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# Atmospheric Mercury Deposition to Lake Michigan during the Lake Michigan Mass Balance Study

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Wet and dry mercury (Hg) deposition were calculated to Lake Michigan using a hybrid receptor modeling framework. The model utilized mercury monitoring data collected during the Lake Michigan Mass Balance Study and the Atmospheric Exchange Over Lakes and Oceans Study together with high-resolution over-water meteorological data provided by the National Oceanic and Atmospheric Administration (July, 1994–October, 1995). Atmospheric deposition was determined to be the primary pathway for mercury input to Lake Michigan, contributing approximately 84% of the estimated 1403 kg total annual input (atmospheric deposition + tributary input). Wet ( $10.6 \mu\text{g m}^{-2}$ ) and dry deposition ( $9.7 \mu\text{g m}^{-2}$ ) contributed almost equally to the annual atmospheric Hg deposition of  $20.3 \mu\text{g m}^{-2}$  (1173 kg). Re-emission of dissolved gaseous Hg from the lake was also significant ( $7.8 \mu\text{g m}^{-2}$ ), reducing the net atmospheric deposition to  $12.5 \mu\text{g m}^{-2}$  (720 kg). A strong urban influence was observed in the over-water mercury deposition estimates in the southern portion of the lake. The Chicago/Gary urban area was estimated to contribute approximately 20% (127 kg) of the annual atmospheric mercury deposition to Lake Michigan. The magnitude of local anthropogenic mercury sources in the Chicago/Gary urban area suggests that emission reductions could significantly reduce atmospheric mercury deposition into Lake Michigan.

## Introduction

Consumption advisories are presently in effect for fish caught in Lake Michigan as well as all inland lakes in the surrounding states of Michigan and Wisconsin and some in Illinois and Indiana because of elevated mercury (Hg) concentrations that may pose a health risk to the general public or sensitive subpopulation(s) (1). The elevated concentrations of Hg in Lake Michigan fish were initially assumed to be the result of direct industrial discharges to the lake. However, fish with elevated levels of Hg were subsequently found in pristine inland lakes in Minnesota and Ontario far from industrial activities (2, 3). Atmospheric deposition was later determined to be the major source of Hg to these remote inland lakes (4, 5) and has been implicated as the primary pathway for inputs of Hg to Lake Michigan (6–8).

The Lake Michigan Mass Balance Study (LMMBS) was initiated by the U.S. Environmental Protection Agency (EPA) Great Lakes National Program Office (GLNPO) to collect the

necessary monitoring data and to develop appropriate models to evaluate the sources of persistent bioaccumulative toxics, such as Hg. The mass balance modeling approach provided a quantitative framework for integrating atmospheric and riverine loadings, air–water exchange, transport and fate, and food web bioaccumulation of Hg. A companion manuscript describes the atmospheric Hg component of the LMMBS and summarizes the atmospheric Hg measurements (9).

This manuscript describes a hybrid-modeling framework that was developed for estimating both wet and dry atmospheric Hg deposition to Lake Michigan in support of the mass balance model. Since the sources of atmospheric Hg were numerous and generally not well characterized, an accurate emissions inventory that included both speciated anthropogenic and natural sources was not available. This reality, coupled with an incomplete understanding of atmospheric processes for Hg, limited the reliability of deterministic models in predicting the atmospheric behavior and deposition of Hg over short temporal and large spatial scales (10, 11). Therefore, a hybrid-modeling framework was developed to estimate wet and dry Hg deposition. The hybrid deposition model utilizes high-resolution Eulerian gridded meteorological data and long-term Hg measurements made at multiple receptor sites as part of the LMMBS.

## Modeling Approach

Deposition estimates to Lake Michigan were calculated onto a 5 km over-water grid developed by the National Oceanic and Atmospheric Administration (NOAA) Great Lakes Environmental Research Laboratory (GLERL) for the LMMBS modeling effort (2318 grid cells). The 5 km high resolution over-water meteorological fields were generated by the NOAA enhanced hydrodynamic model (12).

**Mercury Monitoring Data.** Atmospheric Hg monitoring data utilized for deposition modeling was collected at four sites around Lake Michigan (Figure 1) in Kenosha (KEN), WI ( $42.50^{\circ}\text{N}$ ,  $87.81^{\circ}\text{W}$ ); Chicago (IIT), IL ( $41.83^{\circ}\text{N}$ ,  $87.62^{\circ}\text{W}$ ); Sleeping Bear Dunes (SBD), MI ( $44.76^{\circ}\text{N}$ ,  $86.06^{\circ}\text{W}$ ); and South Haven (SHN), MI ( $42.46^{\circ}\text{N}$ ,  $86.16^{\circ}\text{W}$ ) from July 1994 through October 1995 as part of the LMMBS (9). Event precipitation samples were collected for Hg determination using automatic wet-only precipitation collectors. Twenty-four h integrated total particulate phase Hg (Hg(p)) and total vapor phase Hg (Hg(v)) samples were collected every sixth day from 8:00 a.m. local time to the following morning at 8:00 a.m. local time. Although funding for only four sites along the lakeshore was allocated, the LMMBS was the most comprehensive atmospheric Hg monitoring project completed to date in the Great Lakes Region. Previous estimates of atmospheric deposition to Lake Michigan were typically calculated using data collected exclusively from a remote location(s), using climatologically averaged precipitation depths, and generic dry deposition velocities (8, 13, 14).

