Environ. Sci. Technol. **2006**, *40,* 741–747

Historical Perspective of Industrial Lead Emissions to the Atmosphere from a Canadian Smelter

CÉLINE GALLON,[†] ANDRÉ TESSIER,* AND CHARLES GOBEIL

Institut national de la recherche scientifique, Centre Eau, Terre et Environnement, Université du Québec, 490 rue de la Couronne, Québec, Québec G1K 9A9, Canada

RICHARD CARIGNAN

Département de sciences biologiques, Université de Montréal, C. P. 6128, Montréal, Québec H3C 3J7, Canada

Dated sediment cores from four remote Canadian Shield headwater lakes, where atmospheric deposition has been the only input of anthropogenic Pb, situated along a transect extending 300 km from a nonferrous metal smelter, were analyzed for both lead concentrations and isotopic composition; porewater samples collected at the same sites were analyzed for Pb and other geochemical variables. The depth distributions of stable Pb isotope ratios show the presence of several isotopically distinct Pb types since the preindustrial period. Lead from the smelter emissions had an isotopic signature (e.g., ^{206}Pb/^{207}Pb ~ 0.993) that was clearly distinct from those of Pb in aerosols collected at sites remote from point sources in Eastern Canada (e.g., ^{206}Pb/^{207}Pb usually ~1.15–1.20) and the United States (e.g., ^{206}Pb/^{207}Pb usually ~1.15–1.22), allowing the geographical area impacted by the smelter Pb emissions to be traced. On the basis of the sediment Pb isotopic composition, it is estimated that lead from the smelter accounts for 89%, 88%, and 5–34% of the total inventory of anthropogenic Pb deposited in the sediments of lakes located 10, 25, and 150 km from the smelter, respectively; but lead from this point source was not detected in sediments of a fourth lake that is 300 km from the smelter. We also estimate that the amount of smelter-derived Pb deposited within a distance of 150 km is equivalent to 5–10% of the amount released by leaded gasoline combustion in all of Canada. Sharp decreases in the recent Pb fluxes to lake sediments indicate that the measures taken to mitigate metal emissions from the smelter were effective.

Introduction

It is widely recognized that combustion of leaded gasoline and coal, nonferrous metal smelting, and cement production contributed to the major part of anthropogenic Pb emissions to the atmosphere (e.g., refs *1–5*). While Pb emissions to the atmosphere from leaded gasoline usage are relatively well assessed, those from industrial point sources, such as nonferrous metal smelters, are less well understood (*6*). Therefore, in this study, we measured Pb concentrations and stable lead isotope ratios in lake sediments to assess the relative importance of historical Pb emissions from the Horne smelter, Rouyn-Noranda, Québec, Canada, and to delineate their geographical zone of influence.

The Horne copper smelter was set up in 1927 and increased gradually its production since then. It currently has the capacity to process 800 000 tons year^{-1} of copper and precious metal-bearing materials, yielding 180 000 tons year^{-1} of anode copper and 600 000 tons year^{-1} of sulfuric acid (see www.noranda.com). The plant processed exclusively local ores (Abitibi copper sulfides) until 1976, after which it began to smelt and refine relatively large proportions of ores (50–80%) from other parts of the world (*7*). The company also developed recycling facilities for metal-rich materials such as electronic circuit boards and computer parts in the mid-1970s and is now the largest and most advanced plant for recycling used materials in North America.

Materials and Methods

Sampling. The study was conducted in four headwater oligotrophic Canadian Shield lakes (Despériers, Vose, Carpe, and N56) located along an east–west transect with the smelter situated in the west (Figure 1). Locations and general characteristics of these lakes are summarized in Table 1. Lakes with high lake to watershed surface area ratios were purposely chosen to reveal Pb atmospheric deposition. Their hypolimnions, except that of Lake Carpe, become seasonally anoxic, and their uninhabited drainage basins have not been affected by forest fires or wood harvesting for the last 100 years. The only inputs of anthropogenic lead to these entirely forested watersheds are therefore assumed to be via atmospheric deposition.

Sediment cores were collected between 1999 and 2002 at the deepest site of each lake by scuba divers using 9.5 or 12 cm internal diameter butyrate tubes. Within 2 h of collection, the sediments were extruded and sectioned at every 0.5 cm interval to a depth of 10 cm and then at every 1 cm interval to the bottom of the cores. These samples were put in 100 mL plastic vials and frozen until freeze-dried. Acrylic in situ diffusion samplers (peepers; 1-cm vertical resolution), similar to those described by Carignan et al. (*8*), were deployed to collect duplicate or triplicate sets of porewater and overlying water samples at the coring sites in three of the lakes (Despériers, Vose, and N56). Details on the methods to withdraw the samples from the peeper cells and to preserve their integrity for the subsequent chemical analyses have previously been reported by Alfaro-De la Torre and Tessier (*9*).

Analyses. To date the sediments, freeze-dried subsamples were placed in sealed Al vials for at least 1 month to allow for secular equilibrium of ^{222}Rn and ^{214}Pb with ^{226}Ra. Radioisotope (^{210}Pb, ^{214}Pb and ^{137}Cs) activities were then measured by Compton-suppressed γ spectrometry (Canberra equipment) and corrected for sample geometry and self-absorption (*10*). Details on sediment dating are available in Supporting Information. Lead concentrations were measured in sediments [total digestion of 250 mg of freeze-dried sediment with a mixture of ultrapure (Seastar) HNO_3, $HClO_4$, and HF] by quadrupole inductively coupled plasma mass spectrometry (ICP-MS; Thermo Instrument X7) or inductively coupled plasma optical emission spectrometry (ICP-OES; Vista AX CCD) and in porewaters by ICP-MS or by graphite furnace atomic absorption spectrometry (GFAAS; Perkin-Elmer SIMAA 6000; Zeeman correction). For the measurements by ICP-MS, we used an external calibration with Pb standards and Rh as an internal standard. Analyses of lead

---

* Corresponding author phone: (418)654-2632; fax: (418)654-2600; e-mail: atessier@ete.inrs.ca.

[†] Present address: Environmental Toxicology, University of California at Santa Cruz, 1156 High Street, Santa Cruz, CA 95064.

