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ATMOSPHERIC MERCURY MEASUREMENTS: RECENT OBSERVATIONS IN THE GREAT LAKES BASIN

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ABSTRACT

In order to characterize ambient levels of vapor phase and particle mercury at source and receptor locations in the Great Lakes Basin, and to diagnose source regions of atmospheric mercury, samples were collected at three locations: Illinois Institute of Technology (IIT) in Chicago, IL and South Haven, MI (SHA) and aboard the R/V Laurentian (LAU). Vapor phase mercury samples were collected onto gold coated sand traps and analyzed by cold vapor atomic fluorescence (CVAFS). Particulate phase mercury samples were collected onto both Teflon filters and pre-fired glass fiber filters. Teflon filters were analyzed by neutron activation analysis (NAA) and glass fiber filters were analyzed by CVAFS after acid digestion/extraction. Results of particle phase analysis from glass fiber filter samples and results of vapor phase mercury samples are presented here.

Mean vapor phase mercury concentrations were 8.7 ng/m^3 at IIT, 2.3 ng/m^3 on the LAU and 2.0 ng/m3 in SHA. Mean particle phase mercury concentrations by site were 97.5 pg/m^3 at IIT, 28.4 pg/m^3 on the LAU and 18.6 pg/m^3 in SHA. Particulate phase mercury comprised 1.7% (IIT), 1.3% (LAU) and 1.2% (SHA) of total mercury measured on the average.

INTRODUCTION

Currently atmospheric mercury deposition to surface waters is a topic of intense interest due to the high incidence of mercury contamination of fish in the Great Lakes Basin. To the extent that these fish are found in remote lakes where direct discharges can be ruled out, the atmosphere must necessarily present a significant pathway for this

toxic metal (Nriagu, 1990; Johansson *et al.*, 1988; Glass *et al.*, 1990; Barrie *et al.*, 1987). While the concentration of mercury in the atmosphere in remote locations is typically quite low (ppt), mercury can bioaccumulate in animal tissue, such that, even in the presence of extremely low concentrations of mercury in the water column, concentrations of mercury in fish tissue can reach levels that pose a significant human and wildlife health risk. In Michigan alone 40 of the 107 lakes studied by the Michigan Department of Natural Resources from 1987-1990 were found to contain at least one fish with levels of mercury greater than the public health fish consumption advisory level of 0.5 mg Hg/Kg (MDNR, 1991).

To investigate the sources and transport of mercury in the Great Lakes Basin, vapor and particulate phase samples were collected during the Lake Michigan Urban Air Toxics Study (LMUATS), a cooperative project between the USEPA and The University of Michigan Air Quality Laboratory. Sampling sites utilized for the one month study included a site at the Illinois Institute of Technology (IIT) in Chicago, IL, aboard the Research Vessel Laurentian (LAU), and a farm near South Haven, MI (SHA). Vapor and particulate mercury measurements were taken as part of the LMUATS in order to: 1) provide accurate mercury measurements for the Great Lakes Region using state-of-the art clean sampling and analysis techniques; 2) to investigate spatial and temporal variations in vapor and particulate mercury; 3) to investigate the deposition and transport of mercury; and 4) to begin to investigate the potential sources and source regions for the observed mercury.

Sample Analysis

Ultra-clean techniques were used in all phases of the mercury sampling and analysis. Filter packs and sample storage containers were prepared using a two-week acid-cleaning procedure, the last step of which must be completed in an ultra-clean room. Sample analysis was also carried out in the class 100 clean room.

Vapor phase mercury was collected onto gold-coated sand traps at a flow rate of 0.3 lpm. Elemental mercury levels were determined using the dual amalgamation technique described by Bloom and Fitzgerald (1988) followed by cold vapor atomic fluorescence spectroscopy.

Vapor phase samples at SHA were collected for a duration of 12 hours (8am-8pm, CDT). At IIT 12 hour daytime vapor phase samples were collected when the R/V Laurentian was in port and two six hour daytime (8am-2pm, 2pm-8pm) and one 12-hour night time sample was collected when the R/V Laurentian was at station. Vapor phase samples on the R/V Laurentian (LAU) were also collected for two six-hour periods during the day (8am-2pm and 2pm-8pm) and for 12-hours during the night. Two traps in series were run at various times throughout the study with no discernible breakthrough observed.

Particulate phase mercury was collected onto 47 mm glass fiber filters (Gelman, Type A/E) which were fired at 500°C for one hour to drive off mercury before sampling. Twenty-four hour particulate samples were collected using acid-cleaned open-faced Teflon filter packs at a nominal flow rate of 30 lpm. Exposed filters were placed in 25 ml acid-cleaned Teflon vials which were capped tightly, sealed with Teflon tape, triple-bagged in polyethylene and frozen until analysis. Field blanks were routinely taken at each site during the study to ensure that contamination was not occurring. Field blanks were prepared, placed in the samplers, stored, and analyzed exactly the same way as the actual samples.

Particulate mercury was extracted from the glass fiber filter samples using a nitric/sulfuric acid solution followed by 30 minutes of sonication, one hour oxidation in bromine monochloride and finally, reduction with stannous chloride and liberation of mercury from solution by bubbling with a mercury-free stream of nitrogen. The liberated mercury was captured on a gold-coated sand trap which was analyzed by CVAFS. The detection limit for total mercury concentrations as presently performed in the UMAQL is about 9 pg/m^3. All particulate samples were analyzed in duplicate with a precision of better than 15%. It should be noted that the data given in this paper are not corrected to STP.

