

Distribution of particulate, colloidal, and dissolved mercury in San Francisco Bay estuary. 2. Methylmercury

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Abstract

The phase speciation and estuarine behavior of methylmercury (MeHg) were determined in surface waters of the San Francisco Bay estuary in September–October 2000 (low flow) and March 2001 (high flow). Colloidally associated MeHg was isolated using a cross-flow ultrafiltration technique with a nominal molecular weight cutoff of 1 kDa. Filter-passing MeHg was $57 \pm 18\%$ of the MeHg in unfiltered water in the fall and $39 \pm 12\%$ in the spring. Colloidal MeHg averaged $34 \pm 11\%$ of the filter-passing MeHg in the fall and $56 \pm 15\%$ in the spring. Significantly higher particle–water partition coefficients were observed between colloidal and dissolved MeHg ($\log K_c = 5.6 \pm 0.3$, $n = 21$) compared with those between particulate and dissolved MeHg ($\log K_p = 4.9 \pm 0.5$, $n = 21$), which suggests that MeHg is preferentially associated with colloidal material. Strong correlations of MeHg with organic carbon content in the filter-passing, colloidal, and dissolved fractions confirmed the importance of organic matter in the MeHg cycle. Both absolute and relative (as a percentage of Hg) MeHg concentrations were highest in the river water end-member under both flow regimes, which suggests that riverborne MeHg is the major source of MeHg introduced to the estuary. A nonconservative estuarine mixing model suggests that significant amounts of colloidal and dissolved MeHg are removed in the estuary under both flow regimes, standing in marked contrast to Hg, which had a source within the estuary under the low flow condition.

Methylmercury (MeHg) biomagnifies up the food chain more efficiently than inorganic mercury (Watras and Bloom 1992; Mason et al. 1996). As a result, MeHg is usually the dominant Hg species concentrated in the soft tissue of fish and shellfish (Bloom 1992). Methylmercury is a potent neurotoxin that impairs the nervous system, posing a potential human health risk through the consumption of MeHg-contaminated fish. Numerous studies have been conducted on MeHg formation (Gilmour et al. 1992, 1998), bioavailability (Watras and Bloom 1992; Mason et al. 1996; Benoit et al. 1999), and transport in rivers (Hurley et al. 1995, 1998) and estuaries (Leemakers et al. 1995, 2001; Benoit et al. 1998). Mason et al. (1999) suggested that in situ MeHg formation in sediments was the major source of MeHg to Chesapeake Bay.

Colloidal material has received significant attention because of its strong reactivity with trace metals (Honeyman and Santschi 1989) and the possible effects of trace metal complexation with colloids on its bioavailability to microorganisms (Tessier and Turner 1995; Guo et al. 2001). There have been several articles that have dealt with the mercury (inorganic Hg + MeHg) association with colloids in natural waters (Guentzel et al. 1996; Stordal et al. 1996). Only a few studies, however, have quantitatively measured colloidally associated MeHg in natural waters (Cai et al. 1999; Babiarez et al. 2001) because of difficulties in measuring MeHg. Those studies confirmed the importance of colloidal material in MeHg cycling in aquatic systems. However, those investigations were conducted only in freshwater systems, so very little is known about the interaction between MeHg and colloids and the phase speciation of MeHg in estuarine environments.

In the present study, the distribution of particulate, colloidal, and dissolved MeHg was investigated in the San Francisco Bay estuary, one of the most heavily Hg-contaminated regions in the United States (Domagalski 1998, 2001). This is the first study conducted on the phase speciation of MeHg in an estuarine environment, as well as the first reported measurements of filter-passing MeHg in San Francisco Bay. The major focus of the present work is to characterize the distribution of MeHg in unfiltered, particulate ($>0.45 \mu\text{m}$), filter-passing ($<0.45 \mu\text{m}$), colloidal (1 kDa– $0.45 \mu\text{m}$), and dissolved (<1 kDa) fractions and to examine the importance of natural colloidal material on the speciation of MeHg. In addition, results for MeHg are compared with those for Hg reported in our companion article (Choe et al. 2003).

Materials and methods

The operational definitions for different phase fractions described in Choe et al. (2003) are also used in the present article. Particulate concentrations were determined by the difference between unfiltered and filter-passing concentrations, and the colloidal MeHg concentration was calculated by the difference between filter-passing and dissolved MeHg concentrations.

Surface water samples were collected 29 September–3 October 2000 (low flow) from 15 sites in the northern reach and 5–6 March 2001 (high flow) from 14 sampling sites, including 3 South Bay stations (see the map of the study area in Choe et al. 2003). Both filtered and unfiltered water samples were drawn from ~50 cm depth through Teflon tubing with a peristaltic pump. Filtered water was ultrafiltered to isolate colloidal MeHg with a regenerated-cellulose membrane with a nominal molecular-weight (MW) cutoff of 1 kDa (Amicon model S1Y1). Membranes were calibrated with vitamin B-12 (average MW, 1,350) and rhodamine 6G