10.1021/es051326g CCC: $33.50

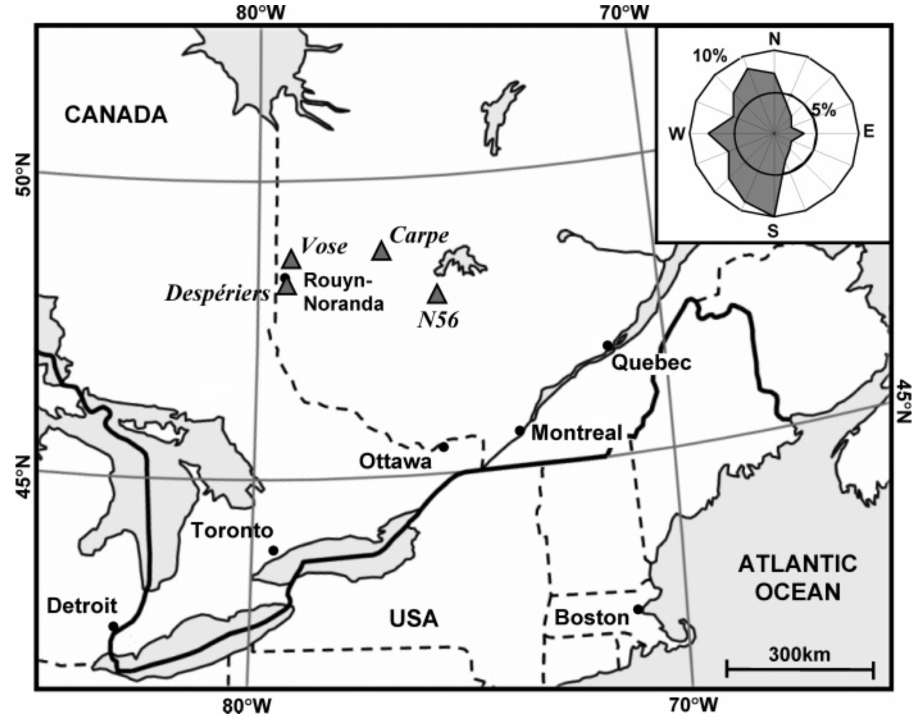

FIGURE 1. Location map of Lakes Despériers, Vose, Carpe, and N56 (indicated by gray triangles). Inset: direction of wind occurrence for the period 1954–1993 (data provided by Noranda, Inc.).

TABLE 1: Locations and Characteristics of the Study Sites

	Despériers	Vose	Carpe	N56
location	48°11′N, 79°09′W	48°28′N, 78°50′W	48°45′N, 76°43′W	48°00′N, 75°24′W
distance from Horne smelter (km)	10	25	150	300
altitude (m)	418	350	395	440
lake area (km^2)	0.10	0.12	0.51	0.80
watershed area (km^2)	0.82	4.5	2.62	1.26
volume (10^6 m^3)	0.51	0.85	1.75	0.75
maximum depth (m)	14	17	10	10
mean depth (m)	5.1	6.7	2.8	2.8
pH (water column)	5.9	6.4–6.7	5.7	6.0–6.3
hypolimnion	seasonally anoxic	seasonally anoxic	oxic	seasonally anoxic
sediment mass accumulation rate (mg cm^{-2} year^{-1})	4	8–16	21–46	7–11
sediment porosity	0.97–0.99	0.97–0.99	0.91–0.97	0.86–0.98
sediment bioturbation	no	no	no	no

in the National Institute of Standards and Technology (NIST) reference materials RM8704 for sediment and 1643d for water were within 4% and 5% of their certified values, respectively. Precision of repeated measurements of certified samples was 3% for NIST 1643d ($n = 10$) and 4% for NIST RM8704 ($n = 16$). Detection limits, defined as 2.5 times the standard deviation of a sample of low concentration, were 0.01 nmol g^{-1} and 0.5 nM for the sediments and porewaters, respectively. Determination of stable lead isotope ratios (^{206}Pb/^{208}Pb, ^{206}Pb/^{207}Pb, and ^{206}Pb/^{204}Pb) was also made in the sediment solutions by ICP-MS (three channels reading; dwell time of 30 ms for $^{206-8}$Pb and 100 ms for ^{204}Pb; 100 sweeps; 5 replicates). Mass bias and drift in Pb isotope ratios were corrected by use of the measurements of the certified lead reference material NIST SRM-981 analyzed after every second sample (*11*). External precisions, from measurements of replicate digestions ($n = 10$) of the reference material PACS-2 from the National Research Council of Canada (NRCC), were 0.14%, 0.13%, and 0.26% for the ^{206}Pb/^{208}Pb, ^{206}Pb/^{207}Pb, and ^{206}Pb/^{204}Pb ratios, respectively. Details on the other analyses carried out on porewater samples [pH and concentrations of dissolved organic carbon (DOC), sulfide (ΣS(-II)), Fe, Mn, and major ions] and on sediments (Al, Ca, Fe, Mn, Ti, and organic carbon concentrations) have been reported elsewhere (*9*).

In this paper, { } and [ ] refer to concentrations in the solid and dissolved phases, respectively, and errors are standard deviations (±1 SD).

Results and Discussion

Sedimentary Records of Pb Concentrations and Stable Pb Isotope Ratios. The profiles of solid-phase Pb concentrations ($\{Pb\}_{meas}$) in the four lakes are characterized by subsurface maxima (Figure 2a,e,i,m). The Pb concentrations increase from constant low preindustrial values (20 ± 2 to 44 ± 7 nmol g^{-1} prior to 1870) to maximum values between 1970 and 1980, and then diminish to present-day values that are about 6–42% lower than peak values. The highest maximum Pb concentration (3100 nmol g^{-1}) occurs in Lake Despériers, located 10 km from the smelter, and the lowest concentration (260 nmol g^{-1}) occurs in Lake Carpe, located 150 km from the smelter.

