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A REGIONAL MASS BALANCE OF METHYLMERCURY IN SAN FRANCISCO BAY, CALIFORNIA, USA

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Abstract—The San Francisco Bay (California, USA) is a water body listed as impaired because of Hg contamination in sport fish for human consumption, as well as possible effects on resident wildlife. A legacy of Hg mining in local watersheds and Hg used in Au mining in the Sierra Nevada (USA) has contributed to contamination seen in the bay, with additional more recent and ongoing inputs from various sources. Methylmercury is the species of Hg most directly responsible for contamination in biota, so better understanding of its sources, loads, and processes was sought to identify the best means to reduce impacts. A regional scale model of San Francisco Bay was developed to characterize major methylmercury inputs and processes. The model was used to evaluate the potential impact of uncertainties in estimates for methylmercury loading pathways and environmental processes, identify major data gaps, and explore management prospects for reducing methylmercury contamination. External loading pathways considered in the mass balance include methylmercury loads entering via atmospheric deposition to the bay surface, and discharges from the Sacramento/San Joaquin Delta, local watersheds, municipal wastewater, and fringing wetlands. Internal processes considered include exchange between bed and suspended sediments and the water column, in situ production and demethylation, biological uptake, and losses via hydrologic transport to the ocean through the Golden Gate. In situ sediment methylation and demethylation were dominant sources and losses determining ambient steady-state concentrations in the model, with changes in external loads and export causing smaller changes. Better information on methylation and demethylation is thus most critical to improving understanding of methylmercury balances and management. Environ. Toxicol. Chem. 2011;30:88–96. © 2010 SETAC

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INTRODUCTION

Mercury is a pollutant of high concern in San Francisco Bay, California, USA. The San Francisco Bay is a water body listed as impaired because of Hg contamination in sport fish for human consumption, as well as possible effects on resident wildlife. As a result, a total maximum daily load development process has been undertaken to estimate the reductions in Hg loads needed to avoid impairment. Mercury has been introduced to the bay environment through historic Au and Hg mining in California, as well as through ongoing inputs from other global and local anthropogenic activities. The Regional Monitoring Program for Water Quality (RMP) in the San Francisco estuary has monitored mercury in the bay since its inception in 1993.

Methylmercury is the form of Hg that bioaccumulates and biomagnifies in the food web. The RMP monitoring of methylmercury, starting in 1999 (http://www.sfei.org/rmp/wqt), typically has found a very small proportion (average $<1\%$) of total Hg in the San Francisco Bay waters and sediments. Therefore, any strategies for managing Hg impacts will likely especially benefit from improved understanding of methylmercury processes.

Concentrations of total Hg in the bay are expected to slowly decline as new releases of Hg decrease. A previous regional-scale mass budget for total Hg [1] estimated gross export (i.e., not counting inputs) from the bay of approximately 500 kg/year, of a total inventory of approximately 60,000 kg, mostly in bay sediments, a maximum change of less than 1% per year. Therefore, even without any new inputs, decades to centuries are needed before current ambient concentrations (2002–2006 RMP average approximately 0.23 μg/kg) return to pre-anthropogenic levels of approximately 0.08 μg/kg [2]. However, if specific fractions or sources of Hg entering or already in the bay contribute disproportionately to methylmercury accumulation in biota, then reducing Hg impacts more rapidly may be possible.

Objectives of the mass balance exercise were to collate information on methylmercury distributions and processes in the San Francisco estuary; estimate methylmercury loads from various pathways including atmospheric deposition, urban storm water, delta outflow, wetlands, and municipal wastewater; and develop an annually averaged mass balance for San Francisco Bay using empirical data on local processes wherever possible. The current work is an important step towards developing a better understanding of the factors controlling methylmercury concentrations on a baywide scale.

MATERIALS AND METHODS

Location and physiography

San Francisco Bay, California, USA (see map, Fig. 1), receives water, sediments, and pollutants from local watersheds (area ~8,200 km^2), discharging 1.05 km^3 water annually [3], as well as from the Sacramento/San Joaquin River watershed (area, 154,000 km^2), discharging 24.9 km^3 water [4]. The volume of the San Francisco Bay is approximately 5.5 km^3, with a surface area of 1,100 km^2 at mean sea level. In addition, a discontinuous fringing marsh of 950 km^2 (greatly reduced from its historical extent) occupies the area between the uplands and the open bay. Tides in the bay are semidiurnal, with a range at the Golden Gate Bridge (mean lower low water to mean higher high water at the National Oceanic and Atmospheric Administration station) of 1.78 m, varying in magnitude in various parts of the bay.

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Fig. 1. Map of the San Francisco Bay Region, California, USA.

Environmental monitoring

The RMP for Water Quality in the San Francisco estuary has conducted annual monitoring of open water areas in San Francisco Bay since 1993. Other projects and programs have monitored other locations and ecosystem components, information useful in building our understanding of methylmercury processes in San Francisco Bay, described in sections addressing those loads and processes.