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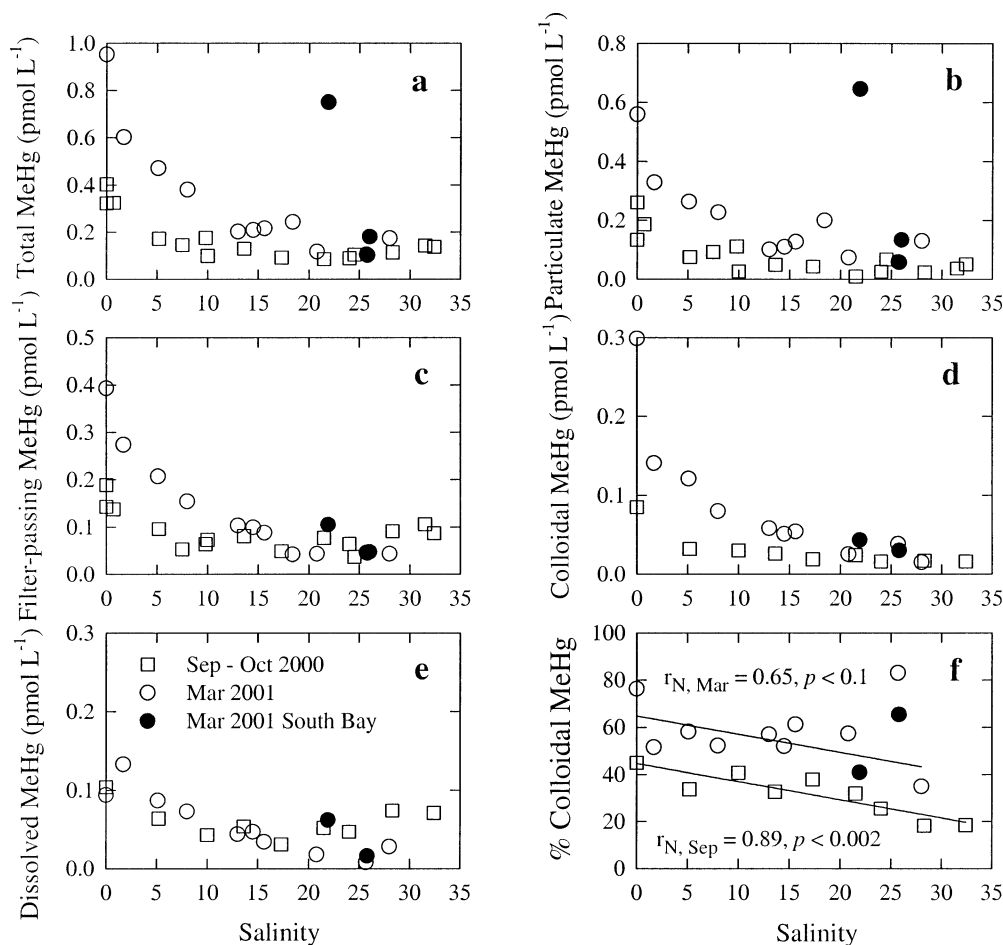


Fig. 1. Monomethyl mercury distributions as a function of salinity. (a) Total, (b) particulate ($>0.45 \mu\text{m}$), (c) filter-passing ($<0.45 \mu\text{m}$), (d) colloidal (1 kDa– $0.45 \mu\text{m}$), and (e) dissolved (<1 kDa) Hg and (f) percentage of colloidal MeHg in the filter-passing fraction in September–October 2000 and March 2001. $r_{N, \text{Sep}}$ and $r_{N, \text{Mar}}$ represent the correlation coefficients for the northern reach data in September–October 2000 and March 2001, respectively.

(average MW, 480) prior to use. Additional details on the study area, river flow conditions, sample collection, ultrafiltration, and membrane calibration results are described in Choe et al. (2003).

Mass balance—The mass balance recovery of MeHg was also tested as a quality control check of the ultrafiltration procedures. The mass balance for MeHg averaged $86 \pm 15\%$ ($n = 21$), which is lower than that for Hg ($94 \pm 15\%$) or organic carbon (OC) ($99 \pm 8\%$). It is not clear whether the slightly lower recovery of colloidal MeHg results from greater sorptive losses of MeHg onto this particular type of membrane, a slight analytical bias due to the extremely low MeHg concentrations in filter-passing and permeate samples, or another mechanism.

MeHg measurement—MeHg measurements were conducted using aqueous-phase distillation for purification, ethylation to gaseous phase (methyl ethyl mercury) by 1% sodium tetraethylborate solution, trapping on a Tenax TA column, gas chromatography separation, thermal ($\sim 700^\circ\text{C}$)

reduction to Hg^0 , and detection by cold vapor atomic fluorescence spectrometry (Liang et al. 1994). A distillation volume of 150 ml was used for the unfiltered, filtered, and permeate solutions, and a volume of 45 ml was used for the retentate and wash solutions. The detection limit estimated as three times the standard deviation of the method blank was 0.01 pmol L^{-1} . Matrix spike recoveries were generally $>90\%$, and analytical precision was $<15\%$.

Results

Estuarine distributions of suspended particulate matter (SPM) and OC were presented in Choe et al. (2003). Total (unfiltered), particulate, filter-passing, colloidal, and dissolved MeHg exhibited nonconservative estuarine mixing distributions for both estuarine transect profiles (Fig. 1). The highest unfiltered MeHg concentration during the low flow condition in September–October 2000 occurred in the San Joaquin River (0.40 pmol L^{-1}) (Fig. 1a). The unfiltered MeHg concentration at the Golden Gate Bridge (the seawater end-member) was slightly higher (0.14 pmol L^{-1}) than the

Table 1. Comparison of particulate and filter-passing MeHg concentrations in estuarine environments.

Estuarine system	Salinity	Particulate (nmol kg ⁻¹)	Filter-passing (pmol L ⁻¹)
Galveston Bay*	0–28	1.7–2.9	0.03–0.15
Patuxent†	0–15	—	<0.10–0.50
North San Francisco Bay‡	0–32	1.2–12	0.04–0.40
South San Francisco Bay‡	22–26	5.0–24	0.05–0.11
Scheldt§	0–30	~2–~50	0.05–2.0

* Choe and Gill (2001).

† Benoit et al. (1998).

‡ Present study.

§ Leermakers (2001).

lowest concentration (0.09 pmol L⁻¹) measured at midestuary. During the high flow season in March 2001, unfiltered MeHg concentrations were a factor of ~2 higher in the upper estuary than those observed during September–October 2000. However, it appeared that significant temporal changes occurred only in the upper estuary (salinity, <10). The unfiltered MeHg concentration at the extreme South Bay (Sta. 1) was markedly high compared with other regions with a similar salinity.

Particulate MeHg concentrations averaged 43 ± 18% of the MeHg in unfiltered water during September–October 2000 and 61 ± 12% during March 2001 (Fig. 1b). These values are significantly lower than those for particulate Hg, which constituted 88 ± 7% of total Hg throughout both sampling periods. The estuarine distribution pattern of particulate MeHg was similar to that of unfiltered MeHg. As was found for Hg (Choe et al. 2003), most MeHg (85%) was associated with particulate material in the extreme South Bay (Sta. 1). Average particulate MeHg concentrations normalized to SPM were not statistically different during both seasons (e.g., 4.2 ± 3.3 nmol kg⁻¹ during the fall and 5.2 ± 2.6 nmol kg⁻¹ during the spring, *p* > 0.3). In general, a maximum concentration of particulate MeHg (in nmol kg⁻¹) in San Francisco Bay was significantly higher than that observed in Galveston Bay but lower than that in Scheldt estuary (Table 1).