The concentration of solid-phase Pb contributed by diagenesis ($\{Pb\}_{diag}$) was estimated by modeling porewater

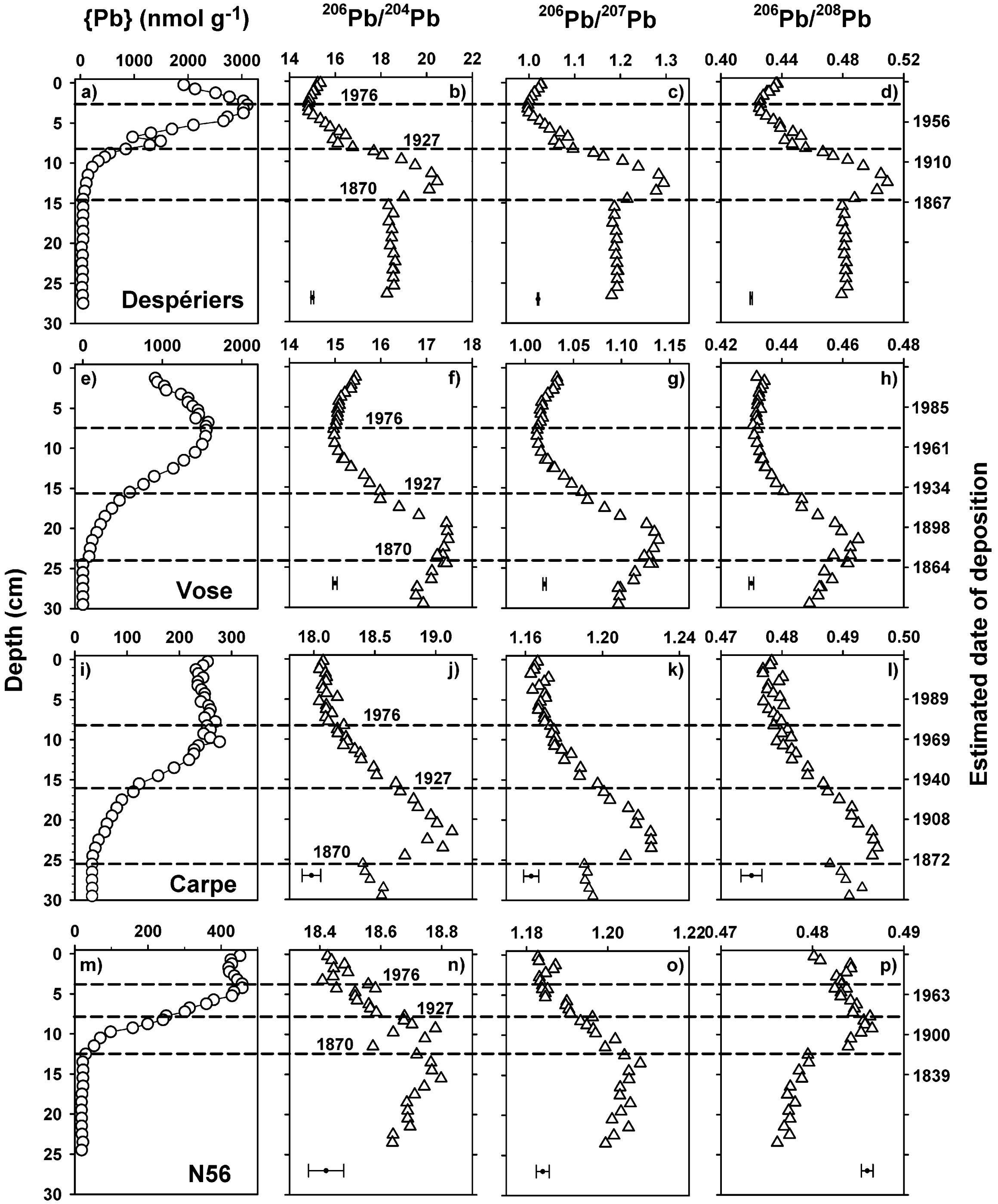

FIGURE 2. Vertical distribution of measured total Pb concentrations and $^{206}Pb/^{204}Pb$, $^{206}Pb/^{207}Pb$, and $^{206}Pb/^{208}Pb$ ratios in sediments from Lakes Despériers, Vose, Carpe, and N56. The error bars represent the mean standard deviation. The dates are derived from ^{210}Pb and ^{137}Cs geochronologies (see Supporting Information). Note that the horizontal scales vary among graphs.

[Pb] profiles with a one-dimensional transport-reaction equation at steady state (see Supporting Information). Subtracting $\{Pb\}_{diag}$ from $\{Pb\}_{meas}$ in Lakes Despériers, Vose, and N56 yielded $\{Pb\}_{hist}$ (herein referred to as historical Pb). With the assumption of no bioturbation in these seasonally anoxic lakes, the reconstructed profiles represent estimated chronologies of the Pb inputs at the sediment surface. The results of these calculations indicate that, for example, during the last 50 years, $\{Pb\}_{diag}$ contributed negligibly to $\{Pb\}_{meas}$ in Lakes Despériers ($\leq$0.5%) and N56 ($\leq$0.3%), which is in line with findings for another Canadian Shield lake (*12*). In the case of Lake Vose, the diagenetic contribution to solid Pb was greater (e.g., $\{Pb\}_{diag}$ of ~200 nmol g^{-1}) and represented about 20% of $\{Pb\}_{meas}$ at the sediment surface; however, the profile of $\{Pb\}_{hist}$ remained very similar to that of $\{Pb\}_{meas}$ in this lake. Diagenetic modeling was not performed for Lake Carpe, for which porewater data were not obtained.

Variations in stable Pb isotope ratios as a function of sediment depth are shown in Figure 2. The depth profiles of the three stable Pb isotope ratios display similar trends in Lakes Despériers, Vose, and Carpe. The values increase above preindustrial ratios (average values given in Table 2) from ~1870 to ~1900 and progressively decrease to values lower than the preindustrial values from 1900 to 1975; after 1975, the stable Pb isotope ratios increase again in Lakes Despériers and Vose as the Pb concentration decreases. The trends in

TABLE 2: Stable Pb Isotope Ratios Used as End-Members To Deconvolute Total Anthropogenic Pb[a]

	^{206}Pb/^{204}Pb	^{206}Pb/^{207}Pb	^{206}Pb/^{208}Pb
	Natural Pb Types		
Despériers	18.49	1.190	0.481
Vose	16.87	1.099	0.452
Carpe	18.53	1.193	0.492
	Anthropogenic Pb Types		
type 1	20.6	1.299	0.510
type 2	14.7	0.993	0.425

[a] Deconvolution is into type 1 Pb (mainly coal combustion) and type 2 Pb (mainly Abitibi sulfide ore); the stable Pb isotope ratios for natural Pb are also given.

the Pb isotope ratios differ slightly in Lake N56 in that the ^{206}Pb/^{208}Pb ratio does not parallel the other two isotopic ratios (Figure 2): whereas the ^{206}Pb/^{207}Pb and ^{206}Pb/^{204}Pb ratios progressively decrease from about 1870 to present time, the ^{206}Pb/^{208}Pb ratio first increases from 1870 to 1925 and then diminishes.

