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A mercury transport and fate model (LM2-Mercury) for mass budget assessment of mercury cycling in Lake Michigan

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ABSTRACT

LM2-Mercury, a mercury mass balance model, was developed to simulate and evaluate the transport, fate, and biogeochemical transformations of mercury in Lake Michigan. The model simulates total suspended and resuspendable solids (TSRS), dissolved organic carbon (DOC), and total, elemental, divalent, and methylmercury as state variables. Simplified processes among the mercury state variables including net methylation, net reduction of divalent mercury, and reductive demethylation are incorporated in the model. Volatilization of elemental mercury as a kinetic (phase transfer) process and partitioning of total, divalent, and methylmercury as a set of instantaneous equilibrium processes were also simulated. The model was calibrated to data collected in 1994 and 1995 and corroborated by comparing model output generated from a long-term model hindcast to total mercury measured in high quality sediment profiles. Model hindcast predictions of total mercury in the water column were within estimates of total mercury calculated from observed lake trout bioaccumulation factors. Using the model, a mass budget assessment of mercury cycling in the lake was conducted. Atmospheric deposition, including wet and dry (particle) deposition and absorption of gaseous divalent mercury, was the dominant source of total mercury to the lake, followed by sediment resuspension, and then tributary loads. The major loss mechanism of total mercury from the water was associated with the settling of solids, followed by net volatilization. Methylmercury loading associated with wet deposition was the dominant source to the lake, followed by tributary loadings, and *in situ* net methylation.

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Introduction

Mercury is a global, persistent, and bioaccumulative toxic pollutant. Its organic form, CH_3Hg (methylmercury or MeHg), is the most biologically active and toxic form of mercury. It can accumulate in organisms within the food chain, such as fish, posing a risk to wildlife and humans.

Smaller lakes have the potential to have more severe mercury problems than large lakes, such as the Great Lakes in the United States. With relatively large ratios of area/volume, smaller lakes are likely to have relatively higher mercury concentrations than the larger lakes in response to atmospheric deposition, which is usually the most predominant source of mercury to both small and large lakes (Mason and Sullivan, 1997). In addition, small lakes warm up more quickly and attain higher summer temperatures than large lakes such as Lake Michigan. Mercury methylation rate constants increase with increasing water temperatures (Ulrich et al., 2001), thereby increasing the potential for the production of MeHg in a smaller lake.

A series of linked numerical models are often used to simulate complex physical and chemical cycling of mercury in aquatic ecosystems and to evaluate the effects of external mercury inputs on aquatic and terrestrial organisms and humans that consume them. As an important component in the linked modeling framework, water quality models provide both short-term and long-term predictions on the mercury environmental exposure concentrations in the water column and sediments of a water body. The predicted environmental exposure concentrations are used for further predicting the level of mercury accumulated in the organisms such as fish and their predators.

Mercury transformation processes in an aquatic ecosystem can be very complex, and some of the processes have not been well defined. In general, most of the rate constants for these processes have not been experimentally determined. However, over the last few decades, significant modeling efforts have been made to describe and simulate the fate, transport, and biogeochemical transformation of mercury in aquatic ecosystems. Several notable mechanistic models have been

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developed and applied to various aquatic ecosystems that utilized simplifying assumptions such as those used in this paper (key processes modeled, equilibrium speciation of mercury complexes, and first-order biogeochemical kinetics among mercury components). These models include the MCM (Mercury Cycling Model) by Hudson et al. (1994), SERAFM by Knightes (2008), SERAFM and Wasp7 by Knightes et al. (2009), MERC4 by Martin (1992), and WASP5 by Tsiros and Ambrose (1998).

The United States Environmental Protection Agency (USEPA) selected mercury as one of the target contaminants for the Lake Michigan Mass Balance Project (LMMBP) to support the development of a Lake Wide Management Plan (LaMP) for Lake Michigan. A mercury mass balance model, LM2-Mercury, was developed to: 1) describe and evaluate the fate, transport, and biogeochemical transformations of mercury in Lake Michigan; 2) forecast mercury concentrations in the lake (both water column and sediment); and 3) provide insights for policy makers to evaluate the long-term responses of the lake to various mercury loading scenarios. The mercury transport and fate model independently simulates total mercury (tHg, an analytical measurement that combines all mercury components) and the three individual mercury components (elemental mercury (Hg^0), divalent mercury (Hg^{2+}), and methylmercury (MeHg)) and their interactions with total suspended and resuspendable solids (TSRS) and dissolved organic carbon (DOC). MINTEQA2 (Allison et al., 1991), an equilibrium metal speciation model applied to Lake Michigan water with mean estimates of 22 major cation and anion concentrations for the year 1991, predicted that >99% of the dissolved Hg^{2+} and MeHg was $Hg(OH)_2$ and MeHgOH, respectively. The LM2-Mercury model was designed to have enough sophistication in overall model conceptualization to capture key processes while maintaining simplicity of speciation processes where permitted. This paper provides details on model development, conceptual framework, and model input. The results of model calibration and corroboration as well as a mass budget are presented and discussed. A future paper will provide results and a discussion on forecasts with the consideration of impacts of global and local contributions to mercury concentrations in the lake and a post-audit corroboration.

