

# ANTHROPOGENIC MERCURY ENRICHMENT IN REMOTE LAKES OF NORTHERN QUÉBEC (CANADA)

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**Abstract.** In a sub-Arctic region of the province of Québec, at sites situated 200 to 1400 km away from the closest industrial centers, we find the ubiquitous presence of anthropogenic Hg, reflected by steadily increasing concentrations of this metal in lake sediments, since about 1940, to rates averaging 2.3 times the preindustrial levels. Mercury concentrations in lake sediments were found to be proportional to the amounts of terrestrial organic carbon from the catchment area. It would, therefore, be misleading to derive continental-scale gradients of this pollutant based on Hg concentrations in oligotrophic lake sediments, unless they are normalized to their organic carbon content. Our normalized data for sediments of remote lakes along a 1200 km transect (45 to 55°N) clearly indicate that the distribution pattern of long-range Hg contamination is independent of the latitude over the boreal forest domain. This uniform contamination contrasts with that of Pb, which decreases towards the north over the same latitudinal span, away from the industrial centers of the St Lawrence Valley and the U.S. Mid-West.

## 1. Introduction

The deleterious effects of mercury (Hg) resulting from long range atmospheric transport (Verta *et al.*, 1989; Iverfeldt, 1991; Swain *et al.*, 1992) are a cause of concern, as a growing number of aquatic systems in the northern hemisphere have been reported to bear high mercury burdens (Hakanson *et al.*, 1988; McMurtry *et al.*, 1989; Lindqvist, 1991; Meili, 1991; Lathrop *et al.*, 1991; Wren *et al.* 1991). The presence of mercury may either be predominantly a reflection of local anthropogenic sources (Iverfeldt, 1991; Lathrop *et al.*, 1991; Johansson *et al.*, 1991; Nater and Grigal, 1992) or of more global scale processes (Steinnes and Andersson, 1991; Slemr and Langer, 1992 Swain *et al.*, 1992) and therefore uniformly distributed over large continental areas. In Canada, substantial increase in sediment mercury loadings have been reported in lakes situated in south-eastern Canada (Speyer, 1980; Evans, 1986; Rybak *et al.*, 1989). Because of their geographic positions, all these lakes were under the direct influence of westerlies carrying mercury from industrial centers in their paths (Delisle *et al.* 1979; Ouellet and Jones, 1982; Mierle, 1990). In more septentrional regions of the Canadian boreal forest domain, the history of mercury atmospheric contamination remains to be elucidated.

Following its release into the atmosphere, particulate Hg is deposited locally or

regionally within a few weeks (Iverfeldt, 1991; Slemr and Langer, 1992). In contrast, the residence time of gaseous  $\text{Hg}^0$  or  $\text{Hg}^{\text{II}}$  fixed on aerosol size particles is estimated to be about one year, and may therefore be transported over thousands of kilometers from its source before being deposited (Glass *et al.*, 1986; Slemr and Langer, 1992). Mapping the extent of Hg transport, however, is an elusive quest because the direct determination of Hg in precipitation is hampered by temporal variability and low concentrations (Iverfeldt, 1991). Alternatively, lake sediment records can provide time-averaged patterns of Hg deposition, as demonstrated in northern Minnesota and Wisconsin, where modern fluxes of Hg were shown to reach 3.7 times the pre-industrial levels (Swain *et al.*, 1992). Resolving the controversy concerning widespread as opposed to regional contamination by anthropogenic Hg is of special interest in Québec where the development of hydroelectric reservoirs results in Hg release from flooded soils and subsequent bioaccumulation through the food chain (Verdon *et al.*, 1991). The present study was undertaken to evaluate the level of mercury contamination of the Québec boreal forest domain. Inspired by the findings reported for the north central U.S. (Nater and Grigal, 1992), we hypothesized that Hg concentrations in lake sediments would show a clear pattern of distribution with increasing distance away from urban and industrial sources (from 200 km for the southernmost sampling sites to 1400 km for the northernmost). Furthermore, our initial hypothesis was influenced by an earlier report (Ouellet and Jones, 1982) of the existence of a strong gradient in wet sulphate deposition in our study area. In parallel, we analysed Pb concentrations in lake sediments because the spatial distribution of this element in the environment is also governed by atmospheric transport (Evans and Rigler, 1985; Johansson, 1989; Sturges and Barrie, 1989).

