer is a 60-cm long \times 10-cm diameter Teflon tube, which is thoroughly washed in distilled dilute HCl and nanopure water before sampling, and kept sealed in precleaned polyethylene bags. At all times, manipulation of the corer involved the use of sterile Latex gloves. At the sampling site, the tube is “precontaminated” by driving it into the accumulated snow several times. The sample is obtained by driving down the corer, from an upwind position, using a lid at the top, which induces compaction of the snow column inside the tube such that the effective length of the snowpack sampled may be as long as 1.0 to 1.5 m. Note that most of the snow cores did not sample the entire winter’s snowfall accumulation, thus the profiles probably reflect the integrated atmospheric signal for the latter part of the winter season. The sample-bearing corer is immediately sealed in a cleaned polyethylene bag and transferred into a cleaned icebox for transportation. The snow cores are melted within hours of collection and the meltwaters collected in precleaned polyethylene bottles. Typically, 2 to 3 L of water are recovered and stored in a cleaned icebox located in the vehicle (i.e., simulate a cold room environment). Upon return to the laboratory, the samples are stored in a cold room at 4°C. Except where noted (Table 1), all analytical results were obtained on filtered (0.45- μm) aliquots of the bulk samples using a precleaned acetate cellulose filter and a peristaltic pump equipped with Teflon tubing. Cleaning procedure for the acetate cellulose filters and Teflon tubing involved “filtering” approximately 1 L of nanopure water prior to sample processing. Table 2 also lists the average blank trace element concentra-

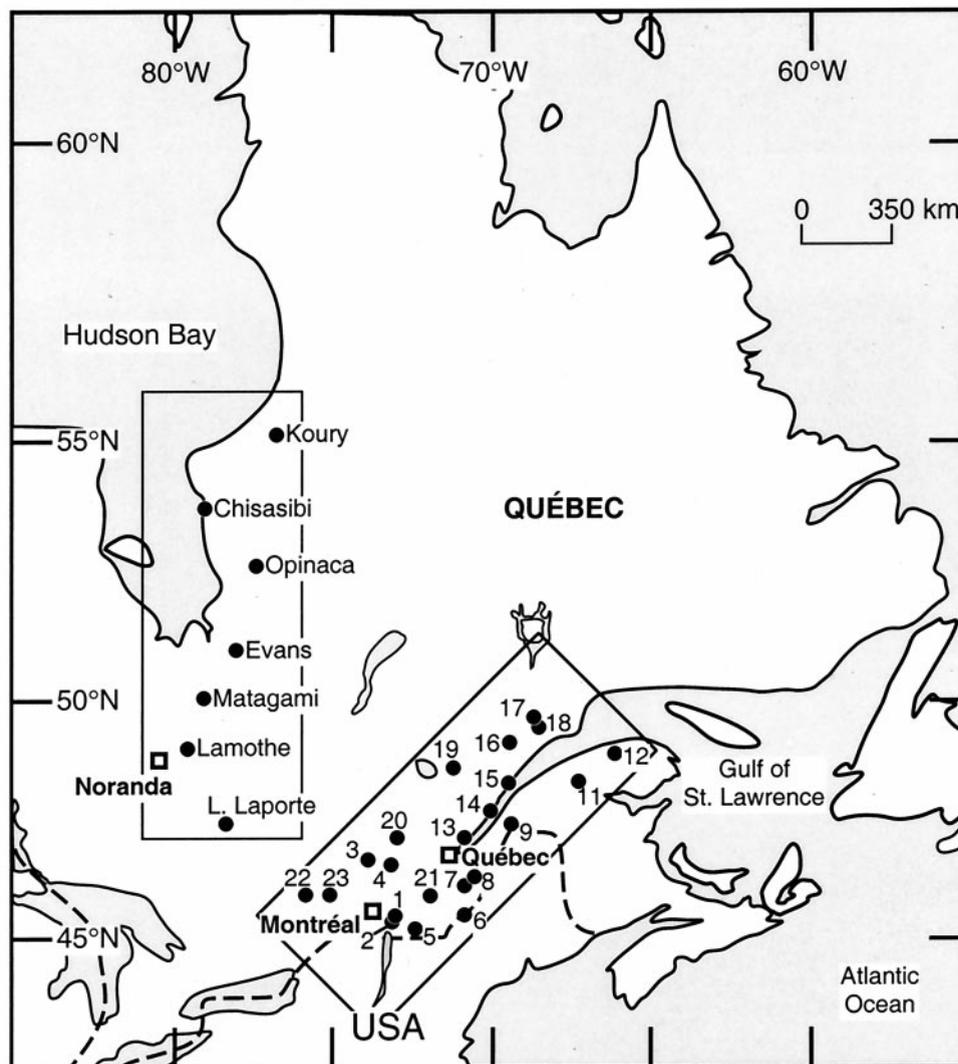


Fig. 1. Location of snowpack sampling sites. Samples along the N-S transect were retrieved during the 1994 winter, whereas those along the St. Lawrence Valley were obtained during the 1997 winter. Sample numbers for sites along the St. Lawrence Valley correspond to those listed in Tables 1, 2, and 4.

tions for two filtered nanopure water ("cleaning") solutions. Subsequent to cleaning, the first ≈ 30 mL of filtered meltwater was discarded as part of the filter and tubing precontamination procedure.

All laboratory treatments were carried out in a class 100 clean-room environment. Separation of Pb from a 100-mL aliquot of meltwater was obtained using a two-step anion-exchange chromatographic procedure (modified after Manhès et al., 1980). Strontium was separated from the very same aliquot of water using the wash fraction from the Pb chemistry and conventional cation-exchange chromatography. Total procedural blanks were ≤ 100 pg for Pb and ≈ 70 pg for Sr. The blank-to-sample ratio for Pb and Sr in the least abundant samples (≈ 0.05 ppb for Pb and ≈ 0.07 ppb for Sr) is at most 2% and 1%, respectively, and are both negligible. The isotopic compositions for Pb and Sr were determined by thermal ionization mass spectrometry (TIMS). Sr aliquots were loaded using a TaF solution on a single Re filament, whereas Pb aliquots were loaded on a single Re filament using a silica gel- H_3PO_4 acid mixture. Repeated measurements of the NIST SRM 981 Pb standard yielded an average external reproducibility of $\pm 0.1\%$ amu^{-1} (2σ). Pb concentrations were measured by isotope dilution TIMS using a separate ≈ 10 -mL aliquot and a ^{206}Pb spike (99.997% pure). The latter was calibrated against the NIST SRM 981 metal standard using a series of spike-standard mixtures. pH measure-

ments were obtained with a Fisher Accumet portable meter using a one-point standardization with automatic temperature compensation technique on a ≈ 30 -mL aliquot of meltwater. pH values measured for filtered and nonfiltered aliquots of the same sample yielded results within the relative accuracy of the instrument (± 0.01 unit). Samples from the N-S transect were acidified to pH 2 with suprapure HCl before storage, thus pH values are not available (Table 2).

Trace element data were determined at the CNRS Centre de Recherches Pétrographiques et Géo-chimiques (Nancy) by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Instrumental parameters were adjusted such that the signals from oxides and doubly charged ions were $\leq 3\%$ and $\leq 2\%$, respectively. Reference solutions were prepared using ultrapure reagents and certified NTRM' reference standards. Only external calibration was used and correction for instrumental drift was not required. The blank signal (Table 2) subtracted from that of the snow samples was determined using acidified nanopure water that was filtered and stored in an identical manner as for the samples. The blank correction was negligible except for seven samples (97-QC-8, 9, 14, 19, 20, 21, and Lac Laporte) with relatively low abundances for certain trace elements (Pb, Cd, Cu, and Rb). Four of these samples were analyzed in duplicate and yielded reproducible results. The overall uncertainties, based on replicate analyses of mul-

Table 1. Locations, pH values and elemental concentrations (ppb) for 1997 snow samples.

