Methylmercury in San Francisco Bay Surface Sediments

D. Yee[1], S. Lowe[1], J. Ross[1], G. Scelfo[2], C. Conaway[2] [1 San Francisco Estuary Institute, 7770 Pardee Lane, 2nd Floor, Oakland, CA 94621 2 Department of Environmental Toxicology, University of California, Santa Cruz, CA 95064]

ABSTRACT

Surface sediments (0-5cm) were collected for the Regional Monitoring Program (RMP) from San Francisco Bay sites summer 2002-2004. Mercury (Hg), methylmercury (MeHg), and a suite of ancillary sediment parameters (total organic carbon (TOC), total nitrogen (TN), oxidation-reduction potential (ORP), grain size) were measured in the field or in the laboratory. Reports in the literature show correlations of MeHg to Hg, TOC [1], and other sediment characteristics, relationships examined in samples collected for the RMP. However, Hg and TOC showed weak or no relationship to MeHg in RMP samples. Of measured ancillary parameters, sediment TN and ORP were most strongly correlated to MeHg. Sulfate reducing bacteria (SRB) under anaerobic conditions are expected to produce the majority of MeHg in estuarine sediments, and the parameters correlating with sediment MeHg support this expectation. These findings suggest options other than just reducing total Hg for managing ecosystem methylmercury exposure.

INTRODUCTION

The Bay is listed as an "impaired" water body because Hg adversely impacts established beneficial uses; Hg in Bay fish caught and consumed may threaten human health, and Hg in bird eggs may increase risk of eggs failing to hatch or other developmental problems. SF Bay surface sediments are widely contaminated with Hg from sources including historic loads from Sierra Nevada gold mining and nearby mercury mines, and ongoing inputs via atmospheric deposition, wastewater discharge, and runoff from local watersheds. Although elemental and ionic Hg account for most of the mass in the Bay, MeHg is a major concern due to its rapid uptake and accumulation in the food web. MeHg is primarily produced by SRB under anoxic conditions [2]. However, MeHg degrades [3] in days, so MeHg produced locally in Bay sediments is likely the majority of MeHg found.

FIELD METHODS

Sediment was collected with a Young-modified Van Veen grab (surface area 0.1m^2). Two grabs were taken at each site. A short core subsample (5cm diameter) was taken from one grab for measuring ORP on board (WTW 340i Multimeter, Sentix ORP electrode). The top 5cm from both grabs was composited for each site. Composite aliquots were split into containers for various laboratory analyses. MeHg samples were then frozen on board.

LABORATORY ANALYSIS METHODS

SEDIMENT QUALITY

Grain size fractions were determined with an x-ray transmission analyzer (Sedigraph 5100). Aliquots for TOC and TN were dried, ground, and acidified prior to analysis to remove carbonates. TOC in 2002 samples was analyzed with a Coulometrics CM 150 (UIC Inc.), while TOC and TN in 2003-4 were measured with a Carlo Erba 2500 Elemental Analyzer.

METHYLMERCURY & MERCURY

Hg samples were freeze dried and stored. Samples were digested by a weak acid mix (60:40 HNO_3:H_2SO_4), oxidized with BrCl, and analyzed using an automated instrument (Tekran) with $SnCl_2$reduction, gold-amalgamation trap, and cold vapor atomic fluorescence spectrometry (CVAFS) detection (EPA Method 1631 modified).

MeHg was analyzed by a method similar to Bloom and Fitzgerald (1988) and EPA 1630. Wet sediments were stored frozen. Thawed samples were digested in an acid mix, then extracted into CH_2Cl_2 with agitation. The organic solvent was back-extracted into an aqueous buffer and removed by gas bubbling. Soluble MeHg was ethylated using sodium tetraethyl borate. Derivatives were purged with N_2 gas, collected on a Tenax trap, and dried. Hg species were thermally desorbed, separated by gas chromatography (GC), reduced in a pyrolytic column, and detected by CVAFs.

RESULTS AND DISCUSSION

SF Bay surface sediment Hg ranged from ND<0.005 to 0.78mg/kg dry weight (dw), averaging 0.24mg/kg, and MeHg sediments averaged 0.48µg/kg dw (ND< 0.005 to 2.4µg/kg dw). Averaged over the whole Bay, MeHg and Hg showed little interannual variation in RMP summer samples. Differences among Bay segments in mean MeHg and Hg were significant, with northern stations showing significantly lower concentrations than the rest of the Estuary (Figures 1-2).

