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Spatial and Temporal Patterns in Mercury Contamination in sediments of the Laurentian Great Lakes

By:
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Data from recent sediment surveys have been collated and mapped in order to determine the spatial distribution of mercury in sediments across the entire Great Lakes basin. Information from historical surveys has also been collated in order to evaluate temporal trends. Lake Huron (2002) exhibited the lowest mercury concentrations (lake-wide average concentration 0.043 μg/g); Lakes Michigan (1994-1996) and Superior (2000) also exhibited relatively low levels (lake-wide averages of 0.088 μg/g and 0.078 μg/g, respectively). The western basin of Lake Erie (1997-1998, 0.402 μg/g) and Lake Ontario (0.586 μg/g) exhibited the highest levels. Sources of mercury contamination in Lake Erie and Ontario are primarily attributed to loadings from historical sources, including chlor-alkali production in the Detroit, St. Clair and Niagara Rivers. The spatial distributions of mercury in sediments of Lakes Huron and Superior suggest that natural geochemical factors are an influence. Surficial sediment mercury contamination was found to have decreased markedly since the late 1960s and 1970s. Decreases in lake-wide average sediment concentrations of mercury over this time period ranged from approximately 25% for Lake Ontario to 80% for Lake Huron.

Profils spatiaux et temporels de la contamination par le mercure des sédiments dans les Grands Lacs laurentiens

Chris Marvin*, Scott Painter et Ronald Rossmann

Résumé

On a colligé et cartographié les données de relevés récents sur les sédiments afin de déterminer la distribution spatiale du mercure dans les sédiments de l'ensemble du bassin des Grands Lacs. On a aussi recueilli des informations des relevés historiques afin d'évaluer les tendances temporelles. Le lac Huron (2002) présentait les plus faibles concentrations de mercure (concentration moyenne pour l'ensemble du lac de 0,43 μg/g); les lacs Michigan (1994-1996) et Supérieur (2000) présentaient aussi des concentrations relativement faibles (avec des concentrations moyennes pour l'ensemble du lac de 0,088 μg/g et de 0,078 μg/g, respectivement). Les concentrations des bassins de l'ouest des lacs Érié (1997-1998, 0,402 μg/g) et Ontario (0,586 μg/g) étaient les plus élevées. Dans les lacs Érié et Ontario, on a déterminé que les sources de contamination par le mercure étaient surtout dues aux charges des sources historiques, notamment à la production de chlore et de soude sur les rivières Detroit, St. Clair et Niagara. La distribution spatiale du mercure dans les sédiments des lacs Huron et Supérieur semble indiquer des influences de facteurs géochimiques naturels. On a noté que la contamination des sédiments de la surface par le mercure avait fortement diminué depuis la fin des années 1960 et 1970. La diminution à l'échelle du lac des teneurs moyennes en mercure des sédiments en fonction du temps était comprise entre environ 25 % pour le lac Ontario et 80 % pour le lac Huron.

NWRI RESEARCH SUMMARY

Plain language title
Spatial and Temporal Trends in Mercury Contamination in Sediments of the Laurentian Great Lakes

What is the problem and what do sicentists already know about it?
Presence of contaminants in bottom sediments can be a primary source to higher trophic levels resulting in deleterious health impacts on fish and wildlife.

Why did NWRI do this study?
The Great Lakes Sediment Assessment Program is currently assessing sediment quality in the Great Lakes. Results of sediment surveys are compared with data from earlier Departmental surveys conducted in the late 1960s and early 1970s. This information is important to the understanding of the anthropogenic activities on open lake environments, and allows assessment of changes in contaminant concentrations since the advent of measures to reduce sources and loadings. The results of these surveys also allow assessment of sediment quality in the context of sediment quality guidelines for the protection of aquatic biota. This body of work represents a collation of mercury surficial sediment data from the major agencies mandated with monitoring temporal and spatial distributions of contaminants across the Great Lakes Basin. These data sets are unparalleled in their resolution and scope, and convey a reasonable understanding of the general prevailing spatial and temporal trends in mercury in sediments of the Great Lakes.

What were the results?
The highest levels of sediment mercury contamination were detected in the major lake depositional basins. Overall, levels of mercury have significantly declined over the period 1968 to 1998 throughout the Great Lakes. These conclusions were drawn from comparisons with the results of previous EC surveys, and assessment of dated sediment cores. In general, levels of mercury were estimated to have been reduced by a range 25% in Lake Ontario to 80% for Lake Huron, since peak contamination in the late 1960s. However, sediments in Lake Ontario, Lake St. Clair, and the western basin of Lake Erie still generally exceed guideline levels.

How will these results be used?
This report was solicited by the IJC as a result of a joint presentation by EC and USEPA at the IJC Health Effects of Mercury in the Great Lakes Workshop held in Windsor, Feb 26-27, 2003. The results of joint EC and USEPA studies have further demonstrated the value of open lake research and monitoring, and that the focus of government agencies on some AOCs is well justified. Further collaboration between State, Provincial and Federal agenices has been initiated to further study sources and loadings of contaminants that appear to be associated with local sources. These efforts are critical as elimination of sources is the only feasable management option for reducing deep water open-lake sediment mercury contamination.

Who were our main partners in the study?
Ontario Region, NOAA, USEPA

Sommaire des recherches de l'INRE

Titre en langage clair
Tendances spatiales et temporelles de la contamination par le mercure des sédiments des Grands Lacs laurentiens.

Quel est le problème et que savent les chercheurs à ce sujet?
La présence de polluants dans les sédiments de fond peut être une source majeure de contamination pour les niveaux trophiques supérieurs, ce qui a des effets nuisibles sur les poissons et sur la faune.

Pourquoi l'INRE a-t-il effectué cette étude?
Le Programme d'évaluation des sédiments des Grands Lacs est actuellement en train d'évaluer la qualité des sédiments dans les Grands Lacs. On compare les résultats des relevés des sédiments avec ceux d'autres relevés plus anciens, effectués par le Ministère vers la fin des années 1960 et le début des années 1970. Ces informations sont importantes pour la compréhension des activités anthropiques sur les milieux des lacs ouverts, et elles permettent d'évaluer les changements dans les concentrations de contaminants depuis l'introduction des mesures visant à réduire les sources et les charges. Les résultats de ces relevés permettent aussi d'évaluer la qualité des sédiments dans le contexte des nouvelles Recommandations canadiennes pour la qualité des sédiments du gouvernement fédéral, destinées à assurer la protection du biote aquatique. Ces travaux présentent une compilation des données sur le mercure dans les sédiments de surface, qui proviennent de principaux organismes chargés de la surveillance de la distribution temporelle et spatiale des contaminants dans le bassin des Grands Lacs. La résolution et la portée de ces ensembles de données sont sans précédent, et elles permettent d'obtenir une assez bonne compréhension des tendances spatiales et temporelles générales du mercure dans les sédiments des Grands Lacs.

