

# Response of a Macrotidal Estuary to Changes in Anthropogenic Mercury Loading between 1850 and 2000

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Methylmercury (MeHg) bioaccumulation in marine food webs poses risks to fish-consuming populations and wildlife. Here we develop and test an estuarine mercury cycling model for a coastal embayment of the Bay of Fundy, Canada. Mass budget calculations reveal that MeHg fluxes into sediments from settling solids exceed losses from sediment-to-water diffusion and resuspension. Although measured methylation rates in benthic sediments are high, rapid demethylation results in negligible net in situ production of MeHg. These results suggest that inflowing fluvial and tidal waters, rather than coastal sediments, are the dominant MeHg sources for pelagic marine food webs in this region. Model simulations show water column MeHg concentrations peaked in the 1960s and declined by almost 40% by the year 2000. Water column MeHg concentrations respond rapidly to changes in mercury inputs, reaching 95% of steady state in approximately 2 months. Thus, MeHg concentrations in pelagic organisms can be expected to respond rapidly to mercury loading reductions achieved through regulatory controls. In contrast, MeHg concentrations in sediments have steadily increased since the onset of industrialization despite recent decreases in total mercury loading. Benthic food web MeHg concentrations are likely to continue to increase over the next several decades at present-day mercury emissions levels because the deep active sediment layer in this system contains a large amount of legacy mercury and requires hundreds of years to reach steady state with inputs.

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## Introduction

High levels of exposure to methylmercury (MeHg) from fish consumption causes adverse health effects on humans and wildlife (1, 2). Approximately 90% of fish consumed in the U.S. population are from estuarine and marine systems (3). Since MeHg is actively produced in coastal and shelf sediments (4–6) and tidal salt marshes (7), these systems are an important vector for entry of MeHg into marine food webs. Evaluating the magnitude of Hg loading reductions needed to maintain fish tissue levels below regulatory guidelines considered safe for human consumption requires a quantitative analysis of estuarine mercury (Hg) cycling processes (8). Here we develop an ecosystem model of Hg dynamics to investigate anthropogenic impacts on estuarine MeHg levels. To do this, we reconstruct historical mercury loading (1850–2000) from atmospheric deposition, tides, and rivers to a coastal embayment in eastern Canada using sediment core data and global models.

Anthropogenic Hg emissions in eastern Canada and the northeastern United States peaked in the 1970s and have declined by over 50% since this time (9, 10). Despite these reductions in emissions, Hg concentrations in some freshwater and marine fish and wildlife remain high (11, 12). Fish consumption advisories throughout this region warn of health risks associated with Hg exposure for pregnant women and other sensitive groups (13). Time scales required for Hg to cycle through freshwater and marine ecosystems are highly variable and can range from several years to many decades (14–17). Environmental fate and bioaccumulation models are critical for synthesizing best-available process understanding and for determining how the legacy of anthropogenic Hg loading has affected biological MeHg concentrations. Such information is essential for developing effective management strategies and emission reduction targets. Here we develop such a fate and transport model and apply it to Passamaquoddy Bay, a macrotidal estuary located at the mouth of the Bay of Fundy, Canada. This region has historically supported large fish populations and provides critical habitat for wildlife (18), in part due to its unique hydrography and extreme tidal range that reaches up to 16 m at the mouth of the Bay of Fundy (19). Protecting coastal water quality is vital for the local economy because approximately 20,000 U.S. and Canadian fishers depend on marine resources in this region (20).

This study's main objective is to develop an analytical framework for better understanding the biogeochemical cycling of Hg in coastal ecosystems. The model developed here simulates changes in MeHg concentrations between 1850 and 2000 using the trajectory of historical loading from several data sources (4, 16, 21). We evaluate the model's performance using sensitivity analyses and by comparing results to measurement data from our previous research (4, 21–24). We apply the model to (a) quantify the relative importance of different sources of mercury loading (atmospheric, tidal, riverine); (b) characterize time scales required for anthropogenic Hg to cycle through this ecosystem; and (c) assess impacts of anthropogenic Hg on MeHg reservoirs and fluxes driving the bioavailable Hg pool at the base of the food web. To our knowledge, this is the first ecosystem-scale simulation of how changing loading from anthropogenic sources over the last 150 years has impacted estuarine MeHg levels.

