

## Distribution of particulate, colloidal, and dissolved mercury in San Francisco Bay estuary. 1. Total mercury

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### Abstract

Surface water samples were collected from the San Francisco Bay estuary in September–October 2000 (low flow) and March 2001 (high flow). Total mercury (Hg) concentrations were measured in unfiltered, filter-passing ( $<0.45 \mu\text{m}$ ), colloidal (1 kDa– $0.45 \mu\text{m}$ ), and dissolved ( $<1$  kDa) fractions. Particulate Hg was the dominant phase ( $88 \pm 7\%$ ,  $n = 29$ ) in unfiltered water. Suspended particulate matter (SPM) explained most particulate Hg concentrations in the northern reach. A significant portion of filter-passing Hg was associated with colloidal Hg, accounting for  $38 \pm 18\%$  ( $n = 9$ ) in the fall and  $57 \pm 10\%$  ( $n = 12$ ) in the spring. Seasonal variability of the filter-passing Hg concentration observed in the upper estuary was attributed to the temporal change in the riverine colloidal Hg. The strong correlation observed between Hg and organic carbon in the filter-passing fraction indicates that organic material is an important transport medium of Hg in San Francisco Bay. Assessment of various forms of the particle–water distribution coefficient revealed that Hg was preferentially associated with SPM during the low flow period but that colloidal material played as important a role in Hg phase speciation as SPM during the high flow condition. A steady-state nonconservative estuarine mixing model suggested that the northern reach had an internal source of colloidal Hg in September–October, possibly from resuspended sediments, and a sink of colloidal Hg within the estuary in March 2001.

Phase speciation (or size distribution) of trace metals is important to their bioavailability, toxicity, and fate in aquatic environments. For instance, many investigators have shown that only the solution-phase or free ion species are bioavailable to phytoplankton (Tessier and Turner 1995 and references therein). Colloids are operationally defined as inorganic or organic material in the size range of  $\sim 1$  nm to  $\sim 1 \mu\text{m}$ . Because of their short residence time (Baskaran et al. 1992; Moran and Buesseler 1992) and strong reactivity with trace metals (Honeyman and Santschi 1989), colloidal materials have been receiving considerable attention recently with respect to the biogeochemistry of trace metals in natural waters (Benoit et al. 1994; Dai and Martin 1995; Powell et al. 1996; Wen et al. 1999). In contrast to traditional approaches that have used conventional filters with pore sizes between 0.1 and  $1.0 \mu\text{m}$ , where colloid-sized macromolecules are included in the solution phase, cross-flow ultrafiltration techniques provide a great capability to isolate colloids and associated trace elements from the filter-passing fraction.

Numerous investigations have been conducted on total mercury (Hg) (inorganic Hg + monomethyl Hg) biogeo-

chemistry in estuaries. Mercury often exhibits nonconservative estuarine mixing behavior from various Hg sources and sinks (Cossa and Martin 1991; Guentzel et al. 1996; Stordal et al. 1996a; Benoit et al. 1998; Mason et al. 1999). Several studies have reported that a significant fraction of the filter-passing Hg ( $<0.45 \mu\text{m}$ ) is bound to colloidal material in estuarine environments (Guentzel et al. 1996; Stordal et al. 1996a).

Mercury contamination in the San Francisco Bay estuary and its tributaries has long been recognized as a serious concern. Water-column Hg concentrations often exceed the California state standard of  $12 \text{ ng Hg L}^{-1}$  (Domagalski 1998, 2001). Mercury accumulation in fish has been observed, and advisories on the consumption of certain species of fish have been issued in the bay (San Francisco Regional Water Quality Control Board 1995). The Sacramento and San Joaquin rivers have extensive Hg sources in their drainage basins. Large amounts of Hg had been mined in the California Coast Range and were used in Sierra Nevada gold mines to recover gold. Once released to the aquatic environment in soluble form, Hg is readily mobilized and can undergo a variety of complex biogeochemical processes: adsorption/desorption by colloids and suspended particles (Stordal et al. 1996b), methylation by microorganisms to produce monomethyl mercury (MeHg) (Gilmour et al. 1998), bioaccumulation, and biomagnification (Mason et al. 1996). Even though locations of Hg sources are known (Ganguli et al. 2000), little is understood about the speciation of Hg in the submicron fraction and its principal sources, sinks, and geochemical behavior within the San Francisco Bay estuary.

The present study reports the first Hg phase speciation measurements in the San Francisco Bay estuary. The major focus of this work is to characterize the size fractionation, distribution, transportation, and fate of Hg and to examine the importance of natural colloidal material on the speciation

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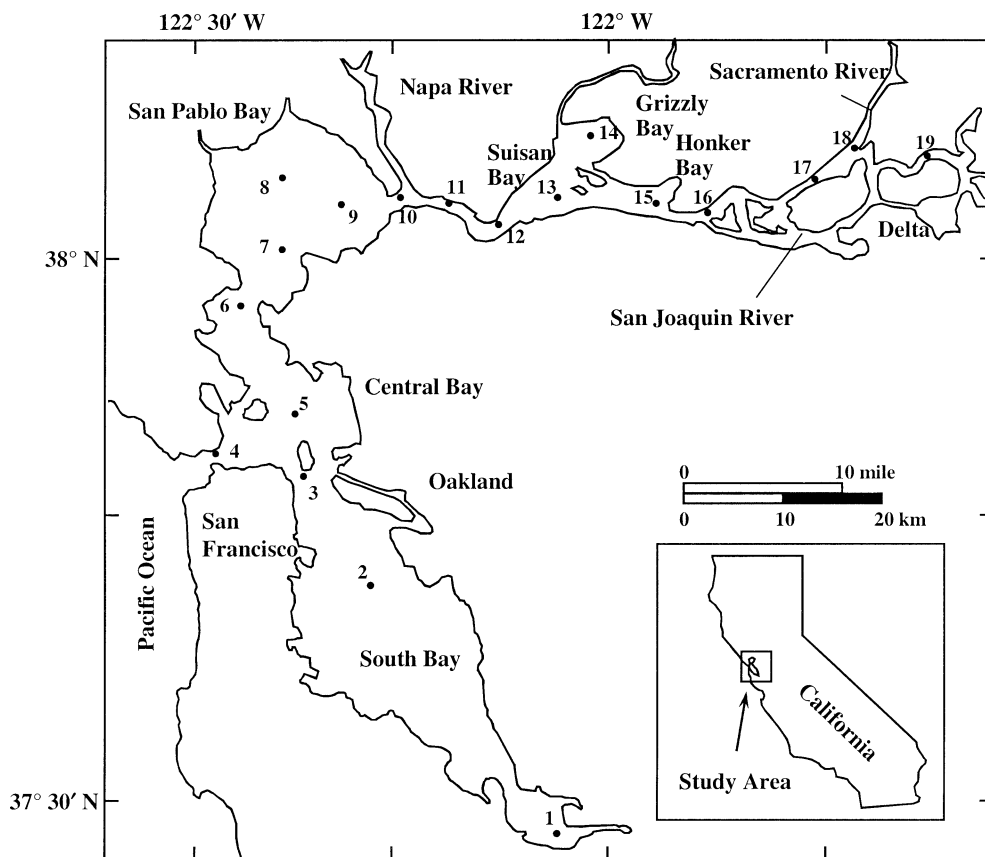


Fig. 1. The San Francisco Bay estuary and surface water sampling sites.

of Hg. The related study of MeHg is presented separately in this issue (Choe and Gill 2003).

## Materials and methods

**Operational definitions**—Particulate ( $>0.45 \mu\text{m}$ ) and filter-passing (or filtered) ( $<0.45 \mu\text{m}$ ) fractions are defined as the portion that is retained by or passes through a  $0.45\text{-}\mu\text{m}$  pore-size filter, respectively. Particulate concentrations were determined by the difference between unfiltered and filter-passing concentrations. Colloidal ( $1 \text{ kDa}$ – $0.45 \mu\text{m}$ ) and dissolved ( $<1 \text{ kDa}$ ) fractions refer to the filter-passing fraction that is retained by and passes through a  $1\text{-kDa}$  pore-size membrane, respectively. The colloidal Hg concentration was calculated by the difference between filter-passing and dissolved Hg concentrations.

