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San Francisco Bay Methylmercury Mass Budget

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Title:

A Simple Mass Budget of Methylmercury in San Francisco Bay, California

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Abstract

San Francisco Bay is a water body listed as impaired due to mercury contamination in sport fish for human consumption, as well as possible effects on resident wildlife. A legacy of mercury mining in local watersheds and mercury used in gold mining in the Sierra Nevada have contributed to contamination seen in the Bay, with additional more recent and ongoing inputs from various sources. Even without continued mercury inputs, it would likely be decades or centuries before ambient mercury concentrations return to pre-industrial levels. Methylmercury is the species of mercury 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 simple one box model of San Francisco Bay was applied to evaluate uncertainties in estimates for methylmercury loading pathways and environmental processes, to identify major data gaps, and test various management scenarios for reducing methylmercury contamination. External loading pathways considered in the mass budget include methylmercury loads entering via atmospheric deposition to the Bay surface, and discharges from the Sacramento/San Joaquin Delta, local watersheds, industrial and municipal wastewater, and fringing wetlands. Internal processes considered include exchange between bed and suspended sediments and the water column, *in-situ* production and degradation, and losses via hydrologic transport to the Pacific Ocean. *In situ* sediment methylation and demethylation rates were dominant sources and losses determining mass budget steady state concentrations, with changes in external loads and export causing smaller changes. Better information on methylation and demethylation rates are thus most critical to improving methylmercury budgets and management.

1. Introduction

Mercury is a pollutant of high concern in San Francisco Bay, due to its listing for impairment of beneficial uses such as human fish consumption and potential impacts on survival of resident wildlife. As a result, a Total Maximum Daily Load (TMDL) development process has been undertaken to address the impairment. Mercury has been introduced to the Bay environment through historic gold and mercury 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.

Mercury in the environment is necessary but not alone sufficient to cause negative impacts on biota, as mineral and elemental forms of mercury are less bioaccumulative than methylmercury. RMP monitoring of methylmercury starting 1999 has found that it typically is a very small proportion (average <1%) of total mercury in the San Francisco Bay ecosystem. Therefore, any strategies for managing mercury impacts benefit from improved understanding of methylmercury processes in particular.

Concentrations of total mercury in the Bay are expected to slowly decline as new releases of mercury decrease. However, even without any new inputs, it will likely be decades if not centuries before current ambient concentrations (2002-2006 RMP average ~0.23 μg/kg) return to pre-anthropogenic levels of around 0.08 μg/kg [1]. However, if there are specific fractions or sources of mercury entering or already in the Bay that contribute disproportionately to bioaccumulation in species of concern, then it may be possible to reduce mercury impacts more rapidly.

The RMP has already conducted a substantial amount of monitoring to better understand

distributions, loads, and exposure of mercury and methylmercury, with more information collection planned. Objectives of this mass budget exercise were to 1) collate information on methylmercury distributions in the urbanized San Francisco estuary; 2) estimate methylmercury loads from various pathways including atmospheric deposition, urban stormwater, Delta outflow, wetlands, municipal wastewater, and other discharges; 3) develop an annually averaged one-box mass balance for San Francisco Bay using empirical data on local processes where possible and data for other regions in the literature otherwise. This was a first step towards developing a better understanding of the factors most likely controlling methylmercury concentrations on a Bay-wide scale. Much of the available information was from intensive studies with limited temporal and spatial distribution, so potential pitfalls of a simplified one-box mass budget include: 1) extrapolation of limited data to wider temporal and spatial scales than appropriate, and 2) under-interpretation of finer details of spatial and temporal data critical to local processes. These limitations will be discussed and could be addressed in future work.

2. Methods

2.1 Location and Physiography

San Francisco Bay, California, USA, receives water, sediments and pollutants from local watersheds, as well as from the Sacramento/San Joaquin River watershed (commonly called the Central Valley), which covers an area of 154,000 km^2 (~37% of California). Local watersheds account for an additional 6,650 km^2 , with a mix of urban (35% of the land area), agricultural, and open space (e.g. park and other undeveloped) land uses. The volume of 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 uplands and the open Bay. Tides in the Bay are semi-

diurnal with a range (MLLW to MHHW) of 1.78 m at the Golden Gate Bridge, varying in magnitude in various parts of the Bay. Average water discharge for the period 1971-2000 from the Sacramento/San Joaquin watershed past Mallard Island was 24.9 km^3 annually [2]. Another 1.05 km^3 of freshwater input is provided by the local watershed drainages. Suspended sediment loads entering the Bay from the Delta average 1 billion kg/year [2]. There is no recent estimate of suspended sediment loads from local tributaries; the latest best estimate was 0.75 billion kg/year [3]. The nine-county Bay Area population reached 6.78 million in the 2000 U.S. Census, growing at a rate of about 5% a year (http://www.abag.ca.gov/planning/currentfcst/proj07.html), with another 6 million people in the Central Valley, upstream of Mallard Island. Some of the larger industrial facilities in the Bay area include oil refineries, a cement plant, an automobile plant, steel manufacturing and fabrication, and computer and electronics manufacturers.

2.2 Environmental Monitoring

The Regional Monitoring Program (RMP) for Water Quality in the San Francisco Estuary has conducted annual monitoring of open water areas in San Francisco Bay since 1993. Additionally, RMP has conducted pilot and special studies examining pollutant concentrations and loads entering the Bay by a variety of pathways at various locations. Other projects and programs have monitored other locations and ecosystem components, information useful in building our understanding of methylmercury processes in San Francisco Bay.

Bay Ambient Water and Sediment

Although the RMP has been monitoring mercury in the Bay since its inception in 1993, methylmercury measurements in water and surface (0-5cm) sediment have only been

included since 1999. Samples were collected during the dry season (summer) at fixed locations from 1999 to 2001, and primarily at probabilistic sites with some fixed locations since 2002. Historical fixed locations were located along a transect primarily following the deep channel spine of the Bay. A Generalized Random Tessellation Stratified design used by the U.S. EPA's Environmental Monitoring and Assessment Program was applied to select spatially unbiased probabilistic sampling locations locally [4]. Water was collected via peristaltic pump from ~1m 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.

Sacramento – San Joaquin River Delta

A methylmercury Total Maximum Daily Load (TMDL) report for the Delta [5] by the Central Valley Regional Water Quality Control Board (RWQCB) estimated net methylmercury exported from the Delta to the San Francisco Bay. In the Central Valley TMDL, a major export site of water from the Delta is through the channel cross section adjacent to Mallard Island, roughly the boundary of the Central Valley and San Francisco Bay RWQCB jurisdictions. To obtain export load estimates, methylmercury concentrations were measured at X2, the location in the estuary with 2 $^{o}/_{oo}$ bottom salinity (which ranges up to ~10 miles upland or seaward of Mallard Island), or at Mallard Island in more recent studies. For the TMDL, Central Valley RWQCB staff monitored aqueous methylmercury at X2 monthly from March 2000 to September 2001 and from April to September 2003. Concentrations at Mallard Island were measured in a subsequent CALFED study. Net daily Delta outflow water volumes were determined by the DAYFLOW model (http://www.iep.ca.gov/dayflow/index.html).