## Methods

**Site Description.** Passamaquoddy Bay is a semienclosed macrotidal estuary (Figure 1). Strong currents and tidal mixing

inhibit thermal stratification of the water column during summer months. Forests cover most of the watershed (4225 km<sup>2</sup>), with the exception of a narrow floodplain that supports mixed farming and light industry (25). Water temperatures vary from a low of -1 °C in winter to 16 °C in summer (26). The average water depth is 30 m (maximum of ~70 m) and salinities range between 26‰ and 33‰ (26). As a smaller and tidally dynamic system enclosed by the Bay of Fundy, Passamaquoddy Bay differs from previously studied larger estuaries such as Long Island Sound (27) and Chesapeake Bay (28) that have much longer water residence times.

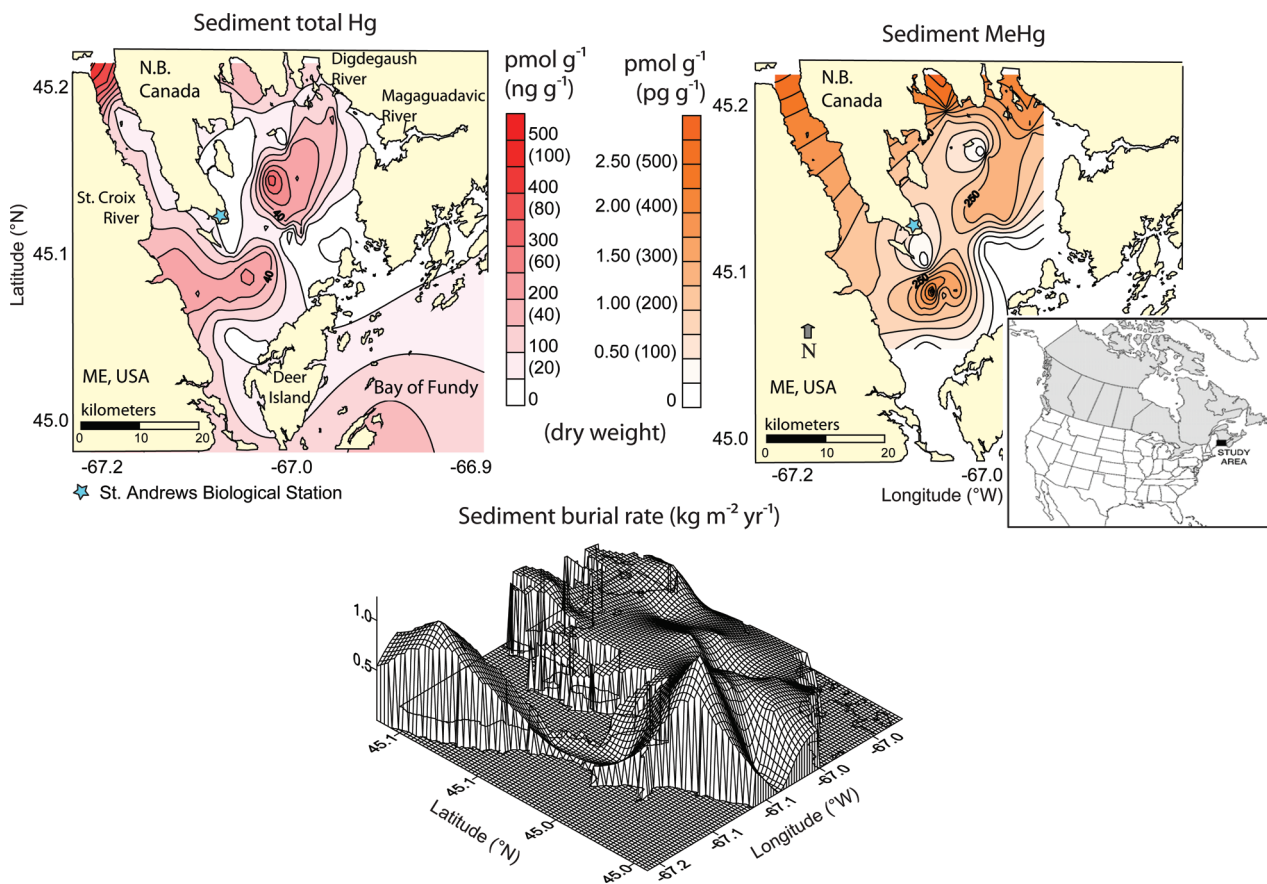
**General Model Description.** We developed equations to describe the transport and partitioning of each of the three main forms of mercury (elemental Hg: Hg(0), divalent Hg: Hg(II), and MeHg) in water and sediments (Supporting Information (SI) Figure S1) using the general fate and transport modeling framework developed by Gobas et al. (29, 30). All model compartments are assumed to be well-mixed, and benthic sediments are divided into an active layer and a truly buried inaccessible sediment layer (4). External loading from atmospheric deposition (*A*), rivers (*R*), and tidal inflow (TL) drives the model, which is run with a temporal resolution (*t*) of one day. A larger time-step results in numerical instability because many of the reaction rates are very fast (e.g., oxidation and reduction). One-step forward Euler-type numerical integration is used to compute changes in the mass of each Hg species in water (*M<sub>w</sub>*) and sediments (*M<sub>s</sub>*) over time. For total Hg this is represented by the following general equations:

$$\frac{dM_w}{dt} = (A + R + TL) + (k_{res} + k_{diff})M_s - (k_{ev} + k_o + k_{sett})M_w \quad (1)$$

$$\frac{dM_s}{dt} = k_{sett}M_w - (k_{res} + k_{bur} + k_{diff})M_s \quad (2)$$

Rate coefficients (*d*<sup>-1</sup>) shown in eqs 1 and 2 and Figure S1 represent tidal outflow (*k<sub>o</sub>*), sediment resuspension (*k<sub>res</sub>*), sediment settling (*k<sub>sett</sub>*), diffusion (*k<sub>diff</sub>*), burial (*k<sub>bur</sub>*), and Hg(0) evasion (*k<sub>ev</sub>*). Rates of interspecies conversions in the differential equations for MeHg, Hg(0) and Hg(II) (SI Section II, Figure S1) are described using rate coefficients for Hg(II) reduction (*k<sub>red</sub>*), Hg(0) oxidation (*k<sub>ox</sub>*), Hg(II) methylation (*k<sub>m</sub>*), MeHg demethylation (*k<sub>dm</sub>*), and MeHg photodecomposition (*k<sub>dmw</sub>*). All rate coefficients represent annually averaged values and include in their calculation partitioning of Hg species between the dissolved and solid phases (see SI for details). Additional information on methods and data used to derive model rate coefficients is provided in SI Section IV.

**External Inputs from Rivers, Tides, and Atmospheric Deposition.** In previous research, we estimated mean anthropogenic enrichment factors (AEF = 2000 loading/1850 loading) for atmospheric deposition (3.2 ± 0.4) and freshwater inputs (3.6 ± 1.9). Here we reconstruct annual loading between 1850 and 2000 by combining measured present-day (year 2000) inputs with historical loading information from sediment cores and global models. For atmospheric deposition and fluvial inputs, we multiplied measured contemporary inputs by the relative changes in loading indicated by sediment core data (4, 21). Sediment cores used to reconstruct historical atmospheric deposition were from



**FIGURE 1.** Map of study region showing spatially interpolated measured total Hg and MeHg concentrations and burial rates used to calculate the contemporary (ca. 2000) reservoirs in sediments and burial fluxes. Information on sampling locations, analytical methods, and correlations with ancillary sediment characteristics can be found in Sunderland et al. (4, 24).

tidal salt marshes, lakes, and bogs in the region, while cores from the mouth of the St. Croix River (the major freshwater tributary) were used to reconstruct historical loading from rivers. To characterize changes in Hg fluxes from tidal inflows, we used data from Sunderland and Mason (16) showing the Atlantic Ocean (35°S–55°N) has been enriched in total Hg by 58% since preindustrial times. Because no historical oceanic Hg trend data are available, we assume that changes in tidal inputs increase linearly between 1850 and 2000 to the contemporary enrichment level (16).