Sample	Latitude (°N)	Longitude (°W)	pH	Pb	Zn	Cd	Cu	Rb	Sr	Al	Ba	Mg	Mn
Montréal-Québec City													
97-QC-1	45°29'41"	73°02'29"	4.64	1.17	27.7	1.94	3.79	0.120	1.06	6.9	1.17	36.9	2.28
97-QC-2	45°21'11"	73°09'12"	5.08	0.23	23.8	0.024	0.36	0.043	0.73	2.3	0.35	14.8	0.92
97-QC-2 NF				0.95	169	0.115	0.92	0.086	2.72	10.2	1.16	51.1	3.84
97-QC-3	46°40'27"	73°54'07"	4.18	0.33	4.7	0.057	0.30	0.060	0.33	2.7	0.62	7.6	1.24
97-QC-3 NF				0.24	17.6	0.084	0.94	0.170	0.46	3.4	0.79	11.7	1.51
97-QC-4			4.24	0.53	9.0	0.043	0.84	0.088	0.44	7.3	0.60	13.0	1.59
97-QC-4 NF				0.59	11.7	0.049	1.01	0.120	0.54	9.6	0.82	16.1	1.93
97-QC-5A	46°12'35"	72°23'33"	4.58	0.44	70.5	0.029	0.45	0.047	0.49	3.0	0.42	16.3	1.86
97-QC-5A dup.				0.45	76.0	0.029	0.44	0.043	0.48	2.9	0.41	16.1	1.86
97-QC-6	45°31'29"	70°49'58"	4.63	0.12	23.2	0.011	0.24	0.084	0.16	1.8	0.20	5.9	2.00
97-QC-6 dup.				0.13	25.9	0.014	0.26	0.085	0.17	1.7	0.20	5.9	2.02
97-QC-7	46°07'36"	70°51'13"	4.18	0.20	16.4	0.010	0.20	0.029	0.11	1.9	0.18	9.6	0.68
97-QC-8	46°19'49"	70°33'00"	4.59	0.11	4.5	0.006	0.06	0.029	0.07	0.9	0.16	3.5	2.28
97-QC-8 dup.				0.10	3.8	0.007	0.06	0.031	0.07	0.9	0.17	3.5	2.28
97-QC-13	47°10'17"	70°52'30"	4.30	0.32	297	0.019	1.95	0.054	0.64	6.5	0.59	14.7	1.71
97-QC-20	47°11'42"	72°58'57"	4.68	0.08	58.7	0.002	0.08	0.009	0.12	1.9	0.18	3.4	0.61
97-QC-21	45°55'55"	71°56'19"	4.47	0.06	8.2	0.004	0.06	0.010	0.07	1.0	0.17	3.7	1.57
97-QC-21 dup.				0.07	8.2	0.004	0.06	0.020	0.07	1.0	0.18	3.6	1.57
97-QC-22	45°56'10"	75°49'43"	4.66	0.16	230	0.019	0.15	0.100	0.60	2.3	0.54	11.8	1.20
97-QC-23	45°56'56"	75°06'12"	4.55	0.21	25.0	0.012	0.14	0.140	0.49	2.9	0.62	16.2	3.13
North Shore-Gaspé regions													
97-QC-9	47°29'00"	69°23'15"	4.68	0.06	45.4	0.004	0.10	0.044	0.13	1.1	0.16	5.0	0.56
97-QC-9 dup.				0.07	43.3	0.006	0.12	0.045	0.13	1.2	0.17	5.0	0.57
97-QC-11	48°22'07"	67°17'36"	4.43	0.15	77.8	0.013	0.18	0.036	0.37	2.0	0.54	21.4	3.50
97-QC-11 dup.				0.15	74.2	0.012	0.18	0.040	0.38	2.1	0.55	21.3	3.55
97-QC-12	48°56'58"	66°07'34"	4.40	0.26	162	0.014	0.36	0.032	0.41	2.7	0.13	37.2	0.64
97-QC-14	47°45'10"	70°00'34"	4.80	0.04	24.7	0.007	0.04	0.060	0.18	0.7	0.34	9.8	7.28
97-QC-14 dup.				0.04	24.7	0.007	0.04	0.060	0.18	0.8	0.39	9.9	7.27
97-QC-15	48°20'43"	69°27'17"	4.72	0.12	37.1	0.007	0.05	0.023	0.18	1.3	0.16	15.3	0.67
97-QC-16	49°11'20"	69°26'30"	4.39	0.35	208	0.021	0.92	0.040	0.42	3.9	0.28	12.1	1.09
97-QC-17	49°42'54"	68°43'16"	4.51	0.19	110	0.006	0.14	0.022	0.21	3.0	0.13	7.4	0.53
97-QC-18	49°28'30"	68°32'37"	4.64	0.36	181	0.016	0.28	0.070	0.32	3.6	0.21	11.2	0.82
97-QC-19	48°38'11"	71°11'36"	4.64	0.09	48.7	0.004	0.05	0.010	0.10	1.5	0.12	2.8	0.38

NF = analysis from nonfiltered fraction. dup. = duplicate analysis. The relative uncertainties (of the quoted value) are the following: Pb: <2% for 1–5 ppb, <5% for 0.1–1 ppb; Zn: <3% for 1–100 ppb, <2% for >100 ppb; Cd: <10% for 0.01–0.1 ppb; Cu: <5% for 0.1–1 ppb; Mg: <4% for 1–50 ppb; Mn: <10% for 0.1–1 ppb, <2% for 1–10 ppb.

elemental standard solutions ranging in concentrations from 0.1 to 100 ppb are listed in Table 1. Average values measured for the SLRS-4 water standard are in agreement with the accepted concentrations (Table 2). The average measured value of Zn (64.5 ± 4.2 ppb) for the NIST 1643d water standard, which was analysed because of its similar content of Zn compared with the snow samples, is within the analytical uncertainty (2σ) of its certified value (72.5 ± 7.9 ppb; Table 2). Moreover, Table 4 lists the Pb concentrations determined by isotope dilution TIMS. Comparison between the Pb concentrations determined by ICP-MS (Tables 1 and 2) and TIMS exhibits an excellent correlation for all samples.

3. RESULTS

3.1. Elemental Concentrations

The pH values for samples within the St. Lawrence Valley vary from 4.2 to 5.1 (Table 1), a range that is typical for wet precipitations recorded in the U.S., east of the midwest region (Office of Technology Assessment, 1984), and the province of Quebec (Boulet and Jacques, 1995; Poissant et al., 1997). This range in pH values for the snow samples is also consistent with the episodic acidification of surface waters in northern Europe (Henriksen and Wright, 1977) and North America (Galloway et al., 1983) during the period of spring melt.

Tables 1 and 2 list the elemental concentrations determined by ICP-MS for the snow samples. These have been divided into three groups on the basis of their geographic locations and year of collection: (1) samples proximal to the St. Lawrence Valley within the Montréal-Québec City corridor; (2) samples from the North Shore-Gaspé regions located at the northeastern extremity of the St. Lawrence Valley; and (3) samples from the N-S transect. The sampling sites within these three regions cover areas of approximately 250,000 km², 150,000 km², and 300,000 km², respectively.

Figure 2 illustrates the geographic variation in the concentrations of Pb, Cu, Zn, and Mn. Lead concentrations of the snow samples range from 0.05 to 2.5 ppb (Tables 1 and 2) and are of the same magnitude as those measured in rain and snow for various sites within North America (e.g., Barrie et al., 1987; Poissant et al., 1994, 1997). These Pb concentrations are, on average, 5 to 10 times higher than those determined in Greenland snow during the period of 1960 to 1988 (e.g., Rosman et al., 1994; Savarino et al., 1994). The snow samples bearing >0.5 ppb of Pb all occur either within the Montréal-Québec City corridor, proximal to Noranda, or adjacent to the shore of James Bay (Fig. 2). In a simple scenario, the highest Pb, Cu,

Table 2. Locations and elemental concentrations (ppb) for 1994 snow samples, and measured values for reference water standards.