## 2. Materials and Methods

The sediments were collected with either a remotely-triggered stainless steel box corer or a 15 cm diameter core tube manually inserted by divers, in the deepest part of ten remote lakes, distributed along a  $10^\circ$  of latitude transect on the Canadian Shield, extending from southwestern Québec to eastern Hudson Bay (Figure 1). Minimal disturbance of flocculent surface sediments was achieved by these coring methods. The lakes were chosen on the basis of their size (small lakes:  $\sim 0.04$  to  $\sim 6$  km<sup>2</sup>), maximum depth (6 to 13 m), pH (6.0 to 7.3) and oligotrophic characteristics. To complement the pristine environments, we collected cores from four lakes whose respective water levels were raised through impoundment of hydroelectric reservoirs (LG-2 and Cabonga, impounded 14 and 65 years ago, respectively). All sediments were subsampled at one centimeter intervals.

The Hg content of the sediments was determined by atomic fluorescence following acid digestion, employing recent analytical developments (Bloom, 1989; Pichet *et al.*, 1994). Analyses for Pb were conducted on the Hg digests by graphite furnace atomic absorption spectrophotometry. Sedimentation rates were determined from the decay of excess  $^{210}\text{Pb}$  below the mixed surface layer and average rates were corrected for

porosity change with core depth. Organic carbon concentrations were measured with a Carlo Erba CHN analyser. Stable C isotope ratios ( $^{13}\text{C}/^{12}\text{C}$ ) of particulate organic C were determined with a PRISM mass spectrometer following the standard combustion in presence of cupric oxide. The results are reported as  $\delta^{13}\text{C}$  (‰) values relative to the Pee Dee Belemnite limestone standard (PDB).

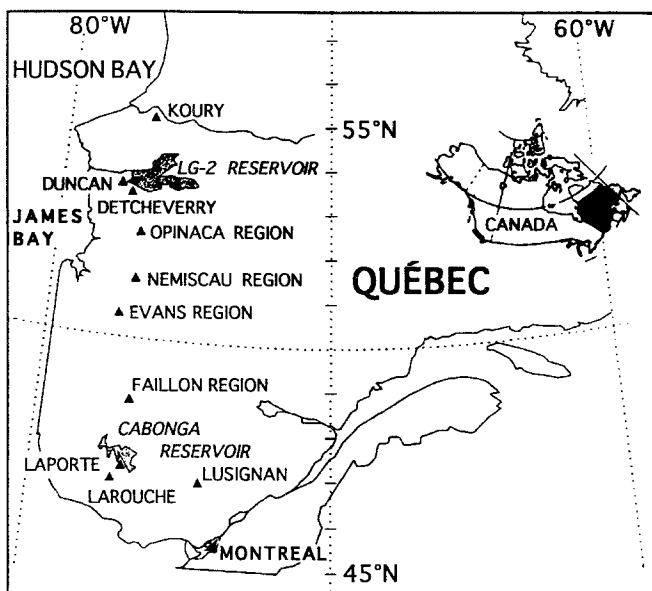


Fig. 1. Sample locations

### 3. Results and Discussion

For all sampled lakes, sedimentation rates fall within a narrow range of 0.1 to 0.3 cm/yr (Table I). Bioturbation by chironomids is responsible for sediment mixing in the top 2 to 6 cm. All Hg and Pb profiles are characterized by constant concentrations at depth (Figure 2). In the top 10-20 cm, Hg and Pb profiles follow the same trend and clearly show a dramatic increase in the flux of these metals to the sediment (Figure 2 & Table I). Both Hg and Pb are only weakly susceptible to diagenetic remobilization in lake sediments, being strongly bound to refractory organic matter (Rybak *et al.*, 1989; Verta *et al.*, 1989; Dominik *et al.*, 1991; Louchouart *et al.*, 1993). Thus, the departure in Hg and Pb concentrations above background values may be interpreted as the record of the airborne contamination of the pristine lacustrine systems. In each sedimentary profiles, the age of the onset of contamination was calculated after subtracting the time required for the deposition of one mixed layer. We estimate that the uncertainty in the historical reconstructions of local contamination does not exceed ten years. Variations in absolute Hg and Pb baseline concentrations between lakes reflect dissimilar pre-industrial inputs of these metals from their respective drainage basins. The ratios of the surface to baseline

