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Mercury in the Canadian Environment: Current Research Challenges

R. E. Rasmussen, P. W. B. Friske, L. M. Azzaria et R. G. Garrett

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Résumé de l'article

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ARTICLES

Mercury in the Canadian Environment: Current Research Challenges

P.E. Rasmussen[1], P.W.B. Friske[1]
L.M. Azzaria[2] and R.G. Garrett[1]
[1]*Geological Survey of Canada*
Natural Resources Canada
601 Booth Street
Ottawa, Ontario K1A 0E8
[2]*Département de géologie et*
de génie géologique
Université Laval
Québec City, Québec G1K 7P4
(Present address: Case Postale 705
Ste-Julienne, Québec JOK 2T0)

SUMMARY
Elevated methylmercury concentrations are common in fish and other wildlife in ecosystems remote from any industrial point sources. Concern about chronic exposure to methylmercury for people who depend on fish as a dietary staple has focused attention on mercury sources and cycling processes in rural and remote areas, and on the potential for airborne mercury to travel hundreds to thousands of kilometres. A number of other studies have demonstrated that elevated concentrations of mercury in fish may be attributable to local geological sources. Compared to the large body of literature that is emerging on anthropogenic sources, however, there is a relative lack of research aimed at quantifying the contribution of mercury from natural sources. This has resulted in a debate over the relative significance of anthropogenic and natural mercury inputs to rural and remote lakes. Geoscience research is needed to improve our understanding of the biogeochemical cycling of mercury species released from common sulphide minerals and other crustal sources into soil, sediments, air, water, vegetation and ultimately into the human food chain.

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RÉSUMÉ
Les niveaux de mercure méthylé sont souvent élevés dans les tissus des poissons et ceux d'autres animaux de la faune des écosystèmes éloignés des sources industrielles. Découlant des préoccupations concernant les risques d'une exposition régulière au mercure méthylé pour les populations dont la diète est basée sur le poisson, les recherches ont porté sur les sources possibles du mercure, ses cycles de transport ainsi que sur la possibilité que le mercure atmosphérique puisse être transporté sur des milliers de kilomètres. D'autres études ont démontré que des sources géologiques pourraient être à l'origine de concentrations élevées en mercure dans les poissons. Si la documentation sur les sources anthropogéniques de mercure est abondante, on constate en contrepartie qu'il n'y a pas assez de recherches scientifiques visant à chiffrer l'apport des sources naturelles. En conséquence, la question de l'apport relatif en mercure des sources anthropogéniques et naturelles en milieu rural et dans les lacs éloignés demeure-t-elle encore matière à discussion. Des études géoscientifiques devront être réalisées afin d'améliorer nos connaissances sur le cycle biochimique des composés du mercure provenant des minéraux de sulfures usuels et d'autres sources crustales, dans le sol, les sédiments, l'air, l'eau, la végétation, et en bout de piste, dans la chaîne alimentaire des humains.

INTRODUCTION

The need for stringent controls on the use and release of mercury became widely recognized after the acute poisoning events of the 1950s and 1960s, most notably the Minamata Bay and Niigata tragedies (D'Itri, 1972). Another landmark episode was the Iraqi disaster, where grain dressed with organic mercurial fungicide was accidentally ground into flour to make bread (Bakir *et al.*, 1973). These tragedies brought widespread public awareness of the neurological and developmental disorders that are caused by toxic doses of methylmercury. By the end of the 1970s most governments had responded by restricting industrial discharges of mercury and its compounds to water bodies. In Canada, particular attention was focused on discharges from chloralkali plants and pulp and paper mills. Later regulations reduced or eliminated the use of mercury compounds in agricultural chemicals, paper, paint and batteries.

There is now a growing concern about a different type of exposure: the chronic or long-term exposure to low levels of mercury that are commonly described as "background" concentrations. Thus, in the past decade, many researchers have turned their attention to mercury cycling in rural and remote areas, meaning ecosystems located hundreds or thousands of kilometres away from industrial point sources. Surveys indicate that mercury concentrations in fish of rural and remote lakes and hydroelectric reservoirs commonly exceed recommended consumption guidelines. In Ontario, for example,

consumption restrictions apply to several hundred lakes which are remote from industrial sources, as indicated in the *Guide to Eating Ontario Sport Fish* (OMEE/OMNR, 1993) which provides size-specific consumption advice for sport and game fish at more than 1600 locations across the province.

Concern about potential effects of chronic low-level exposure to mercury in the environment has focused public attention on atmospheric emissions and the potential for airborne mercury to travel long distances from industrial centers to rural and remote lakes (Mahoney, 1997; Spears, 1997). The major industrial sources of atmospheric mercury are fossil fuel combustion, waste incineration, smelting and manufacturing processes. Canada has achieved significant reductions in industrial releases through regulatory activities such as the *Chlor-Alkali Mercury Release Regulations* under the Canadian Environmental Protection Act (CEPA), and non-regulatory/voluntary activities such as the Accelerated Reduction/Elimination of Toxics (ARET) initiative. According to the National Pollutant Release Inventory (www.ec.gc.ca/pdb/npri.html), industrial emissions of mercury to the atmosphere in Canada have decreased about 49%, from 39 tonnes·a^{-1} in 1990 to 20 tonnes·a^{-1} in 1995. During the past year, the three NAFTA partners (Canada, the United States and Mexico) identified the need to improve existing mercury emissions inventories and to obtain unambiguous information on relative contributions from different sources. The resulting North American Regional Action Plan (NARAP), an undertaking that stems from the North American Agreement on Environmental Cooperation, may be accessed *via* the internet (www.cec.org).

As the quantity and quality of information on anthropogenic mercury releases improve, there is a growing recognition of the need to quantify the natural sources and pathways of mercury in the environment. Areas where mercury concentrations in biota are elevated due to local geological sources and biogeochemical cycling processes will always remain a public health concern. Governments will need to continue to identify such areas and communicate these findings to sport fishers, northern communities, land use planners and public health authorities. The purpose of this article is to highlight geoscience research needed to improve our understanding of the biogeochemical cycling of mercury species released from common sulphide minerals and other crustal sources into soil, sediments, air, water, vegetation and ultimately into the human food chain.

ENVIRONMENTAL PATHWAYS OF MERCURY EXPOSURE

Mercury accumulates in fish and marine mammals predominantly in the form of methylmercury (CH_3Hg^+). Much current research is focused on the biotic and abiotic processes that transform the mercuric ion (Hg^{2+}) into methylmercury, in particular factors controlling the rates of methylmercury production and decomposition, and on the toxicological effects of methylmercury consumption (Gilmour and Henry, 1991; Sellers *et al.*, 1996; Wiener and Spry, 1996; Pierce and Williams, 1997; Egeland and Middaugh, 1997). The production of methylmercury occurs in nature whether the source of the mercuric ion is anthropogenic (generated by human activity) or geogenic (arising from a geological source, such as weathering of sulphides). The mercuric ion is strongly sequestered by organic compounds in soils, sediments, and natural waters. Consequently, total mercury concentrations tend to correlate with organic matter concentrations in these media. In both freshwater and marine systems the mercuric ion may be reduced to elemental mercury (Hg^0). Under aerobic conditions, mercuric sulphide (HgS) undergoes chemical or microbial oxidation leading to the formation of elemental mercury, mercuric carbonates and hydroxides, or mercuric chlorides and sulphates. Elemental mercury also undergoes numerous chemical and physical changes within the soil, including co-precipitation, sorption and complexation, which change the proportions of volatilizable or easily extractable mercury and fixed forms.