**Wet Deposition.** Mercury wet deposition estimates to Lake Michigan were calculated using the LMMBS Hg in precipitation database and the National Climatic Data Center (NCDC) TD3220 digital precipitation depth database. Atmospheric wet deposition at land-based sampling locations was calculated as the product of the Hg concentration and precipitation depth. Estimating over-water wet deposition fluxes required the land-based chemical and precipitation depth data to be interpolated over the lake surface.

Precipitation depth estimates were kriged (15) onto the NOAA-GLERL over-water grid on a monthly basis utilizing data from approximately 700 National Weather Service (NWS)

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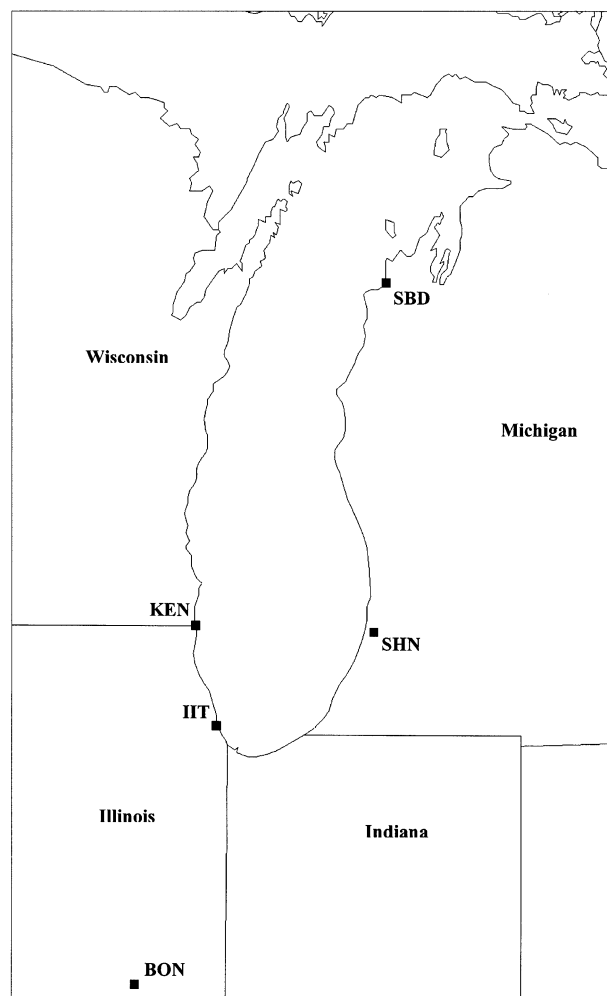


FIGURE 1. Location of sampling sites used in the Lake Michigan Mass Balance Study.

cooperative stations in Illinois, Indiana, Michigan, and Wisconsin included in the NCDC database with complete data records. The kriging procedure was configured to use a 150 km radius of influence across the model domain. An average of  $54 \pm 17$  precipitation gauge stations were used to estimate precipitation depth to each of the over-water grid cells. The mean total over-water estimated precipitation depth during the LMMBS sampling period was 113 cm (Figure 2a). The mean kriging standard error for all the over-water precipitation depth estimates was 26%.

The relative accuracy of the kriging technique for predicting precipitation depth was determined using a sensitivity analysis. The NWS cooperative station data was used to predict the monthly precipitation depth at eight LMMBS sampling site locations, including the five Hg monitoring sites. The kriged estimates were then compared to the precipitation depth measured using a Belfort rain gauge. The average difference between the monthly kriged estimates and the measured precipitation depths was 7.9% (range = 1.4–11.6%). The results of this analysis were considered excellent since the uncertainty for a Belfort gauge measurement was considered to be approximately 10%.

Monthly volume-weighted Hg in precipitation concentrations were also interpolated over Lake Michigan on a monthly basis. Since there were only four land-based sampling locations, a modified interpolation scheme was utilized to limit the sphere-of-influence of each of the sites to 100 km. Grid cells with no monitoring sites within this radius were assigned the value of its nearest neighbor site.