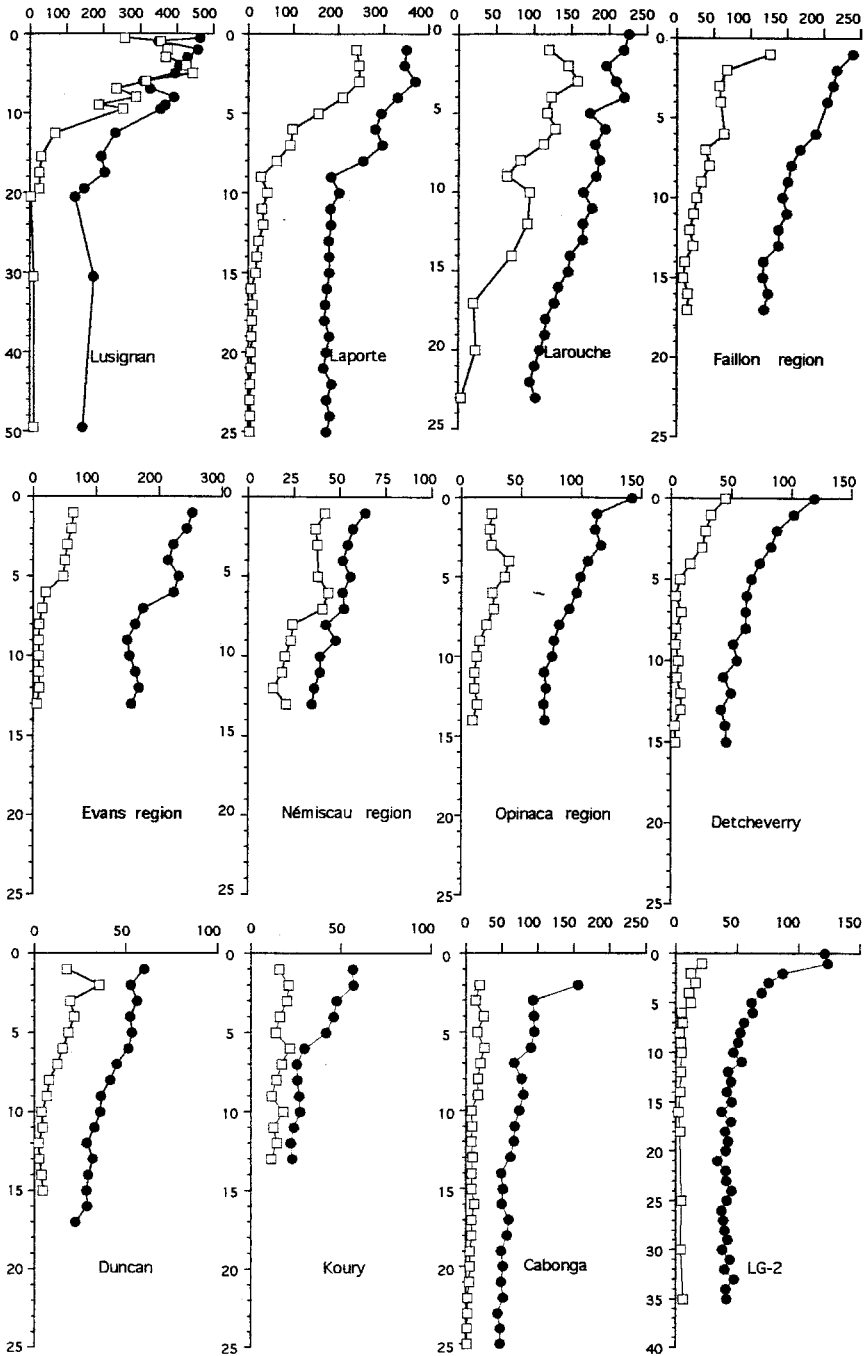


Fig. 2. Mercury (●, ng/g) and lead (□, μg/g) profiles in the sediments of 10 natural lakes and 2 flooded lakes.