Ambient water and sediment methylmercury samples were collected primarily at sites selected by a generalized random tessellation stratified design [5] with some fixed locations since 2002. Water was collected via peristaltic pump from approximately 1-m depth as either total (unfiltered) or dissolved (filtered, 0.45 μm nominal pore size) samples and frozen in the field. Sediment samples were collected using a modified Van Veen grab sampler, with surface (top 5 cm) sediments composited in the field and immediately frozen. Monitoring data up to the previous year are available online (http://www.sfei.org/rmp/wqt); ambient concentrations for 2002 to 2006 were used for the current exercise.

Regional mass balance model

A regional model of water and sediment processes was employed to integrate existing monitoring data and to enhance our understanding of methylmercury fate in San Francisco Bay. The model was initially developed by Davis [6] to predict the long-term fate of polychlorinated biphenyls (PCBs) in San Francisco Bay and has been used for developing mass balances for polycyclic aromatic hydrocarbons, organochlorine pesticides, and polybrominated diphenyl ethers [7–9]. The current model of San Francisco Bay treats the bay as two well-mixed compartments representing the water column and surface sediments for the region. Conceptually, the model ignores differences in the geographic subregions of the bay, a simplification that limits its ability to capture spatial variations on a subregional scale, but allows a first-order evaluation of the system given limited spatial resolution and availability of data for most processes regionally.

In situ production is a major component missing from the earlier mass balance models, because it is negligible for the previously modeled organic contaminants but is critical for methylmercury, given its facile transformation to and from

inorganic forms. A previous mass balance of Hg in the San Francisco Bay treated these transformations as a pseudo-equilibrium characteristic, using a fixed percentage of total Hg [1] to model a pseudo–steady-state methylmercury concentration, but methylmercury is not always well correlated to total Hg in the bay and delta [10,11]. The current model instead treats methylmercury production as an internal input in a methylating zone of sediment. With total Hg estimated to be changing by less than 1% annually [1], even if methylmercury production depended on total Hg, it would be approximately constant for short modeling periods.

External loads

External loads, not dependent on concentrations in the bay, include inputs entering from the air via direct deposition or from the land via rivers, tributaries, channels, and discharge pipes. External loads are described later and summarized in Table 1. Although flows and loads are not uniform over the course of the year or evenly distributed in space, all external loads were combined and applied uniformly to allow a regional annual-scale evaluation.

Sacramento–San Joaquin River Delta. Net methylmercury exported from the delta to the San Francisco Bay was estimated by the Central Valley Regional Water Quality Control Board (RWQCB) in a methylmercury total maximum daily load report for the delta ([12]; http://www.swrcb.ca.gov/rwqcb5/water_issues/tmdl/central_valley_projects/delta_hg/staff_report_feb08/tmdl_full_rpt.pdf) and a subsequent California Bay–Delta Authority–funded study. Net daily delta outflow water volumes determined by the DAYFLOW model (http://www.iep.ca.gov/dayflow/index.html) were used with water column concentrations to derive loads, resulting in an estimated average methylmercury export flux of 9.8 g/d. Adjustments for dispersive flux can reduce advective flux by approximately 15% for periods of delta outflow over 500 m^3/s [4]. Temporal variability in annual flux is somewhat larger (relative standard deviation ~30%). Impacts of uncertainties for external loads combined are later assessed together through sensitivity analysis.

Local watersheds. A small number of local tributaries with a mix of land uses have been monitored by the RMP for total Hg and methylmercury. The Guadalupe River watershed below reservoirs is 13% industrial, 13% commercial, and 58% residential land use. The Hayward Zone 4 Line A storm drain is almost 100% urban land use, similar to many small urban drainages on the bay margin. Methylmercury concentrations in Guadalupe River and Zone 4 Line A have been reported previously ([13]; http://www.sfei.org/sites/default/files/424_Guadalupe_2005Report_Final_0.pdf; [14]; http://www.sfei.org/sites/default/files/563_Z4LA_Year1final4_web.pdf). Few to no measurements have been taken for other local watersheds, so watershed loads for the region are estimated by extrapolation from these watersheds.

The methylmercury found in storm water at these sites ranged 0.5 to 1.6% of total mercury. In RMP ambient bay monitoring, methylmercury averaged less than 1% of total mercury in the water column, and an average 0.7% was found in the delta to Central Bay for another study [11]. Thus, methylmercury loads for local watersheds were estimated as 1% of total Hg loads.

Watershed total Hg loads have previously been estimated at a regional scale for the San Francisco RWQCB ([15]; http://www.scvurppp-w2k.com/pdfs/0102/Joint_Stormwater_Agency_Project_to_Study_Urban_Sources_of_Mercury-PCBs_and_Organochlorine_Pesticides_(Year%202).pdf; [16]) and for local storm water management agencies (Kinnetic Laboratories, 2002, Santa Cruz, CA, USA). Estimates from these previous studies ranged from 123 to 185 kg/year. Methylmercury loads based on 1% of those total mercury loads are thus 1.2 to 1.9 kg/year. A simple rainfall/runoff model [17] was also used to estimate total mercury load for different land uses. Using that total mercury load with average methylmercury percentages resulted in 3.3 kg/year loads. A load of 2.3 kg/year (6.2 g/d), between these estimates was used as the baseline estimate of local watershed loads for the mass balance.

