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Deposition and Emission of Gaseous Mercury to and from Lake Michigan during the Lake Michigan Mass Balance Study (July, 1994–October, 1995)

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This paper presents measurements of dissolved gaseous mercury (DGM) concentrations in Lake Michigan and the application of a mechanistic approach to estimate deposition and emission fluxes of gaseous mercury (Hg^{2+} and Hg^0) to and from Lake Michigan. Measurements of DGM concentrations made during May and July, 1994 and January, 1995 indicate that Lake Michigan was supersaturated with DGM suggesting that transfer of Hg^0 occurs from the water to the atmosphere. Over-water concentrations of gaseous Hg^{2+} were estimated from total gaseous Hg (TGM) concentrations measured at five sites in the basin and used to model dry deposition fluxes of Hg^{2+}. The modeling approach combines estimates of dry deposited Hg^{2+} with known photochemical and biotic reduction rates to form Hg^0, which is available for re-emission. The model accounts for temporal and spatial variations in the deposition velocity of gaseous Hg^{2+} and the transfer velocity of Hg^0 using high temporal and spatial resolution meteorological data. The modeled DGM concentrations agree well with the observed DGM concentrations in Lake Michigan. The modeled dry deposition fluxes of Hg^{2+} (286–797 kg yr^{-1}) are very similar to the emission fluxes of Hg^0 (320–959 kg yr^{-1}), depending on the gaseous Hg^{2+} concentration used in the model.

Introduction

Elevated concentrations of mercury (Hg) in fish have led to consumption advisories for fish taken from many lakes in the Great Lakes region. Wet deposition has been identified as the most likely source of Hg to the water surface even in regions far from direct discharges of Hg (*1–3*). Mercury is incorporated into precipitation via conversion of elemental Hg vapor (Hg^0) to water soluble divalent Hg (Hg^{2+}) by gas-phase reactions with ozone (*4*) and in-cloud oxidation processes (*5, 6*). Although Hg^{2+} has been recognized as a significant component of wet deposition, the influence of Hg^{2+} on dry deposition fluxes to water bodies is poorly understood. Reliable and proven methods were not available until recently to directly measure concentrations and dry deposition fluxes of Hg^{2+} or reactive gaseous Hg (RGM).

Significant progress has been made in evaluating current methods for measuring concentrations of RGM using a variety of methods (*7*). Nonetheless, dry deposition fluxes of Hg^{2+} are often lacking in atmospheric Hg budgets for water bodies due to the paucity of available data. Recent modeling efforts, however, have shown that dry deposition of Hg^{2+} may contribute as much as 65% of the total atmospheric deposition of Hg to the Great Lakes (*8*). Using an emissions inventory approach coupled with a Eularian transport modeling framework, Pai et al. (*9*) concluded that dry deposition of Hg is dominated by deposition of gaseous Hg^{2+}.

Once deposited to the water surface, Hg^{2+} may be converted to the toxic methyl-Hg form (which bioaccumulates in the aquatic food chain), reduced to form gaseous Hg^0, or scavenged by particles and deposited to the sediment. Mechanisms of reduction involving photolysis (*10–12*) and biota (*13, 14*) are known to be important in the formation of dissolved gaseous Hg (DGM). Measurements of DGM in freshwater lakes indicated that Hg^0 comprises > 98% of gaseous Hg in water (*15*) and is present at supersaturated concentrations with respect to the atmosphere (*10, 15*). Volatilization of Hg^0 has been recognized as an important removal process from water bodies and may reduce the Hg burden available for methylation (*16*). Current global estimates indicate that volatilization from the oceans may account for ~30% of the total flux of Hg to the atmosphere (*17*).

Previous attempts to model gaseous Hg cycling at the air–water interface have not addressed the factors that affect the temporal and spatial variations in deposition and emission fluxes of gaseous Hg. Shannon and Voldner (*8*) calculated dry deposition fluxes for Hg^{2+} using an implied diurnal and seasonal relationship in deposition velocity but did not include horizontal variations due to over-water wind speed and atmospheric stability. Estimates of Hg^0 emission from water surfaces are typically calculated using a two-film gas exchange model (e.g. ref *18*). This approach combines an equilibrium partitioning model with an estimated transfer velocity to estimate emission fluxes. The concentration gradient of Hg^0 at the air–water interface is generally assumed to be constant (both temporally and spatially) since limited data exist on measurements of DGM in the water column. The transfer velocity is also usually assumed to be constant but is known to vary as a function of wind speed, water temperature, and wave conditions for other gases (*19, 20*). Estimates of Hg^0 emission calculated for Lake Michigan using this approach indicate that volatilization may remove ~50 (*21*) to 500% (*8*) of the Hg deposited by the atmosphere on an annual basis.

The objective of this study was to determine the contribution of gaseous Hg cycling at the air–water interface to the overall Lake Michigan mass balance. As a component of the Lake Michigan Mass Balance Study (LMMBS), this work provided information regarding the importance of gaseous Hg deposition and emission in comparison to wet and dry particle deposition as well as tributary inputs of Hg to Lake Michigan. Gaseous Hg deposition and emission fluxes were estimated by integrating measurements of gaseous Hg in air and water with high-resolution meteorological data. Measurements of DGM in water were made during the Atmospheric Exchange Over Lakes and Ocean Surfaces (AEOLOS) study in May and July, 1994 and January, 1995. Total gaseous Hg (TGM) in air was measured during the LMMBS at four sites on the lakeshore from July, 1994 to October, 1995 and over-water during the AEOLOS study periods. Over-water meteorological data were used to calculate the horizontal