Year 2000 inputs are based on measured Hg concentrations and hydrological fluxes for each source. Inflowing tidal water volume ( $T_i$ ) is estimated from the difference between tidal outflow ( $T_o$ ) and the sum of freshwater inflow ( $R$ ) and inputs through precipitation ( $P$ ) (i.e.,  $T_i = T_o - R - P$ ). Concentrations of Hg species in tidal water are based on data from Dalziel et al. (22), who measured unfiltered seawater concentration profiles at 15–50 m vertical intervals in the Bay of Fundy between 2000 and 2002 (mean Hg:  $1.20 \pm 0.34$  pM; mean MeHg:  $0.29 \pm 0.11$  pM). No data are available for Hg(0), therefore we assumed that the fraction of total Hg present as Hg(0) in tidal waters is  $13 \pm 6\%$  corresponding to the overall mean and standard deviation of the fraction present in the Atlantic Ocean at comparable latitudes compiled by Sunderland and Mason (16).

Monthly fluvial discharges into Passamaquoddy Bay are reported by Gregory et al. (19). Annually averaged Hg concentrations in the three major freshwater tributaries (Hg:  $19.0 \pm 7.6$  pM; MeHg:  $1.22 \pm 0.25$  pM) are based on previous studies (22, 31) that measured unfiltered Hg concentrations and suspended particulate content over several seasons (SI Table S2). Total (wet + dry) atmospheric deposition ( $54.8 \pm 0.5$  nmol  $m^{-2} yr^{-1}$ ) is based on measurements and models described in detail elsewhere (21). Wet atmospheric deposition rates (mean  $30.9 \pm 6.7$  nmol  $m^{-2} yr^{-1}$ ) were taken from measurements at the St. Andrews Mercury Deposition Network (MDN) Station (NB-02) (SI Table S2). Inputs of MeHg in precipitation are from Environment Canada measurements at nearby field stations showing MeHg is on average  $1.6 \pm 1.2\%$  of total Hg in precipitation (22).

**Empirically Constrained Mass Budget.** We developed an empirically constrained mass budget for the year 2000 using measured sediment and water concentrations. We used depth integrated seawater concentrations for total Hg ( $1.27 \pm 0.23$  pM) and MeHg ( $0.25 \pm 0.07$  pM) measured in Passamaquoddy Bay (November 2001) and the four closest Bay of Fundy sampling stations (June 2001–August 2002) (SI Table S2) to characterize the contemporary water column reservoirs of total Hg and MeHg (22). Because no direct measurements of Hg(0) concentrations in seawater are available, we specified rate coefficients for oxidation and reduction measured in other coastal systems (SI Section IV) and allowed concentrations to reach steady state. We also estimated the accumulation of Hg and MeHg in primary producers based on a reported primary productivity of  $296$  g  $C m^{-2} yr^{-1}$  (32), measured concentrations in dinoflagellates and diatoms (total Hg:  $14.0 \pm 4.1$  and MeHg:  $0.75 \pm 0.55$  pmol  $g^{-1}$  wet weight) in the Bay of Fundy (11), an 80% moisture content, and assumed that 50% of the plankton dry weight is carbon (32).

In previous work, we measured a deep active sediment layer of 0.15 m (4) that exchanges Hg with the water column and buried sediments through resuspension, diffusion, and burial (33). Spatial heterogeneity in sediment Hg concentrations (34, 35) can introduce substantial error into box model calculations that are based on mean concentrations from a limited sampling population. To account for this heterogeneity, we spatially interpolated measurement data for total Hg ( $n = 56$ ) and MeHg ( $n = 52$ ) reported in our previous work (4, 24) using several algorithms (Variogram, Drift Type,

and Nugget Effect models) (36). Sediment reservoir calculations were completed by summing volume estimates for each cell defined in the spatial grid (see burial flux diagram Figure 1) using the Trapezoidal Rule, Simpson's Rule, and Simpson's 3/8 Rule, where the difference among methods was used to estimate the error among volume calculations (37). Figure 1 shows the spatially interpolated concentrations of total Hg and MeHg in benthic sediments used to derive mass budgets shown in Figure 2.

#### **Preindustrial Budget and Time-Dependent Simulation.**

We developed a preindustrial budget for Hg by assuming local steady state with 1850 loading, and that no changes in present-day sedimentation rates have occurred in the Bay. We drive the preindustrial steady state model with reconstructed historical loading between 1850 and 2000, and force the simulation for an additional 50 years (to 2050) with constant 2000 loading rates to project changes in water and sediment concentrations over time.

