

# Mass Balance Assessment for Mercury in Lake Champlain

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A mass balance model for mercury in Lake Champlain was developed in an effort to understand the sources, inventories, concentrations, and effects of mercury (Hg) contamination in the lake ecosystem. To construct the mass balance model, air, water, and sediment were sampled as a part of this project and other research/monitoring projects in the Lake Champlain Basin. This project produced a STELLA-based computer model and quantitative apportionments of the principal input and output pathways of Hg for each of 13 segments in the lake. The model Hg concentrations in the lake were consistent with measured concentrations. Specifically, the modeling identified surface water inflows as the largest direct contributor of Hg into the lake. Direct wet deposition to the lake was the second largest source of Hg followed by direct dry deposition. Volatilization and sedimentation losses were identified as the two major removal mechanisms. This study significantly improves previous estimates of the relative importance of Hg input pathways and of wet and dry deposition fluxes of Hg into Lake Champlain. It also provides new estimates of volatilization fluxes across different lake segments and sedimentation loss in the lake.

## 1. Introduction

Lake Champlain, on the border of New York, Québec, and Vermont, is facing mercury (Hg) contamination problems similar to many other inland lakes around the globe (1–7).

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Hg has both natural and anthropogenic sources and enters Lake Champlain via many different pathways (8–13). Hg contamination has resulted in the need for fish consumption advisories for certain species. In addition, recent research has identified hot spots of elevated levels of Hg and other metals in sediments (up to 0.80  $\mu\text{g Hg/g}$  dry weight at nonmunicipal sites) in the lake (8), compared to the maximum value of 0.26  $\mu\text{g Hg/g}$  dry weight for 118 samples taken from Lake Michigan (14).

An effective management strategy for Hg contamination in a large lake system is predicated on a quantitative understanding of the relations between sources, inventories, and sinks of Hg to the lake; e.g., a mass balance accounting of Hg in the lake system. Such a model may be used to predict steady-state concentrations throughout the lake in response to future changes in Hg sources and sinks. This approach has been validated by a number of previous studies for large or small water bodies including Lake Michigan (2, 3), Lake Superior (4), the Everglades and Florida Bay (5), St. Lawrence River (6), and Lochnagar, Scotland (7). Herein, we present a mass balance model to assess sources, sinks, and internal transfers of total Hg in Lake Champlain. The primary sources of Hg to Lake Champlain are tributary inputs, direct wet and dry atmospheric loading, and effluent from wastewater treatment facilities. Hg sinks include sedimentation, evasion, and export from the lake outlet.

The Lake Champlain Hg mass balance model was constructed using results from previous work as well as newly acquired measurements in the basin. Atmospheric Hg concentrations in three phases, vapor, precipitation, and fine particles (9–11), have been measured at the Proctor Maple Research Center (PMRC) in Underhill, Vermont since 1992. A small number of water samples were collected from one large tributary and one small stream draining into the lake in the early 1990s (12). Since 2000, a more systematic water sampling effort has been carried out. These sampling results showed that both natural and anthropogenic sources of Hg enter Lake Champlain via many different pathways.

Dissolved total Hg concentrations in a headwater stream in the basin were typically low, ranging from 0.5 to 2.6 ng/L, while peak concentrations in unfiltered samples reached 79 ng/L during high flow, suggesting a large percentage of the total Hg in stream flow is in the particulate phase (13). Snowmelt can have a very large effect on the annual tributary loading due to concurrent increases in stream discharge and Hg concentration (15). During the 1994 snowmelt, total Hg in snowmelt at PMRC ranged from 2 to 9 ng/L and averaged 4.8 ng/L (12). Perhaps of greater importance is the release of stored Hg from watershed soils during high flows as runoff erodes near-stream soils and rising water tables flush Hg from the forest floor (13). The median total Hg concentration was approximately 200 ng  $\text{g}^{-1}$  in sediment at the mouths of Lake Champlain tributaries sampled in 1991 by the U.S. Geological Survey (USGS) (16).

Using a limited dataset collected in the early 1990s, Shanley et al. (12) developed an initial Hg input–output budget for the Lake Champlain Basin. They estimated that stream flow delivered an average of 27  $\text{mg ha}^{-1} \text{ year}^{-1}$  of Hg to the lake (equivalent to 54 kg/year to the lake) while direct atmospheric deposition to the lake surface contributed 30  $\text{mg ha}^{-1} \text{ year}^{-1}$  of Hg (equivalent to 60 kg/year to the lake). No estimate was made of removal of Hg from the water column due to evasion or sedimentation.

Since 2000, a multidisciplinary team of researchers has been working to refine the mass balance model by addressing the relations between Hg sources and Hg concentrations in