Municipal wastewater. The San Francisco Bay RWQCB requested monthly information on methylmercury discharges from the 16 largest municipal wastewater plants (95% of the regional effluent discharge) over one year (2007–2008). Dischargers collected monthly effluent grab samples, reporting discrete and annually averaged concentrations. Average concentrations (0.37 ng/L) combined with annual discharge rates for each of the plants yielded methylmercury loads of 0.29 kg/year (0.79 g/day). Concentrations at treatment plants were highly variable (mean relative standard deviation ~65%), but loads were small relative to other pathways.

Wetland discharge. The current extent of tidal marsh area in the San Francisco Bay region is approximately 40,000 acres, greatly reduced from 190,000 acres historically ([18]; http://www.sfei.org). Wetlands vary widely in characteristics, but to simplify the current mass balance exercise, we treated all these areas as similar. Assuming wetland surfaces have constant slopes, and an average difference of 0.7 m between mean high water and mean tide level from local National Oceanic and Atmospheric Administration benchmarks, a tidal prism with an average 0.35 m water depth covers the marsh surface on high tides (twice daily), equivalent to 200-m depth of water transported on and off wetlands annually. Wetland evapotranspiration is only 1 m/year [19], and annual rainfall is less than 0.5 m/year (http://www.wrcc.dri.edu/summary/climsmcca.html), so water movement via tides dominates other hydrologic transport pathways in most tidal wetland areas.

Petaluma Marsh water column concentrations were monitored over 24 h to obtain first-order estimates of methylmercury loads ([20]; http://nrm.dfg.ca.gov/FileHandler.ashx?DocumentID = 4001). Dissolved methylmercury concentrations on ebb tide averaged 0.136 ng/L, higher than on flood tide (0.083 ng/L), exporting 6.0 g/d if applied regionwide to 40,000 acres of wetlands. Particulate concentrations averaged higher during flood tide (0.098 ng/L) compared with ebb tide (0.092 ng/L), 0.7 g/d of methylmercury transported from the bay to wetlands. Thus, net methylmercury loads from wetlands to the bay were 5.3 g/d (1.9 kg/year). Estimates of leachable methylmercury in a study of the Hamilton Army Air Field wetland ([21]; http://el.erdc.usace.army.mil/elpubs/pdf/trel05-

Table 1. Estimated external loads of methylmercury to bay waters

Source	g/d	Data sources
Sacramento–San Joaquin Delta	9.8	[12]
Local watersheds	6.2	[13–17]
Wetland discharge	5.3	[20,21]
Atmospheric deposition	0.37	[22–24]
Wastewater	0.79	SFBRWQCB[a]
Total	22	

[a] SFBRWQCB = San Francisco Bay Regional Water Quality Control Board, Oakland, CA, USA.

15.pdf) suggested a similar magnitude of methylmercury exported from wetlands, 4.0 g/d.

Atmospheric deposition. Like most mercury deposition network sites, a station in Lower South Bay measured total mercury in precipitation for six years, but not methylmercury. The mean of methylmercury concentrations in studies from Indiana ([22]; http://pubs.usgs.gov/sir/2007/5063/pdf/sir2007-5063_web.pdf), Experimental Lakes Area of Northwestern Ontario [23], and North Olympic Peninsula in western Washington State, USA [24], was 0.087 ng/L. Applying this mean to San Francisco Bay area mean annual rainfall (0.4–0.5 m/year) yielded direct wet deposition of 0.1 g/d (0.37 kg/year) methylmercury to the bay, a small portion of external loads.

Methylmercury in dry deposition is seldom measured. A recent study estimated dry deposition of methylmercury in the Experimental Lakes Area, collecting throughfall and litterfall, and subtracting open field deposition [25]. The net rates were similar to rates of wet deposition, so dry deposition would likely be a similarly minor load to the bay.

Uptake to biota

Methylmercury biouptake was modeled as a removal from the water compartment to evaluate its impact on the overall mass budget. Because the primary interest was a mass balance of methylmercury on an annual time scale, small fish were reasonable candidates for estimating annual methylmercury transfer to biota. The California Department of Fish and Game conducts monthly trawls in the bay and delta. The size/age relationship for various species in the bay have been studied, so the Hg body burden in the young-of-year cohort was used to estimate annual-scale net uptake.

The mean pelagic fish biomass in trawls for areas in northern San Francisco Bay in the intermediate and high-salinity areas (SB Slater, California Department of Fish and Game, Stockton, California, Oakland, CA, USA) is approximately 0.17 g/m^3 in young-of-year fish. The average Hg wet weight concentration in small fish measured in the San Francisco Bay by the RMP was 0.049 μg/g, so 0.046 kg/year (0.13 g/d) methylmercury is transferred to small fish biomass. Mid-water trawls likely underrepresented benthic residing fish, whereas pelagic fish mass is likely overestimated by applying their density to the entire bay water volume. Bottom trawl data supplied by the California Department of Fish and Game suggest these errors roughly offset, because demersal fish density averages 0.21 g/m^3. Biouptake removal of methylmercury in fish was thus estimated to be very small (~0.5%) compared with external loads to the bay.