Local Watersheds

A number of local tributaries with a mix of urban and other land uses have been monitored by the RMP for total mercury and other pollutants, starting with monitoring of the mining contaminated Guadalupe River in Water Year 2003, continued with a mix of funding through to Water Year 2006. The Guadalupe River watershed area below reservoirs is 236 km^2, with 13% industrial, 13% commercial and 58% residential land use. Sampling began at a Hayward storm drain in Water Year 2007. Hayward Zone 4 Line A was selected for monitoring in recognition that the Guadalupe River watershed is not representative of the smaller urban drainages on the Bay margin which have no mercury mines, are more heavily industrialized, and have almost 100% urban land use designation. Samples typically were collected over the course of storm events and on a few occasions during base flow. Concentrations in Guadalupe River and Zone 4 Line A have been reported previously [6-9]. Few to no measurements have been taken for other local watersheds, so estimates of combined watershed loads for the region are made by extrapolation of methylmercury percentage from these watersheds and regional estimates for mercury loading, with high uncertainty given likely differences in watershed characteristics and mercury sources.

Municipal Wastewater

The San Francisco Bay RWQCB recently requested information on methylmercury concentrations from local municipal wastewater dischargers over the course of a year (2007-2008). Using clean techniques, dischargers collected monthly effluent grab samples and reported discrete and annually-averaged concentrations. These average concentrations were combined with annual discharge rates for each of the plants to estimate annual methylmercury loads. The reporting municipal dischargers account for 95% of the regional effluent discharge.

Wetland concentrations

Concentrations of methylmercury in wetland waters have been reported in a number of studies. Studies in wetlands of the North Bay (e.g., Petaluma Marsh [10]; Suisun Marsh [11]), have reported water column concentrations on incoming and outgoing tides for specific events, but comprehensive monitoring across many days over spring/neap cycles in multiple seasons has not been performed due to the large field and laboratory effort this would entail. Data on water column concentration differences between incoming and outgoing tides measured in the Petaluma study, and estimates of leachable methylmercury produced in the Hamilton Army Air Field wetland [12] can be used to provide an estimate of wetland methylmercury discharge, albeit with large uncertainties. However, such first order estimates based on existing information could indicate whether wetland discharges are a potential source of concern given the range of concentrations and loads in the sparse data found thus far.

2.3 Mass Budget Model

A one-box model of water and sediment processes was employed to integrate existing monitoring efforts and to enhance our understanding of methylmercury fate in San Francisco Bay. The model was initially developed by Davis [13] to predict the long-term fate of PCBs in San Francisco Bay and has been used for developing mass budgets for PAHs, organochlorine pesticides, and PBDEs [14-16]. The one-box model of San Francisco Bay treats the Bay as two well-mixed compartments representing the water column and surface sediments. Conceptually, the model ignores differences in the geographic sub-regions of the Bay, a simplification that precludes deeper understanding of temporal and spatial variations, but allows a first-order evaluation of the system. The model includes parameters for describing major physical and chemical processes governing the transport and fate of

contaminants in the system. These processes include:

1. external loads,
2. settling and resuspension of sediment particles,
3. water-solid partitioning (sorption/desorption),
4. sediment-water diffusive exchange,
5. volatilization,
6. degradation in water and sediment,
7. tidal flushing and outflow, and
8. *in-situ* production.

In-situ production is a major component missing from the earlier one-box models, as 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 effort for a mass balance of mercury in the San Francisco Bay treated these transformations as a pseudo-equilibrium characteristic, using a fixed percentage of total mercury [17] to model a pseudo-steady state methylmercury concentration. However, in this model we do not attempt to express methylmercury as a function of total mercury concentration. Instead, methylmercury production is treated as a specified (input) rate in a methylating zone of sediment. A rate calculated based on total mercury would effectively have been a specified methylmercury input rate, unless it was linked to a concurrent model of long-term large change in total mercury mass balance.

2.3.1 Model External Loads

In the model, some inputs to the Bay are external and not dependent on concentrations in the Bay; these include inputs entering from the air via direct deposition or from the land via rivers, tributaries, channels, and discharge pipes. External loads are discussed below, and

summarized in Table 1. Although flows and loads (e.g. from precipitation runoff in the Delta and local watersheds) are not uniform over the course of the year or evenly distributed in space, this model simplifies temporal loads by treating inputs as occurring uniformly throughout the year and simplifies spatial heterogeneity by assuming all loads enter the Bay evenly spatially (one well-mixed box). These simplifications are important to the system response and will be discussed in detail later.

Sacramento – San Joaquin River Delta

In the Delta methylmercury TMDL [5], average annual methylmercury exports were estimated for water years (WY) 2000 to 2003 (relatively dry years). Concentration data for samples collected at X2 from two sampling periods (March 2000 to September 2001, and April to September 2003) were combined to derive monthly average concentrations, and the DAYFLOW program was used to derive average monthly flows. Methylmercury concentrations at X2 ranged from below detection limits to 0.241 ng/L, averaging 0.075 ng/L over all periods combined. Monthly average concentrations were multiplied by monthly average flows for WY2000-2003 to estimate monthly loads. Monthly loads were summed to calculate an annual average methylmercury load of 1.7 kg/year (4.7 g/day). A simple model regressing Delta outflow to methylmercury concentration for that period resulted in a similar estimate, with export of 2.1 kg/year. Given their similarity, the monthly average derived export was used in the TMDL mass balance.

A subsequent CALFED funded study measured methylmercury concentrations at both Mallard Island and at X2 from October 2004 to November 2005 to examine differences between estimated fluxes for the two locations, but no significant differences were found. Combining previous data used in the TMDL with the new data resulted in an estimated average export flux of 9.8 g/day, These export calculation sonly attempted to estimate

advective flux from the Delta, but dispersive flux could also affect net export. Ignoring dispersive transport generally results in an overestimate of advective flux by around 15% for periods of Delta outflow over 500 m^3/s [2]. The error in estimated mercury advective flux would be expected to be of a similar magnitude, but even with correction for dispersive flux, temporal variability in annual flux is still larger (stdev ~30/% of average). Potential impacts of all these uncertainties are later assessed together through sensitivity testing of the estimate for Delta flux in combination with other external loads.

Local Watersheds

Concurrently collected samples were analyzed for methylmercury and total mercury in the Guadalupe River and Hayward Zone 4 Line A watersheds for events in one or more rainy seasons for RMP special studies of local watershed loads. Guadalupe River total (combined dissolved and particulate phase) methylmercury concentrations ranged 0.05 to 2.2 ng/L (average 0.7 ng/L), which was an average 0.45% of total mercury concentrations (0.05 to 1.9%). Total methylmercury concentrations in Hayward Zone 4 Line A samples ranged from 0.08 to 1.3 ng/L (average 0.44 ng/L, 1.6% of total mercury in water). Other urban sites around San Jose had similar concentrations, with San Pedro Street storm drain ranging 0.02 to 3.1 ng/L (average 0.84 ng/L) , and 0.95 ng/L for a single sampling event at Airport Parkway. Methylmercury was 0.43% and 1.4% of total mercury for those sites, respectively. Because methylmercury concentrations and percentages (of total mercury) were not yet known for other watersheds, estimates for the rest of the region required extrapolation of the limited existing data. Methylmercury percentages in the literature ranged widely, although percentages reported were generally below 10%. Thus the concentrations and percentages found here in stormwater (methylmercury between 0.02 to 3 ng/L, averaging 0.4 to 1.5% of total mercury, for various land use types) did not seem unreasonable. In RMP ambient

monitoring throughout the Bay, methylmercury averaged <1% of the total mercury in the water column, and a similar percentage (average 0.7%) was found in the Delta to Central Bay for another study [18]. A synoptic study of the upper portions of the Guadalupe River watershed [19] also found similar distributions at the station furthest downstream (Los Gatos Creek near its confluence with the Guadalupe River), with methylmercury 1.2% of total mercury. Thus average methylmercury loads at around 1% of total mercury loads were likely to be a reasonable first order estimate.