Hg concentrations (Anthropogenic Sedimentary Enrichment Factor, ASEF) average 2.3 for all sampled lakes and are independent of latitude. In contrast, variations in the organic carbon content in any given lake sediment core are negligible, indicating that fairly stable sedimentary conditions prevailed over the period represented by the sampled interval.

TABLE I

Location, chemical and sedimentological characteristics of the lakes investigated, including the Hg and Pb anthropic sedimentary enrichment factor (ASEF) and the time elapsed since the beginning of significant Hg enrichment in the lake sediments (n.r.: baseline concentration not reached.; \* mean values over the length of the core, with a standard deviation smaller than 0.8).

Site	Latitude North	C <sub>surface</sub> (%)	C <sub>deep</sub> (%)	$\delta^{13}\text{C}$ (PDB) (‰)*	Hg ASEF	Pb ASEF	Sedimentation (cm/year)	Record of Hg enrichment (years)
Natural lakes								
Lusignan	46°41'	24.8	25.8	-28.5	3.5	147	0.24	80
Laporte	47°12'	17.9	19.7	-28.6	2.0	62	0.135	55
Larouche	47°12'	11.3	11.9	-28.9	2.2	40	0.30	57
Faillon region	48°22'	14.1	13.6	-27.9	2.0	13	0.20	57
Evans region	50°36'	17.4	17.7	-28.7	1.6	11	0.075	66
Némiscau region	51°36'	3.9	3.1	-27.5	1.8	3	0.20	50
Opinaca region	52°40'	8.5	6.6	-27.6	2.0	4	0.16	50
Detcheverry	53°27'	8.3	8.7		1.7	10	0.19	53
Detcheverry	53°27'	9.5	8.9		2.8	7.5		
Duncan	53°29'	4.1	2.8		2.6	7		
Koury	55°07'	2.8	1.5	-27.8	2.5	1.5		
Flooded lakes								
Cabonga	47°17'	4.6	3.9	-27.5	2.1	13		
Cabonga	47°17'	7.2	7.8	-26.4			0.12	n.r.
Cabonga	47°17'	4.4	4.4	-27.6	1.5			
LG-2	53°29'	9.4	5.7	-27.6	2.3	10	0.17	53
LG-2	53°29'	9.4	5.7		2.3	1.3	0.26	50
LG-2	53°31'	9.8	13.0	-26.6	3.0	3.5		
LG-2	53°32'	8	3.8	-27.1	6.2	6		

The sharp rise in the Hg deposition rate above background levels occurred, for all lakes situated north of 47° latitude, in the early 1940's irrespective of latitude (Table I). This observation is consistent with what was reported for Hg and other metals in the sediments of undisturbed lakes of southern Québec (Ouellet and Jones, 1982), and for one headwater lake in Newfoundland (Rybak *et al.*, 1989). The only exception to our recorded mid-1940's increase in Hg concentration was observed in the southernmost lake, Lake

Lusignan. It corresponds to a change initiated ca. 1910 and may be attributed to the local influence of a small copper mine. In comparison, Hg accumulation records from the industrialized regions of Minnesota and Wisconsin show that the increased fluxes of Hg date back nearly 140 years (Swain *et al.*, 1992). Mercury concentrations in Finnish lake sediments (Verta *et al.*, 1989) and peat bogs of southern Sweden (Jensen and Jensen, 1991) also started to rise dramatically at the turn of this century, as opposed to the 1960's for peat bogs of northwestern Norway (Jensen and Jensen, 1991). Thus, anthropogenic Hg seems to have reached northern sites of North America and Europe at a later date. The reason for this variation may be attributed to their remoteness from industrial centers and their lack of exposure to short range fallout of particulate Hg.

Although surface sediments in the two latitudinally extreme lakes contain the lowest and highest recorded Hg concentrations, neither the absolute Hg maximum surface concentrations, nor the Hg ASEF appear to be correlated with latitude (Table 1). The influence of large regional inputs, such as from the mining area of Abitibi, between 48 and 49 °N, could not be resolved either. The most noticeable difference between the sampled lake sediments is their organic matter content,  $C_{org}$ , which ranges from 3 to 25 % dry weight (Table 1). Our  $^{13}C$  measurements (Table 1) indicate that the  $C_{org}$  in the sampled lake sediments of southwestern Québec is composed mainly of terrestrial material (LaZerte, 1983; Meili *et al.*, 1993). This observation attests to the oligotrophic nature of the 10 sampled lakes.

