

## Sediment–water exchange of total mercury and monomethyl mercury in the San Francisco Bay–Delta

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### *Abstract*

Five field trips were conducted in the San Francisco Bay–Delta between May 2000 and October 2001 to investigate the sediment–water exchange of total mercury (Hg) and monomethyl mercury (MMHg). Solid-phase Hg averaged  $\sim 1 \text{ nmol g}^{-1}$  and did not show any variability with depth or time or among sites. In contrast, solid-phase MMHg showed considerable vertical, temporal, and spatial variability ( $0.4\text{--}66 \text{ pmol g}^{-1}$ ), with the highest values occurring at a peat-rich environment in May 2001, suggesting that MMHg production was largely controlled by temporal factors and habitat type. In pore water, both Hg and MMHg concentrations were generally elevated near the sediment–water interface during warm months. Sediment–water exchange flux of MMHg, determined with benthic chamber deployments, ranged from  $-92$  to  $850 \text{ pmol m}^{-2} \text{ d}^{-1}$ , with higher values occurring in May. In most cases, diffusional fluxes of Hg and MMHg, estimated with the use of interfacial concentration gradients, constituted only a minor portion of the measured fluxes, suggesting the importance of advective processes on sediment–water exchange. Surface-water transect and time series studies conducted in Franks Tract support the commonly held belief that wetland and marsh regions are major sources for MMHg within the Delta. The integrated sediment–water fluxes of Hg and MMHg in the study area were estimated to be  $130$  and  $6 \text{ mmol d}^{-1}$ , respectively, and the benthic input was as important a source of Hg and MMHg as the riverine input within the Delta during low-flow months.

Historically, about 90% ( $\sim 100$  million kg) of the mercury (Hg) produced in the United States between 1850 and 1980 was mined in the California Coast Range. During the California gold rush era (1848 to the first part of the 20th century), much of the Hg mined in the Coast Range was transported to the Sierra Nevada Mountains and consumed by Hg amalgamation processes associated with gold mining activities. Large amounts of Hg have been lost into Coast Range and Sierra watersheds during these activities. Today, there are estimated to be 13,000 abandoned gold mines in the Sierra and  $>200$  abandoned Hg mines in the Coast Range. Runoff from many of these mines and mine tailings are the primary source of Hg contamination in the San Francisco Bay–Delta (hereafter referred to as the “Bay-Delta”; Ganguli et al. 2000). It has been demonstrated that at least 100 to  $>800$  kg of Hg are transported annually into the Bay-Delta (Domagalski 1998; Foe and Croyle 1998; Roth et al. 2001; Choe et al. 2003). As a result, widespread Hg contam-

ination has occurred in Bay-Delta sediments (Hornberger et al. 1999; Heim 2003) and biota (Fairey et al. 1997; Hoffman et al. 1998; Davis et al. 2002). Large piscivorous fish such as striped bass and sharks were found to have Hg concentrations exceeding the screening value defined by the U.S. Environmental Protection Agency ( $0.3 \mu\text{g g}^{-1}$  wet weight; Fairey et al. 1997). In 1994, because of concern over human exposure to Hg, health advisories for fish consumption were issued for the Bay-Delta by California State’s Office of Environmental Health Hazard Assessment, recommending no consumption of large striped bass and limited consumption of other sport fish. The advisories are currently still in place.

In shallow estuarine environments, sediment–water exchange processes could be important sources of trace metals and nutrients to the water column and are possibly comparable to riverine inputs. As an example, in the upper Galveston Bay, Texas, it was suggested that benthic inputs of manganese, nickel, zinc, and nutrients were significant enough to increase water column concentrations (Warnken et al. 2000, 2001), resulting in nonconservative estuarine mixing behaviors previously observed in that region of Galveston Bay (Wen et al. 1999). Similarly, recent studies noted that benthic transport of lead and silver could be greater than the fluvial input in South San Francisco Bay (Rivera-Duarte and Flegal 1994, 1997). The importance of benthic transport of Hg has been tested in other coastal (Covelli et al. 1999) and estuarine environments (Gill et al. 1999), but little is known about the sediment–water exchange of Hg in the Bay-Delta.

Among various Hg species, monomethyl mercury (MMHg) has received the greatest attention because of its

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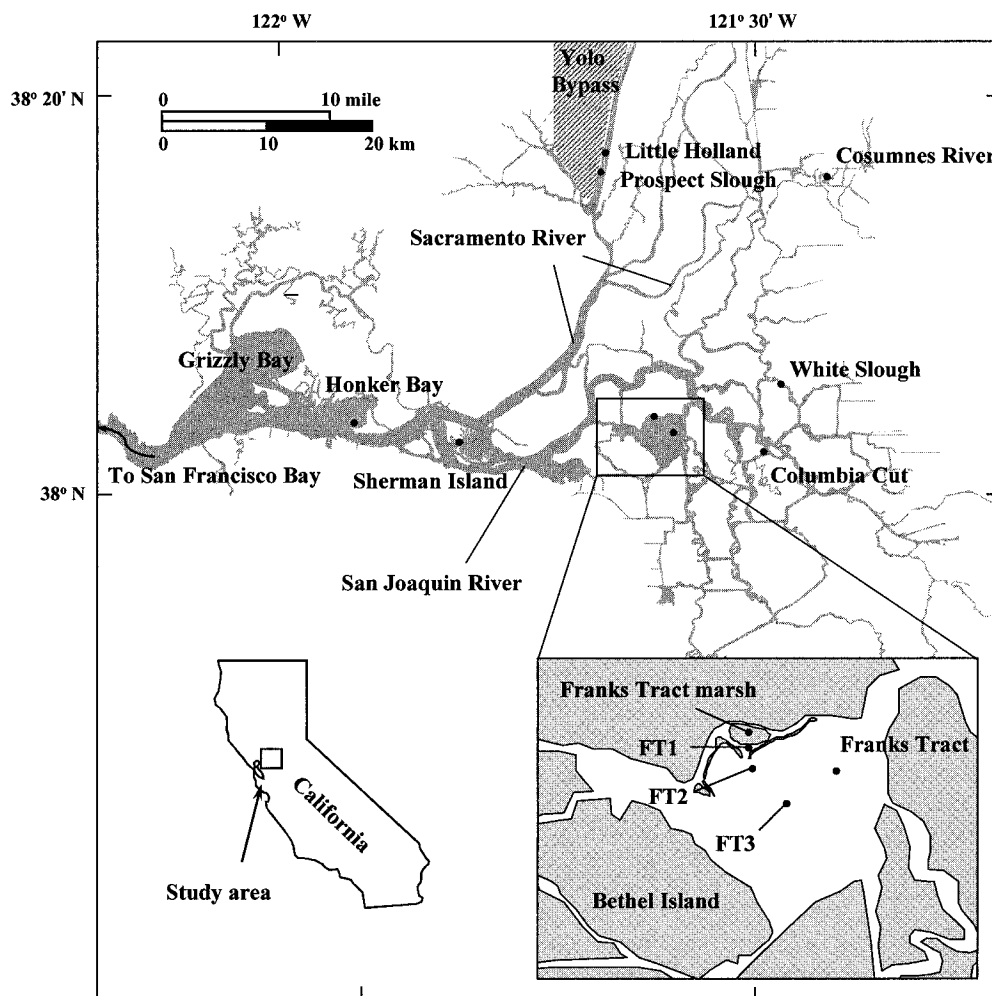


Fig. 1. The San Francisco Bay–Delta system and sampling locations.

toxicity, accumulation in biota, and biomagnification in aquatic food chains (Bloom 1992). It is now widely accepted that MMHg is converted from inorganic Hg principally by sulfate-reducing bacteria in surficial sediments (Compeau and Bartha 1985; Gilmour et al. 1998). It has been suggested that in situ MMHg concentration or the MMHg to Hg concentration ratio (percent MMHg) in sediment can be used as a proxy of the relative Hg methylation rate within an environment (Gilmour et al. 1998; Bloom et al. 1999). Recently, Heim (2003) reported elevated MMHg concentrations and percent MMHg in surface sediments of the central Delta (i.e., near Franks Tract; see Fig. 1). This finding suggests that the central Delta has a greater Hg methylation potential than surrounding tributaries.

This study was conducted as part of the Bay-Delta Hg project sponsored by a consortium of California and federal agencies referred to as “CALFED.” This paper discusses the distribution of Hg and MMHg in pore waters and upper sediments of the Delta, quantifies the sediment–water exchange of Hg and MMHg, and estimates the importance of the sediment–water exchange as a source of MMHg.

Two different sampling approaches were employed in this study. First, intact sediment cores were collected from sev-

eral sites in the Delta, and steady-state diffusional flux was estimated by vertical distributions in pore water. This approach is based on Fick’s first law and has often been used in studies of Hg and MMHg (Gobeil and Cossa 1993; Gagnon et al. 1997; Covelli et al. 1999; Gill et al. 1999). The second approach employed benthic flux chambers; in situ flux was directly determined on the basis of the concentration gradient over time. This method provides information on the effect of advective processes on benthic transport and the temporal scales for which sampling is conducted. Because of analytical difficulties, very few studies have tested the latter approach for Hg and MMHg (Covelli et al. 1999; Gill et al. 1999). The information obtained from this study will be used in future efforts to model the mass balance and biogeochemistry of Hg and MMHg in the Bay-Delta ecosystem.

#### Materials and methods

*Study area and sampling sites*—San Francisco Bay is one of the largest estuarine systems along the Pacific coast of the United States with a surface area of 1,240 km<sup>2</sup>. The average water depth is relatively shallow (~6 m) except for

Table 1. Sampling locations and sample collection matrix.