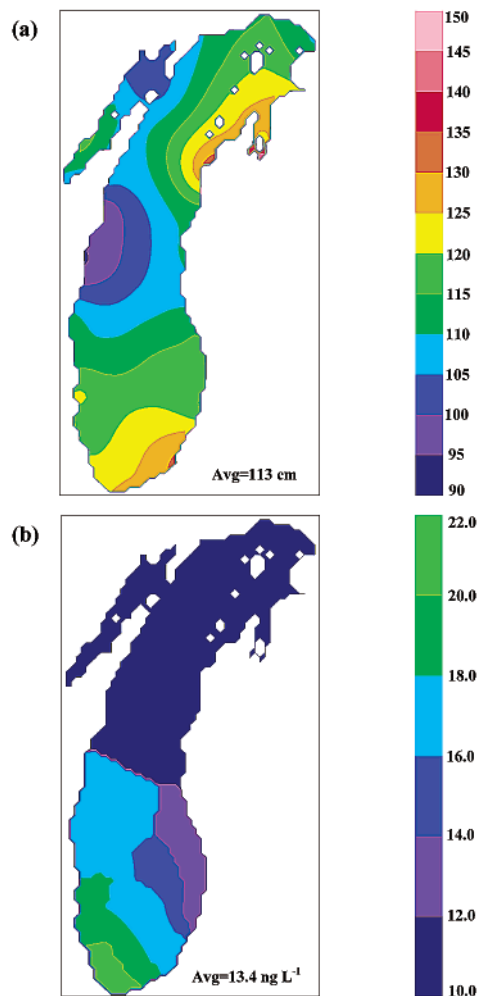


FIGURE 2. Estimated over-water (a) precipitation depth and (b) mercury in precipitation concentrations (July 1, 1994–October 31, 1995).

The result of this interpolation scheme was that the SBD site effectively represented the entire northern part of the lake (1260 of the 2318 grid cells). The spatial limitation (100 km) on the interpolation scheme was set (i) so the KEN and SHN sites would constrain the influence of the urban enhanced IIT site and (ii) because the predominant meteorological flow regime for the northern part of the lake (SBD) was considerably different than the other sites (9). The mean over-water Hg in precipitation estimate for the LMMBS sampling period was  $13.4 \pm 3.5 \text{ ng L}^{-1}$  (Figure 2b). The uncertainty imparted on the final deposition estimates by using only four monitoring locations to interpolate the Hg concentrations over the lake is difficult to quantify. However, the monitoring sites utilized for the LMMBS represented the area of highest anthropogenic source density (IIT) to an area of lowest source density (SBD). The standard deviation of the resulting distribution of over-water grid estimates ( $n = 2318$ ), therefore, represents a conservative upper and lower bounds for the estimated deposition.

**Particulate Dry Deposition.** Dry deposition of Hg(p) to Lake Michigan was estimated using LMMBS aerosol measurements in a mathematical modeling framework. No routine direct measurement technique for Hg dry deposition to natural surfaces was available at the time of this study. Measurements of other trace elements have been made using flat aerodynamic surrogate surfaces (16–18). However, contamination of the grease used to limit the resuspension from the surrogate surfaces precluded their

use for measuring Hg dry deposition flux. Recent work by Keeler et al. (14) using a water surface to measure Hg dry deposition has shown promise, but the technique was not available for routine monitoring at the time of this study.

Dry deposition rates have been shown to depend primarily on meteorological conditions (wind speed, atmospheric stability, relative humidity), depositing surface properties (type, roughness), and the physical and chemical properties of the depositing species (particle size, particle shape, solubility) (16). Of particular importance is wind speed and particle size. The majority of previous estimates of dry deposition flux to large water bodies assumed that deposition velocities and ambient concentrations were constant both spatially and temporally (e.g. refs 13 and 20). The assumption that deposition velocities are constant ignores the reality that the processes affecting the transfer of atmospheric aerosols to a water surface, such as wind speed and atmospheric stability, are extremely dynamic on relatively short time and spatial scales. And since the relationship between dry deposition flux and wind speed is a nonlinear function, the use of averaged meteorological parameters could lead to dramatically underestimated deposition velocities and fluxes (21).

A hybrid Hg(p) dry deposition modeling framework was developed for this study in which size-dependent deposition velocities and fluxes were calculated on an hourly basis for each of the 5 km over-water grid cells. The deposition estimates were made on the same spatial and temporal resolution as the available over-water meteorological data to provide the most realistic estimates possible. Over-water meteorological data (u wind component, v wind component, water temperature, and air temperature) used by the Hg dry deposition model was generated by the NOAA enhanced hydrodynamic model (12). The hydrodynamic model used meteorological input data from numerous surface observation stations around the lake as well as over-water data collected from NOAA's buoys. The Hg dry deposition flux was calculated as the product of the over-water interpolated ambient Hg(p) concentration and the modeled deposition velocity.

The over-water Hg(p) estimates were interpolated on a monthly basis in the same manner as the Hg in precipitation data. Since only total Hg(p) measurements were made during the LMMBS, over-water size fractionated Hg(p) measurements made aboard the research vessel *Lake Guardian* during the Atmospheric Exchange Over Lakes and Oceans Study (AEOLOS) were used to characterize the Hg(p) size distribution (9). The Hg(p) size distribution was determined to be bimodal with 70% of the total Hg(p) in the fine fraction and 30% of the total Hg(p) in the coarse fraction during the study. The mass median aerodynamic diameters for the fine fraction and coarse fraction were 0.68  $\mu\text{m}$  and 3.8  $\mu\text{m}$ , respectively (22).