The estuarine distribution of filter-passing MeHg was similar to that of unfiltered MeHg (Fig. 1c). The highest concentration was observed in the river water end-member during both cruises (0.19–0.40 pmol L⁻¹). The lowest concentration was measured in the seawater end-member during the spring (0.04 pmol L⁻¹) but midestuary during the fall (0.04 pmol L⁻¹). Filter-passing MeHg concentrations averaged 57 ± 18% of the total MeHg during the fall and 39 ± 12% during the spring, indicating that larger amounts of MeHg are transported in the particulate phase when the river flow and SPM concentrations are high. Overall, filter-passing MeHg concentrations in the San Francisco Bay estuary are similar to those determined in other U.S. estuaries but lower than those observed in the Scheldt estuary (Table 1).

A significant portion of the MeHg in the filter-passing fraction was colloiddally bound MeHg, with an average of 34 ± 11% during the fall and 56 ± 15% during the spring, with seasonal concentration variation only in the mid- to upper estuary. The distribution pattern of colloiddal MeHg was similar to those of unfiltered and filter-passing MeHg (Fig. 1d).

Dissolved MeHg (<1 kDa) showed a smaller seasonal change than the other size fractions, which suggests that the temporal variation of the filter-passing Hg found in low-salinity regions is mostly explained by the variation in the colloiddal Hg concentration. The consistency of the dissolved fraction with season and salinity was also observed for total Hg (Choe et al. 2003). Dissolved MeHg concentrations did not exceed 0.1 pmol L⁻¹ at most sampling sites, and the lowest concentrations were measured in a medium-salinity region during the fall (0.03 pmol L⁻¹) and a high-salinity region during the spring (0.01 pmol L⁻¹).

Discussion

Particulate MeHg—MeHg concentrations in both filtered and unfiltered waters were generally higher in March 2001 during the higher flow condition than in September–October 2000 (Fig. 1). This is consistent with other studies that reported higher MeHg concentrations in the water column of the Sacramento River and its tributaries during major flood events (Domagalski 1998, 2001). MeHg, however, does not always increase with flow rate in other estuarine environments (Lawson et al. 2001), when resuspension or erosion of bed sediment contributes mainly inorganic Hg but little MeHg.

Mercury methylation rates are generally greater during warmer seasons (Gilmour et al. 1998), because methylation processes are dominantly mediated by microbial activities (Gilmour et al. 1992). The average surface water temperature measured in the San Francisco Bay and Delta regions was ~22°C during the fall cruise and ~11°C during the spring cruise. Our recent direct measurements also showed that MeHg concentrations in sediment pore waters and the benthic transport of MeHg from sediments to overlying water were greater during warm seasons (Choe 2002). Because sediment-water exchange can influence the overlying water concentrations in shallow environments, higher MeHg concentrations in overlying water have been more often observed during warm than cold seasons (Hurley et al. 1995; Leermakers et al. 2001). Nevertheless, MeHg concentrations in the San Francisco Bay estuary were generally higher in March. This result suggests that estuarine MeHg concentrations are dependent not only on MeHg production rates in sediments but also on the mobilization of MeHg during flood events (Domagalski 1998).

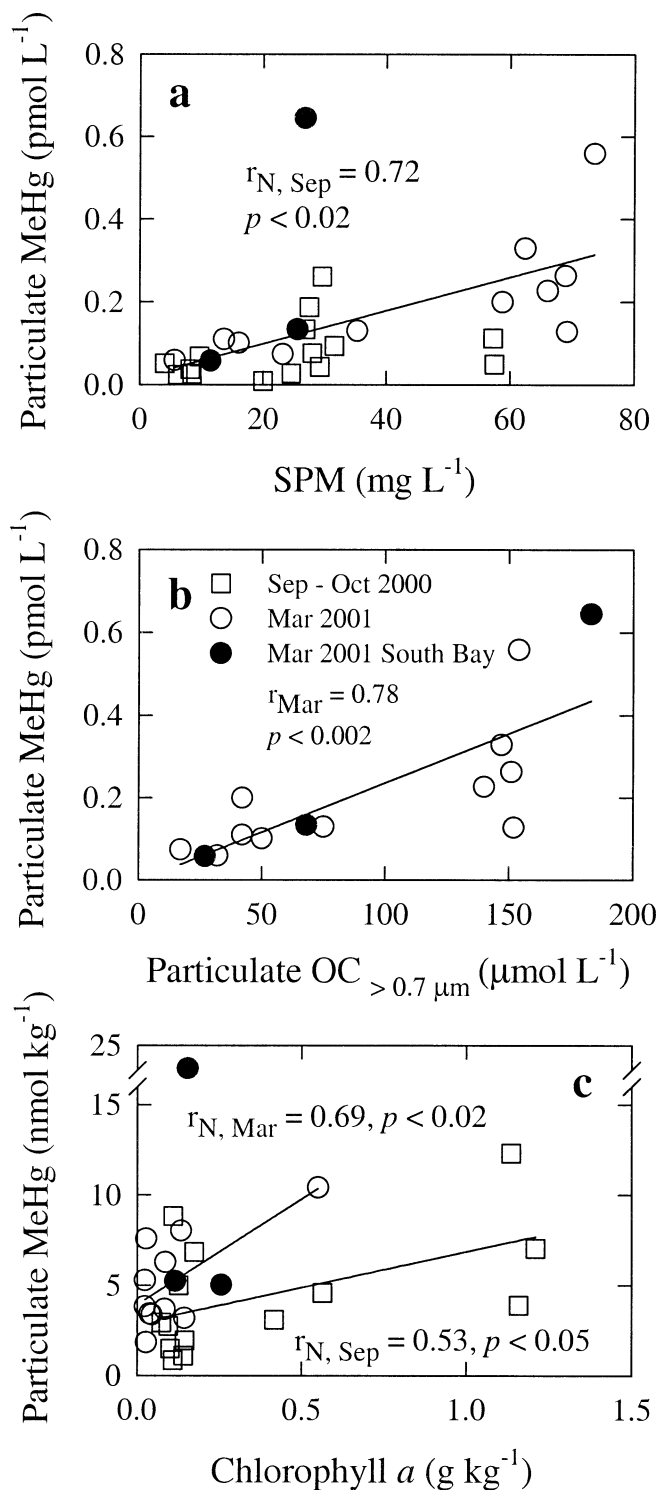


Fig. 2. The relationship between MeHg and particulate material in September–October 2000 and March 2001. $r_{N, \text{Sep}}$ and $r_{N, \text{Mar}}$ represent the correlation coefficients for the northern reach in September–October 2000 and March 2001, respectively and r_{Mar} for the entire bay in March 2001.