**TABLE 1. Physical Dimensions (25) and MB Modeling Results for Each of the 13 Lake Segments<sup>a</sup>**

segment (sampling location)	surface area (km <sup>2</sup> )	vol (km <sup>3</sup> )	length (km)	trib input (g Hg/ year)	WWTFs input (g Hg/year)	wet dep input (g Hg/year)	dry dep input (g Hg/year)	volatile loss (g Hg/year)	sedim ent loss (g Hg/year)	sampled [Hg] (ng Hg/L)	modeled [Hg] (ng Hg/L)
Isle LaMotte (at Point Au Fer)	185.59	1.892	40.3	2417	0	1455	1581	3613	5194	0.27	0.18
Cumberland Bay	10.75	0.063	3.4	2241	80	84	115	694	309	0.38	0.49
Main Lake	414.14	16.787	47	8216	13	3255	3077	1856.7	7399	0.33	0.35
Port Henry (at Cole Bay)	75.55	1.463	20.1	188	3	605	278	2233	1387	0.32	0.25
Missisquoi Bay	89.94	0.205	16.8	2340	3	738	699	1842	1525	0.38	0.18
St. Albans Bay	7.21	0.023	3.4	71	9	57	50	16	158	0.30	0.06
Northeast Arm (at Inland Sea)	248.25	3.38	33.5	243	0	1959	1884	414	4670	0.24	0.05
Malletts Bay	55.06	0.722	6.7	3165	0	433	426	1181	2655	0.28	0.19
Burlington Bay (at Burlington Harbor)	5.51	0.063	2	52	38	44	39	179	251	0.27	0.27
Shelburne Bay	9.62	0.14	3.4	213	3	77	69	374	181	0.26	0.31
Otter Creek (at Diamond Island)	28.49	0.955	10.1	3690	2	229	101	1286	542	0.32	0.36
South Lake A (at Crown Point)	43.27	0.125	33.5	1424	2524	353	160	3482	766	0.52	0.60
South Lake B (at Benson's Landing)	5.79	0.0078	20.1	2203	2	47	21	984	179	0.98	1.23
total	1179.17	25.826	N/A	2646.3	2677	9336	8479	3486.5	25216	avg 0.37	avg 0.35

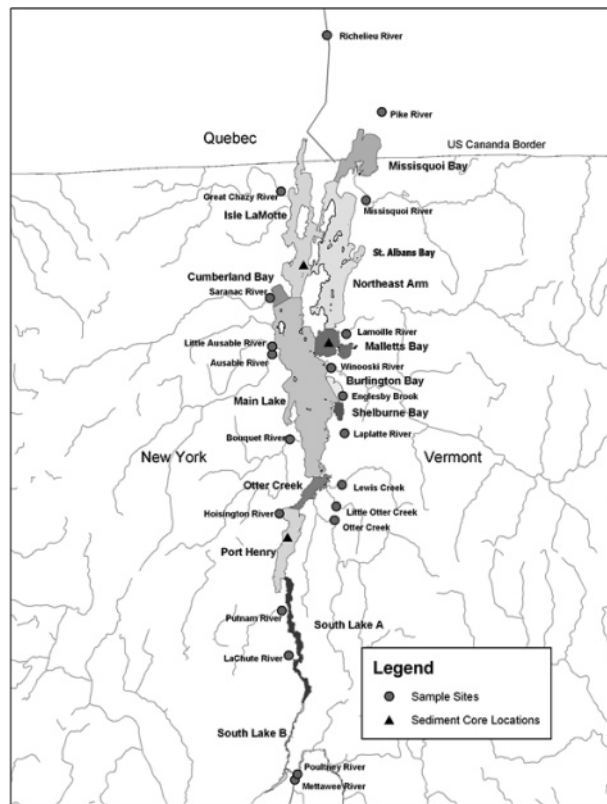
<sup>a</sup> The modeling results were from the MB model using the tributary conditions in 2001 and the assumption that [DGM] = 20%[THg].

air, water, sediment, and biota in Lake Champlain. This initiative is being undertaken in two phases. Phase I entailed model construction and calibration/validation with new field data. Phase II involves model refinement and incorporation of biotic transfers and sinks of Hg and is ongoing. For Lake Champlain, as elsewhere, once Hg enters the lake, it is transported by dispersive and advective flows (17), becomes entrained in the biological mercury cycle (18–20), and contributes to the sediment pool (21). Chemical and biochemical transformations (oxidation, reduction, methylation) occur in water and sediment (22, 23) and in the food web (e.g., biomagnification). Sediment resuspension often allows mercury to re-enter the aquatic environment. Volatilization or evasion allows some of the deposited mercury to return to the atmosphere (3, 24).

As a part of this project and an independent USGS project, we undertook a field campaign from 2000 to 2003 to generate data necessary to calibrate the model. Total Hg (unfiltered) water samples were collected from the lake outlet, 14 gauged tributary inputs, and 14 locations on the lake (2001 only), and sediment cores were collected from three lake sites to provide Hg sedimentation flux estimates. We obtained estimates of Hg wet and dry deposition rates to the lake based on data from atmospheric monitoring at PMRC (13) and algorithms developed by Miller et al. (25). All these data were used in phase I of this project, to develop a mass balance model that accounts for the physical cycling of Hg in the lake. Phase II of the project, commencing in 2005, expands the existing physical cycling model to include Hg bioaccumulation and trophic transfer. The present paper focuses exclusively on the mass balance assessment for total Hg in Lake Champlain (phase I), while a future paper will address Hg methylation and biotic cycling (phase II).

## 2. Development of a Mass Balance Model for Hg in Lake Champlain

Lake Champlain is a complex aquatic system due to wide variation in its width, depth, hydrodynamic circulation, and nutrient inputs (26–28). Lake Champlain stretches 250 km from south to north, draining north to the St. Lawrence River via the Richelieu River. It has a maximum width of 20.2 km and maximum depth of 122 m (26). Lake Champlain has a large drainage area/lake surface ratio of 18 to 1 (26). Therefore, most of the incoming atmospheric Hg deposits first onto the



**FIGURE 1. Thirteen segments of Lake Champlain and sampling sites.**

mostly forested lands surrounding the lake before possible transport to the lake by surface runoff and tributary flow.