**Study area**—San Francisco Bay is one of the largest estuarine systems in the Pacific coast. The average water depth is relatively shallow ( $\sim 6 \text{ m}$ ), and the surface area encompasses  $1,240 \text{ km}^2$ . In the present study, “the northern reach” is operationally defined as the upper estuary combining Central Bay, San Pablo Bay, Carquinez Strait, Suisan Bay, Grizzly Bay, Honker Bay, and the Delta area. “South Bay” refers to the southern reach only (Fig. 1). Two major freshwater sources (i.e., the Sacramento and San Joaquin rivers) enter the northern reach, joining at the Delta with numerous in-

terconnected waterways. The South Bay is a large lagoon with limited freshwater inputs.

The Sacramento River drains  $>80\%$  of the total freshwater feeding the estuary. In contrast, a large amount of freshwater is exported from the San Joaquin River for irrigation and municipal water supplies. The Sacramento River flow rate measured at Freeport near Sacramento, California, 1 July 2000–30 June 2001 ranged  $1,300\text{--}200 \text{ m}^3 \text{ s}^{-1}$ , with an average of  $450 \pm 170 \text{ m}^3 \text{ s}^{-1}$ . On the other hand, the San Joaquin River flow rate monitored at Vernalis near Tracy, California, ranged  $160\text{--}40 \text{ m}^3 \text{ s}^{-1}$ , with an average of  $70 \pm 30 \text{ m}^3 \text{ s}^{-1}$  during the same period (California Data Exchange Center, <http://cdec.water.ca.gov>). The highest flow rate occurred in February–April.

**Sample collection and ultrafiltration**—Surface water samples were collected on 29 September–3 October 2000 (low flow) from 15 sites in the northern reach and on 5–6 March 2001 (high flow) from 14 sampling sites covering the major geographic regions of the northern reach and the South Bay (Fig. 1 and Table 1). Surface water was drawn from  $\sim 50 \text{ cm}$  depth through acid-cleaned Teflon tubing with a peristaltic pump. The water was filtered with an acid-cleaned  $0.45\text{-}\mu\text{m}$  pore-size polypropylene cartridge filter directly into acid-cleaned Teflon bottles. The bottles were double-bagged using an inner bag that was cleaned with Micro-90 cleaning solution and stored on ice for transport to the laboratory.

Table 1. Sampling location and salinity in September–October 2000 and March 2001.

Sta. number	Sta. name	Location		Salinity	
		Latitude (N)	Longitude (W)	Sep–Oct 2000	Mar 2001
1	Extreme South Bay	37.467	122.062	—	<u>21.9</u>
2	Central South Bay	37.699	122.302	—	26.0
3	Bay Bridge	37.792	122.372	—	<u>25.8</u>
4	Golden Gate	37.916	122.477	<u>32.4</u>	<u>28.0</u>
5	Angel/Treasure Islands	37.852	122.386	31.5	<u>25.7</u>
6	San Pablo Strait (Richmond Bridge)	37.943	122.457	<u>28.3</u>	<u>20.8</u>
7	West San Pablo Bay	38.006	122.397	—	18.4
8	Central San Pablo Bay	38.074	122.399	24.5	—
9	East San Pablo Bay	38.045	122.336	<u>24.0</u>	<u>15.6</u>
10	Napa River Mouth (I-80 Bridge)	38.067	122.250	<u>21.5</u>	<u>14.5</u>
11	Carquinez Strait	38.059	122.197	<u>17.3</u>	<u>13.0</u>
12	Martinez (I-680 Bridge)	38.039	122.149	<u>13.6</u>	<u>8.0</u>
13	Suisan Bay	38.057	122.068	<u>10.0</u>	<u>5.1</u>
14	Grizzly Bay	38.125	122.031	9.8	—
15	Honker Bay	38.047	121.938	7.5	<u>1.7</u>
16	Pittsburg	38.041	121.882	<u>5.2</u>	<u>0.0</u>
17	Sacramento River (Sherman Is.)	38.086	121.743	0.7	—
18	Sacramento River (Rio Vista)	38.113	121.712	<u>0.0</u>	—
19	San Joaquin River	38.101	121.616	0.0	—

Sites with salinity underlined represent where ultrafiltration was conducted.

Mercury samples were acidified to pH < 2 with low-Hg content HCl and were refrigerated until analyzed. Ultrafiltration samples were stored in a refrigerator and processed within 10 h after collection.

Nine filtered samples were used for ultrafiltration during the September–October cruise and 12 samples in March 2001. The colloidal-size (1 kDa–0.45  $\mu\text{m}$ ) Hg was isolated using a compact cartridge with regenerated-cellulose membrane with a nominal molecular weight cutoff of 1,000 Da (Amicon model S1Y1). Ultrafiltration was carried out with  $\sim 2$  liters of sample and a concentration factor (CF, the initial volume/retentate volume) of  $\sim 15$  was used throughout the present study. Additional details on membrane cleaning and ultrafiltration protocol are reported in Choe and Gill (2001). The average procedural blanks for Hg are 0.1 pmol L<sup>-1</sup> in permeate and 0.015 pmol L<sup>-1</sup> in retentate solution and 1  $\mu\text{mol L}^{-1}$  in both permeate and retentate solution for organic carbon (OC).

**Membrane calibration**—Membranes used for the study were “calibrated” with vitamin B-12 (molecular weight [MW], 1,350) and rhodamine 6G (MW = 480) before use (Table 2). The average retention coefficients ( $R_c$ , the ratio of retentate concentration to initial concentration) of rhodamine 6G and vitamin B-12 were 0.22 ( $n = 2$ ) and  $0.81 \pm 0.02$  ( $n = 5$ ), respectively. For vitamin B-12, the  $R_c$  values for both membranes were close, indicating both membranes had the same effective pore sizes. The retention coefficient of rhodamine 6G in deionized water was lower than that in seawater, whereas the  $R_c$  of vitamin B-12 did not vary with matrix. This implies that the ionic strength of a sample may affect the performance of the ultrafiltration, especially for low-molecular-weight organic macromolecules. The calibration was conducted in September 2000 and February 2001.

No significant temporal change in  $R_c$  was observed, which indicates that the membranes did not undergo any serious deformation between two sampling periods.

**Mass balance**—Colloidal concentrations were determined and mass balance recovery was evaluated as a quality control check of the ultrafiltration procedures using

$$\begin{aligned} & [\text{colloidal}]_{\text{measured}} \\ &= \frac{[\text{retentate}] - [\text{permeate}]}{CF} + \frac{[\text{wash}] - [\text{permeate}]}{CF_w} \\ & \text{mass balance (\%)} \\ &= \frac{[\text{dissolved}] + [\text{colloidal}]_{\text{measured}}}{[\text{filter-passing}]} \times 100 \end{aligned}$$

where  $CF_w$  is the ratio of the initial ultrafiltration volume to the wash volume. The mass balance recovery averaged  $94 \pm 15\%$  ( $n = 21$ ),  $99 \pm 8\%$  ( $n = 21$ ),  $102 \pm 1\%$  ( $n = 5$ ), and 89% for Hg, OC, vitamin B-12, and rhodamine 6G, respectively, which suggests that a portion of the Hg and rhodamine 6G sorbed onto the membrane was not recovered.

**Analyses of Hg and ancillary parameters**—Mercury measurements in the present work represent total Hg measurements, which includes the inorganic Hg (II) and monomethyl mercury forms. For Hg analysis, samples were digested by ultraviolet (UV) irradiation (8 lamps of 15 W each) for >12 h. Mercury concentrations were measured using aqueous-phase reduction with sodium borohydride, trapping onto a gold-coated quartz column, thermal desorption, and detection by cold-vapor atomic fluorescence spectrometry (Stordal et al. 1996a). The detection limit was 0.1 pmol L<sup>-1</sup>, and

Table 2. Retention coefficients of organic macromolecules by 1-kDa membranes.