Site	Location		Sample collection*				
	Latitude (°N)	Longitude (°W)	May 2000 (28 May–1 Jun)	Sep 2000 (23 Sep–27 Sep)	Feb 2001 (27 Feb–1 Mar)	May 2001 (18 May–24 May)	Oct 2001 (16 Oct–20 Oct)
Columbia Cut	38.0301	121.4905	LCO	LC	—	—	—
Cosumnes River	38.2582	121.4262	C	C	LC	LC	LC
Franks Tract	38.0528	121.5920	LCO	LCO	—	—	LC
Franks Tract marsh	38.0594	121.6116	—	—	LC	LC	LC
Honker Bay	38.0585	121.9331	LC	—	—	—	—
Little Holland	38.2904	121.6615	LC	LC	—	—	—
Prospect Slough	38.2862	121.6645	—	—	LC	LC	—
Sherman Island	38.0413	121.8194	LCO	LCO	—	LC	LC
White Slough	38.0873	121.4784	LCO	CO	—	LC	LC

\* L, light chamber; C, core; O, O<sub>2</sub> microelectrode.

narrow channels that are typically 10–20 m deep. The water column in San Francisco Bay is relatively well mixed over the majority of the estuary. Stratification occurs only in deeper regions of the bay and channel areas, with seaward low-salinity surface currents and landward high-salinity bottom currents (Smith 1987).

Located in the northern reach of San Francisco Bay, the Delta is a complicated system with two major rivers—the Sacramento and San Joaquin—numerous interconnected waterways, and other tributaries (Fig. 1). The Delta receives runoff draining approximately 40% of California's land. The Sacramento River is the largest freshwater source to the Bay-Delta, draining major Hg and gold mining areas. The freshwater flow is dominated by the unique climatic cycle in the area: high flow in winter and low flow in summer. During high-flow months, a portion of storm water runoff originating from the upper Sacramento River is diverted at Fremont Weir and routed down the Yolo Bypass. Nichols et al. (1986) reported that 40% (~13 km<sup>3</sup> yr<sup>-1</sup>) of the freshwater inflow into the Delta was removed for local consumption and 24% (~8 km<sup>3</sup> yr<sup>-1</sup>) was pumped from the Delta and exported for agricultural irrigation and municipal water supplies for central and southern California. The water flow in the interconnected channels is relatively slow and partially influenced by tidal forces. However, operation of the pumps during low-

flow periods at the southern end of the Delta causes water in Delta channels to flow upstream (Nichols et al. 1986).

Sediment cores were collected at nine sites in the central Delta region during five periods, beginning in May 2000 and ending in October 2001 (Table 1). Except at Columbia Cut and Honker Bay, sampling trips were conducted four times or more at each site. Sampling sites were chosen to be representative of various hydrological and habitat types in the central Delta (Table 2): tributary streams (Cosumnes River, Little Holland, and Prospect Slough), interconnected waterways (Columbia Cut, Franks Tract marsh, Sherman Island, and White Slough), and open water (Franks Tract, and Honker Bay). Salinity measured in the water column remained near zero (<0.1) at most sites all year but varied from 0.2 to 6 at Sherman Island and from 0.7 to 9 at Honker Bay, depending on the freshwater inflow. The percent fines (<63 μm) in surface sediments was highest at Franks Tract and White Slough (99%) and lowest at Sherman Island (26%; Heim 2003). Percent fines varied from 48% to 78% at the other sites. Organic matter content, estimated by loss on ignition (LOI), generally ranged from 5% to 30%. The LOI was highest (>20%) at Franks Tract marsh and Sherman Island, both of which have peat-rich sediments, and was lowest at Honker Bay, Little Holland, and Prospect Slough (Heim 2003). Most sampling sites, except Honker Bay, Little

Table 2. Characteristics of sampling locations.

Site	Average water depth (m)	Sample area	Aquatic vegetation	Benthic macrofauna	% fine sediment (<0.063 mm)	% loss on ignition*
Columbia Cut	2	Channel	Elodea, tule	Corbicula	79±9 (n=5)	7.4±0.9 (n=5)
Cosumnes River	1.5	Tributary	Egaria	None	51±18 (n=5)	7.8 ±1.0 (n=5)
Franks Tract	3	Open water	Egaria, elodea	Corbicula	99±1 (n=4)	9.5±0.5 (n=9)
Franks Tract marsh	1.5	Backwater	Egaria	None	ND	23.5±5.9 (n=5)
Honker Bay	3	Open water	None	None	69±4 (n=5)	3.7±0.9 (n=5)
Little Holland	1	Tributary	None	Corbicula	68±24 (n=5)	5.8±0.4 (n=5)
Prospect Slough	1.5	Tributary	None	Corbicula	48 (n=1)	5.3±0.3 (n=3)
Sherman Island	1.5	Channel	Tule	Corbicula	26±6 (n=3)	29.8±15.2 (n=3)
White Slough	3	Channel	Egaria, elodea	Corbicula	99±1 (n=5)	11.9±1.9 (n=7)

\* Measured at 0–0.5 cm (Heim 2003).

Holland, and Prospect Slough, had patches or dense mats of submerged plants on the surface sediment. Brazilian waterweed (*Egeria densa*) and Canadian waterweed (*Elodea canadensis*) were the most frequently observed, and tule (*Scirpus acutus*) was common at Sherman Island. Macrofauna such as Asian clams (*Corbicula fluminea*) were commonly observed in surface sediments at most sites.

**Pore water collection**—Intact sediment cores (9 cm I.D.) were collected by SCUBA divers. The core collection was conducted with polycarbonate core liners fitted with sampling ports at 1-cm intervals. The sediment cores were pressurized with high-purity nitrogen gas (~10 psi) through a valve located in the top core lid. Pore water was forced into acid-cleaned polypropylene syringes through Porex® rods that were inserted about halfway into the sediment core (Jahnke 1988). The sampling interval was 1 cm near the sediment–water interface and 2–3 cm at depth. After squeezing, samples collected in syringes were filtered through 0.45- $\mu$ m pore-sized syringe filters and acidified to pH <2 with low-Hg content HCl. The typical sample volume extracted was 4–6 ml to minimize the vertical movement of pore fluid or overlying water. Two cores were collected within a relatively small area (<1 m<sup>2</sup>). Separate cores were needed for Hg and MMHg measurements because of the small sample volumes obtained. Sediment cores were sliced at 1-cm intervals after the pore water was extracted, placed in small polyethylene bags, and refrigerated until processed for Hg and MMHg analyses. Additional details of the sampling procedure are given elsewhere (Mason et al. 1998; Warnken et al. 2000, 2001). For several sites, a separate core was collected for high-resolution microelectrode profiling of oxygen.

**Diffusive flux estimation**—The benthic diffusive flux of Hg and MMHg was estimated on the basis of the concentration gradient between Hg in the top sediment and Hg in the overlying water column. According to Fick's first law, diffusive flux ( $F_D$ ) is modified for application to sediments in the absence of biological irrigation.

$$F_D = - \left( \frac{\varphi D_w}{\theta^2} \right) \frac{\partial C}{\partial x}$$

$\varphi$  is the sediment porosity,  $\theta$  is the tortuosity,  $D_w$  is the diffusion coefficient of Hg in water without the presence of the sediment matrix,  $C$  is the concentration of Hg in pore water, and  $x$  is the sediment depth. The value of  $\theta^2$  can be estimated from porosity by the relationship  $\theta^2 = 1 - \ln(\varphi^2)$  (Boudreau 1996). Porosity of surface sediments averaged  $0.83 \pm 0.09$  ( $n = 20$ ) in the study area. In general, sites with low hydraulic energy had higher porosity (0.85–0.91 at Columbia Cut, Cosumnes River, Franks Tract, and White Slough) than sites with high hydraulic energy (0.66–0.79 at Honker Bay, Little Holland, and Prospect Slough). A diffusion coefficient ( $D_w$ ) of  $5 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> was chosen for both Hg and MMHg (Bothner et al. 1980; Gobeil and Cossa 1993; Gagnon et al. 1997; Covelli et al. 1999) and then corrected for temperature effects (Li and Gregory 1974). Resultant  $D_w$  values ranged from 3.3 to  $4.8 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>.

**Benthic chamber deployment**—The benthic chambers employed are very similar to those used in our previous studies (Gill et al. 1999; Warnken et al. 2000, 2001). Each side of these dual polycarbonate chambers has a surface area of 0.0962 m<sup>2</sup> and an internal volume of ~8.1 liters, preset by a collar fastened to the outside of the chambers. Water within the chamber is continuously and gently stirred with a Teflon®-coated stirrer operated by an external motor. A sample volume of ~120 ml was drawn by SCUBA divers directly into polypropylene syringes from each chamber, typically every hour. Samples for Hg and MMHg measurements were filtered through 0.45- $\mu$ m syringe filters immediately on retrieval and were transported to the laboratory and preserved at pH <2 with low-Hg content HCl. The dissolved oxygen (DO) concentration inside the chambers was monitored to test for bias in the benthic input of Hg and MMHg by low DO. Initial DO content of  $240 \pm 30$   $\mu$ mol L<sup>-1</sup> ( $n = 35$ ) decreased only by ~17% after ~4 h of deployment, suggesting that the alteration of benthic flux by low DO was insignificant.