Total mercury loads at a regional scale have been estimated using multiple methods (e.g. the SIMPLE model [20], or combining bed sediment concentrations with regional suspended sediment loads estimates [21]). Regional total mercury loads estimates from these previous studies ranged from 123 to 185 kg/year. The corresponding methylmercury loads based on 1% of total mercury loads would be between 1.2 to 1.9 kg/year.. Given uncertainties associated with estimating methylmercury as a fixed percentage of total mercury described previously, a second method was applied to provide a comparison. A first order estimate of methylmercury can also be developed using the limited existing data for general land use types and the SIMPLE model [22]. Mass loads of methylmercury estimated in this manner were 1.3kg/year (0.4 kg/year for urban watersheds, 0.4 kg/year for non-urban watersheds, and 0.5 kg/year from the Guadalupe River alone). Using the SIMPLE model to estimate total mercury loads for different watershed types in the region and multiplying by average methylmercury percentages for those land use types resulted in slightly (~3x) higher methylmercury load estimates, with about 1.5 kg/year from urban watersheds, 1.3 kg/year from non-urban areas, and 0.5 kg/year from the Guadalupe River. Summing these gives a total estimated annual average methylmercury load entering the Bay of 3.3 kg/year. Given no way to know which of the estimates was "better", we elected to use a load between the two

described. Thus, a load of 2.3 kg/year was chosen as the default estimate of local watershed loads for the mass budget exercise. Given the limited available data, there was substantial uncertainty in the possible range of methylmercury concentrations and percentages. In acknowledgement of this uncertainty, the mass balance model developed here was tested over a one order-of-magnitude range of for local watershed loads.

Wastewater

Monthly methylmercury data from the 16 largest treatment plants were compiled, and combined with data on mean annual discharge volume [23] to estimate mean annual methymercury loads. These plants account for around 95% of wastewater discharged to the Bay, yielding a total methylmercury load of 0.8 g/day. Concentrations at treatment plants were highly variable (mean RSD ~65%), so testing an order of magnitude range of loads for the model sensitivity runs would likely include the true load.

Wetland Discharge

Net import or export from tidal wetlands can be calculated from measured concentrations and flows in the water column during flood and ebb tides. Neither currents nor methylmercury concentrations are uniform over the course of a tidal cycle, and most wetlands have multiple inlets and outlets, so many measurements at many locations would be needed to get an accurate estimate of net transport for even a single wetland. Given the paucity of data on net import or export for the numerous wetlands fringing the Bay, simplifying assumptions and extrapolations were made to estimate export rates, which could be compared to standing methylmercury inventories and production rates in wetlands to determine their reasonableness.

The current extent of tidal marsh area in the San Francisco Bay region is about 40,000 acres, greatly reduced from 190,000 acres historically, due to diking and infill [24]. These wetlands

vary widely in elevation, vegetation, and hydrological connectivity, but to simplify for this mass budget exercise, we treated all these areas as similar. Long term tidal data for NOAA benchmark stations around San Francisco Bay (Port Chicago, Mare Island, Richmond, San Francisco, Alameda, Redwood City) show differences between mean high water (MHW) and mean tide level (MTL) averaging 0.7 m. Assuming wetland areas have constant slopes, a tidal prism with an average of 0.35 m water covers the marsh surface on each high tide (twice daily), an equivalent depth of over 200m of water is transported on and off wetlands annually. Local wetland evapotranspiration rates are estimated around 1m/year [25], and average annual rainfall around 0.5m/year (http://www.wrcc.dri.edu/summary/Climsmcca.html), so water movement via tides swamps other hydrologic transport pathways in most tidal wetland areas. Although episodic flows from storm events may transport greater volumes for short periods, on an annual basis, transport via daily tidal flows likely dominate in wetland areas other than directly along stream banks, areas already counted as tributary loads.

In a wetland near the mouth of the Petaluma River studied in a Calfed-funded project, water column concentrations over 24 hours were monitored to obtain estimates of the net flux of methylmercury [10]. Peak water column dissolved methylmercury concentrations on ebb tide were up to ten times higher than concentrations seen during flood tide, with the average ebb concentration (0.136 ng/L) almost double the average flood concentrations (0.083 ng/L). In contrast, particulate concentrations averaged slightly higher during flood tide (0.098 ng/L) compared to ebb tide (0.092 ng/L). Extrapolating the difference in dissolved methylmercury between flood and ebb tides, with hydrologic transport primarily by approximately equal volumes of tidal flows in and out of wetlands, methylmercury mass exported from 40,000 acres of tidal marshes around San Francisco Bay would total 6.0 g/day. Similarly, from the

difference in particulate methylmercury concentrations between incoming and outgoing tides, about 0.7 g/day of methylmercury would be transported from the Bay to wetlands. Thus net methylmercury transport would be 5.3 g/day exported from wetlands to the Bay. In a study of the Hamilton Army Air Field (HAAF) wetland, the USACE [12] estimated potential methylmercury export by another methodology. They assumed that solubility would control methylmercury transferred from wetland sediments to overlying water. The net methylmercury production rate was estimated to be 3.1 $\mu g/m^2$/day at HAAF. Based on mercury solubility [26], 0.4% of methylmercury was estimated to be exchangeable with the water column. Combined with twice daily tides, 0.8% of daily net methylmercury production would be removed through tidal transport. Extrapolating the HAAF rates to the total wetland area around the Bay, 4.0 g/day of methylmercury would be discharged to the Bay from wetlands. This export rate is of the same order-of-magnitude as that estimated by the difference in flood and ebb tide concentrations at Petaluma.

Studies in Suisun Marsh [11] found mixed results in net methylmercury transport, with some studied periods and locations showing net import to the marsh, and others showing net export. Although dissolved and particulate methylmercury were not measured separately in those studies, the authors hypothesized that differences in net transport resulted from differences in hydrology and particulate and dissolved phase methylmercury between events and locations. This is consistent with findings in the Petaluma wetland, with higher particulate concentrations in flood tides and higher dissolved concentrations in ebb tides. An accurate determination of net methylmercury transport between a wetland and the Bay would require monitoring over a long term under a wider range of hydrologic conditions (flood and ebb tides under spring and neap tide periods during wet and dry seasons, including rainfall events of different intensities and durations), a task beyond the scope of

most studies, including this exercise. However, the rough estimates provided by studies conducted to date provide a starting point to evaluate the relative importance of refining wetland load estimates.