Identifying the Sources of Anthropogenic Pb. The occurrence of two predominant anthropogenic lead types is revealed from the depth profiles of stable Pb isotope ratios in Lakes Despériers and Vose (Figure 2), which show higher values in the early 20th century and lower values in the mid-1970s than those of natural Pb (<1870). Figure 3 displays variations in ^{206}Pb/^{208}Pb as a function of ^{206}Pb/^{207}Pb and ^{206}Pb/^{204}Pb; the linear distribution of all the isotopic ratios of these two lakes between two end-members of isotopic composition different from that of natural Pb (Table 2) indicates the presence of two isotopically distinct anthropogenic Pb types in the sediments of these lakes.

One type of Pb was dominant in the sediments of these two lakes at the beginning of the industrialized era, and this type of Pb (herein called type 1 Pb) had elevated isotopic ratios. For example, the ^{206}Pb/^{207}Pb ratio measured in the sediments deposited around 1890 reached a value of 1.29 in Lake Despériers (Figure 2c). It should be noted that the maximum values in the Pb isotope ratios occurred in sediments deposited in 1890, in which Pb concentrations were about twice those of preindustrial sediments. This Pb type most likely originated from coal and wood combustion, and perhaps from metal smelting in the United States, which were the major sources of anthropogenic Pb emissions from 1850 to 1930 (*2*, *13*, *14*). From the mid-19th century to the early 20th century, coal has been widely used for home heating and as a source of energy in a number of industries in North America, including the Horne smelter. Peaks of high ^{206}Pb/^{207}Pb ratios (1.32−1.65), observed in the sediments of the Pettaquamscutt River, Lake Michigan, and Lake Ontario were attributed to smelting of Pb ores in the Upper Mississipi Valley region, the main Pb ore producer from 1830 to 1870 (*13*).

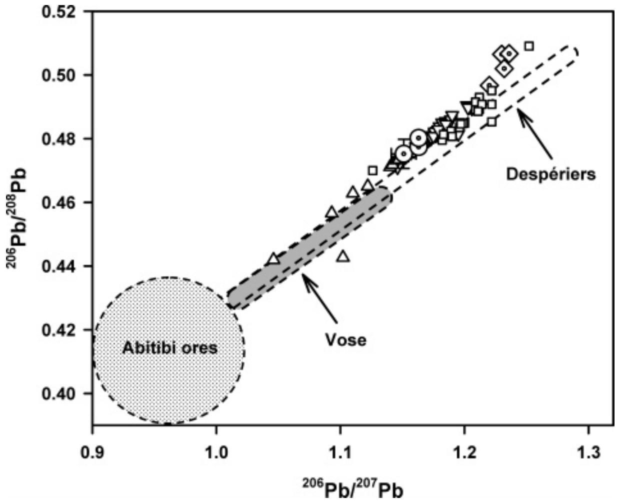

FIGURE 4. Plot of the ^{206}Pb/^{207}Pb ratio vs ^{206}Pb/^{208}Pb ratio reported for Abitibi ores (*15*), for lichens from the St. Lawrence Valley (▽; ref *16*) and from a 47−55°N transect comprising Rouyn-Noranda (△; ref *16*), for aerosols from Eastern Canada (○; refs *3*, *4*, *17*) and from Eastern/Midwest regions of the United States (◇; refs *3*, *4*, *18*, and *19*), and for North American coals (□; ref *20*). Areas comprising the Pb isotopic ratios measured for Lake Despériers and Lake Vose sediments are given for comparison.

The other predominant type of anthropogenic lead (herein called type 2 Pb) in the sediments of Lakes Despériers and Vose had a less radiogenic Pb isotopic composition. For example, the lowest ^{206}Pb/^{207}Pb ratio measured in Lake Despériers in 1976, when {Pb} reached its maximum, was 0.997 (Figure 2c). It is noteworthy that this isotopic signature is very different from that of the Pb in aerosols collected remote from point sources in North America (Figure 4). Specifically, a ^{206}Pb/^{207}Pb ratio of 0.997 is distinct from that reported for Pb in aerosols from Eastern Canada (~1.15; ref *4*) and from the Eastern and Midwest United States (~1.22; refs *4*, *18*), which most likely originated from leaded gasoline combustion.

The low values of the ^{206}Pb/^{207}Pb ratio found in sediments of Lakes Despériers and Vose at maximum {Pb} fall within the range of those (0.900−1.025) reported for the Abitibi

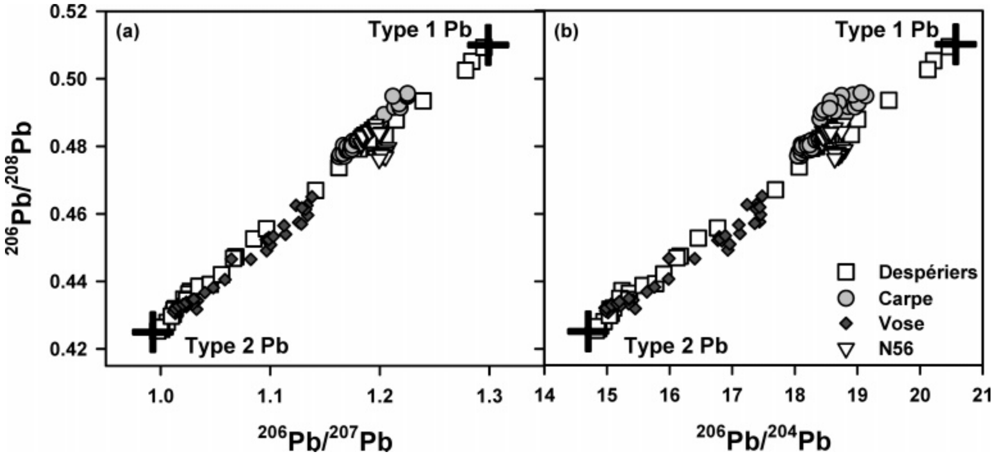

FIGURE 3. Plot of the ^{206}Pb/^{208}Pb vs ^{206}Pb/^{207}Pb (a) and ^{206}Pb/^{204}Pb (b) ratios in sediments from Lakes Despériers, Vose, Carpe, and N56 and assigned isotopic ratios (indicated as black crosses) for the anthropogenic type 1 and type 2 Pb.