Quels sont les résultats?
On a détecté les plus forts niveaux de contamination des sédiments par le mercure dans les principaux bassins de dépôt des lacs. En général, les teneurs en mercure ont connu une diminution notable de 1968 à 1998 dans l'ensemble des Grands Lacs. On a établi ces conclusions grâce à des comparaisons avec les résultats de relevés antérieurs d'EC, et à des évaluations de carottes de sédiments datées. En général, on estimait que les concentrations ont été réduites de 25 % (dans le lac Ontario) à 80 % (dans le lac Huron), depuis les maximums de contamination observés vers la fin des années 1960. Toutefois, les teneurs des sédiments du lac Ontario, du lac St. Clair et de l'ouest du bassin du lac Érié dépassent encore habituellement les limites des lignes directrices.

Comment ces résultats seront-ils utilisés?
Ce rapport était demandé par la CMI dans le cadre d'une présentation conjointe par EC et l'EPA à l'atelier de la CMI sur les effets sanitaires du mercure dans les Grands Lacs, tenu à Windsor les 26 et 27 février 2003. De plus, les résultats d'études conjointes d'EC et de l'EPA ont montré que les activités de recherche et de surveillance dans les eaux libres du lac sont utiles, et que l'accent mis par les organismes gouvernementaux sur certains SP est justifié. On a également entrepris d'autres travaux faisant appel à la collaboration entre des organismes des États, des provinces et du gouvernement fédéral, qui permettent de mieux examiner les sources et les charges de contaminants qui semblent associées aux sources locales. Ces efforts sont d'une importance cruciale, étant donné que l'élimination des sources est la seule option de gestion réalisable pour la réduction de la contamination par le mercure dans les sédiments profonds en eau libre.

Quels étaient nos principaux partenaires dans cette étude?
Région de l'Ontario, NOAA, EPA

Spatial and Temporal Patterns in Mercury Contamination in Sediments of the Laurentian Great Lakes

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Abstract

Data from recent sediment surveys have been collated and mapped in order to determine the spatial distribution of mercury in sediments across the entire Great Lakes basin. Information from historical surveys has also been collated in order to evaluate temporal trends. Lake Huron (2002) exhibited the lowest mercury concentrations (lake-wide average concentration 0.043 μg/g); Lakes Michigan (1994-1996) and Superior (2000) also exhibited relatively low levels (lake-wide averages of 0.088 μg/g and 0.078 μg/g, respectively). The western basin of Lake Erie (1997-1998, 0.402 μg/g) and Lake Ontario (0.586 μg/g) exhibited the highest levels. Sources of mercury contamination in Lake Erie and Ontario are primarily attributed to loadings from historical sources, including chlor-alkali production in the Detroit, St. Clair and Niagara Rivers. The spatial distributions of mercury in sediments of Lakes Huron and Superior suggest that natural geochemical factors are an influence. Surficial sediment mercury contamination was found to have decreased markedly since the late 1960s

and 1970s. Decreases in lake-wide average sediment concentrations of mercury over this time period ranged from approximately 25% for Lake Ontario to 80% for Lake Huron.

Key Words: Great Lakes, mercury, heavy metals, sediment

Introduction

Agricultural, industrial and municipal activities, both within the Great Lakes basin and in upwind areas, have resulted in pollution by a variety of contaminants and the subsequent degradation of ecosystem health. Accumulation of pollutants in sediments, tissues of benthic invertebrates, and fish are the result of both historical and contemporary inputs. Information on the occurrence and spatial distribution of toxic substances in the Great Lakes furthers understanding of the role human activities play in discharging these chemicals to the environment, and can also serve as a benchmark in assessing contaminant discharge reduction strategies. These initiatives include the Great Lakes Water Quality Agreement and the Great Lakes Binational Toxics Strategy that are collaborative processes through which levels of government, environmental organizations, the public and industry work toward reduction of persistent toxic substances.

There is a considerable body of literature documenting the accumulation of persistent contaminants in Great Lakes sediments up until the period of the late 1960s through the mid-1970s. These intensive lake-wide sediment surveys detected the presence of compounds including PCBs (Frank et al., 1979, Frank et al., 1977), organochorine pesticides (Frank et al., 1977, Van Hove Holdrinet et al., 1978) and mercury (Cahill, 1981, Thomas, 1972, Thomas, 1974, Kemp and Thomas, 1976, Thomas and Jaquet, 1976) in sediments of the Great Lakes at elevated concentrations due to the influence of anthropogenic activities. In the case of Lake St. Clair, these early reports of high concentrations of mercury in sediments, coupled with

reports of mercury contamination in fish in 1969, led to implementation of a commercial fishing ban in 1970. In addition to studies of mercury in surficial sediments, sedimentation rates and mercury loadings were estimated using sediment cores from Lakes Huron, Erie and Ontario (Kemp et al., 1974). The aforementioned studies pre-dated binational strategies to mitigate deleterious environmental impacts due to persistent toxics, including banning of PCBs and phasing-out of leaded gasoline. Studies in the 1990s using sediment cores concluded that deposition rates for a number of persistent toxics in the Great Lakes generally peaked during the period 1960 – 1980, with subsequent decreases after this time (Pearson et al., 1998, Wong et al., 1995, Schneider et al., 2001). However, these studies of temporal trends using sediment cores were generally restricted to a small number of sample sites in each lake.

Over the period 1994 – 2002, Environment Canada, the United States Environmental Protection Agency (EPA) and other collaborating government agencies conducted sediment surveys in the Great Lakes and Lake St. Clair on a rotational basis to fulfill commitments under binational contaminant reduction initiatives, to measure compliance with sediment quality guidelines, to evaluate spatial and temporal trends, and to identify emerging contaminant issues. Sediment sampling during these recent surveys was designed in part to enable comparison of contemporary sediment contamination with the results of Great Lakes surveys conducted over the period 1968 – 1975. Our recent surveys, with the exception of Lake Michigan, included a subset of stations from the grid-sampling program used for the 1968 – 1973 surveys. These comparisons can be used to investigate changes in types and magnitudes of sources, dispersal, and subsequent deposition of sediment-bound mercury throughout the Great Lakes. The most recent sediment surveys were conducted in each of Laurentian Great Lakes, and Lake St. Clair; detailed reports of recent surveys of Lake Michigan (Rossmann, 2002), Lake Erie (Painter et al., 2001) and Lake Ontario (Marvin et al.,

2002a,b) have previously been published. In this paper, we present general information on spatial trends for total mercury in bottom sediments from the Great Lakes, and an assessment of temporal trends through comparisons with previously reported data.

Materials and Methods

Sample collection

Surficial sediment samples from Lakes Erie (1997), Ontario (1998), Superior (2000) and St. Clair (2000) were collected aboard the CCGS Limnos using a mini box core sampling procedure. Samples collected from these surveys consisted of fine-grained sediments classified as glacio-lacustrine clay, sand, silt or mud. The top 3 cm of the sediment was sub-sampled for analyses of persistent organic pollutants, metals, particle size, and nutrients. Detailed descriptions of sampling procedures and locations in Lakes Erie and Ontario can be found in Marvin et al. (2002a,b) and Painter et al. (2001). Lake Michigan surficial sediments (1994 – 1996) were collected using a box corer (preferred method) or Ponar dredge; the top 1 cm section of the sample was sub-sampled for subsequent analyses. Detailed descriptions of sampling procedures and locations for Lake Michigan (1994 – 1996) can be found in Rossmann (2002).