Sample	Latitude (°N)	Longitude (°W)	Pb	Zn	Cd	Cu	Rb	Sr	Al	Ba	Mg	Mn
North-South transect												
Lac Laporte	47°12'12"	76°44'19"	0.11	2.1	0.018	1.17	0.026	0.13	1.7	0.15	7.8	0.92
Lamothe	48°24'17"	78°00'10"	2.44	5.4	0.092	4.01	0.043	0.42	6.9	0.71	17.3	2.65
Lamothe dup.			2.54	5.0	0.097	3.89	0.057	0.42	6.6	0.74	16.5	2.56
Matagami	49°52'56"	77°15'07"	0.45	2.2	0.034	0.64	0.025	0.21	2.0	0.29	8.9	1.18
Evans	50°35'40"	77°34'00"	0.09	3.7	0.049	0.54	0.036	0.46	2.2	4.54	18.4	1.09
Evans dup.			0.08	3.6	0.046	0.53	0.036	0.46	2.1	4.53	18.3	1.09
Opinaca	52°39'47"	77°23'24"	0.08	3.6	0.048	0.53	0.034	0.46	2.1	4.53	18.1	1.09
Opinaca dup.			1.49	3.3	0.072	0.84	0.042	0.63	4.1	1.47	69	1.19
Chisasibi	53°48'42"	78°55'27"	1.52	3.1	0.068	0.85	0.054	0.61	4.0	1.48	65	1.14
Koury	55°08'02"	76°44'06"	0.77	2.9	0.047	0.71	0.214	2.16	9.1	1.12	138	2.50
SLRS-4			0.52	2.0	0.045	0.39	0.037	0.91	2.1	0.32	119	0.62
standard			0.091 ± 0.01	1.57 ± 0.17	0.011 ± 0.001	1.76 ± 0.02		28.7 ± 1.1	52.9 ± 1	13.3 ± 0.5		3.41 ± 0.06
NIST 1643d			0.086 ± 0.007	0.9 ± 0.1	0.012 ± 0.002	1.81 ± 0.08		26.3 ± 3.2	54 ± 4	12.2 ± 0.6		3.37 ± 0.18
standard				64.5 ± 4.2								
Blank ^b			0.01	72.5 ± 7.9 ^a	0.001	0.01	0.001	0.008	0.09	0.006	0.27	0.01
				0.04								

dup. = duplicate analysis; trip. = triplicate analysis. **Standards:** Measured values are in boldface and accepted values beneath. Associated errors (2σ level) with the measured values are based on repeated analyses ($n = 7$). ^a Certified value for NIST 1643d water standard. ^b Blank concentration determinations were obtained from an aliquot of nanopure water acidified to pH ~ 4.3, filtered at 0.45 μm , and subsequent to storage (at $T \sim 4^\circ\text{C}$) in a cleaned polyethylene bottle for a period of several months. See caption of Table 1 for analytical uncertainties of concentration determinations.

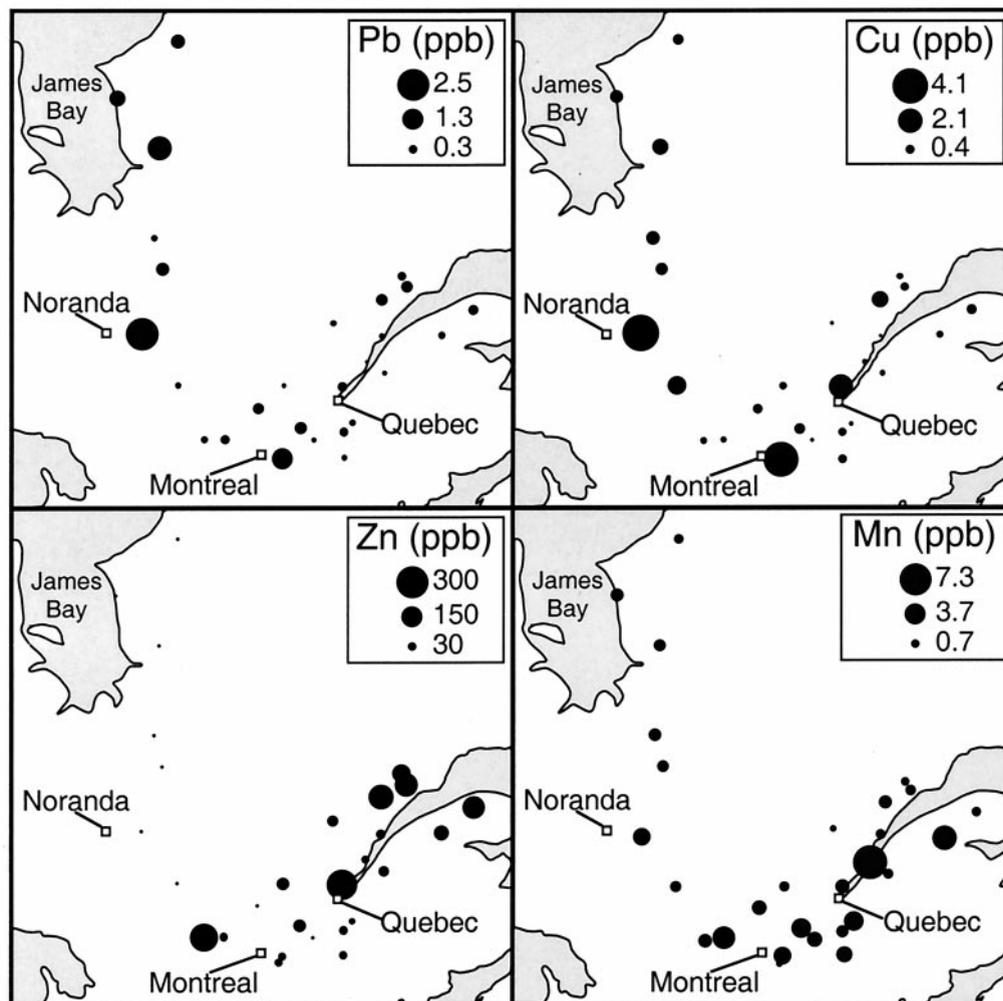


Fig. 2. Thematic maps illustrating the geographic variation in the abundances of Pb, Cu, Zn, and Mn for sample locations shown in Figure 1. Symbol size follows a square-root scale.

and Mn concentrations within the Montréal–Québec City corridor and proximal to Noranda may readily be attributed to inputs from local pollution sources such as urban activity associated with Montréal and Québec City and the smelting operations at Noranda, respectively (Fig. 2). The snow sample retrieved at the Lamothe site, the most proximal to the Noranda smelting operations, indeed contains the highest levels of Cd, Cu, and Zn compared to the remaining samples along the N–S transect (Table 2). However, there is no such simple explanation for samples from the James Bay area, a relatively uninhabited region with no significant industrial infrastructure.

Figure 3 shows the relation between the Pb content and levels of Cd, Cu, Mn, Zn, Al, and Sr for the snow samples. There are three important features to note from Figure 3. First, the abundances of Cd and Cu are roughly correlated with the Pb content (Fig. 3a, b), whereas those for Mn and Zn are not (Fig. 3c, d). Second, snow from the 1994 N–S transect clearly possesses the highest average content of Pb and Cd (Table 2; Fig. 3a). Last, a large proportion of the samples within the Montréal–Québec City corridor and the Gaspé–North Shore region, with Pb contents < 0.5 ppb, have Zn abundances two to

six times higher than the remaining samples (Fig. 3d). In addition, the variation in the contents of Al and Sr, two elements derived primarily from non-anthropogenic sources vs. the abundances of Pb (Fig. 3e,f) show a somewhat positive correlation between Al and Pb, in particular for samples with < 0.5 ppb Pb. In contrast, no clear relationship is apparent between the values for Sr and Pb (Fig. 3f). The positive correlation shown in Figure 3e suggests that the abundances of heavy metals in the atmosphere are related to sources of urban dust.