The relationship between particulate MeHg and SPM or particulate OC is plotted in Fig. 2. Correlations between particulate MeHg and SPM were not as significant as those observed between Hg and SPM, varying from weak ($r = 0.31$, $p < 0.3$) in the fall to significant ($r = 0.72$, $p < 0.05$) in the spring (Fig. 2a). The interaction between particulate MeHg and SPM appeared to vary seasonally in the northern reach. During the high flow period, the river was the dominant source of both SPM and particulate MeHg (Fig. 1), leading to a strong correlation between SPM and MeHg. In contrast, during the low flow condition, the river was still the dominant source of particulate MeHg, but the resuspension of sediments that are relatively poor in MeHg was a significant source of SPM in the midestuary, possibly resulting in a weak correlation.

A poor correlation was observed between MeHg and SPM in the South Bay. Although there are only three data points, particulate MeHg was correlated with particulate OC in the South Bay, which suggests that particulate OC in the South Bay may be important in MeHg cycling (Fig. 2b). This relationship was also observed for Hg in the South Bay. In the northern reach, significant correlations were observed between particulate MeHg and chlorophyll a during both sampling periods (Fig. 2c), as has been reported in other estuarine systems (Coquery et al. 1995, 1997), possibly because of the biological uptake of MeHg (Mason et al. 1996).

A correlation that was observed between the percentage of particulate Hg and SPM (Choe et al. 2003) appeared to be negligible for MeHg (no figure shown). The percentage of particulate MeHg was weakly correlated with SPM concentration in September–October 2000 ($r = 0.41$, $p < 0.2$) but was relatively constant ($63 \pm 11\%$) under the high flow condition, independent of the SPM concentration. Overall, these results show that bulk SPM is not the dominant parameter that governs the geochemical cycling of MeHg in the San Francisco Bay estuary.

Filter-passing, colloidal, and dissolved MeHg—For both estuarine transects, there was a strong correlation between ($r = 0.95$, $p < 0.001$) unfiltered and filter-passing MeHg concentrations in the northern reach (Fig. 3a). This is particularly noteworthy because a correlation existed between filter-passing and unfiltered Hg only during September–October 2000. A strong correlation ($r = 0.96$, $p < 0.001$) was also observed between colloidal and filter-passing MeHg (Fig. 3b). In the northern reach, the filter-passing : unfiltered MeHg concentration ratio averaged 0.50 ± 0.17 , and the colloidal : filter-passing MeHg concentration ratio averaged 0.46 ± 0.18 . Because these concentration ratios are fairly constant, it is possible to estimate both the filter-passing and colloidal MeHg concentrations using unfiltered MeHg concentrations and the ratios observed. These strong correlations suggest that concentration ratios among particulate, filter-passing, and colloidal MeHg are set at the river water end-member and are independent of changes in water chemistry across the salinity gradient. A second possibility is that processes controlling partitioning between particulate, colloidal, and dissolved MeHg are kinetically fast (e.g., shorter than the freshwater flushing time).

The correlations of MeHg with OC during the filter-pass-

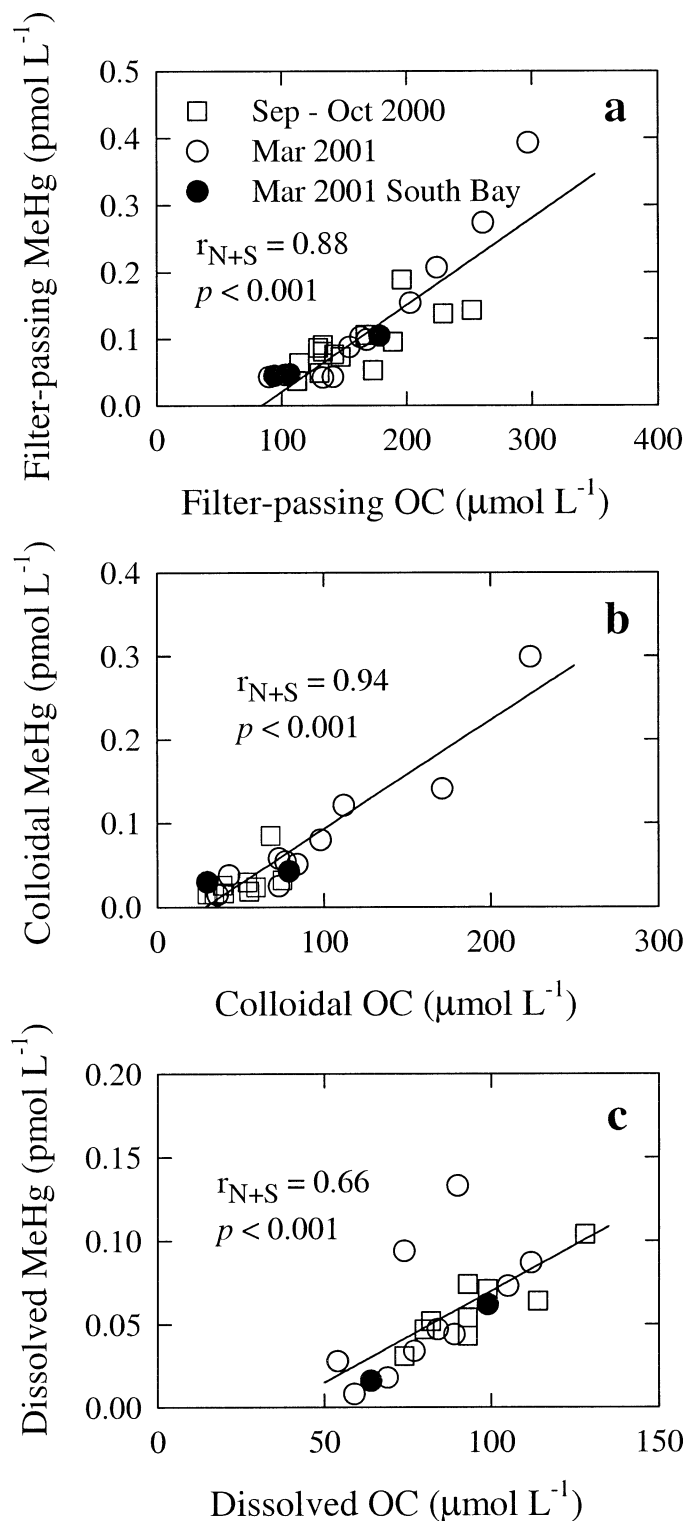
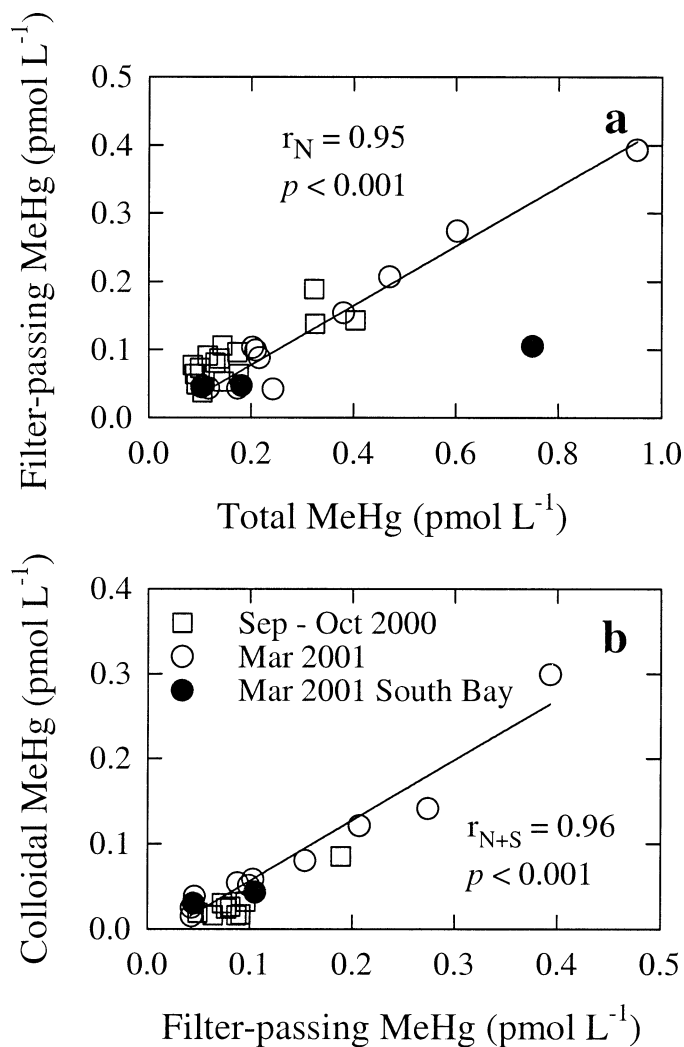