Sediment–water exchange fluxes ( $F_M$ ) were directly measured by the time course increase in Hg concentration in the chambers.

$$F_M = \frac{\Delta C}{\Delta t} \cdot \frac{V}{A}$$

$C$  is the Hg concentration,  $t$  is the chamber deployment time,  $V$  is the internal volume of the chamber (8.1 liters), and  $A$  is the surface area the chamber encloses (0.0962 m<sup>2</sup>).

**Total Hg analysis**—Sediment samples for Hg analysis were first oxidized with aqua regia. Water samples for Hg analysis were digested in an ultraviolet irradiation box (eight lamps of 15 W each) for ~12 h. Total Hg was measured by aqueous-phase reduction with sodium borohydride solution, trapping onto a gold-coated quartz column, thermal desorption, and detection by cold-vapor atomic fluorescence spectrometry (CVAFS; Gill and Bruland 1990). The analytical performance was checked on a daily basis with a certified reference material, PACS-2 (marine sediment,  $3,040 \pm 200$  ng g<sup>-1</sup>), supplied by the National Research Council of Canada (NRCC). A typical matrix spike recovery was 97% for sediment and 99% for water samples. The method detection limit, defined as three times the standard deviation of method blanks, was 1.5 pmol L<sup>-1</sup> for 5 ml of pore water and 0.3 pmol L<sup>-1</sup> for 30-ml aliquots of benthic chamber samples.

**MMHg analysis**—Sediments for MMHg measurement were processed by the KBr/CH<sub>2</sub>Cl<sub>2</sub> extraction procedure described by Bloom et al. (1999), which is designed to minimize potential artifacts of MMHg formation during the distillation procedure (Bloom et al. 1997). Approximately 0.5–1.0 g of wet sediment was digested with acidic potassium bromide solution and extracted into 10 ml of methylene chloride in a Teflon® centrifuge tube. An aliquot (2 ml) of methylene chloride was then back-extracted to deionized water by purging out methylene chloride with high-purity nitrogen gas. Water samples for MMHg analysis were distilled to liberate MMHg. Typically, 5.0–30.0 ml of acidified sam-

Table 3. Results of intercomparison study for water samples (ng L<sup>-1</sup>) and sediments (ng g<sup>-1</sup>).

Sample matrix	Expected value*	Mean value†	Measured value‡	RPD (%)§
<b>Mercury</b>				
Freshwater	5.4	5.1±0.3 (n=12)	5.1±0.1	5.7
Freshwater	5.5	5.0±1.1 (n=15)	4.9±0.1	12
Freshwater	7.5	7.4±1.0 (n=12)	6.0±0.1	22
Freshwater	20.4	20.5±1.6 (n=15)	19.8±0.1	3.0
Seawater	5.3	5.2±0.4 (n=9)	5.1±0.0	3.6
Seawater	15.3	14.6±0.4 (n=12)	15.1±0.1	1.3
Sediment	4860	5060±264 (n=15)	4820±63	0.8
Soil	32.6	32.6±1.8 (n=18)	29.4±0.3	10
<b>Monomethyl mercury</b>				
Freshwater	3.0	3.1±0.4 (n=7)	3.3±0.2	9.5
Seawater	3.0	3.0±0.2 (n=9)	2.7±0.1	11
Sediment	5.7	5.0±0.9 (n=12)	5.5±0.4	3.6

\* Samples were prepared and distributed by Frontier Geosciences.

† Average values were calculated from results submitted by participants of the intercomparison study.

‡ Samples were analyzed in triplicate (n=3).

§ Relative percent difference (RPD) =  $\frac{[\text{expected}] - [\text{measured}]}{([\text{expected}] + [\text{measured}])/2} \times 100$ .

ple was diluted to 45 ml with deionized water before aqueous-phase distillation.

Extracts or distillates were analyzed for MMHg with the use of aqueous-phase ethylation by sodium tetraethylborate, trapping on a Tenax TA<sup>®</sup> column, gas chromatography separation, thermal decomposition to Hg<sup>0</sup>, and detection by CVAFS (Liang et al. 1994). The analytical recovery was checked regularly with a certified reference material, DORM-2 (dogfish muscle, 4,470 ± 320 ng g<sup>-1</sup>), supplied by the NRCC. Duplicate measurements were conducted for most analyses, and typical reproducibility, in terms of the relative percent difference, was 13 ± 12% (n = 53 pairs) for sediments and 20 ± 18% (n = 141 pairs) for water samples. Matrix spike recovery averaged 94 ± 15% (n = 20) for sediments and 90 ± 10% (n = 196) for aqueous samples. The detection limit was 0.05 pmol g<sup>-1</sup> for sediments, 0.4 pmol L<sup>-1</sup> for 5-ml samples of pore-water, and 0.075 pmol L<sup>-1</sup> for 30-ml benthic chamber samples.

Intercomparison samples for both Hg and MMHg were received from Frontier Geosciences as part of the CALFED quality assurance requirements. Results of the intercomparison study are listed in Table 3. The sample matrices analyzed were natural sediments, freshwater, and seawater. With one exception, the relative percent difference between our results and expected values or mean values was ≤12%.

## Results and discussion

**Total Hg in sediments**—Figure 2 illustrates the vertical distribution of total Hg in sediment cores collected in the Delta. In general, Hg concentrations averaged ~1 nmol g<sup>-1</sup> (all Hg and MMHg concentrations based on the dry weight of sediment), without any appreciable vertical or temporal variability. The average concentrations we observed are consistent with Hg concentrations measured in surface sediments of San Francisco Bay (Conaway et al. 2003). The highest concentrations occurred at Cosumnes River, with an average of 2.1 ± 0.9 nmol g<sup>-1</sup>, and the lowest concentrations

were at Sherman Island, with an average of 0.29 ± 0.25 nmol g<sup>-1</sup>. The Hg concentrations we observed are generally lower than those found in the surface sediments of Saguenay fjord, Quebec (~2.5 nmol g<sup>-1</sup>; Gagnon et al. 1997), or Lavaca Bay, Texas (~2 nmol g<sup>-1</sup>; Bloom et al. 1999), both of which have been affected by Hg discharge from chloro-alkali plants. However, Hg levels for most sampling sites are higher than the natural background concentration (0.3 ± 0.05 nmol g<sup>-1</sup>), which was estimated with long cores collected from San Francisco Bay (Hornberger et al. 1999).

The cores collected at Cosumnes River had elevated Hg concentrations (~5 nmol g<sup>-1</sup>) at a depth interval of 9–10 cm. Hornberger et al. (1999) observed a similar peak Hg concentration of 4.7 nmol g<sup>-1</sup> at depths between 45 and 65 cm in Grizzly Bay and attributed it to recent deposition (i.e., after ~1950s) of Hg-contaminated sediments from historical hydraulic mining activities. The Cosumnes River is the only river unobstructed by dams flowing into the Delta, and the observed elevation in Hg at depth in Cosumnes River cores is likely from the deposition of Hg-contaminated sediments. However, it remains uncertain whether elevated Hg concentrations at depth in the Cosumnes River can be attributed to historical mining activities.

**MMHg in sediments**—Figure 3 presents the distribution of MMHg in upper sediments (0–10 cm). Depth profiles of MMHg clearly have greater spatial, seasonal, and vertical variability than those of total Hg in sediments. A positive relationship was observed between Hg and MMHg at the surface sediments (0–5 cm) collected in San Francisco Bay (Conaway et al. 2003). However, a lack of correlation between Hg and MMHg concentrations in surface sediments (0–1 cm,  $r = -0.02$ ,  $n = 19$ ) or within the depth interval of 0–10 cm ( $r = -0.09$ ,  $n = 90$ ) suggests that Hg concentration is not a key factor controlling the variability of MMHg concentrations in subsurface sediments.

In contrast to Hg, there was large spatial variability of MMHg concentration in sediments. The peat-rich Franks

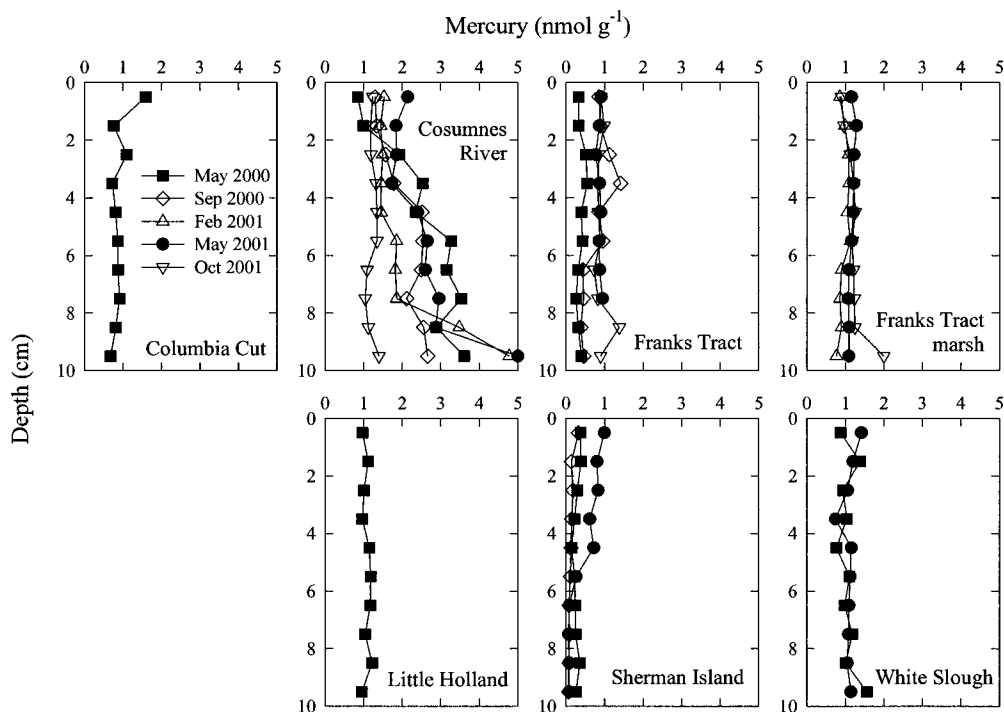


Fig. 2. Depth profiles of Hg concentration in sediments.