Model internal process estimates

Bay internal processes (other than methylmercury production) were modeled as functions of ambient concentrations in bay waters and sediments. Demethylation was modeled as a first-order reaction proportional to methylmercury concentration in the modeled compartment. For transport and partitioning, relative concentrations between water and sediment and adjoining compartments such as the nearshore ocean and the atmosphere were used. Many of the key model parameters are listed in Table 2 and discussed in following sections.

The overall mass balance tracked methylmercury inventories in the water and sediment (shown in Eqns. 1 and 2),

$$M_W(t) = M_W(t-1) + (L(t) - \text{bio}(t) + M_S(t-1) \cdot K_{SW} - M_W(t-1) \cdot (K_V + K_O + K_{WR} + K_{WS})) \cdot dt \quad (1)$$

Table 2. Key parameters used in model base case

Parameter	Magnitude	Data source
Bay freshwater inflow (m^3/s)	820	IEP
Tidal/fresh flow ratio	3.75	[30]
Demethylation rate in water (1/day)	0.1	[20]
Demethylation rate in sediment (1/day)	0.083	[26]
Sediment methylmercury production (ng/g/day)	0.11	[26]
Bay average water MeHg (pg/L)	95.7	RMP
Bay average Sediment MeHg (μg/kg)	0.558	RMP
Golden Gate Water MeHg (pg/L)	8	[31]
Water column partitioning K_d (L/kg)	12,500	RMP
Porewater partitioning K_d (L/kg)	45,700	[11]
Sediment burial rate (cm/y)	0.83	[34]
Water-side evaporation coefficient (m/day)	1.5	[38]
Air-side evaporation coefficient (m/day)	0.26	[38]
Water-sed diffusion coefficient (m/day)	0.001	[11]

IEP = Interagency Ecological Program (http://www.iep.ca.gov/dayflow/index.html); RMP = Regional Monitoring Program (http://www.sfei.org/rmp/wqt) (2002–2006 data); MeHg = methylmercury.

$$M_S(t) = M_S(t-1) + \text{mpr}(t) + (M_W(t-1) \cdot K_{WS} - M_S(t-1) \cdot (K_{SW} + K_B + F_{DM} \cdot K_{SR})) \cdot dt \quad (2)$$

where bio = baywide biouptake per time step; dt = size of each time step; F_{DM} = fraction of sediment layer demethylating; K_O = rate of outflow (riverine + tidal); K_{SR} = rate of demethylation in sediment; K_{SW} = rate of sediment to water flux; K_V = rate of volatilization; K_{WR} = rate of demethylation in water; K_{WS} = rate of water to sediment flux; L = water mass loads introduced each time step; mpr = sediment methylmercury production input per time step; M_S = mass in the sediment at a given time (t); M_W = mass in the water column at a given time (t); t = a given time step ($t-1$ = previous step).

In the current application of the model, biouptake (bio), methylmercury production (mpr), and external loads (L) were treated as constant input or removal rates (g/d) from sediment or water inventories, but these could be modified to introduce time dependence (e.g., seasonal or interannual trends) if desired.

Sediment methylmercury production. Methylmercury production (mpr) was treated as a zero-order rate of internal input to the anoxic portion of the active sediment layer. Factors affecting methylation such as total Hg concentration were approximated to be at steady state, because total mercury concentrations change slowly in the bay [1]. Methylmercury production rates in anoxic laboratory incubations of San Pablo Bay sediment ranged between less than 0.03 and 1.0 ng/g/d [26]. Rates are likely site specific, but for regional scale application we used a geometric mean of 0.11 ng/g/d, examining higher and lower rates via sensitivity analysis.

Demethylation in water and sediment. Demethylation in the sediment and the water column was modeled as a first-order decay of methylmercury. In bay sediment, oxidative demethylation was posited to be a primary mode of demethylation based on the byproducts of ^{14}C-methylmercury demethylation experiments [26]. Rate constants in sediment ranged from 0.019 to 0.25/d (i.e., 1.9–25% degraded per d) in that study. We applied the geometric mean (0.083/d) as the rate constant for sediments throughout the bay. Most rates in that study were for surface (0–4 cm depth) samples, but demethylation rates in sections below 8 cm were nearly 10-fold lower in the one site where they were measured. We estimated that sediment demethylation occurred

in the top 7 cm, with potential impacts of assumptions explored in sensitivity analysis.

Methylmercury demethylation in the water column also may occur through biotic oxidative pathways such as in sediments; however, photodemethylation is the focus of most demethylation studies in surface waters. Demethylation rate constants of 0.11 to 0.22/d were measured in delta surface waters ([27]; http://www.abag.ca.gov/abag/events/estuary/pdfs/SOE_2005_abstracts_poster.pdf). Similar rates were seen in photo-irradiated water samples from Petaluma Marsh, with half-lives of 5 to 20 d for filtered waters, and longer half-lives (11–20 d) for unfiltered waters.

Shallow waters typically experience more irradiation and thus higher rates of photodemethylation [28]. Shallow bay surface waters are likely to have demethylation half-lives similar to those at Petaluma Marsh, averaging 7 d (rate of 0.1/d). Light penetration in northern San Francisco Bay as measured by Secchi disk ranged 0.3 to 1.6 m [29] and was 1.1 m or less in all but two measurements. Thus, assuming that demethylation occurs only over the top 1 m of the water column, the water column average demethylation rate was modeled as being fivefold lower (0.02/d).