The deposition velocities for fine and coarse fraction Hg(p) were calculated using a model formulated for natural water surfaces. The approach was based upon a model described by Williams (23) and is procedurally similar to electrical circuit analysis (resistance). The Williams model divides the atmosphere into two layers, the turbulent layer and the deposition layer. Aerosol movement through the upper layer is controlled by gravitational settling and turbulent transfer, while movement through the lower layer is controlled by two parallel paths. One path represents the transfer resistance from air to a smooth water surface and the second path represents the transfer resistance to a broken water surface. The broken surface path was intended to characterize the increased deposition due to breaking waves and spray formation. The model was applied to Lake Michigan using optimized broken water transfer coefficients ( $K_{bs}$ ) and lateral transfer coefficients ( $K_m$ ) coefficients (24) from over-

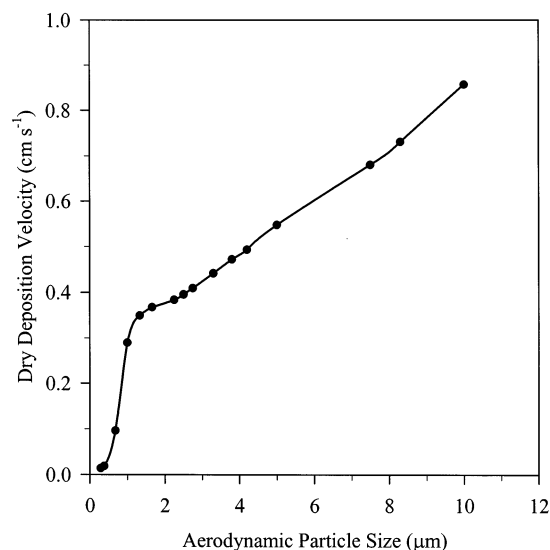


FIGURE 3. Annualized over-water size-dependent Hg(p) dry deposition velocities (July 1, 1994–October 31, 1995).

water measurements made aboard the University of Michigan research vessel *Laurentian* during the Lake Michigan Urban Air Toxics Study (7). The optimized transfer coefficients were particle size dependent. Based on these results  $K_{bs} = 27 \text{ cm s}^{-1}$  and  $K_m = 0.9 \text{ cm s}^{-1}$  were used for the fine fraction (0.68  $\mu\text{m}$ ) Hg(p) and  $K_{bs} = 225 \text{ cm s}^{-1}$  and  $K_m = 1.2 \text{ cm s}^{-1}$  were used for the coarse fraction (3.8  $\mu\text{m}$ ) Hg(p). Since the aerodynamic surrogate surface is thought to represent a minimum deposition flux, the estimates for the  $K_{bs}$  and  $K_m$  are thought to be quite conservative.

A sensitivity analysis of the model's particle size parametrization was conducted. Sixteen discrete particle sizes, ranging from 0.29  $\mu\text{m}$  to 10.0  $\mu\text{m}$ , were modeled onto the 5 km over-water grid for the entire LMMBS sampling period. Figure 3 depicts a plot of the resulting annualized average deposition velocities as a function of particle size. The deposition velocities increased rapidly with particle size up to about 1.5  $\mu\text{m}$  when the particles started to approach their terminal settling velocities. The result of this relationship is that a 10% error in parametrizing the Hg(p) fine fraction particle size would equate to a 24% error in the calculated deposition velocity. Conversely, a 10% error in parametrizing the Hg(p) coarse fraction particle size would result in only a 4% error in the calculated deposition velocity.

The size-specific deposition velocities, calculated by the model for the entire LMMBS sampling period, were extremely variable. The hourly deposition velocities for each grid cell varied by over an order of magnitude during the course of the study period. Size-specific overall average deposition velocities varied by approximately a factor of 2 across the lake domain (Figure 4a and 4b). The overall mean fine fraction Hg(p) deposition velocity from the distribution of over-water grids was  $0.09 \pm 0.01 \text{ cm s}^{-1}$  and the overall mean coarse fraction Hg(p) deposition velocity from the distribution of over-water grids was  $0.46 \pm 0.04 \text{ cm s}^{-1}$ . Consequently, the Hg(p) dry deposition flux was dominated by coarse particles.

**Air/Water Gaseous Mercury Exchange.** Hg(v) measurements were made during the LMMBS to be incorporated into an air/water exchange model to estimate  $\text{Hg}^0$  flux in and out of Lake Michigan. Measurements of elemental dissolved gaseous mercury (DGM) in the water column during AEOLOS (May 1994, July 1994, and January 1995) found that Lake Michigan was always supersaturated with respect to the atmosphere (25). Saturation levels of DGM in Lake Michigan during AEOLOS were determined to be  $286 \pm 99\%$ , indicating that exchange of  $\text{Hg}^0$  will be always