The primary route of exposure of Canadians to methylmercury is food consumption, with fish and shellfish being the greatest contributors (Richardson *et al.*, 1995). Native people living a traditional lifestyle are potentially more vulnerable, owing to the fact that fish from lakes and streams, and sea mammals such as seals and whales, form a greater proportion of their diet (Wheatley and Paradis, 1995; Girard and Dumont, 1995).

In Canada, there is evidence of an overall reduction in human exposure to mercury over the past two decades, but the degree to which this trend can be attributed to the reduction in mercury releases to the environment is unknown. Wheatley and Paradis (1995) observed an overall downward trend in mercury concentrations in residents of First Nations communities across Canada, based on hair and blood data collected from 1974 to 1992. In this study the authors note that it is not clear whether the downward trend reflects decreased mercury concentrations in fish or a decrease in fish consumption. Richardson *et al.* (1995) estimated that the average Canadian adult ingests 3.93 micrograms (μg) of mercury per day, which is significantly less than earlier estimates of 10 μg per day to 16 μg per day reported in the literature of the 1970s (Richardson *et al.*, 1995, and references cited therein). While a decline in mercury pollution may be partly responsible for this apparent trend, Richardson *et al.* (1995) indicate that differences in methods for risk assessment and improved analytical techniques also contribute.

Scientists from the Department of Fisheries and Oceans (DFO) have observed distinct geographic trends in mercury and cadmium (Cd) concentrations in Canadian Arctic mammals, trends which suggest that natural occurrences of these two metals are the predominant sources for mercury and cadmium found in the Arctic food chain (Muir *et al.*, 1992; Wagemann *et al.*, 1995). Generally, higher mercury concentrations are found in ringed seals and in beluga whales in the western Canadian Arctic compared to the east. Evidence of temporal changes in mercury concentrations in the Arctic food chain remains contradictory, and there is a need for well-designed temporal trend studies using retrospective analyses of samples stored in tissue banks (Muir *et al.*, 1996, and references cited therein).

Research into geological sources of mercury has particular relevance to the environmental assessment of lands proposed for hydroelectric reservoir creation. The flooding of landscapes enriched in mercury due to local geological sources can lead to particularly high concentrations of mercury in fish. In British Columbia, for example, elevated concentrations of mercury in the fish of Williston Reservoir have been attributed to the adjacent mercuriferous Pinchi fault zone (Watson, 1992). In Manitoba, elevated concentrations in fish of the Churchill River Diversion have been attributed to the mobilization of mercury from volcanogenic sulphides (Rannie and Punter, 1987, in the Canada Manitoba Agreement, 1987). Based on their study of the Churchill River Diversion, Rannie and Punter (1987) rec-

ommended the use of soil and vegetation surveys to evaluate geological sources of mercury in assessing future reservoir development proposals. Elevated mercury concentrations in aquatic organisms may arise from flooding even in areas where mercury concentrations are naturally low, as it has been demonstrated that the immersion of soil and vegetation releases mercury into the aquatic ecosystem and creates conditions which favor methylation processes (Hecky *et al.*,1987; Morrison and Thérien, 1991).

NATURAL SPATIAL VARIATIONS REVEALED BY REGIONAL GEOCHEMICAL SURVEYS

Research in a variety of geological settings across Canada has shown that physical and chemical weathering and erosion of bedrock, glacial deposits and soil enriched in mercury ultimately increases the mercury load to lakes and streams (Hornbrook and Jonasson, 1971; Allan *et al.*, 1974; Jonasson, 1976; Rasmussen, 1993; Painter *et al.*, 1994; Cook and Jackaman, 1994; Richardson, 1994; Friske and Coker, 1995; Coker *et al.*, 1995; Shilts and Coker, 1995; Cook *et al.*, 1996; Sibbick and Laurus, 1995; Kettles *et al.*, 1997). Thus, regional geochemical data can provide useful preliminary information about areas where geological sources of mercury might lead to elevated levels of mercury in fish and other wildlife. For example, a study of mercury distribution in the Muskoka-Haliburton region of Ontario indicates wide variation in sediment mercury concentrations (from <5 ppb to >450 ppb) among lakes in close proximity, comparable to the variation reported for lakes across the whole of Canada (Rasmussen *et al.*, 1998a). In this area, the spatial pattern of mercury concentrations in pre-colonial lake sediments (>800 years before present) mirrors the pattern of mercury concentrations in modern surface sediments (*i.e.*, the *Ambrosia* horizon). This observation is supported by a strong positive correlation between mercury contents of pre-colonial and modern sediments of 25 lakes (R^2 = 0.85), indicating that natural processes govern the unequal distribution of Hg among the lakes. Sediment mercury concentrations normalized to organic carbon (Hg/C) are also reflected by mercury concentrations in smallmouth bass (R^2 = 0.63; n = 15 lakes). These relationships show that, in this watershed system, smallmouth bass and lake sediment indicators provide mutually supportive information regarding mercury loading to the lacustrine environment from natural sources (Rasmussen, 1993; Rasmussen *et al.*, 1998a).

The National Geochemical Reconnaissance (NGR) is a compilation of lake sediment, stream sediment, and surface water surveys completed by the Geological Survey of Canada (GSC) in co-operation with provincial and territorial geological survey organizations (Friske and Horn-

