



Spatial distribution and trends of total mercury in waters of the Great Lakes and connecting channels using an improved sampling technique

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ABSTRACT

Environment Canada recently developed a clean method suitable for sampling trace levels of metals in surface waters. The results of sampling for total mercury in the Laurentian Great Lakes between 2003 and 2009 give a unique basin-wide perspective of concentrations of this important contaminant and represent improved knowledge of mercury in the region. Results indicate that concentrations of total mercury in the offshore regions of the lakes were within a relatively narrow range from about 0.3 to 0.8 ng/L. The highest concentrations were observed in the western basin of Lake Erie and concentrations then declined towards the east. Compared to the offshore, higher levels were observed at some near-shore locations, particularly in lakes Erie and Ontario. The longer-term temporal record of mercury in Niagara River suspended sediments indicates an approximate 30% decrease in equivalent water concentrations since 1986.

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1. Introduction

Inorganic mercury is present in the environment in trace amounts, but methylation increases its toxicity. Due to the processes of bioaccumulation and biomagnification, even very low quantities in water can result in elevated levels in aquatic organisms (Morel et al., 1998). Mercury is also responsible for the majority of fish consumption advisories in the Great Lakes (Health Professionals Task Force, 2004).

Surveys of total mercury throughout the Great Lakes were conducted in the 1970s (Pascoe and Stewart, 1977) and in each lake except Lake Ontario in the 1980s (Rossman, 1983, 1984, 1986), but laboratory detection limits were in the 26–50 ng/L range and resulted in the majority of data being reported as below the detection limit. Detection limits for studies conducted in the late 1980s were improved but still in the 1–2 ng/L range, and only single lakes were surveyed (e.g., Sorensen et al., 1990; Glass et al., 1990).

More recent improvements in analytical methods (e.g., USEPA, 2002, Environment Canada, 2002) and the adoption of more stringent sample handling procedures (e.g., USEPA, 1996) have significantly reduced the detection limits for total mercury in water samples. Considerable success has been achieved, for example, in measuring sub-ng/L levels of total and methyl-mercury in boreal

forest lakes and wetlands (St. Louis et al., 1994), in prairie surface waters (Hall et al., 2009) and in Arctic water and snow samples (St. Louis et al., 2007; Kirk et al., 2008) using clean laboratory and field methods. With shifts toward more sensitive analytical detection methods using fluorescence rather than atomic absorption, and using closed rather than open vessel digestion, the challenge has become the prevention of sample contamination, whether during sample bottle preparation, sample collection and transportation, or sample processing in the laboratory. When attempting to measure ultra-trace ambient values, even slight exposure (to particles or gasoline fumes, for example) can lead to significant sample contamination. Clean sample collection techniques typically involve transferring waters from a sampling vessel (e.g., Go-Flo bottle), which must be adequately cleaned before surveys and between sampling sites, to a container used for sample storage and/or acidification. In the laboratory, a subsample is taken for analysis, and the samples may be exposed to air contamination during sample digestion. Mason and Sullivan (1997) and Amyot et al. (2000) achieved sub-ng/L detections of total mercury in the Great Lakes, but they employed a clean laboratory in the field.

Sub-ng/L determinations of total and methyl-mercury concentrations have been made in Great Lakes waters, but these studies focused on single lakes (Mason and Sullivan, 1997; Rolfhus et al., 2003; Jeremiason et al., 2009). The objective of our work is to describe the spatial trend of total mercury throughout the Great Lakes, and to examine historical data for temporal trends. We present basin-wide information on the levels of total mercury in the Great Lakes and their connecting channels using clean

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techniques developed by Environment Canada that are simple to execute and do not require the use of a clean laboratory in the field. A specialized sampler, sample bottles and isolation containers, as well as stringent sample handling procedures, are all employed. The results for water are compared with those obtained from the Niagara River, where the specialized procedures were not utilized. Quantifying mercury levels in sediment is more straightforward than for water; concentrations tend to be higher and samples are therefore not as prone to contamination. The long-term record for mercury on suspended sediments in the Niagara River is therefore used here to provide a longer-term temporal trend of mercury in the Great Lakes environment.