In the case of snow samples 97-QC-2, -3, and -4, aliquots of the bulk (nonfiltered) and filtered meltwater were analysed separately for trace element concentrations (Table 1). The trace element abundances are higher in the bulk fractions compared to the filtered aliquots, although this is only marginal in sample 97-QC-4, indicating that the predominant trace element carrier is within the “solid” (particle emissions) aerosol phase. A similar feature was noted from separate analyses of meltwaters and filter residues for samples of snowpack from northwestern Russia and Scandinavia (1992 winter), as the former contained only between 10 to 80% of the total trace element concentra-

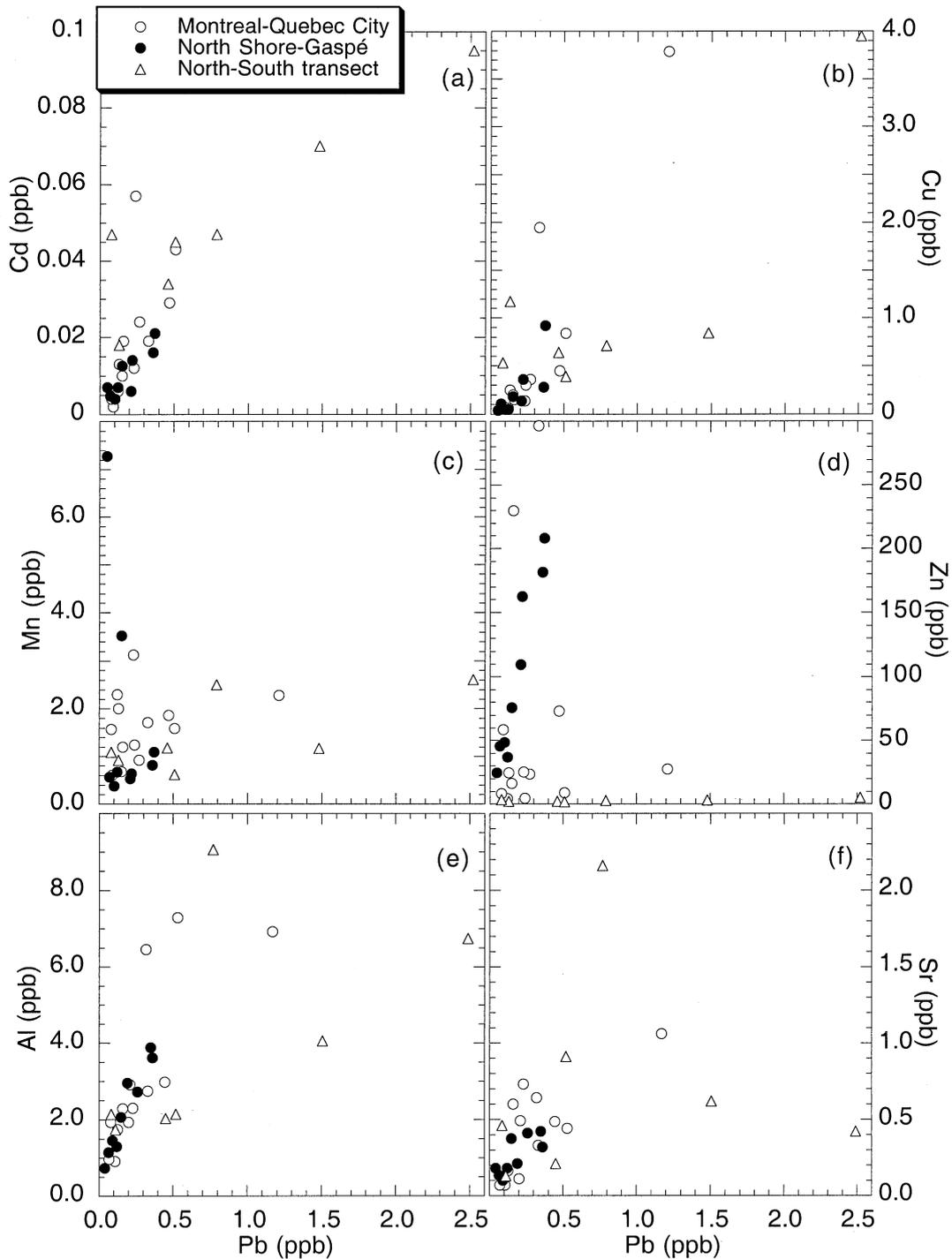


Fig. 3. Variations of concentrations for different elements vs. abundances of Pb (a to f) for all the snow samples. Note that in (a) sample 97-QC-1 is not shown (Cd = 1.94 ppb; Table 1) for scaling consideration.

tions (Riemann et al., 1996). The higher trace element concentrations in the nonfiltered meltwater fractions are most probably the result of increased particulate input, in particular for sample 97-QC-2, and attributable to local sources of anthropogenic dust (≈ 50 km away from Montreal). Moreover, estimates of dry vs. wet deposition totals for a variety of trace metals in the Great Lakes region (during 1993 and 1994) indicate that for a

majority of the metals investigated (except Se), dry deposition is dominant by several orders of magnitude, and related to the presence of proximal urban and industrial facilities (Sweet et al., 1998). However, it must be noted that with the single exception of the Pb concentrations for sample 97-QC-3, all elemental abundance ratios are essentially similar for both the bulk and filtered aliquots.

Table 3. Average and median values for enrichment factors.^a

Region	Pb	Cd	Zn	Cu	Mn	Rb	Sr	Ba	Mg
Montréal–Québec City									
Average	370 (146)	23,100 (59,800)	22,900 (30,500)	470 (428)	102 (87)	17 (10)	30 (18)	20 (8)	24 (9)
Median	292	5,400	9,700	350	60	13	23	20	23
North Shore–Gaspé									
Average	306 (68)	4,100 (1,670)	47,000 (11,300)	287 (193)	207 (404)	17 (16)	30 (12)	22 (21)	43 (29)
Median	290	4,200	42,000	250	40	13	26	12	26
North–south transect									
Average	800 (518)	12,530 (4,552)	1,093 (445)	1,051 (789)	54 (16)	26 (38)	42 (27)	63 (98)	92 (104)
Median	890	11,600	1,000	980	52	11	35	21	92

^aRelative to upper crustal values taken from Taylor and McLennan (1995). Values in brackets represent one standard deviation.

To evaluate the relative contribution from natural (i.e., soil dust) vs. anthropogenic sources in the atmosphere, elemental abundances of metals are usually expressed in the form of enrichment factors (EF). The latter is defined as the concentration ratio of a given element to that of Al (or any other element thought to be derived exclusively from a crustal source, such as Si) normalized to the same concentration ratio characteristic of the upper continental crust (e.g., Taylor and McLennan, 1995). For example, the enrichment factor for Pb is thus: $(EF)_{Pb} = [Pb/Al]_{sample}/[Pb/Al]_{crust}$. However, given the large natural variations in the composition of crustal materials exposed to surface erosion and the diversity of biogeochemical processes affecting soil development at a global scale, enrichment factors within ± 10 times the mean crustal abundances (i.e., EF between 0.1 to 10) do not likely identify the presence of materials other than aerosols of a crustal origin (Duce et al., 1976). Conversely, any $(EF)_{metal} \geq 10$ strongly suggests contributions from other sources, whether they be related to biological functions on land or ocean, physical transfer of water droplets to the atmosphere, or human activities.

Table 3 lists the average and median values of the (EF) for all the trace elements analysed in this study. The high $(EF)_{heavy\ metal}$ values (≥ 100), in particular for Cd (up to $\approx 23,000$) and Zn (up to $\approx 45,000$), clearly indicate that their atmospheric abundances must be from non-natural sources. In contrast, the median values of (EF) for Ba (12 to 20), Mg (23 to 60), Rb (10 to 13), and Sr (23 to 29) in snow are much lower, suggesting that these elements were derived primarily from non-anthropogenic sources. In addition, the $(EF)_{heavy\ metal}$ values listed in Table 3 overlap with those reported for precipitations collected at the meteorological stations of Montréal (Poissant et al., 1994) and Villeroy (Poissant et al., 1997), located south of Québec City.

3.2. Pb Isotope Results

The Pb isotope results for all snow samples are listed in Table 4. Duplicate isotopic analyses were carried out on seven filtered aliquots of meltwater; only one duplicate pair (97-QC-6) yielded results that are well outside the expected analytical uncertainty (Table 4). In addition, snow cores 97-QC-3 (C1) and (C2) were taken from the same site, but ≈ 40 m apart from one another, then melted, filtered, stored, and analyzed separately. These yield similar Pb isotopic ratios (Table 4),

which supports the notion that the snowpack is relatively homogeneous at a local scale.