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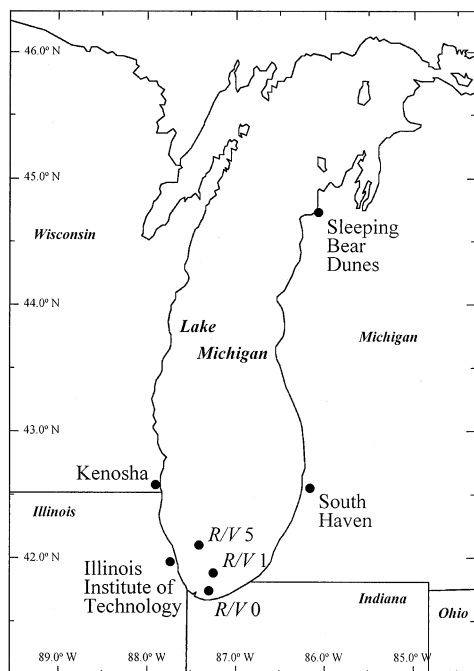† Current address: U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

FIGURE 1. Location of the land-based and over-water sampling sites during the Lake Michigan Mass Balance and the Atmospheric Exchange Over Lakes and Ocean Surfaces studies. R/V represents the location of the EPA R/V *Lake Guardian* at stations 5, 1, and 0.

and temporal variations in the dry deposition velocity of Hg^{2+} and the transfer velocity of Hg^0.

We developed a mechanistic model that, for the first time, linked dry deposition fluxes of Hg^{2+} with known in-lake processes to convert Hg^{2+} to Hg^0, which was subsequently available for re-emission. Dry deposition fluxes of Hg^{2+} were calculated using Hg^{2+} concentrations estimated from measurements of TGM in air. This treatment of gaseous Hg cycling at the air−water interface represents a unique approach at understanding the behavior of gaseous Hg and the relationship between gaseous Hg in air and the water column.

Methods

Dissolved and Total Gaseous Mercury Measurements. Water samples for DGM analysis were collected from the EPA Research Vessel (R/V) *Lake Guardian* during the AEOLOS study from May 17−19, 1994, July 17−28, 1994, and January 16−19, 1995. During the studies, the R/V was anchored at three stations approximately 30 km from Chicago, IL (Figure 1). Station 5 was located 18 km from shore (42°00′N, 87°25′W), station 1 was located 10 km from shore (41°46′N, 87°20′W), and station 0 was located 5 km from shore (41°40′N, 87°22′W). Samples were collected at a depth of 5 m below the surface. This depth represented the mid-epilimnion in July, 1994 and the mixed layer during May, 1994 and January, 1995 when the lake was not thermally stratified. Diurnal profiles of DGM concentrations were determined by collecting samples several times daily during both sunny and cloudy days. A metal-free submersible bilge pump with silastic tubing (Cole Parmer) was used to collect sample water into previously acid-cleaned (*22*) 2-L Teflon bottles. After the pump and tubing were rinsed with at least 150 L of water, the Teflon bottles were rinsed three times with sample water and samples were collected without agitation to prevent losses of DGM. The samples were immediately taken to the laboratory on board the R/V and purged with Hg-free nitrogen for 90 min at a flow rate of 0.5 LPM. The gaseous Hg released from solution was captured onto gold-coated glass bead traps. Periodically, field blanks ($N = 8$) were collected by replacing

the gold trap after the initial purge and the sample was purged for an additional 90 min. The concentration of DGM in field blanks was 7 ± 2 pg L^{-1} (mean $\pm$ SD). All reported DGM concentrations have been blank corrected. As an additional quality assurance measure, duplicate samples were collected ($N = 12$) and agreed within $17 \pm 11\%$. The Teflon bottles were stored with purged DGM-free sample water between sampling periods.

Measurements of total gaseous Hg (TGM) in air were made once every sixth day from July, 1994 to October, 1995 as part of the LMMBS and every day during the AEOLOS study periods. Samples for TGM in air were collected at four land-based sites near the shore of Lake Michigan during the LMMBS and aboard the R/V during the AEOLOS study (Figure 1). The land-based sites included south Chicago on the campus of the Illinois Institute of Technology (41°50′N, 87°37′W) located 1.6 km from the shore, Kenosha, WI (42°30′N, 87°48′W) about 0.5 km from the shore, South Haven, MI (42°27′N, 86°10′W) about 3.6 km from the shore, and Sleeping Bear Dunes National Seashore (44°45′N, 86°03′W) in Empire, MI about 0.5 km from the shore. Samples were collected at a height of ∼2 m above ground at the land-based sites and from a suspended sampling platform mounted off the bow of the R/V at a height of ∼10 m above the water. Samples for TGM in air were collected from the R/V concurrently with DGM samples. Air samples for TGM analysis were captured on gold-coated glass bead traps placed downstream of a prefired glass fiber filter. Additional details may be found elsewhere (*23*).

The gold traps used to measure TGM and DGM were analyzed at the University of Michigan Air Quality Laboratory within 5 days of collection. The gold traps were blanked prior to use by heating to ∼500 °C and sealed with Teflon end plugs. Before and after sampling the traps were stored in sealed plastic tubes and double bagged to avoid contamination. The gold traps were analyzed for elemental Hg by cold vapor atomic fluorescence spectrometry (CVAFS) using the dual-amalgamation procedure (*24*).

Deposition−Emission Model. The modeling approach used in this study treated gaseous Hg at the air−water interface as a two species system involving Hg^0 and Hg^{2+} (Figure 2). While other gas phase Hg species (e.g. dimethyl-Hg) may exist in the atmosphere and water, the concentrations are often below detection and normally represent a very small portion of the TGM in air and DGM in water (*15*). Therefore, we assumed DGM in the water column consisted entirely of Hg^0 and TGM in air consisted of Hg^0 and Hg^{2+}. Divalent Hg^{2+} in the atmosphere (i.e. reactive gaseous Hg, RGM) is very soluble in water causing transfer of RGM exclusively from the atmosphere to the water surface. Elemental Hg vapor is sparingly soluble in water but typically present at supersaturated concentrations with respect to the atmosphere. As a result, the net transfer of Hg^0 is almost entirely from the water to the atmosphere except when DGM concentrations are below saturation with respect to the atmosphere.