Tidal flushing and outflow. Bay-specific model parameters were identical to those used in predicting the long-term fate of PCBs in the bay [6], with the addition of a tidal flushing ratio ($\alpha = 3.75$), a ratio of tidal exchange flow to net freshwater flow in the system. Tidal flushing was not included in the original mass balance model for PCBs but was added in response to review comments [30] and used in more recent applications of the model, such as the polybrominated diphenyl ethers mass balance [9]. Tidal flow rate determined the volume of bay water replaced with water from outside the Golden Gate (the seaward boundary) in each model time step.

For the base case assumption running the model, waters at the Golden Gate were assumed to have a concentration of 8 pg/L, the lowest detected concentration at the Golden Gate in another study [31]. The load carried in by tides was added to external loads in the model. The model was also run using different seaward methylmercury concentrations to assess the sensitivity to this parameter.

Sediment–water partitioning. Kinetics of methylmercury adsorption and desorption are relatively fast, reaching equilibrium on the order of hours [32], compared with the model daily time step, hydrologic turnover times on the order of a week or greater, and the annual or longer time scale scenarios being modeled. Thus, although equilibrium assumptions may not be strictly correct, they were reasonable approximations given rates of other model processes. Using the baywide mean particulate (49.6 pg/L) and dissolved (44.5 pg/L) methylmercury concentrations in water, and the baywide mean concentration of suspended particles in water (0.085 g/L), the partition coefficient was estimated to be 13,100 L/kg ($\log K_d = 4.11$), consistent with other estimates in the bay [31] and Guadalupe River [13]. If instead the average bed sediment methylmercury concentration (0.558 μg/kg) was used, the resultant K_d between sediment and the water column was 12,500 ($\log K_d = 4.09$), virtually the same. A value of 13,100 L/kg was used as the water column K_d for the base case in the model.

The K_d in sediment pore water may potentially differ from that in the overlying water column because of differences in factors affecting solubility, such as organic carbon concentrations and sulfide speciation. Work in northern San Francisco Bay [11] examined sediment and pore-water concentrations of methylmercury and derived a K_d of 45,700 ($\log K_d = 4.7 \pm 0.4$ (average ± SD), a similar order-of-magnitude as for the water column. A pore water K_d of 45,700 ($\log K_d = 4.7$) was used for the base case model scenario. Effects of higher and lower water column and pore water K_d were evaluated during sensitivity analysis.

Sediment–water column particle exchange. Although the exchange of particles between the water column and the bed sediment of the bay is not spatially uniform, this regional-scale mass balance model did not attempt to capture such spatial heterogeneity. Although model assumptions of uniform mixing and equilibrium may not reflect any specific location at a particular time, on a regional annually averaged basis, the system might be reasonably modeled as a steady state as long as the kinetics of the modeled processes are much shorter than the modeled period. Similarities in suspended sediment and bed surface sediment partitioning constants suggest that a model of continuous exchange between these two compartments is reasonable.

One major simplification was the treatment of suspended sediment concentration as approximately constant. Although a long-term trend has been observed toward reduced sediment loads coming from the delta in recent decades [3,33], given the high turnover rate of other modeled processes compared with the slow long-term change in suspended sediment concentration, water–sediment particle exchange was simplified and modeled as a steady state (i.e., all inputs roughly equal all losses). Another simplification was the treatment of the mixed sediment layer as a uniformly mixed compartment. For conservative pollutants, a uniform mixing assumption accelerates system response to changes in loads, which would be modeled as occurring instantly equally throughout the bay. However, methylmercury is not a conservative pollutant; given turnover times of days to weeks for some processes such as demethylation, the impacts of a uniform mixing assumption are lessened. Also, despite simplifying assumptions shortening the system response time to changes, the resulting steady-state mass achieved would be essentially the same in the longer term.

Sediment–water column pore water exchange. Pore water exchange flux rates may be empirically determined via flux box measurements or through mesocosm experiments, although each approach presents artifacts differing from in situ conditions. Nonetheless, in situ flux box experiments likely represent the best available measurement of actual fluxes in the native ecosystem and provide at least lower bound estimates of net flux because of possible exclusion of some abiotic forces such as resuspension by waves and stronger currents. Flux measurements were made in benthic chamber deployments in Suisun Bay and the delta [11], with median flux rate measured of 13 ng/m^2/d (10–90th percentile range 2–55 ng/m^2/d). Applying the flux rate to the bay surface results in a net flux of 14 g/d. Empirical flux rates, which include biologically mediated exchange, were converted to a transfer velocity (V_d) (Eqn. 3),

$$Flux(\mathrm{ng/m^2/d}) = V_d(\mathrm{m/d}) \times [C_{sed} - C_{water}](\mathrm{ng/m^3}) \quad (3)$$

where C_{sed} and C_{water} are dissolved concentrations in sediment porewater and overlying water, respectively. The resultant estimated V_d was 0.001 m/d, which was used to parameterize the model.

Sediment burial or erosion. Net burial or erosion of bed sediments could also result in methylmercury loads to or losses from the mixed sediment layer. Methylmercury concentrations at depth were lower than those in surface samples [26]. Thus, unlike persistent organic pollutants such as PCBs and inorganic

metals such as total Hg or Cu, no substantial high concentration legacy deposits of methylmercury that can be exposed through erosion were found.