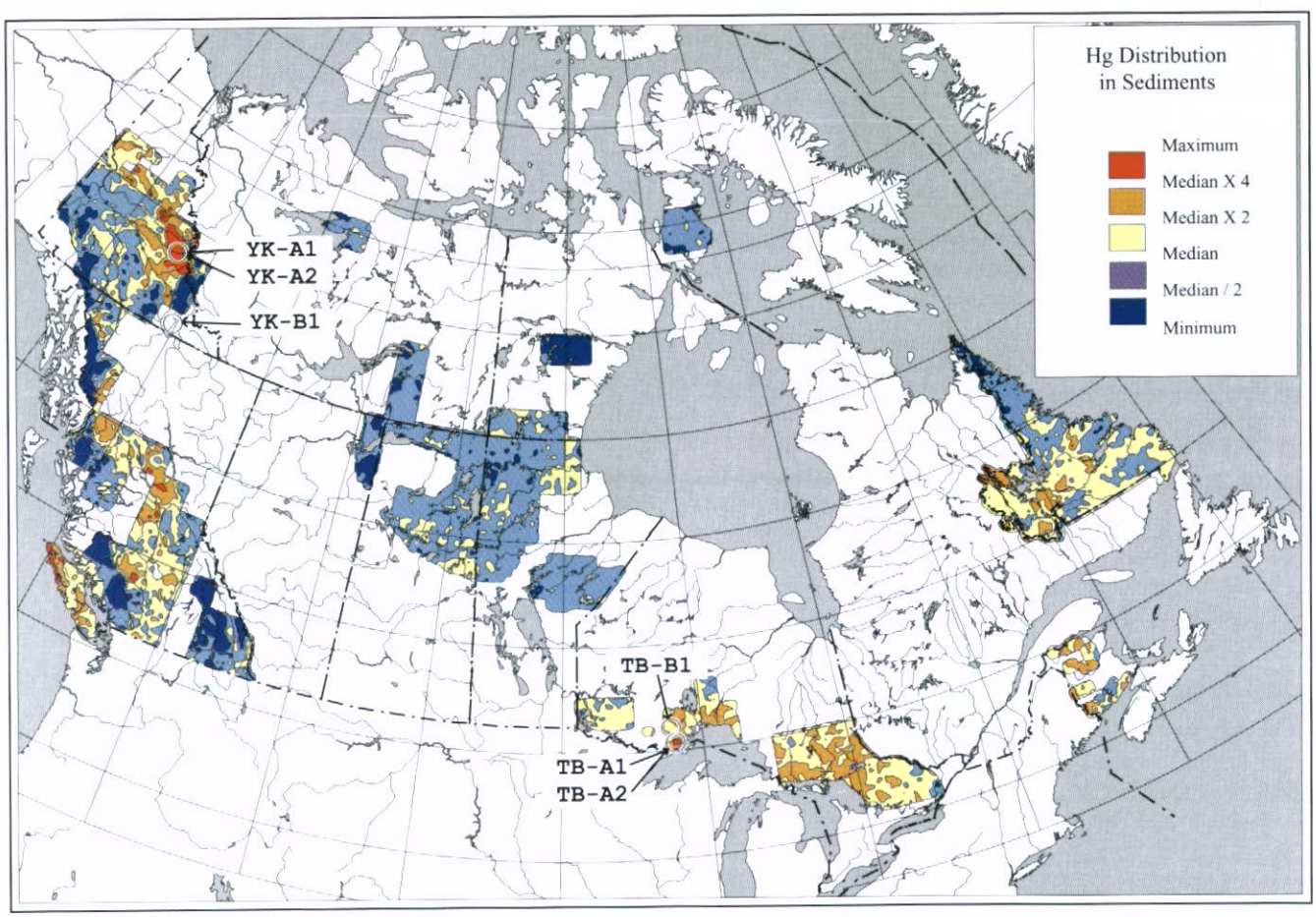

Figure 1 Smoothed contour map of National Geochemical Reconnaissance (NGR) data from across Canada. Refer to Table 1 for maximum, median and minimum values. The "median" is the 50th percentile in Table 1 (40 ppb for stream sediments and 60 ppb for lake sediments). The contours were calculated by converting the raw data (Table 1) to $\log_{10}$ values, interpolating to a 2.5 km^2 grid, and smoothing using an IDW function. Lake sediments are collected from 10-20 cm below the sediment-water interface; see Friske and Hornbrook (1991) for further description of the NGR survey methodology.

brook, 1991). To date, about 200 surveys have been completed consisting of more than 185,000 sites covering 2.2 million km² of Canada. The development of the NGR analytical protocol for the routine determination of mercury in sediments (acid digestion and cold-vapor AAS) included interlaboratory comparisons by the GSC and Environment Canada (John Lynch, unpublished data). Mercury data have been collected systematically since 1980 and are now available for about 75% of the total NGR data base. The mercury data acquired to 1995 are presented in Figure 1 as a geochemical map.

Stream sediment coverage shown in Figure 1 (61,744 samples) is restricted to Yukon, British Columbia, New Brunswick and the Torngat Mountain region of northern Labrador. Lake sediment coverage (76,072 samples) is largely confined to the Canadian Shield and includes parts of Baffin Island, Manitoba, Saskatchewan, Ontario and Labrador. The contour intervals for the map (Fig. 1) are referenced to the median values (50th percentile) of the lake and stream sediment data provided in Table 1. In other words, the red areas in Figure 1 indicate mercury concentrations above 240 ppb for lake sediments, and above 160 ppb for stream sediments. The blue areas in Figure 1 indicate mercury concentrations below 30 ppb for lake sediments, and below 20 ppb for stream sediments. Assuming that the 5th and 95th percentiles are reasonable estimates of background variation, the contrast between lower and upper limits of variation is almost nine-fold for lake sediments (5th = 20 ppb; 95th = 175 ppb), and almost 20-fold for stream sediments (5th = 10 ppb; 95th = 199 ppb).

Although the NGR coverage of Canada is far from complete, the areas surveyed to date (Fig. 1) indicate that there are large regions characterized by elevated mercury concentrations in lake and stream sediments. The surveys are not evenly distributed across Canada and tend to be located in remote areas far from major population centres, where the NGR sampling protocol is applicable. The stream sediments are collected at sites removed from obvious contamination sources and stream bank slumps. The lake sediments are collected from 10-20 cm below the sediment-water interface to selectively sample sediment that is uninfluenced by recent diagenetic processes or human activity. By following this protocol the geochemistry of the lake catchments becomes the major controlling factor on the geochemical patterns observed in the surveys, as discussed previously by Painter *et al.* (1994) and Friske and Coker (1995).

According to the *Canadian Sediment Quality Guidelines for Mercury* (Environment Canada, 1997) the "threshold effect level" for freshwater sediment is 174 ppb (dry weight). The threshold effect level, which is defined as the concentration below which toxicological effects are expected to occur rarely, corresponds with the 94th percentile of the lake sediment NGR data. The *Guidelines* also provide a "probable effect level" of 486 ppb (corresponding to the 99.55th percentile of the NGR data), which represents the concentration of mercury in sediments above which toxicological effects are expected to occur frequently. These guidelines are for total mercury concentrations as quantified by digestion with a strong acid (*e.g.*, aqua regia). The report notes that these are interim guidelines due to the absence of sufficient spiked sediment toxicity test data. Background information and the rationale for the derivation of the guidelines are provided in Environment Canada (1997) and CCME (1995). The guidelines have not been formulated for organomercury species (methylmercury compounds) owing to a paucity of data that associates toxicological effects with concentrations of organomercurials in lake sediments (Environment Canada, 1997).

Two areas in Canada where natural sediment mercury concentrations exceed the *Canadian Sediment Quality Guide-*

Table 1 Mercury concentration (ppb) summary statistics for lake and stream sediment data from the National Geochemical Reconnaissance (NGR) data base.

	Streams	***Lake***
Number of Values	61,744	76,072
Mean	75*	74
Std Deviation	478	96
Minimum Value	<10	<10
5th Percentile	**10**	**20**
10th Percentile	10	27
25th Percentile	23	40
50th Percentile	**40**	**60**
75th Percentile	80	90
90th Percentile	135	140
95th Percentile	**199**	**175**
98th Percentile	320	220
Maximum Value	>10,0000	21,000

*Detection limit 10.0 ppb. Values <10.0 set to 5.0 for calculations.