2. Methods

2.1. ISOMET sampler

Environment Canada has developed a system for sampling mercury and trace metals that is suitable for water sampling at both low-level and contaminated sites. Full details of the method is provided in the [Supplementary Information](#), including information about the sampler, its testing, bottle cleaning, field methods and results of quality assurance studies. Briefly, the ISOMET (ISolation Strategy for METals Sampling) comprises a sampler and also a procedure that emphasizes containment of the sample to isolate it from external sources of contamination. Two versions of the sampler have been designed: a hand-held sampler suitable for rivers, streams and lake surface water sampling from a small boat; and a larger electric version that is suitable for lake sampling from a ship. Both sampler types uncap and recap the sample bottles *underwater* to avoid any sample exposure to the atmosphere, fumes, or particles, and avoiding transfer of waters from the sampler into a container. The bottle is permanently labeled with a unique identification number so that the number can be cross referenced when sampling and there is no need to label the bottle in the field. Instead of double bagging, we use a system of nested rigid containers to contain the sample bottles during transportation. In the laboratory, the entire (closed) bottle is subjected to the digestion procedure, rather than opening the bottle and taking a subsample. By emphasizing these isolation procedures, we have been successful in reliably determining sub-ng/L concentrations of total mercury in samples collected by a number of technicians in the field.

2.2. Field methods – Great Lakes

As part of its commitment to the Canada-United States Great Lakes Water Quality Agreement, Environment Canada has run the Great Lakes Surveillance Program (<http://www.ec.gc.ca/scitech/default.asp?lang=en&n=3F61CB56-1>) since 1968. The program conducts ship-based monitoring cruises to measure physical, chemical and some limited biological parameters at a number of locations on each of the lakes which Canada borders. A suite of physical and chemical parameters, including nutrients, major ions, trace metals and organic contaminants are monitored. The Surveillance Program produces long-term trend information for the measured parameters as well as information about their spatial distributions, within each lake and across the Great Lakes basin as a whole. Currently, monitoring is conducted on a rotating cycle so that each lake is generally monitored during the spring every second year, with multiple cruises (consisting of one spring, one summer and occasionally one fall cruise) conducted every four or five years. In 2006, some limited sampling was additionally conducted on Lake Michigan. Across the entire basin, the Surveillance Program comprises approximately 300 stations. For organic contaminants and metals, samples are collected from about 80 stations.

Since the development and field testing of the ISOMET in 2003, mercury sampling is routinely conducted during Surveillance Program spring water quality surveys. Full field methodology is provided in the [Supplementary Information](#). Total mercury results from 14 Great Lakes monitoring cruises from 2003 to 2009 are considered here ([Supplementary Information Table S8](#)). Monitoring was generally conducted using the Canadian Coast Guard Ship (CCGS) *Limnos*, except for samples from Lake Huron and Georgian Bay in 2007 which were taken from the CCGS *Griffon*. During the spring, the Great Lakes waters are isothermal (i.e., not vertically stratified), and near-surface samples (taken 1–4 m below the surface) are assumed to be representative of the majority of the water column.

2.3. Laboratory methods – Great Lakes

Due to program constraints, two laboratories, Flett Research Limited and the mercury laboratory at Environment Canada's Aquatic Ecosystem Protection Research Division, were used by the Great Lakes Surveillance Program for analysis of total mercury. Flett is accredited for these analyses with the Canadian Association for Laboratory Accreditation (CALA). Both laboratories use bromine monochloride (BrCl) to convert the mercury to ionic Hg²⁺, a purge and trap methodology using Sn²⁺ reduction to convert the ionic Hg²⁺ into metallic Hg⁰, followed by gas purging

with nitrogen or argon. Flett Research incorporates gold amalgamation to pre-concentrate the Hg vapour while the EC lab uses a direct detection method (USEPA, 2005) and both labs utilize atomic fluorescence spectrometric detection (USEPA, 2002). The method detection limit for Flett is 0.04 ng/L, based on a 50 mL sample (0.012 ng/L for 170 mL) and for NWRI is below 0.1 ng/L based on a 40 mL sample (0.024 ng/L for 170 mL).