Mercury Analyses

Mercury analyses for surficial sediment surveys, with the exception of Lake Michigan, were performed by Caduceon Laboratories (Ottawa, ON). Briefly, total mercury was determined by digestion with hot nitric acid and hydrochloric acid followed with measurement by cold vapour atomic absorption spectrometer (USEPA 1981). A detailed description of the analysis of mercury in Lake Michigan sediments can be found in Rossmann (2002). Briefly, Lake Michigan sediments were extracted by automated digestion (Leeman

Labs, Inc. 1993), or microwave digestion (Uscinowicz and Rossmann 1997), and subsequently analyzed using an automated mercury analysis system (Leeman Labs, Inc. 1991). The automated mercury analysis system was based on cold vapour atomic absorption spectrophotometry.

Results and Discussion

Spatial Trends in Surficial Sediment Mercury Contamination

Sediments in the Great Lakes generally represent a primary sink for contaminants, and can act as a source through resuspension and subsequent redistribution within the individual lakes. Surficial sediments, defined as the top 1-3 cm, represent the bulk of material available for resuspension. However, deposition and subsequent burial represents a primary mechanism by which contaminants are sequestered and prevented from re-entering the water column. Environment Canada conducted intensive lake-wide surveys in the late 1960s and early 1970s to determine the severity of surficial sediment contamination, and to investigate spatial trends. As a result, historical trends and distributions related to mercury in the Great Lakes are well documented (Frank et al. 1977, Kemp and Thomas, 1976, Thomas and Jaquet, 1976, Thomas, 1974, Cahill, 1981). During the period 1997 to 2002, Environment Canada revisited sites sampled in these historical surveys. In addition, the United States Environmental Protection Agency (USEPA) surveyed Lake Michigan during the period 1994 – 1996. Data presented in this paper represent the collation of mercury data for 380 samples collected during these most recent studies. Based on ^{210}Pb dating of sediment cores collected in offshore deep-water depositional during these surveys, data for surficial sediments generally represents the following dates of accumulation: Lake Superior, 1980 – 2000; Lake Michigan, 1990 – 1996; western basin of Lake Erie, 1995 – 1997; Lake

Ontario, 1990 – 1998. Therefore, with the exception of Lake Superior, data from these surveys generally represents mercury contamination accrued during the 1990s.

According to Thomas (1974), who studied distribution and transport of mercury in the Great Lakes during the late 1960s and early 1970s, an understanding of the sedimentology of the Great Lakes is in turn fundamental to understanding spatial distributions of mercury in sediments. Modern sediments of the Great Lakes reflect the post-glacial history of the area. Presently, the general sedimentology of the Great Lakes is characterized by continued deposition of fine clayey sediments in deep-water areas over older deposits that include glaciolacustrine clays, tills and glacial features. Glacial moraines segregate areas of lakes into individual depositional basins, of which there are six in Lake Huron, four in Lake Huron and three in Lake Ontario. Lake Superior is characterized predominately by a single large depositional basin (Thomas, 1974). We have adopted the conventions of sediment classification of Thomas et al., who characterized sediments for all the Great Lakes (Thomas, 1974, Sly and Thomas, 1974, Thomas et al., 1976, Thomas et al., 1972, Thomas et al., 1973). Sediments from our most recent surveys are classified either as non-depositional, consisting of bedrock, glacial till and glaciolacustrine clay, or depositional, consisting of fine-grained postglacial muds comprised mostly of material in the silt and clay particle size ranges. Non-depositional sediments including bedrock and till are found predominantly in nearshore areas, and are overstepped in turn by the glaciolacustine clays moving offshore into the areas of postglacial muds that correspond to the deep-water depositional basins.

The spatial distribution of mercury in Great Lakes surficial sediments is shown in Figure 1. The lake-wide and basin-specific (where applicable) average concentrations for mercury and other selected metals are shown in Table 1. Mercury data for Lake Erie sediments are also presented for the individual basins to illustrate the trend toward increasing concentrations from east to west. Conversely, mercury concentrations among the three major

depositional basins in Lake Ontario are generally similar. Table 1 also shows background levels of mercury in each lake represented by concentrations in the deepest sections of benthos core samples that generally pre-date industrial activity. Therefore, the ratios of surficial to background mercury concentrations reflect the impact of anthropogenic activity. The highest concentrations of mercury in sediments of Lakes Michigan, St. Clair, Erie and Ontario were observed in offshore depositional areas characterized by fine-grained sediments. Contaminant concentrations are generally correlated with particle size, hence the distribution of mercury shown in Figure 1 is not only a function of loadings and proximity to sources, but of the influence of substrate type and bathymetry as well. The correlation of mercury with sediment type in Lakes Erie and Ontario has been previously reported (Thomas, 1972, Thomas and Jaquet, 1976); concentrations of mercury increased from shallow nearshore areas of coarser sediments outwards into deep-water depositional basin sediments composed of silts and clays. Our most recent lake-wide surveys of Lakes Superior, Huron, St. Clair, Erie and Ontario did not match the spatial intensity of surveys conducted in the late 1960s and early 1970s (Thomas, 1974, Table 2). In addition, we specifically targeted deep-water depositional sediments comprised of fine-grained silts and clays. Therefore, the mercury concentrations shown in Figure 1 and Table 1 generally represent contamination in deep-water depositional areas. More intensive sampling in nearshore areas, which should be considered in the inter-lake comparisons, may have influenced the lake-wide average mercury concentration in the Lake Michigan data set. The spatial distribution of mercury across the Great Lakes was generally representative of the distributions of other metals, with the exception of lead, where the magnitude of contamination in Lake Michigan was similar to Lake Ontario. Mercury contamination, based on a comparison of lake-wide average concentrations, was lowest in Lakes Michigan and Superior (lake-wide averages of 0.077

μg/g and 0.088 μg/g, respectively) and highest in Lake Ontario (lake-wide average 0.586 μg/g).

Lake Superior

The relatively low mercury levels in Lake Superior sediments in 2000, and the relatively small number of stations sampled (N = 20), did not result in a definitive spatial trend in contamination as with some other lakes (Figure 1). Thomas (1974) reported the presence of elevated mercury concentrations in Lake Superior in 1973 that were anomalous in that they were not related to sediment type. It was concluded that these elevated mercury levels were related to local sources and the prevailing circulation patterns in the lake. However, our most recent survey was not conducted with great enough spatial resolution to support or refute these findings. Rossmann (1999) has provided a detailed discussion of horizontal and vertical distributions of mercury in sediments of Lake Superior collected in 1983. In addition, it was estimated the surficial 2 cm of sediment represented an inventory of 29 metric tons of mercury, of which 22 metric tons (76%) was anthropogenic. Estimates of fluxes of anthropogenic mercury ranged from –0.42 ng/cm^2/year to 10 ng/cm^2/year with a mean of 2.7 ng/cm^2/year. Estimates of the relative contributions of anthropogenic sources of mercury in Lake Superior vary somewhat; Rossmann (1999) reported that local point sources dominated mercury loadings to Lake Superior in 1983, and estimated that 38% of the total mercury flux was derived from atmospheric deposition from outside the basin, while Rolfhus et al. (2003), using data from water and suspended particulate samples collected in 2000, estimated that 58% of the total mercury flux was derived from atmospheric deposition. It is important to note that Rossmann (1999) included atmospheric deposition from local industrial sources as a component of the approximately 60% of mercury loadings originating within the Lake Superior basin.