Organic macromolecule	Average molecular weight	Matrix solution	Retention coefficient*	Initial concentration ( $\mu\text{mol L}^{-1}$ )	CF	Mass balance (%)	Membrane	Date
Rhodamine 6G	480	DI water	0.16	0.094	15.2	90	1	Sep 2000
Rhodamine 6G	480	Seawater	0.27	0.072	15.3	88	2	Sep 2000
Vitamin B-12	1,350	DI water	0.82	0.53	14.1	102	1	Sep 2000
Vitamin B-12	1,350	DI water	0.83	0.53	15.4	101	2	Sep 2000
Vitamin B-12	1,350	Seawater	0.80	0.71	14.9	101	1	Sep 2000
Vitamin B-12	1,350	DI water	0.79	0.42	14.9	101	1	Feb 2001
Vitamin B-12	1,350	DI water	0.82	0.43	15.8	103	2	Feb 2001

\* Retention coefficient =  $1 - [\text{permeate}]/[\text{initial}]$ .

analytical precision was <5%. OC concentrations in filter-passing, permeate, retentate, and wash solutions were measured by a high-temperature combustion method (Guo et al. 2000), particulate OC by a Perkin Elmer CHN analyzer, and rhodamine 6G and vitamin B-12 by a UV/visible spectrophotometer.

## Results

*Suspended particulate matter (SPM) and OC*—The estuarine concentrations of SPM were generally higher in March 2001 than in September–October 2000 (Fig. 2a). A maximum SPM concentration was observed in a midestuarine region (salinity,  $\sim 14$ ) in September–October 2000 but in the river water end-member in March 2001. Particulate matter concentrations in the South Bay were comparable to those found in the northern reach sites with similar salinities (i.e., salinity, 21–26).

The estuarine transect profiles of particulate, filter-passing, colloidal, and dissolved OC concentrations are given in Fig. 2b–f. Particulate OC measurements were conducted only in March 2001 (Fig. 2b). The particulate OC distribution in the northern reach agreed well with the SPM distribution ( $r = 0.86$ ). In the northern reach, particulate OC was highest in the Sacramento River water, decreased to a minimal value at salinities of  $\sim 20$ , and then slightly increased near the Golden Gate. The extreme South Bay (Sta. 1) had the highest particulate OC concentration. Filter-passing OC in September–October 2000 revealed nonconservative estuarine mixing behavior, with higher concentrations in river waters and the Golden Gate. In contrast, it decreased nearly conservatively with increasing salinity in March 2001 (Fig. 2c). Seasonal variation in the filter-passing fraction was not significant. The greatest temporal change was observed in the colloidal fraction (1 kDa– $0.45 \mu\text{m}$ ) (Fig. 2d). During the high flow condition, colloidal OC was the dominant species, constituting 32%–75% of the filter-passing OC pool, and a significant concentration gradient was observed across the salinity gradient (Fig. 2f). During the low flow condition, colloidal OC concentrations as a percentage in the filter-passing phase, as well as its absolute concentrations, were lower than those measured in March 2001. The colloidal OC constitutes only 35% even in the river water end-member. In addition, there was a minor concentration gradient across the estuary. The dissolved OC concentration did not vary significantly either across the salinity gradient or with season (Fig. 2e). Overall, these results suggest that temporal variation of the filter-passing OC in the estuary is mainly explained by the colloidal OC and that riverine input is an important source of the colloidal OC during the high flow condition.

*Hg distributions*—Estuarine Hg concentrations for September–October 2000 and March 2001 are plotted in Fig. 3. During both low and high flow conditions, total Hg concentrations in unfiltered water were  $\sim 50 \text{ pmol L}^{-1}$  in the river water end-member, increased to  $\sim 100 \text{ pmol L}^{-1}$  in the midestuarine region around a salinity of 15, and dropped to  $< 20 \text{ pmol L}^{-1}$  at higher salinities (Fig. 3a). These values measured in river water end-members were consistent with those



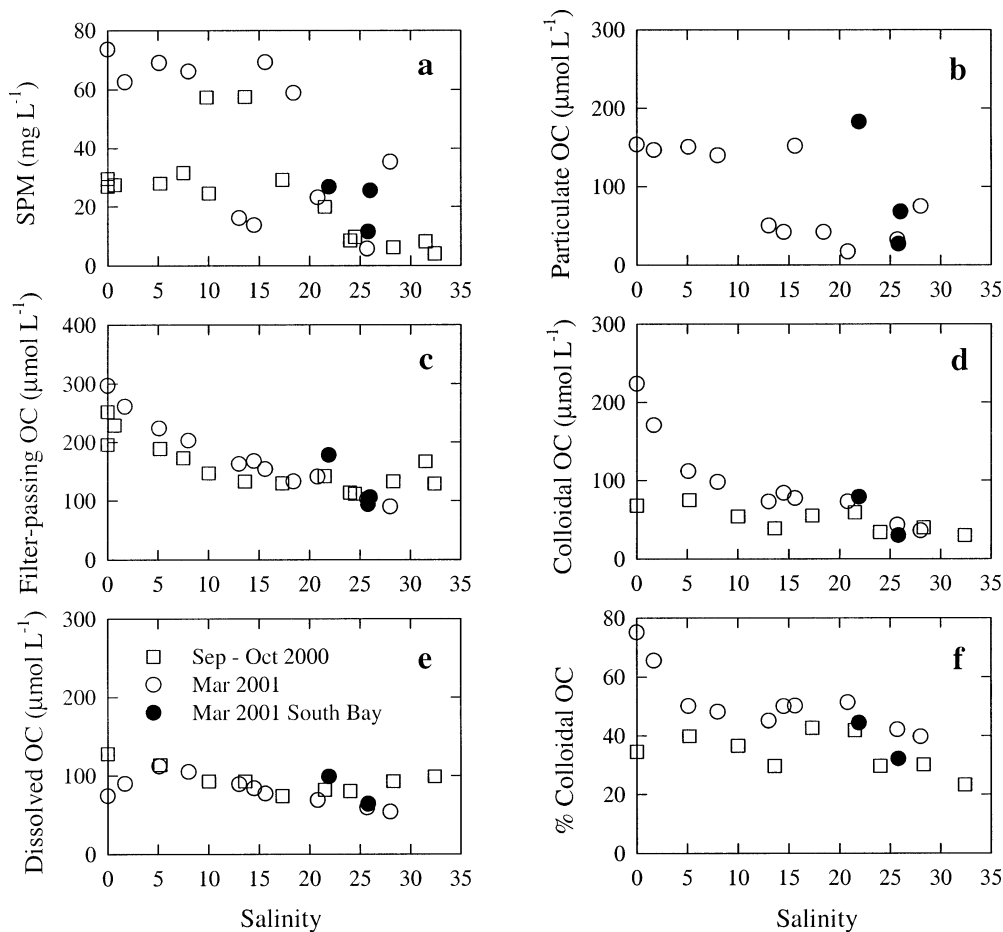


Fig. 2. SPM and OC distributions as a function of salinity. (a) SPM ( $>0.45 \mu\text{m}$ ), (b) particulate ( $>0.7 \mu\text{m}$ ), (c) filter-passing ( $<0.45 \mu\text{m}$ ), (d) colloidal (1 kDa– $0.45 \mu\text{m}$ ), (e) dissolved ( $<1 \text{ kDa}$ ) OC, and (f) percentage of colloidal OC in the filter-passing fraction.

reported in studies by Domagalski (1998, 2001). The seasonal variation in unfiltered Hg distribution was not significant. The highest total Hg concentration ( $163 \text{ pmol L}^{-1}$ ) was found in the extreme South Bay (Sta. 1) in March, which suggests that large amounts of Hg are being transported by local streams draining an inactive mercury mine area, such as the New Almaden mercury mine. Particulate Hg averaged  $88 \pm 7\%$  ( $n = 29$ ) of the Hg in unfiltered samples, and particulate Hg distributions were similar to those for total Hg (Fig. 3b). Particulate Hg concentrations normalized to SPM ranged  $0.60\text{--}2.0 \mu\text{mol kg}^{-1}$  in the northern reach and  $0.90\text{--}5.9 \mu\text{mol kg}^{-1}$  in the South Bay (Table 3). These are significantly higher than those determined in Galveston Bay but are similar to or lower than those reported in European estuaries.

