A First-Order Mass Budget for Methylmercury in San Francisco Bay, CA.

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Abstract

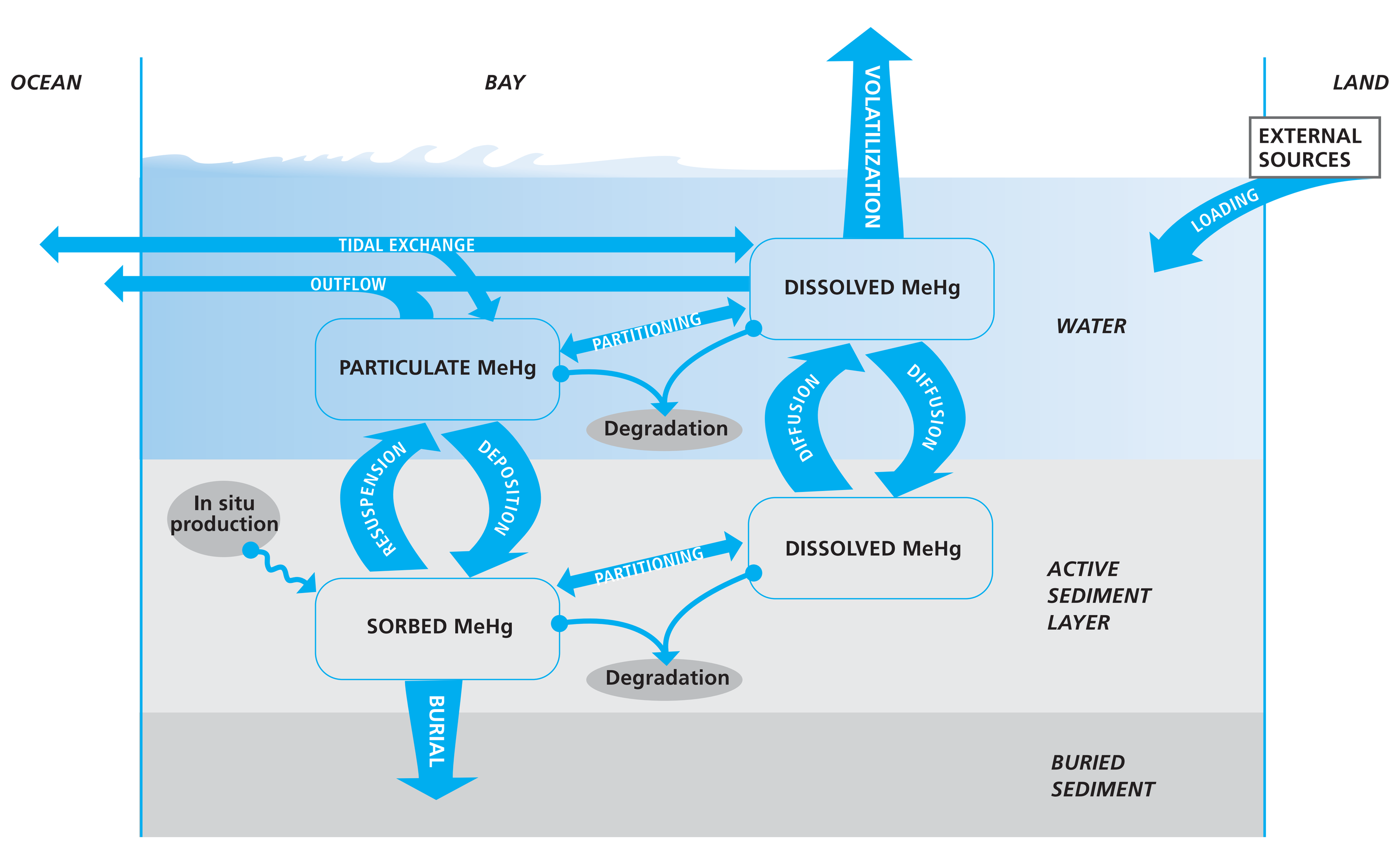
San Francisco Bay is listed as impaired due to mercury contamination in sport fish for human consumption. A legacy of local mercury mining and mercury from gold mining in the Sierra Nevada and more recent/ongoing urban inputs have contributed to contamination of the Bay. Even without continued mercury inputs, it would likely be centuries before mercury concentrations return to pre-industrial levels. Because methylmercury is the mercury species most directly responsible for contamination in biota, a better understanding of its sources, loads, and processes is sought to identify means to manage its impact in the Bay in the near term. A simple one-box model of San Francisco Bay was applied to evaluate estimates for methylmercury loading pathways and environmental processes, to identify major data gaps, and test various management scenarios. External loading pathways considered in the mass budget include loads entering via atmospheric deposition, and discharges from the Sacramento/San Joaquin Delta, local watersheds, industrial and municipal wastewater, and fringing wetlands. Internal processes examined included exchange between bedded sediment and the water column, degradation, in situ production, and losses via hydrologic transport to the Pacific Ocean. The largest uncertainties and information needs are explored.