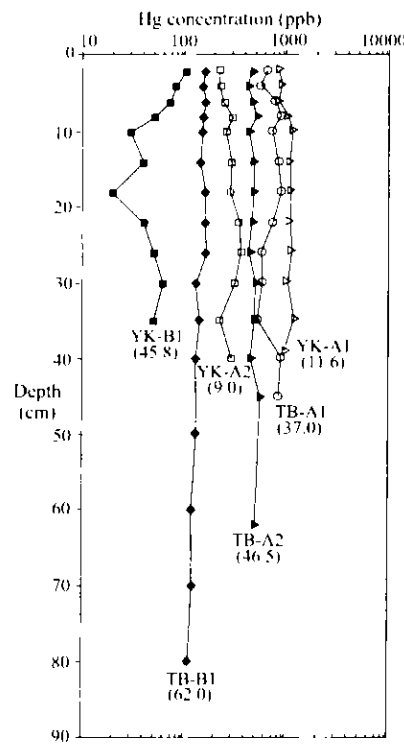

Figure 2 Vertical profiles of mercury concentration (ppb) in lake sediment cores collected in the Yukon (YK) and northwestern Ontario (TB). Values in brackets are LOI (loss-on-ignition at 500°C) averaged for all depths in each core. The sediment-water interface is at 0 cm depth. Locations are shown in Figure 1.

lines for Mercury are indicated in Figure 1: one within the Road River and Earn Groups of the Selwyn Basin, east-central Yukon (YK), and the other within the Animikie Group, west of Thunder Bay, Ontario (TB). The Selwyn Basin is an elongate fault-controlled epicratonic marine basin, in places consisting of highly carbonaceous black shale (Goodfellow, 1989; Gordey and Anderson, 1993). Prominent mercury anomalies in stream sediments within the Selwyn Basin are related to high mercury levels in the black shales, and also to extensive base metal sulphide mineralization in Cambrian to Mississippian bedrock sequences (Bonham-Carter and Goodfellow, 1986; Painter *et al.*,1994). This anomaly (YK; Fig. 1) covers an area of about 5200 km^2, and is based on 1148 sampling sites out of which 955 sites exceed the "threshold effect level", and 142 sites exceed the "probable effect level." A follow-up study undertaken in 1995 determined that the mercury enrichment is also reflected in lake sediments in this area. For example, Figure 2 compares mercury concentration profiles for sediment cores collected from three Yukon lakes: two sites within the YK anomaly in the Itsi Lakes region of the Selwyn Basin (YK-A1 and YK-A2) and one background site located outside the Selwyn Basin (YK-B1) in Watson Lake, which is about 300 km to the south-southeast. Mercury concentrations in coreYK-A1 from the Selwyn Basin are more than 10 times higher than concentrations in the background core (YK-B1; Fig. 2), and are more than twice as high as the "probable effect level" of 486 ppb.

The mercury anomaly west of Thunder Bay, Ontario (TB; Fig. 1) is attributed to mercury concentrations in the early Proterozoic Rove and Gunflint Formations of the Animikie Group. This anomaly covers an area of about 295 km^2, and is based on samples from 22 lakes, out of which 21 sites exceed the "threshold effect level," and four sites exceed the "probable effect level." Mercury concentration profiles obtained by follow-up lake sediment coring are displayed in Figure 2. Two cores were collected within the anomalous area in the vicinity of Oliver Lake (TB-A1, TB-A2; Fig. 2). The anomalous area is underlain by the black (carbonaceous) Rove shale which extends across the Canada-United States border into Minnesota (Geul, 1970). A background core (TB-B1; Fig. 2) was collected from Adrian Lake about 25 km to the northwest, in an area underlain by Archean metavolcanics of the Wawa Subprovince of the Superior Province (Rogers and Berger, 1995). Concentrations of mercury and other elements (Zn, As and Cd) are enriched in bedrock and stream sediments collected in the anomalous area compared to those collected in the background area (Table 2). As indicated above, relative enrichments of trace metals are common in carbonaceous shales such as the Rove Formation (Table 2) and in stream and lake sediments derived from carbonaceous shale parent material (as shown in Table 2 and Fig. 2). Note that mercury concentrations in both sediment cores collected from within the anomalous area (TB-A1 and TB-A2; Fig. 2) exceed the "probable effect level" of 486 ppb.

As noted above, a significant positive relationship between organic carbon content and total mercury is commonly reported in sediments, due to the strong affinity of the mercuric ion for organic substances. This relationship may be investigated for lake sediments across Canada using the NGR data base (Fig. 3), where the organic content of the lake sediments is estimated by determining the loss-on-ignition (LOI) at 500°C (Sheldrick, 1984). For sediments containing up to about 40-50% LOI, which corresponds to 79% of the total data set, median mercury concentrations increase with increasing LOI by a factor of 2.7. If the sediment data up to 50-60% LOI are included (corresponding to 89% of the total data set), the trend is for mercury concentrations to increase to 30% LOI and then plateau at an average of 74 ppb, a factor of 2.5 increase over the 1-10% LOI median level of 30 ppb. The implication of this finding is that whereas comparisons of mercury contents in lake sediments containing 30-60% LOI may be made with some confidence, comparisons to and between lake sediments containing less than 30% LOI need to be made with care, recognizing the matrix effect that the organics, as estimated by LOI, exert on the mercury contents. Failure to take this natural adsorption phenomenon into account can lead to misleading or incomplete interpretations of the processes that control mercury distribution in lake sediments.

INFLUENCES ON REGIONAL MERCURY DISTRIBUTION PATTERNS

Natural variations in mercury contents are caused by a combination of geological,

Table 2 Concentrations of mercury (Hg), zinc (Zn), arsenic (As) and cadmium (Cd) in stream sediment and bedrock samples from the "anomalous" area (Proterozoic Rove Formation) and "background" area (Archean metavolcanics) in the Thunder Bay area.

Anomalous Area	*Hg (ppb)*	*Zn (ppm)*	*As (ppm)*	*Cd (ppm)*
Stream sediment	**323**	**329**	**38**	**1.2**
(N=7)	(170 - 900)	(251 - 590)	(19 - 88)	(0.7 - 2.1)
Bedrock	**537**	**234**	**30**	**0.6**
(N=3)	(90 - 1390)	(159 - 280)	(7 - 56)	(0.2 - 1.0)

Background Area	*Hg (ppb)*	*Zn (ppm)*	*As (ppm)*	*Cd (ppm)*
Stream sediment	**35**	**140**	**12**	**0.2**
(N=4)	(20 - 60)	(127 - 168)	(7 - 28)	(<0.2 - 0.3)
Bedrock	**<10**	**111**	**5**	**0.2**
(N=3)	(all <10)	(94 - 122)	(1 - 14)	(<0.2 - 0.3)

climatic and topographic influences. The strong positive relationship between organic carbon and total mercury at the regional scale (Fig. 3) demonstrates that the interpretation of regional distribution patterns requires knowledge of mercury accumulation processes in a wide geographic and latitudinal range of environments. Vegetation is also a key pathway through which mercury enters the food chain from geological sources (Jonasson and Boyle, 1979; Siegel *et al.*, 1985; Rasmussen *et al.*, 1991; Rasmussen, 1994a; 1995; Moore *et al.*, 1995). The fact that many plant species readily accumulate mercury means that changes in vegetation type and density are an important influence on regional distribution patterns.

Bedrock Influences

The above examples of natural regional-scale anomalies (Fig. 1) illustrate certain factors that are particularly important in evaluating the natural distribution of mercury in the environment: the bedrock lithology and age, and the abundance of sulphide mineralization. In general, black shales tend to have elevated concentrations of mercury and other trace metals (Reichenbach, 1993); particularly pyritic types of early Proterozoic age (Cameron and Jonasson, 1972). The pyrite content is important because it provides a mobilizing leachate upon exposure and oxidation. Jonasson and Sangster (1974) noted that sulphide deposits of Proterozoic age also have higher mercury contents than their Phanerozoic and Archean counterparts. They compiled a map showing regions of Canada where elevated mercury contents might be inferred in the surface environment based on the widespread distribution of mercury-bearing sphalerite (ZnS). A comparison of the current NGR map (Fig. 1) with their 1974 compilation indicates that, at a regional scale, elevated mercury concentrations in pre-industrial lake sediments in several regions of Canada, notably British Columbia, Yukon, Ontario and Labrador can be related to the distribution of mercury-bearing sulphides, mainly sphalerite. The only major cinnabar (HgS) occurrences in Canada are in British Columbia, although cinnabar is also associated with some Ontario deposits such as Hemlo and minor occurrences at Clyde Forks. The most important inference is that natural background concentrations of mercury are determined not just by the distribution of cinnabar deposits, as is sometimes assumed, but rather by the presence of mercury in variable amounts in a number of more common geological materials.