Deposition and emission fluxes of gaseous Hg were independently calculated and integrated for each 1-h time step to calculate the concentrations of the Hg species in the water column. The RGM deposited to the water surface, termed dissolved reactive Hg (DRM), was subject to either scavenging by suspended particulate matter (SPM) in the water column or conversion to DGM (Figure 2) via competing processes. The resulting DGM concentrations were used to calculate the emission flux. Monthly data for SPM in Lake Michigan (*25*) was used with the particulate distribution coefficient (K_d; see Figure 2) to estimate particulate Hg scavenging in the water column. The log K_d values for Lake Michigan measured during the LMMBS time period ranged from 5.5 to 5.8 (*21*). Monthly settling velocities for SPM in
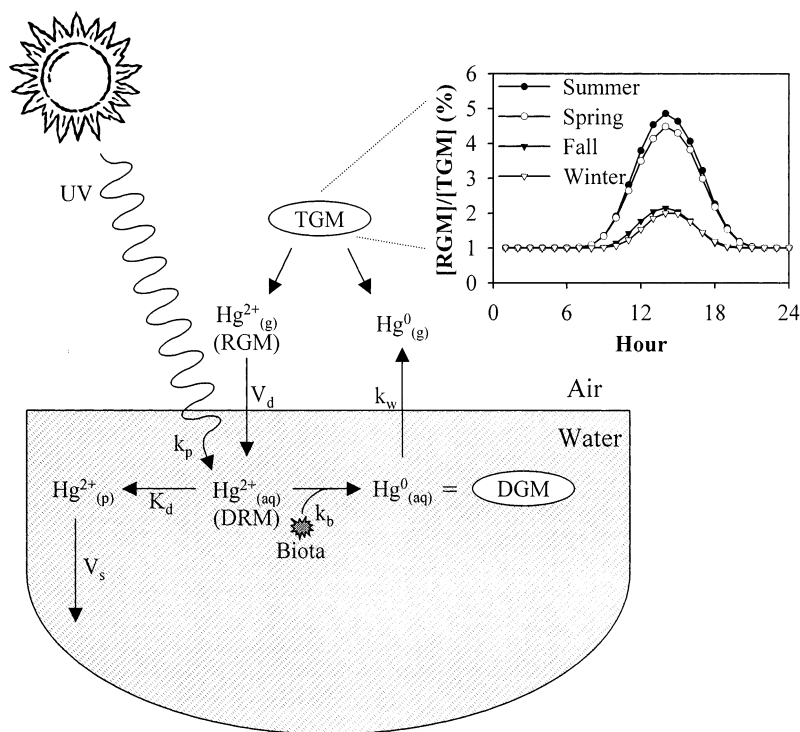
FIGURE 2. Conceptual framework of the modeling approach used in this study. The RGM concentration used in the dry deposition model was estimated from the measured TGM concentration as shown in the plot (based on data in ref *32*). The photochemical reduction rate (k_p) was obtained from ref *29* and the biotic reduction rate (k_b) was estimated from data in ref *31*. Adsorption of DRM to suspended particulate matter (SPM) was calculated using the particulate distribution coefficient ($K_d = ([Hg^{2+}_{(p)}]/[SPM])/[DRM])$; monthly SPM data were obtained from ref *25* and particle settling velocity (V_s) were obtained from ref *26*.

Lake Michigan ranged from 0.2 to 10 m day^{-1} (*26*). At the end of each time step, the inputs and losses of the Hg species were used to calculate the DGM and DRM concentrations in the water column for subsequent time steps.

The DGM and DRM concentrations in the water column were calculated every hour at each grid cell using a mass balance approach. We assumed that DGM was produced by photochemical, biotic and dark reduction of DRM and lost by emission from the water surface. Oxidation of DGM has been shown to occur only in waters with elevated levels of Cl$^-$ (*27, 28*) and, therefore, was not considered as a DGM loss term in this model for freshwater. Photochemical reduction of DRM in the Great Lakes has been shown to occur only in the UV region of the solar spectrum (*29*), similar to results obtained in field incubation studies in a low DOC lake (*10*). The photoreduction rate of DRM was calculated using UV$_B$ irradiance data from Pellston, MI obtained from the USDA-UV$_B$ monitoring program. The photochemical reduction rate varied from ~0−4% day^{-1} in winter to ~0−8% day^{-1} in summer (*29*). These DGM production rates are similar to those previously determined in inland freshwater lakes (*10, 11*). Because UV light is attenuated by water, photoreduction was limited to the top 3 m of the water column based on the equations described by Scully and Lean (*30*). The biotic reduction rate was calculated based on data in Sullivan and Mason (*31*) and varied as a function of solar radiation to produce a diurnal and seasonal variation of ~0−2% day^{-1} in winter to ~0−5% day^{-1} in the summer. Dark reduction was assumed to occur at a rate of 2% day^{-1} (*31*) during all times of the year. We assumed that biotic and dark reduction occurred throughout the mixed layer of the water column.