copper sulfides (*21*), the only feed material to the nearby Horne smelter until 1976. Since then, the smelter has processed both local (20−50% of the feed material) and imported ores. In addition, in 1984, the plant began to recover precious metals by smelting metal-rich materials (e.g., computer parts and circuit boards), which may release recycled Pb to the atmosphere. Simonetti et al. (*15*) reported that the stable Pb isotope ratios of aircraft-sampled emissions from the Horne smelter in 2000 varied widely (e.g., ^{206}Pb/^{207}Pb ~1.12−1.17) over the two 2-week sampling periods, likely due to the smelting of recycled materials containing Pb from various origins. The influence of recycled materials on the ^{206}Pb/^{207}Pb ratio does not show up in our sediment cores, because they cannot provide the resolution necessary to observe such short-term events.

The present-day values of the ^{206}Pb/^{207}Pb ratios in Lakes Despériers and Vose (1.027 and 1.033, respectively) are very similar to those measured in epiphytic lichens collected near the city of Rouyn-Noranda between 1990 and 1994 (1.046; ref *16*), but they differ from those of lichens collected along the St. Lawrence River Valley (Figure 4; ref *16*). The low ratios for lichens collected near Rouyn-Noranda have been attributed to Pb emissions from the smelting of Abitibi sulfide ores (*16*).

Figure 2 panels b−d and f−h also show that the three Pb isotope ratios start to decrease sharply as the {Pb} increases about 20 years before the onset of the Horne smelter in 1927. This discrepancy is attributed to either a higher-than-expected diagenetic redistribution of lead in these two lakes or dating errors, since there is no important atmospheric source of anthropogenic Pb with low radiogenic signatures in the area other than the Abitibi sulfide ores.

The vertical profiles of stable Pb isotope ratios also illustrate the presence of two major anthropogenic Pb types in Lake Carpe (Figure 2j−l) and Lake N56 (Figure 2n−p), but Pb from the smelter is not predominant in the sediments of these lakes. At the sediment depth where the Pb concentration is maximal in Lake N56 (mid 1970s), the isotopic Pb composition (e.g., ^{206}Pb/^{207}Pb ~ 1.183) differs strongly from that of Pb deriving from the Abitibi sulfide ore (^{206}Pb/^{207}Pb ~ 0.990−1.025), indicating that another source of Pb contamination, that is, combustion of gasoline, prevailed in this lake during the second part of the 20th century. Indeed, a ^{206}Pb/^{207}Pb ratio on the order of 1.183 is consistent with a mixture of Pb from leaded gasoline usage in Canada and in the United States (*3*, *4*). It also agrees with the value of 1.184 reported for this time period in the sediments of Lake Tantaré, near Québec City (*14*). Apportionment among source regions of Pb deposited in the sediments of this lake during the period 1970−1980, when leaded gasoline dominated atmospheric Pb emissions, showed that approximately 50% of this Pb originated in the United States (*14*). Thus, our results suggest that the smelter does not contribute Pb to the sediments of Lake N56. However, for Lake Carpe, a ^{206}Pb/^{207}Pb ratio of 1.163 at sediment depths corresponding to 1970−1980 (Figure 2k) is lower than the ^{206}Pb/^{207}Pb ratios (1.183−1.184) found in Lakes N56 and Tantaré; this result indicates that Pb from another less radiogenic source is also present (if we assume a similar apportionment of Pb derived from leaded gasoline between Canada and the United States for Lakes Carpe, N56, and Tantaré). This source is probably Pb derived from the Abitibi sulfide ores processed at the Rouyn-Noranda smelter.

Inputs of Type 2 Pb to Lakes Despériers and Vose. To estimate the flux contribution of type 2 Pb (Pb from smelter emissions) at each sediment depth of Lakes Despériers and Vose, we multiplied the measured Pb concentrations by the sediment accumulation rates to yield total burial fluxes of Pb ($J_{\mathrm{meas}}^{\mathrm{Pb}}$), from which the contribution of the natural (≤1870) Pb fluxes was subtracted to yield anthropogenic Pb fluxes ($J_{\mathrm{an}}^{\mathrm{Pb}}$). The corresponding values of the anthropogenic stable Pb isotope ratios (R$_{\mathrm{an}}$) were obtained with eq 1:

$$R_{\mathrm{an}} = \frac{R_{\mathrm{meas}}\, J_{\mathrm{meas}}^{\mathrm{Pb}} - R_{\mathrm{nat}}\, J_{\mathrm{nat}}^{\mathrm{Pb}}}{J_{\mathrm{meas}}^{\mathrm{Pb}} - J_{\mathrm{nat}}^{\mathrm{Pb}}} \tag{1}$$

where the index nat refers to ≤1870 data. The flux contribution from type 2 Pb was then estimated with the $J_{\mathrm{an}}^{\mathrm{Pb}}$ and R_{an} values, assuming a binary mixture of Pb with ^{206}Pb/^{207}Pb ratios of 1.299 (type 1 Pb) and 0.993 (type 2 Pb) (Table 2); the following mass balance equations were used:

$$J_1^{\mathrm{Pb}} + J_2^{\mathrm{Pb}} = J_{\mathrm{an}}^{\mathrm{Pb}} \tag{2}$$

$$\left(\frac{^{206}\mathrm{Pb}}{^{207}\mathrm{Pb}}\right)_1 J_1^{\mathrm{Pb}} + \left(\frac{^{206}\mathrm{Pb}}{^{207}\mathrm{Pb}}\right)_2 J_2^{\mathrm{Pb}} = \left(\frac{^{206}\mathrm{Pb}}{^{207}\mathrm{Pb}}\right)_{\mathrm{an}} J_{\mathrm{an}}^{\mathrm{Pb}} \tag{3}$$

where the indices 1 and 2 refer to type 1 and type 2 Pb, respectively. Using either of the other two isotope ratios (^{206}Pb/^{208}Pb or ^{206}Pb/^{204}Pb) in eq 3 instead of ^{206}Pb/^{207}Pb would yield similar results, since the three isotope ratios are well correlated ($r^2 > 0.99$ by simple linear regression; Figure 2).