Fig. 3. Correlations between (a) unfiltered and filter-passing and (b) filter-passing and colloidal MeHg in September–October 2000 and March 2001. r_N and r_{N+S} represent the correlation coefficients in the northern reach and in the entire bay, respectively, during both sampling periods.

ing, colloidal, and dissolved phases are plotted in Fig. 4. Filter-passing Hg was correlated with OC only under the high flow condition (Choe et al. 2003), but MeHg was highly correlated with OC during both seasons and in all phases (i.e., filter-passing, colloidal, and dissolved). These results confirm that the processes that control the OC concentration also influence the MeHg cycling in the San Francisco Bay estuary. The importance of organic association was also observed for other trace metals in the study area: Al, Fe, Cu, and Mn in the northern reach (Sanudo-Wilhelmy et al. 1996) and Cu and Zn in the South Bay (Kuwabara et al. 1989). The y-intercepts of the regression line for MeHg–OC plots are highly deviated from zero (Fig. 4). These observations imply that only a fraction of the organic matter rather than bulk OC controls MeHg concentration in each fraction.

Covariance has been observed between trace metals (Cu, Ni, Cd, Zn, and Co) and nutrient (phosphate and nitrate) concentrations in San Francisco Bay (Flegal et al. 1991).

Fig. 4. Correlations between MeHg and organic carbon in filter-passing ($<0.45 \mu\text{m}$), colloidal, and dissolved ($<1 \text{ kDa}$) fractions in September–October 2000 and March 2001. r_{N+S} refers to the correlation coefficient for all data.

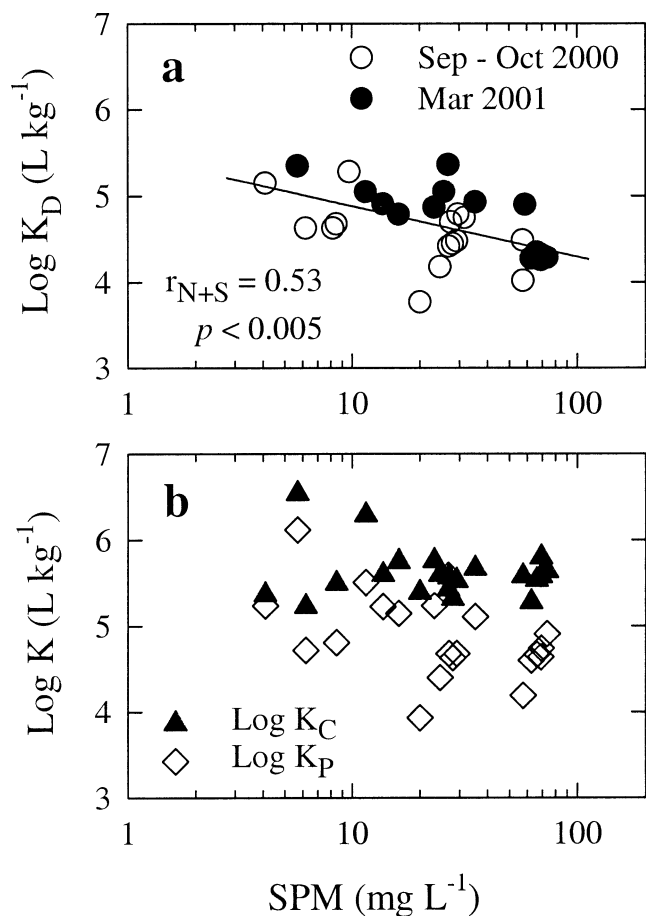


Fig. 5. Particle-water partition coefficients of MeHg as a function of SPM.