A number of nearshore areas of Lake Superior are reported to exhibit elevated sediment mercury concentrations as a result of industrial activities. Sediments offshore of Thunder Bay in the depositional area between the bay and Isle Royale were found in previous surveys (Rossmann, 1999, Kemp et al., 1978, Thomas, 1974) to exhibit relatively high concentrations of mercury (0.34 μg/g to 0.67 μg/g). These elevated concentrations were attributed to industrial activities in the Thunder Bay area including mining, chlor-alkali production, and pulp and paper production (Rossmann, 1999). Other impacted areas included the upper peninsula of Michigan (iron, copper, gold and silver mining, Rossmann, 1999) and the Batchewana Bay, Agawa Bay and Whitefish Bay areas of southeast Lake Superior (iron, silver, gold and copper mining, Rossmann, 1999). Mercury from shoreline tailings, parent ores and smelters has reportedly influenced concentrations in sediments in the area of the Keweenaw Peninsula in the south-central area of the lake (Kerfoot et al., 2002). Interestingly, mercury concentrations in the area of Silver Bay on the north shore between Duluth and Thunder Bay are lower than background concentrations due to dilution of sediments with taconite tailings (Rossmann, 1999).

Although the predominant mercury loadings to Lake Superior have been reported to be the result of anthropogenic activities, including long-range atmospheric transport and subsequent deposition, the distribution of mercury in Lake Superior sediments may be partially the result of the influence of local natural sources as well. Sedimentary rocks can contain high burdens of mercury that can result in elevated concentrations in tributary and lakebed sediments in areas such as Thunder Bay (Painter et al., 1994). The highest mercury concentrations detected in the 2000 Lake Superior survey (0.30 μg/g and 0.33 μg/g) were observed near Thunder Bay and Nipigon Bay, which are in proximity to areas in the watershed characterized by sedimentary rocks of lower Proterozoic age containing naturally high mercury contents (Painter et al., 1994). Large areas of Precambrian shales containing

mercury in excess of 0.500 μg/g are common (Cameron and Jonasson, 1972). However, the Thunder Bay is also a region historically associated with silver mining and chlor-alkali production, both of which used mercury in their processes (Rossmann, 1999). Thomas (1974) suggested that mercury contamination derived from sediments in the Thunder Bay area has influenced concentrations in deep-water areas of the western area of the lake, including the Duluth basin.

Lake Michigan

Surficial sediment (top 1 cm) mercury concentrations in Lake Michigan in 1994 – 1996 ranged from 0.002 μg/g to 0.260 μg/g with a lake-wide mean of 0.078 μg/g (Rossmann, 2002). Mercury concentrations were highest in the deep-water depositional basins and exhibited a spatial distribution that conformed to the lake's bathymetry. There was little variation in mercury concentrations within the depositional basins; all concentrations ranged between 0.120 μg/g and 0.160 μg/g. Only two samples from the 1994 – 1996 survey exceeded 0.200 μg/g. These results are exclusive of Green Bay, which was most recently intensively sampled (N=74) over the period 1987 – 1990 (Table 2). Green Bay was found to have a considerably higher degree of sediment mercury contamination (mean of 0.360 μg/g, range of 0.006 to 1.10 μg/g) due to the historical contamination from pulp and paper industry discharges (Rossmann and Edgington, 2000).

Comparison of the 1994 – 1996 data with data from surveys conducted over the period 1969 – 1975 (Cahill, 1981, Kennedy et al., 1971, Table 2) indicate reductions in mercury contamination in Lake Michigan. The 1994 – 1996 mean concentration of 0.078 μg/g represents a roughly 30% decrease from the mean value derived from the most comprehensive historical survey conducted (N=254) by Cahill (1981) in 1975. In addition, comparison of the spatial distributions of mercury in the recent and historical surveys result

in a generally similarity pattern that roughly conforms to the lake bathymetry. There may have been a shift in the highest mercury concentrations toward northern offshore areas of the depositional basins over the period 1969 – 1975; however, this apparent shift may have been due in part to differences in sampling strategy.

Rossmann (2002) also calculated mercury fluxes to the depositional basins in Lake Michigan using box cores. Mean total mercury fluxes ranged from 3.3 – 14 ng/cm^2/year. As with the total mercury concentrations, there were no significant inter-basin variations in mercury fluxes. Relatively high mercury fluxes were estimated for depositional areas in the southeastern areas of the lake, which were attributed to potential transport of material from southwestern and southern shore areas. As part of the same study, the relative importance of regional atmospheric sources and point sources of mercury were assessed. The mercury flux to Lake Michigan sediments was estimated to be divided roughly equally between regional atmospheric and local mercury sources. In contrast, mercury fluxes to Green Bay were dominated by local sources resulting from historical industrial contamination (Rossmann and Edgington (2000).

Lake Huron

As with Lake Superior, there was no spatial trend in sediment-bound mercury in Lake Huron in 2002 (Figure 1). The lake-wide average of 0.043 μg/g (Table 1) was the lowest calculated for any of the lakes. Previously, Thomas (1974) the Thomas et al. (1973) discussed trends in mercury contamination in Georgian Bay and the North Channel, which are headwaters of Lake Huron, and are therefore potential source regions to the open-water areas. In the 1969 Lake Huron survey, elevated concentrations of mercury (>1.00 μg/g) were found near the Spanish River area of the North Channel (Thomas, 1974). Concentrations ranging from 3.0 μg/g to 9.5 μg/g were found in an area of Nottawasaga Bay on the eastern

side of the Bruce Peninsula in Georgian Bay. None of these observations could be related to specific sources; the high levels near the Bruce Peninsula were attributed to sphalerite mineralization in limestones of the area (Liberty, 1966). For the 1969 survey, the mean mercury concentrations in surficial sediments of the North Channel (range of 0.008 μg/g to 1.11 μg/g) and Georgian Bay (range of 0.012 μg/g to 9.50 μg/g) were 0.151 μg/g and 0.257 μg/g, respectively. The mean mercury concentration in 1969 in the open-lake area of 0.222 μg/g (range of 0.054 μg/g to 0.805 μg/g) was similar to the mean concentration in Georgian Bay. Two areas of elevated mercury contamination in sediments of the open-lake were identified; an area in the northeastern section of the lake, referred to as the "Bruce anomaly" that was attributed to the geochemical influence of sphalerite mineralization, and; an area of elevated concentrations emanating from Saginaw Bay and spreading out over the southern area of the lake. Thomas (1974) therefore concluded that Saginaw Bay was a source of contaminants to Lake Huron.