Deposition fluxes of RGM were calculated as the product of the RGM concentration and the deposition velocity

$$F_{RGM} = V_{d*}[RGM]$$

where F_{RGM} is the deposition flux of RGM to the water surface (ng m^{-2} hr^{-1}), V_d is the deposition velocity of RGM (m h^{-1}), and [RGM] is the concentration of RGM in air. Recent measurements of RGM have shown that, on average, RGM represents about 3% of TGM at rural sites in Indiana and Tennessee (*32*). The RGM/TGM ratio varied diurnally from ~1−6% in summer with the maximum occurring during midday (*32*). The RGM concentration used in this model was estimated under two different scenarios. Under the first scenario, the measured TGM concentrations were combined with solar radiation data to produce a diurnal and seasonal variation in the RGM/TGM ratio (Figure 2), similar to that observed by Lindberg and Stratton (*32*). In the second scenario, the RGM/TGM ratio was held spatially and temporally constant at 1% (lower bound estimate) and 3% (upper bound estimate). The RGM deposition velocity, V_d, was calculated using the model developed by Lo (*33*). This model uses single-level atmospheric data of wind speed and air temperature coupled with water surface temperature to calculate the surface parameters of friction velocity, u*, and the atmospheric stability parameter, z/L. The molecular diffusivity of RGM (assumed to be HgCl$_2$) was calculated as a function of air temperature (*34*) and used with the atmospheric parameters to calculate the RGM deposition velocity to water.

Emission fluxes of DGM were calculated using an equilibrium-partitioning model as follows

$$F_{DGM} = k_w([Hg^0_{air}]/H - [Hg^0_{water}])$$

where F is the flux of DGM (Hg^0) at the air−water interface (ng m^{-2} h^{-1}), k_w is the mass transfer coefficient (m h^{-1}), [Hg$^0_{air}$] is the concentration of Hg^0 in air, H is the Henry's Law constant, and [Hg$^0_{water}$] is the concentration of dissolved Hg^0 in water. The Henry's Law constant, a dimensionless constant defined as [Hg$^0_{air}$]/[Hg$^0_{water}$] at equilibrium, was temperature

TABLE 1. Measured Concentrations of Dissolved Gaseous Hg (DGM) in Lake Michigan, Over-Water Concentrations of Total Gaseous Hg (TGM) in Air, Water Temperature (T_{water}), and Degree of DGM Saturation (DGM Sat.) in Lake Michigan (Mean $\pm$ SD) during the Atmospheric Exchange over Lakes and Ocean Surfaces Study[a]

study dates	[DGM] (pg L^{-1})	[TGM] (ng m^{-3})	T_{water} (°C)	DGM sat. (%)
May 17−19, 1994	18 ± 4 (9)	2.8 ± 0.8 (5)	9.3 ± 0.2 (6)	160 ± 60 (6)
July 17−28, 1994	20 ± 6 (44)	1.9 ± 0.3 (17)	21.5 ± 0.4 (30)	320 ± 80 (30)
Jan 16−19, 1995	20 ± 6 (9)	1.9 ± 0.4 (5)	4.6 ± 0.1 (9)	260 ± 90 (9)

[a] Number of observations is shown in parentheses.

corrected using the equation proposed by Sanemesa (*35*).

The transfer velocity, k_w, was calculated as a function of wind speed and water temperature using the model developed by Liss and Merlivat (*36*). The model was developed based on empirical measurements of CO_2 exchange on the open ocean, and we modified it for Hg by relating the Schmidt number (Sc) for Hg^0 to that of CO_2. The model combines the principles of the surface renewal model and the boundary layer model to derive k_w. The surface renewal model, applicable at low wind speeds, assumes that a stagnant film at the air−water interface is periodically replaced by fluid from the bulk water (*37−39*). The rate-limiting step in this process is the film replacement rate. The boundary layer model, applicable at higher wind speeds, incorporates micrometeorological processes including mass and momentum transfer to calculate k_w (*40*). A comparison of modeling approaches to estimate k_w specifically for Hg, including this one, may be found elsewhere (*41*).

The meteorological data used to calculate the RGM V_d and the DGM k_w were obtained from the National Oceanic and Atmospheric Admininstration − Great Lakes Environmental Research Laboratory hydrodynamic model (*42*). The gridded meteorological data were available with a spatial and temporal resolution of 5 km and 1 h, respectively. The modeling domain consisted of 2318 over-water grid cells with dimensions of 5 × 5 km (*42*). The TGM concentrations measured at each site during the LMMB and AEOLOS studies were averaged by month and spatially interpolated over the Lake at each grid cell using a kriging technique (*43, 44*) with specific modifications for the Lake Michigan basin (*1*). The RGM deposition and DGM emission fluxes were calculated at each grid cell on an hourly basis.

Results and Discussion

Dissolved and Total Gaseous Mercury. The DGM concentrations measured during the AEOLOS surveys indicated that Lake Michigan was supersaturated with respect to the atmosphere during May and July, 1994, and January, 1995. The degree of DGM saturation was calculated using

$$S = (([Hg^0_{water}] * H) / [Hg^0_{air}]) * 100$$

where S is the degree of DGM saturation (%), Hg$^0_{water}$ is the concentration of dissolved Hg^0 in water, H is the temperature corrected Henry's Law constant (*35*), and Hg$^0_{air}$ is the concentration of Hg^0 in air. For the purposes of this calculation, the concentrations of Hg$^0_{water}$ and Hg$^0_{air}$ were assumed to be equal to the measured DGM and TGM concentrations, respectively. The results in Table 1 show that mean DGM concentrations during the three surveys were very similar and above saturation with respect to the atmosphere. The mean observed degree of DGM saturation was 286 ± 99% (mean ± SD; median = 294%) indicating that the concentration gradient of gaseous Hg^0 favors exchange from the water to the atmosphere. These results are similar to measurements made during August, 1994 (28 ± 17 pg L^{-1}) at several locations on Lake Michigan, including northern sites (*21*).
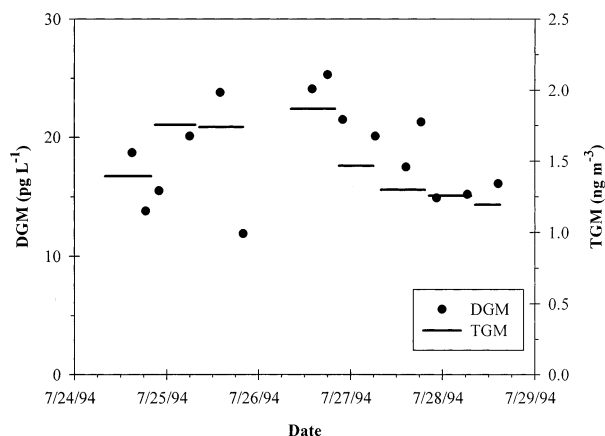