Filter-passing Hg ranged  $1.8\text{--}4.6 \text{ pmol L}^{-1}$  in September–October 2000 and  $2.5\text{--}7.8 \text{ pmol L}^{-1}$  in March 2001, averaging  $12 \pm 7\%$  of the unfiltered Hg (Fig. 3c). These concentration ranges are generally comparable with those observed in the Galveston Bay, Patuxent, Loire, and Seine estuaries but are slightly lower than those determined in the Ochlockonee, Rhone, and Scheldt estuaries (Table 3). The filter-passing Hg distribution in the fall was consistent with

that of unfiltered Hg. There was a source of Hg at salinities between 10 and 15. The filter-passing Hg distribution in the spring was not consistent with the unfiltered Hg distribution, with the highest concentration in the Sacramento River. A local introduction of Hg was observed in the west San Pablo Bay (salinity, 20–25). Total Hg introduced into the extreme South Bay (Sta. 1) was mostly in the particulate phase, and the filter-passing Hg concentration constituted only 3% of the unfiltered fraction.

Colloidal Hg (1 kDa– $0.45 \mu\text{m}$ ) as a percentage of the filter-passing Hg (% colloidal Hg), which was estimated by the difference between filter-passing and dissolved concentrations, was higher in low-salinity regions and under the high flow condition. The % colloidal Hg averaged  $38 \pm 18\%$  ( $n = 9$ ) of the filter-passing Hg pool in the fall and  $57 \pm 10\%$  ( $n = 12$ ) in the spring. Dissolved Hg ( $<1 \text{ kDa}$ ) represented 25%–81% of the filter-passing concentration (Fig. 3f). This phase did not show a significant concentration change with salinity or season, which indicates that seasonal variation in the filter-passing Hg observed in the upper estuary is mostly explained by the seasonal variation in the colloidal Hg.

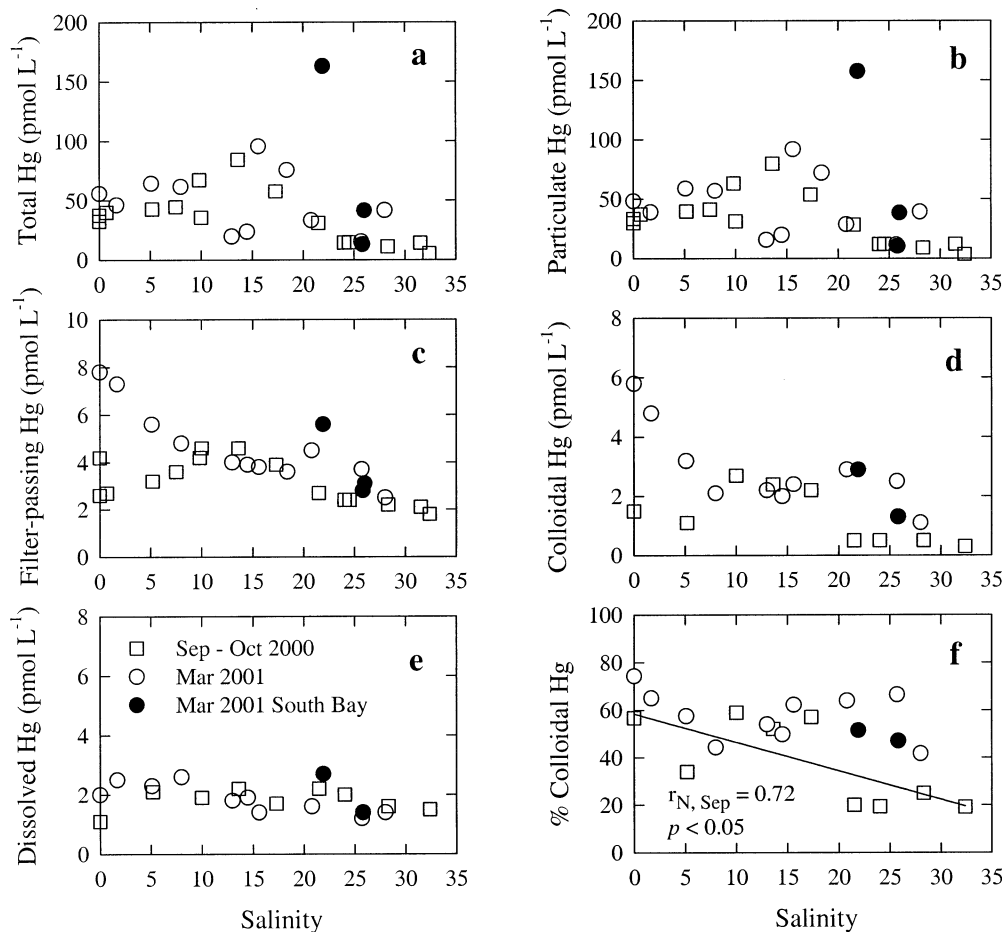


Fig. 3. Mercury distributions as a function of salinity. (a) Total, (b) particulate ( $>0.45 \mu\text{m}$ ), (c) filter-passing ( $<0.45 \mu\text{m}$ ), (d) colloidal (1 kDa– $0.45 \mu\text{m}$ ), (e) dissolved ( $<1 \text{ kDa}$ ) Hg, and (f) percentage of colloidal Hg in the filter-passing fraction.  $r_{N, \text{Sep}}$  represents the correlation coefficient for the northern reach data in September–October 2000.

Table 3. Comparison of particulate and filter-passing Hg concentrations in estuarine environments.

Location	Salinity	Particulate Hg ( $\mu\text{mol kg}^{-1}$ )	Filter-passing Hg ( $\text{pmol L}^{-1}$ )
American			
Galveston Bay*	0–30	0.1–0.4	0.3–6.8
Ochlockonee†	0–32	—	3.4–30
Patuxent‡	0–15	—	2.0–7.5
North SF Bay§	0–32	0.6–2.0	1.8–7.8
South SF Bay§	22–26	0.9–5.9	2.8–5.6
European			
Rhone	0.2–23	1.2–8.5	2.9–16
Loire¶	0–35	~0.5–5	~1–3
Seine¶	0–35	~2–10	~2–6
Scheldt#	0–~30	~0.5–9.5	~2–15

\* Stordal et al. (1996a).

† Guentzel et al. (1996).

‡ Benoit et al. (1998).

§ Present study.

|| Cossa and Martin (1991).

¶ Coquery et al. (1997).

# Leermakers (2001).

## Discussion

**Particulate Hg**—Particulate Hg concentrations are plotted as a function of SPM concentrations in Fig. 4a. As was demonstrated above, the variation of total and particulate Hg in the northern reach is primarily explained by a single parameter, SPM. The Hg-SPM relationship has also been reported elsewhere (Coquery et al. 1995, 1997; Leermakers et al. 1995; Stordal et al. 1996a). A previous study conducted in Sacramento River basin (Domagalski 2001) also found a relationship between Hg in unfiltered water and SPM. However, the relationship observed was second order instead of the linear correlation that was observed in the present study. Resuspended sediments and particulate material transported by riverine water were considered to be a major source of Hg (Hurley et al. 1998).