Figure 4a shows that the $^{206}Pb/^{207}Pb$ ratios for all analyzed snow samples correlate with their geographic position: (1) samples retrieved from the Montréal–Québec City corridor have the highest $^{206}Pb/^{207}Pb$ values, in the range of 1.180 to 1.190; (2) this ratio is always < 1.180 in the North Shore–Gaspé region, decreasing to values as low as ≈ 1.160 ; and (3) the $^{206}Pb/^{207}Pb$ ratios for the samples along the N–S transect decrease systematically northwards of Noranda (from 1.179 to 1.148) but are > 1.180 for the two sample sites adjacent to the James Bay shoreline (Fig. 4a). Also shown in italics on Fig. 4a are the $^{206}Pb/^{207}Pb$ ratios of lichens collected at the same time of year, proximal to the snow sampling sites of the N–S transect (Carignan and Gariépy, 1995). The lichens are characterized by much lower $^{206}Pb/^{207}Pb$ values compared to those of snowpack collected in their vicinity. Carignan and Gariépy (1995) attributed the unradiogenic character of the Pb isotope signatures in these lichens ($^{206}Pb/^{207}Pb = 1.04$ to 1.14) to atmospheric emissions of Pb from the Cu-smelting activities at Noranda.

Figure 5 compares the Pb isotopic compositions of the snow samples collected in the St. Lawrence Valley during 1997 to those of lichens retrieved from the Montréal–Québec City corridor and the northeastern U.S. during the summers of 1994 and 1995 (Carignan and Gariépy, 1995, and Carignan, Simonetti and Gariépy, unpublished data). Also shown in Figure 5 is the linear array that would result from a simple two-component mixture of typical Canadian and U.S. anthropogenic emissions (e.g., Carignan and Gariépy, 1995). The lichen and the snowpack samples from within the Montréal–Québec City corridor define a similar range of $^{206}Pb/^{207}Pb$ values but the snow samples have, on average, lower $^{208}Pb/^{204}Pb$ (Fig. 5a) and higher $^{206}Pb/^{207}Pb$ (Fig. 5b) ratios. Compared to the snow samples from the Montréal–Québec City corridor, those from the N–S transect and the Gaspé–North Shore region exhibit a much wider range of $^{208}Pb/^{204}Pb$ values and in general, plot outside the two-component Canada–U.S. Pb “mixing array” (Fig. 5).

Lead isotope data (Figs. 4a and 5) and the $(EF)_{heavy\ metal}$ (Table 3) recorded in snowpack from the province of Québec clearly show that Cu, Zn, Pb, and Cd (Fig. 2) are not evenly distributed over the areas of study, and that their atmospheric emissions are controlled by anthropogenic sources. On the

Table 4. Pb and Sr isotope ratios and Pb concentrations for snow samples.

Sample	Pb (ppb)	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{87}\text{Sr}/^{86}\text{Sr}$
Montréal–Québec City						
97-QC-1	1.21	18.56	15.64	38.15	1.187	0.70897 ± 1
97-QC-1 dup.		18.55	15.62	38.08	1.187	
97-QC-2	0.27	18.57	15.60	38.08	1.190	0.70905 ± 3
97-QC-2 dup.		18.53	15.60	38.14	1.188	
97-QC-3 (C1)	0.24	18.50	15.63	38.22	1.183	0.71002 ± 2
97-QC-3 (C2)		18.34	15.57	37.96	1.178	
97-QC-4	0.51	18.63	15.64	38.21	1.190	9.70917 ± 5
97-QC-5A	0.47	18.37	15.60	38.07	1.177	0.70985 ± 1
97-QC-5A dup.		18.31	15.52	37.86	1.179	
97-QC-6	0.13	18.29	15.56	37.89	1.176	0.70956 ± 2
97-QC-6 dup.		18.52	15.57	38.04	1.189	
97-QC-7	0.15	18.50	15.64	38.18	1.183	0.71009 ± 2
97-QC-7 dup.		18.49	15.55	37.95	1.188	
97-QC-8	0.12	18.43	15.62	38.13	1.180	0.70998 ± 2
97-QC-8 dup.		18.41	15.60	38.14	1.181	
97-QC-13	0.33	18.46	15.56	38.06	1.187	0.70752 ± 3
97-QC-20	0.09	18.42	15.56	38.00	1.183	0.70791 ± 3
97-QC-21	0.08	18.32	15.45	37.60	1.188	0.71023 ± 2
97-QC-22	0.16	18.36	15.55	37.97	1.181	0.70791 ± 2
97-QC-23	0.23	18.38	15.57	37.99	1.180	0.71043 ± 9
North Shore–Gaspé regions						
97-QC-9	0.07	18.36	15.59	38.09	1.176	0.70806 ± 1
97-QC-9 dup.		18.37	15.61	38.12	1.177	
97-QC-11	0.16	18.09	15.49	37.70	1.167	
97-QC-12	0.22	17.81	15.31	37.25	1.161	0.70817 ± 2
97-QC-14	0.05	18.08	15.46	37.53	1.170	0.71045 ± 1
97-QC-15	0.12	17.99	15.46	37.54	1.163	0.70883 ± 2
97-QC-16	0.37	17.84	15.34	37.19	1.162	0.70915 ± 2
97-QC-17	0.21	18.06	15.48	37.41	1.168	0.70751 ± 2
97-QC-18	0.36	18.15	15.41	37.49	1.176	0.70722 ± 2
97-QC-19	0.10	18.11	15.36	37.38	1.178	0.70768 ± 2
North–south transect						
Laporte	0.13	18.32	15.54	37.87	1.179	0.71220 ± 3
Lamothe	2.52	18.09	15.43	37.55	1.172	0.71286 ± 3
Matagami	0.46	17.96	15.47	37.56	1.161	0.71469 ± 6
Evans	0.08	17.78	15.38	37.18	1.156	0.71162 ± 3
Opinaca	1.48	17.81	15.51	37.56	1.148	0.71045 ± 2
Chisasibi	0.79	18.55	15.56	37.98	1.193	
Koury	0.51	18.42	15.56	37.98	1.184	0.71028 ± 2

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. Pb concentrations determined by isotope dilution and associated uncertainty <1%. Sr isotope analyses measured in dynamic, multicollection mode. Sr isotope ratios normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. Repeated analyses of the NBS 987 Sr standard yielded an average value of 0.710245 ± 0.000018 (2σ , $n = 6$). Precision for individual Sr isotope measurements is quoted at the 2σ level.

basis of the Pb isotope systematics for the snow samples (Fig. 5), in particular those from the North Shore–Gaspé region, these require the involvement of at least three anthropogenic end-members.

3.3. Sr Isotope Results

The $^{87}\text{Sr}/^{86}\text{Sr}$ values of the snow samples are listed in Table 4 and shown on Figure 4b. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios also correlate, in general, with their geographic position: (1) samples within the Montréal–Québec City corridor vary between ≈ 0.7090 and ≈ 0.7100 ; (2) those from the North Shore–Gaspé region have values ≤ 0.7080 ; and (3) samples from the N–S transect contain the highest Sr isotope values, all > 0.7100 .