The 2002 Lake Huron survey did not provide any substantive evidence of potential regional sources of mercury, including areas of the North Channel, Georgian Bay and Saginaw Bay; rather, the distribution of mercury on a lake-wide basis was generally characterized by concentrations that we estimate to be roughly equivalent to background concentrations. The mean background sediment mercury concentration, estimated from mercury concentrations in the deepest sections of benthos cores that predated modern industrial activity, including gold and silver processing, was 0.026 μg/g. Using a similar method, Mudroch et al. (1988) estimated background concentrations of the depositional basins of Lake Huron to be in the range 0.040 – 0.080 μg/g. These estimated background concentrations were not substantially different from the 2002 lake-wide mean value (0.043 μg/g), which indicates that the current degree of mercury contamination in Lake Huron

sediments does not represent a significant degree of anthropogenic enrichment. Most mercury concentrations measured during the 2002 survey were less than 0.100 μg/g, and only a single site in Georgian Bay (0.367 μg/g) exceeded the Canadian Threshold Effect Level (TEL, CCME, 1998) guideline of 0.170 μg/g. As with Lake Superior, the natural geochemistry of the watershed may provide a source of mercury to open-lake areas of Lake Huron. Inland lake sediments in areas of the Georgian Bay and North Channel watersheds, including Elliot Lake and Sudbury, typically exhibit mercury concentrations in the range 0.200 μg/g to 0.400 μg/g (Painter et al., 1994).

Lake St. Clair

The distribution of mercury in surficial sediments of Lake St. Clair in 2000 exhibited a distinct pattern in that the highest concentrations were observed in the central and east-central areas (Figure 1). This distribution is very similar to that observed by Thomas (1974) in a 1970 survey; the highest mercury concentrations were positively correlated with increased levels of total organic carbon (TOC) and fine clay-sized sediment (Thomas, 1974). According to Thomas (1974), the pattern of contamination also relates to the predominant flow patterns, and major sources of mercury. The observed distribution reflects two features: mercury contamination in the central area of the lake in proximity to the shipping channel as a result of the predominant flow along the axis between the St. Clair and Detroit Rivers, and; contamination in the east-central area as a result of mercury entering the lake from the eastern network of stream and tributaries associated with the Lake St. Clair delta. Mudroch and Hill (1989) found mercury concentrations as high as 3.7 μg/g in surficial sediments of the Chenal Ecarte, which is a channel flowing east off the St. Clair River through the delta into the east-central area of the lake. These features, and the corresponding lack of contamination in the

western area of the lake and Anchor Bay, indicate the influence of upstream sources of mercury on the Canadian side of the St. Clair River.

The lake-wide average surficial sediment mercury concentration for Lake St. Clair in 2000 was 0.196 μg/g (Table 1), which was roughly five-fold higher than the average for Lake Huron. The highest individual mercury concentration in the 2000 survey (1.2 μg/g) was detected at a site roughly corresponding to the center of the lake. Thomas (1974) calculated a lake-wide average of 0.632 μg/g in Lake St. Clair in 1970 (Table 2), which was roughly three-fold higher than the corresponding value for Lake Huron in 1969. In contrast to Lake Huron, the 2000 surficial sediment mercury lake-wide average concentration in Lake St. Clair was roughly ten-fold higher than the estimated background concentration (0.023 μg/g). Many parts of the central and east-central areas of the lake exhibited an even greater degree of enrichment. The substantially higher mercury values in Lake St. Clair, compared to Lake Huron, support the conclusion that there are significant sources of mercury in the upper areas of the St. Clair River. There are areas of sediment in the upper St. Clair River highly contaminated by mercury as a result of chlor-alkali production and other industrial processes (Mudroch and Hill, 1989). However, we are currently unable to assess the relative contributions of these local sources, and mercury contamination in Lake St. Clair originating in the upper lakes and connecting channels.

Lake Erie

There was a spatial distribution in contamination in Lake Erie with a trend toward decreasing concentrations from the western basin to the eastern basin, and from the southern area to the northern area of the central basin (Figure 1). This spatial pattern was also evident for a variety of other contaminants in Lakes Erie and Ontario, including PCBs and organochlorine pesticides (Painter et al. 2001, Marvin et al., 2002a,b). The spatial trend in

mercury in Lake Erie sediments may have been influenced by industrial activities in the watersheds of the major tributaries, including the Detroit River, and areas along the southern shoreline (Painter et al. 2001). A number of reports in the early 1970s implicated mercury cell chlor-alkali facilities in the Detroit and St. Clair Rivers as the primary sources of mercury in sediments of the western basin (Thomas and Jaquet, 1976, Kovacik and Walters, 1973, Walters et al., 1972, Walters et al., 1974). Since these facilities are no longer in operation, current loadings of mercury to the western basin probably represent a combination of the influence of contamination originating in the upper lakes and connecting channels, and material from historically contaminated sediment deposits in the lower Detroit and upper St. Clair Rivers.

The distribution of mercury in the western and central basin areas of Lake Erie in 1997 – 1998 was similar to that observed in the historical surveys (Thomas, 1974, Thomas and Jacquet, 1976), and corroborated results of studies in the individual basins using sediment cores (Rossmann and Robbins, 1994); this pattern generally corresponded to the distribution of fine-grained depositional sediments. The gradient of mercury contamination across the lake limits the value of calculating a lake-wide average; therefore, we have presented data for the individual Lake Erie basins (Table 1). The mean concentration in the western basin (0.402 μg/g) represents a roughly two-fold increase over Lake St. Clair, and the second highest value calculated for the Great Lakes. As with Lake St. Clair, current levels of mercury contamination in the western basin of Lake Erie represent significant enrichment due to anthropogenic activities; the mean western basin concentration was roughly twelve-fold higher than the estimated background concentration of 0.034 μg/g (Painter et al., 2001). The observation of relatively low mercury concentrations in sediments of the eastern basin (basin average of 0.069) stood in contrast to results from the 1971 survey (Thomas and Jaquet, 1976). In the 1971 survey, two areas of high sediment mercury contamination were observed

in the area between Erie, Pennsylvania and the Niagara River. While the 1971 survey was carried out with greater spatial resolution (N=243) than the 1997 – 1998 survey (N=68), it is unlikely that the reduced number of sample sites in the most recent survey can account for this discrepancy. The 1997 – 1998 eastern basin average concentration of 0.069μg/g represents only a minor degree of enrichment over the estimated background concentration of 0.042 μg/g (Painter et al. 2001). Significant reductions in local sources of mercury from areas along the southern shore in the eastern basin represent the most logical explanation for these reductions; remediation of a number of hazardous waste facilities in this area has been reported (Townsend, 1998). However, the results of the 1997 – 1998 survey do not provide evidence of significant transport of mercury-contaminated sediment from the western basin to the eastern basin via a flow pattern along the southern shore, as reported by Thomas and Jaquet (1976). Other studies of contaminant cycling processes in Lake Erie suggest that the majority of chemical loadings entering Lake Erie via the Detroit River are deposited in the western basin, and do not experience significant easterly transport (Carter and Hites, 1992, Koslowski et al., 1994).