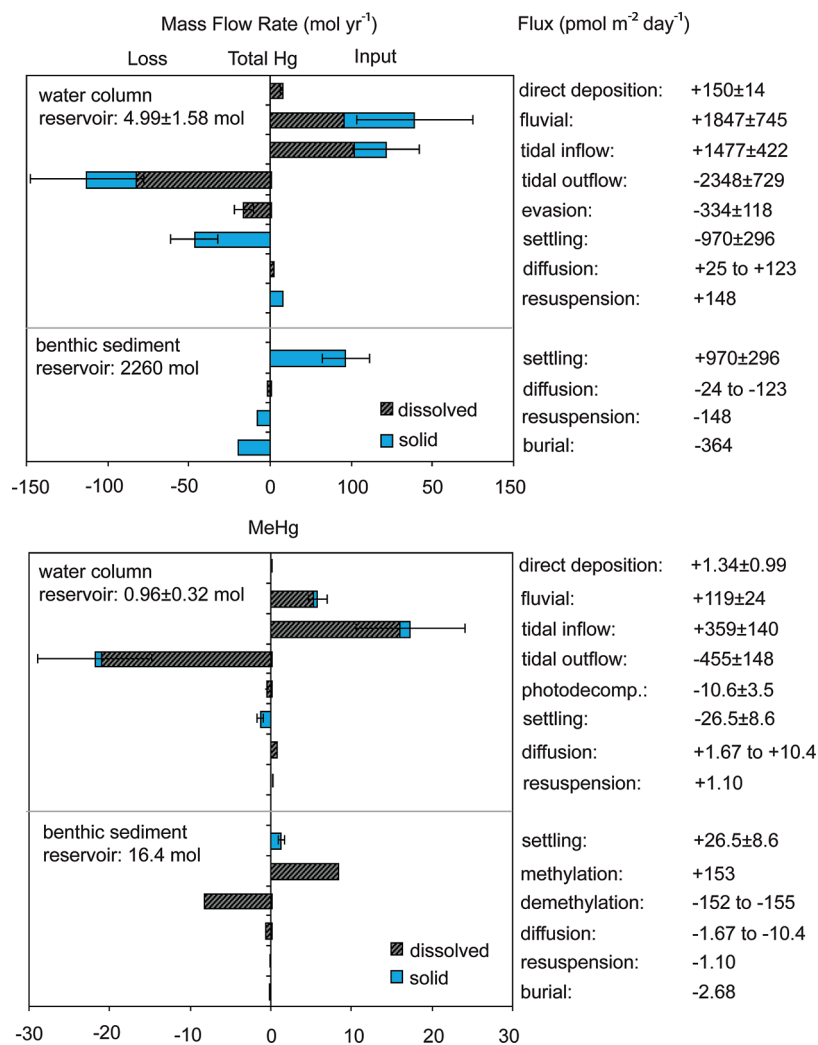
**Model Evaluation and Sensitivity Analysis.** For all simulations and mass budget calculations we show upper and lower bounds for modeled Hg concentration changes based on 95% confidence intervals for measured inputs from rivers, tides, and atmospheric deposition. We conducted detailed sensitivity analysis on model inputs and parameters, including the net methylation rate in benthic sediments, the reduction rate coefficient, the depth of the active sediment layer, alternate formulations of the gas exchange flux (38, 39), and upper and lower bounds for diffusion coefficients (27, 34). We also compare results from the time-dependent model simulation to available measured Hg concentrations.

## **Results and Discussion**

**Model Evaluation.** Comparing model simulated water and sediment Hg concentrations to independent data shows reasonable agreement given the error and uncertainty in historical loading (Figure 3). Year 2000 measurements of water column total Hg and MeHg (Figure 3) suggests that model predicted concentrations are biased slightly high relative to observations. However, natural stochasticity in Hg concentrations (16) and limited sample sizes means observations are also subject to error and uncertainty. We could not comprehensively test model performance by comparing results to measurement data because limited information on temporal trends in Hg concentrations are available. We use model sensitivity analysis to further investigate factors controlling results presented in the remaining sections.