Because of the lake's diverse characteristics, our mass balance model divides the lake into 13 segments to simplify the system (29). Table 1 shows the different physical characteristics of the lake for each of the 13 segments, the boundaries of which are displayed in Figure 1 (29). For each lake segment in the model, Hg influxes and outfluxes are constrained by mass balance. Hg influxes to a segment include tributary loading, effluent from wastewater treatment facilities, dry deposition, wet deposition, and advective flow

from upstream segments. The outfluxes for a given segment include volatilization, sedimentation, and advective flow to downstream segments. The model also accounts for dispersive bidirectional exchange across each segment interface.

The following equation is applied to each lake segment in the mass balance model. With respect to total Hg (THg), each lake segment is treated as a mixed reactor.

$$dC(t)_i/dt = \Sigma(L_{\text{influx}})/V_i + \Sigma(Q_{ji}C(t)_j)/V_i - \Sigma(Q_{ik}C(t)_k)/V_i + DF_{ik}(C(t)_k - C(t)_i)/V_i - \Sigma(L_{\text{outflux}})/V_i \quad (1)$$

where  $C(t)_i$ ,  $C(t)_j$ , and  $C(t)_k$  represent the instantaneous total Hg concentrations (ng/L) in the three lake segments,  $i$ ; its upstream neighbor  $j$ ; and its downstream neighbor  $k$ .  $L$  represents Hg loading (g/year) for an influx or outflux;  $Q_{ji}$  and  $Q_{ik}$  represent net advective flows (km<sup>3</sup>/year) from segment  $j$  to segment  $i$ , and from segment  $i$  to segment  $k$ , respectively.  $DF_{ik}$  (km<sup>3</sup>/year) represents the bulk dispersive flow between segments  $i$  and  $k$  (the bulk dispersive flow in this model is always calculated for the downstream interface of two neighboring segments); and  $V_i$  represents a lake segment volume (km<sup>3</sup>). The lake system was allowed to reach an equilibrium ( $dC(t)_i/dt = 0$  in all lake segments), and the steady-state total Hg concentrations for all the lake segments are reported as modeling outputs.

**2.1. Influx Variables. Tributaries.** From 2000 to 2003, approximately 30–50 water samples per year were collected from the tributaries discharging into Lake Champlain (Figure 1) for total Hg determination in unfiltered water. Tributary water sampling and analytical methods are presented in the Supporting Information section.

Fluxes of total Hg were calculated for water years 2001 through 2003 (a water year runs from October 1 of the previous year through September 30 of the water year) for 14 of the main inlet streams representing 67% of the terrestrial basin, as well as for the lake outlet (Richelieu River). Because Hg concentrations are strongly correlated with total suspended sediment (TSS) (15), we used the more frequent TSS determinations as a surrogate for Hg to refine the Hg flux calculations. The Hg flux was calculated at a 15-min interval (frequency of the stream discharge record) by first calculating a TSS concentration from the TSS–discharge relation, then converting to a Hg concentration from the Hg–TSS relation, and finally multiplying Hg concentration by stream discharge. The 15-min Hg fluxes were summed for each water year to compute annual Hg fluxes. Because TSS and Hg concentrations increase markedly with flow, keying this calculation to the detailed hydrograph captures the exponential increases in Hg flux that occur at high flow.

For each lake segment, the Hg input from tributaries was tallied from the fluxes for the measured streams contributing to a given segment. For segment watershed area not draining to a measured tributary, we assumed that the flux per unit areas was the same as that for the measured streams. Total tributary Hg input to the lake from the terrestrial watershed averaged 31.8 kg/year during the 3 years of observation. The average Hg flux per unit area was 1.60  $\mu\text{g}/\text{m}^2\cdot\text{year}$ , which can be compared to Hg input in wet deposition of  $\sim 7.98 \mu\text{g}/\text{m}^2\cdot\text{year}$ . The output in Richelieu River (outlet of the lake) averaged 0.37  $\mu\text{g}/\text{m}^2\cdot\text{year}$ , or 23% of the tributary influx.

**Atmospheric Dry and Wet Deposition.** Atmospheric deposition fluxes to Lake Champlain were estimated using a modified version of the high-resolution deposition model for mercury (HRDM–Hg) described in Miller et al. (25). The HRDM was initially designed to predict deposition to terrestrial ecosystems and small water bodies. Here we describe the modifications to the dry deposition component of the model needed to estimate deposition to a large water body such as Lake Champlain.

The turbulent transfer of material across the air–water interface ( $F_i$ ) can be described by