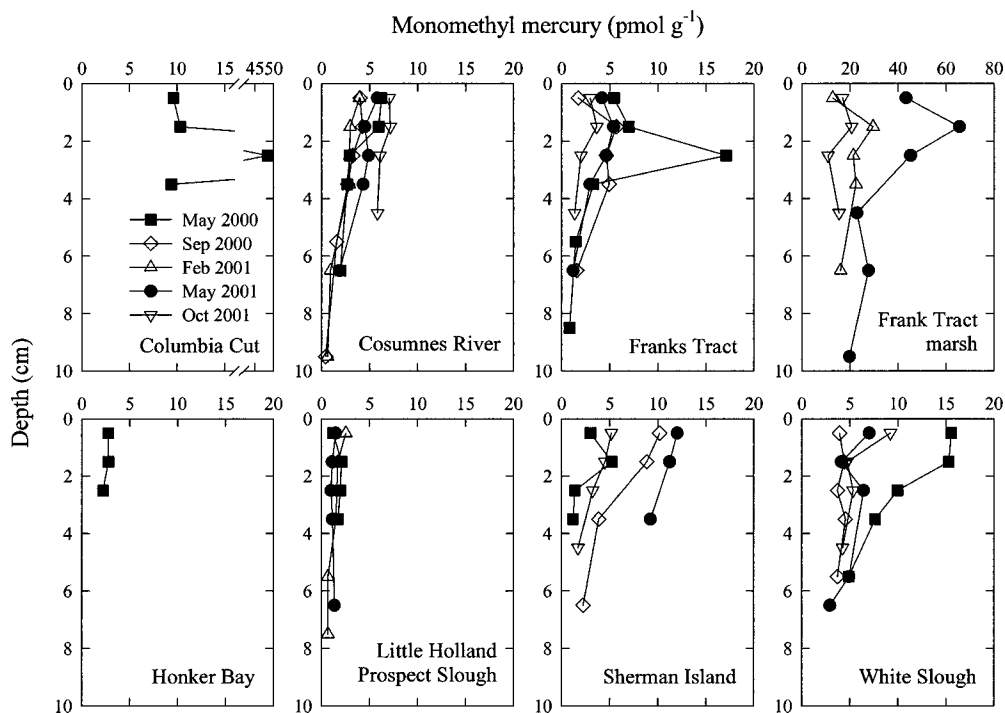


Fig. 3. Depth profiles of MMHg concentration in sediments. Note that the concentration scale for the Franks Tract marsh is different from those for the other sites. For the Little Holland and Prospect Slough panel, the data for year 2000 refer to Little Holland and for 2001 to Prospect Slough.

Tract marsh had the highest MMHg concentration, ranging from 13–30 pmol g<sup>-1</sup> in February 2000 to 20–66 pmol g<sup>-1</sup> in May 2001. Columbia Cut also had elevated MMHg concentrations in May 2000, ranging from 9.4 to 48 pmol g<sup>-1</sup>. Both areas could be considered important source regions of MMHg production. Relatively low MMHg concentrations were found at Honker Bay, Little Holland, and Prospect Slough (0.7–2.8 pmol g<sup>-1</sup>) with no significant seasonal variability. Cosumnes River, Franks Tract, Sherman Island, and White Slough had medium concentrations, ranging from 0.4 to 17 pmol g<sup>-1</sup>. These results are consistent with a recent study conducted by Marvin-DiPasquale et al. (2003) in San Pablo Bay located in northern San Francisco Bay, where MMHg concentrations were higher at a salt marsh site (27 ± 18 pmol g<sup>-1</sup>) than at open-water sites (<4 pmol g<sup>-1</sup>).

Several studies have observed that MMHg concentrations covary with organic matter content in estuarine sediments (Benoit et al. 1998; Conaway et al. 2003). Unfortunately, organic material content was not directly measured in this study, but LOI was measured at the sediment surface (0–0.5 cm) in a concurrent study (Heim 2003). There was a significant correlation ( $r = 0.91$ ,  $P < 0.001$ ,  $n = 9$ ) observed between MMHg and LOI in samples collected in May 2000, suggesting that MMHg concentration in surficial Delta sediments might be related to organic matter content. It should be noted, however, that LOI values used here are measured in surface sediments (0–0.5 cm), and the correlation does not necessarily account for the vertical variability of MMHg in Delta sediments.

It has also been suggested that mean grain size or percent fine sediment (i.e., <63 μm) could also be an important factor controlling MMHg concentration in estuarine sediments (Conaway et al. 2003). However, the correlation between MMHg concentration and the content of fine-grain sediment was negligible because LOI was poorly correlated with fine-grained sediment content ( $r = 0.26$ ,  $n = 6$ ).

A maximum sediment MMHg concentration was measured at (e.g., Cosumnes River and Prospect Slough) or near the sediment–water interface (1–3 cm; e.g., Columbia Cut, Franks Tract, Franks Tract marsh, Sherman Island, and White Slough), followed by a rapid concentration decrease with increasing depth. At most sites, the maximum concentrations observed in May 2000 or May 2001 were about two- to threefold higher than those found during other sampling periods. The shape of the vertical distribution profile and seasonal changes in sediment MMHg concentrations observed here are similar to those reported in other Hg-affected estuaries such as Lavaca Bay, Texas (Bloom et al. 1999).

It is widely recognized that MMHg production is mainly mediated by sulfate-reducing bacteria (Compeau and Bartha 1985; Gilmour et al. 1992), and temperature is an important parameter influencing Hg methylation rate (Gilmour et al. 1998). In this study area, the overlying water temperature during the day averaged ~23°C in May and September and ~10°C in February. As a result, the vertical and temporal variation of MMHg in the study area suggests that Hg methylation processes occur predominantly at or within a few centimeters of the sediment–water interface, with an active methylation period in spring. Higher MMHg concentrations in May 2000 and May 2001 than those in September 2000

and October 2001 might be attributed to Hg methylation stimulated by the high supply of fresh organic matter after the spring plankton bloom.

*Total Hg in pore waters*—Vertical concentration profiles of filter-passing Hg (<0.45 μm) in sediment pore waters are shown in Fig. 4. Clearly, the distribution of Hg in pore water was not proportional to Hg associated with the solid phase ( $r = -0.084$ ), suggesting that pore-water Hg concentrations are not simply controlled by an exchange equilibrium between dissolved and solid phases (Gagnon et al. 1997; Covelli et al. 1999). Mercury concentrations generally ranged from ~10 to 50 pmol L<sup>-1</sup>, with elevated values (140–260 pmol L<sup>-1</sup>) at Cosumnes River, Franks Tract, and White Slough. Most sites had higher Hg concentrations in May 2000 and May 2001 than other sampling periods. Intersite variation also was greater in May 2000 and May 2001 than for other sampling periods.

Subsurface Hg maximums were observed at depths between 1 and 2 cm in May 2000 or May 2001. Two explanations could be suggested for this observation. First, production of MMHg by microbial activity can increase the apparent solubility and mobility of total Hg (Bloom et al. 1999). Enhanced activities of Hg methylators during warm periods resulted in elevated MMHg concentrations in both sediment and pore water in May and September 2000 (Fig. 5). At Franks Tract marsh, for example, maximum Hg and MMHg concentrations in May 2001 were, respectively, about 30 pmol L<sup>-1</sup> and 20 pmol L<sup>-1</sup> higher than those measured in February 2001, suggesting that Hg methylation in sediment followed by the release of MMHg into pore water influences Hg solubility. However, this hypothesis does not appear to be important at other sites. A maximum concentration of Hg in pore water was generally greatest in May, whereas a peak concentration of MMHg was observed both in May and September (Fig. 5).