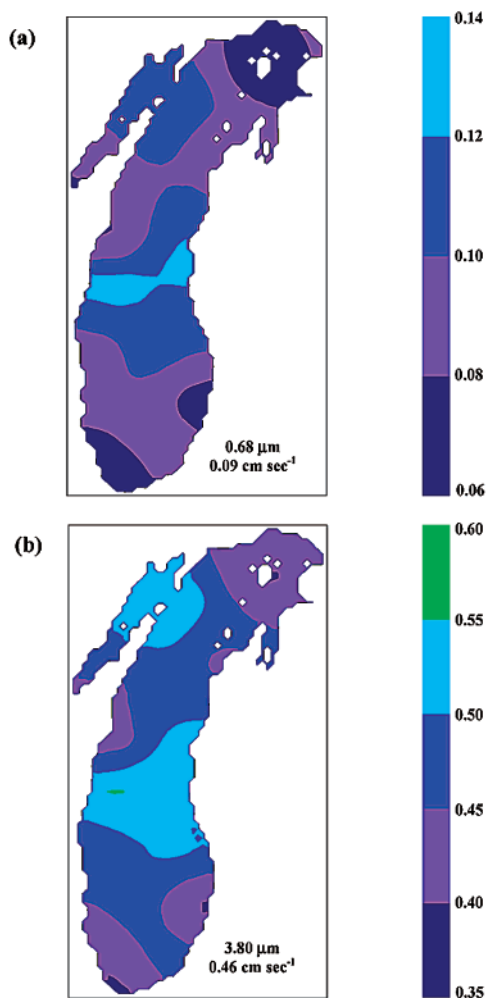


FIGURE 4. Estimated over-water (a) fine fraction deposition velocities (b) coarse fraction deposition velocities (July 1, 1994–October 31, 1995).

from the water to the atmosphere. However, subsequent research has found that divalent  $\text{Hg}^{2+}$  species (e.g.  $\text{HgCl}_2$ ,  $\text{HgBr}_2$ ) may play an important role in atmospheric dry deposition. Stevens et al. (26) found that 75–95% of the total Hg emitted from two incinerators in Florida was divalent or reactive gaseous mercury (RGM). In subsequent measurements of ambient air in rural Indiana and Tennessee, Lindberg and Stratton (27) found that approximately 3% of  $\text{Hg}(\text{v})$  was RGM.

The presence of RGM in remote midwestern ambient air has major implications on atmospheric Hg deposition to Lake Michigan. Unlike  $\text{Hg}^0$ , RGM is water soluble and will efficiently dry deposit to natural water bodies at rates comparable to nitric acid ( $1\text{--}5\text{ cm s}^{-1}$ ) (27, 28). Although no RGM measurements were made during the LMMBS, it was critical to estimate the potential impact of RGM to atmospheric Hg deposition to Lake Michigan. Estimates of RGM deposition were needed to outline additional uncertainty in the total lakewide Hg deposition model and to determine the importance of conducting future atmospheric RGM measurements in the Lake Michigan basin. Vette et al. (25) constructed an air/water Hg exchange model that independently calculated DGM emission and RGM deposition to Lake Michigan on the NOAA GLERL over-water 5 km grid during the LMMBS period assuming the RGM concentrations based upon the  $\text{Hg}(\text{v})$  measurements.

TABLE 1. Lake Michigan Monthly Hg Wet Deposition Estimate Summary (July 1994–October 1995)

month	total wet deposition mean $\pm$ SD (kg)	grid cell mean $\pm$ SD ( $\mu\text{g m}^{-2}$ )	grid cell range ( $\mu\text{g m}^{-2}$ )
Jul 1994	103 $\pm$ 51	1.78 $\pm$ 0.89	0.67–5.41
Aug 1994	103 $\pm$ 31	1.79 $\pm$ 0.53	0.92–3.68
Sep 1994	68 $\pm$ 16	1.18 $\pm$ 0.27	0.49–1.88
Oct 1994	24 $\pm$ 5	0.42 $\pm$ 0.08	0.21–0.82
Nov 1994	48 $\pm$ 29	0.83 $\pm$ 0.50	0.30–2.39
Dec 1994	18 $\pm$ 24	0.32 $\pm$ 0.41	0.04–2.39
Jan 1995	29 $\pm$ 14	0.50 $\pm$ 0.25	0.11–0.95
Feb 1995	10 $\pm$ 5	0.18 $\pm$ 0.08	0.04–0.44
Mar 1995	40 $\pm$ 12	0.70 $\pm$ 0.21	0.35–1.23
Apr 1995	72 $\pm$ 33	1.25 $\pm$ 0.57	0.57–2.44
May 1995	80 $\pm$ 16	1.38 $\pm$ 0.28	0.92–2.32
Jun 1995	35 $\pm$ 23	0.61 $\pm$ 0.40	0.19–2.19
Jul 1995	76 $\pm$ 21	1.32 $\pm$ 0.36	0.60–2.07
Aug 1995	91 $\pm$ 37	1.58 $\pm$ 0.64	0.65–4.04
Sep 1995	36 $\pm$ 10	0.63 $\pm$ 0.18	0.33–1.06
Oct 1995	58 $\pm$ 19	1.01 $\pm$ 0.33	0.65–2.28
total	895 $\pm$ 243	15.49 $\pm$ 4.20	10.26–26.97