RESULTS

Vapor-phase mercury measurements

Vapor phase mercury concentrations measured at IIT during the period July 10-August 9, 1991 ranged from 1.8 - 62.7, with an average of 8.7 ng/m^3 (Table 1). On the R/V Laurentian, 25 vapor phase mercury samples were collected during three separate cruises. The average vapor phase mercury concentration measured on the LAU was 2.3 ng/m^3. Of the 38 samples collected in South Haven resulted in a mean vapor phase mercury concentration was 2.0 ng/m^3. Duplicate samples taken at South Haven agreed quite well with a better than 15% variability with concentrations near 1 ng/m^3.

Table I. Vapor phase mercury measurements in Chicago (IIT), on the R/V Laurentian (LAU) and in South Haven (SHA) in ng/m^3.

SITE	N	MEDIAN	MEAN	STD DEV	MIN	MAX
IIT	58	4.5	8.7	12.0	1.8	62.7
LAU*	25	2.2	2.3	0.7	1.3	4.9
SHA	38	1.8	2.0	0.6	1.8	4.3

***Sampling Dates: 7/11-7/12, 7/25-7/27, 8/5-8/8**

Diurnal Variations in Vapor Phase Mercury

At IIT 18 samples were collected between 8am-2pm (designated as AM), 17 samples were collected between 2pm-8pm (PM), 11 daytime 12 hour samples were collected between 8am-8pm (DAY) and 12 night time samples from 8pm-8am were collected (NIGHT) in order to investigate potential diurnal behavior of vapor phase mercury. The average concentration (ng/m^3) for AM samples was 3.3 times larger than the NIGHT samples and the average concentration for PM samples was 2.1 times larger than NIGHT samples. The average vapor phase mercury concentration for AM and PM samples was 10.1 while the average vapor phase concentration for DAY samples was 9.9.

Particulate mercury measurements

Total particulate mercury was measured at the three sites for periods when the R/V Laurentian was at station. At IIT 16 samples were collected and the concentrations varied from 22.0-518.0 pg/m^3 (Table 2). The average concentration of particle phase mercury at IIT was 97.5 pg/m^3. On the R/V Laurentian 9 samples were collected giving an average particulate phase mercury concentration of 28.4 pg/m^3, with a range of 9.0-54.0 pg/m^3. In SHA 18 glass fiber filters were collected and the average particulate phase mercury concentration was 18.6 pg/m^3 with a range of 9.0-29.0 pg/m^3.

Particle phase mercury represented 1.7% of the total atmospheric Hg measured (elemental vapor phase + particulate mercury) at IIT, 1.2% at SHA and 1.3% on the LAU. The range in vapor phase mercury was largest at IIT where the percentage of mercury found in the particle phase varied from 0.07% to 7.3%. Particle phase mercury at SHA and LAU varied from 0.6-1.9% and 0.6-2.3% of vapor phase mercury, respectively.

Table II. Particle phase mercury measurements in Chicago (IIT), on the R/V Laurentian (LAU) and in South Haven (SHA) in pg/m^3.

SITE	N	MEDIAN	MEAN	STD DEV	MIN	MAX
IIT	16	60.0	97.5	118.1	22.0	518.0
LAU*	9	24.0	28.4	16.7	9.0	54.0
SHA	18	18.5	18.6	5.7	9.0	29.0

***Sampling Dates: 7/23-7/27, 8/5-8/7**

CONCLUSIONS

The vapor and particulate mercury concentrations measured during the one month study decreased from Chicago to downwind sites on the R/V Laurentian and in South Haven MI. Diurnal variation in vapor phase mercury observed at IIT indicated that samples collected between 8am-2pm may be influenced by local sources impacting the sampling site during typical daytime flow patterns, while predominant nighttime wind patterns (from Lake Michigan) may not result in local point source impacts at IIT.

Vapor phase concentrations measured in SHA were similar to those measured in other rural and remote locations in the Great Lakes Basin (Fitzgerald, 1990). Vapor phase mercury levels measured in South Haven did not demonstrate episodic behavior with flow from the southwest urban source region as did other pollutants measured. However, fine fraction (< 2.5 μm) particulate Hg concentrations as determined by NAA did reveal a peak during the main episode with SW transport. While ambient mercury levels at SHA were uniformly low, these low concentrations are present in remote environments where the atmosphere is implicated as a dominant source of mercury to waterbodies.

Particulate mercury concentrations varied widely at IIT, possibly due to local source influence. However the processes that control formation of particulate mercury are not well understood. Volatilization of mercury from the particle phase during sampling probably represents a small loss of particulate mercury during the 12-24 hour duration samples at the flow rates used in this study.

Fine fraction and total suspended particulate samples collected onto Teflon filters will be analyzed and results will be compared to those for glass fiber filter digestion collected simultaneously.

This data will be merged with measurements taken for organic and elemental carbon, volatile organic carbon, polyaromatic hydrocarbons, fine and coarse trace elements and acidic aerosol and gaseous species. Receptor modeling techniques will be applied to the combined data sets to determine sources and source strengths of the observed atmospheric mercury.

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