$$F_i = K(C_w - C_a/K'_H) \quad (2)$$

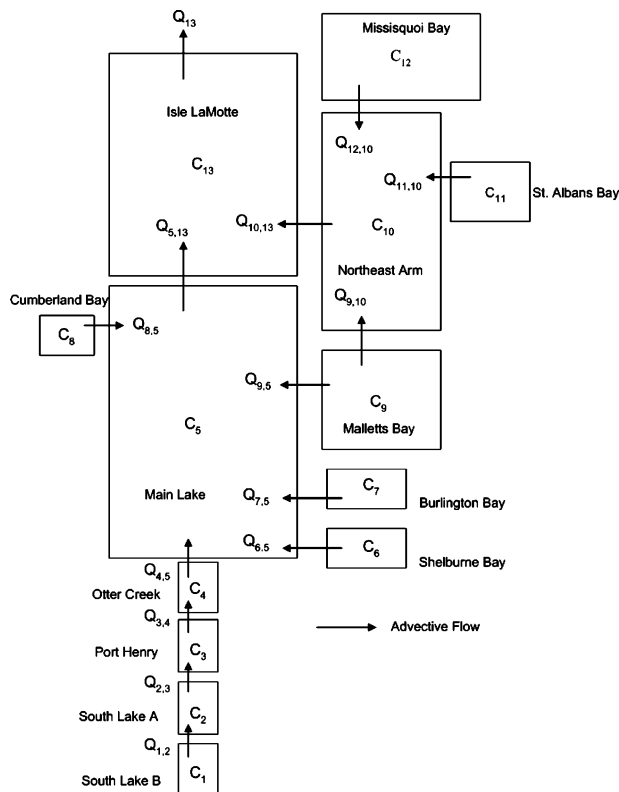
where  $K$  is the mass transfer coefficient,  $C_w$  is the concentration in water,  $C_a$  is the air concentration, and  $K'_H$  is the Henry's law constant describing the solubility in water. The mass transfer coefficient can be decomposed into the air-side ( $K_a$ ) and water-side ( $K_w$ ) of the interface (30). For reactive gaseous mercury (RGM = HgCl<sub>2</sub> + HgBr<sub>2</sub>), which is extremely soluble, and for particulate mercury, transport is controlled by conditions on the air-side of the interface ( $K_a$ ) and by particle mass and composition (only PM<sub>2.5</sub>, i.e., particles less than 2.5  $\mu\text{m}$  are accounted for). For gaseous elemental mercury (GEM = Hg<sup>0</sup>), which has a very low solubility, transport is controlled by conditions on the water-side ( $K_w$ ) of the interface.  $K_w$  was estimated as a function of surface water temperature and wind speed following the approach of Lin and Tao (31) and Poissant et al. (32).  $K_a$  was estimated following the general approach of Xu et al. (33) but using Monahan (34) rather than Asher and Wanninkhof (35) to account for the effects of breaking waves at high wind speeds.

Atmospheric Hg input to the model was derived from several monitoring programs in the northeastern North America and represents an average of atmospheric conditions during the period of 1996–2001 (25). Keeler et al. (36) reported that the annual variability of Hg flux in wet deposition at the Underhill, VT monitoring station in the Lake Champlain Basin was just 12% from 1993 to 2003. Meteorological data input to the model were derived from two stations on Lake Champlain operated by the Vermont Monitoring Cooperative. The Colchester Reef station (longitude, 73.328983° W; latitude, 44.555066° N) provided a record of wind speed and direction (model 40C cup-anemometer by NRG Systems) and air temperature (HMP45C by Vaisala and Campbell Scientific) from 1994 to 2004. Data were recorded as 15-min averages from sensors mounted  $\sim 10$  m above the mean lake level. Monthly mean values for each hour of the day were calculated across the 11-year period, including only those months where  $>90\%$  of observations were valid. Only a 2-month record (September–November 2004) at the more southern Diamond Island station (longitude, 73.333695° W; latitude, 44.236617° N) overlapped with the Colchester Reef station. During each of the two overlapping months, the average wind speed at Diamond Island was 71% of the value measured at Colchester Reef. This difference is due, in part, to the steep topography and narrow lake basin in the southern part of the lake compared to the main and northern lake sections. Winds over the southern four segments of the lake (Figure 1) were estimated to be 71% of the wind speed measured at Colchester Reef. Winds over the other nine segments were assumed to be the same as that observed at Colchester Reef.

Surface water (mixed-layer) temperatures were measured during lake water sampling by the Vermont Agency of Natural Resources for six segments of the lake during 1995–2003. A large number of measurements were made during May through October. To estimate the surface water temperature from November through April, regression equations relating surface water temperature to the air temperature measured at Colchester Reef were developed for both the warming and cooling cycle. The seven lake segments without direct observations were assigned water temperatures based on their proximity to a measured segment and accounting for basin characteristics. For example, Missisquoi Bay (shallow) was assumed to have the same surface water temperature as Malletts Bay (shallow), even though data for the more proximal Northeast Arm (deep) were available.

Atmospheric Hg dry deposition rates (including particulate, reactive, and gaseous elemental mercury) to the various





**FIGURE 2. Advective flows routing through the 13 lake segments (29).**

parts of the lake range from 3.56 to 8.52  $\mu\text{g}/\text{m}^2\cdot\text{year}$  and wet deposition rates range from 7.84 to 8.21  $\mu\text{g}/\text{m}^2\cdot\text{year}$ . The total atmospheric deposition of Hg to different parts of the lake ranges from 11.6 to 16.4  $\mu\text{g}/\text{m}^2\cdot\text{year}$ . The Hg dry and wet deposition loadings ( $\text{g}/\text{year}$ ) were obtained by multiplying the deposition rates by the lake segment surface areas.

**Wastewater Treatment Facilities.** There are 17 wastewater treatment facilities (WWTF) around Lake Champlain that discharge either directly to the lake or to tributary reaches downstream of the tributary monitoring locations. WWTFs must comply with Hg discharge restrictions only to a reporting limit of 200 ng/L—a very coarse measurement. We therefore estimated WWTF Hg inputs based on literature values (37) for communities of comparable sizes. The effluent Hg concentrations used in this mass balance model ranged from 3.1 to 7.0 ng/L for municipal wastes. A conservative estimate of 105 ng/L Hg (50% of the reviewed literature average for industrial wastes) was applied to one major pulp and paper manufacturing facility. The Hg concentration values were converted to units of  $\text{g}/\text{km}^3$  and then multiplied by the mean annual waste discharge volumes ( $\text{km}^3$ ) taken from the Lake Champlain diagnostic feasibility study (LCDFS) phosphorus budget model (29) to produce the WWTF Hg input loadings ( $\text{g}/\text{year}$ ) for the lake segments.