Methylmercury Mass Balance Model

A one-box model of water and sediment processes was previously used to predict the long-term fate of PCBs in San Francisco Bay, adapted here for a methylmercury (MeHg) mass balance. The one-box model of San Francisco Bay treats the Bay as two well-mixed compartments representing the water column and surface sediments, ignoring spatial differences within the Bay. This simplification precludes deeper understanding of system dynamics, but allows a first-order macroscopic evaluation of the system given limited information.

The model includes loads and major physical and chemical processes governing MeHg transport and fate. A conceptual diagram of the model is shown in Figure 1.

Figure 1.
One Box Mass Balance Model of SF Bay



External Loads

External load estimates were derived for a number of sources, summarized in Table 1. Outflow from the Sacramento/San Joaquin Delta was estimated for the California Central Valley Regional Water Quality Control Board (RWQCB) mercury TMDL (Foe et al. 2008 draft). Wetland discharge was determined by the difference in average flood versus ebb tide MeHg concentrations measured in a northern SF Bay wetland (Yee et al. 2008) for a CALFED funded study. Local watershed loads were estimated in current SF Bay Regional Monitoring Program (RMP) pilot studies for urbanized, mine impacted, and mixed land use watersheds. Wastewater loads were derived from information provided by municipal dischargers to the SF Bay RWQCB. Atmospheric deposition was estimated using precipitation concentrations in other areas of North America (Bloom and Watras 1989; St. Louis et al. 1995; Risch 2007) applied to average SF Bay rainfall. There is substantial uncertainty for many of these loads from extrapolation of limited data due to potential spatial and temporal variability.

Table 1.
Estimated MeHg External Loads to San Francisco Bay. (g/d)

Loading Pathway	Loads g/day
Delta	9.8
Net wetland discharge	5.3
Local Watersheds	6.2
Wastewater	0.79
Atmospheric deposition	0.10
Total	**22.2**

In Bay Processes

Other key parameters for the one-box model (Table 2) were populated using data from regional studies, or studies in the literature from other areas in the absence of local data. Like external loads, there is uncertainty in some of these parameters due to their derivation from temporally and/or spatially limited data, but the impact can be assessed through model testing.

Table 2. Key Parameters used in MeHg One-Box Model

Parameter	Value	Data Source
Bay freshwater inflow (m^3/s)	820	CA Dept. Water Resources
Tidal/fresh flow ratio	3.75	(Connolly et al. 2005)
Degradation rate in water (1/d)	0.1	(Yee et al. 2008)
Degradation rate in sediment (1/d)	0.083	(Marvin-DiPasquale et al. 2003)
Methylation rate in sediment (ng/g/d)	0.11	(Marvin-DiPasquale et al. 2003)
Water column partitioning Kd (l/kg)	12500	RMP
Porewater partitioning Kd (l/kg)	45700	(Choe et al. 2004)
Sediment burial rate (cm/y)	0.83	(Fuller et al. 1999)
Water-side evaporation coefficient (m/d)	1.5	(Hoff et al. 1996)
Air-side evaporation coefficient (m/d)	0.26	(Hoff et al. 1996)
Water-sed diffusion coefficient (m/d)	0.001	(Choe et al. 2004)

Base Case Scenario

The model was initialized with the best estimate of the current MeHg mass in the Bay using RMP ambient monitoring data. The base case scenario model run allowed us to assess whether the model could reasonably simulate the current state of the Bay using default parameters. Given that many of the model parameters used averages from local data, not surprisingly the base case scenario steady state mass was similar to the initial mass (Figure 2).

The processes governing ambient MeHg mass in the water column in the base case were the external load, outflow/exchange to the ocean, and water column degradation, with the largest of these accounting for nearly 6% of the steady state MeHg mass (Table 3). Major factors determining the sediment MeHg mass were the in situ methylation rate and the sediment degradation rate, which were ~6% of the sediment MeHg mass. Given these processes each turn over 6% of the MeHg inventory each day, a steady state was readily achieved in less than one month.

Figure 2.
MeHg Mass in Sediment and Water, Base Case Model Run

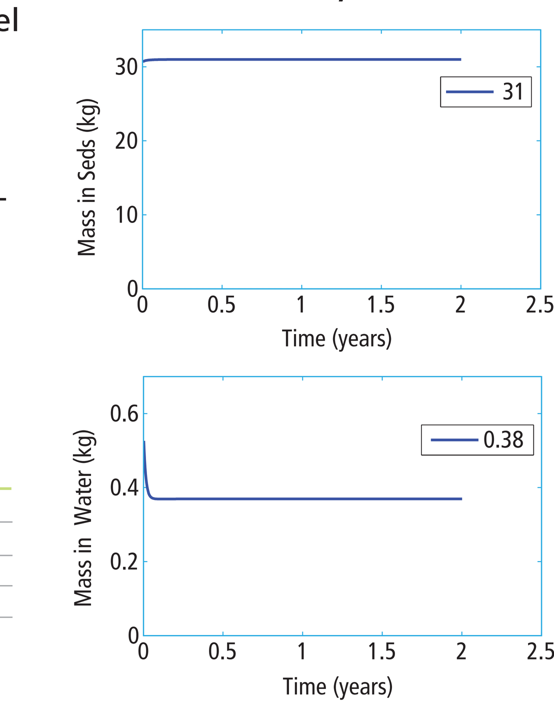


Table 3.
SF Bay MeHg Masses versus Loading, Exchange, and Loss Processes, Model Base Case