Atmospheric deposition

The majority of atmospheric mercury monitoring under the Mercury Deposition Network measures only total mercury in wet deposition, although sites have occasionally monitored methylmercury concentrations. Although an MDN station measuring total mercury was maintained near San Jose for 6 years, methylmercury in precipitation was not measured at that local station. The U.S. Geological Survey, in cooperation with the Indiana Department of Environmental Management monitored both total and methyl mercury in precipitation at several stations in Indiana between 2001 to 2003 [27]. For the 3-year period, the median methylmercury concentration in weekly samples was 0.058 ng/L with a maximum of 5.77 ng/L. Methylmercury was also found in precipitation in a similar concentration range (0.01 to 0.179, average 0.052 ng/L) in the Experimental Lakes area of Northwestern Ontario [28]. Rain samples collected during a storm event passing over the North Olympic Peninsula in western Washington State showed average methylmercury concentrations of 0.15 ng/L [29]. Taking the mean methylmercury concentrations in rainfall of these various studies, (0.087 ng/L) and applying San Francisco Bay area mean annual rainfall (typically between 0.4 to 0.5 m/year), direct wet methylmercury deposition to the Bay is estimated to be 0.1 g/day. Methylmercury in dry deposition is seldom measured. A recent study characterized dry deposition of methylmercury in Canada's ELA through collection of throughfall and litterfall, subtracting open field deposition [30]. Although it is possible to measure throughfall and litterfall in surrounding watersheds, dry deposition of methylmercury onto watersheds is already accounted for in the estimation of watershed loadings via tributaries.

The combined throughfall and litterfall deposition rates in the ELA study were up to double the rates of wet deposition, so as a first-order approximation, any dry deposition directly to the Bay would likely be a similar order-of-magnitude as wet deposition.

2.3.2 Model uptake loss to biota

Potential methylmercury bio-uptake was modeled as a loss, using biota for which relatively good inventories exist to evaluate their impact on the overall mass budget. With sufficient information methylmercury uptake into biota might eventually be modeled using concentration dependent relationships. However, a lack of good inventories for many types of biota and a lack of sufficiently detailed information on the relationship between various biota and water or sediment concentrations precluded explicit modeling of these processes for the mass balance developed here.

Estimating uptake of methylmercury by primary producers would be a possible starting point towards quantifying bio-uptake of methylmercury, but the rapid turnover rate of phytoplankton (0.2-0.7/day [31]) suggests that much of the methylmercury in phytoplankton could be rapidly cycled, with a large fraction returning to the water column and sediment. That fraction recycled would depend on what proportion of phytoplankton was consumed by higher tropic organisms and the methylmercury assimilation efficiency of those biota. Because the primary interest of this exercise was to model the fate of methylmercury on annual and interannual time scales, small fish seemed reasonable candidates for estimating annual methylmercury transfer to biota. Small fish are relatively well studied in the Estuary, with the California Department of Fish and Game conducting monthly trawls in the Bay and Delta for the California Department of Water Resources Interagency Ecological Program (I.E.P). The size/age relationship for various species in the Bay have been studied, so the mercury body burden in the young-of-year cohort was used to represent annual-scale net

uptake.

The mean pelagic fish biomass in June-October trawls for areas in northern San Francisco Bay in the intermediate and high salinity areas typically ranged 100 to 1000 g carbon (g C) per 10,000 m^3 trawled [32]. Using the geometric mean of the year 2000 to 2006 range (~0.02 to 0.03 g C/m^3), and converting back into wet weight (original data were expressed as wet weight catch per unit effort), we found about 0.17 g/m^3 in (pelagic) young-of-year fish biomass. The average mercury wet weight concentration in small fish measured in San Francisco Bay by the RMP was 0.049 μg/g. Applying the young-of-year fish density to the total Bay volume, assuming the uptake rate is uniform over the course of a year, an estimated 0.13 g/day of methylmercury is transferred to small fish biomass each day. The data from mid-water trawls likely under-represented benthic residing fish. However, the mercury mass estimate also likely overestimated pelagic fish in deep waters by applying their density to the entire Bay water volume.

Subsequent otter (bottom) trawl data supplied by CDFG (Steven Slater, CDFG, Stockton, CA, *personal communication*) suggested these errors roughly offset. Combining all the Bay segments for 2000 to 2006 resulted in a wet weight average 0.21 g/m^3 for demersal fish density. Thus the estimated net biouptake loss of methylmercury to fish likely was of the right order of magnitude and was a very small component (~0.5%) of overall methylmercury loads to the Bay.

This fish biomass estimate might also have been spatially biased as the mid-water trawls only sampled water 2.5 m or deeper. The US Fish and Wildlife Service conducts beach seining in waters up to ~1m deep as part of the Delta Juvenile Fish Monitoring Program (http://www.fws.gov/stockton/jfmp/monitoring.asp). Biomass catch per unit effort in that program was about ten-fold higher than in the open-water trawls (around 2 g/m^3) but

waters <2.5 m deep account for around one tenth of the Bay volume. Including the beach seine data to derive a volume weighted average biomass would thus only double the amount of methylmercury to biomass (to ~1% of external methylmercury loads).

2.3.3 Model Internal Process Estimates

A majority of the Bay internal processes in the one-box model were dependant on ambient concentrations in Bay waters and sediments. Degradation 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 Pacific Ocean and the atmosphere were needed. Many of the key model parameters are listed in Table 2 and discussed below.

Atmospheric volatilization

Methylmercury can volatilize as the charge neutral species MeHgCl. Air-water partitioning of MeHgCl was measured for 0.7 M NaCl [33] with a dimensionless Henry's law constant of $\sim 2 \times 10^{-5}$ at 25 °C. The volatilization rate calculated by the model using this constant was likely biased high, as the Bay water surface temperature is below 25 °C for most of the year. Furthermore, not all the "dissolved" phase methylmercury in surface waters is present as MeHgCl, as methylmercury may also complex with dissolved organic matter or partition to colloidal material in the operationally defined (<0.45 μm) "dissolved" phase. Binding constants with humic acids in freshwater [34] and gel permeation chromatography [35] suggest that half or more of dissolved methylmercury may be complexed to various forms of DOC. Heavy organically complexed and adsorbed colloidal methylmercury are not volatile, so given dissolved methylmercury concentrations are only partially MeHgCl or similarly light charge-neutral species, the rate of volatilization calculated from literature constants [36] represents an upper bound estimate of the loss rate by this pathway.

Degradation in water and sediment

Degradation in the sediment and the water column was modeled as an internal loss pathway for methylmercury. Degradation can occur through a number of biotic and abiotic pathways. In San Pablo Bay sediment, oxidative demethylation was posited to be a primary mode of degradation based on the by-products of ^{14}C-methylmercury demethylation experiments [37]. Sediment first-order degradation rate constants ranged from 0.019 to 0.25 /day (i.e. 1.9 to 25% of methylmercury degraded per day) in that study. We applied the geometric mean (0.083 /day) as the rate constant for sediments throughout the Bay. Most degradation rates in the San Pablo Bay study were determined for surface (0-4 cm depth) samples, but in the one site where degradation rates were measured at multiple depths (8 cm and deeper), degradation rates were up to about 10-fold lower below 8 cm. Therefore for purposes of the mass balance model, we assumed that sediment methylmercury degradation primarily occurred in the top 7 cm of sediment, with negligible degradation in the deeper anoxic layers.