These correlations suggest that trace metals and nutrients have similar natural and anthropogenic processes. In the present study, however, MeHg did not covary with any nutrients ($r = 0.17$ for nitrate, $r = 0.11$ for ammonium, and $r = -0.26$ for phosphate).

Particle-water partition coefficients—Three forms of the particle-water partition coefficient, K_D , K_p , and K_C (see definitions given in Choe et al. 2003) were calculated to investigate the partitioning of MeHg among the particulate, colloidal, and solution phases. Figure 5 shows the partition coefficients of MeHg as a function of SPM. As noted for Hg (Choe et al. 2003), traditional partition coefficients (K_D)

reveal a particle concentration effect (Fig. 5a) that is possibly due to the inclusion of colloidal MeHg in the filter-passing fraction. The partition coefficient between the colloidal and the dissolved phase (K_C) is independent of particle concentration, whereas the partition coefficient between the filter-retained particulate and the dissolved fraction (K_p) is still influenced by particle concentration.

The average particle-water partition coefficients are listed in Table 2 for the two sampling periods. In both seasons, the average $\log K_C$ values (5.45 ± 0.13 in the fall and 5.74 ± 0.35 in the spring) were significantly ($p < 0.001$, one-way analysis of variance) greater than the average $\log K_p$ values (4.59 ± 0.38 in the fall and 5.13 ± 0.46 in the spring) and $\log K_D$ values (4.66 ± 0.40 , $n = 29$). The average $\log K_p$ for MeHg (4.90 ± 0.50) was significantly lower than that for Hg (5.85 ± 0.22), but the average $\log K_C$ for MeHg (5.62 ± 0.31) was similar to that of Hg (5.63 ± 0.26) (Table 2). These results suggest that colloidal abundance is more important than SPM abundance in influencing MeHg cycling and transport in the San Francisco Bay estuary. Additionally, colloids have a similar binding capability with Hg and MeHg, whereas suspended solids have a greater binding capacity with Hg. There is a paucity of literature data, but average $\log K_D$, $\log K_p$, and $\log K_C$ values during the low flow period in San Francisco Bay were comparable with those observed in Galveston Bay and Florida Everglades (Table 2). During the high flow season, however, values from San Francisco Bay were slightly greater (for K_D and K_p) or significantly greater (for K_C) than those from the other areas. Lower $\log K_C$ values observed in Midwestern U.S. rivers may be attributed to larger nominal MW cutoff (10 kDa) of the membrane used for the isolation of colloidal MeHg.

A positive correlation was observed between the K_D of MeHg and salinity during the high flow season ($r = 0.85$, $p < 0.001$) (Fig. 6). A similar relationship was observed for K_D and K_p with Hg (Choe et al. 2003). The low K_p (and K_D) values in the upper estuary may be attributed to a decrease in surface area and surface complexation sites for MeHg as the suspended particle size becomes larger under high hydraulic energy (Benoit 1995).

Sources of MeHg—The MeHg:Hg concentration ratio (percentage of MeHg) in surface water of the estuary was determined as a function of salinity for unfiltered, filter-passing, colloidal, and dissolved fractions, to demonstrate the source of MeHg (Fig. 7). Because Hg is the substrate for MeHg production processes, one may anticipate the per-

Table 2. Particle-water partition coefficients of MeHg in natural waters.

System	$\log K_D$	$\log K_p$	$\log K_C$	Reference
Galveston Bay	4.57 ± 0.21 ($n=3$)	4.83 ± 0.25 ($n=3$)	5.20 ± 0.20 ($n=3$)	Choe and Gill (2001)
Florida Everglades*	4.14 ($n=2$)	4.46 ($n=2$)	5.12 ± 0.16 ($n=4$)	Cai et al. (1999)
Midwestern U.S. Rivers†	4.79 ± 0.50 ($n=14$)	5.11 ± 0.48 ($n=14$)	4.90 ± 0.40 ($n=15$)	Babiarz et al. (2001)
San Francisco Bay (low flow)‡	4.56 ± 0.39 ($n=15$)	4.59 ± 0.38 ($n=9$)	5.45 ± 0.13 ($n=9$)	Present study
San Francisco Bay (high flow)‡	4.77 ± 0.39 ($n=14$)	5.13 ± 0.46 ($n=12$)	5.74 ± 0.35 ($n=12$)	Present study

* A nominal molecular weight cutoff of 3 kDa was used.

† A nominal molecular weight cutoff of 10 kDa was used.

‡ For K_C , total colloid concentrations were estimated as 2.7 times colloidal OC concentrations (Guo and Santschi 1997).

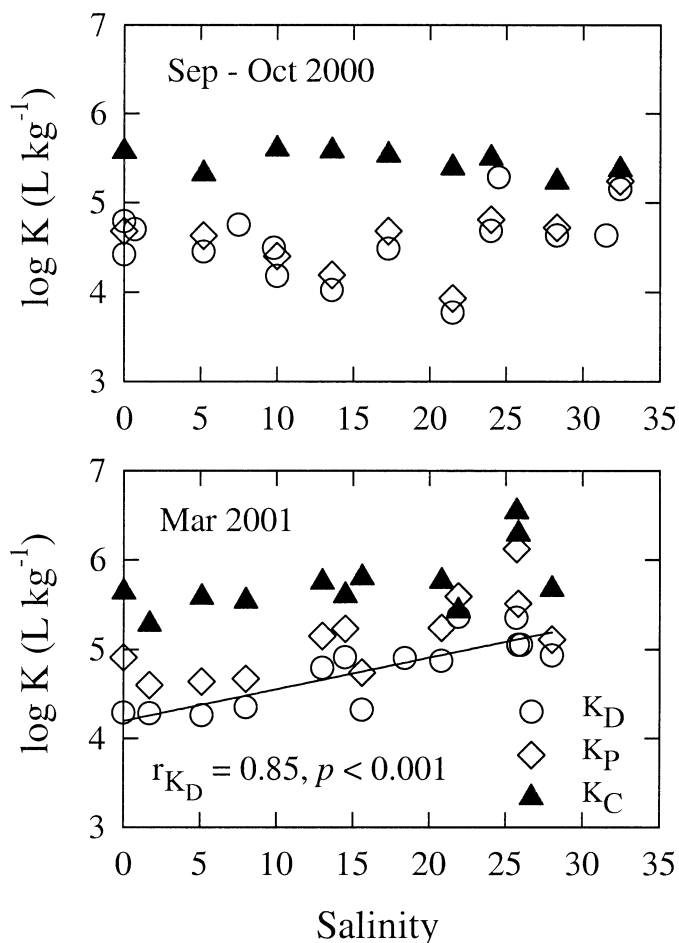


Fig. 6. Particle-water partition coefficients of MeHg as a function of salinity. The lower panel includes the South Bay data.

centage of MeHg to be high in a region where significant MeHg production takes place (Gill et al. 1999; Leermakers et al. 2001). Similarly, Bloom et al. (1999) used the percentage of MeHg in sediments to evaluate the seasonal variation of Hg methylation.