The surficial sediment Hg anthropogenic enrichment concentrations (EHg, surface minus baseline concentrations) are directly proportional to their  $C_{org}$  ( $EHg = 12.3 \times C_{org} - 23.8$ ,  $r^2 = 0.932$ ; Fig. 3). These variables and the residuals from the least squares fits (7% of EHg) are strongly of latitude. It is well documented that Hg forms stable complexes with organic matter (Lindqvist, 1991). As a matter of fact, several authors hypothesized that most Hg present in the water column (Iverfeldt and Johansson, 1998; Mierle, 1990; Mierle and Ingram, 1991; Meili, 1991; Lee and Iverfeldt, 1991) or buried in the sediments (Evans, 1986; Meili, 1991; Swain *et al.*, 1992) of various natural lakes could be transported by surface runoff along with the outwash of terrestrial organic matter, in both dissolved and particulate forms. The strong relationship reported here between the allochthonous  $C_{org}$  concentration and the sediment EHg concentrations of the 10 oligotrophic lakes confirm the latter hypothesis. Sediment focussing in the deeper parts of a lake, however, would only help to amplify this relationship. The external loading of fine grained particles, including organic matter, to a lake is dependent upon the physiography (slope, drainage area : lake surface ratio) and the composition of the catchment (vegetation type, acidity of runoff) (Meili, 1991; Nelson and Campbell, 1991; Rowan *et al.*, 1992). The local flux of carbon is then modulated by in-lake depositional processes.

Our data reinforce previous findings (Swain *et al.*, 1992) from which it was postulated that the quantity of Hg brought to a lake is directly proportional to the amount of carbon leached from the surrounding soils, regardless of soil type. Calculated

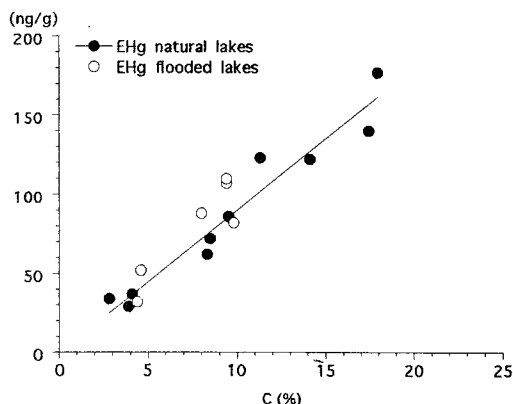


Fig. 3. The Hg surficial sediment anthropic enrichment (EHg) as a function of the organic carbon content for the natural lake sediments sampled along the North-South transect.

sedimentary fluxes of Hg range from 35 to 76  $\mu\text{g}/\text{m}^2/\text{yr}$ , for all cored sites, which is systematically 3 to 5 times higher than the direct atmospheric Hg deposition rates presently proposed for central North America (Glass *et al.*, 1986; Mierle, 1990; Fitzgerald *et al.*, 1991; Swain *et al.*, 1992). As indicated above, our estimated sedimentary fluxes may be overestimated because of particle focussing in the deeper parts of the lake where we sampled. Nevertheless, these high values corroborate our conclusions that most Hg found in these lake sediments must have been brought by the outwash of terrestrial organic matter.

The relationship between EHg and  $C_{\text{org}}$  also holds true for sediment samples of lakes presently incorporated into the LG-2 and Cabonga hydroelectric reservoirs, where, respectively, 2-3 cm and  $\approx 20$  cm of sediment has accumulated since impoundment. Thus, Hg inputs are directly related to the accumulation of organic matter, even if the latter has varied through time in response to a major change in the sedimentary regime following impoundment.