**2.2. Internal Exchange: Advective and Bulk Dispersive Flow.** Advective flows,  $Q_i$  ( $\text{km}^3/\text{year}$ ), and bulk dispersive flows,  $DF_{ij}$ , were routed through or applied to the 13 lake segments based on previous hydrologic modeling (28, 29, 38). Bulk dispersive flow values ( $\text{km}^3/\text{year}$ ) are given for the downstream boundary of each lake segment based on the flow routing scheme shown in Figure 2.

**2.3. Outflux. Volatilization.** Hg volatilization flux from the lake segments was determined by the air–water exchange model (30, 39) used for the atmospheric dry deposition estimates (eq 2). Annual average lake water temperature, air temperature, and 10-m wind speed from the Colchester Reef station were used in the calculation. The only unknown value

in eq 2 is the mass transfer coefficient,  $K$ , which can be solved with the following equation,

$$F_i = K(C_w - C_a/K'_H) \quad (2)$$

$$K = [1/K_w(\text{Hg}) + 1/K'_H K_a(\text{Hg})]^{-1} \quad (3)$$

where  $K_w(\text{Hg})$  is the mass transfer coefficient (or velocity) of Hg in the thin layer of water at the interface and  $K_a(\text{Hg})$  is the mass transfer coefficient (or velocity) of Hg in the thin layer of air at the interface. Both of these velocity functions are altered by the wind speed above the surface.

The velocities of the Hg in both air and water,  $K_w(\text{Hg})$  and  $K_a(\text{Hg})$ , were calculated using the following equations (39).

$$K_a(\text{Hg}) = K_a(\text{H}_2\text{O})[D_a(\text{Hg})/D_a(\text{H}_2\text{O})]^\alpha \quad (4)$$

$$K_w(\text{Hg}) = K_w(\text{O}_2)[D_w(\text{Hg})/D_w(\text{O}_2)]^\beta \quad (5)$$

where  $D_a(\text{Hg})$  (0.131  $\text{cm}^2/\text{s}$ ) and  $D_a(\text{H}_2\text{O})$  (0.260  $\text{cm}^2/\text{s}$ ) are the diffusion coefficients in air of Hg and  $\text{H}_2\text{O}$ , respectively, and  $D_w(\text{Hg})$  ( $2.9 \times 10^{-5}$   $\text{cm}^2/\text{s}$ ) and  $D_w(\text{O}_2)$  ( $2.1 \times 10^{-5}$   $\text{cm}^2/\text{s}$ ) are the diffusion coefficients of Hg and  $\text{O}_2$  in water, respectively.  $K_a(\text{H}_2\text{O})$  is the velocity of water vapor in air, and  $K_w(\text{O}_2)$  is the velocity of dissolved oxygen. The two diffusion constants  $\alpha$  and  $\beta$  used in eqs 4 and 5 are 0.5 and 0.67 (39, 40), respectively.

$$K_w(\text{O}_2) = 4.0 \times 10^{-4} + 4.0 \times 10^{-5}(U_{10})^2 \quad (6)$$

$$K_a(\text{H}_2\text{O}) = 0.2U_{10} + 0.3 \quad (7)$$

Using eqs 6–7 and the average wind speed at 10 m above water surface ( $U_{10} = 6.228$  m/s), we estimate the average  $K_a(\text{H}_2\text{O})$  as 1.54 cm/s and the average  $K_w(\text{O}_2)$  as  $1.95 \times 10^{-3}$  cm/s, which are the standards that reflect the physical conditions of the boundary for both the air and the water.

With  $K_a(\text{Hg})$  and  $K_w(\text{Hg})$  values from the above calculations determined to be  $2.29 \times 10^{-3}$  and 0.973 cm/s, respectively,  $K$  can be solved by using appropriate values of the other parameters in eq 3. For  $T_{\text{air}} = 7.52$  °C (based on the average air temperature at the Colchester Reef sampling station),  $K'_H = 0.0093T_{\text{air}} + 0.1333 = 0.203$ . Hence,  $K = 2.26 \times 10^{-3}$  cm/s (39), a value then applied to eq 2.

Finally the volatilization flux ( $F$ ) in eq 2 is solved in terms of  $C_w$ . This yields the equation that is used in our mass balance model, where  $C_w$  varies with each time step. This flux equation is

$$F(\text{g}/\text{m}^2\cdot\text{year}) = 7.127 \times 10^{-7}C_w(\text{ng}/\text{m}^3) - 5.617 \times 10^{-6} \quad (8)$$

According to O'Driscoll et al. (41), dissolved gaseous Hg (DGM) in freshwater lakes makes up from 10% to 30% of the total dissolved Hg. If we assume that nearly all the unfiltered Hg in lake water is dissolved Hg, a fairly reasonable assumption, then eq 8 becomes

$$F(\text{g}/\text{m}^2\cdot\text{year}) = 7.127 \times 10^{-7}RC_w(\text{ng}/\text{m}^3) - 5.617 \times 10^{-6} \quad (9)$$

where  $R$  varies from 10% to 30%. Equation 9 is valid as long as DGM is produced in lake water faster than its evasion into the air, i.e.,  $\text{Hg}^0$  evasion is the rate-limiting step for the volatilization process. On the basis of the observation that Lake Michigan surface water has a mean degree of DGM saturation of 286% (3), it is reasonable to apply such an assumption for Lake Champlain. The total amount of Hg evasion ( $\text{g}/\text{year}$ ) from each lake segment is then calculated

**TABLE 2. Modern Average Hg Flux Values ( $\mu\text{g m}^{-2} \text{ year}^{-1}$ , Corrected for Sediment Focusing) and Flux Ratios for Lake Champlain**

flux values:	site			ave for the 3 cores
	Cole Bay	Malletts Bay	Point au Roche	
modern mean (1994–present)	19.4	54.4	47.4	40.4
ratio: modern mean/baseline peak	2.3	3.9	2.4	2.8
year of peak	1959	1922	1944	
ratio: peak/baseline	6.9	9.8	4.2	7.0

by multiplying the areal flux from eq 9 by the surface area of the lake segment.