The correlation between particulate Hg and SPM was weaker in the South Bay (Fig. 4a). For example, the particulate Hg concentration at the extreme South Bay (Sta. 1) in March 2001 ( $157 \text{ pmol L}^{-1}$ ) was several fold higher than that found at San Pablo Strait (Sta. 6) ( $38 \text{ pmol L}^{-1}$ ), although both sites had similar SPM concentrations of  $\sim 25 \text{ mg L}^{-1}$ . This is not explained only by the SPM dependency. For the spring transect, where the particulate OC concentration was measured, the relationship between particulate OC and particulate Hg is plotted in Fig. 4b. Despite the paucity of data, a correlation was observed between particulate OC and unfiltered Hg in the South Bay, which suggests that particulate organic matter may play an important role in Hg concentration in the South Bay. A good correlation between chlorophyll *a* and particulate Hg has often been noted in estuarine environments—for example, the Arctic (Coquery et al. 1995) and European estuaries (Coquery et al. 1997)—because Hg uptake by phytoplankton may represent the initial stage of trophic transport through the food chain (Mason et al. 1996). The average Chl *a* concentration, normalized to SPM, in the central and extreme South Bay was  $0.13 \text{ mg g}^{-1}$ , which is twofold greater than that in the upper estuary ( $0.06 \pm 0.05 \text{ mg g}^{-1}$ ; salinity,  $<20$ ). This indicates that SPM in the South Bay is more biogenic than in the northern reach and that phytoplankton may be a more important substrate for Hg adsorption in the South Bay than in the northern reach. In the northern reach, Chl *a* correlated with particulate Hg, when normalized to SPM concentrations, during the high flow period ( $r = 0.84$ ,  $p < 0.005$ ) but not during the low flow condition. More information is needed to evaluate the role of phytoplankton as a substrate for scavenging Hg in the northern reach.

An interesting relationship was found in the partitioning between particulate and filter-passing fractions relative to the SPM concentration (Fig. 4c). The contribution of particulate Hg to the total in unfiltered samples is small when the SPM concentration is low ( $< \sim 20 \text{ mg L}^{-1}$ ) and increases nonlinearly with increasing SPM concentration. When the SPM concentration is high ( $> 30 \text{ mg L}^{-1}$ ), the Hg exists predominantly ( $> 90\%$ ) in particulate phase. Even though the SPM concentration did not always explain the particulate Hg concentration (Fig. 4a,b), the relative abundance of particulate Hg appeared to be controlled by the SPM concentration to a significant extent throughout the estuary.

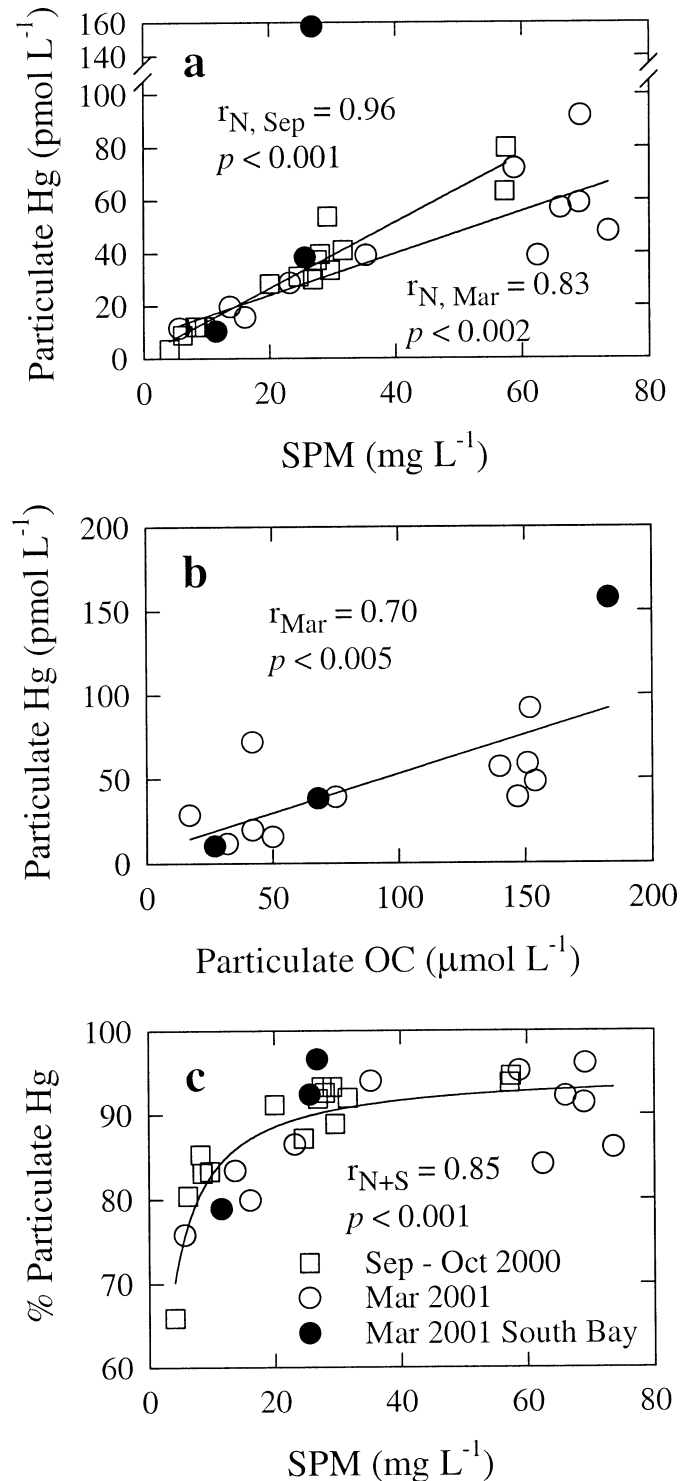


Fig. 4. The relationship between Hg and particulate material.  $r_{N, \text{Sep}}$  and  $r_{N, \text{Mar}}$  represent the correlation coefficients for the northern reach in September–October 2000 and March 2001, respectively,  $r_{\text{Mar}}$  for the entire bay in March 2001, and  $r_{N+S}$  for all data.

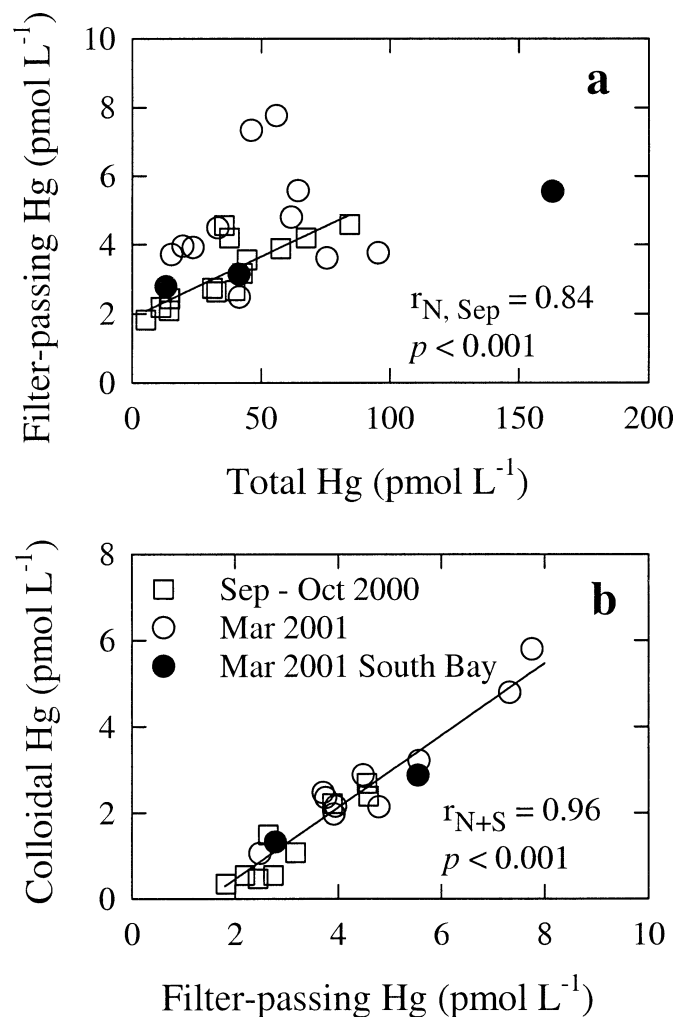


Fig. 5. Correlations between (a) unfiltered and filter-passing and (b) filter-passing and colloidal Hg.  $r_{N, \text{Sep}}$  refers to the correlation coefficient for the northern reach in September–October 2000 and  $r_{N+S}$  to that for all data.