Seasonal variations were observed in the percentage of MeHg (Fig. 7), with higher ratios occurring when the river flow was low and the water temperature was high in the fall. This result suggests that more MeHg was produced during the warm season, even though water-column MeHg concentrations were higher during the spring. During the fall of 2000, the percentage of MeHg averaged $0.7 \pm 0.6\%$, $3.0 \pm 2.3\%$, and $3.0 \pm 1.7\%$ in unfiltered, colloidal, and dissolved fractions, respectively. Lower MeHg:Hg ratios observed in unfiltered water compared with those in the colloidal and dissolved fractions are consistent with high particulate Hg concentrations, as discussed in Choe et al. (2003). The percentage of MeHg was highest in the Sacramento River, with 5.7% in the colloidal fraction and 9.1% in the dissolved fraction. All phases dropped to a minimum value in midestuarine regions. These observations suggest that riverborne MeHg is a major source of the MeHg introduced to the San Francisco Bay estuary.

During the March 2001 sampling period, the percentage

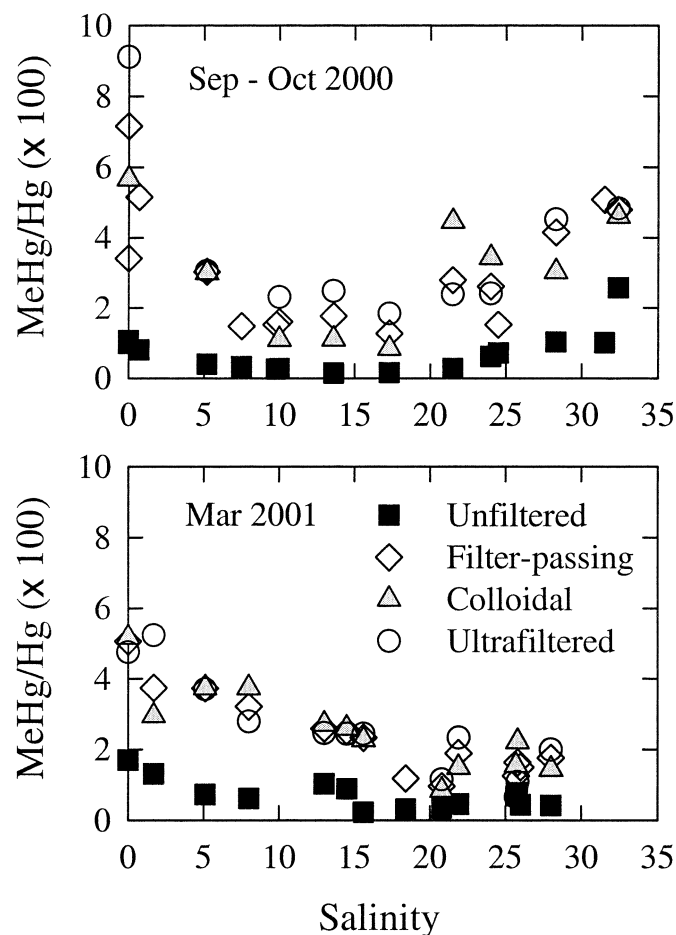


Fig. 7. MeHg:Hg concentration ratio (%) in surface water of the San Francisco Bay estuary (both the northern reach and South Bay).

of MeHg was highest in the river water end-member, and the ratio nonconservatively decreased with increasing salinity. Similar to the results in September–October 2000, the ratio was lowest in unfiltered water, with an average of $0.7 \pm 0.4\%$. The MeHg:Hg concentration ratios in the colloidal ($2.6 \pm 1.4\%$) and dissolved ($2.6 \pm 1.2\%$) fractions were lower than those in the fall. A lower percentage of MeHg during winter has been reported in other estuaries (Leermakers et al. 2001). There was no elevated percentage of MeHg found in the lower estuary during March 2001, possibly because of the dilution by low MeHg content estuarine water under extremely high flow condition.

A striking feature observed under the low flow condition is that the percentage of MeHg increased with increasing salinity in the lower estuary. Furthermore, the percentage of MeHg in the unfiltered fraction was highest at the Golden Gate Bridge (2.6%). Several hypotheses could explain the high percentage of MeHg in the lower estuary. First, seasonal upwelling may elevate MeHg distribution in the lower estuary. The peak of California coastal upwelling occurs around June (Robinson 1981). Previous studies have demonstrated that cadmium (Flegal et al. 1991) and nitrate (Peterson et al. 1985) in San Francisco Bay were influenced by

Table 3. Monomethyl mercury flux estimates in the northern reach of San Francisco Bay, determined from estuarine geochemical modeling.

	C_o ($\mu\text{mol L}^{-1}$)	C_s ($\mu\text{mol L}^{-1}$)	F_r	F_i	F_e
Sep–Oct 2000 (river flow = 3.0×10^{10} L d ⁻¹) (mmol d ⁻¹)					
Particulate MeHg	0.13	—	3.9	—	—
Filter-passing MeHg	0.19	0.00	5.7	-5.7	0.0
Colloidal MeHg	0.09	0.02	2.7	-2.1	0.6
Dissolved MeHg	0.10	-0.02	3.0	-3.6	-0.6
Mar 2001 (river flow = 7.7×10^{10} L d ⁻¹) (mmol d ⁻¹)					
Particulate MeHg	0.56	—	43	—	—
Filter-passing MeHg	0.40	0.11	30	-22	8.5
Colloidal MeHg	0.30	0.08	23	-17	6.2
Dissolved MeHg*	0.09	—	6.9	-4.6	2.3
Annual flux (mol yr ⁻¹ and g Hg yr ⁻¹)†					
Particulate MeHg			3.0 (600)	—	—
Filter-passing MeHg			3.5 (700)	-3.0 (-600)	0.5 (100)
Colloidal MeHg			2.2 (440)	-1.6 (-320)	0.6 (120)
Dissolved MeHg*			1.3 (260)	-1.4 (-280)	-0.1 (20)

C_o and C_s are the actual and hypothetical MeHg concentrations in the Sacramento River end-member, respectively. F_r and F_e refer to the Hg flux into and out of the estuary. A negative F_i value represents a net internal sink, whereas a positive F_i value indicates a net internal source within the estuary.