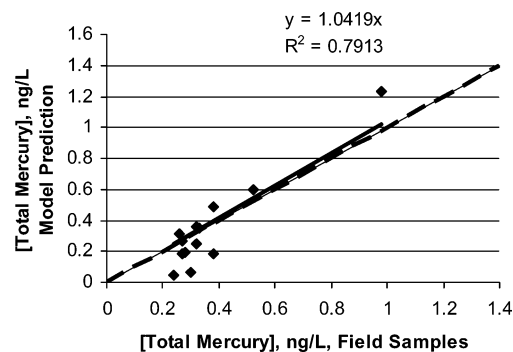
**Sedimentation Flux.** Prior to this study, no surveys had generated estimates of Hg sedimentation fluxes to Lake Champlain due to the lack of collocated sediment core dating and Hg concentration data. To address this need, three short sediment cores were collected from Cole Bay off Port Henry-Westport, NY (July 17, 2003), outer Malletts Bay, VT (July 31, 2002), and south of Point au Roche, on the open waters of the northern Main Lake (August 5, 2003) (Figure 1). These locations were selected to represent likely deposition patterns in the major sections of Lake Champlain, while avoiding areas of lake bottom that are known to exhibit deepwater currents.

Sediment coring, Hg analysis, and radiometric analysis methods are presented in the Supporting Information section. Sedimentation fluxes were corrected for sediment focusing by dividing sediment fluxes by the ratio of cumulative unsupported  $^{210}\text{Pb}$  flux to the regional average unsupported flux of  $0.5 \text{ pCi cm}^{-3}\cdot\text{year}^{-1}$  (42).

Estimated areal Hg fluxes ( $\mu\text{g}/\text{m}^2\cdot\text{year}$ ) for each core, as well as average fluxes across the three cores, are summarized in Table 2. Also summarized are peak Hg fluxes, the year of those peaks, and modern to peak flux ratios. Enrichment factors were calculated as the ratio of the peak or modern flux to the baseline flux. Except for some hot spots, Hg concentrations in the sediments of Lake Champlain overall are low relative to other Vermont lakes. However, sedimentation rates in Lake Champlain are relatively high, and thus on balance, Hg fluxes to the sediments of Lake Champlain are largely consistent with those at other sites in the northeastern United States (42–44).

To incorporate the sedimentation fluxes into our mass balance model, lake bottom areas for the 13 lake segments were calculated (see the Supporting Information), and the sedimentation loss (g/year) for a lake segment was calculated by multiplying the assigned modern flux value by the lake segment bottom area. For the Malletts Bay segment, the modern flux value from the sediment core taken there was used. For the Isle Lamotte segment, the average of the modern flux values from the cores taken at Point au Roche (Isle Lamotte segment) and Cole Bay (Port Henry segment) was used. For all other lake segments, the modern flux value from the sediment core taken in the Cole Bay (Port Henry segment) was used. This is a conservative approach because the Cole Bay sediment core carries the lowest modern Hg flux value of the three cores.

**2.4. Modeled Variables: Concentrations of Total Hg in the 13 Lake Segments.** This mass balance approach is designed to model the net accumulation of the total Hg in each lake segment. All of the lake segments are integrated so that a change in a single influx or outflux value in one segment will trigger changes in the total Hg concentrations in all the lake segments. The Hg mass balance model for



**FIGURE 3. Correlation plot of MB model predicted Hg concentrations vs the observed values (solid line, regression; dash line, 1:1).**

Lake Champlain was constructed using STELLA version 7.0 (45), a finite differential-equation-based modeling package. STELLA was used to solve (eq 1) simultaneously across all lake segments. The model allows variation of most input parameters in order to investigate differing conditions on Hg accumulation in the lake. Given sufficient equilibration time, the model generates steady-state Hg concentration by lake segment.

### 3. Modeling Results and Discussion

The Hg mass balance model is reasonably successful at apportioning the various Hg input pathways and losses and reproducing measured Hg concentrations in the 13 segments of Lake Champlain (Table 1). On the basis of the historical sedimentation flux profiles displayed by the three lake sediment cores acquired in this study, the modern flux rates (2000–2004) are at or near historical lows since they peaked in the 1920s to 1950s. Also, the change in Hg sedimentation fluxes in recent years is constrained to a few percent. As such, a steady-state mass balance model is an appropriate choice for the modeling of total Hg in Lake Champlain. With an initial total Hg concentration value of zero for all the lake segments, the system appears to achieve steady state within one input step (1 year). So the lake system is able to reach a new equilibrium rather quickly after a perturbation.