FIGURE 3. Dissolved gaseous Hg (DGM) in Lake Michigan ($n = 15$) and 12-h integrated mean total gaseous Hg (TGM) in air ($n = 8$) from July 24 to July 29, 1994 measured concurrently from the R/V *Lake Guardian.*

Concentrations of DGM were similar during each season, although differences were found in degree of DGM saturation between seasons. The DGM concentrations measured in May and July, 1994 and January, 1995 were very similar, and no significant differences were found between any seasonal sampling periods ($p < 0.85$). However, DGM saturation was significantly higher in July, 1994 than May, 1994 and January, 1995 ($p < 0.01$). The difference in degree of DGM saturation between periods was due to differences in water temperature and the over-water TGM concentration in air, while the DGM concentration remained relatively constant at about 20 pg L^{-1} (Table 1). During May, 1994, the degree of DGM saturation was significantly lower than July, 1994 because the TGM concentrations were higher and the water temperatures were lower (Table 1). The difference in degree of DGM saturation between July, 1994 and January, 1995 was due to differences in water temperature, while the DGM and TGM concentrations were similar during both periods (Table 1). No significant diurnal relationship was observed between DGM saturation or concentration and solar radiation ($p < 0.20$). Incubation studies have also shown a lack of photoinduced DGM production in Lake Erie, which has very similar DGM and total Hg concentrations as Lake Michigan (*10*).

Day-to-day variations in DGM concentrations were correlated with TGM concentrations. The DGM and TGM concentrations during July, 1994 varied simultaneously over a period of about 4 days (Figure 3). A similar relationship was observed with all data collected during the AEOLOS studies ($r^2 = 0.20$; $p < 0.02$). One possible explanation for this observed relationship may be that TGM in air controlled the DGM concentration by reducing air−water exchange. If the rates of DGM formation and loss are comparable and independent processes, then a decrease in the DGM loss term will result in increased DGM concentrations at a constant formation rate. For instance, when TGM concentrations are elevated the rate of DGM loss from the water column by volatilization (~2−15% day^{-1}; assuming a flux of 0.3−2 ng m^{-2} h^{-1} and an epilimnion depth of 10 m) may be
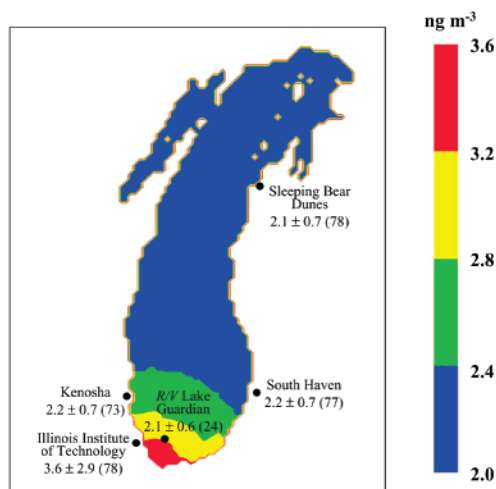
FIGURE 4. Spatial interpolation of total gaseous Hg (TGM) concentrations measured during the Lake Michigan Mass Balance and Atmospheric Exchange Over Lakes and Ocean Surfaces studies. The TGM concentrations (mean ± SD) measured at each site during the study is also shown with number of observations in parentheses.

slower than the rate of DGM formation ($\sim$2−15% day^{-1}), thus causing an increase in DGM concentrations.

The mean TGM concentrations measured at all sites from July, 1994 to October, 1995 ranged from 2.1 ng m^{-3} at Sleeping Bear Dunes to 3.6 ng m^{-3} at IIT (Figure 4). The spatial interpolation of these data show a gradient of increasing TGM concentration from the northern, rural Sleeping Bear Dunes site to the source areas in the southern part of the basin (Figure 4). Although the source areas are located in the

southern part of the basin, the Sleeping Bear Dunes site periodically received air masses containing elevated levels of TGM similar to the South Haven and Kenosha sites. These periodic events of elevated TGM levels transported from the source areas were responsible for the higher than background TGM concentrations at the monitoring sites. In general, TGM concentrations were very similar at all of the sites except IIT (23).

Deposition−Emission Model. The modeled RGM deposition velocities (V_d) to water shown in Figure 5(a) ranged from 0.6 ± 0.1 cm s^{-1} (mean ± SD) in spring and summer to 1.0 ± 0.1 cm s^{-1} in fall and winter. The V_d's were lowest during spring and summer because the temperature gradient between the air and the water surface was either positive ($T_{air} > T_{water}$) or neutral ($T_{air} \sim T_{water}$; Figure 5(b)). This caused a stable or neutral layer in the atmosphere at the air−water interface which reduced turbulence and, hence, the V_d's. The over-water wind speeds plotted in Figure 5(c) show that wind speeds were also lower, on average, during spring and summer. The combination of low wind speeds and a positive temperature gradient between the air and the water surface during spring and summer resulted in the lowest V_d's. Conversely, the V_d's were highest in the fall and winter because of a negative temperature gradient ($T_{air} < T_{water}$) coupled with higher wind speeds. For a water soluble gas, such as RGM, the main resistance to deposition is atmospheric transfer to the water surface. The atmospheric resistance is minimized during unstable periods, which enhances turbulent transport of RGM to the water surface.