Figure 6 plots the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios versus 1/Sr abundances to evaluate the relative contributions of sea salt and soil-derived aerosols. Linear trends on such a diagram indicate simple

mixing between two end-members with different isotopic compositions. On Figure 6, the snow samples define three broad trends that correlate with their geographic position. Snow samples from the N–S transect exhibit a positive correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ values and 1/Sr values, whereas most of the samples from the North Shore–Gaspé region define a negatively sloped array (Fig. 6). In contrast, samples from the Montréal–Québec City corridor exhibit little variation in their Sr isotopic composition as a function of Sr abundances. The samples define broad arrays rather than plotting along tightly constrained linear trends indicating that simple mixing of two singular aerosols sources, in space and time, is an oversimplification. Nevertheless, the isotopic compositions of snow samples with the highest Sr concentrations (lowest 1/Sr values) converge toward $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.709 to 0.710, values that are on average only slightly more radiogenic than that of

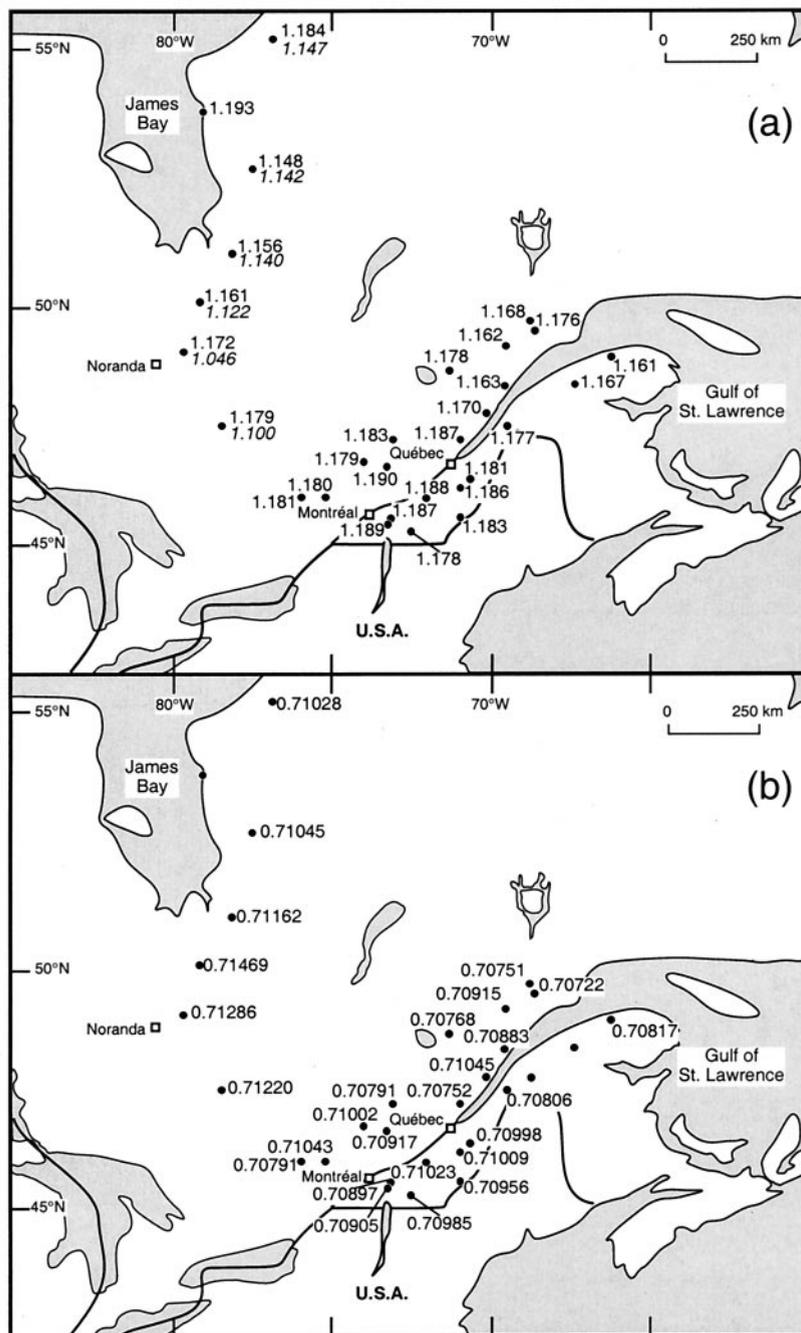


Fig. 4. (a) Map illustrating the geographic distribution of $^{206}\text{Pb}/^{207}\text{Pb}$ values for snow samples along the two transects. For the N–S transect, italicized Pb isotope values are for lichens (from Carignan and Gariépy, 1995) obtained from proximal areas within the individual snow sampling sites during the same period of time. (b) Map illustrating the geographic distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ values for snow samples along the two transects.

present-day seawater. The trends shown in Figure 6 may suggest, therefore, that sea salt aerosols are, for the Sr-rich samples, the predominant source of atmospheric Sr in the three geographic areas. The other end-members, however, must be different for samples from the North Shore–Gaspé region and those from the N–S transect. The radiogenic Sr isotope values in snow from the latter transect may reflect soil dust inputs, as

these are typically characterized by $^{87}\text{Sr}/^{86}\text{Sr} > 0.720$. It is also noteworthy that the two samples adjacent to James Bay contain the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ values (≈ 0.710) and highest abundances of Sr (0.6 to 0.9 ppb; Table 2) compared to the remaining samples along the transect, features suggesting a more effective contribution of sea salt aerosols in the littoral environment of Hudson Bay. The unradiogenic character ($^{87}\text{Sr}/^{86}\text{Sr} < 0.709$) of most snow

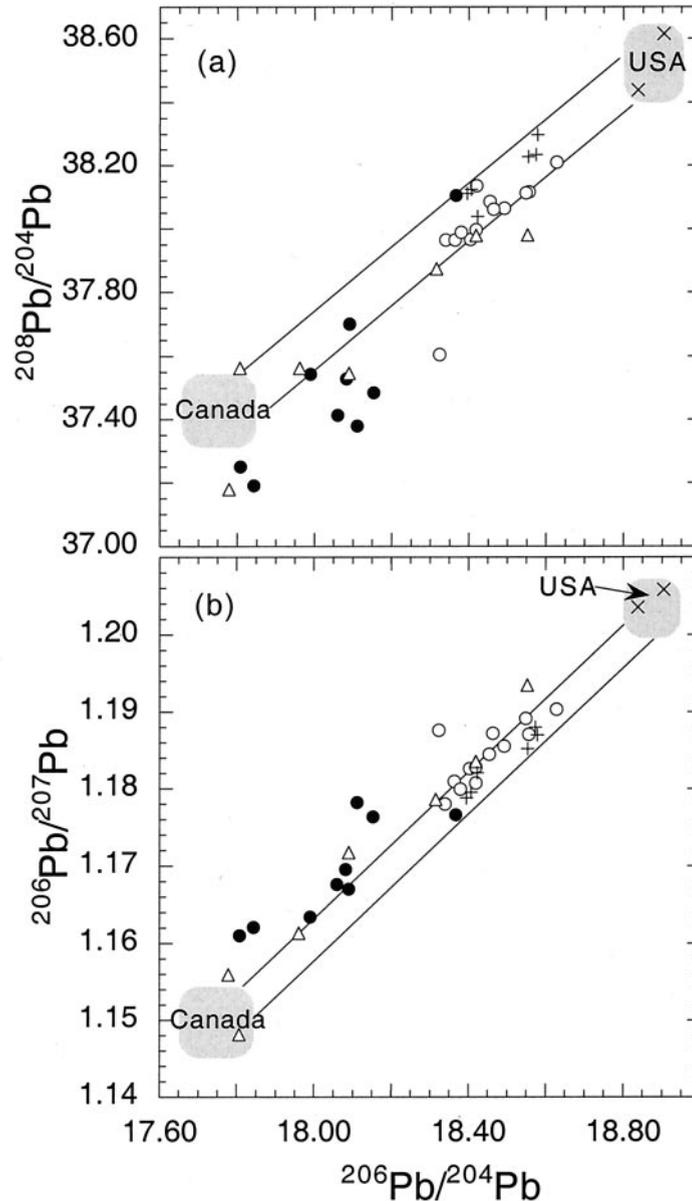


Fig. 5. (a) $^{208}\text{Pb}/^{204}\text{Pb}$ and (b) $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ showing the data for all the snow samples (Table 3). + = isotopic data for lichens from within the St. Lawrence Valley (Carignan and Gariépy, 1995); X = isotopic data for lichens from Maryland and New Jersey (Carignan, Simonetti, and Gariépy, in prep.), which plot within the field (shaded gray) defined for U.S. anthropogenic emissions (Véron et al., 1992, 1993; Rosman et al., 1994). Field for Canadian anthropogenic emissions (shaded gray) taken from Carignan and Gariépy (1995). Analytical uncertainties are within the size of the symbol. Other symbols as in Figure 3.

samples from the North Shore–Gaspé region remains somewhat problematic. It may reflect the presence of soil or vegetation particles that developed on Paleozoic carbonate rocks, a lithology that is relatively abundant in the northern Appalachians.