Tributary input is the largest Hg contributor to the lake, at  $26.5 \text{ kg/year}$  (56.4% of total inputs), followed by total atmospheric deposition ( $17.8 \text{ kg/year}$ , or 38% of total inputs). These estimates comprise a significant improvement to the rough estimates provided by a previous study (12) that identified atmospheric deposition of Hg to the surface of the lake as the dominant contributor. Given the large ratio of watershed area to lake surface (18:1), it is not surprising that tributary streams contribute the largest share of mercury to the lake. However, because much of the tributary load is understood to originate from atmospheric deposition to the watershed, atmospheric deposition is ultimately the leading source of Hg to the lake (46). Both wet and dry Hg deposition rates are greater in the terrestrial uplands because of increasing precipitation with elevation and because of the scavenging of atmospheric  $\text{Hg}^0$  and RGM by the forest canopy (25). Certain lake segments, such as the Northeast Arm, have a large surface area and little tributary input, and therefore Hg loading is dominated by direct atmospheric deposition.

The loss of Hg through the lake outlet into the Richelieu River is  $1.6 \text{ kg/year}$  (2.6% of total losses). The major sinks for Hg are volatilization loss, at  $34.9 \text{ kg/year}$  (56.6% of total losses), and sedimentation loss,  $25.2 \text{ kg/year}$  (40.8%). Overall, for the modeling run summarized in Table 1 (based on tributary Hg fluxes from water year 2002), the steady-state total Hg concentrations for most of the lake segments relate well to measured values from September 2001 ( $R^2 = 0.79$ , Figure 3). The simulated mercury concentrations from a few lake segments in the northern section of the lake are markedly

**TABLE 3. MB Modeling Results with Varying Tributary Loadings and Volatilization Rates**

lake segment	[THg], ng/L (DGM = 10% THg)			[THg], ng/L (DGM = 20% THg)			[THg], ng/L (DGM = 30% THg)			[THg], ng/L (9/2001)
	WY01	WY02	WY03	WY01	WY02	WY03	WY01	WY02	WY03	(field samples)
Burlington Bay	0.93	0.54	0.64	0.45	0.27	0.32	0.28	0.17	0.20	0.27
Cumberland Bay	1.16	0.76	0.83	0.70	0.49	0.52	0.53	0.38	0.40	0.38
Isle LaMotte	0.65	0.39	0.45	0.28	0.18	0.20	0.16	0.11	0.11	0.27
Main Lake	1.06	0.63	0.74	0.58	0.35	0.42	0.41	0.25	0.30	0.33
Malletts Bay	0.17	0.34	0.16	0.09	0.19	0.08	0.06	0.13	0.06	0.28
Missisquoi Bay	0.26	0.32	0.34	0.14	0.18	0.19	0.10	0.13	0.13	0.38
Northeast Arm	0.17	0.14	0.14	0.06	0.05	0.05	0.03	0.03	0.03	0.24
Otter Creek	1.09	0.63	0.76	0.60	0.36	0.44	0.42	0.25	0.32	0.32
Port Henry	0.99	0.54	0.65	0.45	0.25	0.30	0.26	0.15	0.18	0.32
Shelburne Bay	1.02	0.59	0.70	0.54	0.31	0.38	0.36	0.21	0.26	0.26
South Lake A	2.06	1.08	1.21	1.13	0.60	0.69	0.74	0.41	0.47	0.52
South Lake B	4.61	1.67	2.01	3.60	1.23	1.56	2.96	0.99	1.28	0.98
St. Albans Bay	0.15	0.13	0.13	0.05	0.06	0.05	0.03	0.04	0.03	0.30

lower than the actual measurements. These low modeled Hg concentrations may be an artifact of the unusually high modern Hg sedimentation flux value from Malletts Bay used in the model.

Field measurements of tributary THg concentrations confirmed significant seasonal and interannual variability. For example, [THg] in the Little Otter Creek decreased from 10.4 ng/L in March to 6.68 ng/L in April, to 1.58 ng/L in July, and 0.81 ng/L in September in 2003, while [THg] in April of 2001 was only 3.11 ng/L. Since tributary input is the main contributor of Hg to the lake, we expect the concentrations of the lake water to reflect such variability as well, but subannual variability is not presently included in the modeling due to the lack of mercury sampling data for lake water over different seasons. We conducted sensitivity tests on the mass balance model by using a range of tributary Hg input loads based on the sampling for water years 2001–2003. We also explored uncertainty in the volatilization estimate by varying the assumed level of dissolved gaseous mercury (DGM) in the lake from 10% to 30% of the total dissolved Hg. This range is consistent with accepted values as mentioned in section 2.3. The output results are tabulated in Table 3. The model run for year 2001 yielded the highest Hg concentrations in the lake segments. The model run using water year 2002 inputs and DGM at 20% of total Hg produced the closest agreement with measured water column Hg concentrations from September 2001. The potential variability in modeled steady-state total Hg concentrations is supported by our more recent field measurement findings in phase II of our project, which showed lake segment total Hg concentrations vary by a factor of 2 to 3 from year to year, a finding that is not uncommon for lake systems when highly variable tributary input is driving the lake systems. For example, in the Lake Michigan mass balance project, total Hg concentration ranged from a minimum of 7.81 to a maximum of 182 ng/L during 1994 for the Fox River, tributary to Lake Michigan (14).