**Filter-passing, colloidal, and dissolved Hg**—As was mentioned earlier, the filter-passing Hg fraction contained only a small portion (i.e.,  $12 \pm 7\%$ ) of the Hg in the unfiltered sample. The filter-passing concentration generally increased with increasing unfiltered concentration, but the correlation was significant only in September–October 2000 (Fig. 5a). In contrast, colloidal Hg concentrations were highly dependent on the filter-passing Hg concentrations ( $r = 0.96$ ) within the estuary (Fig. 5b), which suggests that processes controlling partitioning between filter-passing and colloidal Hg are kinetically fast or that the concentration ratio of colloidal Hg to filter-passing Hg is set at the river water end-member and then diluted gradually with the seawater end-member.

Colloidal Hg averaged  $49 \pm 16\%$  ( $n = 21$ ) of the filter-passing fraction during the 2000–2001 sampling period. This result is similar to that observed previously by Guentzel et al. (1996) in the Ochlockonee estuary in Florida ( $68 \pm 12\%$ ) and by Stordal et al. (1996a) in Texas estuaries ( $57 \pm 20\%$ ). The average % colloidal Hg was higher in the spring ( $57 \pm 10\%$ ), when both absolute and relative colloidal OC concen-

trations were enhanced, compared with that in the fall ( $38 \pm 18\%$ ).

Filter-passing Hg was markedly correlated with OC (Fig. 6a), especially during the high flow season, which suggests that organic material is the dominant transport medium of filter-passing Hg in the San Francisco Bay estuary. A good correlation was also observed between colloidal Hg and colloidal OC during high flow condition ( $r = 0.26$  for all samples but 0.96 for March 2001 samples) (Fig. 6b), which is consistent with previous studies conducted in other estuarine environments (Guentzel et al. 1996; Stordal et al. 1996a). Colloidal and dissolved Hg did not covary with colloidal and dissolved OC in September–October 2000. This suggests that a fraction of the organic matter may be a more important carrier phase of Hg than bulk OC under lower flow conditions.

**Particle–water partition coefficients**—The partitioning of metals between filter-passing (i.e.,  $<0.45 \mu\text{m}$ ) and particulate (i.e.,  $>0.45 \mu\text{m}$ ) fractions is often quantified in terms of a particle–water partition coefficient ( $K_D$ ):

$$K_D (\text{L kg}^{-1}) = \frac{[\text{particulate Hg (pmol kg}^{-1})]}{[\text{filter-passing Hg (pmol L}^{-1})]}$$

Although it is not a true thermodynamic parameter, because of its simplicity it has been widely used to describe the interaction of solution components with heterogeneous solids in estuarine environments (Stordal et al. 1996a; Wen et al. 1999; Leermakers et al. 2001). A common observation in aquatic systems is that  $K_D$  is negatively proportional to SPM concentration, an artifact termed the “particle concentration effect” (Benoit 1995). The colloidal material concentration is known to be proportional to SPM concentration:

$$[\text{colloidal}] = k(\text{SPM})^x$$

where  $k$  is a constant and  $x$  is a slope that ranges between 0.5 and 1.0 (Honeyman and Santschi 1989; Benoit 1995). The concentration of a colloiddally associated trace metal increases as SPM concentration increases, and the inclusion of the colloidal fraction in the filter-passing fraction results in a decrease in  $K_D$  (Honeyman and Santschi 1988; Benoit et al. 1994; Benoit 1995; Sanudo-Wilhelmy et al. 1996; Quémérais et al. 1998; Benoit and Rozan 1999). A particle concentration effect was observed for Hg in the present study (Fig. 7a). To minimize this artifact, two other variations of a particle–water partition coefficient can be developed on the basis of ultrafiltration results:

$$K_p (\text{L kg}^{-1}) = \frac{[\text{particulate Hg (pmol kg}^{-1})]}{[\text{dissolved Hg (pmol L}^{-1})]}$$

$$K_C (\text{L kg}^{-1}) = \frac{[\text{colloidal Hg (pmol kg}^{-1})]}{[\text{dissolved Hg (pmol L}^{-1})]}$$

Figure 7b shows that both operational definitions greatly reduced the particle concentration effect but did not eliminate it.

The three forms of the partition coefficient described above are plotted along the salinity gradient in Fig. 8. By definition,  $K_p$  values would always be greater than  $K_D$  values if colloidal Hg is present in the filter-passing fraction. When



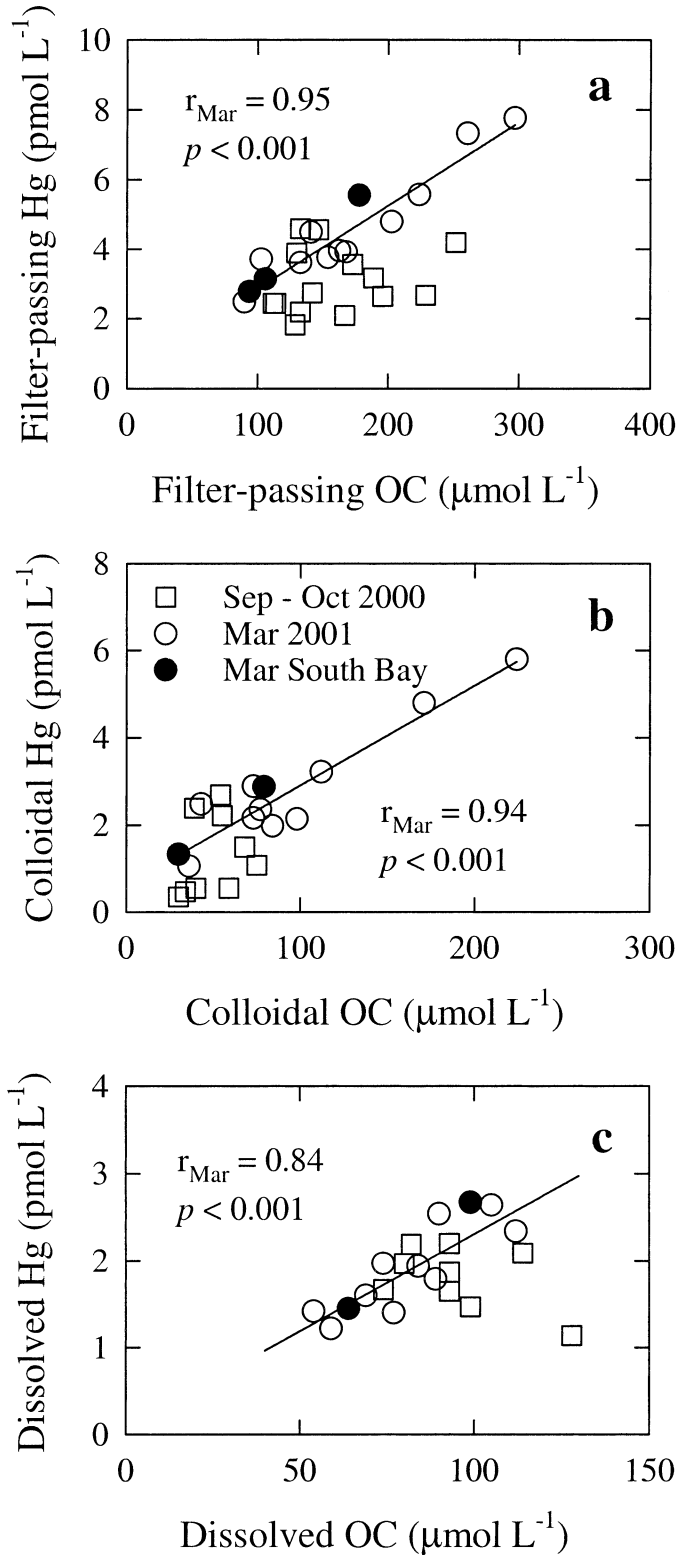


Fig. 6. Correlations between Hg and organic carbon in filter-passing, colloidal, and dissolved fractions.  $r_{\text{Mar}}$  refers to the correlation coefficient in March 2001.

