

MERCURY CONCENTRATIONS IN TWO "GREAT WATERS"

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Abstract. Although many sources of Hg to surface waters have been identified including atmospheric deposition, re-suspension of contaminated sediments, and direct discharges, there are very few recent data on ambient concentrations in the large lakes. Thus, an investigation of Hg concentrations in Lake Champlain and Lake Michigan was completed in the summer of 1993. Three depths of water including the microlayer, 30 cm below the surface, and 1 m below the thermocline were collected for each sampling event using ultra-clean techniques. All samples were processed in the field for dissolved and particulate fractions in a portable plastic enclosure equipped with a HEPA filter, and then analyzed by dual amalgamation and cold vapor atomic fluorescence spectroscopy in a Class 100 clean room at the University of Michigan. In addition, samples were analyzed for other trace metals by ICP-MS. Results from the two field investigations include the following: (1) On average, Lake Michigan water samples had higher concentrations of Hg than Lake Champlain; (2) There was no consistent pattern of Hg concentrations in the water column; (3) There was variability in the concentrations of Hg from the same depths over consecutive sampling periods. This paper discusses these results, and examines the relationship between the patterns in mercury concentrations and other physical and chemical data collected during the investigation.

1. Introduction

Concentrations of mercury (Hg) in surface waters are of great concern and interest because of fish consumption advisories triggered by elevated Hg levels. In the Great Lakes, the ingestion of fish with high concentrations of Hg has been associated with reproductive problems in eagles, otters, mink, and other animals (Douglas, 1991). Because of its ability to bioaccumulate, even the lowest surface water concentrations of Hg are important.

There is a surprising paucity of Hg data for many freshwater systems. This is especially true for the "Great Waters", that includes among others, the Great Lakes, Lake Champlain and Chesapeake Bay. Since many of these bodies of waters have restrictions or warnings on fish consumption due to high Hg levels, more information is needed about the levels and forms of Hg found in the surface waters. Thus, the purpose of this investigation was to measure the concentrations of Hg and other trace metals at three different depths in Lake Champlain and Lake Michigan, and describe the temporal variability of these pollutants over a 4 to 6 day period at each site. A secondary objective was to determine if there were any relationships between levels of Hg and other trace metals at the different sampling depths and between the lakes.

Lake Champlain, bordered by New York, Vermont and Quebec, is the sixth largest natural freshwater lake in the United States. It is about 193 km long, 19 km across at its widest point and has a surface area of 1,124 km² (Watzin, 1992). The ratio of the drainage basin to the surface area of the lake is about 19. In contrast, Lake Michigan has a surface area of 57,800 km² with a ratio of drainage basin to surface area of only about 2 (Watzin, 1992). Thus, the two lakes have very different physical characteristics, which in turn, are likely to affect the input and cycling of Hg and other trace metals in the respective ecosystems.

2. Materials and Methods

2.1. SAMPLE COLLECTION AND PROCESSING

All collection, processing and analysis of Hg and metals samples were performed using ultra-clean techniques. This included putting all supplies through an 11-day acid cleaning procedure (Hoyer and Keeler, 1994) and transporting all materials to the field triple-bagged. Once in the field, all sample handling was performed with particle-free gloves and upwind of the handlers so as to minimize possible sample contamination.

The Lake Champlain samples were collected 20 - 25 July 1993 at a location approximately 1.6 km west of Burlington, VT (44°29'N, 73°14'W) in the main lake where the depth of the water is approximately 33 m. This part of the lake has the deepest, coldest water and is most similar to the Great Lakes. Ten sets of water samples were collected including 0.3 and 15 m depths. Due to choppy waves and high winds, only 6 concurrent microlayer samples were collected. The Lake Michigan samples were collected from 2 - 5 September 1993 at a location about 6.4 km east of Chicago, IL (41° 50'N, 87°50'W) where the water depth was approximately 12 m. Eight sets of water samples were obtained at depths of 0.3 and 10 m, as well as 7 microlayer samples.