Wet deposition to the lake surface appears to be the second largest contributor, at 9.3 kg/year (19.9%), followed closely by dry deposition at 8.5 kg/year (18.1%) and a small contribution from WWTFs at 2.7 kg/year (5.7%) to total mercury inputs. The wet deposition rates are estimated to be fairly homogeneous across the lake at  $7.98 \pm \text{SD } 0.12 \mu\text{g}/\text{m}^2\text{-year}$ . The dry deposition rates are estimated to be more variable at  $6.46 \pm \text{SD } 1.78 \mu\text{g}/\text{m}^2\text{-year}$ . Estimates of atmospheric wet and dry deposition of Hg produced as part of this project were considerably improved relative to the previous estimates made in the 1990s (13). The improvements result from the refinement of dry deposition modeling methods, the inclusion of newly available RGM measurements, and a considerably longer monitoring period. Since start-up in 1992, the Hg monitoring program at PMRC

measured only elemental gaseous Hg and particulate Hg. RGM, a potentially important component of total Hg deposition, was not measured until 2004. Our estimates of dry deposition of RGM, based on the new data and calculation methods of Miller et al. (25), ranged from 1.5 to 5.5  $\mu\text{g}/\text{m}^2\text{-year}$  to the 13 lake segments. Dry deposition was spatially adjusted by accounting for variations in water and air temperature and wind speed among the 13 lake segments.

A comparison of the relative importance of the main Hg input pathways at Lake Champlain to those at Lake Michigan (47) reveals some interesting similarities but many important differences. First, direct atmospheric deposition (wet and dry) is the largest source of Hg to Lake Michigan at 84%, whereas it accounts for only 38% of the Hg input to Lake Champlain. Annual wet and dry deposition fluxes of Hg to Lake Champlain (average  $7.98 \mu\text{g}/\text{m}^2\text{-year}$  and  $6.5 \mu\text{g}/\text{m}^2\text{-year}$ , respectively) are somewhat lower than those to Lake Michigan (average  $10.6 \mu\text{g}/\text{m}^2\text{-year}$  and  $9.7 \mu\text{g}/\text{m}^2\text{-year}$ , respectively). However, these estimates reflect different time periods. The much smaller watershed area/lake surface ratio (2:1) also enhances the importance of direct atmospheric deposition at Lake Michigan.

This modeling effort provides a better understanding of the Hg transport and removal mechanisms in Lake Champlain. For example, we have demonstrated the importance of tributary runoff as a Hg source to lakes with large watershed/lake area ratios. We also made some initial estimates of the rates of Hg sedimentation in the lake. Two of the three sediment cores taken from the lake during this study (Cole Bay and Point au Roche) displayed a typical modern Hg flux to baseline Hg flux ratio of 2.3 and 2.4, respectively. These ratios are comparable to those obtained in a comprehensive survey of sediment Hg levels in a large number of lakes in Vermont and New Hampshire (42–44). The Malletts Bay core yielded an atypically high ratio of 3.9. This high apparent Hg flux is likely due to a consequence of higher particle sedimentation rate in that lake region owing to highly constrained bulk dispersive flow to the adjacent Inland Sea and Main Lake segments. The historical Hg sedimentation flux highs observed in the three core profiles occurred in the 1920s to 1950s. Lake sediments in many other regions of the United States display Hg sedimentation maxima in the 1960s to 1990s, a result of increased Hg use, and fossil fuel and waste combustion, during that period of time. In Lake Champlain, Hg sedimentation appears to be strongly tied to sediment loading events. The sedimentation flux peaks in two of the three cores are temporally coincident with the catastrophic flood of 1927. The volatilization component of this mass balance model is another refinement over the simple Hg budget produced in the 1990s (12). By incorporating volatilization and sedimentation pathways and by improved modeling of other pathways, we were generally



able to reproduce the field Hg measurements.

Even though we limit the focus of this paper to phase I of this study—physical cycling of total Hg, our most recent field measurements provided some interesting preliminary findings regarding MeHg. For example, tributary MeHg concentrations around Lake Champlain are 0.4–16% of the THg concentrations, compared to 0.5–5.9% for tributaries to Lake Michigan. The lake water MeHg concentrations are 4–6% of the THg concentrations in Lake Champlain, consistent with Little Rock Lake, Wisconsin (48), but considerably lower than values measured across 90 smaller Vermont and New Hampshire lakes (44). Watras and Bloom found that when a lake basin is slightly acidic (mean pH of 6.1), as in the case of part of the New York portion of the Lake Champlain, the average lake water MeHg concentration is 5% of the THg concentration (49). When a lake is highly basic, as in the case of Lake Michigan (mean pH of 8.2) and the majority of the Lake Champlain Basin, the lake water MeHg concentrations are lower, at only 2–3% of THg concentrations (1). We also discovered that MeHg concentrations in lake segment are about 0.3–0.6% of THg summertime concentrations in lake water.

The findings and progress made in phase I of this study have helped to identify certain deficiencies in the current mass balance model, several of which are being addressed by phase II of this study. Specifically, we need (1) additional sediment coring at representative locations for improved understanding of the spatial variation in Hg sedimentation rates in the lake; (2) more detailed modeling of water and air temperature and wind speed variations across the lake to refine Hg volatilization estimates; (3) expanded spatial and temporal tributary sampling that includes the smaller streams to more accurately account for total tributary Hg input; (4) actual measurements of Hg concentrations in WWTF effluent; (5) expanded sampling of lake water for THg and MeHg, and new analyses of DGM to provide more accuracy in inputs to the model; (6) finer temporal resolution of Hg inputs, e.g., using monthly wet and dry deposition and monthly tributary inputs, which would allow for an understanding of the short-term variations in the accumulation of Hg in the lake; (7) coordinated water, sediment, and biota sampling and analysis for THg, MeHg, stable isotopes, and DOC to allow incorporation of Hg dynamics in the food web.

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## Supporting Information Available

Tributary water sampling and Hg analysis methods, sedimentation coring, Hg analysis, and radiometric analysis methods, and calculation of lake bottom areas. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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