Lake Ontario

Mercury contamination in Lake Ontario was relatively consistent among the three major depositional basins (Figure 1), as a result of the predominant circulation pattern that distributes particulate material around the lake in a counterclockwise fashion (Pickett and Bermick, 1977). In both the 1968 and 1998 surveys, mercury concentrations increased moving offshore into the deep-water areas of the major depositional characterized by fine-grained sediments. The distribution, composition and characteristics of Lake Ontario sediments have been thoroughly described by Thomas et al. (1972); three major depositional basins (west – Niagara, central – Mississauga, east – Rochester) are located in the main body

of the lake, which are separated from each other by sills of glacial material. In addition to the trend in mercury contamination being generally associated with sediment particle size, the 1968 survey indicated regions of high mercury concentrations emanating from the Niagara River and extending northwestward into the Niagara basin and eastward along the southern shore of the lake (Thomas, 1972). After application of a quartz correction to the 1968 data set, the highest mercury concentrations were observed directly offshore of the mouth of the Niagara River, which implicated this area as the primary source of mercury to Lake Ontario (Thomas, 1972). The distribution resulting from the 1998 survey did not readily distinguish this definitive mercury plume, which may have been due in part to the reduced sampling intensity (N=70 in 1998 vs. N=248 in 1968); rather, mercury contamination was essentially equally distributed across the three major depositional basins. These results do not necessarily contradict those of Thomas (1972), as the spatial pattern we observed may result from the prevailing circulation pattern that generally moves particulate material from west – to – east in a counterclockwise motion, but also includes a secondary mechanism by which material emanating from the Niagara River is deposited into the Niagara basin.

The lake-wide average mercury concentration of 0.586 μg/g represented the highest value for all of the Great Lakes and Lake St. Clair, and represented only a marginal reduction from the results of the 1968 survey (N=287, mean concentration of 0.651 μg/g, range of 0.032 to 2.10 μg/g, Thomas, 1972, Table 2). However, the lake-wide average mercury concentration for the 1968 survey, based on the same 70 stations that were resampled in 1998, was 0.790 μg/g and indicates a more substantial decrease in mercury concentrations than is apparent from using the entire 1968 data set. The 1998 average mercury concentration represents a roughly sixteen-fold enrichment over the estimated background concentration of 0.04 μg/g (Marvin et al., 2002). The relatively higher mercury concentrations in Lake Ontario, compared to the other lakes, are reportedly the result of local

sources including the Niagara River, as opposed to Lake Superior where atmospheric sources dominate (Diamond et al. 1993, Pirrone et al. 1998). Pirrone et al. (1998) reported that wastewater sources were the dominant source of mercury in Lake Ontario sediments over the period 1940 – 1970, but atmospheric sources were predominant after this period. The relatively high concentrations of mercury in surficial sediments of the major depositional basins of Lake Ontario, compared to the other Great Lakes, is presumably a result of historical loadings combined with intra-lake mixing processes prior to deposition and ultimately burial. Therefore, considering the delayed response of sediments to reduced loadings, further decreases in mercury levels in Lake Ontario are to be expected.

Temporal Trends in Mercury Contamination

Comparisons with data from historical surveys conducted during the period 1968 to 1975 show a general decrease in mercury sediment concentrations in all lakes, with the exception of Lake Superior (Table 2), where sediments generally have not been significantly impacted and approach geological norms. Both the lake-wide average mercury concentrations, and the range of concentrations expressed as maximum and minimum values, were similar for the 1973 and 2000 Lake Superior surveys (Table 2). However, sediments collected in the 2000 Lake Superior survey (top 3 cm) represent accumulation over roughly a 20-year time period from 1980 – 2000, while sediments from the other lakes represent accumulation during the period 1990 – 1998. Therefore, sampling of Lake Superior at greater resolution than the top 3 cm would be required to better estimate trends in mercury contamination over the past 30 years. Reductions in mercury contamination in sediments across the entire Great Lakes basin, estimated through comparisons of lake-wide average concentrations from the most recent surveys and historical surveys (Table 2), ranged from 24% for Lake Ontario to 80% for Lake Huron. Rossmann (2002) reported a decrease in

mercury concentrations in Lake Michigan between 1969 and 1994; the rate of decrease between 1969 and 1981 was 10 ng/g/year and 3.8 ng/g/year between 1981 and 1994. The rate of decrease for mercury in Lake Ontario sediments, using data from Marvin et al. (2002b), was estimated to be roughly 7 ng/g/year.

The most recent surveys included sampling of sediment cores in the individual lakes, the analysis of which provided information complementary to surficial sediments in the assessment of temporal trends. Direct comparisons of trends over time in mercury contamination assessed using surficial sediments vs. core profiles are difficult, given that sediment core studies are site-specific, while comparisons of data from surficial sediment studies conducted over several decades may be influenced by differences in analytical and sampling methods. Profiles of mercury in selected sediment cores sampled from the Mississauga (central) basin of Lake Ontario and Lake Michigan are shown in Figure 2. For all of the Great Lakes and Lake St. Clair, temporal trends derived from sediment core profiles of mercury generally proved to be consistent with those obtained through comparisons of recent and historical surficial sediment surveys.

The core profiles shown in Figure 2 represent the general trend in mercury accumulation in Great Lakes sediments over the past 150 years. Sediments of the Great Lakes were generally impacted after 1850 due to mercury emissions from gold and silver extractions. Pirrone et al. (1998) estimated that maximum atmospheric emissions of mercury in North America occurred in 1879 (roughly 1,708 t/yr) and 1920 (roughly 940 t/yr) as a result of gold and silver mining. However, these dates of maximum atmospheric deposition do not represent the periods of maximum accumulation in sediments, which are more closely correlated with estimates of total anthropogenic loadings to the Great Lakes (Pirrone et al., 1998). Based on profiles of cores sampled during our recent lake-wide sediment surveys, maximum accumulation of mercury in sediments of western Lake Erie, Lake Ontario and

Lake Superior occurred during the period 1964 – 1970. These dates of maximum accumulation have been corroborated by other studies using sediment cores, e.g., Gottgens et al. (1999) estimated that peak concentrations of mercury in western Lake Erie occurred in 1970. Core data reported by Thomas (1974), although conducted near these periods of maximum mercury accumulation, indicate that peak concentrations of mercury occurred in the late 1960s in Lakes Erie and Ontario. Rossmann (2003, unpubl. data) is currently assessing trends in mercury contamination in Lake Michigan using a large number of sediment cores; these data generally show dates of maximum accumulation of mercury during the mid – 1950s. All of the aforementioned core profiles from the most recent lake-wide sediment surveys exhibited subsequent declines, as illustrated in Figure 2, from peak concentrations at depth to levels commensurate with current surficial sediments. Percent reductions in mercury concentrations in sediment cores ranged from 48% - 54% for western Lake Erie and 55% - 65% for cores from the depositional basins of Lake Ontario. In comparison, the percent decrease in the mean surficial sediment concentration from the late 1960s – early 1970s to the late 1990s for was roughly 60% for western Lake Erie and 25% for Lake Ontario.