Glacial History

In many parts of Canada, an overriding influence on the distribution of trace metals, including mercury, is the glacial history and the geochemical makeup of the deposited glacial debris. When ice sheets moved across the North American land-

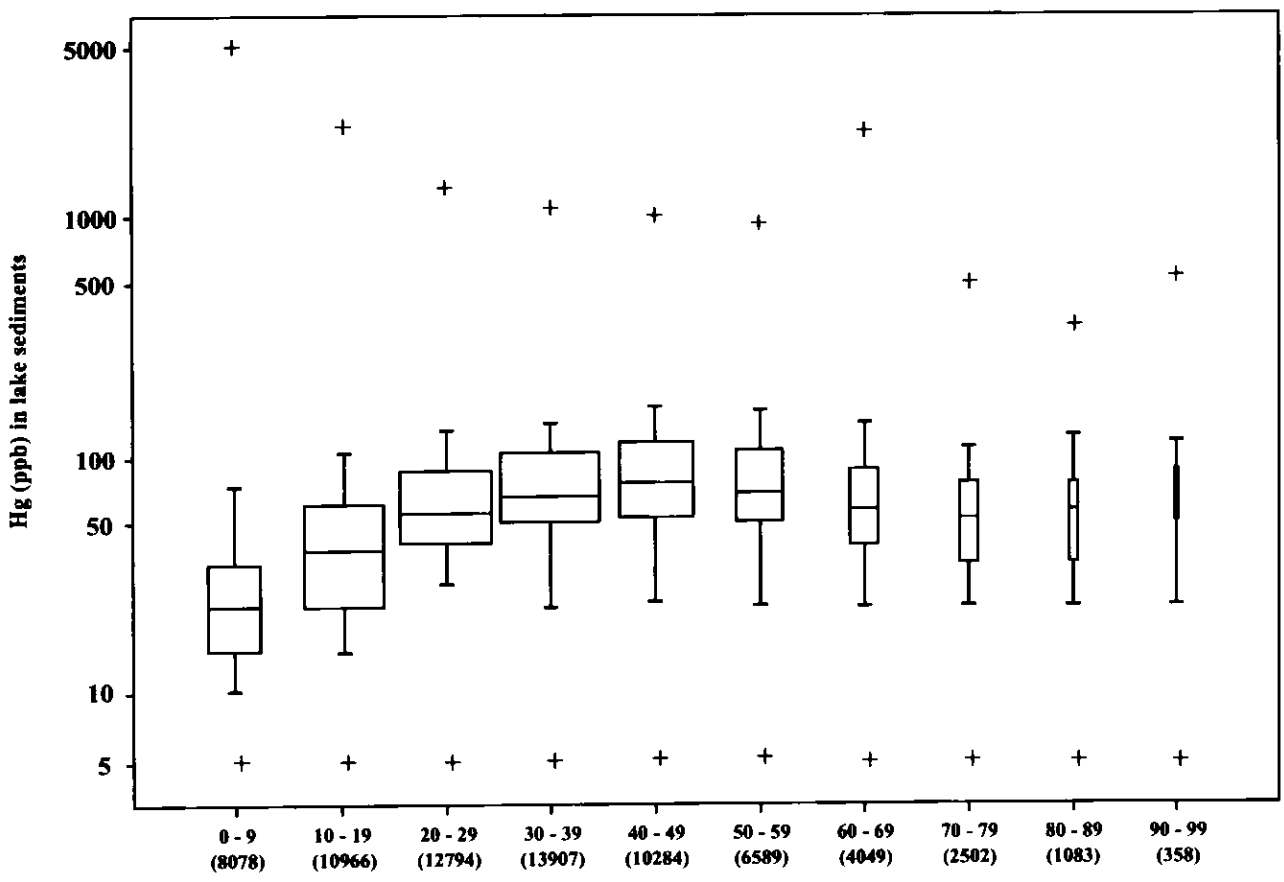

Figure 3 Relationship between Hg and organic matter (loss-on-ignition) in lakes sampled in the National Geochemical Reconnaissance Programme. The boxes represent the middle 50% of the data for each of the 10% intervals of LOI content starting at zero (*i.e.*, 0-9.99%, 10.00-19.99%, 20.00-29.99%, *etc.*) The bar inside each box indicates the median of the data; the whiskers extend to the 5th and 95th percentiles; and the crosses represent the minimum and maximum values.

scape, they eroded and pulverized the underlying bedrock, leaving behind deposits of chemically reactive clay, silt and sand. This means that, in some areas, the distribution pattern of mercury in the unconsolidated surface material may be substantially different from a distribution pattern that might be predicted from bedrock geology alone. In central British Columbia, for example, Plouffe (in press) reported significant detrital glacial transport of mercury eastward from the Pinchi fault zone. Based on heavy mineral analysis, he defined a dispersal train of mercury-enriched drift at least 24 km in length. Similar geochemical surveys such as those of Kettles and Shilts (1994), Henderson and McMartin (1995), Plouffe (1995), Parent *et al.* (1995b, 1996) and McMartin *et al.* (1996) indicate the complexity of natural and anthropogenic mercury occurrences in unconsolidated materials of the terrestrial environment. Such data sets have wide and sometimes unexpected applications. An assessment of Canadian exposure to mercury in household dust, for example, was based on surveys of mercury concentrations in the fine fraction (<2 μm) of glacial deposits of southern Ontario, which have a geometric mean of 0.060 ppm for 1684 sites (Richardson *et al.*, 1995, citing data of Kettles and Shilts, 1994).