A second possibility is that solubilization and precipitation reactions involving iron (Fe), manganese (Mn), or both, which depend on redox conditions in the sediment, control the solubility and mobility of Hg (Gobeil and Cossa 1993; Gagnon et al. 1997; Covelli et al. 1999). The reduction of Fe or Mn (hydro)oxides at the redox boundary as a consequence of microbial degradation of organic matter results in the associated dissolution of Hg. Pore-water Fe and Mn concentrations were not measured in this study. However, the depth of oxygen penetration in the sediments determined with a microelectrode was only a few millimeters (data not shown), possibly leading to an environment favorable to Fe and Mn reduction below this depth. Depth profiles of Fe and Mn measured in other areas of San Francisco Bay showed a sharp subsurface maximum at a depth between 1 and 4 cm (Rivera-Duarte and Flegal 1994), which is consistent with depths where the Hg maximum was observed in this study. Increases of the supply of organic matter to the sediment after plankton blooms could also enhance the reduction of Fe or Mn (hydro)oxides (Roitz et al. 2002), possibly resulting in higher Hg concentrations in pore water in May 2000 and May 2001 compared with other sampling periods. The sharp decrease in dissolved Hg observed at depths <4 cm could be attributed to the precipitation of insoluble metacin-

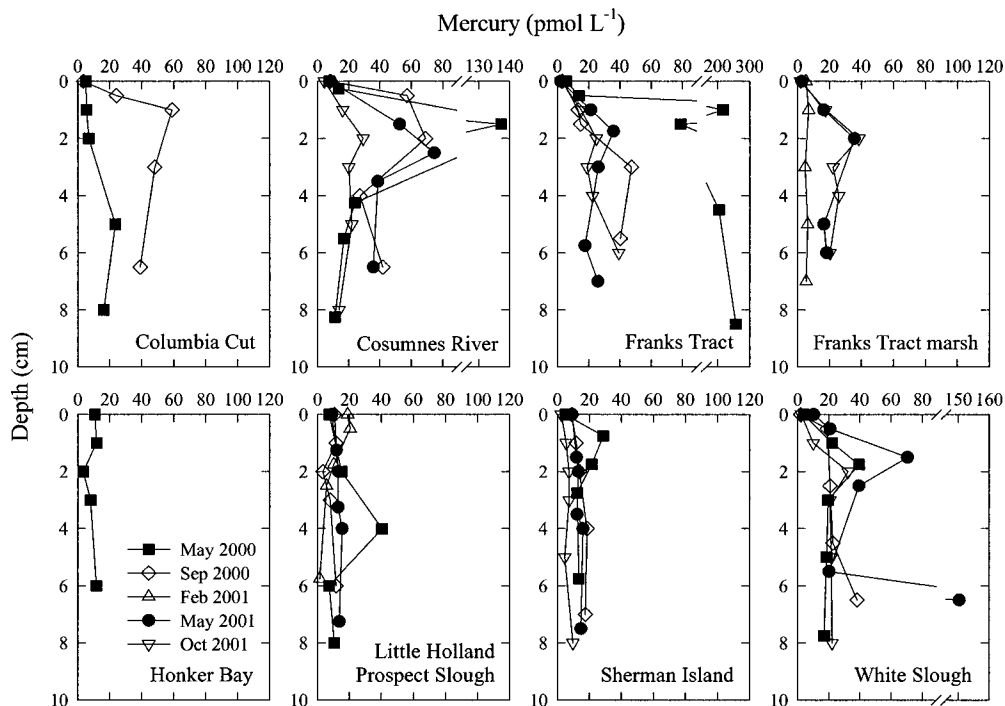


Fig. 4. Depth profiles of filter-passing Hg concentration ( $<0.45 \mu\text{m}$ ) in pore water. Concentrations at 0 cm represent those measured in the overlying water.

nabar (HgS) or coprecipitation of Hg with iron sulfides (Gobeil and Cossa 1993). The mechanism for the elevation of Hg concentrations in deep sediments of Franks Tract in May 2000 and White Slough in May 2001 is not clear. One possibility could be the significant heterogeneity in the sediments because such enhancements were not noted to be reproducible.

**MMHg in pore waters**—Most sampling sites had MMHg concentrations in pore water ranging from 1 to 20 pmol L<sup>-1</sup> (Fig. 5). In general, the spatial variability of pore-water MMHg is consistent with that of sediment MMHg discussed earlier; Cosumnes River, Franks Tract, Franks Tract marsh, and White Slough had higher MMHg concentrations than other sampling sites. Like sediment MMHg, pore-water MMHg showed significant seasonal variability at Cosumnes River and Franks Tract marsh, with the lowest concentrations measured in February 2001. In contrast to the sediment MMHg, which showed a maximum concentration in spring, the pore-water MMHg concentration did not decrease from spring to fall, and MMHg concentrations in September often exceeded those in May.

Maximum MMHg concentrations occurred at depths between 0.5 and 2 cm in most cores, which is consistent with the depth where a maximum MMHg concentration occurred in sediment. This distributional feature is in good agreement with those reported in Lavaca Bay (Mason et al. 1998; Bloom et al. 1999) and the Florida Everglades (Gilmour et al. 1998). Bloom et al. (1999) noted that the particle–water partition coefficient ( $K_D = [\text{MMHg}_{\text{sed}}]/[\text{MMHg}_{\text{pw}}]$ ) for MMHg was lowest at the depth where the filter-passing Fe concentration was at its maximum. This suggests that the

solubility and mobility of MMHg in this area might be controlled by adsorption and dissolution processes involving Fe (hydro)oxides or Fe sulfides, as previously discussed for Hg. It has been suggested that Fe and Mn oxides could also serve as a geochemical barrier limiting the release of Hg and MMHg from pore water to overlying bottom waters (Gagnon et al. 1997; Gill et al. 1999).

The fraction of Hg in methylated form (percent MMHg) in pore water ranged from  $<0.5\%$  to 120%, with few values  $>100\%$ . Sample heterogeneity in pore water could be contributing to the variability in the data (Mason et al. 1998; Bloom et al. 1999) because pore-water Hg and MMHg analyses were performed on separate replicate cores. The highest percent MMHg was observed at Franks Tract marsh in May and October 2001, averaging  $60 \pm 35\%$  and  $33 \pm 19\%$ , respectively, suggesting that the marsh area could be an important source of MMHg into Franks Tract or the Delta. The fraction of MMHg in pore water averaged  $19 \pm 21\%$  ( $n = 94$ ), which is significantly higher than observed in sediment ( $1.0 \pm 1.2\%$ ,  $n = 90$ ) or overlying water ( $7.0 \pm 8.4\%$ ,  $n = 24$ ), suggesting a higher solubility for MMHg compared with Hg.

Figure 6 summarizes traditional particle–water partition coefficient ( $K_D$ ) determinations based on MMHg concentrations in pore water and sediment. The average log  $K_D$  for MMHg ( $3.3 \pm 0.7$ ,  $n = 97$ ) was an order of magnitude lower than that of Hg ( $4.6 \pm 0.4$ ,  $n = 80$ ), which agrees with the elevated percent MMHg values in pore water compared with those in solid phase. In general, log  $K_D$  values for MMHg in sediment were lower than those measured in Sacramento River suspended particles, which had a log  $K_D$  between 4.3 and 4.8 (Choe and Gill 2003), but were an order of magni-

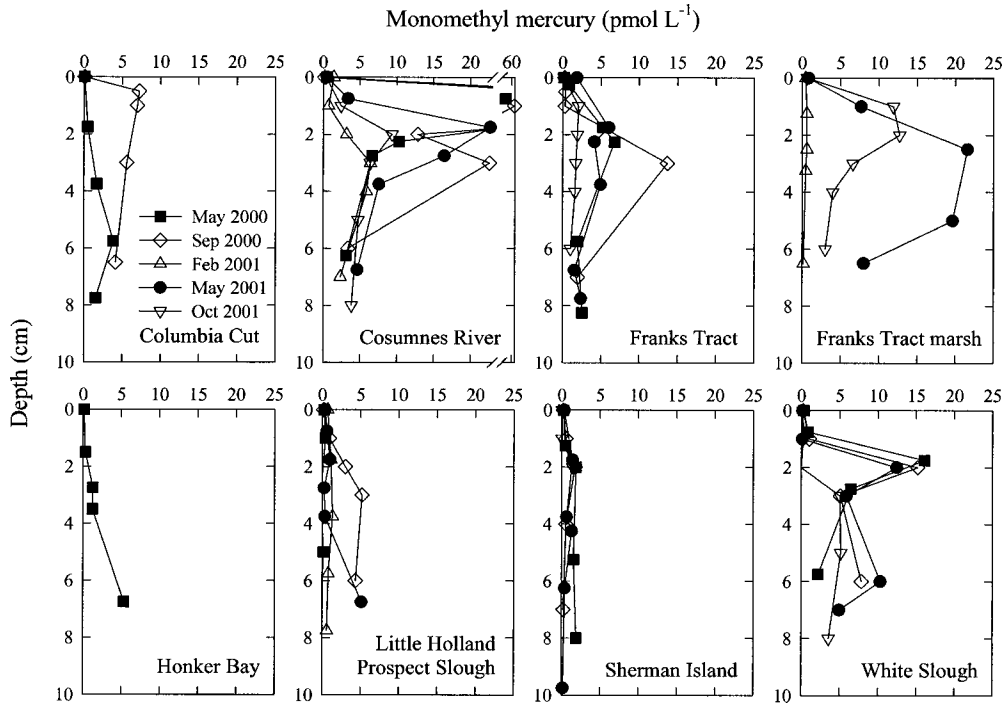


Fig. 5. Depth profiles of filter-passing MMHg concentration ( $<0.45 \mu\text{m}$ ) in pore water. Concentrations at 0 cm represent those measured in the overlying water.

tude higher than those estimated in Lavaca Bay ( $2.7 \pm 0.8$ ,  $n = 69$ ; Bloom et al. 1999). At Cosumnes River, there was a distinctive seasonality in the upper sediments ( $\leq 2$  cm), with higher values during February 2001. Extremely low  $K_D$  values in May and September 2000 occurred when pore-

water MMHg concentrations were highest seasonally. Franks Tract, Sherman Island, and White Slough showed a similar depth profile (e.g., high  $K_D$  values near the surface, a rapid decrease in depths between 2 and 4 cm, and a fairly constant distribution in deeper sediments). At Franks Tract marsh,