Core profiles can also be used in the assessment of primary sources of mercury through the comparison of accumulation in sediments with estimates of atmospheric mercury deposition. Pirrone et al. (1998) found a correlation between atmospheric deposition and mercury accumulation in sediment cores in Lakes Erie and Michigan, indicating atmospheric contributions as the primary source of mercury. In contrast, accumulations in Lake Ontario cores indicated the influence of local point sources, including atmospheric deposition from mercury emitted within the Lake Ontario basin, and direct wastewater discharges. Atmospheric deposition is also reported to be the dominant source of total mercury to Lake Superior (Rolfhus et al., 2003).

Conclusions

Spatial and temporal trends in surficial sediments indicate progress toward significant reductions in mercury in the Great Lakes basin. These conclusions are supported by the results of studies in which core profiles were used to assess mercury accumulation rates and reductions in loadings over the past several decades. These conclusions are also in concurrence with assessments of reductions in sources of mercury in North America as reported through initiatives including the Great Lakes Binational Toxics Strategy; source reductions in Canada and the United States currently stand at approximately 80% and 40%, respectively (GLBTS, 2002). As a result, further reductions in mercury concentrations in sediments of the Great Lakes are anticipated, but at rates that are subject to factors including physical processes within lakes including sedimentation rates, and regional/global influences.

Relatively higher sediment mercury concentrations, compared to other areas within the same lake, or compared to the other lakes, indicated local, i.e., within the individual lake basin, sources of mercury as in the case of Lake Ontario. These spatial trends in mercury contamination may have been influenced by industrial activities in the watersheds and along major tributaries; mercury from sources within tributary watersheds or even derived through atmospheric deposition, can ultimately be deposited in deep-water areas. This process is sometimes referred to as sediment focusing (Rossmann, 2002). However, even in the case of Lake Ontario, areas of the highest sediment mercury contamination appear to be the result of historical loadings, particularly from areas associated with mercury cell chlor-alkali facilities. Management actions have undoubtedly been a primary contributor to the marked declines in mercury contamination. Other actions have presumably contributed to the general declines in mercury concentrations in sediments, including the remediation of contaminated sites,

reduction and/or elimination of discharges from hazardous waste facilities, reduction of open-lake disposal of contaminated sediments, and reductions in loadings from atmospheric sources. A thorough review of atmospheric deposition of toxics to the Great Lakes can be found in Hoff et al. (1996).

It is interesting to compare the major conclusions of Thomas (1974) related to mercury distribution and movement in Great Lakes sediments in the late 1960s and early 1970s with our interpretations of current trends. We have summarized the comparisons as follows:

1. Sediments in Lakes Superior (1973) and Michigan (1975) exhibited low mercury levels, with subsequently little throughput of mercury to Lake Huron. Lake Superior exhibited localized areas of mercury enrichment that reflected source locations and the physical processes of the lake. The results of recent surveys are in agreement with these historical trends; lake-wide average concentrations of mercury in Lakes Michigan (1994 – 1996) and Superior (2000) were 0.078 μg/g and 0.088 μg/g, respectively. In addition, geochemical factors, i.e., natural mercury enrichment due to rocks in the Pre-Cambrian Shield, are potential influences near the northern shore of Lake Superior near Thunder Bay and Nipigon Bay. The geochemical characteristics of this area have been well documented (Painter et al., 1994).
2. Levels of mercury in Lake Huron in 1969 were low, but substantially higher than Lakes Michigan and Superior. There were localized areas of high sediment mercury in Georgian Bay, and Saginaw Bay appeared to be a source of mercury to the southern area of the lake, which was ultimately transmitted to Lake St. Clair. The results of the 2002 Lake Huron survey contrasted somewhat with those of Thomas; the lake-wide average concentration of 0.043 μg/g was the lowest of all the lakes. The combination

of the low mercury levels in Lake Huron, combined with the non-descript spatial distribution, did not provide evidence of any local or regional sources of mercury.

3. Thomas reported that levels of mercury in Lake St. Clair in 1970 were roughly three-fold higher than Lake Huron (1969), a trend that was related to major sources in the St. Clair River. Mercury-contaminated sediment was likely transitory and subject to transport downstream into the Detroit River and western Lake Erie. The 2000 survey corroborated these results; the lake-wide average of 0.196 μg/g was roughly five-fold higher than Lake Huron. The spatial distribution of mercury in the open lake implicated upstream sources in the St. Clair River as a primary influence.
4. The spatial distribution of mercury resulting from the 1972 Lake Erie survey indicated that the Detroit River was the major source. The predominant lake circulation pattern resulted in sediment-bound mercury being ultimately deposited in the eastern basin, with very little transport through the Niagara River to Lake Ontario. Although the results of the 1997 – 1998 survey also implicated the Detroit River as the primary vector for mercury contaminated material entering Lake Erie, we found no evidence of significant cross-lake transport. The mean mercury concentration for the eastern basin (0.069 μg/g) did not indicate any significant degree of enrichment.
5. Mercury detected in Lake Ontario in 1968 was derived predominately from sources in the Niagara River, the distribution of which reflected the prevailing circulation patterns in the lake. The 1998 survey resulted in the highest lake-wide average mercury concentration (0.600 μg/g) of all the lakes; however, it appears that this contamination is the result of historical sources and further declines in mercury contamination in Lake Ontario are expected.