2.4. Field methods – connecting channels

The Niagara River flows 60 km from Lake Erie to Lake Ontario. Environment Canada has been conducting water quality monitoring on the river as part of its commitment to the Niagara River Toxics Management Plan on behalf of the Four Parties (Environment Canada, U.S. Environmental Protection Agency Region II, Ontario Ministry of the Environment and New York State Department of Environmental Conservation). Monitoring has been conducted downstream at Niagara-on-the-Lake (NOTL) since 1976 and upstream at Fort Erie (FE) since 1984. By comparing water and suspended sediment concentrations of priority chemicals at the upstream (FE) and downstream (NOTL) locations, the program can measure concentrations of chemicals in the river in order to determine loads of contaminants and report on trends, specifically in relation to implemented control measures. The record for mercury on suspended sediments extends from 1986 to the present time.

Suspended sediments (which include inorganic and organic matter) are collected according to the standard operating procedure for the Niagara River upstream–downstream program (Harrison et al., 2009). Briefly, water is pumped from the river upstream near FE and downstream near NOTL via a magnetic drive submersible pump with glass-filled polypropylene head and a ceramic impeller (March 5C-MD). The water is pumped from mid-depth, approximately 30–50 m from the Canadian shore, to base stations located on the shore. The river water is filtered through an in-line polypropylene basket filter to remove any large debris such as algae, fish or weeds. A T-fitting after the filter splits the water flow into two lines, one for collecting whole-water samples, and the other for feeding the centrifuge. The centrifuge (Westfalia model KA-02-06-075) is fitted with a four-chamber all stainless steel bowl and it runs for 24 h, extracting suspended sediment from a volume of approximately 8600 L of water. Beginning in 1986, suspended sediment samples were collected weekly; since 1997, sampling has been biweekly.

Whole-water mercury measurements were also made between July 2002 and March 2006 in the Niagara River at FE and NOTL (approximately biweekly) and in the St. Lawrence River at Wolfe Island (WI; approximately monthly). The ISOMET method was not used here; instead samples were collected from the whole-water line at each station into purchased pre-cleaned 125 mL Wheaton glass bottles. Although gloved hands were used, the samples were exposed to the atmosphere during sampling.

Surveys of whole-water total mercury were conducted in the St. Clair River – Detroit River from April to November, 2004. A total of 100 samples plus replicates were collected using the ISOMET methodology from nine stations along the corridor. A small fibreglass-hulled boat with an in-hull motor was used, and it was scrubbed-down prior to each survey to remove particulates and/or fuel contaminants. Five surveys were conducted on the St. Clair River. Samples were collected upstream near the inlet from Lake Huron to the St. Clair River, downstream on the St. Clair River on the US side at Roberts Landing, and on the Canadian side of the river at Port Lambton. A total of 17 surveys were conducted along the Detroit River. Samples were collected upstream of the inlet in Lake St. Clair in the navigational channel and upstream in the Detroit River at Fleming Channel (on the US side of the river). Downstream in the Detroit River, samples were collected on the US side in the Trenton Channel and on the Canadian side in the Amherstburg Channel. Further downstream, samples were collected at Sugar Island Channel (US side) and Livingstone Channel (Canadian side), prior to the Detroit River discharge to the western basin of Lake Erie.

2.5. Laboratory methods – connecting channels

Samples of total mercury in all connecting channels waters (i.e., Niagara River, St. Lawrence River and St. Clair – Detroit River corridor) were analyzed at Flett Research Limited using the methodology described above for Great Lakes samples.

Mercury on suspended sediments was analyzed by Environment Canada's National Laboratory for Environmental Testing (NLET). Samples were analyzed in a wet state and results converted to dry weight by correcting for moisture content. From 1985 until March 1999, an open digestion method, employing strong acids and oxidizing agents at 60 °C for 2 h, was conducted (detection limit 2 ng/g dw; Environment Canada, 1994). Since April 1999, a closed vessel microwave assisted acid digestion, conducted at 200 °C for 15 min, instead was performed (detection limit 4 ng/g dw; Environment Canada, 1999). The improved sample digestion provided a 5% increase in extraction efficiency, compared to the traditional open digestion. In both methods, the analysis of mercury was carried out by cold vapour atomic absorption spectrometry (CVAAS). NLET is CALA accredited for the analysis of sediment mercury.

Mercury on suspended sediment (ng/g) was converted to an equivalent water concentration (ng/L) by multiplying by the suspended sediment concentration

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