**MeHg Production and Diffusion from Benthic Sediments.** In previous work we measured substantial Hg(II) methylation in sediments ( $153$  pmol  $m^{-2} d^{-1}$ ). Year 2000 mass budget results shown in Figure 2 indicate that in situ MeHg production in sediments is not the major MeHg source for the water column and pelagic organisms, assuming MeHg from different sources is equally bioavailable. Figure 2 further shows that the sum of MeHg inputs from settling particles and losses from sediment-to-water diffusion and resuspension results in a net contribution from the water column to benthic sediments of at least  $25$  pmol  $m^{-2} d^{-1}$ . Thus, sediments in this system are an overall sink for water column MeHg. Even combining the upper bound for diffusive fluxes of MeHg with the lower bound for Hg(II) (maximizing methylation and minimizing demethylation) does not result in appreciable net MeHg formation in the sediments given the magnitude of inputs from settling particles (Figure 2) and constraints imposed by measured MeHg concentrations in sediments (0.7–0.8% of total Hg in sediments, Figure 1). Time dependent model simulations show MeHg inputs from settling particles are sufficient to account for observed MeHg accumulation in sediments (Figure 3). Even if all MeHg produced in situ were demethylated, it is plausible that MeHg could continue to accumulate in sediments due to





**FIGURE 2.** Empirically constrained mass budgets for total Hg and MeHg in the year 2000 based on measured water and sediment Hg and MeHg concentrations. Error bars represent 95% confidence intervals around loading and measured concentrations except for sediment reservoirs and mass flow rates, which are based on spatial interpolations of field data. Ranges for diffusion and methylation/demethylation represent scenarios based on high/low diffusion coefficients for Hg species in interstitial waters. Large mass flow rates in the water column compared to the reservoir size results in rapid concentration changes with alterations in inputs, while the larger Hg and MeHg reservoirs and smaller mass flow rates in sediments results in a slower temporal response.

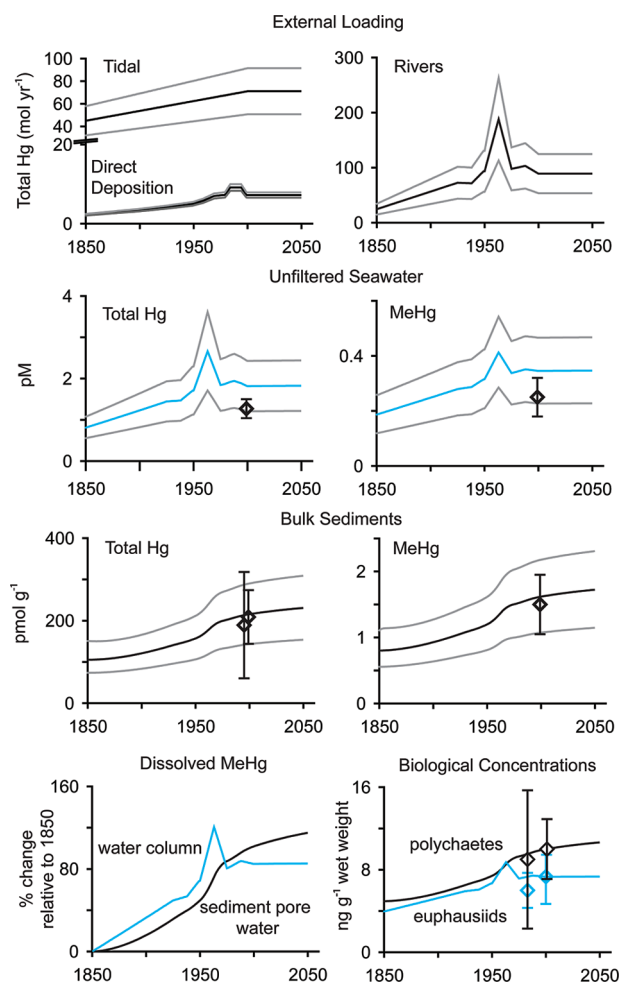
inputs from settling particles, assuming MeHg sorbed to settling solids is sufficiently recalcitrant to survive transit.