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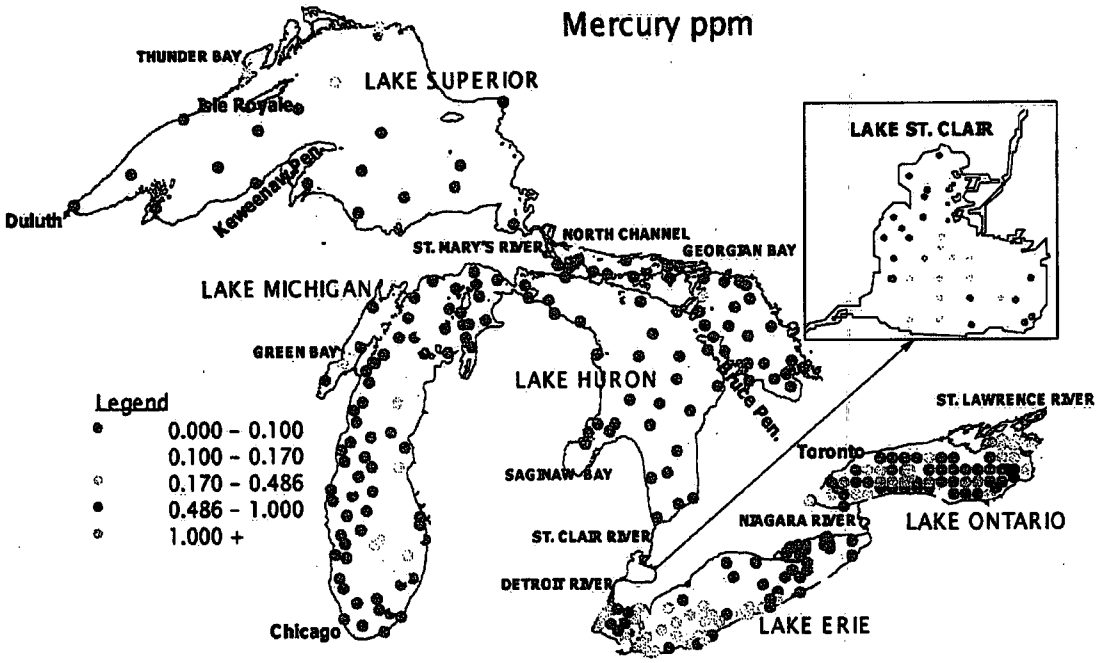
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GREEN BAY
LAKE HURON
Bruce Pen.
SAGINAW BAY
ST. CLAIR RIVER
DETROIT RIVER
Chicago
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ST. LAWRENCE RIVER
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NIAGARA RIVER
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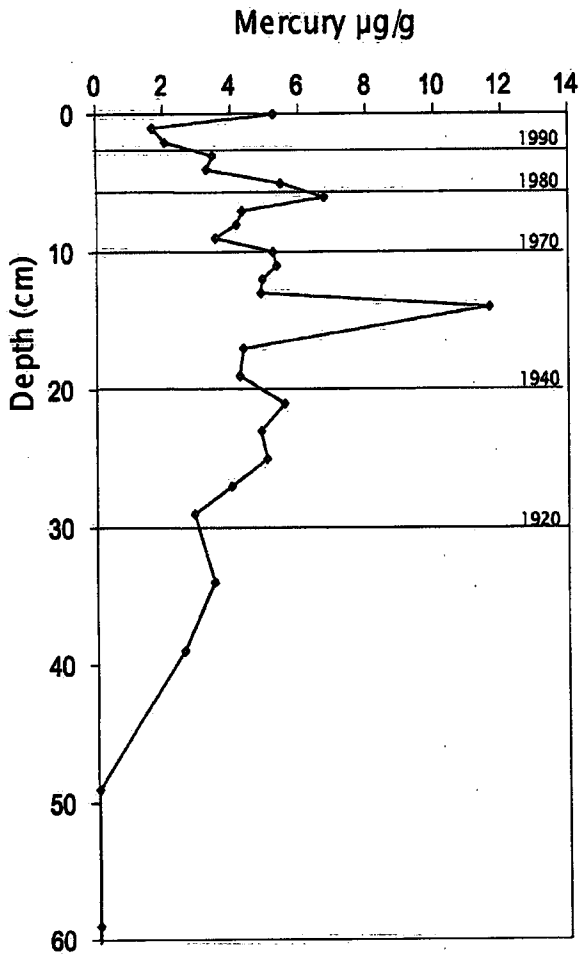
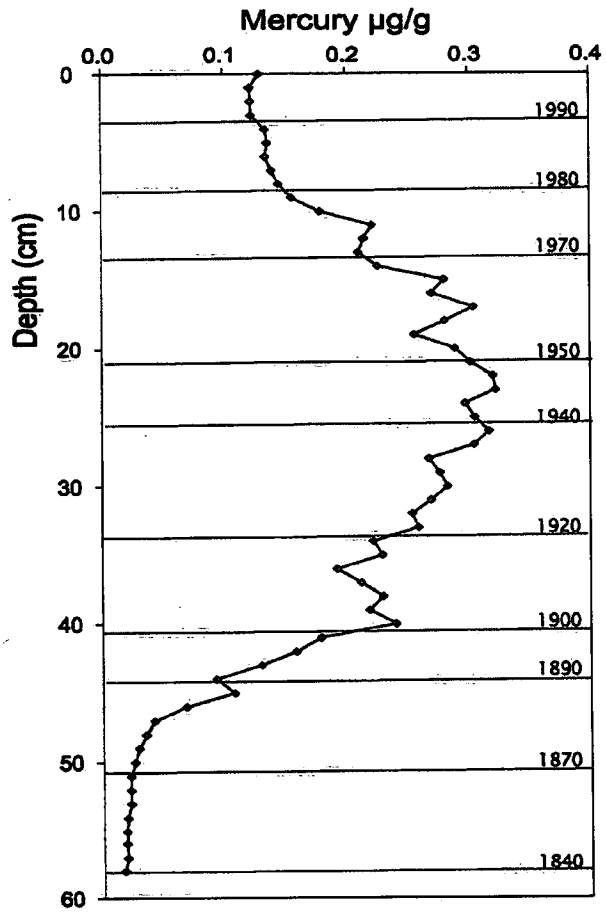


Lake Ontario



Lake Michigan

List of Tables.

Location	Mean Concentration	Background Concentration
	μg/g	μg/g
Western Lake Erie	0.402	0.034
Central Lake Erie	0.167	0.049
Eastern Lake Erie	0.069	0.042
Ontario	0.586	0.040
St. Clair	0.196	0.023
Huron	0.043	0.026
Superior	0.088	0.029[a]
Michigan	0.077	0.012

Location	Year	N	Mean	Std. Dev.	Median	Range (Min. – Max.)	Reference
			µg/g		µg/g	µg/g	
Southern Michigan	1969 – 1970	31	0.150	0.100	0.120	0.030 – 0.670	Kennedy et al., 1971
Michigan	1975	254	0.110	0.110	0.060	0.020 – 0.670	Cahill, 1981
Green Bay	1987 – 1990	74	0.360	0.270	0.280	0.006 – 1.10	Rossmann and Edgington, 2000
Michigan	1994 – 1996	118	0.078	0.065	0.073	0.002 – 0.260	Rossmann, 2002
Superior	1973	405	0.083	0.056		0.004 – 0.584	Thomas, 1974
Superior	1983	31	0.180	0.180	0.140	0.027 – 0.960	Rossmann, 1999
Superior	2000	20	0.088	0.093	0.069	0.005 – 0.328	Current study
St. Clair	1970	55	0.630	0.630		0.070 – 2.60	Thomas, 1974
St. Clair	2000	38	0.200	0.220	0.097	0.014 – 1.20	Current study
Huron	1969	163	0.220	0.160		0.008 – 9.50	Thomas, 1974
Huron	2002	67	0.043	0.052	0.024	0.005 – 0.367	Current study
Erie	1971	243	0.610	0.700		0.013 – 7.50	Thomas and Jaquet, 1975
Erie	1997 – 1998	68	0.190	0.170	0.160	0.006 – 0.940	Painter et al., 2001
Ontario	1968	248	0.650 (*0.79)	0.510		0.032 – 2.10	Thomas, 1972
Ontario	1998	69	0.586	0.350	0.650	0.005 – 1.40	Marvin et al., 2002

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