Model development and construct

LM2-Mercury is based on the principle of conservation of mass. The lake water and sediments are represented in the model as a series of discrete computational elements (segments). The sediment compartments are linked to the water compartments *via* particle settling, resuspension, and diffusion processes.

LM2-Mercury adapted the generic code and structures from the Lake Michigan PCB model, LM2-PCBs (Zhang et al., 2008), including the water transport fields and the sediment transport scheme. The spatial segmentation for LM2-Mercury is the same as that used by LM2-PCBs. The segmentation includes forty-one water segments (Fig. 1 shows only the surface water segments) with five horizontal layers and 53 surficial sediment segments categorized to address distinct sediment non-depositional, transitional, and depositional zones. Details of the model segmentation scheme including sediment segmentation are provided in the Electronic Supplementary Material (ESM Appendix B). Several specific modifications were made in the adaptation of LM2-PCBs for mercury components: 1) the temperature-dependent Henry's Law constant for tHg and Hg^0; 2) air–water exchange formulations for tHg and Hg^0; 3) an approach similar to that used by Vette, 1998 and Vette et al., 2002) to estimate absorption of gaseous divalent mercury (reactive gaseous mercury abbreviated as RGM) to Lake Michigan; 4) a distribution factor was added to specify the fraction of the dissolved phase of total mercury allowed to be volatized; and 5) simplified speciation processes (Tsiros and Ambrose, 1998) were added for transformation among the mercury components for both the water column and the sediment. A detailed model description including numerical method, general mass balance equations for the state variables (total mercury, mercury components, TSRS, and DOC) in water column and sediments, and aggregation of the inputs of hydrodynamic fields based on the outputs from the hydrodynamic model (POMGL — Princeton Ocean Model for the Great Lakes) can be found in the ESM Appendix B.

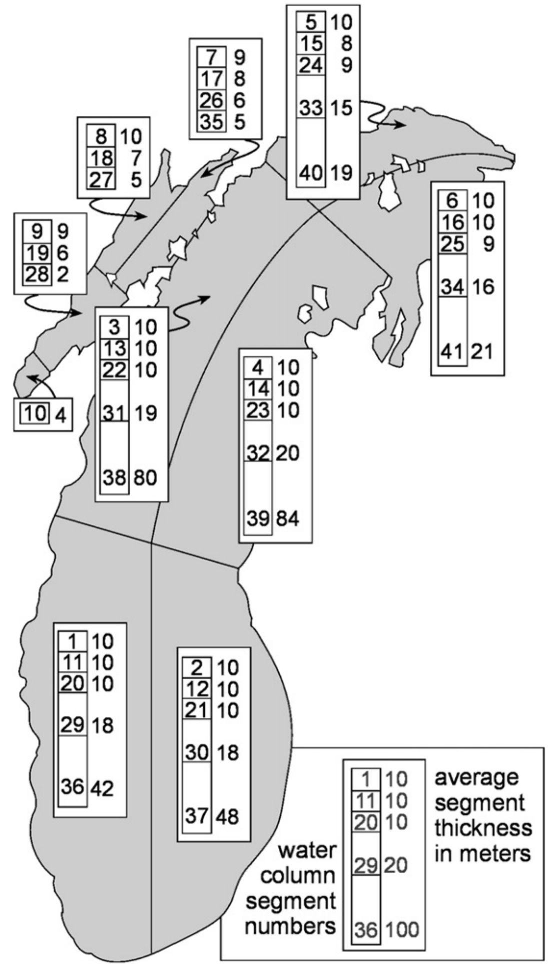

Fig. 1. LM2-Mercury water column segmentation. The numbers on the left side of the boxes are segment numbers. The numbers on the right side of the boxes are average segment thickness. This figure is from Zhang et al. (2008) and reused with permission from Elsevier.

LM2-Mercury simulates TSRS, DOC, total mercury (tHg), and three mercury components (Hg^0, Hg^{2+}, MeHg) as model state variables. Among the mercury state variables, tHg, Hg^{2+}, and MeHg exist in both the water column and the sediment as dissolved and associated with particulate phases. In this paper, whenever tHg, Hg^{2+}, and MeHg are used without a qualifier, they should be interpreted as containing Hg in both dissolved and particulate phases. Hg^0 exists in the system only in the dissolved phase. Equilibrium partitioning is assumed between the dissolved and particulate-associated mercury components in both the water and sediment. The time step used in the model simulations is about 3 h which is assumed to be long enough for mercury or a mercury component to reach equilibrium between the dissolved and particulate phases in a large fresh water system. The transport and fate of mercury is closely linked to the movement of water, TSRS, and DOC, including processes such as advection, dispersion, settling, resuspension, partitioning to TSRS and DOC, etc. In addition, the transformation processes among the mercury components, including net reduction of inorganic mercury, net methylation, and reductive demethylation, are critical to the fate of mercury in the lake. Conceptualizations of the dynamics of TSRS, mercury components, and total mercury in the lake are given in Appendix A. The conceptual framework