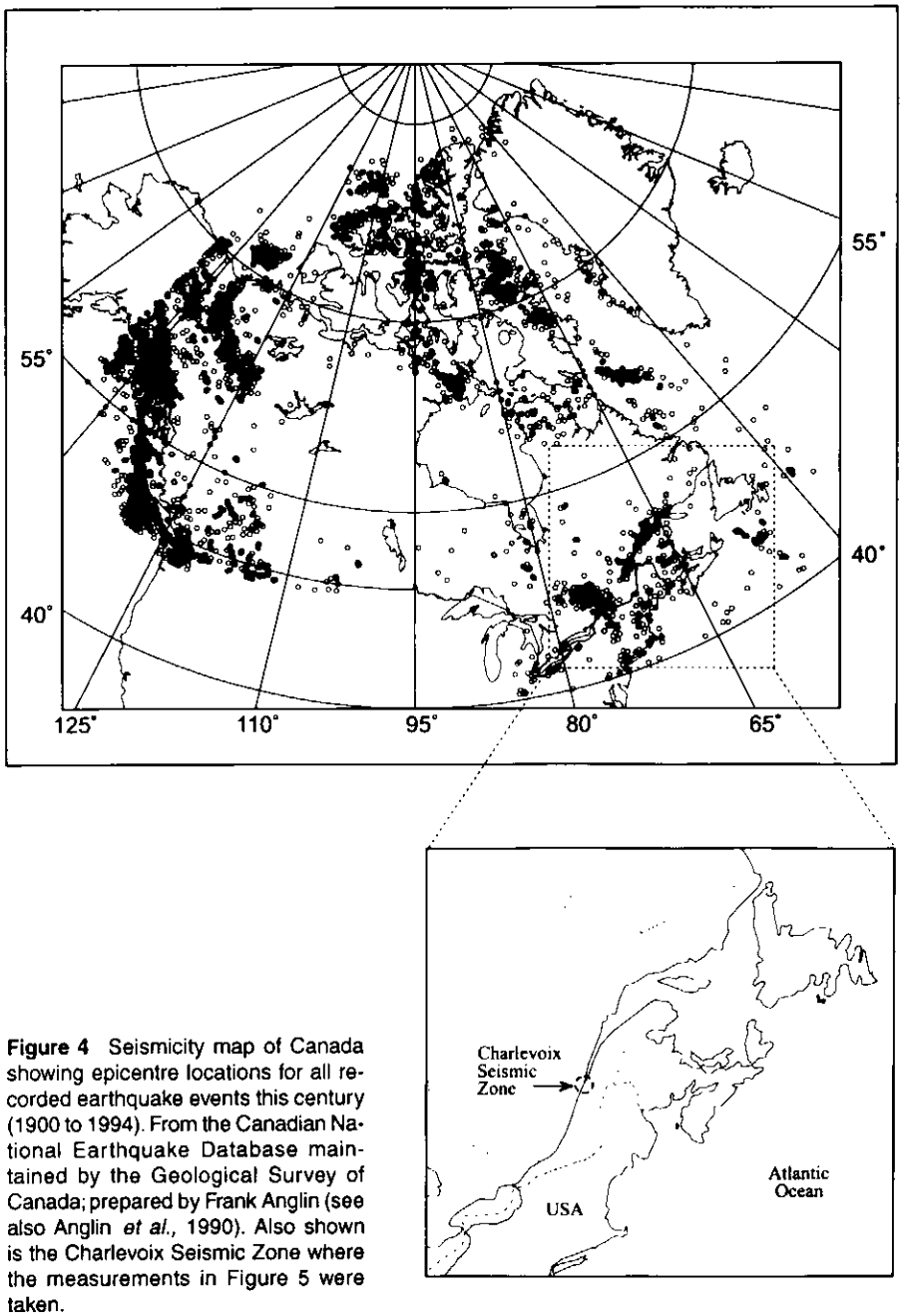

Figure 4 Seismicity map of Canada showing epicentre locations for all recorded earthquake events this century (1900 to 1994). From the Canadian National Earthquake Database maintained by the Geological Survey of Canada; prepared by Frank Anglin (see also Anglin *et al.*, 1990). Also shown is the Charlevoix Seismic Zone where the measurements in Figure 5 were taken.

Tectonic Setting

Natural mercury concentrations are also determined by a number of factors related to the tectonic setting, including bedrock structure, crustal heat flow, and seismic activity. Elevated mercury concentrations in soil are associated with geothermal hotspots in western North America (Openshaw, 1983; Kodosky, 1989; Priest *et al.*, 1983). A risk assessment conducted in Oregon showed that human exposure to lithogenic mercury occurs through consumption of fish containing elevated mercury from geothermal sources (Dunnette, 1988). Even in "background" areas, meaning non-mineralized areas with low crustal heat flow, groundwater transport along permeable zones created by bedrock faults and fractures is an important mechanism for the transport of mercury to the surface environment. For example, in a study of a pristine granitic area of coastal Maine, Sidle (1993) showed that a system of bedrock faults and fractures resulted in elevated mercury concentrations in about 19% of sampled residential water wells (*i.e.*, above the EPA maximum contaminant level of 2 $\mu g \cdot L^{-1}$. Studies in eastern Canada also indicate that mercury enrichment related to fault systems is not necessarily related to sulphide mineralization (Azzaria and Carrier, 1976; Debicki, 1982; Azzaria, 1992; and Rasmussen, 1993).

Seismic Activity

Elemental mercury is known to migrate from depth to the earth's surface during earthquake activity, a phenomenon that has been researched in Russia and China as a potential method for predicting earthquakes (Varshal *et al.*, 1985; Jin *et al.*, 1989). Some areas of Canada where earthquakes tend to occur frequently, such as Vancouver Island and eastern Yukon (Fig. 4), also tend to have elevated concentrations of mercury in sediments (Fig. 1), although long-term mercury vapor monitoring would be required to establish a causal relationship. The only Canadian study of this kind was conducted in Quebec by Azzaria (1988, 1989, 1990). On 25 November 1988, Azzaria happened to be working in the Charlevoix seismic zone (CSZ), and was in the process of setting up his equipment to sample mercury vapor in soil air when the Saguenay earthquake (magnitude 6) occurred. Azzaria started his measurements about four hours after the quake, and continued for a period of nine months (Fig. 5), observing significant temporal increases related to the Saguenay quake and two other

Charlevoix earthquakes of 9 and 11 March 1989 with magnitudes of 4.3 and 4.4, respectively (Wetmiller and Adams, 1990). The CSZ is located about 100 km northeast of Quebec City along the St. Lawrence River valley (Fig. 4), and is characterized by buried faults and seismic activity. The Saguenay earthquake (epicentre 48.12° north, 71.19° west), located about 70 km northwest of the CSZ, is the largest earthquake to occur in eastern North America since 1935 and is twice as deep (29 km) as most previously studied earthquakes in this region (Lamontagne *et al.*, 1990). During aftershocks immediately following the Saguenay earthquake, mercury vapor concentrations in soil air increased to 205 ng·m^{-3} from a background of <5 ng·m^{-3} (Fig. 5). Mercury concentrations remained elevated for about three weeks following the Saguenay earthquake. Following the two Charlevoix earthquakes, mercury concentrations in soil air reached a maximum of 80 ng·m^{-3} (Fig. 5). These observations demonstrate that tectonic stability is an important factor in the interpretation of temporal and spatial variations of mercury in the environment.

THE CHALLENGE OF DISTINGUISHING AMONG VARIOUS SOURCES OF MERCURY

As noted in a recent United States Environmental Protection Agency (EPA) study (Gubala *et al.*, 1995), the highly variable background concentrations of mercury and other metals found in the bedrock and soils of remote Arctic regions make it difficult, if not impossible, to isolate and describe the phenomenon of long range atmospheric transport. Similarly, Wagemann *et al.* (1995) observed that as mercury is not introduced into the environment