Previous studies have constructed estuarine Hg mass budgets without considering the relative magnitude of MeHg inputs to sediments from settling solids (27, 28, 40). These studies have postulated that diffusive fluxes of MeHg from estuarine sediments account for the majority of water column MeHg and accumulation in estuarine biota. In contrast, Figure 2 shows that MeHg concentrations in the water column of Passamaquoddy Bay are most affected by external MeHg inputs from tides and rivers ( $23.1 \text{ mol yr}^{-1}$ ) rather than MeHg from estuarine sediments ( $-0.83 \text{ mol yr}^{-1}$ ). Model sensitivity analysis reveals that increasing the benthic sediment methylation rate by 60% increases water column MeHg concentrations by only 2.1% (SI Figure S2). The relative importance of sediment-to-water diffusion of MeHg compared to external MeHg inputs to the water column (40) and/or water column methylation (41) could be similarly tested using data from other systems such as Chesapeake Bay and Long Island Sound (28, 40).

Although model calculations show that methylation and demethylation rates in sediments are approximately balanced, these processes turn over approximately 50% of the sediment MeHg reservoir on an annual basis (Figure 2). Time-

dependent simulations presented in Figure 3 do not account for environmental changes that could alter sedimentary methylation and demethylation rates (4, 24). Model sensitivity analysis (SI Figure S2) shows that such changes in the balance of sediment methylation and demethylation would cause large and near proportional changes in sediment MeHg concentrations. Increases in sediment methylation rates could therefore rapidly increase benthic food web exposures.

**Water Column Hg Fluxes.** For the year 2000 mass budget, the largest inputs of total Hg are from rivers, and the largest output is associated with tidal outflow (Figure 2). Evasion of Hg(0) at the air-sea interface ( $334 \pm 118 \text{ pmol m}^{-2} \text{ d}^{-1}$ ) is greater than the total Hg inputs from direct deposition ( $150 \pm 14 \text{ pmol m}^{-2} \text{ d}^{-1}$ ) indicating that the estuary is a net Hg source to the atmosphere. Comparing evasion of Hg(0) for the year 2000 calculated using the scheme developed by Nightingale et al. (38) ( $16.1 \text{ mol yr}^{-1}$ ,  $334 \text{ pmol m}^{-2} \text{ d}^{-1}$ ) used in our standard simulation to the low-end estimate (42, 43) from the model developed by Liss and Merlivat (39) ( $11.1 \text{ mol yr}^{-1}$ ,  $230 \text{ pmol m}^{-2} \text{ d}^{-1}$ ) shows a 30% decline in water column Hg(0) losses. Aqueous reduction of Hg(II) and subsequent evasion of Hg from seawater removes inorganic Hg that could potentially be converted to bioavailable MeHg. However, MeHg concentrations in seawater are



**FIGURE 3. Reconstructed historical Hg loading to Passamaquoddy Bay between 1850 and 2000 and modeled changes in water, sediments, and biota. Constant loading is assumed between 2000 and 2050. Gray lines represent 95% confidence intervals around loading and concentrations based on measured variability in inputs from atmospheric deposition, rivers, and tides. Measured concentrations are shown as diamonds. Projected changes in polychaetes (biota sediment accumulation factor =  $8.6 \times 10^3$ ) and euphausiids (bioaccumulation factor =  $1.1 \times 10^5$ ) are calculated by assuming steady state with dissolved MeHg concentrations.**

relatively insensitive to both the choice of evasion scheme and reduction rate coefficients. Model sensitivity analysis showed that a 60% increase in the water column Hg(II) reduction rate coefficient results in a less than 1% decline in MeHg concentrations in the year 2000 (SI Table S1). Similarly, the low (Liss and Merlivat) evasion estimates increase water column MeHg for the year 2000 by less than 1%.

For MeHg, tidal inflow represents the largest MeHg input into the water column due to large inflowing water volumes and a relatively high fraction of total Hg as MeHg (~24%) (Figure 2). Ambient MeHg concentrations that determine exposure of organisms will therefore be most affected by tidal inflow MeHg contributions. Primary producers take up  $0.29 \pm 0.21$  mol MeHg yr<sup>-1</sup> and  $5.5 \pm 1.7$  mol Hg yr<sup>-1</sup>, which is a small portion of water column fluxes on an annual basis (Figure 2). There is a net export of MeHg in tidal outflow of  $4.5 \pm 0.3$  mol yr<sup>-1</sup> or  $93 \pm 6$  pmol m<sup>-2</sup> d<sup>-1</sup> (normalized to water surface area). Since fluxes of MeHg from the sediments to the water column through diffusion and resuspension are smaller than inputs from settling of suspended solids, MeHg inputs from rivers likely account for the majority of MeHg exported in tidal outflow. Other studies have suggested that the impacts of fluvial Hg discharges are limited to a relatively

small geographical region surrounding the river mouth (44, 45). Burial fluxes for the study site shown in Figure 1 illustrate the high rates of solids deposition around the mouth of the St. Croix river (the major freshwater tributary) but do not preclude offshore transport of MeHg since a substantial portion of MeHg inputs (>90%) is in the dissolved phase (Figure 2).