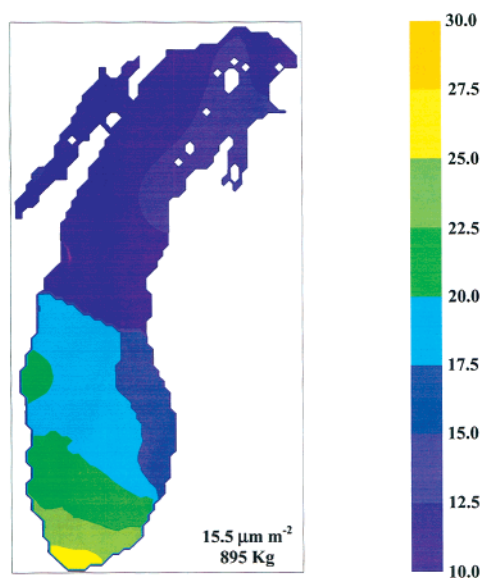


FIGURE 5. Estimated over-water wet deposition flux (July 1, 1994–October 31, 1995).

## Results and Discussion

**Atmospheric Mercury Deposition to Lake Michigan.** Mercury wet deposition was calculated for each of the over-water grid cells on a monthly basis by taking the product of the estimated precipitation depth and estimated mercury in precipitation concentration. A summary of the Hg wet deposition estimates for the entire LMMBS sampling period is summarized in Table 1 and depicted in Figure 5. The average Hg wet deposition for the LMMBS period was  $15.5 \pm 4.2\text{ } \mu\text{g m}^{-2}$  (mean  $\pm$  standard deviation) based upon the distribution of over-water 5 km grid estimates (equating to  $895 \pm 243\text{ kg}$ ). Since atmospheric deposition estimates are typically expressed in terms of annual flux, annualized wet deposition fluxes to Lake Michigan were calculated from the entire LMMBS data set by averaging the over-water flux estimates for months that had 2 years of data (July–October). The mean annualized over-water Hg wet deposition flux was estimated to be  $10.6 \pm 3.2\text{ } \mu\text{g m}^{-2}$  (equating to  $614 \pm 186\text{ kg}$ ). The highest Hg wet deposition rates occurred during the spring and summer months (May–August) when both precipitation depths and volume weighted mean Hg concentrations were higher. Elevated Hg wet deposition in the

TABLE 2. Lake Michigan Monthly Hg(p) Dry Deposition Estimate Summary (July 1994–October 1995)

month	total dry deposition mean $\pm$ SD (kg)	grid cell mean $\pm$ SD ( $\mu\text{g m}^{-2}$ )	grid cell range ( $\mu\text{g m}^{-2}$ )
Jul 1994	4.8 $\pm$ 2.3	0.08 $\pm$ 0.04	0.05–0.31
Aug 1994	6.7 $\pm$ 6.0	0.12 $\pm$ 0.10	0.04–0.58
Sep 1994	5.8 $\pm$ 4.0	0.10 $\pm$ 0.07	0.04–0.39
Oct 1994	7.6 $\pm$ 2.8	0.13 $\pm$ 0.05	0.06–0.25
Nov 1994	8.0 $\pm$ 6.8	0.14 $\pm$ 0.12	0.04–0.52
Dec 1994	6.1 $\pm$ 4.3	0.11 $\pm$ 0.07	0.03–0.35
Jan 1995	4.8 $\pm$ 4.0	0.08 $\pm$ 0.07	0.02–0.28
Feb 1995	8.1 $\pm$ 4.2	0.14 $\pm$ 0.07	0.06–0.36
Mar 1995	6.5 $\pm$ 2.7	0.11 $\pm$ 0.05	0.05–0.29
Apr 1995	3.4 $\pm$ 1.2	0.06 $\pm$ 0.02	0.03–0.12
May 1995	5.2 $\pm$ 2.2	0.09 $\pm$ 0.04	0.05–0.22
Jun 1995	3.3 $\pm$ 1.5	0.06 $\pm$ 0.03	0.03–0.14
Jul 1995	4.1 $\pm$ 1.7	0.07 $\pm$ 0.03	0.04–0.20
Aug 1995	3.7 $\pm$ 1.5	0.06 $\pm$ 0.03	0.03–0.13
Sep 1995	8.6 $\pm$ 4.5	0.15 $\pm$ 0.08	0.07–0.50
Oct 1995	5.8 $\pm$ 3.0	0.10 $\pm$ 0.05	0.04–0.25
total	92.4 $\pm$ 50.5	1.60 $\pm$ 0.87	0.76–4.81

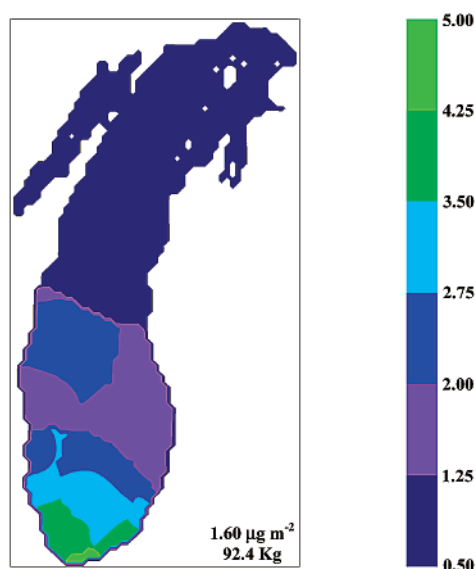


FIGURE 6. Estimated over-water Hg(p) dry deposition flux (July 1, 1994–October 31, 1995).

southern portion was also a function of both higher Hg concentrations in the Chicago/Gary urban area and higher precipitation depths.