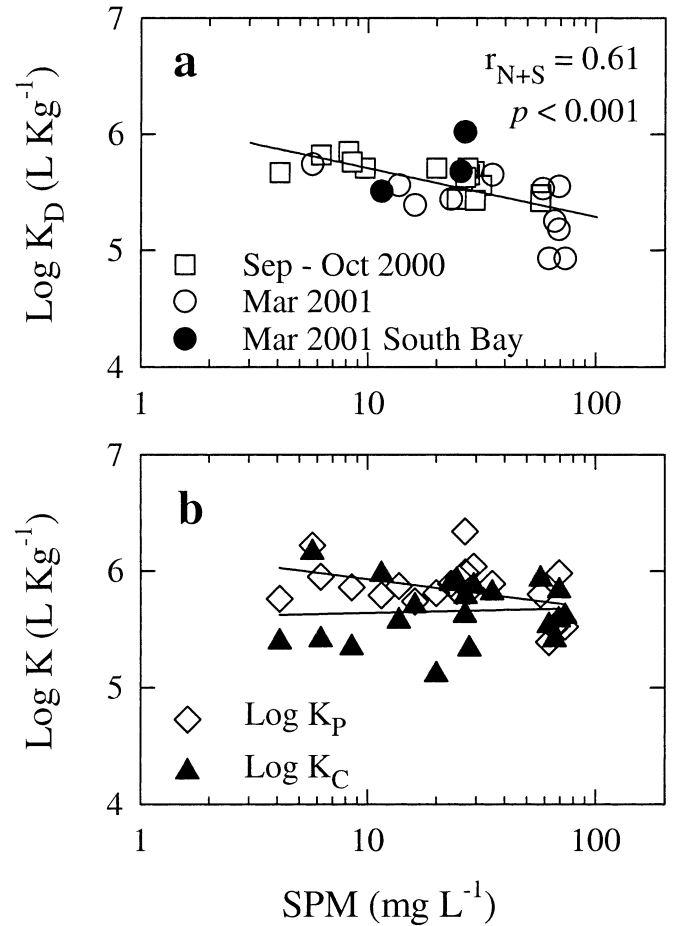


Fig. 7. Particle-water partition coefficients of Hg as a function of SPM.  $r_{\text{N+S}}$  refers to the correlation coefficient for all data.

$K_p$  values are greater than  $\log K_c$  values, this indicates that bulk SPM is a more important carrier phase of Hg than colloidal matter. In September–October 2000,  $\log K_D$ ,  $K_p$ , and  $K_c$  values averaged  $5.64 \pm 0.16$  ( $n = 15$ ),  $5.87 \pm 0.10$  ( $n = 9$ ), and  $5.56 \pm 0.31$  ( $n = 9$ ), respectively. In March 2001,  $\log K_D$ ,  $K_p$ , and  $K_c$  values averaged  $5.46 \pm 0.30$  ( $n = 14$ ),  $5.81 \pm 0.29$  ( $n = 12$ ), and  $5.72 \pm 0.21$  ( $n = 12$ ), respectively. The magnitudes of  $K_D$  are consistent with those determined in other estuarine environments (Cossa and Martin 1991; Stordal et al. 1996a; Leermakers et al. 2001). The lower  $K_D$  values ( $p < 0.05$ , one-way analysis of variance) observed during the high flow season are possibly attributed to the particle concentration effect. The  $K_c$  values were significantly ( $p < 0.05$ ) smaller than  $K_p$  values in September–October 2000, but both values were statistically similar in March 2001 ( $p < 0.5$ ). Collectively, these results suggest that colloidal material played as important a role in Hg phase speciation as particulate material during the high flow condition.

Positive correlations were observed between partition coefficients and salinity in March 2001. There are many factors that influence partition coefficients other than SPM concentration, such as pH (Stumm and Morgan 1996), salinity (Benoit 1995; Turner 1996; Turner et al. 2001), and the OC

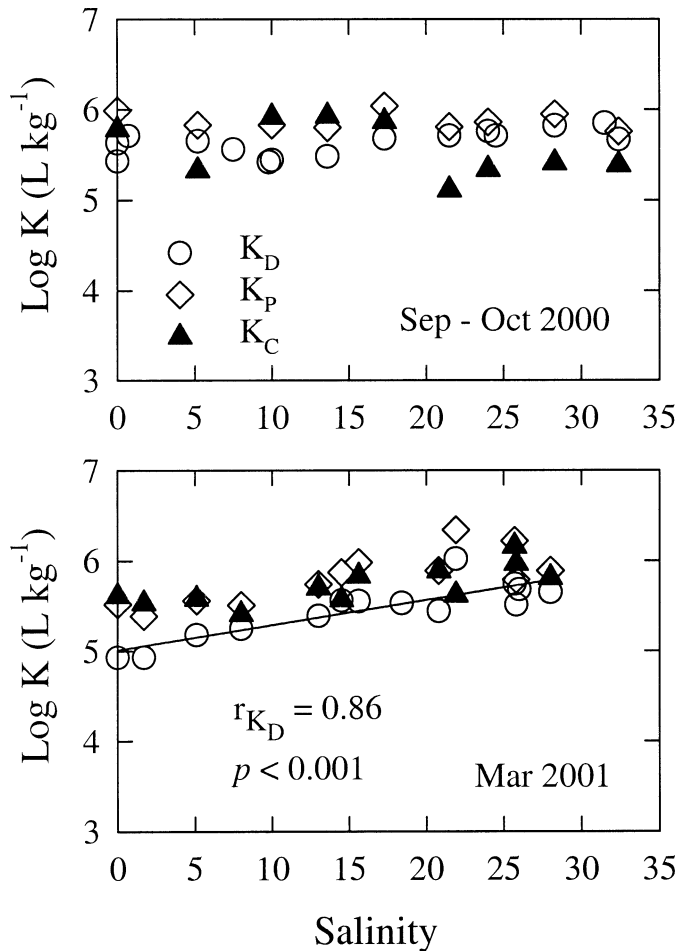


Fig. 8. Particle–water partition coefficients of Hg as a function of salinity.

content in filtered water (Benoit 1995). Increasing pH down the estuary could increase partition coefficients because of an increase in negatively charged surface, as shown in Fig. 8b. Increasing salinity could also enhance  $K_D$ , because Hg and organically associated Hg are “salted out” in high-salinity regions (Turner et al. 2001). However, estuarine pH and salinity do not seem to be important in influencing Hg partitioning, because the salinity dependence of Hg occurs only in the spring. The seasonal variation in partition coefficient values was greatest in low-salinity regions and lowest in high-salinity regions. Therefore, low  $K_D$  (and  $K_P$ ) values in the upper estuary during the high flow condition appear to result from a Hg deficiency in larger suspended particles with smaller surface area (and surface complexation sites) (Benoit 1995). It is not clear whether, as was suggested by Benoit (1995), resuspension followed by reversible desorption/disaggregation of trace metals from particles or colloids at low salinity decreased  $K_D$  during the high flow season.