**Relative Importance of Inputs from Rivers, Tides, and Atmospheric Deposition.** Direct atmospheric deposition accounted for a small fraction of cumulative external loading between 1850 and 2000 (Hg: 4%; MeHg: 0.2%) compared to rivers (Hg: 53%; MeHg: 26%) and inflowing tidal waters (Hg: 43%; MeHg: 75%) (Figure 3). However, atmospheric deposition indirectly accounts for the majority of external inputs, because the watershed is much larger than the water surface area. Differences between atmospheric and fluvial AEFs for each year between 1850 and 2000 provide a first estimate of local watershed sources and suggest that approximately 78% of the cumulative loading from rivers is from atmospheric deposition transported through the catchment. Constraining the time required for atmospheric Hg to travel through different types of watersheds is therefore important for predicting temporal responses of estuaries to changes in Hg deposition (14).

**Temporal Trends in Hg Concentrations.** Figure 3 shows that water column Hg and MeHg concentrations in Passamaquoddy Bay peaked in the 1960s due to elevated discharges from local industry (pulp and paper mills) along the St. Croix river (46) and have declined substantially since this time. Water column Hg concentrations respond rapidly to changes in loading, requiring approximately 60 days to reach 95% of steady state. These relatively fast changes occur because the annual magnitude of Hg and MeHg flows out of the water column exceeds the size of water column reservoirs resulting in rapid turnover (Figure 2).

The deep active sediment layer in Passamaquoddy Bay exacerbates slow changes in sediment and benthic food web concentrations. Approximately 200 years are required for sediment Hg and MeHg concentrations to reach 95% of steady state. More than 90% of the total mass of Hg and MeHg is contained in the sediment compartment (Figure 2). Fluxes of Hg and MeHg through resuspension, diffusion, burial, and particle settling are small compared to the reservoirs in benthic sediments (Figure 2), explaining why sediment concentrations respond much more slowly than the water column to changes in external loading. Concentrations of Hg and MeHg in benthic sediments reflect the integrated signal of inputs from the water column. Sensitivity analysis of model results (SI Figure S2) shows that the depth of the active sediment layer drives the temporal response of benthic sediments (e.g., steady state would be achieved in several decades if the active sediment layer depth was 1 cm rather than centuries for 15 cm (4)).

Dissolved pools of MeHg in water and sediments provide the best measure of available Hg at the base of pelagic and benthic food webs, respectively (27, 47). Model simulations suggest that MeHg exposures and concentrations in pelagic biota have declined by almost 40% since their peak in the 1960s because of declines in water column concentrations (Figure 3). Figure 3 shows that MeHg concentrations in the water column and pelagic organisms are expected to remain stable at present emissions levels. In contrast, sediments and benthic organisms will gradually increase at a rate of 0.13% per year, which leads to a 6% increase by 2050 relative to 2000 levels. Even with substantial Hg emissions reductions achieved by national and international agreements benthic food web Hg concentrations will likely exhibit a long temporal lag before declines are achieved, while rapid and proportional declines in MeHg concentrations in the pelagic food web can be expected. Other estuaries with substantial tidal

resuspension and perturbation of benthic sediments can be expected to respond over time scales similar to those of Passamaquoddy Bay, while those with a shallower active sediment layer will respond more rapidly (SI Figure S2). Results presented here also suggest that water column and pelagic food web MeHg concentrations in estuaries with significant fluvial and tidal influx (short water residence times) will respond rapidly to changes in anthropogenic Hg loading.

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### Note Added after ASAP Publication

Due to a production error, this paper published ASAP February 1, 2010 without the Acknowledgments section; the corrected version published ASAP February 8, 2010.

### Supporting Information Available

Additional information on model sensitivity analysis, field data used to parametrize model, differential equations, and derivation of model rate coefficients are available in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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