* Dissolved MeHg fluxes were calculated by the difference between filter-passing and colloidal MeHg fluxes.

† Fluxes in parentheses are in g Hg yr⁻¹.

seasonal upwelling. However, no evidence is currently available to test this hypothesis for MeHg. Nitrate and phosphate concentrations (no data shown) were not elevated at the seawater end-member or correlated with MeHg in the lower estuary during the fall sampling period. No direct measurement of MeHg is available in California coastal water, making it difficult to test this hypothesis. A second possibility could be that MeHg is elevated in the South Bay and influences the seawater end-member concentration when South Bay water mixes with the main estuarine water. Unfortunately, no samples were collected from the South Bay during September–October 2000. The South Bay may be a major source of MeHg because the local streams (e.g., Guadalupe River) emptying into the South Bay have a historic Hg mine (e.g., New Almaden mine) in their drainage basin. However, these freshwater sources are not significant enough to transport particulate MeHg to the Golden Gate Bridge. Even during spring, when the river flow was high, very low MeHg concentrations and MeHg:Hg ratios were observed at the two sampling sites in the South Bay (1.5–1.6% in the filter-passing fraction). A third possibility is that municipal and industrial waste discharge from the Oakland–San Francisco metropolitan area is influencing MeHg to Hg concentration factors. Effluents could be elevated in MeHg compared with Hg, or the Hg released could be highly bioavailable and served as the substrate for in situ Hg methylation processes in the Central Bay. Ammonium concentrations measured at the Golden Gate Bridge ($3.2 \mu\text{mol L}^{-1}$) and Angel/Treasure Island ($5.1 \mu\text{mol L}^{-1}$) were significantly higher than the concentrations found in other stations ($1.8 \pm 0.6 \mu\text{mol L}^{-1}$), which probably implies the evidence of waste discharge in the lower estuary. Further study will be needed to elucidate the source of MeHg in the lower estuary during low flow periods.

Estuarine fluxes of MeHg—MeHg fluxes in the northern reach were estimated with a steady-state nonconservative estuarine mixing model (see description in Choe et al. 2003). As was pointed out by Officer and Lynch (1981), rapid temporal changes in riverine concentrations may cause inconsistencies between actual and apparent constituent-salinity profiles within the estuary. The filter-passing MeHg concentration in Sacramento River water in March 2001 was approximately twofold greater than that measured in September–October 2000, which suggests that the temporal riverine concentration variation could account for some of the observed nonconservative distribution for MeHg (Officer and Lynch 1981; Cifuentes et al. 1990). No time-series riverine MeHg data were measured in the present study. It seems plausible that the temporal variations of MeHg and Hg were similar because the ratio of filter-passing MeHg to filter-passing Hg concentrations in the river varied within a narrow range (5.1–7.2%). As a result, the influence of MeHg variation in the river may not be significant, because the influence of riverine Hg variation on Hg-salinity distributions was insignificant.

Estuarine flux modeling results for MeHg are summarized in Table 3. The riverine fluxes were calculated under the assumption that the Sacramento River is the dominant freshwater source. The estuarine flux of dissolved MeHg for March 2001 was estimated by the flux difference between filter-passing and colloidal MeHg. This alternate approach was necessary because the inconsistent distribution of dissolved MeHg near the seawater end-member makes it difficult to determine a hypothetical river water end-member concentration. The riverine MeHg fluxes in the particulate, colloidal, and dissolved fractions during the high flow condition were significantly greater than those under the low flow condition because of both higher river flow and higher

riverine MeHg concentrations. There was a midestuarine sink for all MeHg phases during both periods. More than 65% of the riverine colloidal and dissolved MeHg was removed during estuarine mixing in March 2001 and >80% in September–October 2000.

Flegal et al. (1991) investigated the estuarine biogeochemistry of several trace metals, including copper, nickel, cadmium, zinc, cobalt, and iron, in San Francisco Bay. They found that only iron was elevated in the river water end-member and was removed nonconservatively (>90%) at low salinities of the northern reach during both high and low flow conditions (April, August, and December 1989). Sando-Wilhelmy et al. (1996) conducted the first trace metal speciation study in San Francisco Bay. They reported that only iron, in both the colloidal (10 kDa–0.2 μm) and dissolved (<10 kDa) phases, was removed during estuarine mixing, with a maximum concentration in the river water end-member. Even though iron concentrations were not directly measured in the present study, these results imply that the removal of MeHg may be also coupled with iron removal in San Francisco Bay. There could also be other sinks of MeHg within the estuary, such as photodegradation. In a recent study, Sellers et al. (2001) showed that MeHg removal by photodegradation in Canadian lakes is greater than the loss through outflow. However, it is unclear whether photodegradation is an important loss mechanism of MeHg in an estuarine environment.

Annual estuarine MeHg fluxes were estimated using the flux data listed in Table 3. Approximately 60 d in winter were assumed to be the high flow condition and the rest of year as the low flow condition. The Sacramento River introduces 1.3 kg of MeHg annually to the estuary, of which 46% is particulate MeHg (600 g Hg yr⁻¹). This percentage of particulate MeHg is much lower than that of particulate Hg (90%). The annual riverine flux of filter-passing MeHg was 700 g Hg yr⁻¹, with a significant fraction (63%) associated with colloidal material. A significant portion of riverine colloidal (73%) and dissolved (108%) MeHg is removed during estuarine mixing. The fractions of MeHg in total Hg in the riverine flux were 0.6%, 5.5%, and 6.8% in the particulate, colloidal, and dissolved phases, respectively, which confirms that MeHg is preferentially associated with low-MW organic or inorganic ligands.

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