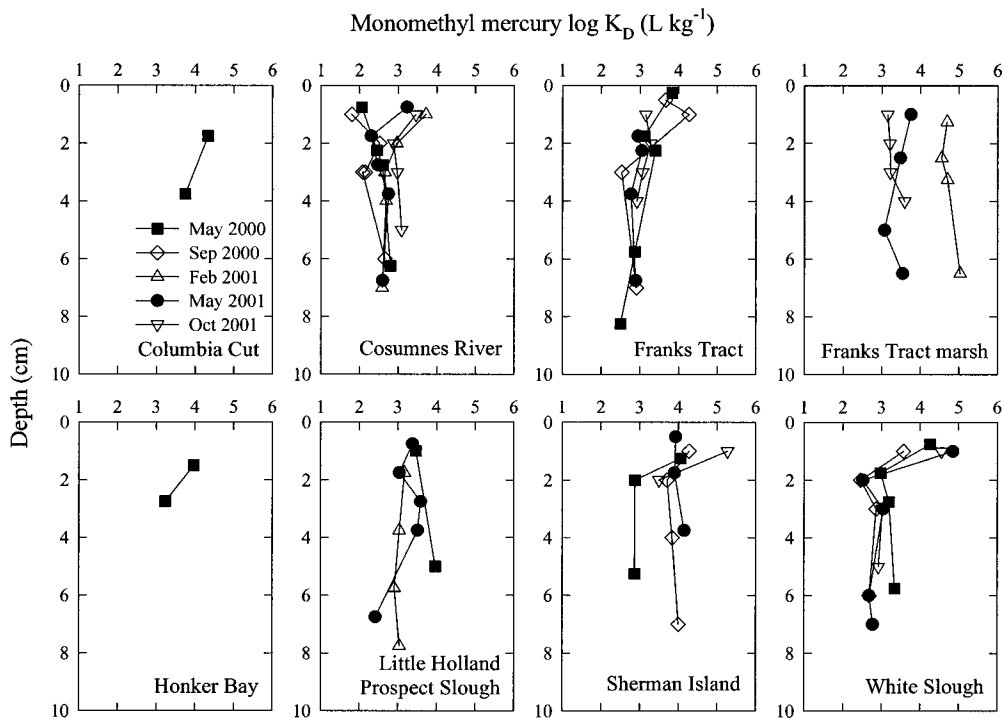


Fig. 6. Depth profiles of particle-water partition coefficients for MMHg.

Little Holland, and Prospect Slough,  $K_D$  values did not vary significantly with depth. Franks Tract and Prospect Slough did not show seasonality, and Franks Tract marsh revealed the largest seasonal variability among the sampling sites.

*Diffusive flux estimation*—Table 4 summarizes diffusive flux estimates for Hg and MMHg. Diffusive flux estimates for Hg ranged from 1.3 to 220 pmol m<sup>-2</sup> d<sup>-1</sup>, with higher values in warm seasons (May–October) than in February (Fig. 7), mainly because of higher pore-water Hg concentrations in May–October. In general, higher Hg fluxes were observed at Cosumnes River, Franks Tract, Franks Tract marsh, and White Slough than at Little Holland and Sherman Island.

Diffusive fluxes for MMHg ranged from -4.4 to 440 pmol m<sup>-2</sup> d<sup>-1</sup> with seasonal and spatial variability (Fig. 8). Diffusive flux estimates were lowest in February 2001. Columbia Cut, Cosumnes River, Franks Tract, and Franks Tract marsh had higher diffusive fluxes than Honker Bay and Sherman Island. The fraction of MMHg contributing to the Hg flux was greatest at Cosumnes River (48% in September 2000 and 10% in May 2001) and Franks Tract marsh (29% in February 2001 and 37% in May 2001), consistent with the sampling sites where elevated diffusive fluxes of MMHg were observed.

*Benthic chamber deployments*—Direct measurements of the sediment–water exchange flux of Hg obtained with benthic chamber deployments are shown in Fig. 7 along with diffusive flux estimates. Direct flux measurements ranged from -1,900 to 2,600 pmol m<sup>-2</sup> d<sup>-1</sup>, showing no significant relationship with diffusive fluxes ( $r = -0.23$ ,  $n = 20$ ). Even though there was a substantial amount of temporal variability at each site, Prospect Slough, Sherman Island, and White Slough had relatively high fluxes, averaging 1,400 ( $n = 2$ ), 1,600 ± 1,200 ( $n = 3$ ), and 1,200 ± 1,100 pmol m<sup>-2</sup> d<sup>-1</sup> ( $n = 3$ ), respectively. In contrast, Cosumnes River and Little Holland had relatively low or possibly negative fluxes (i.e., flux into the sediment), averaging -480 ± 920 ( $n = 3$ ) and -820 pmol m<sup>-2</sup> d<sup>-1</sup> ( $n = 2$ ), respectively.

It is difficult to generalize any seasonal changes in the sediment–water exchange flux of Hg because of the paucity of data collection in different seasons. Moreover, only a few sites showed reproducible seasonal patterns. Franks Tract showed higher fluxes in May 2000 and May 2001 than in September 2000 and October 2001. In contrast, White Slough had higher Hg fluxes in October than in May. Franks Tract marsh had relatively constant Hg fluxes during the period of February 2000–October 2001. Sherman Island and White Slough had the highest fluxes in October 2001.

Measured fluxes for MMHg ranged from -92 to 850 pmol m<sup>-2</sup> d<sup>-1</sup> (Fig. 8), which are comparable to those measured in Lavaca Bay (75–770 pmol m<sup>-2</sup> d<sup>-1</sup>; Bloom et al. 1999) but markedly lower than those measured in the Gulf of Trieste, northern Adriatic Sea (-530–12,000 pmol m<sup>-2</sup> d<sup>-1</sup>; Covelli et al. 1999), which also has been affected by historical Hg mining activities. Cosumnes River (80 ± 57 pmol m<sup>-2</sup> d<sup>-1</sup>,  $n = 3$ ), Franks Tract (48 ± 49 pmol m<sup>-2</sup> d<sup>-1</sup>,  $n = 4$ ), Franks Tract marsh (310 ± 470 pmol m<sup>-2</sup> d<sup>-1</sup>,  $n = 3$ ), and Little Holland/Prospect Slough (51 ± 53 pmol m<sup>-2</sup>

d<sup>-1</sup>,  $n = 3$ ) had higher fluxes than Sherman Island (-29 ± 47 pmol m<sup>-2</sup> d<sup>-1</sup>,  $n = 4$ ) and White Slough (-21 ± 55 pmol m<sup>-2</sup> d<sup>-1</sup>,  $n = 3$ ). This spatial variability is considerably different from that observed for Hg, which had higher fluxes at Sherman Island and White Slough than at Columbia Cut and Cosumnes River. In general, sites with relatively high diffusive MMHg fluxes (i.e., Columbia Cut, Cosumnes River, Franks Tract, Franks Tract marsh) also had elevated measured fluxes, and sites with low diffusive MMHg fluxes (i.e., Sherman Island and White Slough) had low or negative measured fluxes. However, there was a poor linear relationship between average diffusive and measured fluxes ( $r = 0.37$ ,  $n = 8$ ).

White Slough is a site of special interest. This site had relatively high pore-water MMHg concentrations (~15 pmol L<sup>-1</sup>) during all three sampling periods (Fig. 5). These concentrations are comparable to those found at Franks Tract and Franks Tract marsh. However, MMHg fluxes measured with flux chambers at White Slough in May 2000 and May 2001 were -84 and 5 pmol m<sup>-2</sup> d<sup>-1</sup>, respectively, accounting for <10% of those measured at Franks Tract and Franks Tract marsh during the same period. This implies that MMHg does not diffuse freely through the sediment–water interface in this region. There are several possible hypotheses to explain this anomaly. First, the presence of a thin oxic surface sediment layer would serve as a geochemical barrier for MMHg diffusion (Gagnon et al. 1996, 1997; Gill et al. 1999). A second possibility could be the absence or insignificance of bioirrigation and bioturbation at this site that would ordinarily enhance the exchange of interstitial pore water. A third possibility is that the predominance of demethylation processes over methylation processes could occur near the sediment–water interface (Oremland et al. 1991). The last hypothesis could explain why a low MMHg flux but high Hg flux occurs at this site. Further studies are clearly needed to examine these processes.

Directly measured fluxes for MMHg in May 2000 and May 2001 were generally greater than those observed in other sampling periods, except for the abnormally high flux observed at Franks Tract marsh in October 2001 (850 pmol m<sup>2</sup> d<sup>-1</sup>). Figure 9 shows typical time series MMHg measurements in flux chambers deployed at selected sites. Time course concentration increases (i.e., slope of a regression line) were similar at all sites in May 2001, ranging from 0.040 to 0.046 pmol L<sup>-1</sup> h<sup>-1</sup>. On the other hand, in February 2001, Prospect Slough did not show any concentration increase with time, and Franks Tract marsh showed a decreasing MMHg concentration with time. These results suggest that MMHg production during the warm period enhanced the sediment–water exchange of MMHg at these sites.