The modeled DGM transfer velocities (k_w) were also dependent on wind speed and water temperature (Figure 5(b)−(d)). The modeled k_w's ranged from 6.2 ± 1.1 cm h^{-1} (mean ± SD) in spring to 11.6 ± 2.2 cm h^{-1} in fall. The lowest k_w's occurred in spring due to low wind speeds combined
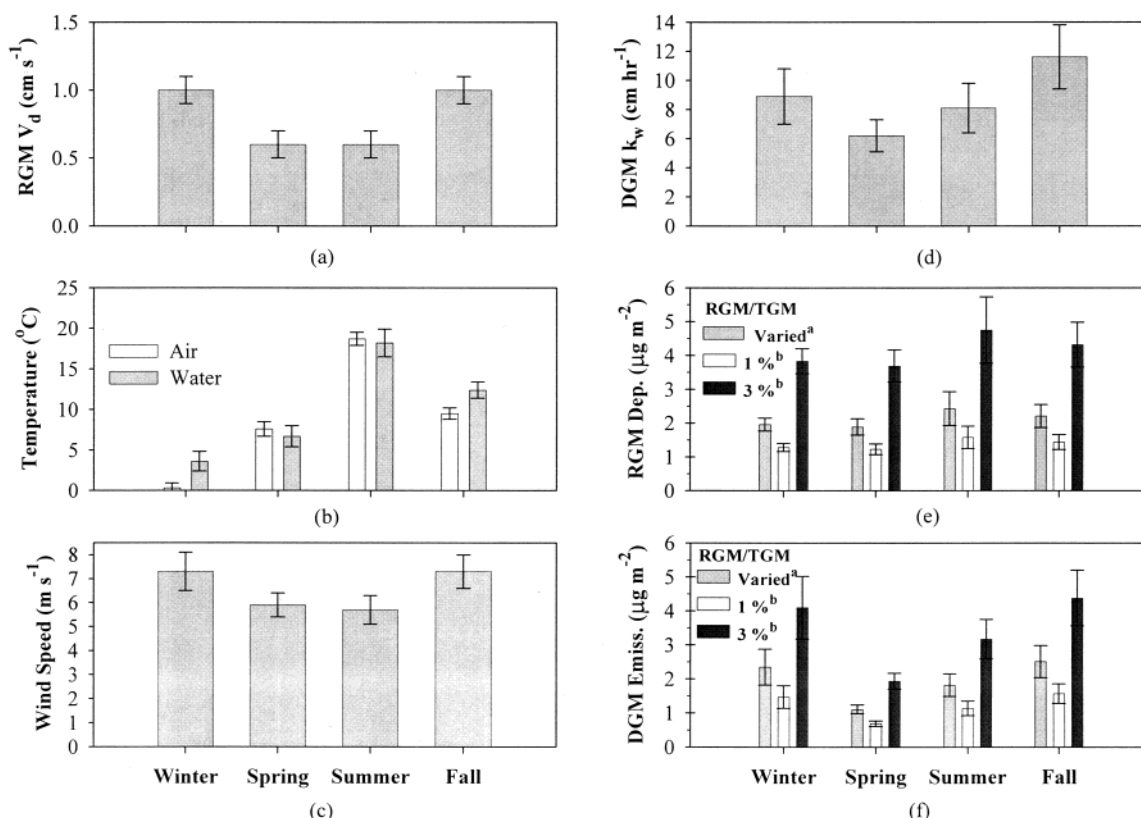

FIGURE 5. Seasonal plots (mean ± SD) of the (a) modeled reactive gaseous Hg (RGM) dry deposition velocities (V_d), (b) air and water temperature, (c) over-water wind speed, (d) modeled dissolved gaseous Hg (DGM) transfer velocities (k_w), (e) modeled RGM deposition fluxes, and (f) modeled DGM emission fluxes. Error bars indicate temporal variance. a − RGM/TGM ratio varied according to data shown in Figure 2, b − RGM/TGM ratio held constant.

with relatively low water temperatures. Since DGM is relatively insoluble, the main resistance to atmospheric exchange is liquid phase resistance. This resistance is minimized during periods of mixing in the water column, often a result of increased wind speed and water temperature causing increased transfer rates of DGM to the water surface. These conditions were prevalent during fall when both wind speed and water temperature were relatively higher than other times of the year (Figure 5(b),(c)). Although water temperatures were highest in the summer, the k_w's did not peak during summer because wind speeds were significantly lower, on average, than during the fall.

The modeled RGM deposition fluxes (Figure 5(e)) were strongly dependent on the RGM concentration. The lack of a strong seasonal relationship in the RGM deposition fluxes was due to the seasonally opposing relationship between the V_d's (Figure 5(a)) and the estimated RGM concentration. The highest RGM/TGM ratio in Figure 2 and thus the highest RGM concentrations occurred during spring and summer when the V_d's were lower than during winter and fall (Figure 5(a)). In contrast, the lower RGM/TGM ratios during winter and fall coupled with higher V_d's resulted in similar deposition fluxes as during spring and summer. The estimated RGM deposition fluxes were slightly higher during summer and fall when the RGM/TGM ratio was held constant and this was due to generally higher estimated RGM concentrations. It is essential to verify that the estimated over-water RGM concentrations used in this model are appropriate, since the modeled estimates of RGM concentration and deposition were based on limited measurements of RGM concentrations at land based sites in the literature. To date, only limited over-water RGM measurements have been made, but the available data (RGM/TGM ∼ 2%; (45)) are similar to those used in this model. Contemporary over-land measurements of RGM/TGM ratios conducted in the Great Lakes region range from <0.1% to ∼3% (46).