**Estuarine Hg flux**—Filter-passing, colloidal, and dissolved mercury fluxes within the estuary were estimated with a steady-state nonconservative estuarine mixing model (Officer 1979). In the model, the net internal flux,  $F_i$ , is estimated using

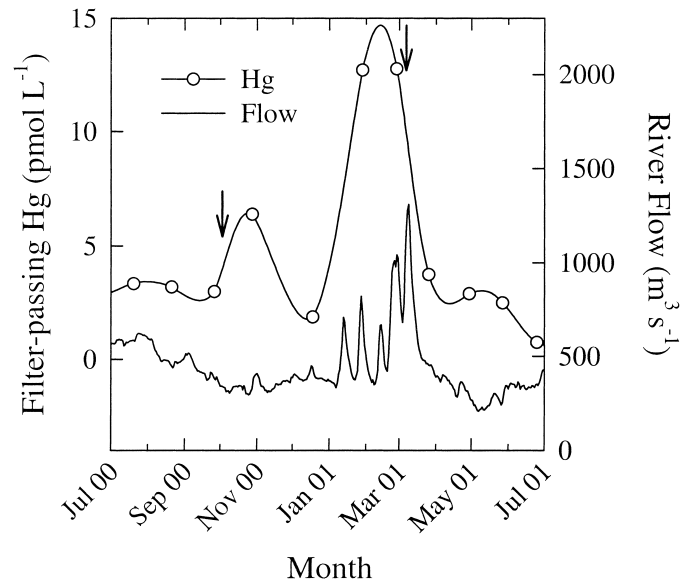


Fig. 9. Filter-passing Hg in the Sacramento River measured at Greene’s Landing (38°34’N, 121°55’W) (Foe unpubl. data) and flow rate monitored at Freeport, California (38°45’N, 121°50’W). The arrows represent the sampling periods during the present study.

$$F_i = F_e - F_r = RC_* - RC_o = R(C_* - C_o)$$

where  $F_r$  and  $F_e$  refer to the flux into and out of the estuary (in  $\text{mmol d}^{-1}$ ), respectively;  $R$  refers to river flow (in  $\text{L d}^{-1}$ ); and  $C_o$  and  $C_*$  are the actual and hypothetical Hg concentrations in the river water end-member (in  $\text{pmol L}^{-1}$ ), respectively. A hypothetical value,  $C_*$ , is extrapolated from the linear portion of estuarine concentration near a seawater end-member. A negative  $F_i$  value represents a net internal sink, whereas a positive value represents a net internal source. This approach has been used for the estimation of trace metal fluxes in the San Francisco Bay estuary (Cutter 1989; Flegal et al. 1991).

Rapid variations in the river water end-member concentration can result in the inconsistency between actual and apparent Hg-salinity profiles within the estuary (Officer and Lynch 1981). This influence is dependent on (1) the direction of river water end-member variation (i.e., whether riverine concentration increases or decreases), (2) the relative magnitude of the riverine concentration variation, and (3) the freshwater residence time in the estuary. Figure 9 clearly shows that filter-passing Hg concentrations in the Sacramento River varied with time and river flow rate (Foe unpubl. data). Riverine Hg concentrations were increasing with time during the fall sampling period and decreasing during the spring sampling period. If river source variations were significant enough to influence estuarine Hg-salinity distributions, the mixing curves would be concave upward in the fall and concave downward in the spring. These estuarine Hg distributions were not observed (Fig. 3), which suggests that the influence of Hg variation in the river is insignificant.

Officer and Lynch (1981) demonstrated that a ratio of freshwater residence time to the period of riverine concentration variation,  $\tau:T$ , of 0.33 can cause curvature in the constituent salinity profile in the lower half of the salinity

Table 4. Mercury flux estimates in the northern reach of San Francisco Bay determined from estuarine geochemical modeling.

	$C_o$ (pmol L <sup>-1</sup> )	$C_s$ (pmol L <sup>-1</sup> )	$F_r$	$F_i$	$F_e$
Sep.–Oct. 2000 (river flow = $3.0 \times 10^{10}$ L d <sup>-1</sup> ) (mmol d <sup>-1</sup> )					
Particulate Hg	30.0	—	900	—	—
Filter-passing Hg	2.6	6.0	78	100	180
Colloidal Hg*	1.5	—	45	67	110
Dissolved Hg	1.1	2.2	33	33	66
Mar. 2001 (river flow = $7.7 \times 10^{10}$ L d <sup>-1</sup> ) (mmol d <sup>-1</sup> )					
Particulate Hg	38.8	—	3,700	—	—
Filter-passing Hg	7.8	5.6	600	-170	430
Colloidal Hg*	5.8	—	450	-230	220
Dissolved Hg	2.0	2.7	150	60	210
Annual flux (mol yr <sup>-1</sup> and kg Hg yr <sup>-1</sup> )†					
Particulate Hg			490 (98)	—	—
Filter-passing Hg			59 (12)	21 (4.2)	80 (16)
Colloidal Hg*			40 (8.0)	8 (1.6)	48 (9.6)
Dissolved Hg			19 (3.8)	13 (2.6)	32 (6.4)

$C_o$  and  $C_s$  are the actual and hypothetical Hg 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.

\* Colloidal Hg fluxes were calculated by the difference between filter-passing and dissolved Hg fluxes.

† Fluxes in parentheses are in kg Hg yr<sup>-1</sup>.

range. Similarly, Cifuentes et al. (1990) observed the influence of riverine concentration variation on alkalinity–salinity distributions in the north San Francisco Bay when  $\tau:T$  was 0.37. In the present study, the riverine concentration variation was largest under the high flow condition (Fig. 9), which suggests the greatest effects of riverine source variation occur during winter. However, given a freshwater residence time of 22 d, estimated with a river flow rate of 800 m<sup>3</sup> s<sup>-1</sup> (Cifuentes et al. 1990) and a period of riverine Hg variation of ~120 d (Fig. 9),  $\tau:T$  for Hg was estimated at 0.18. This result further supports that the effects of riverine source variation on the estuarine Hg distribution are minimal.

A summary of the modeling results is given in Table 4. The riverine fluxes have been calculated on the basis of the assumption that the Sacramento River is the only dominant freshwater source. Colloidal Hg fluxes were calculated using dissolved Hg fluxes subtracted from filter-passing fluxes, given its complicated estuarine distribution pattern. The riverine Hg fluxes in colloidal and dissolved fractions during the high flow condition were significantly greater than those in the low flow condition because of high river flow and high riverine Hg concentrations. There were net internal sources of colloidal and dissolved Hg during the low flow period, which increased the estuarine export flux (relative to freshwater inputs) by 140% and 100%, respectively. During the high flow season, however, ~50% of the colloidal Hg that was transported by the river was removed during early estuarine mixing. Although there was internal input of dissolved Hg (60 mmol d<sup>-1</sup>), this flux was less than the internal removal of colloidal Hg (-230 mmol d<sup>-1</sup>), resulting in the net loss of filter-passing Hg during the high flow condition.

Annual Hg fluxes can be estimated using the short-term flux data for both flow regimes (Table 4). The 2 months during winter were assumed to be a high flow period and the rest of year to be a low flow condition (Fig. 9). Approx-

imately 90% (98 kg Hg yr<sup>-1</sup>) of the total Hg (110 kg Hg yr<sup>-1</sup>) carried by the Sacramento River is in the suspended particulate form. Filter-passing Hg has an annual riverine flux of 12 kg Hg yr<sup>-1</sup>, which is greater than the internal input (4.2 kg Hg yr<sup>-1</sup>). A significant fraction (67%) of riverine Hg flux is associated with colloidal material. The annual riverine flux of colloidal Hg (8.0 kg Hg yr<sup>-1</sup>) is fivefold greater than the internal fluxes (1.6 kg Hg yr<sup>-1</sup>), whereas the annual riverine flux of dissolved Hg (3.8 kg Hg yr<sup>-1</sup>) is ~30% greater than the internal flux (2.6 kg Hg yr<sup>-1</sup>). These results show that the river is an important source of Hg in the estuary.

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