Methylmercury degradation in the water column also may occur through biotic pathways similar to those in sediments, but abiotic pathways such as photodemethylation are the focus of most degradation studies in surface waters. Degradation rate constants of 0.11 to 0.22 /day were measured in Delta surface waters [38]. Similar rates were seen in photo-irradiated water samples from Petaluma wetlands, with half-lives of 5 to 20 days for filtered waters, and generally longer half-lives (11 to 20 days) for unfiltered waters. Petaluma samples nearest San Pablo Bay had the shortest half-lives in filtered samples of 5 to 6 days, but wetland waters are much shallower than those in most areas of the Bay (typically 1 m maximum depth at high slack tide compared to the Bay average of around 5 m).

Waters at shallow depths typically experience higher levels of irradiation and thus show

higher rates of photodemethylation [39]. Shallow Bay surface waters are likely to have a demethylation half-life similar to that seen in the wetland nearest San Pablo Bay of 7 days (first order degradation rate of approximately 0.1 /day). Unlike in the wetlands however, light penetration in much of the Bay is not likely to extend the entire depth of the water column to the sediment surface. Light penetration in northern San Francisco Bay as measured by Secchi disk in three segments (Suisun, San Pablo, and Central Bay) over four seasons, ranged 0.3 to1.6 m [40]. In all but 2 measurements (Central and San Pablo Bay in the fall), average Secchi depths were 1.1 m or shallower. Thus, assuming that demethylation occurs only over the top ~1 m of surface waters, the demethylation rate applied to the entire water column was modeled as being five-fold lower (0.02 /day).

Tidal flushing and outflow

Bay-specific model parameters were identical to those used in predicting the long-term fate of PCBs in the Bay [13], with the addition of a tidal flushing ratio ($\alpha = 3.75$), which is the ratio of tidal exchange flow to net freshwater flow in the system. Tidal flushing was not included in the original application of the one-box model to PCBs, but was added to the one-box model in response to review comments [41] and used in more recent applications of the one-box model such as the PBDE mass balance [16].

Methylmercury concentrations in the water column measured by the RMP at the Golden Gate station outside of San Francisco Bay typically have not been detected (<20 pg/L). For the base case assumption running the one-box model, ocean waters were assumed to have no methylmercury (concentration of 0 pg/L), which would maximize the estimated net export rate, as methylmercury would only be transported with the ebbing tide, transporting methylmercury from the Bay to the ocean. The model was also tested using different oceanic methylmercury concentrations to assess the sensitivity to this assumption.

Sediment-water partitioning

Partitioning of methylmercury between the water and sediment phases is an important characteristic of the system. The sediment-water partition coefficient (Kd) determines the degree to which methylmercury in sediments adsorb to or desorb from particle surfaces. Methylmercury loads introduced via the water column may adsorb to suspended particles and settle to the sediment bed. Conversely, methylmercury produced in sediment may dissolve from bed sediments into porewater or desorb from resuspended particles into the water column. The partition coefficient is treated as the equilibrium ratio (L/kg) between concentrations in solid (μg/kg) and liquid (μg/L) phases. The use of partition coefficients relies on the assumptions that the kinetics of partitioning are fast relative to other processes; for example, the Kd would become elevated as the apparent water column concentration were decreased by biological degradation or hydrologic exchange that removed methylmercury much faster than it could be replenished by desorption.

Kinetics of methylmercury adsorption and desorption are relatively fast, reaching equilibrium on the order of hours [42], compared to 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 of partitioning in the system for the one-box model. Using the Bay-wide mean particulate methylmercury concentration in water (49.6 pg/L), the Bay-wide mean dissolved methylmercury concentration in water (44.5 pg/L), and the Bay-wide mean concentration of suspended particles in water (0.085 g/L), the methylmercury partitioning coefficient was estimated to be 13,100 L/kg (log Kd=4.11), consistent with other measurements in the San Francisco Estuary [43] and similar to that reported for the Guadalupe River [8]. If instead the average bed sediment methylmercury concentration

(0.558 μg/kg) was used, the resultant Kd between sediment and the water column was 12,500 (log Kd = 4.09), virtually the same. A value of 13,100 L/kg was used as the water column Kd for the base case in the model, with higher and lower partition coefficients used for sensitivity analysis.

The partitioning of methylmercury in sediment porewater may potentially differ from that in overlying water column due to differences in various factors that affect its solubility such as organic carbon concentrations and sulfide speciation. Work in northern San Francisco Bay [18] examined sediment and porewater concentrations of methylmercury and derived Kd for those sites (log Kd = 4.7 ± 0.4 (average ± stdev)). This translates to a mean porewater Kd of 45,700, about the same order-of-magnitude as the partition coefficient for the water column as estimated above. A porewater Kd of 45,700 (log Kd = 4.7) was used for the base case model scenario. Effects of higher and lower porewater Kd were tested during sensitivity analysis.

Sediment-water column particle exchange

The exchange of particles between the water column and the bed sediment of the Bay is not spatially uniform and highly dependant on many environmental factors, such as tidal currents, water depth, wind waves, and particle export from local watersheds and the Delta. The one box mass balance model did not capture such spatial heterogeneity, and given its simplifying assumptions it is best suited to simulating a simple system achieving a long-term pseudo-steady state condition, rather than dynamically modeling episodic or transient events. Although the simplifying assumptions of uniform mixing and equilibrium were not accurate synoptic representations of the system at any particular time, in the longer term, the system tends to range around a mean, which might be reasonably modeled as a steady state condition so long as the kinetics of the modeled processes are much shorter than the

modeled period. The 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 there has been a long-term trend toward reduced sediment loads coming from the Delta in recent decades [44, 45], given the high turnover rate of other modeled processes compared to the long-term change in SSC, modeling of water-sediment particle exchange was simplified and treated as a steady state (i.e. all inputs roughly equal all losses). Another major simplification is the treatment of the mixed sediment layer as a uniformly mixed compartment. In the case of conservative pollutants, a uniform mixing assumption tends to accelerate the response of the system to changes in loads, as increases or reductions in loads will be modeled as occurring instantly equally throughout the Bay. However, methylmercury is not a conservative pollutant; given turnover times on the order of days for some processes such as degradation, the impacts of an instantaneous mixing assumption are lessened. Although the system response time to changes will be shortened by the uniform mixing assumption, the resulting steady state mass achieved should be essentially the same in the long term.