Net sedimentation and burial is modeled as loss from a fixed-depth active sediment layer, replaced by suspended sediment from water column. The net sedimentation rate used was 0.83 cm/year for a core taken from Richardson Bay in 1992 [34], which would bury less than 10% of the methylmercury inventory in the mixed sediment layer of the model each year. Maps of bathymetric change by the U.S. Geological Survey suggest low burial rates for the bay, with most areas showing little change or slight erosion (typically <1 cm/year) in recent history.

Atmospheric volatilization. Methylmercury can volatilize as the charge neutral species MeHgCl. Air–water partitioning of MeHgCl was measured for 0.7 M NaCl [35], with a dimensionless Henry's law constant of 2×10^{-5} at 25 °C, but this constant was likely biased high, because the bay water surface temperature is less than 25 °C for most of the year. Binding constants with humic acids in freshwater [36] suggest that half or more of dissolved methylmercury may be complexed to dissolved organic carbon, so this rate of volatilization estimated from literature constants [38] is at least a factor of 2 too high. Even so, volatilization was still a minor part (<0.03%) of the overall budget.

RESULTS AND DISCUSSION

Initial condition evaluation

Unlike models for PCBs or polybrominated diphenyl ethers [6,9], little or no information exists regarding the history of likely changes in global or local emissions and loading rates for methylmercury, nor of changes in other processes. Sensitivity of the model to historical conditions was assessed by adjusting the initial ambient concentrations. Current loading and process rates in the model are linked to historical rates only through their dependence on ambient concentrations. To limit the possibilities, given no knowledge of the prior condition, we assumed that initial ambient methylmercury concentrations in water and sediment were either zero or 10-fold higher than the current condition.

The zero initial condition represented a minimum lower bound, assuming that before any anthropogenic mercury releases, ambient methylmercury inventories were negligible. The model was run for two years with continuous external loading at current rates (8 kg/year) and internal processes using contemporary rates and coefficients until a steady-state was achieved. The system reached steady-state quickly, stabilizing within 100 d (Figs. 2 and 3). The opposite case, with the initial condition set at 10 times the current ambient inventory, quickly reached the same steady-state within approximately 100 d. Thus, prior condition had negligible influence on the methylmercury steady-state inventory for the modeled bay system.

Base case

The model was then initialized with the best estimate of the current methylmercury mass in the bay and the same annual external loads totaling 8 kg/year. Not surprisingly, given the lack of dependence on initial condition, the base case scenario quickly arrived at the same steady-state final inventory (Figs. 2 and 3). The magnitudes of various methylmercury loading and process rates (kg/d) are listed along with the base case steady-state inventory (kg) in Table 3 and are shown in Figure 4 (in g).

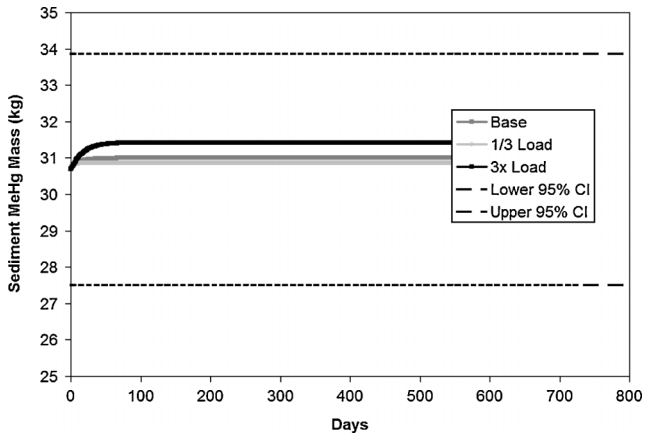

Fig. 2. Modeled methylmercury mass in San Francisco Bay (CA, USA) sediment for loading rates one-third, one, and three times the base case estimate. Dashed lines indicate ±95% confidence intervals (CI) of the current mean inventory.

For the sediment, methylation and demethylation produce and remove, respectively, nearly 6% of the bay sediment methylmercury inventory each day. Fluxes to (0.045 kg/d, mostly sediment resuspension) and from (0.038 kg/d, mostly particle settling) the water column were next, but only 0.15 and 0.12% of sediment inventory. Methylmercury removed by sediment accretion leading to net burial was next largest, at only 0.007 kg/d (0.02%). Given slow net burial, masses of sediment resuspended and settling out of the water column each day were roughly equal in the base case, so the differences in downward versus upward flux were primarily attributable to differences in methylmercury concentrations of suspended versus bed sediments.

For methylmercury in the water column, the largest inputs were flux from the sediment and (combined) external loads, daily 12 and 6% of inventory in the base case. At steady-state, these inputs were offset by water to sediment flux, outflow from the bay, and demethylation in the water column (10, 6, and 2% of inventory, respectively). The other removal pathways included biouptake into fish and volatilization of methylmercury, were 0.03% or less of inventory daily.