Hg(p) dry deposition fluxes to Lake Michigan were summarized on a monthly basis by multiplying the mean over-water deposition flux by the surface area of the lake (57 800 km<sup>2</sup>). The monthly dry deposition fluxes are presented in Table 2. Although there was not a lot of temporal variability, there was a definite spatial pattern (Figure 6). Significantly higher Hg(p) concentrations in the Chicago/Gary urban area resulted in Hg(p) dry depositional fluxes that were almost 10 times higher than in the northern portion of the lake. The mean over-water Hg(p) dry deposition flux for the entire LMMBS period was  $1.6 \pm 0.9 \mu\text{g m}^{-2}$  based upon the distribution of over-water grid estimates (equating to  $92 \pm 51 \text{ kg}$ ). The annualized Hg(p) deposition flux was  $1.2 \pm 0.7 \mu\text{g m}^{-2}$  (equating to  $69 \pm 38 \text{ kg}$ ).

Gas-phase Hg exchange across the air/water interface of Lake Michigan during the LMMBS was found to be significant (25). The emission flux of DGM was calculated to be  $10.6 \pm 2.9 \mu\text{g m}^{-2}$  ( $615 \pm 162 \text{ kg}$ ), and the deposition flux of RGM was calculated to be  $11.7 \pm 2.7 \mu\text{g m}^{-2}$  ( $676 \pm 156 \text{ kg}$ ). On

TABLE 3. Net Atmospheric Hg Deposition to Lake Michigan Summary

type	LMMBS period total $\pm$ SD (kg)	LMMBS period mean $\pm$ SD ( $\mu\text{g m}^{-2}$ )	annualized total $\pm$ SD (kg)	annualized mean $\pm$ SD ( $\mu\text{g m}^{-2}$ )
wet	895 $\pm$ 243	15.5 $\pm$ 4.2	614 $\pm$ 186	10.6 $\pm$ 3.2
Hg(p)	92 $\pm$ 51	1.6 $\pm$ 0.9	69 $\pm$ 38	1.2 $\pm$ 0.7
RGM	676 $\pm$ 156	11.7 $\pm$ 2.7	490 $\pm$ 139	8.5 $\pm$ 2.4
DGM	−615 $\pm$ 162	−10.6 $\pm$ 2.9	−453 $\pm$ 144	−7.8 $\pm$ 2.5
total	1048 $\pm$ 335	18.2 $\pm$ 5.8	720 $\pm$ 276	12.5 $\pm$ 4.8

an annualized basis, the DGM emission and RGM deposition fluxes were  $7.8 \pm 2.5 \mu\text{g m}^{-2}$  ( $453 \pm 144 \text{ kg}$ ) and  $8.5 \pm 2.4 \mu\text{g m}^{-2}$  ( $490 \pm 139 \text{ kg}$ ), respectively.

The total atmospheric Hg budget for Lake Michigan during the LMMBS study period is summarized in Table 3. On an annual basis, the net Hg deposition to the lake was  $12.5 \mu\text{g m}^{-2}$  or 720 kg. Wet deposition was determined to be the major contributor of atmospheric Hg deposition to the lake (54%). The deposition and emission fluxes of gaseous Hg species were very similar. However, the uncertainty of the RGM deposition estimate is unknown and potentially large. If the amount of RGM is found to be significantly higher or lower in the Lake Michigan basin, then its relative importance to total Hg deposition to the lake can dramatically increase or decrease, respectively. While this modeling effort represents the best estimate of atmospheric Hg deposition to Lake Michigan to date, it also highlights the critical need for monitoring RGM in the Great Lakes Region.

**Relative Importance of Atmospheric Deposition.** One of the main objectives of the LMMBS was to determine the Hg loading rates by media (e.g. atmospheric, tributaries). Atmospheric deposition and tributary inputs were hypothesized to be the major loading terms. Mercury loadings to Lake Michigan during the LMMBS study period from tributaries have been reported (29). Hurley et al. (29) estimated the annual tributary Hg flux to be  $230 \text{ kg year}^{-1}$ . The total annualized Hg input into Lake Michigan from the atmosphere and the tributaries during the LMMBS was  $1403 \text{ kg year}^{-1}$ . Direct atmospheric deposition was determined to be the dominant source of Hg inputs to Lake Michigan, contributing approximately 84% ( $1173 \text{ kg year}^{-1}$ ) of the annualized total. The actual contribution of atmospheric deposition of Hg may be even greater since the tributaries include Hg that has been atmospherically deposited directly to the tributaries and Hg atmospherically deposited on terrestrial systems and swept into the tributaries from stormwater runoff.