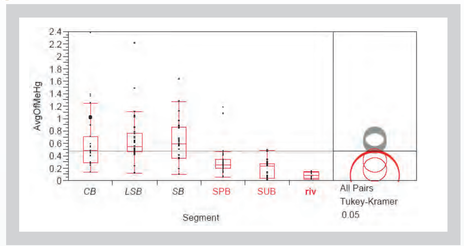
Total Hg was not well-correlated with MeHg (R^2 = 0.06, Figure 3). The lowest MeHg was found in samples with low Hg, but these samples had coarse-grained material. Samples over a narrow range of total Hg (0.20~0.30mg/kg dw), showed nearly the entire range of MeHg.

Total Hg showed positive correlation with %fines (linear regression R^2=0.39, Figure 4). However the MeHg with %fines correlation was much weaker (R^2=0.15, Figure 5), as MeHg ranged widely for sediments with >90% fines.

Sediment MeHg showed a moderate negative correlation to surface (1-6cm depth) ORP (R^2=0.27, Figure 6). MeHg was higher in reduced (negative ORP) sediments. Although oxic sediments often had lower %fines, among sediments with fines>90%, samples with lower ORP had higher MeHg.

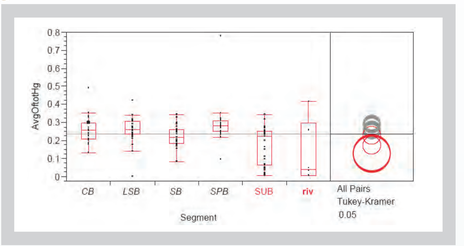
Mercury methylating SRBs require organic matter to metabolize, but MeHg showed no correlation to TOC (Figure 7, R^2=0.008). However, MeHg correlated much better to TN (Figure 8, R^2=0.32). Some high TOCs in 2002 may have been analytical artifacts (excess carbonate) but even removing high (>2%) TOCs, the correlation was poor, as MeHg vary widely over a narrow range of TOC (1-1.5%). Sediment TOC could also include refractory organic compounds which would not promote activity of SRBs. In constrast TN could represent more labile biogenic organic matter easily metabolized by anaerobic bacteria.

1 Sediment MeHg by Segment



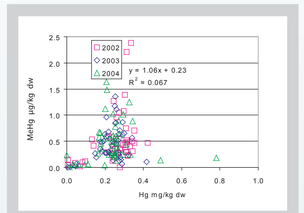
CB=Central Bay, LSB=Lower South Bay, SB =South Bay, SPB=San Pablo Bay, SUB=Suisun Bay, and Riv=Rivers (Sacramento and San Joaquin)

2 Sediment Hg by Segment

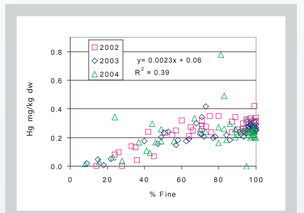


CB=Central Bay, LSB=Lower South Bay, SB =South Bay, SPB=San Pablo Bay, SUB=Suisun Bay, and Riv=Rivers (Sacramento and San Joaquin)

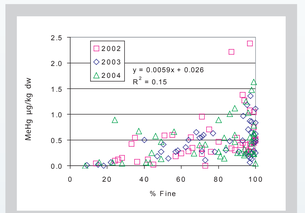
3 MeHg vs Hg



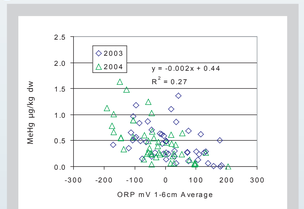
4 Hg vs %Fine



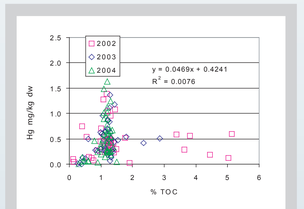
5 MeHg vs %Fine



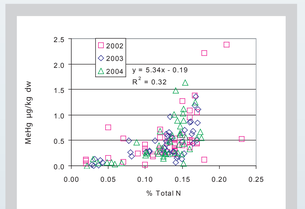
6 MeHg vs ORP



7 MeHg vs TOC



8 MeHg vs Total N



CONCLUSIONS

Surface sediment samples from SF Bay for the RMP showed MeHg concentrations similar to other recent work in the Bay and Delta [4]. Total Hg and TOC showed little correlation to MeHg in RMP samples, as total Hg in the Bay varies little, and TOC includes organic matter not easily metabolized by bacteria. Correlations of TN and ORP to surface sediment MeHg support the expected role of SRB activity under reducing conditions in methylation. Given poor correlation of total Hg to MeHg in Bay samples, the influence of TN (a proxy of labile organic matter) suggests it is a major factor affecting net Hg methylation in the Bay. Controlling organic matter in the Bay may thus represent another avenue to decreasing MeHg more effectively than limiting total Hg alone.

ACKNOWLEDGEMENTS

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