The modeled DGM emission fluxes (Figure 5(f)) showed a strong seasonal dependence, similar to the trend in the modeled k_w's, and were also dependent on RGM concentrations. For each RGM/TGM model scenario, the highest emission fluxes occurred during fall and the lowest emission fluxes occurred during spring, matching the seasonal relationship in the modeled k_w's. The variations in DGM emission fluxes between seasons were a result of the seasonal variation in the modeled k_w's, not seasonal changes in DGM concentration as this was not observed in either the measured (Table 1) or estimated DGM concentrations. The RGM/TGM ratio also had a strong effect on DGM emissions as a result of higher estimated DGM concentrations when the estimated RGM deposition fluxes were higher.

The measured and modeled DGM concentrations were similar during each season (Figure 6) when the RGM/TGM ratio was varied (Figure 2). When the RGM/TGM ratio was held constant at 3% the model predicted considerably higher DGM concentrations than those measured. At an RGM/TGM ratio of 1% the estimated DGM concentrations were generally lower than the measured DGM concentrations. When the RGM/TGM ratio was varied (Figure 2), the modeled DGM concentrations were very similar in both magnitude and variation as the measured DGM concentrations. The model predicted slightly higher DGM concentrations in winter than during other seasons, but these predicted values lie within the observed range of the variations in the measured DGM concentrations. The model was initialized using a DGM concentration of 20 pg L^{-1} (mean measured value). Since limited data exist on DRM, especially for the Great Lakes, the initial DRM concentration (40 pg L^{-1}) was selected based on measurements in Lake Superior (29). The initial DRM concentration used in the model represents about 13% of the total Hg concentration in Lake Michigan (0.3 ng L^{-1} (21)).
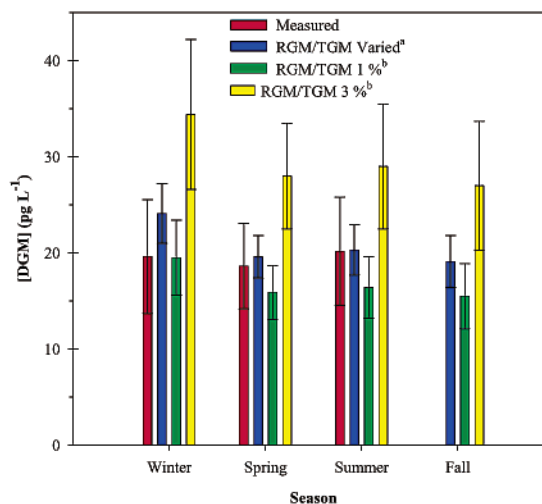

FIGURE 6. Comparison of the measured ($n = 45$) and modeled dissolved gaseous Hg (DGM) concentrations in Lake Michigan (mean ± SD). a — RGM/TGM ratio varied according to data shown in Figure 2, b — RGM/TGM ratio held constant.
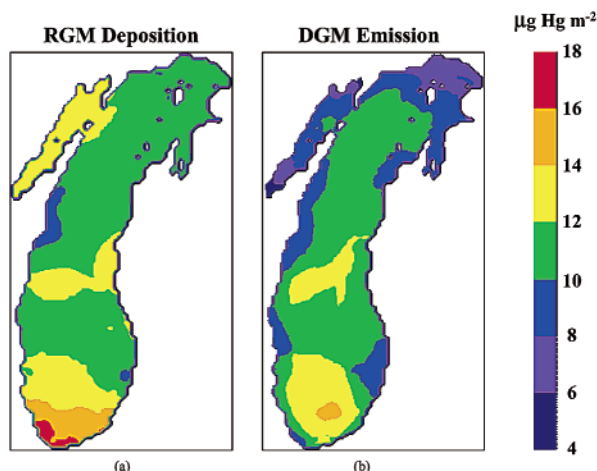

FIGURE 7. Spatial variation in the modeled (a) reactive gaseous Hg (RGM) deposition and (b) dissolved gaseous Hg (DGM) emission fluxes during the Lake Michigan Mass Balance study (July, 1994 to October, 1995). RGM/TGM ratio varied according to data shown in Figure 2.

Measurements of reactive Hg (reducible by SnCl$_2$ and operationally defined as Hg^{2+}) in other freshwater lakes in the Great Lakes region are on the order of 200−500 pg L^{-1} or about 15% of the total Hg concentration (1.5−3 ng L^{-1} (47)). The initial DGM and DRM concentration, however, had little effect on the model estimated DGM concentrations when both were initialized at concentrations that varied from 0 to 100 pg L^{-1} (data not shown). The mechanisms and rates controlling production and loss of each species ultimately determined the estimated concentrations regardless of the initial concentration. However, the RGM/TGM ratio also had a significant effect as illustrated in Figure 6.

The model predicted highest deposition and emission fluxes in the southern and central areas of the lake. The spatial gradient in estimated deposition and emission fluxes generally increased from north to south during the LMMBS period as shown in Figure 7 (a),(b). The higher levels of TGM and, thus, estimated RGM in the southern part of the basin account for the higher RGM deposition flux compared to other areas of the lake. The influence of the source areas in the southern region of the lake is likely conservative, however, because the RGM/TGM ratio was spatially constant. In the vicinity of combustion sources, such as in the southern part of the

TABLE 2. Summary of Estimated Annual Lake-Wide RGM Deposition and DGM Emission Fluxes at Various Ratios of RGM/TGM Concentrations

RGM/TGM	RGM deposition flux		DGM emission flux	
	(kg yr^{-1})	(ug m^{-2} yr^{-1})	(kg yr^{-1})	(ug m^{-2} yr^{-1})
varied[a]	491	8.5	457	7.8
1%[b]	320	5.5	286	4.9
3%[b]	959	16.6	797	13.8