Mass in water (kg)	0.38
External load (kg/d)	0.023
Outflow/exchange past Golden Gate	0.023
Degradation in water	0.0074
Sediment to water exchange	0.0064
Biological uptake into fish	.0001
Volatilization	<0.0001

Mass in sediment (kg)	31.0
Methylation in sediment (kg/d)	1.8
Degradation in sediment	1.8
Burial in sediment	0.0074
Sediment to water exchange	0.0064

Sensitivity Testing

Interactions between water and sediment processes in the model make it difficult to know a *priori* how specific parameter changes will affect model response. Model forecast runs were performed testing various model parameters over a ~one order of magnitude range (±3x). The MeHg inventory change of these scenarios relative to the base case steady state were expressed as a ratio (Table 4):

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

Where $\Delta \text{Input}/\text{Input}_{\text{BASE}}$ is the change in the input parameter relative to the base case input, and $\Delta \text{Output}/\text{Output}_{\text{BASE}}$ is the change in the steady-state mass, relative to the base case mass.

Not surprisingly, the factors most affecting sediment MeHg mass were sediment methylation and degradation rates, which also affected water concentrations due to equilibrium partitioning in the model. Various other factors affected water column mass but had little effect on sediment results, due to the smaller relative mass in water.

Table 4.
Model Response to Input Parameters (100% = Linear Response)

INPUT PARAMETER	SEDIMENT	WATER
Sediment methylation rate	99.3%	66.0%
Sediment demethylation rate	-96.5%	-64.1%
Suspended sediment concentration	-0.8%	49.3%
External load	0.6%	31.1%
Long term net outflow	-0.5%	-23.5%
Tidal flushing ratio	-0.4%	-18.6%
Water column Kd	0.4%	-21.8%
Particle settling rate	-0.3%	16.0%
Sediment burial rate	-0.2%	-11.0%
Water demethylation rate	-0.2%	-9.7%
Ocean MeHg concentration	0.1%	3.2%

Conclusions

The simple one-box methylmercury mass balance model presented here represents a starting point towards a better integrated understanding of the sources and fate of methylmercury in San Francisco Bay. Applying a steady-state one-box model to represent a heterogenous dynamically changing ecosystem presents great uncertainty from extrapolating spatially and temporally limited monitoring data. Nonetheless, it represents the current best integration of our state of knowledge for methylmercury, an ephemeral pollutant species that is of major concern for regional ecological managers. Smaller spatial scales could be more modeled more robustly, provided appropriate local information were available. The sensitive and rapid response of the model and to key parameters such as *in situ* methylation and demethylation rates suggest that there may be management approaches that will help to control methylmercury in a short time frame, compared to reductions in total mercury, which may take decades to show change.

References

Bloom, N. S. and C. J. Watras (1989). "Observations of Methylmercury in Precipitation." Science of the Total Environment 87/88: 199-207.

Choe, K.-Y., G. A. Gill, et al. (2004). "Sediment–water exchange of total mercury and monomethyl mercury in the San Francisco Bay–Delta." Limnology and Oceanography 49(5): 1512-1527.

Connolly, J. P., C. K. Ziegler, et al. (2005). " Comment On "The Long-Term Fate Of Polychlorinated Biphenyls In San Francisco Bay, (USA)"." Environmental Toxicology and Chemistry 24(10): 2397-2398.

Foe, C., S. Louie, et al. (2008 draft). Methylmercury Concentrations and Loads in the Central Valley and Freshwater Delta. Sacramento, CA, Central Valley Regional Water Quality Control Board.

Fuller, C. C., A. van Geen, et al. (1999). "Sediment chronology in San Francisco Bay, California, defined by Pb, Th, Cs, and Pu." Marine Chemistry 64: 7-27.

Hoff, R. M., W. M. J. Strachan, et al. (1996). "Atmospheric deposition of toxic chemicals to the Great Lakes: A review of data through 1994. ." Atmospheric Environment 30: 3505-3527.

Marvin-DiPasquale, M., J. Agee, et al. (2003). "Microbial cycling of mercury in contaminated pelagic and wetland sediments of San Pablo Bay, California." Environmental Geology 43(3): 260-267.

Risch, M. R. (2007). Mercury in Precipitation in Indiana, January 2001–December 2003. U.S. Geological Survey Scientific Investigations Reston, VA, U.S. Geological Survey: 76.

St. Louis, V. L., J. W. M. Rudd, et al. (1995). "Wet deposition of methyl mercury in northwestern Ontario compared to other geographic locations. ." Water, Air and Soil Pollution 80 80(1-4): 405-414.

Yee, D., J. Collins, et al. (2008). Mercury and Methylmercury Processes in North San Francisco Bay Tidal Wetland Ecosystems CalFed ERP02D-P62 Final Report. Oakland, CA, by the San Francisco Estuary Institute for the California Bay Delta Authority.

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