Sediment-Water Column Porewater Exchange

In addition to exchange of particulate matter between the sediment and water column, exchange of porewater with overlying water is another pathway for methylmercury transport. Porewater exchange can occur through abiotic processes such as diffusion or resuspension by wind-wave processes, or through biologically mediated processes, such as bioirrigatation and bioturbation by benthic organisms. Flux rates may be empirically determined via flux box measurements or through mesocosm experiments, although each approach presents

limitations which may lead to differences in net flux from *in-situ* conditions. For example, mesocosms, even if transferred intact, are disconnected from the larger ecosystem and thus may not entirely reflect native conditions. Unless processes such as wind-wave and tidal current shear stresses, tidal pumping, and groundwater flow are adequately simulated, those components of transport will not be included. Similarly, flux box experiments, although maintaining some connection with the surrounding system, tend to isolate the studied patch from waves and currents, and may trap or exclude mobile macrofauna, leading to unrepresentative rate measurements.

Nonetheless, *in-situ* flux box experiments likely represent the best available measurement of actual fluxes in the native ecosystem, and provide a reasonable likely lower bound estimate of net flux due to 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 [18]. The benthic chambers were "gently stirred", which reduced the boundary layer at the sediment-water interface, but likely were not sufficient to resuspend bed sediments. The median flux rate measured was 13 ng/m^2/day (10 to 90^{th} percentile range 2 to 55 ng/m^2/day). Applying that flux rate to the Bay surface results in a net flux of 14 g/day. However, the Bay average concentration differences in porewater and overlying water may not be the same as in that work., so concentrations and measured fluxes were combined to estimate a transfer velocity (Vd) applied in the form:

$$\text{Flux (ng/m}^2\text{/day)} = \text{Vd (m/day)} * [\text{Csed} - \text{Cwater}] \text{ (ng/m}^3\text{)}$$

where Csed and Cwater are dissolved methylmercury concentrations in the sediment porewater and overlying water, respectively. The resultant estimated Vd was 0.001 m/day, which was used to parameterize the one-box model.

Although they did not measure methylmercury flux, the U.S. Geological Survey measured

total mercury flux in a number of South Bay sites [46]. Average dissolved mercury fluxes ranged from 100-400 ng/m^2/day. Assuming porewater ratios of methylmercury:mercury similar to those for the sediment (~1% or less), corresponding methylmercury fluxes would be around 1 to 4 ng/m^2/day, about the same range as found in the North Bay/Delta study of Choe et al. This provides another estimate for methylmercury flux and additional verification that the parameters for estimating benthic flux are reasonable when considered in the larger context of other available data for the Bay.

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. In part due to the relatively rapid sediment degradation rates noted previously, methylmercury concentrations found at depth measured in samples from this region were lower than those in surface samples [37]. Thus unlike the persistent organic pollutants such as PCBs and the inorganic metal pollutants such as mercury or copper, there are not likely to be substantial deeper legacy deposits of methylmercury with higher concentrations that can become exposed through erosion and re-introduced into the ecosystem.

Net sedimentation leading to burial of below the active sediment layer can remove methylmercury from exposure to biota. The average net sedimentation rate of 0.83 cm/year for a core taken from Richardson Bay in 1992 [47] would indicate that less than 10% of the methylmercury inventory in the 10cm mixed sediment layer of the one-box model would be lost by burial each year. Another core in that study from San Pablo Bay suggested a much higher burial rate, averaging 4 cm/year. However, comparisons of bathymetric change suggest that such high burial rates are atypical for much of the Bay [48-50], with most areas showing no net bathymetric change or slight erosion (typically <0.5 m in 30-40 years) in

recent history. However, even assuming such high rates were widespread, burial losses of 40% of the methylmercury in surface sediments over a year are likely dwarfed by potential losses of a similar magnitude in just a week via degradation in sediments. The model response to changes in the burial rate and other assumptions are discussed below.

3. Results and Discussion

3.1. Model Hindcast

Like the PCB and PBDE mass budget models [13, 16], the methylmercury mass budget was run in both hindcast and forecast modes. A hindcast is most useful when there is sufficient data to parameterize the model historically, and the modeled pollutant is sufficiently persistent that prior condition is a significant factor in determining the current state of the system. Unlike for PCBs or PBDEs, little or no information exists regarding the history of likely changes in global or local emissions and loading rates for methylmercury, nor of large changes in partitioning, production, degradation or other processes. Thus, the hindcast scenario was identical to the forecast aside from the initial condition. The sensitivity of the model to historical conditions was tested by adjusting the initial ambient concentrations. Current loading and process rates in the model have no linkage to the historical rates other than through their dependence on ambient concentrations. In the hindcast, to bound the possibilities given no knowledge of the prior condition, we either assumed that ambient methylmercury concentrations in water and sediment were zero, or that they were an order of magnitude (10 times) higher than the current condition.

The zero initial concentration condition represented the hindcast best case scenario, essentially assuming that prior to any anthropogenic mercury releases, ambient methylmercury inventories were negligible. The model was run for two years with continuous loading rates and internal processes using contemporary rates and coefficients

until a steady-state methylmercury mass was achieved. The modeled system reached steady-state quickly, stabilizing within <100 days. The opposite case, with the initial condition set at 10 times the current ambient inventory, quickly reached the same equilibrium within <100 days. This indicated that prior condition had negligible influence on determining the methylmercury steady-state inventory of the modeled Bay system.

3.2 Base Case Forecast

As stated previously, no data exist indicating significant changes in rates and coefficients for various processes. Thus, the same rates and coefficients for these parameters were used in the model hindcast and forecast. In forecast mode, the model was initialized with the best estimate of the current methylmercury mass in the Bay and external loads of between 2.7 and 24 kg/yr (from 1/3 to 3 times the base case) were examined. Given the same final steady state under both the low and high concentration initial condition assumptions in the hindcast runs, not surprisingly, the base case scenario quickly arrived at a steady state with the same final inventory (Figure 1). Varying loading rates over nearly an order of magnitude (9x) range had little effect, with the sediment inventory virtually unchanged, and projected water inventories almost within the 95% confidence interval of the current mean of RMP ambient measurements (Figure 2).

The magnitudes of various methylmercury environmental loading and process rates (kg/day) are listed along with the base case steady state inventory (kg) in Table 3. For the sediment, methylation and demethylation respectively produce and remove nearly 6% of the Bay sediment methylmercury inventory each day. Net methylmercury removed by sediment accretion leading to net burial, was next largest but only 0.007 kg/day, around 250 times smaller. Sediment exchange with the water column was a similar magnitude, 0.007 kg/day. The net exchange was mostly the result of water column suspended particle settling (0.038

kg/day methylmercury) combined with bed sediment resuspension (0.045 kg/day methylmercury). Masses of sediment settling out and resuspended to the water column each day were roughly equal in the base case, so the differences in downward versus upward flux were primarily due to differences in methylmercury concentrations of suspended versus bed sediments.

For methylmercury in the water column, the largest inputs were external loads (including atmospheric deposition, Delta, local tributary, wastewater, and wetlands discharge), and exchange with the bed sediment, which were of roughly the same magnitude in the base case. At steady-state, these inputs were nearly offset by degradation in the water column and outflow from the Bay, which were also of similar magnitudes. The other loss pathways included, biouptake into fish and volatilization of methylmercury, were so small as to be negligible in the mass budget.