4. DISCUSSION

4.1. Sources of Atmospheric Pollution

The elemental and isotopic data for the snow samples (Figs. 2 to 6) are not uniform and correlate with their geographic

position. In contrast to the Sr isotopic data, the Pb isotope results for the snow samples do not define single mixing arrays as a function of their geographic location. Much of the Pb isotopic data from the N–S transect and the North Shore–Gaspé region do not plot along the simple two-component mixture of Canadian and U.S. atmospheric Pb, as defined by lichen data, and exhibit a much wider compositional range than lichens from the St. Lawrence Valley (Fig. 5). Thus, the variation in Pb isotope ratios for the snow samples cannot be attributed solely to the mixing of these two anthropogenic end-members. Similarly, the

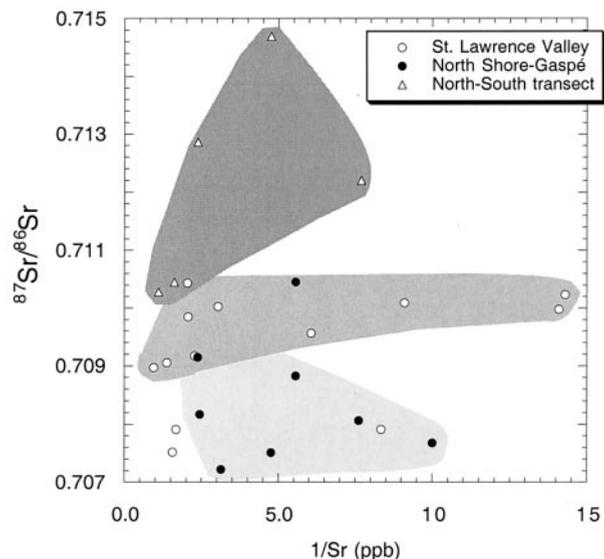


Fig. 6. Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $1/\text{Sr}$ (ppb) for data from all the snow samples.

progressive decrease in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios from Montréal to the North Shore–Gaspé region cannot be attributed solely to a decline of one anthropogenic source with respect to the other.

To account for the Pb isotope compositions for snow samples located north of 47°N , the involvement of an additional anthropogenic source is required that is characterized by $^{206}\text{Pb}/^{207}\text{Pb}$ ratios ≤ 1.150 ; the latter being similar to the value for Canadian anthropogenic emissions (Sturges and Barrie, 1987). On the basis of the $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios, however, the Canadian anthropogenic component does not contain the appropriate Pb isotope compositions to account for the results for snow samples collected north $\approx 47^\circ\text{N}$ (Fig. 5). Figure 7 shows that the Pb isotope ratios for the snow samples collected in 1997 correlate quite well with their latitudinal position, with those situated north of 47° containing $^{206}\text{Pb}/^{207}\text{Pb}$ ratios always < 1.180 . One possible explanation for this latitudinal control of Pb isotope ratios may be related to the migration of the polar front in the northern hemisphere, which is typically situated between 40 and 50°N in the winter season and at 60 to 70°N during the summer (Raatz, 1991). The polar front plays an important role in defining atmospheric transport (isentropic flow) of atmospheric pollutants (e.g., Arctic: Carlson, 1981; Rahn, 1981; Raatz, 1985), as it is a zone characterized by a sharp horizontal temperature gradient that causes strong uplift of moist air parcels originating south of the front (Raatz, 1991). Consequently, the polar front is associated with intense weather activity, and as such moist and warm air masses originating from midlatitudes (south of the front) would lose most of their pollutants due to scavenging effects (Raatz, 1991), a feature that is consistent with the higher average seasonal snowfall accumulation for the more northern regions covered in this study (e.g., North Shore and Gaspé region ≈ 350 to 400 cm) compared to areas further south (e.g., Montréal ≈ 250 cm; Proulx et al., 1987). If the distribution of the Pb isotope ratios are indeed related to this meteorological phenomenon, latitude 47°N represents the mean

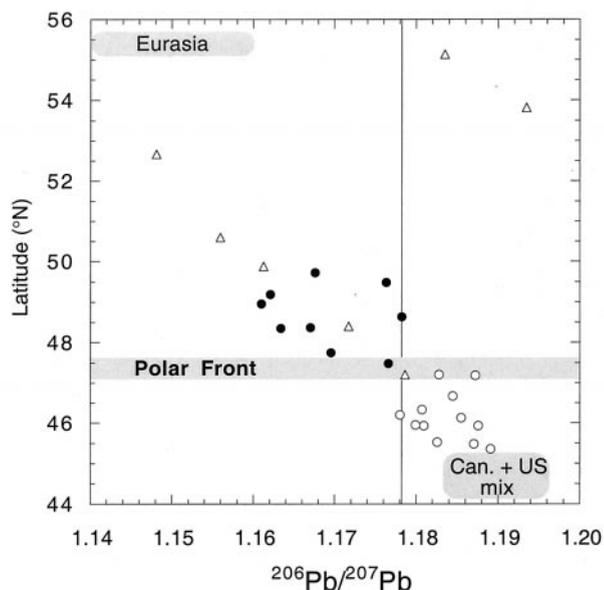


Fig. 7. Diagram showing the variation in $^{206}\text{Pb}/^{207}\text{Pb}$ values vs. latitude. Symbols as in Figure 3. Field labeled “Can. + US mix” represents the range in Pb isotopic compositions of snow (this study) and lichens (Carignan and Gariépy, 1995) along the St. Lawrence Valley, which mostly contain $^{206}\text{Pb}/^{207}\text{Pb}$ ratios between 1.180 and 1.190. These have been attributed to mixing between Canadian and U.S. anthropogenic Pb end members. See text for full details.

position of the polar front over northeastern Quebec during the 1997 winter season.

It is possible that anthropogenic pollution in the northernmost snow samples originated from Eurasia and was transported over the Arctic during the winter season (Iversen, 1984; Raatz and Shaw, 1984). From December to April, meteorological conditions favour the transport of polluted air masses into the Arctic from Eurasia and contributes, in part, to the formation of episodes of Arctic haze (Barrie and Hoff, 1985). Moreover, Barrie et al. (1992) provide strong evidence that only a small fraction (11 to 14%) of the total S, Pb, and Cd transported into the Arctic is actually deposited there, the remainder of which is transported out of the region by winds. However, accurate identification of the Eurasian anthropogenic end-members potentially present in the northerly snow samples is rendered difficult due to the lack of available, precise values for Pb isotope ratios in winter Arctic air masses other than $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ values. On the basis of the average $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (1.160 to 1.161) of aerosols collected in the mid-1980s at the stations of Alert and Mould Bay located in the Canadian High Arctic Islands, Sturges and Barrie (1989b) concluded that these are similar to the mean $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (1.158) for known Soviet nonferrous ore deposits. Similarly, $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of 1.154 were also recorded for aerosols collected at Spitsbergen (Norwegian Arctic) during periods of air flow from the U.S.S.R. Based solely on the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios recorded in the high Arctic, one cannot rule out the possibility that Eurasian pollution is a significant component in snow accumulated north of 47°N . In addition, the snow samples from the North Shore–Gaspé region also contain distinct $^{87}\text{Sr}/^{86}\text{Sr}$ values (in general < 0.7080) compared to the remaining snow samples, also in-

Table 5. Comparison of heavy metal deposition budgets in eastern North America ($\text{g km}^{-2} \text{yr}^{-1}$).