Lead emitted by the smelter started at about the same time (~1930) as the use of leaded gasoline (*22*) and peaked also at about the same time (~1980). However, on the basis of the very high sediment Pb concentrations and very low ^{206}Pb/^{207}Pb ratios observed in Lakes Despériers (Figure 2a,c) and Vose (Figure 2e,g) from 1927 to the present time, we conclude that in these two lakes inputs of Pb derived from leaded gasoline usage were relatively small compared to those originating from the smelter.

The fluxes calculated as above (J^{Pb}) for each type of Pb depend, however, on processes that vary among lakes (e.g., sediment focusing, loss of material by lake outflow). To remove this dependency and allow comparison among lakes, we estimated atmospheric deposition fluxes (J_{atm}^{Pb}) as follows:

$$J_{\mathrm{atm}}^{\mathrm{Pb}} = J^{\mathrm{Pb}} \frac{I_{\mathrm{atm}}^{210Pb}}{A(^{210}\mathrm{Pb})} \tag{4}$$

where A(^{210}Pb) is the inventory of unsupported ^{210}Pb and I_{atm}^{210Pb} (0.44 ±0.05 Bq cm^{-2}) is the cumulative atmospheric input of ^{210}Pb that is assumed to be similar to the inventories of ^{210}Pb$_{\mathrm{un}}$ measured in soils on the Precambrian Shield in Eastern Ontario (*23*).

Figure 5 shows that the flux $J_{\mathrm{atm}}^{\mathrm{Pb}}$ attributed to the smelter emissions (type 2 Pb) peaked in 1975−1980 at 17 nmol cm^{-2} year^{-1} in Lake Despériers and 13 nmol cm^{-2} year^{-1} in Lake Vose. The chronology of this flux in both lakes is consistent with records of the estimated Pb emissions to the atmosphere since 1965 that were provided by Noranda, Inc. for the Horne smelter (Figure 5). There is, however, a possibility that the depth profile of $J_{\mathrm{atm}}^{\mathrm{Pb}}$ shown in Figure 5 for Lake Despériers does not represent the true historical record of atmospheric Pb deposition in this lake. Indeed, the ln ^{210}Pb$_{\mathrm{un}}$ vs cumulative mass plot for Lake Despériers departs from linearity in the top 7 cm (since ~1940), a feature that we attributed to temporal changes in lake pH (see Supporting Information). A pH change would also have affected {Pb} and J^{Pb}, and normalization of J^{Pb} with $A(^{210}\mathrm{Pb})$ would not have corrected adequately for this pH effect. The recent decrease by ~45−50% of the flux of type 2 Pb over the last 25 years demonstrates that the mitigation measures taken to reduce atmospheric emissions from the smelter were effective. Type 1 Pb (data not shown) was discernible earlier, in 1870−1880, and showed a large peak around 1940. The flux of this Pb is, however, more than an order of magnitude lower and less precise than those for type 2 Pb.

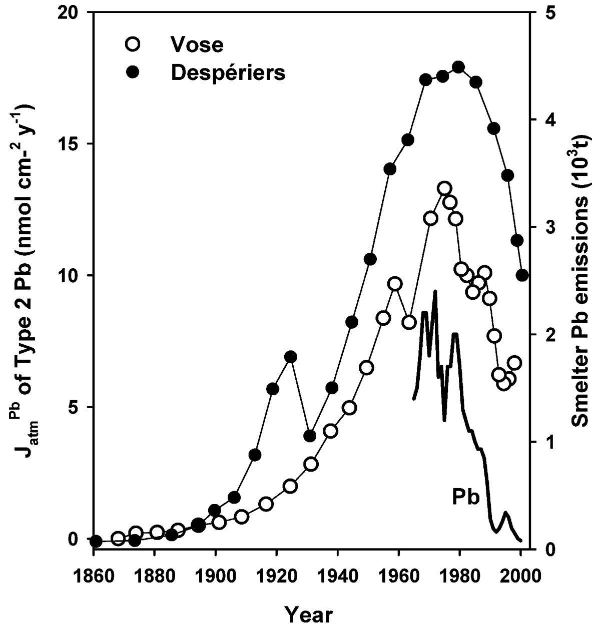

FIGURE 5. Comparison of estimated atmospheric deposition fluxes of type 2 Pb in Lakes Vose and Despériers with Pb emissions from the Horne smelter (thick black line; data provided by Noranda, Inc.).

The total amounts of Pb emitted from the smelter since the beginning of its operation that were delivered to Lakes Despériers and Vose per unit surface area (I^{Pb}_{atm}) were calculated as follows (*24*):

$$I^{Pb}_{atm} = A(\mathrm{Pb})\frac{I^{210Pb}_{atm}}{A(^{210}\mathrm{Pb})} \qquad (5)$$

where A(Pb) is the inventory of type 2 Pb. Table 3 shows that I^{Pb}_{atm} for type 2 Pb is 1040 nmol cm^{-2} for Lake Despériers and 640 nmol cm^{-2} for Lake Vose.

Limits on the Smelter Contribution to L. Carpe. Estimating the contribution of smelter emissions to Pb in Lake Carpe sediments is more difficult because, as discussed previously, the contribution of Pb from leaded gasoline combustion cannot be ignored compared to that from the smelter (type 2 Pb) during the second part of the 20th century. Since values of stable Pb isotope ratios higher than those of natural Pb at depths of 20–25 cm indicate that type 1 Pb is also present, three independent mass balance equations such as Eqns. 2 and 3 would be required to apportion adequately the total Pb flux in this lake among three end-members. However, only two independent equations are available since the three Pb isotope ratios are correlated (Figure 2; $r^2 > 0.99$).