Although the Bay is not truly a steady-state system, gross deviances in the model steady-state from the initial condition (derived using mean concentrations) would suggest major errors or uncertainties in some of the model parameters and/or assumptions. For the sediment, the model methylmercury inventory at the final steady state (30.8 kg) was similar to the initial ambient condition inventory set using averaged RMP monitoring data (30.7 kg). Given that the initial inventory had little influence on the final steady state, the slightly higher final inventory suggested small errors or uncertainties in some model parameters. The direction of difference suggested are errors that introduced too much loading and/or production in sediment, or yielded too little removal and/or degradation.

However, in contrast to the approximately constant sediment inventory in the base case forecast, the base case methylmercury inventory in the water column decreased about 30%, from an initial water column 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 there were factors that might be improved. Some of these factors can be identified through testing the sensitivity of the model to various parameters.

3.3 Sensitivity testing

Given various linkages between water and sediment processes in the model, it is difficult to know *a priori* how much specific parameter changes will affect overall model response. For example, although increasing loads would help the water inventory better match the ambient condition, it would also exacerbate the excess of sediment methylmercury in the model steady-state relative to the actual ambient condition. Model forecast runs were performed testing various model parameters threefold higher and lower (about an order of magnitude). The methylmercury steady-state inventories of these scenarios were compiled and expressed as the response of the model relative to the base case, compared to the relative difference in each input variable to its base case (i.e. a local sensitivity), namely:

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

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

The model output separately tracks inventories in the sediment and water column compartments. Although compartments were linked through modeled exchange and repartitioning among phases, some parameters would have a more direct influence on one compartment versus the other.

The input parameter factors in Table 4 are listed in order of the magnitude of their effect on the sediment response. A positive ratio (>0%) indicates than 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 methylmercury inventory were the sediment methylation and demethylation rates. The final steady-state concentration in sediment was nearly directly related to the changes in these parameters 1 to 1. This result was expected, as *in situ* sediment processes far outpaced all others in the base case scenario, similar to the findings in a mass budget for Cheasapeake Bay [51].

The steady state methylmercury mass in the sediment dwarfed the quantity in water, so given daily uniform mixing and equilibrium partitioning assumptions of the model, not surprisingly those sediment factors also had the greatest influence on water concentrations. Conversely, factors that had moderately large influence on water column inventory (e.g. water demethylation rate, partitioning coefficient, particle settling rate) not surprisingly had only small to minimal effect on sediment methylmercury inventory.

An increase in the steady-state suspended sediment concentration naturally increased the water column methylmercury inventory, as the partitioning coefficient indicates higher concentrations per unit mass in the solid phase compared to the dissolved phase. Increase in external loads, which was modeled as inputs into the water column, also would be expected to increase primarily the water column concentration; water column processes such as demethylation, volatilization, and tidal flushing/outflow would remove much of the daily load before it could impact the sediment. The residual portion of the load that would settle to the sediment would be only about 20% of the water inventory (given a base case settling velocity of 1 m/day and average water column depth of ~5 m), which at steady-state was much smaller than the sediment inventory and thus had little impact on the latter. Similarly, other model effects on the water column steady-state intuitively made sense. Increases in net

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

Some model responses were counterintuitive, but made sense considered in the larger context of the steady-state assumptions 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. However, the steady-state assumption of the model means that the increased particle settling must either be offset by increased resuspension, or increased burial of sediment, in order to maintain a conservation of mass of solids in the water column and mixed surface sediment layer, i.e.

Settling – resuspension = net accretion = burial

This linkage was also seen in the effect of the burial rate; as the burial rate was increased without changing the settling rate, the requirement for steady-state solids mass in the surface sediment layer meant that resuspension solids flux must decrease to offset sediment loss via burial.

Model refinement

There are numerous parameters in the model with significant uncertainties due to the limited spatial and temporal extent of the data used in their derivation for the base case. Although the model could be tuned to optimize the steady-state output to better match the current ambient average state (especially in the water column inventory) these adjustments would generally represent non-unique solutions. For example, given the nearly direct relationship of both methylation and demethylation rate on sediment methylmercury, 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 steady-state outcome virtually identical to the base case. No attempt was made to identify a set of inputs

that would be a "best fit" of the model to existing ambient data, as many combinations of adjustments to other parameters could lead to multiple equally well-fitting solutions.

Given spatial and temporal variability in the Bay, efforts to refine the model would be best spent on improving the spatial and/or temporal specificity the model. Although on a Bay-wide scale external loads appeared to have little impact on the sediment methylmercury budget, at smaller spatial scales on a shorter time scale (e.g. a tributary mouth during the rainy season) external loads would have a more similar magnitude of impact on sediment concentrations as *in-situ* production. A more spatially explicit multi-box model of PCB fate in the Bay has already been constructed, resulting in modeled hindcast PCB distributions more in line with regional differences found in ambient monitoring. However, increased model detail places increased data demands, which may be difficult to meet, particularly for biologically mediated processes such as methylation and demethylation.

In the one box model presented here, processes occurring at small spatial and temporal scales that may are relevant to methylmercury fate and biological uptake were simplified to a Bay-wide average basis. The strength of the model as it currently stands was in integrating an inventory of external loads, and rates and magnitudes of a suite of relevant process parameters. If monitoring efforts indicate potential smaller local problems that could be more easily managed, the increased data collection demands of modeling to understand the ecosystem response at those scales may be warranted, as the ability to tailor management actions to specific problems areas may be more cost effective.

4. Conclusions

The mass budget of methylmercury using a simple one-box model presented here represents a starting point towards a better integrated regional understanding of the sources and fate of methylmercury. Modeling of the current base case and threefold lower and higher external

load scenarios 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 processes, for the most part derived from local data. The limitations of existing local data also have also been shown though, as there is considerable uncertainty in the derivation of current loads and rates from extrapolating spatially and temporally limited monitoring data. Additionally, application of a steady-state one-box model to represent a heterogenous and temporally dynamic ecosystem presents major limitations, as methylmercury processes relevant to biological processes at the base of the food web were modeled only on a Bay-wide average basis. Nonetheless, the exercise here represents the current best integration of the state of knowledge for methylmercury, an ephemeral pollutant species that is of major concern for San Francisco Bay regional ecosystem managers. This initial effort points the way that smaller spatial and temporal scales could be modeled more robustly, provided that sufficiently detailed local information become available. The sensitivity and rapid response of the model to key parameters such as *in-situ* methylation and demethylation rates suggest that there may be management approaches that could control methylmercury in shorter time frames, compared to reductions in total mercury, which would take decades to change even if all external loads were eliminated, given the large inventory already in place in the Bay and slow loss processes.

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Figure 1. Forecast trajectory of methylmercury mass in Bay sediment for loading rates 1/3x, 1x, and 3x the base case estimate. Dashed lines indicate ±95% confidence intervals of the current mean inventory.