Region	Pb	Cd	Zn	Cu	Mn	Reference
This work: total deposition ^a						
Montréal–Québec City (1997)	1300	120	156,000	1580	10,000	
North Shore–Gaspé (1997)	800	40	418,000	780	3600	
North–south transect (1994)	2500	240	14,000	3400	5600	
Mean:	1500	130	196,000	1900	6400	
Great Lakes						
L. Superior (1993–1994)	1500	460	8800	3100	4200	1
L. Michigan (1993–1994)	1600	450	6000	1900	2800	1
L. Erie (1993–1994)	1800	490	17,000	4200	4500	1
Mean:	1600	500	10,600	3100	3800	
L. Michigan (1976)	42,000	—	8600	1400	3800	2
L. Erie (1975)	4200	—	30,000	2600	—	3
Other						
West. Pennsylvania (1975–1980)	10,000	170	4100	—	4800	4
NW Indiana (1975–1980)	60,000	1000	100,000	9000	200,000	5

^a Concentrations from filtered meltwater fractions were multiplied by a factor of 5 based on comparisons between results for filtered versus non-filtered aliquots (Table 1); References 1: Sweet et al. (1998); 2: Sievering et al. (1979); 3: Kuntz (1978); 4: Schell (1986); 5: Cole et al. (1990).

dicative of a different source of atmospheric Sr for this region. As well, these low Sr isotope ratios also exclude a predominant contribution from sea salts, despite their relative proximity to the Atlantic Ocean, suggesting that in these regions the prevailing air masses originate from the north during the winter months.

A potential contribution function analysis was used to study the source–receptor relationships for total gaseous mercury at two meteorological stations along the St. Lawrence River, one being St. Anicet (50 km SW of Montréal) and the other Mingan (in the North Shore region, 50°16'N and 64°14'W; Poissant, 1997). On the basis of the results obtained during the winter season from the Mingan station, Poissant (1997) concluded that a component of the gaseous mercury in this region of Quebec originates from Eurasian air masses providing additional support for the above interpretation.

4.2. Snow vs. Lichen

A comparison of Pb isotope ratios between snow and lichens (for the same site) from the north–south transect (Fig. 4a) indicate that the latter are significantly lower, and hence both are not recording the same time-integrated sources of atmospheric pollution. Carignan and Gariépy (1995) concluded that the unradiogenic Pb isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb} < 1.150$) for these lichens record significant input of atmospheric Pb resulting from smelting activities at Noranda. The reasons being that the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (1.046) for the lichen closest to Noranda is similar to the range (≈ 0.90 to ≈ 1.05) found in Cu sulfides from within the Archean greenstone belt (Delouie et al., 1989), and overlaps with the Pb isotope value reported for a sample of Noranda smelter dust (Sturges and Barrie, 1989a). The difference in Pb isotope ratios between lichens and snow samples from proximal sites along the N–S transect (Fig. 4b), therefore, may reflect that lichens record a time-integrated signal (over several years) of atmospheric conditions predominantly during the nonwinter months, a period during which prevailing wind directions may be different. Alternatively, this difference may indicate that epiphytic lichens record predominantly atmospheric constituents close to ground level (1 to 2 m high),

whereas nucleation of ice crystals and scavenging of aerosols by snow occur at higher altitudes (≈ 1 to 2 km). In contrast, the snow and lichen samples from the Montréal–Québec City corridor define a similar range in Pb isotopic compositions (Fig. 5), and hence confirm the lack of an important local source of anthropogenic Pb.

4.3. Depositional Fluxes

Several assumptions have been made in the estimation of the annual atmospheric deposition fluxes for the areas covered in this study (Table 5). First, median values were calculated using elemental abundances measured in the filtered aliquot for each of the three geographic regions, and these are assumed to be constant year-round. Subsequently, these were multiplied by a factor of 5, as this represents the largest difference between the abundances for nonfiltered and filtered meltwater aliquots, respectively (sample 97-QC-2; Table 1). Consequently, the estimated depositional fluxes for this study represent maximum values (Table 5). Last, for each region, average yearly precipitation totals were calculated from values recorded at individual meteorological stations ($n = 37$) covering the same geographic regions for the years 1992 and 1993 (Boulet and Jacques, 1995). The estimated fluxes are then compared to those reported from several previous investigations (Table 5).

Compared to the results from Sweet et al. (1998) for the Great Lakes region (1993–1994), the average depositional fluxes for Pb, Cd, and Cu estimated in this study are lower by $\approx 6\%$, $\approx 74\%$, and $\approx 39\%$, respectively. In contrast, the average depositional flux for Zn is larger by a factor of ≈ 20 and that for Mn is 68% higher (Table 5). The increase in the depositional budgets estimated for Mn can easily be attributed to the replacement of Pb additives in automotive fuel by Mn-bearing organic substitutes subsequent to the Clean Air legislations adopted in the U.S. and Canada in the late 1970s. The very high depositional values for Zn, in particular for snow samples from the Montréal–Québec City corridor and North Shore–Gaspé regions (Table 5, see also Fig. 2) are most intriguing. It is difficult to reconcile the discrepancy between the high concentrations of Zn compared to those for Cd, as these metals are

typically emitted in tandem to the atmosphere mainly from nonferrous pyrometallurgical production (e.g., Nriagu and Pacyna, 1988). Concentrations of Zn are also not correlated with Pb abundances, a decoupling that was also recorded in recent Greenland snow deposits (Savarino et al., 1994), where a large increase in Zn concentrations (5- to 10-fold) was accompanied by an actual decrease in Pb abundances. Savarino et al. (1994) attributed this feature to atmospheric emissions from smelting operations in the former Soviet Union. If the North Shore–Gaspé region is indeed under the influence of Eurasian atmospheric emissions, as suggested by the Pb isotope results, then this may partly explain the higher concentrations of Zn. Moreover, a major zinc refining industrial plant is located near Valleyfield, approximately 40 km south of Montréal, and right within the St. Lawrence Valley “meteorological corridor.” If it accounts for the higher than expected Zn depositional budgets for the Montréal–Québec City and North Shore–Gaspé regions, then the actual residence time of the Zn “chemical species” emitted to the atmosphere by this industry must be very short. Alternative explanations include, however, increases in the global anthropogenic emissions of Zn (compared to values from Nriagu and Pacyna, 1988, and as qualified by Skeaff and Dubreuil, 1997), and underestimations of atmospheric emissions from natural sources such as biological activity or biomass burning. The former possibility may be related to the increasingly active recycling industry (e.g., plastics, batteries), whereas the latter should be disregarded, in particular during the winter season, as this activity should yield correlations between Cd and Zn abundances.

5. CONCLUSIONS

Lead and Sr isotope ratios, combined with elemental abundances, for samples of snowpack from eastern Canada clearly indicate that this sampling technique is an efficient proxy to monitor atmospheric fallout over a relatively short time scale of 3 to 4 months. Enrichment factors for heavy metals (relative to upper crust) are extremely high (median values range from ≈ 300 to $\approx 42,000$) and indicative of an anthropogenic origin. The Pb isotope data indicate that winter precipitations occurring over eastern Canada are dominated by at least three anthropogenic sources; these originate from the U.S., Canada, and Eurasia, the latter being recorded in the 1997 samples collected north of latitude 47°N. Compared to the Pb isotope results for lichens from the same sample location, those for the snow either overlap (in the Montréal–Québec City corridor) or are significantly different (N–S transect). The latter discrepancy may be attributed to either (1) different time scales for the integration of the atmospheric signal (months for snow and years for lichens); (2) recording of the atmospheric signal at substantially different altitudes; or (3) the presence of an important local point source of atmospheric pollution.

The depositional budgets for Pb, Cd, and Cu are lower compared to those estimated for the Great Lakes region for data collected in 1993–1994 (Sweet et al., 1998). These trends are, therefore, consistent with the concomitant worldwide decrease (since the 1970s) of atmospheric heavy metal emissions. The higher depositional flux of Mn compared to those from the study of Sweet et al. (1998) are attributed to combustion of Mn-bearing fossil fuels by vehicles. The annual depositional

values for Zn are very high and their exact cause remains enigmatic. They could either reflect increased atmospheric industrial emissions from those that prevailed in the mid-1980s, a lower residence time in the atmosphere (compared to Pb, for example), or particular chemical speciation that affects the deposition of Zn from the lower troposphere.

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