The microlayer samples were collected with a Teflon coated rotating drum sampler (Hardy, 1988). Prior to each sampling period, the drum was cleaned with ultra-pure water and particle-free clean wipes and then rinsed with ultra-pure water in the field to remove any possible contamination on the drum. The bulk water samples were obtained using a plastic bilge pump and silicone-based tubing. The pump was lowered to the designated depth from a non-metallic boat, and the tubing was flushed for five minutes with the lake water to be sampled. During this time, approximately 40 L of water passed through the pumping system. Lake water samples were collected in acid-cleaned 10 L low density polyethylene (LDPE) carboys which were rinsed with the respective sample water three times, filled, capped and placed into plastic bags for transport back to the University of Vermont School of Natural Resources (Lake Champlain) or the R/V *Lake Guardian* (Lake Michigan) for processing.

At the laboratory, unfiltered water for Hg and trace metals analysis was dispensed directly into borosilicate glass (BSG) and LDPE bottles, respectively, inside a HEPA-filtered clean space. A filtered sample was processed by passing lake water through a 0.45 μm nitrocellulose filter pre-rinsed with 1 L of ultra-pure water using a desiccator set-up (Rossman and Barres, 1988). Due to a water system problem on the R/V *Lake Guardian*, the water used to rinse the Lake Michigan filters was contaminated with Hg. Thus, only unfiltered Hg values are reported in the results for Lake Michigan. Samples for Hg were preserved with bromine monochloride (1% final concentration) and metals samples were preserved with Seastar nitric acid (0.2% final concentration).

2.2. SAMPLE ANALYSIS

Mercury analysis was performed by dual amalgamation and cold vapor atomic fluorescence spectroscopy inside a Class 100 clean room at the University of Michigan as described in Hoyer and Keeler (1994). Replicate analyses were completed on all samples with an average precision of 9%. Metals samples were analyzed by a Perkin Elmer Elan 5000A Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) equipped with a pneumatic nebulizer.

3. Results and Discussion

Total Hg concentrations of filtered water from Lake Champlain are presented in Figure 1. The average Hg concentrations for the different depths were 3.4 ng/L for the microlayer, 3.2 ng/L for 0.3 m, and 2.2 ng/L for 15 m, while the median concentrations were 3.1 ng/L, 2.6 ng/L, and 1.5 ng/L, respectively.

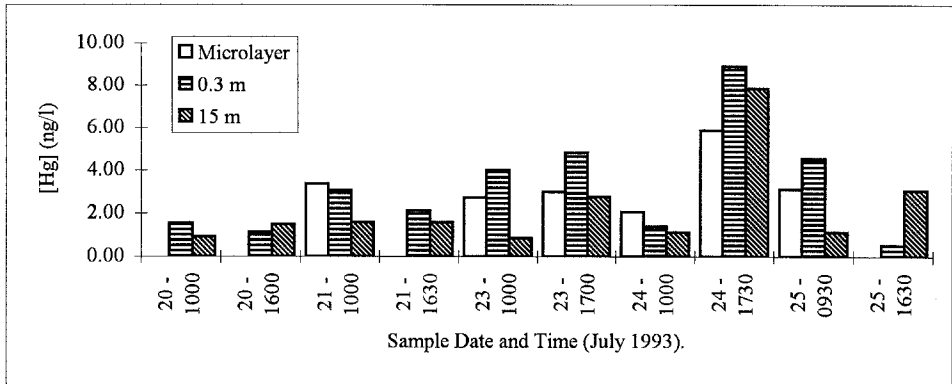


Figure 1. Total Hg Concentrations (ng/l) of Filtered Water from Lake Champlain.

There is a considerable amount of variation in the Hg levels within the respective depths between sampling periods. A similar magnitude of variability was not seen for other dissolved trace metals such as zinc (Zn) (0.76 to 1.58 $\mu\text{g/L}$ for the microlayer, 0.53 to 0.80 $\mu\text{g/L}$ for 0.3 m, 0.51 to 0.81 $\mu\text{g/L}$ for 15 m) and copper (Cu) (0.83 to 0.91 $\mu\text{g/L}$ for the microlayer, 0.50 to 0.84 $\mu\text{g/L}$ for 0.3 m, 0.62 to 0.92 $\mu\text{g/L}$ for 15 m).