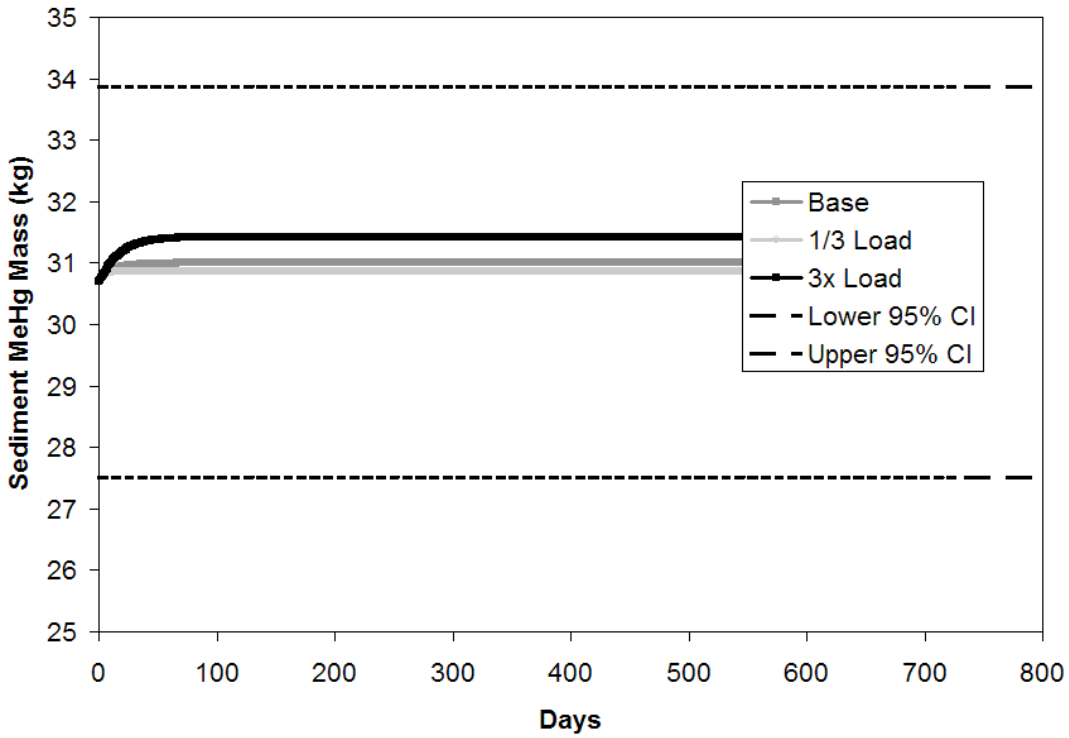

Figure 2. Forecast trajectory of methylmercury mass in Bay water for loading rates 1/3x, 1x, and 3x the base case estimate. Dashed lines indicate ±95% confidence intervals of the current mean inventory.

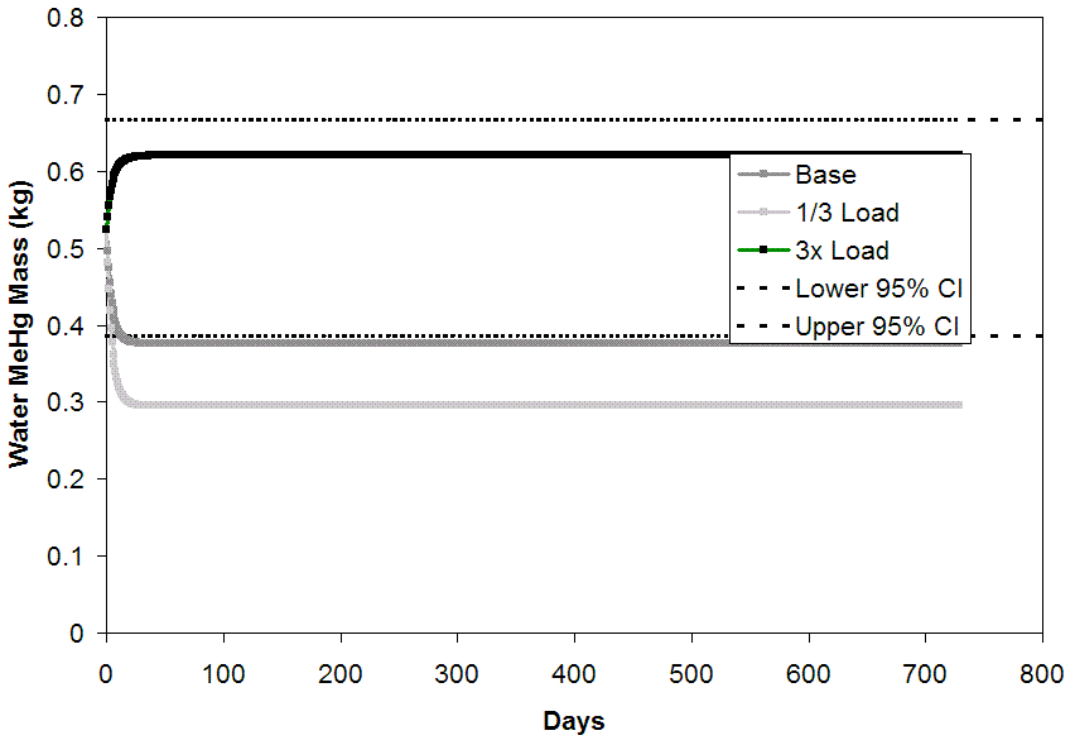

Table 1. Key Parameters Used in Base Case for One-Box Model

Parameter		Data Source
Bay freshwater inflow (m^3/s)	820	(http://www.iep.ca.gov/dayflow/index.html)
Tidal/fresh flow ratio	3.75	[41]
Degradation rate in water (1/day)	0.1	[10]
Degradation rate in sediment (1/day)	0.083	[37]
Methylation rate in sediment (ng/g/day)	0.11	[37]
Bay average water MeHg (pg/L)	95.7	(http://www.sfei.org/rmp/wqt) 2002-2006
Bay average Sediment MeHg (µg/kg)	0.558	(http://www.sfei.org/rmp/wqt) 2002-2006
Pacific Ocean Water MeHg (pg/L)	8	[43]
Water column partitioning Kd (l/kg)	12500	(http://www.sfei.org/rmp/wqt) 2002-2006
Porewater partitioning Kd (l/kg)	45700	[18]
Sediment burial rate (cm/y)	0.83	[47]
Water-side evaporation coefficient (m/day)	1.5	[36]
Air-side evaporation coefficient (m/day)	0.26	[36]
Water-sed diffusion coefficient (m/day)	0.001	[18]

Table 2. Magnitudes of Methylmercury Processes Relative to Inventories, Model Base Case

Model Component	Magnitude (kg/day)	Daily Turnover (%)
Inventory in water = 0.38 kg		
External load	0.024	6%
Outflow past Golden Gate	0.023	6%
Degradation in water	0.0075	2%
Sediment to water exchange	0.0064	2%
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%
Burial in sediment	0.0074	0.02%
Sediment to water exchange	0.0064	0.02%

Table 3. Model Sensitivity to Input Parameters (100% = Direct 1:1 Response)

Input Parameter	Sediment	Water
Sediment methylation 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 Kd	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%
Ocean methylmercury concentration	0.10%	3.20%
Sediment/water transfer velocity	<0.01%	<0.01%
Porewater Kd	<0.01%	<0.01%
Water temperature	<0.01%	<0.01%
Initial Bay methylmercury concentration	<0.01%	<0.01%
Henry's Law constant	<0.01%	<0.01%
Air/water mass transfer coefficient	<0.01%	<0.01%

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