The best that can be done for this lake is to determine the minimum and maximum limits of I^{Pb}_{atm} for smelter-derived Pb. To obtain the upper limit for the smelter contribution to anthropogenic Pb, we calculated the relative contribution of the Pb types 1 and 2 (Table 2) with Eqns 2 and 3 (where fluxes were replaced by concentrations) as if the contribution of Pb from leaded gasoline was negligible. The lower limit was calculated using also a two-component model, where the assumed end-members were Pb from the smelter emissions (^{206}Pb/^{207}Pb = 0.993) and Pb from leaded gasoline (^{206}Pb/^{207}Pb = 1.18). The latter calculation was performed over only the top 11.5 cm (~50 years) since the Pb contribution from coal burning could not be ignored at greater depths. This calculation revealed that 5% to 34% (9–94 nmol cm^{-2}) of the total inventory of anthropogenic Pb in Lake Carpe sediments was derived from the smelter.

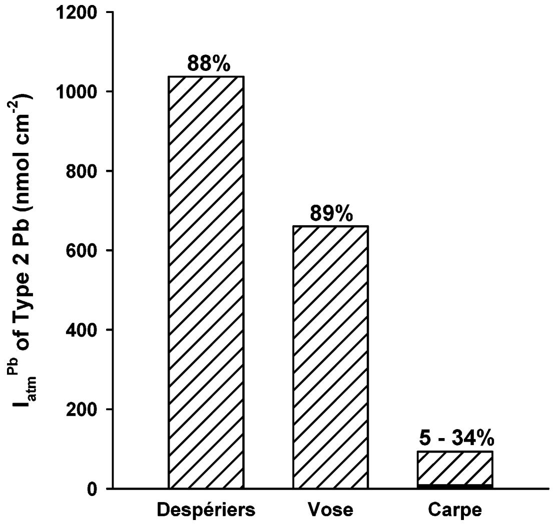

FIGURE 6. Cumulative atmospheric inputs of type 2 Pb for Lakes Despériers, Vose, and Carpe. The percentages indicate the proportion of type 2 Pb to the total anthropogenic Pb input for each lake.

Regional Anthropogenic Pb Inventories. Figure 6 shows that I^{Pb}_{atm} for type 2 Pb decreases sharply with distance from the smelter, for example, from 1040 nmol cm^{-2} in Lake Despériers (10 km) to 9–94 nmol cm^{-2} in Lake Carpe (150 km). We estimated the total burden (B^{Pb}_{sm}) of smelter-derived atmospheric Pb that has been deposited within a radius of 150 km:

$$B^{Pb}_{sm} = \int_{\theta=0}^{\theta=2\pi}\int_{x=0}^{x=150} I^{Pb}_{atm}x \, \mathrm{d}x \, \mathrm{d}\theta \qquad (6)$$

where $I^{Pb}_{atm} = I_0 + a\exp(-bx)$ was obtained by a least-squares fitting of the I^{Pb}_{atm} data given in Table 3. This calculation indicates that 16 000–31 000 metric tons (t) of atmospheric Pb from the smelter have been deposited within 150 km since 1927, depending on the value of I^{Pb}_{atm} used for Lake Carpe sediments; the B^{Pb}_{sm} value corresponds to 5–10% of the total amount of Pb released by leaded gasoline combustion

TABLE 3: Inventories and Cumulative Atmospheric Inputs of ^{210}Pb, Anthropogenic Pb, and Type 2 Pb for Lakes Despériers, Vose, and Carpe

	Despériers	Vose	Carpe
	Inventories		
A (^{210}Pb) (Bq cm^{-2})	0.274	0.753	0.885
A (type 2 Pb) (nmol cm^{-2})	650	1100	17–190
A (total anthropogenic Pb) (nmol cm^{-2})	740	1240	550
	Cumulative Atmospheric Inputs		
I^{210Pb}_{atm} (Bq cm^{-2})	0.44 ± 0.05	0.44 ± 0.05	0.44 ± 0.05
I^{Pb}_{atm} (type 2 Pb) (nmol cm^{-2})	1040	640	9–94
I^{Pb}_{atm} (total anthropogenic Pb) (nmol cm^{-2})	1180	720	270

in all of Canada (305 000 t, estimated on the basis of yearly data from Environment Canada; *22*).

The total quantity of Pb emitted from the smelter (E_{sm}^{Pb}) was also estimated as follows. For the period from 1965 to present, we used emission data from the smelter that were provided by Noranda, Inc. (Figure 5). Since such data are not available for the pre-1965 period, we adopted a mean ($x \pm$ SD) amount of 1.2 ± 0.2 kg of Pb emitted per metric ton of mineral processed by the smelter, a proportion based on the overlap of Pb emissions and quantities of ore processed between 1965 and 1970 (data also provided by Noranda, Inc.). This ratio should be valid before 1970 since only Abitibi ore was processed during this period and major changes in smelting technology occurred later.

This calculation yields an E_{sm}^{Pb} of 88 000 ± 10 000 t, a value of the same order of magnitude as that found for B_{sm}^{Pb}. Our estimated value of E_{sm}^{Pb} corresponds to 29% ± 3% of the burden value for Pb emitted from leaded gasoline combustion in all of Canada. Comparison of B_{sm}^{Pb} and E_{sm}^{Pb} values indicates that 19−36% of the Pb emitted by the smelter is deposited within a radius of 150 km, the remaining being transported over larger distances. Our findings are in agreement with the study of Telmer et al. (*7*), who reported that 15−19% of Pb emitted by the same smelter was deposited within 50 km. On the basis of our results, we calculate that ∼10−12% of the emitted Pb is deposited within this distance.

Finally, we estimate that all of the total Pb emitted by the smelter is deposited within 600−1500 km, depending on the value of I_{atm}^{Pb} for Lake Carpe.

Acknowledgments

Funding is acknowledged from the Natural Sciences and Engineering Research Council of Canada, the Ontario Power Generation Inc., the Mining Association of Canada, and the Fonds de Recherche sur la Nature et les Technologies du Québec. We thank S. Duchesne for her help with the Pb burden calculations and R. Flegal, L. Hare, and an anonymous reviewer for their comments on the manuscript. Permission from Faune et Parcs Québec to work in the Aiguebelle Provincial Park is gratefully acknowledged.