Considerable seasonal variability was observed in the sediment–water exchange flux of MMHg (Fig. 8). Moreover, the seasonal changes in flux did not necessarily follow what one would predict from seasonal changes in physical and biogeochemical parameters. To illustrate, the sediment–water exchange fluxes measured at Cosumnes River were greater in February 2001 than in May 2001 (Fig. 8). It was also surprising that measured fluxes were relatively low in September 2000 and October 2001 at most sites, although there was no significant difference in pore-water MMHg concen-

Table 4. Sediment-water exchange fluxes of Hg and MMHg in the San Francisco Bay-Delta ( $\text{pmol m}^{-2} \text{d}^{-1}$ ) and the percentage of the measured flux ( $F_M$ ) attributed to diffusive flux ( $F_D$ ).\*

Site	May 2000			Sep 2000			Feb 2001			May 2001			Oct 2001		
	$F_M$	$F_D$	$F_D/F_M$ (%)	$F_M$	$F_D$	$F_D/F_M$ (%)	$F_M$	$F_D$	$F_D/F_M$ (%)	$F_M$	$F_D$	$F_D/F_M$ (%)	$F_M$	$F_D$	$F_D/F_M$ (%)
<b>Mercury</b>															
Columbia Cut	—	1.3	—	-260	130	—	—	—	—	—	—	—	—	—	—
Cosumnes River	—	39	—	—	220	—	-1,500	—	—	-210	83	—	280	34	12
Franks Tract	1,900	53	2.8	130	30	23	—	—	—	830	56	6.7	250	29	12
Franks Tract marsh	—	—	—	—	—	—	640	2.9	0.5	870	42	4.8	880	52	5.9
Honker Bay	—	8.0	—	—	—	—	—	—	—	—	—	—	—	—	—
Little Holland	-1,200	6.0	—	-440	1.9	—	—	—	—	—	—	—	—	—	—
Prospect Slough	—	—	—	—	—	—	810	5.0	0.6	1,900	4.0	0.2	—	—	—
Sherman Island	—	79	—	180	6.9	3.8	—	—	—	1,900	4.6	0.2	2,600	7.0	0.3
White Slough	240	58	24	—	110	—	—	—	—	1,100	58	5.3	2,400	21	0.9
<b>Monomethyl mercury</b>															
Columbia Cut	62	0.7	1.1	63	41	65	—	—	—	—	—	—	—	—	—
Cosumnes River	—	120	—	—	140	—	130	-1.3	—	92	10	11	18	5.9	33
Franks Tract	110	8.5	7.7	10	0.9	9.0	—	—	—	62	7.0	11	8.1	4.3	53
Franks Tract marsh	—	—	—	—	—	—	-19	0.2	—	89	21	24	850	37	4.4
Honker Bay	37	0.2	0.5	—	—	—	—	—	—	—	—	—	—	—	—
Little Holland	110	0.3	0.3	14	1.5	11	—	—	—	—	—	—	—	—	—
Prospect Slough	—	—	—	—	—	—	0.0	0.4	—	80	0.5	0.6	—	—	—
Sherman Island	14	0.5	3.6	-92	0.8	—	—	—	—	-36	1.6	—	-3.0	-0.1	—
White Slough	-84	2.3	—	—	2.6	—	—	—	—	5.0	-0.1	—	17	0.1	0.6

\* Negative values indicate fluxes into the sediments.

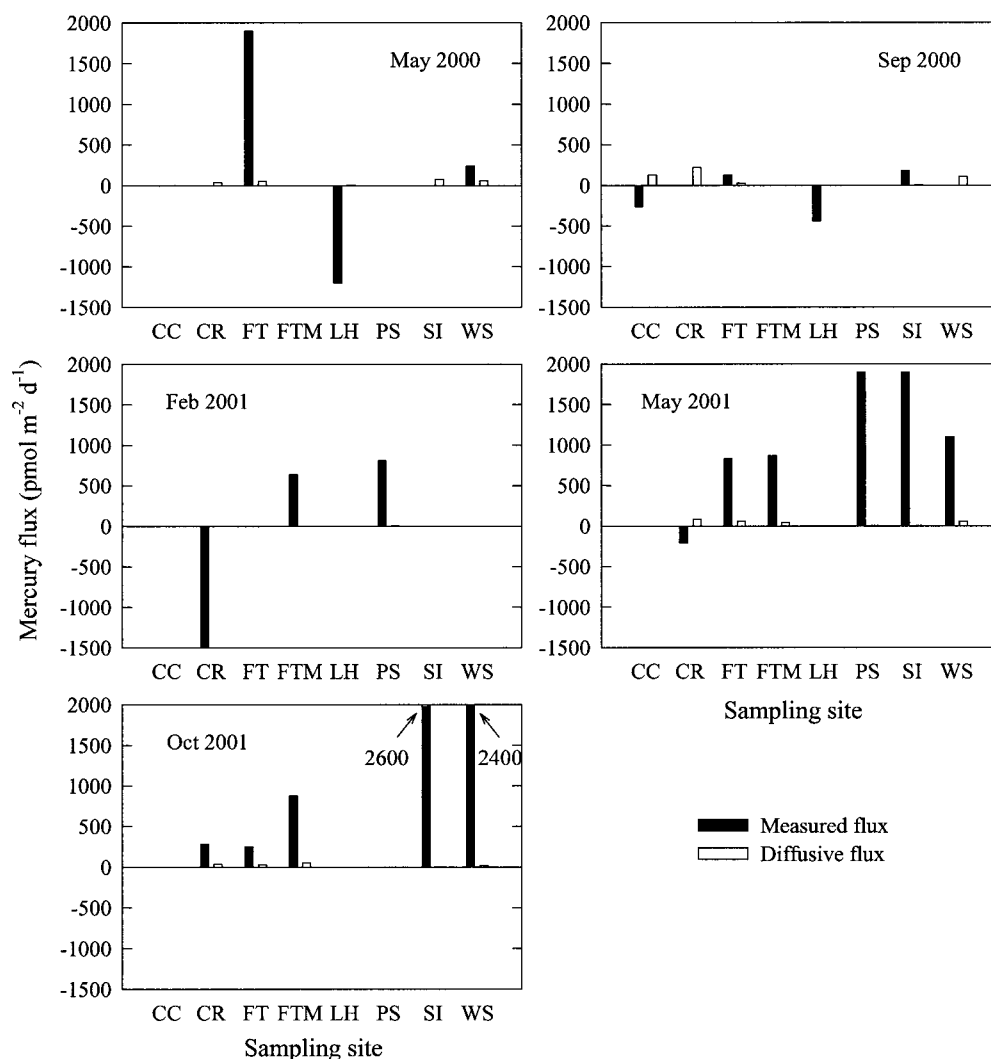


Fig. 7. Sediment–water exchange fluxes of Hg. CC, Columbia Cut; CR, Cosumnes River; FT, Franks Tract; FTM, Franks Tract marsh; LH, Little Holland; PS, Prospect Slough; SI, Sherman Island; WS, White Slough.

trations between May and September or October (Fig. 5). A similar situation was observed in the Gulf of Trieste, where maximum measured sediment–water exchange fluxes and pore-water concentrations of MMHg were observed in fall (November), when the water temperature was at its median level of the annual range (Covelli et al. 1999). Covelli et al. (1999) suggested that elevated sulfide concentrations, resulting from rapid sulfate reduction during the hottest months, could hinder the mobility of Hg and MMHg in sediments. In the Bay-Delta, it is not clear what parameters control Hg and MMHg exchanges across the sediment–water interface on a seasonal basis.

In general, water column MMHg concentrations tend to be higher during warm periods in other aquatic systems (Hurley et al. 1995; Leermakers et al. 2001), most likely because of the temperature dependency of microbial activities on MMHg production. At all sites in this study, however, the initial MMHg concentrations inside benthic chambers were higher in February, when the river flow rate was higher.

This is in agreement with a previous study (Choe and Gill 2003) that particulate, filter-passing, and colloidal MMHg concentrations measured in the surface water of the Sacramento River were about twofold higher under high flow conditions than those measured under low flow conditions. This observation possibly resulted from resuspension and erosion of MMHg-rich surface sediments during storm events (Domagalski 1998), suggesting that the benthic input from sediments could play an important role in the MMHg cycle within the Delta, especially under low river flow conditions, whereas the riverine input is important during high flow conditions.

*Comparison of measured and diffusive fluxes*—For both Hg and MMHg, direct measurements with chamber deployments produced higher fluxes than diffusional fluxes derived from interfacial pore-water concentration gradients. The diffusive flux accounted for only 0.2–24% of the measured flux for Hg and 0.3–65% for MMHg (Table 4). Underestimation