Mercury levels at the 0.3 m depth were significantly correlated ($p < 0.10$) with vanadium (V) and manganese (Mn) while at the 15 m depth Hg concentrations were significantly correlated with V and chloride ions (Cl). (All correlations are positive unless noted). In the microlayer, Hg levels were significantly correlated with strontium (Sr). Thus, Hg in Lake Champlain is related to primarily crustal elements, perhaps indicating a drainage basin or sediment source.

The results of the total Hg analysis of unfiltered water from Lake Michigan are presented in Figure 2. The average Hg concentrations for the respective depths were 7.2 ng/l for the microlayer, 8.0 ng/L for 0.3 m, and 6.3 ng/L for 10 m while the median values were 5.7, 6.3, and 3.3 ng/L, respectively. Once again, a strong impact of the extreme values on the average Hg concentrations is seen. The values are higher than those from Lake Champlain, but Hg in filtered and unfiltered water are being compared. A similar magnitude of variability was not seen for other dissolved trace metals such as Zn (0.83 to 2.59 $\mu\text{g/L}$ for microlayer, 0.61 to 0.89 $\mu\text{g/L}$ for 0.3 m, 0.50 to 1.21 $\mu\text{g/L}$ for 10m) and Cu (0.51 to 0.75 $\mu\text{g/L}$ for microlayer, 0.49 to 0.53 $\mu\text{g/L}$ for 0.3 m, 0.50 to 0.81 $\mu\text{g/L}$ for 10 m).

For Lake Michigan, microlayer Hg levels were significantly negatively correlated with Mn and Zn. At the 0.3 m depth, Hg was significantly negatively correlated with magnesium (Mg) while at the 10 m depth no element correlated with Hg. Thus, in contrast to Lake Champlain, it appears that Hg levels are not associated with elements of

crustal origin. Rather, it is probable that Hg comes from a multitude of sources in the heavily industrialized region surrounding the Southern Lake Michigan Basin.

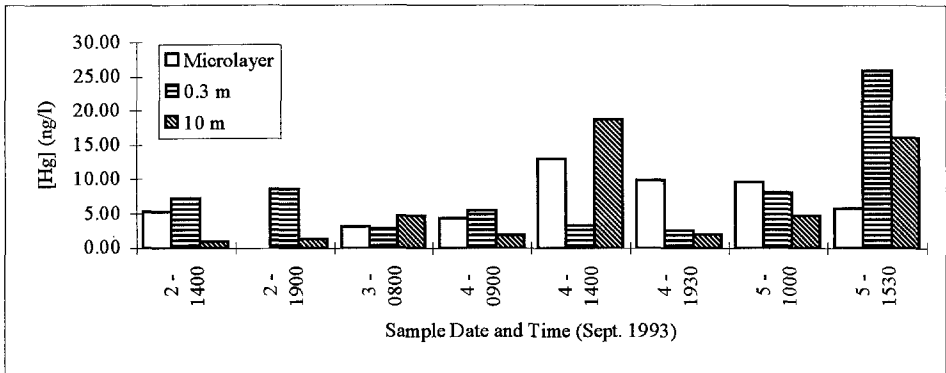


Figure 2. Total Hg Concentrations (ng/l) of Unfiltered Water from Lake Michigan.

The levels of Hg found in water from Lakes Champlain and Michigan are higher than previously reported studies for other lakes (Driscoll *et al.*, 1994; Meili *et al.*, 1991). However, higher values have been found in lakes with known point sources (Bloom and Effler, 1990; Gill and Bruland, 1990). This study shows that more surface waters should be studied in order to determine the range of Hg concentrations present in a variety of water bodies.

4. Conclusions

This intensive field investigation of Hg levels in water from Lakes Champlain and Michigan revealed large fluctuations in concentrations from the same sampling locations and depths over a 4 to 6 day period. Similar variations in levels of other trace metals were not observed. Thus, in order to better describe Hg dynamics in surface waters, spatial surveys should be complemented with intensive sampling at single sites.

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