**Deposition Comparison to IADN Network Estimates.** Most recent estimates of atmospheric deposition of trace elements and organic compounds to the Great Lakes have been made using data from the Integrated Atmospheric Deposition Network (IADN) (13, 30). This network was established in 1988 as a binational program between the United States and Canada to assess the role of atmospheric impacts on toxics substances in the Great Lakes (31). The strategy of this effort was to make measurements from one sampling site on each of the Great Lakes to monitor regional trends and estimate atmospheric deposition. The five sites were established in remote locations to avoid being unduly impacted by local sources. The SBD site is the IADN station for Lake Michigan. During AEOLUS and the LMMBS, Hg measurements at the SBD site were significantly lower in concentration and deposition than all the other sampling locations (9).

The wet and dry Hg deposition models developed for this study were rerun for the LMMBS period using only Hg data measured at the SBD site to determine the importance of the

TABLE 4. Comparison of Annual Hg Deposition Estimates Using All LMMBS Data versus Just SBD Data

deposition	SBD mean ( $\mu\text{g m}^{-2}$ )	SBD (kg)	LMMBS mean ( $\mu\text{g m}^{-2}$ )	LMMBS (kg)	difference (%)
wet	8.4	484	10.6	614	21.2
aerosol dry	0.7	39	1.2	69	43.1
total	9.1	523	11.8	683	23.4

TABLE 5. Chicago/Gary Annualized Hg Wet and Hg(p) Dry Deposition Contribution

deposition	wet mean ( $\mu\text{g m}^{-2}$ )	wet total (kg)	Hg(p) mean ( $\mu\text{g m}^{-2}$ )	Hg(p) total (kg)
all data	10.6	614	1.2	69
modified	9.2	531	0.4	25
Chicago/Gary	1.4	83	0.8	44

more spatially resolved network. The results of the modified deposition model runs are presented in Table 4. Even though the SBD Hg data represented more than 50% of the over-water grid cells on the previous LMMBS model runs, the modified model run calculated 21.2% and 43.1% less Hg wet and particulate dry deposition, respectively. Overall, atmospheric deposition to Lake Michigan was underestimated by approximately 25% when measurements from the southern portion of the lake were not included, highlighting the importance of selecting sampling locations that are more representative of the diversity of the surrounding air basin.

**Influence of the Chicago/Gary Urban Area on Atmospheric Hg Deposition to Lake Michigan.** One of the major goals of AEOLOS was to evaluate the impact of the Chicago/Gary urban area on atmospheric Hg deposition to southern Lake Michigan. Elevated Hg(p) concentrations were observed aboard the *Lake Guardian* during the sampling intensives, suggesting that enhanced over-water dry deposition was occurring (9).

However, a comprehensive quantitative assessment of the urban influence could not be determined from this relatively small data set. While AEOLOS was looking at the over-water urban influence in terms of small spatial scales (20 km), meteorological transport analysis of the entire LMMBS data set found significant large-scale urban influences that impacted all of the monitoring sites (9). The Lake Michigan Hg wet and particulate dry deposition models were reinitialized using modified Hg concentration fields to quantitatively determine the relative importance of the Chicago/Gary urban area to the lake wide flux.

Monthly over-water interpolated Hg concentration fields were recalculated without samples determined to be impacted by the Chicago/Gary urban area. These samples were identified using cluster analysis of meteorological transport data (9). All Hg samples from IIT were eliminated, along with samples from the KEN, SBD, and SHN monitoring sites associated with air transport clusters shown to be enhanced by the Chicago/Gary urban area.

Modeling results using the modified concentration fields indicate the annual Hg deposition from all sources other than those located in the Chicago/Gary urban area was  $9.2 \mu\text{g m}^{-2}$  (531 kg) and  $0.4 \mu\text{g m}^{-2}$  (25 kg) for wet and particle dry deposition, respectively. Table 5 summarizes the atmospheric Hg deposition estimates to Lake Michigan from both sets of model runs. The contribution from the Chicago/Gary urban area was determined by difference to be  $1.4 \mu\text{g m}^{-2}$  (83 kg) for wet deposition and  $0.8 \mu\text{g m}^{-2}$  (44 kg) for dry deposition. The Chicago/Gary urban area enhanced the

overall Hg atmospheric deposition to Lake Michigan by 19% (14% of wet deposition and 63% of particle dry deposition). Although the calculated contribution of the Chicago/Gary urban area on Hg deposition to Lake Michigan presented above was the best estimate possible from the LMMBS dataset, it probably did not accurately detail the magnitude of the urban influence. RGM dry deposition was not included in the analysis and was the largest source of uncertainty in the estimate. The magnitude of local anthropogenic mercury sources in the Chicago/Gary urban area suggests that emission reductions could significantly reduce atmospheric mercury deposition into Lake Michigan.

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