[a] RGM/TGM ratio varied according to data shown in Figure 2. [b] RGM/TGM ratio held spatially and temporally constant.

basin, the RGM/TGM ratio should be greater than in the northern area of the lake far from sources. This was also indicated by limited plume impaction data shown in Lindberg and Stratton (*32*). The higher RGM deposition fluxes near the southern source areas provided additional Hg^{2+} to the water, which resulted in higher estimated DGM concentrations. The estimated RGM deposition fluxes were higher near Green Bay because of a larger negative temperature gradient between the air and the water surface than in other parts of the lake. The negative temperature gradient caused an increase in the atmospheric turbulence at the air−water interface and ultimately led to increased V_d's. Despite higher RGM deposition fluxes in Green Bay, the DGM emission fluxes were not elevated because the k_w's were generally lower than in the southern area of the lake where wind speeds were higher. The elevated deposition and emission fluxes in the central part of the lake were due to higher average wind speeds.

Lake-Wide Deposition and Emission Estimates. The estimated RGM deposition and DGM emission fluxes were integrated over the entire lake to calculate the total deposition and emission fluxes of gaseous Hg. The lake-wide RGM deposition and DGM emission fluxes estimated at different RGM/TGM ratio scenarios is shown in Table 2. There was considerable variation between the lower and upper bound flux estimates, but for each RGM/TGM modeling scenario the dry deposition flux of RGM was comparable to emission losses of DGM. This suggests that in-lake processes may convert dry deposited RGM to DGM, which may be subsequently re-emitted as Hg^0 from the water surface.

The largest source of uncertainty in this modeling approach is selection of an appropriate over-water RGM concentration. To evaluate the effect of RGM concentration on the modeled RGM deposition and DGM emission flux estimates, the concentration ratio of RGM/TGM was either held constant at 1% (lower bound estimate) and 3% (upper bound estimate) or varied diurnally (Figure 2). The results from this analysis provide a reasonable lower and upper

bound estimate for deposition and emission fluxes of gaseous Hg (Table 2).

The model estimates agree well with data in the literature. Table 3 shows that the DGM emission fluxes are similar to those previously estimated for Lake Michigan by Mason and Sullivan (*21*), but considerably less than the model estimates of Shannon and Voldner (*8*). The latter estimates are probably biased high due to the high DGM concentration used in the model. The estimated RGM deposition fluxes and deposition velocities are very similar to the results obtained by Shannon and Voldner (*8*) and Pai et al. (*9*). These results are encouraging because they indicate that independent modeling techniques produced similar results. A comparison of our model estimates to short-term measured gaseous Hg flux data also agree well (Table 3). Clearly, additional work needs to be done to verify these modeled estimates with measurements, but to date, there are no long-term measurements of DGM emission fluxes from the Great Lakes and little data on measured RGM deposition fluxes.

The estimated annual deposition and emission fluxes of gaseous Hg represent a significant contribution to total Hg loadings for Lake Michigan. The estimated deposition and emission fluxes of gaseous Hg when the RGM/TGM ratio was varied (Table 2) are somewhat less than Hg inputs from precipitation (614 kg yr^{-1} (*50*)) and about twice the Hg loading from tributaries (230 kg yr^{-1} (*51*)). Although Hg^{2+} was not measured in precipitation or the tributaries sampled during the LMMBS, these processes may contribute a significant fraction of Hg^{2+} to the water column. However, the Hg loading from tributaries is predominately in the particulate phase (*51*), which will rapidly deposit to the sediments and is not likely available for photolytic reactions.

The mechanistic model developed here illustrates a plausible link between dry deposition of gaseous Hg^{2+}, formation of gaseous Hg^0 in the water column, and the subsequent emission or re-emission of Hg. The results from the model indicate that production and emission losses of DGM are in a near steady-state in Lake Michigan producing DGM concentrations that are nearly constant year-round. This is important because it demonstrates that atmospheric processes (wind, turbulence, etc.) can have a strong impact on DGM concentrations in the water column and may explain the lack of a diurnal cycle in DGM concentrations in Lake Michigan and in other water bodies (*10*, *11*). The results of the model also suggest that dry deposition fluxes of RGM are comparable to gaseous emissions of DGM. This indicates that in-lake conversion of previously dry deposited RGM may be re-emitted back to the atmosphere and represents a significant removal process of gaseous Hg from Lake Michigan.

TABLE 3. Comparisons of Lake-Wide and Short-Term Model Estimates of DGM Emission Fluxes, RGM Deposition Fluxes, and Deposition Velocities to Data Appearing in the Literature

DGM emission flux		RGM deposition flux					
(kg yr^{-1})	(ng m^{-2} h^{-1})	(kg yr^{-1})	(ng m^{-2} h^{-1})	V_d[a] (cm s^{-1})	location	method	reference
286−797	0.6−1.6	320−959	0.6−1.9	0.8	Lake Mich.	estimated	this study
521					Lake Mich.	estimated	(*21*)
1.11−6.1 × 10^3 [b]		583		1.0	Lake Mich.	estimated	(*8*)
				0.52[c]	Regional U.S.	estimated	(*9*)
	1.0−3.4				Lake Superior	measured[d]	(*29*)
	0.7−1.2				Everglades, FL	measured[d]	(*48*)
	0.33				St. Lawrence River	measured[d]	(*49*)
			0.16−6.96		Chesapeake Bay	estimated[e]	(*45*)

[a] Deposition velocity. [b] Estimated using an assumed DGM concentration of 100−500 pg L^{-1}. [c] Over-water estimates from regional Eularian model. [d] Measurements made using flux chamber methodology. [e] Deposition fluxes estimated based on measured RGM concentrations with deposition velocities from the literature.

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