Although the bay is not truly a steady-state system, gross deviances in the model steady-state from the initial condition (using bay mean concentrations) would suggest major errors or

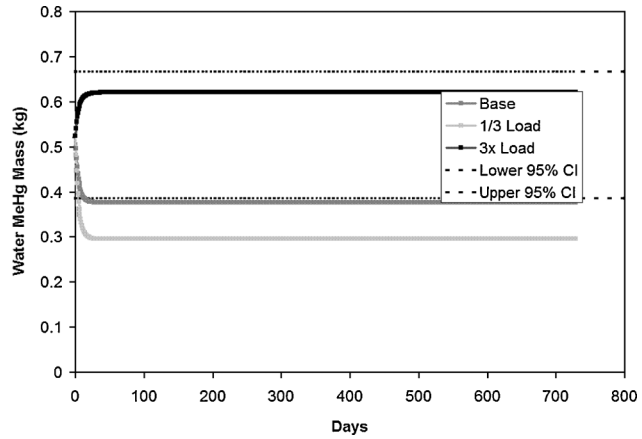

Fig. 3. Modeled methylmercury mass in San Francisco Bay (CA, USA) water for loading rates one-third, one, and three times the base case estimate. Dashed lines indicate ±95% confidence intervals (CI) of the current mean inventory.

Table 3. Magnitudes of methylmercury processes and inventories, base case. Inputs (positive numbers) and losses (negative numbers) in water and sediments compared to the inventories in those compartments in the base case[a]

Model component	Magnitude (kg/d)	Daily turnover (%)
Inventory in water = 0.38 kg		
Sediment to water flux	0.045	12%
Water to sediment flux	−0.038	−10%
Outflow via Golden Gate	−0.023	−6%
External load	0.022	6%
Demethylation in water	−0.0075	−2%
Inflow via Golden Gate	0.0021	1%
Biological uptake into fish	−0.0001	−0.03%
Volatilization	−< 0.0001	−< 0.03%
Inventory in sediment = 31 kg		
Methylation in sediment (kg/day)	1.82	6%
Degradation in sediment	−1.8	−6%
Sediment to water flux	−0.045	−0.15%
Water to sediment flux	0.038	0.12%
Burial in sediment	−0.0074	−0.02%

[a] Daily turnover expresses the inputs and losses as percentages of the base case inventories.

uncertainties in model parameters and assumptions. For the sediment, the model steady-state methylmercury inventory (30.8 kg) was similar to the initial ambient condition inventory from averaged RMP monitoring data (30.7 kg), suggesting small errors that introduced too much loading or production in sediment, or yielded too little removal or demethylation.

However, in contrast, the water column inventory decreased approximately 30% in the base case, from an initial mass of 0.53 kg,to a final steady-state of only 0.37 kg. Although a 30% difference may not be unreasonable for a greatly simplified model of a complex system, the net direction and moderate magnitude of the difference indicates factors that might be improved. Candidate factors were examined by evaluating sensitivity of the model to various parameters.

Sensitivity assessment

Model runs were performed using various model parameters threefold higher and lower (approximately an order of magnitude range). The steady-state inventories of these scenarios were compiled and expressed as the response of the model relative to the base case, compared with the relative difference of each input variable to its base case (i.e., a local sensitivity), namely (Eqn. 4):

$$\text{Response ratio} = (\Delta\text{Output}/\text{Output}_{\text{BASE}})/(\Delta\text{Input}/\text{Input}_{\text{BASE}}) \quad (4)$$

where Δ Output/Output$_{\text{BASE}}$, the change in the output (steady state mass of methylmercury), divided by the output in the base case, is compared with Δ Input/Input$_{\text{BASE}}$, the change in the input parameter divided by its base case value.

The input parameter factors in Table 4 are listed in order of their effect on the sediment response. A positive ratio (>0%) indicates that an increase in the input parameter yields an increase in the steady-state inventory. A negative ratio indicates an inverse relationship. The factors that most influenced the steady-state sediment inventory were the sediment methylation and demethylation rates. The final steady-state concentration in sediment was related to the changes in these parameters, nearly 1 to 1 proportionally. This result was expected, because in situ sediment production and demethylation far outpaced all other inventory gains or losses, similar to the case in a Chesapeake Bay mass budget [37].

The sediment inventory dwarfed the inventory in water, so given water-to-sediment and sediment-to-water fluxes that were larger than external loads, not surprisingly, sediment factors also had the greatest influence on water concentrations. Conversely, factors that had a moderately large influence on water column inventory (e.g., water demethylation rate, partitioning coefficient, particle settling rate) had only a small to minimal effect on sediment methylmercury inventory.