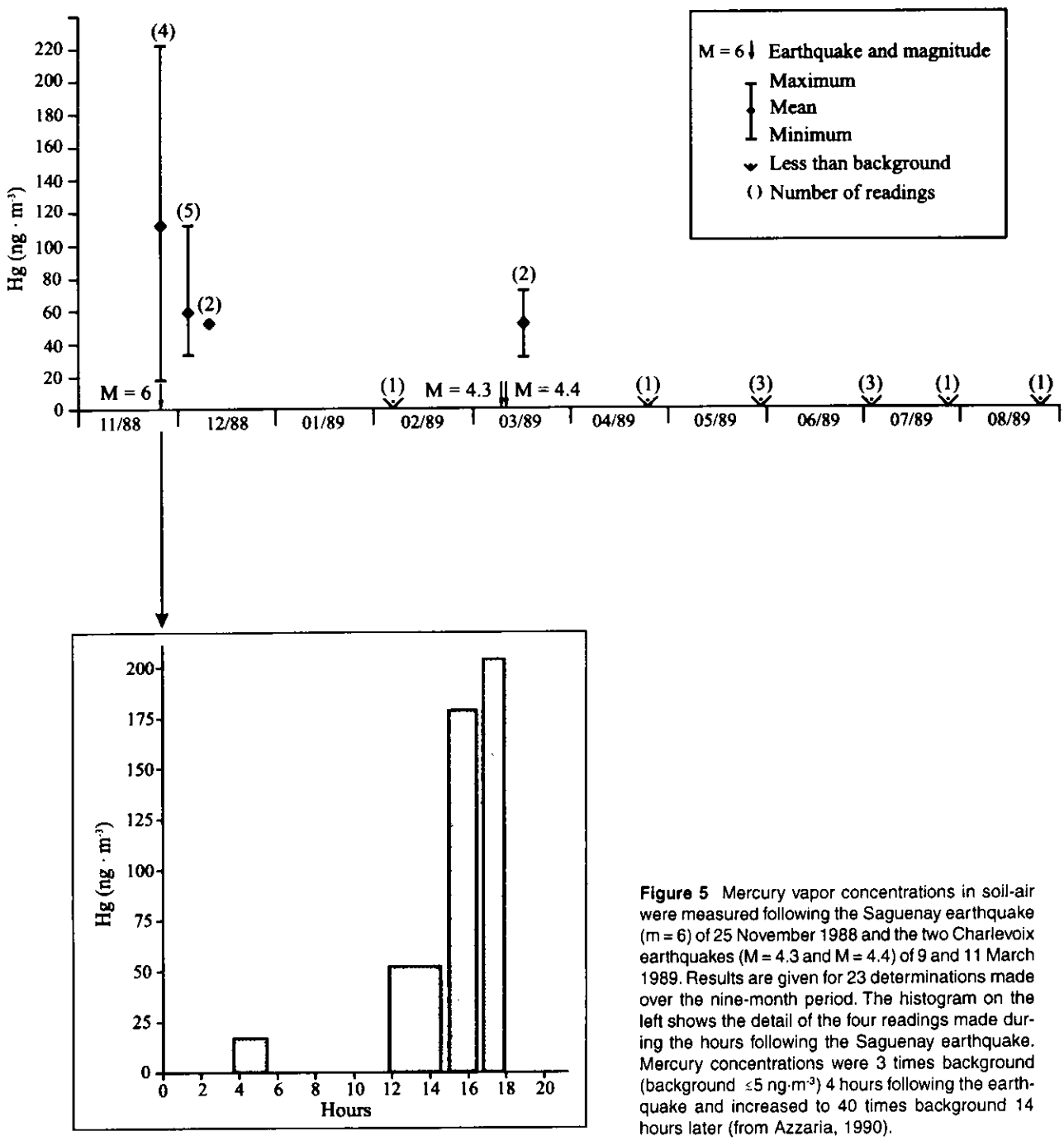

Figure 5 Mercury vapor concentrations in soil-air were measured following the Saguenay earthquake (m = 6) of 25 November 1988 and the two Charlevoix earthquakes (M = 4.3 and M = 4.4) of 9 and 11 March 1989. Results are given for 23 determinations made over the nine-month period. The histogram on the left shows the detail of the four readings made during the hours following the Saguenay earthquake. Mercury concentrations were 3 times background (background ≤5 ng·m^{-3}) 4 hours following the earthquake and increased to 40 times background 14 hours later (from Azzaria, 1990).

exclusively by human activity, it is very difficult to quantify the anthropogenic component.

An underlying cause for such uncertainty is the technical difficulty in distinguishing among the various sources of metals in rural and remote areas. Currently, there is no direct method available for fingerprinting sources of elemental mercury (Hg^0) in the atmosphere, such as the isotopic methods used to distinguish SO_x sources. From the 1960s to the present various instrumental techniques have been used to document elevated concentrations of Hg^0 in the air above both natural and industrial sources, but these studies rely only on observations of increased concentration with proximity to the source to derive clues about the derivation of the Hg^0. The same uncertainty is associated with attempts to determine the sources of methylmercury (CH_3Hg^+) in fish and other biota of remote watershed systems. Methylation and demethylation reactions occur whether the reactant Hg^{2+} ion is derived from the chemical weathering of sulphides or from precipitation: hence, the mere presence of methylmercury in biota of remote ecosytems reveals nothing about its source.

Henderson and McMartin (1995) and McMartin *et al.* (1996) evaluated both atmospheric fall-out and natural variations in background mercury concentrations in a detailed survey of the mercury concentration gradient around a smelter in Flin Flon, Manitoba, using humus and C horizon samples collected from more than 1400 sites in Manitoba and Saskatchewan. Results indicate a large circular "bulls-eye" mercury anomaly around the smelter, having a radius of about 40 km, with smelter-related mercury concentrations becoming indistinguishable from natural background concentrations at less than 100 km from the stack (Henderson and McMartin, 1995; Bonham-Carter and McMartin, 1997). Although the distance of atmospheric transport of significant amounts of mercury and other trace metals is currently a subject of debate (Rasmussen, in press; Jackson, 1997; Fitzgerald *et al.*, 1998), the Flin Flon study supports earlier conclusions that mercury emissions remain airborne for distances in the order of tens of kilometres (Lockeretz, 1974).

With increasing distance from industrial point sources, the proportion of airborne mercury arising from other sources increases, including windblown dust, volcanic emissions and passive crustal degassing, forest fire debris and biological particles such as waxes and pollen (Nriagu, 1989; IPCS, 1989). The existing Canadian natural mercury emissions inventory (EPS, 1981) estimated that the annual flux of mercury to the atmosphere from natural sources was about 3500 tonnes·a^{-1} for Canada. The authors indicated, however, that this estimate only included elemental mercury (Hg^0) and not particulate fluxes, and that it was only an order-of-magnitude approximation serving to provide a framework within which new data may be incorporated (EPS, 1981). To address this need, scientists from the University of Guelph, the GSC and Atmospheric Environment Service are collaborating in field-based research to measure natural Hg^0 emissions from rocks, soils and till in a variety of geological settings. Preliminary results for five contrasting geochemical settings in Canada and the United States indicate a strong positive relationship between Hg^0 flux and total Hg concentrations in the substrate (Rasmussen *et al.*, 1998b).

Compared to the large body of literature that is emerging on atmospheric inputs to lake systems, there is a relative lack of research into methods of quantifying aqueous inputs of mercury from natural watershed sources — plant debris, soil, glacial deposits, and bedrock — in remote ecosystems. Ten years ago, Rannie and Punter (1987) remarked on the gap in understanding of the pathways through which mercury moves from geological sources to the aquatic ecosystem. About 10 years before that, Azzaria and Habashi (1976) expressed similar concerns regarding the lack of research on natural inputs of mercury to lakes. In the 1970s, at the time of their review article, some rivers and lakes in Ontario had been closed to fishing due to industrial mercury pollution. At the same time, the issue of geological sources of mercury was emerging, to the point that the subject was often raised in the Canadian Parliament. By documenting the nature and frequency of these Parliamentary debates, Azzaria (1996) emphasized the importance of ensuring that policy decisions are based on sound scientific data. Even though he and other scientists had identified the lack of basic information on natural sources in northern Quebec (Azzaria and Habashi, 1976), more than 20 years later the relative importance of natural and anthropogenic sources of mercury in this region remains a subject of debate (Girard and Dumont, 1995). While recent GSC studies have determined that the relative enrichment of mercury in the B horizon of till-derived soils in northern Quebec results from biogeochemical (pedogenic) cycling, the question remains whether the soil mercury is derived predominately from long-range atmospheric transport or from local till and bedrock sources (Parent *et al.*, 1995a).