Supporting Information Available

Details on sediment dating, including the ln ^{210}Pb versus depth and versus cumulative mass and the ^{137}Cs versus depth plots for Lakes Despériers, Vose, Carpe, and N56, and estimates of the diagenetic redistribution of Pb in sediments of Lakes Despériers, Vose, and N56. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Ng, A.; Patterson, C. C. Changes of lead and barium with time in California off-shore basin sediments. *Geochim. Cosmochim. Acta* **1982**, *46*, 2307−2321.

(2) Graney, J. R.; Halliday, A. N.; Keeler, G. J.; Nriagu, J. O.; Robbins, J. A.; Norton, S. A. Isotopic record of lead pollution in lake sediments from the northeastern United States. *Geochim. Cosmochim. Acta* **1995**, *59*, 1715−1728.

(3) Sturges, W. T.; Barrie, L. A. Lead 206/207 isotope ratios in the atmosphere of North America as tracers of US and Canadian emissions. *Nature* **1987**, *329*, 144−146.

(4) Sturges, W. T.; Barrie, L. A. Stable lead isotope ratios in arctic aerosols; evidence for the origin of arctic air pollution. *Atmos. Environ.* **1989**, *23*, 2513−2519.

(5) Pacyna, J. M.; Pacyna, E. G. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environ. Rev.* **2001**, *9*, 269−298.

(6) Pacyna, J. M.; Scholtz, M. T.; Li, Y. F. Global budgets of trace metal sources. *Environ. Rev.* **1995**, *3*, 145−159.

(7) Telmer, K.; Bonham-Carter, G. F.; Kliza, D. A.; Hall, G. E. M. The atmospheric transport and deposition of smelter emissions: Evidence from the multi-element geochemistry of snow, Quebec, Canada. *Geochim. Cosmochim. Acta* **2004**, *68*, 2961−2980.

(8) Carignan, R.; Rapin, F.; Tessier, A. Sediment porewater sampling for metal analysis: A comparison of techniques. *Geochim. Cosmochim. Acta* **1985**, *49*, 2493−2497.

(9) Alfaro-De la Torre, M. C.; Tessier, A. Cadmium deposition and mobility in the sediments of an acidic oligotrophic lake. *Geochim. Cosmochim. Acta* **2002**, *66*, 3549−3562.

(10) Carignan, R.; Lorrain, S.; Lum, K. A. A 50-yr record of pollution by nutrients, trace metals, and organic chemicals in the St. Lawrence river. *Can. J. Fish. Aquat. Sci.* **1994**, *51*, 1088−1100.

(11) Jarvis, K. E.; Gray, A. L.; Houk, R. S. *Handbook of Inductively Coupled Plasma Mass Spectrometry*; Blackie Academic & Professional: London, 1996.

(12) Gallon, C.; Tessier, A.; Gobeil, C.; Alfaro-De la Torre, M. C. Modeling diagenesis of lead in sediments of a Canadian Shield lake. *Geochim. Cosmochim. Acta* **2004**, *68*, 3531−3545.

(13) Lima, A. L.; Bergquist, B. A.; Boyle, E. A.; Reuer, M. K.; Dudas, F. O.; Reddy, C. M.; Eglinton, T. I. High-resolution historical records from Pettaquamscutt River basin sediments: 2. Pb isotopes reveal a potential new stratigraphic marker. *Geochim. Cosmochim. Acta* **2005**, *69*, 1813−1824.

(14) Gallon, C.; Tessier, A.; Gobeil, C.; Beaudin, L. Sources and chronology of atmospheric lead deposition to a Canadian Shield lake: Inferences from Pb isotopes and PAH profiles. *Geochim. Cosmochim. Acta* **2005**, *69*, 3199−3210.

(15) Simonetti, A.; Gariepy, C.; Banic, C. M.; Tanabe, R.; Wong, H. K. Pb isotopic investigation of aircraft-sampled emissions from the Horne smelter (Rouyn, Québec): Implications for atmospheric pollution in northeastern North America. *Geochim. Cosmochim. Acta* **2004**, *68*, 3285−3294.

(16) Carignan, J.; Gariepy, C. Isotopic composition of epiphytic lichens as a tracer of the sources of atmospheric lead emissions in southern Québec, Canada. *Geochim. Cosmochim. Acta* **1995**, *59*, 4427−4433.

(17) Outridge, P. M. Lead biogeochemistry in the littoral zones of South-Central Ontario lakes, Canada, after the elimination of gasoline lead additives. *Water, Air, Soil Pollut.* **2000**, *118*, 179−201.

(18) Rabinowitz, M. B.; Wetherill, G. W. Identifying sources of lead contamination by stable isotope techniques. *Environ. Sci. Technol.* **1972**, *6*, 705−709.

(19) Tera, O.; Schwartzman, D. W.; Watkins, T. R. Identification of gasoline lead in children's blood using isotopic analysis. *Arch. Environ. Health* **1985**, *40*, 120−123.

(20) Chow, T. J.; Earl, J. L. Lead isotopes in North American coals. *Science* **1972**, *176*, 510−511.

(21) Simonetti, A.; Gariépy, C.; Carignan, J. Pb and Sr isotopic compositions of snowpack from Québec, Canada: Inferences on the sources and deposition budgets of atmospheric heavy metals. *Geochim. Cosmochim. Acta* **2000**, *64*, 5−20.

(22) Environment Canada. *National Inventory of sources and releases of Lead 1982*. Report EPS 5/HA/3, 1985.

(23) Cornett, R. J.; Chant, L.; Link, D. Sedimentation of Pb-210 in Laurentian Shield lakes. *Water Pollut. Res.* **1984**, *19*, 97−109.

(24) Kada, J.; Heit, M. The inventories of anthropogenic Pb, Zn, As, Cd, and the radionuclides ^{137}Cs and excess ^{210}Pb in lake sediments of the Adirondack region, USA. *Hydrobiologia* **1992**, *246*, 231−241.

Received for review July 8, 2005. Revised manuscript received October 25, 2005. Accepted November 11, 2005.

ES051326G