Increase in the steady-state suspended sediment concentration increased the water column methylmercury inventory, as the partitioning coefficient indicates higher concentrations per unit mass in the solid phase compared with the dissolved phase. Increases in external loads, modeled initially as input into the water column, also would be expected to increase primarily the water column concentration; water column processes such as demethylation and tidal flushing/outflow would remove much of the daily load before it could impact the sediment. Increases

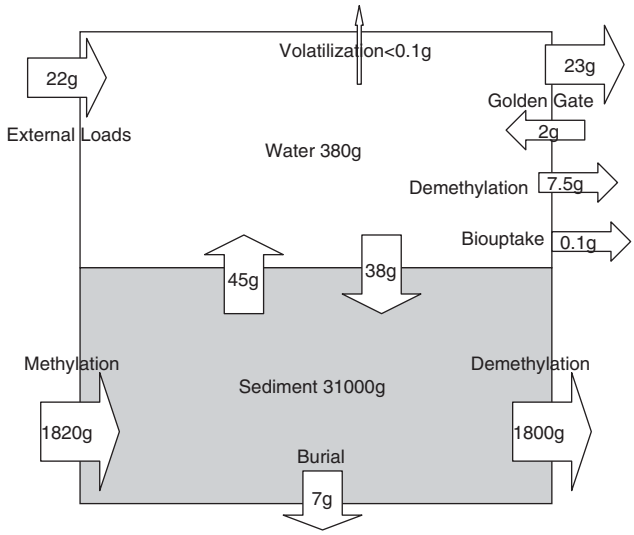

Fig. 4. Model conceptual diagram, with water and sediment methylmercury inventories for base case (in g) and fluxes as arrows (g shown are daily flows).

Table 4. Model Sensitivity to input parameters[a]

Input parameter	Sediment	Water
Sediment methylmercury production rate	99.3%	66.0%
Sediment demethylation rate	−96.5%	−64.1%
Suspended sediment concentration	−0.80%	49.3%
External load	0.60%	31.1%
Long term net outflow	−0.50%	−23.5%
Tidal flushing ratio	−0.40%	−18.6%
Water column K_d	0.40%	−21.8%
Particle settling rate	−0.30%	16.0%
Sediment burial rate	−0.20%	−11.0%
Water demethylation rate	−0.20%	−9.70%
Golden Gate methylmercury concentration	0.10%	3.20%
Sediment/water transfer velocity	<0.01%	<0.01%
Porewater K_d	<0.01%	<0.01%
Water temperature	<0.01%	<0.01%
Initial bay methylmercury concentration	<0.01%	<0.01%
Henry'slaw constant	<0.01%	<0.01%
Air/water mass transfer coefficient	<0.01%	<0.01%

[a] Sensitivity expressed as response ratio of the change in the model output (steady state inventory in sediment or water) relative to its base case value, divided by the change in an input relative to its base case value. A ratio of 100% indicates a direct one-to-one proportional response.

in net outflow and tidal flushing ratio decreased the turnover time of the bay water volume, exporting a greater proportion of water column methylmercury.

Some model responses were counterintuitive, but made sense considering the constraints of the model. For example, one would expect that increasing the particle settling rate would tend to pull methylmercury out of the water column and thus decrease the water inventory, but the fixed active layer depth of the model means that the increased particle settling must be offset by increased resuspension for a given burial rate of sediment (Eqn. 5),

$$\text{Settling} - \text{resuspension} = \text{net accretion} = \text{burial} \quad (5)$$

This linkage was also seen in the effect of the burial rate; as the burial rate was increased without changing settling rate, the fixed depth of the surface sediment layer meant that resuspension flux had to decrease to offset sediment loss via burial.

Model refinement

Although model parameters could be tuned so the steady-state output better matched the average ambient state of the bay, especially the water column inventory, these adjustments would generally be non-unique solutions. For example, given the nearly direct relationship of both methylation and demethylation rate on sediment methylmercury inventory, any adjustment of the sediment methylation rate upward or downward, so long as it were matched by an opposite proportional adjustment of the sediment demethylation rate, would result in a virtually identical steady-state. Therefore, no attempt was made to identify a particular set of inputs that would be a best fit of the model.

In the mass balance model presented here, processes occurring at small spatial and temporal scales that may be relevant to methylmercury fate and biological uptake were simplified to a baywide average basis. Although on a baywide scale external loads have little impact on the sediment methylmercury inventory, at smaller spatial and temporal scales (e.g., a tributary mouth during the rainy season), external loads would have a larger impact. In large part insufficient spatial and temporal resolution of data needed to populate finer-scale models of the region is available, particularly for biologically mediated processes such as methylation and demethylation. The strengths of the current model were in integrating an inventory of external loads and rates and magnitudes of a suite of relevant process parameters. If monitoring efforts indicate potential localized problems that need to be managed, the increased data collection demands of modeling to understand the ecosystem response at those scales may be warranted, to allow tailoring of management actions to specific problems areas cost-effectively.

CONCLUSIONS

The mass balance model of methylmercury presented here has improved our regional understanding of the sources and fate of methylmercury. Modeling of the current base case and scenarios with threefold lower and higher external loads or process rates indicated the importance of in situ production and loss rates to methylmercury fate in the bay. The current model was useful as a framework for integrating an inventory of mass loads and rates for a suite of environmental methylmercury processes, for the most part derived from local and regional data. Although it considers methylmercury only on a baywide average basis, the current study represents the current best integration of the state of knowledge for the region of this ephemeral pollutant species of major concern to ecosystem managers. This initial effort can serve as a template for modeling smaller spatial and temporal scales, provided that sufficiently detailed local information becomes available. The sensitivity and rapid response of the model to key parameters such as in situ methylation and demethylation rates suggest that approaches to control these key methylmercury processes may allow regional managers and stakeholders to reduce mercury impacts more rapidly.

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