Until the geogenic component of mercury in remote ecosystems is quantified, the relative significance of atmospheric loading will remain unknown. To address this information gap, methods are needed to translate regional mercury concentration data, such as the survey data maintained in the GSC geochemical data bases, into annual flux estimates. This will require additional detailed studies identifying and quantifying the pathways through which mercury enters aquatic systems from glacial drift and bedrock sources. Confusion has arisen from the common misconception that mercury associated with the organic fraction of soils and sediments is derived solely from atmospheric deposition. In a critical review of atmospheric flux models in remote areas, Rasmussen (1994b) traced this misconception to the assumption that inorganic mercury species derived from geological sources are confined to the mineral fraction of soil and sediments and are thus immobile and biologically unavailable. In fact, enrichment of mercury in organic matter may be due to a combination of sources and processes, including accumulation in the original plant tissue during the plant's life, release of mercury from minerals through interaction with dissolved organic matter in the weathering zone, and adsorption onto particulate organic matter. This natural partitioning behavior of mercury (and other trace metals) is so complex that it is often impossible to distinguish natural and anthropogenic inputs on the basis of chemical extractions alone.

Central to this debate is the need to determine the influence of diagenesis on mercury concentration profiles in lake sediments. Mercury concentrations in surface sediments of rural and remote lakes (located hundreds or thousands of kilometres from industrial sources) commonly exceed mercury concentrations in deep sediments by a factor of two to five (an example is profileYK-B1; Fig. 2). This phenomenon is widely interpreted as evidence of a two- to five-fold increase in atmospheric loading at the continental or global scale since the onset of industrial

activity. This interpretation is based on the premise that the surface enrichment observed in sediments of remote lakes reflects anthropogenic input and does not arise from natural processes. Based on this interpretation of lake sediment profiles, a number of researchers have concluded that long-range atmospheric transport is the chief source of mercury in remote lakes and hydroelectric reservoirs in Canada (Lockhart *et al.*, 1995; Lucotte *et al.*, 1995; Jackson, 1997 and references cited therein). However, Matty and Long (1995) have demonstrated that diagenetic processes may increase the mercury content of the upper layers of sediment, and caution that if these natural processes significantly alter sediment profiles of mercury, reconstructions of input histories based on mercury profiles could be inaccurate. In the above-mentioned study of multiple sediment cores collected from 25 lakes in the Muskoka-Haliburton region of Ontario, Rasmussen *et al.* (in press) found that the surface-to-deep mercury concentration ratio is about the same for all the lakes despite the variation in mercury concentrations among the lakes, an observation which is not adequately explained by the atmospheric loading model. Instead, similarities between the shape of vertical mercury profiles and vertical LOI profiles, and a lack of correlation between mercury concentrations and sedimentation rates, suggest that the decrease in mercury content down the sediment cores may be related to compositional changes in organic matter during decay. The authors conclude that, in this area at least, the two-to-five fold surface enrichment phenomenon is more consistent with a diagenetic model than with an atmospheric source model (Rasmussen *et al.*, in press). To address these differences in interpretation, a symposium is being held at the 1998 Geological Association of Canada-Mineralogical Association of Canada Annual Meeting in Quebec City, entitled "Diagenesis and remobilization of metals in sediments: effects on vertical concentration profiles."

IMPLICATIONS OF RESEARCH INTO NATURAL SOURCES OF MERCURY

The recognition of the natural variability of mercury and other metals in the environment has at least two important implications. First, different approaches are necessary for the monitoring and modelling of substances such as mercury which have both natural and anthropogenic sources, in contrast to synthetic substances which are solely anthropogenic in origin. There is a lack of simple, reliable methods for distinguishing the origin of mercury observed in remote areas, which has resulted in a confusing and complicated literature. Certainly, to obtain unambiguous information on relative contributions from different anthropogenic and natural sources, mercury releases/emissions need to be monitored at their source. This should ensure that regulatory actions will be well-targeted and result in a measurable improvement in the amount of mercury anthropogenically released to the environment.

Second, research into natural mercury occurrences has important implications for public health, particularly in remote areas where indigenous peoples depend on fish as a dietary staple. A number of North American studies have demonstrated that elevated concentrations of mercury in fish may be attributable to local geological sources, even in the absence of known sulphide mineralization in a given watershed system (Canada-Manitoba Agreement, 1987; Dunette, 1988; Rasmussen, 1993; Shilts and Coker, 1995; Rasmussen *et al.*, in press). Although recent media reports on mercury have tended to overlook natural sources, some practical advice emerges from this research: certain lakes will have high mercury concentrations owing to local geological sources, and the fish from such lakes should be tested to determine if their consumption should be limited according to health guidelines. As discussed above, understanding geological sources of mercury is particularly relevant to the assessment of land slated for hydroelectric reservoir development. Clarifying these issues will require governments to systematically identify areas where natural sources cause elevated mercury concentrations in wildlife and to communicate these findings to land use planners and public health authorities.

Of fundamental importance is the need to determine more precisely what risks are represented by low-level chronic exposure to mercury (Dumont, 1996; Egeland and Middaugh, 1997). The World Health Organization has determined that the general population does not face a significant health risk from long-term methylmercury exposure (references cited in OECD, 1994). It is only within groups having high rates of fish consumption that individuals may acquire an elevated body burden (hair or blood mercury concentrations) and where the dose-response relationship becomes unclear. Dumont (1996) and Egeland and Middaugh (1997) warn of the risks involved in giving wrong advice to people who rely on fish as a basic component of their diet, where the nutritional and cultural value of eating fish may become overshadowed by concerns about exposure to mercury. Wheatley and Paradis (1995) have also expressed concern about the effect of media reports that exaggerate the problem.

CONCLUSIONS

The fact that mercury occurs naturally in the environment is neither an excuse for inaction, nor a rationale for ignoring industrial pollution. Conversely, the mere presence of mercury in the environment is not necessarily evidence of industrial pollution. There are a number of areas in Canada where natural sediment mercury concentrations exceed sediment quality guidelines. Natural background concentrations of mercury are influenced not just by the distribution of cinnabar deposits, as is sometimes assumed, but rather by the presence of mercury in variable amounts in a number of common geological situations. In fact, many geological factors besides bedrock mercury concentrations are important, with the result that there is seldom a one-to-one relationship between bedrock mercury concentrations and the distribution of mercury in the modern environment. In Canada, two other factors are particularly important: the glacial history of an area, and the distribution of organic matter. Natural mercury concentrations are also influenced by factors related to the tectonic setting, including bedrock structure, crustal heat flow and seismic activity.

Present-day regulations and health guidelines are designed to prevent excessive exposure to mercury, with the result that the general population is not at risk. It is important to recognize and understand the tragic poisoning incidents that first raised public awareness of the potential toxicity of this element. However, the current concern is about a different type of exposure — low-level chronic exposure — and we need to determine more precisely the risk that this type of exposure represents, particularly for population groups with high rates of fish consumption.

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