In contrast to the Hg distribution patterns reported for the central U.S. (Nater and Grigal, 1992), southern Ontario (Lathrop *et al.* 1991) and southern Scandinavia (Iverfeldt, 1991; Johansson *et al.* 1991), our data display no clear regional gradient in Hg ASEF or in sedimentary Hg concentrations once they are normalized to  $C_{\text{org}}$  (Figure 4). We can assume that, unlike previously cited reports of local or regional contamination, most of the anthropogenic Hg burden in sediments of our study area must have accumulated from gaseous  $\text{Hg}^0$  or submicron aerosols which remain in the atmosphere for long periods of time, since it was deposited far from the direct influence of heavily industrialized regions. Thus, we propose that, away from major emission sources, Hg is deposited evenly over large continental expanses. Our results concur, but on a much wider latitudinal scale, with previous observations by Swain *et al.* (1992) who reported nearly uniform Hg atmospheric deposition over northern Minnesota and Wisconsin. They also imply that the

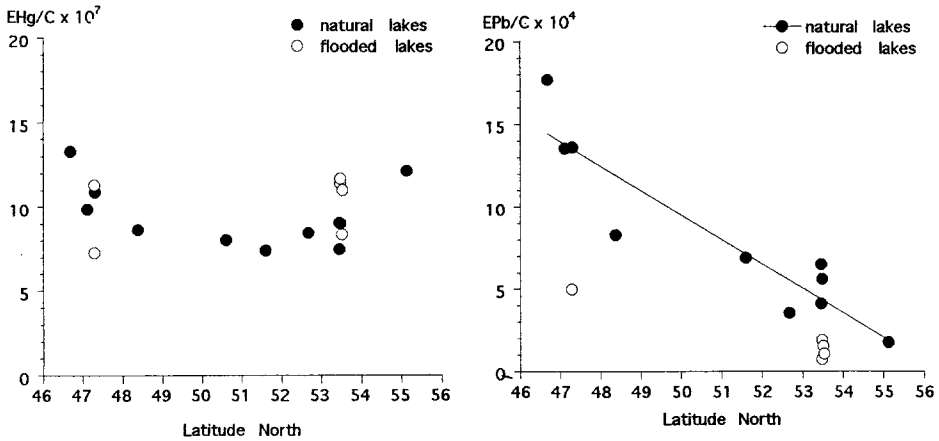


Fig. 4. The Hg and Pb surficial sediment anthropic enrichments normalized to the organic carbon content ( $\text{EHg/C}$  and  $\text{EPb/C}$ ) as a function of the latitude for the lake sediments sampled along the North-South transect.

anthropogenic origin of the airborne Hg in remote regions of northern Québec cannot be clearly traced.

As suggested by previous observations in Québec and Ontario (Rowan and Kalff, 1993), and like for Hg, most of the Pb found in lake sediments should also have been transported with the leaching of the terrestrial organic matter. The EPb values in the sampled lake sediments are indeed linearly correlated to the  $C_{\text{Org}}$  content yet more poorly than for EHg values, particularly when data from the hydroelectric reservoirs are included ( $r^2 = 0.897$ ). One can also observe that, in contrast to Hg, the EPb concentrations normalized with respect to  $C_{\text{Org}}$  decrease linearly with increasing latitude (Figure 4). Likewise, Pb-ASEF values decrease by more than one order of magnitude from the southernmost stations northward (Table 1). This suggests that, in contrast to Hg, the atmospheric transport of anthropogenic Pb over remote areas of northern Québec involves a particulate phase which is preferentially deposited close to the heavily industrialized regions south of the 46th parallel in North America. A similar decreasing gradient of anthropogenic Pb deposition away from industrialized regions was reported for southeastern Canada (Evans and Rigler, 1985) and Sweden (Johansson, 1989).



#### 4. Conclusion

Over time, the spatially uniform and still increasing deposition rates of anthropogenic Hg over the boreal forest domain may lead to a generalized contamination of all natural aquatic ecosystems. So far, Hg contamination is most acute to organisms living in newly impounded hydroelectric reservoirs of northern Québec as mercury transfer to the food chain is promoted by intense microbial and benthic activity in the Hg-laden flooded soils (Verdon *et al.*, 1991; Louchouart *et al.*, 1993). We can only assume that a fraction of the mercury released in this manner is anthropogenic, and has slowly accumulated in the soils over the last half century. In addition, the return to pre-impoundment Hg concentrations in aquatic organisms will be delayed by the continuous deposition of atmospheric Hg over the reservoirs and their watersheds.

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