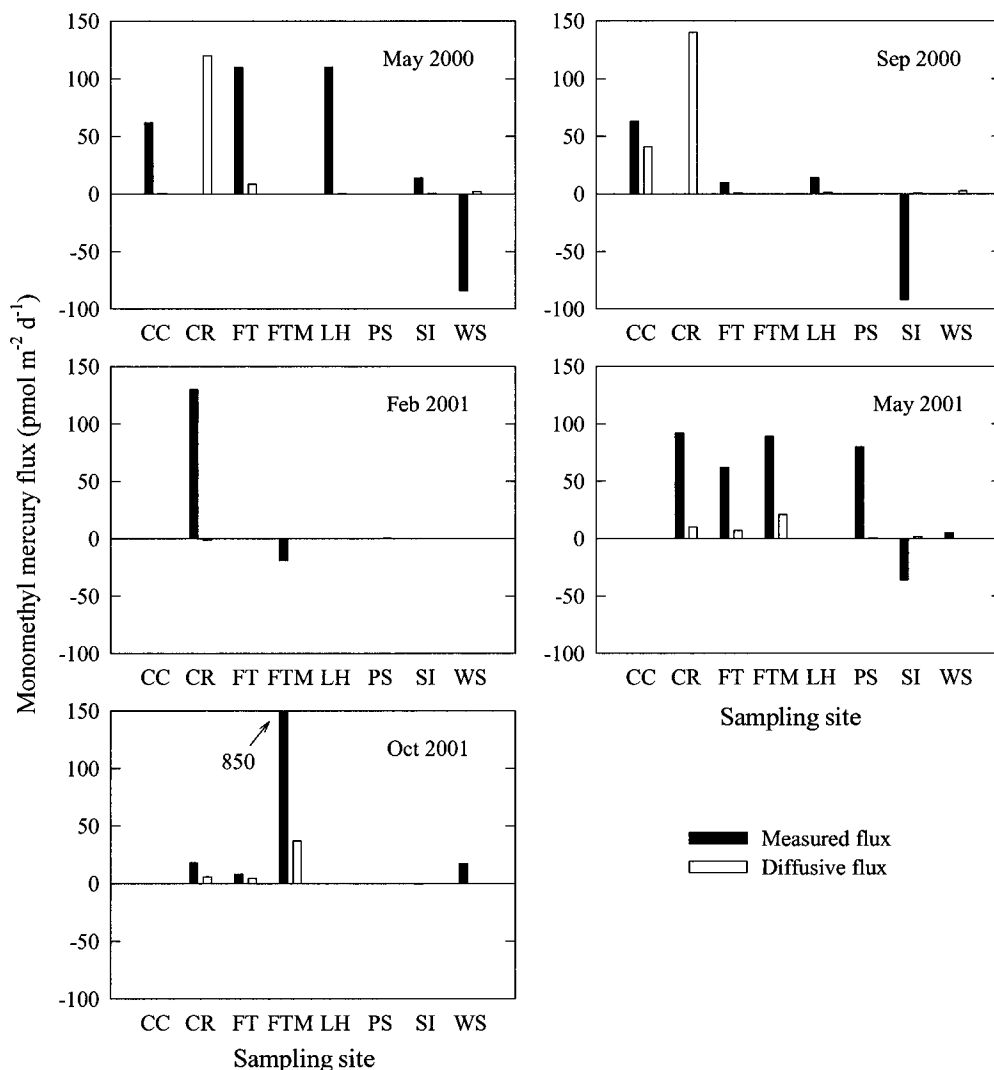


Fig. 8. Sediment-water exchange fluxes of MMHg. CC, Columbia Cut; CR, Cosumnes River; FT, Franks Tract; FTM, Franks Tract marsh; LH, Little Holland; PS, Prospect Slough; SI, Sherman Island; WS, White Slough.

of the measured flux by the diffusive flux for trace elements and nutrients has been commonly reported in the literature (Hammond et al. 1985; Covelli et al. 1999; Gill et al. 1999; Warnken et al. 2001). In a shallow estuarine environment in Texas, Warnken et al. (2001) observed that diffusive fluxes accounted for 5–38% and 25–38% of in situ measured fluxes of manganese and zinc, respectively. Similarly, Covelli et al. (1999) noted that the diffusive flux explained <10% of the MMHg flux measured in the Gulf of Trieste. These discrepancies could arise from benthic organism activities that enhance the exchange of interstitial pore water over pure diffusion or from inappropriate resolution of pore-water concentration gradients near the sediment-water interface. Inadequacy in resolving surficial concentration gradients seems an unlikely explanation, because maximum MMHg concentrations in pore water were below the surface pore-water sampling interval at most sites. Therefore, enhanced exchange of interstitial pore water over pure diffusion ap-

pears to be attributed to advective processes such as biological irrigation in surface sediments (Hammond et al. 1985).

*Significance of sediment-water exchange*—It has been suggested that wetland and marsh regions are major sites for MMHg production (St. Louis et al. 1994; Hurley et al. 1995; Gilmour et al. 1998). Moreover, in shallow estuarine environments, exchange of a constituent across the sediment-water interface could be substantial enough to influence the overlying water column concentration (Rivera-Duarte and Flegal 1994, 1997; Gill et al. 1999; Warnken et al. 2001). To test these hypotheses in the Bay-Delta, a surface-water transect study was conducted in Franks Tract, moving from a nearshore marsh area to open water on 21 May 2001. Mercury and MMHg concentrations were measured in unfiltered and filtered water samples collected at Franks Tract marsh and three open-water stations (FT1, FT2, and FT3; see Fig. 1). As shown in Fig. 10, unfiltered Hg was elevated only in

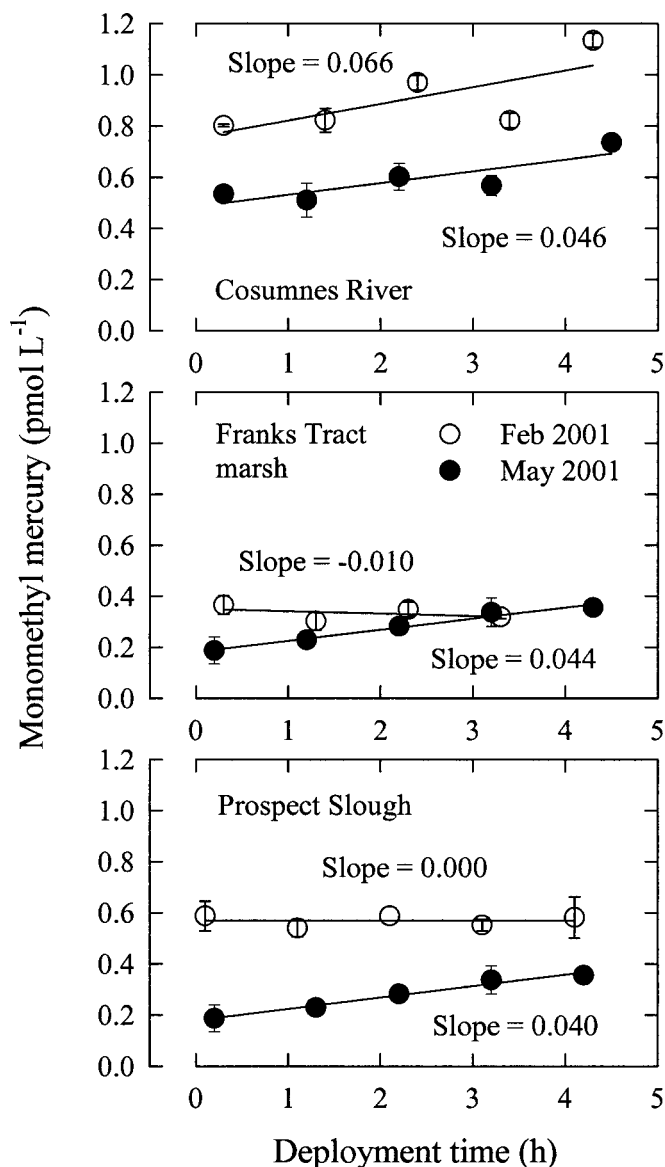


Fig. 9. Time course measurements of MMHg from benthic chambers deployed at Cosumnes River, Frank Tract marsh, and Prospect Slough in February 2001 and May 2001. Error bars and symbols represent the range of duplicate measurements and averages, respectively. The unit of slopes is  $\text{pmol L}^{-1} \text{h}^{-1}$ .

the open-water area (station FT3) and was fairly constant at the other stations. In contrast, filter-passing Hg showed clear evidence of a surface-water concentration gradient between nearshore and open water, with the highest concentration at Franks Tract marsh. Similarly, MMHg revealed a significant concentration gradient, with the highest unfiltered and filter-passing MMHg concentrations occurring at Franks Tract marsh. In addition, higher sediment–water exchange fluxes of Hg and MMHg occurred at Franks Tract marsh compared with the open-water site in Franks Tract during the same sampling period. Collectively, these results demonstrate that sediment–water exchange influences the water column concentrations of Hg and MMHg and that this influence is markedly enhanced in the nearshore marsh environment because

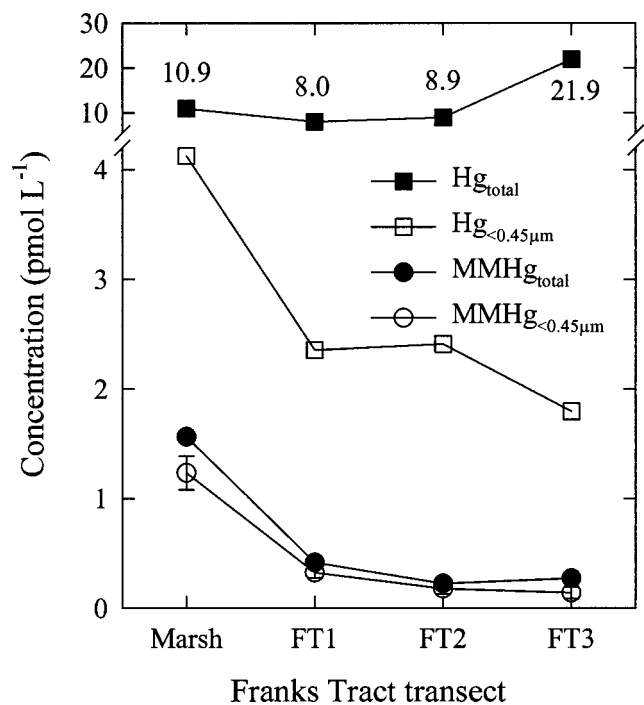


Fig. 10. Mercury and MMHg concentrations in a surface-water transect in Franks Tract on 21 May 2001.

of both shallow water depth and enhanced MMHg production.

Time series measurements of Hg and MMHg were conducted at the entrance to Franks Tract marsh on 19 May 2001 to monitor changes in Hg concentration associated with water entering and leaving the marsh during a tidal event. Unfiltered and filtered surface-water samples collected from the main channel, where water is exchanged with the marsh area, revealed high MMHg fluxes. In Fig. 11, both Hg and MMHg concentrations in unfiltered and filtered surface waters are plotted, showing Hg concentrations changing with time as water is driven into and out of the marsh by a tidal cycle. The total (i.e., unfiltered) Hg concentration was highest between high and low tides when the water flow was believed to be at its maximum. This observation suggests that resuspension or erosion of surface sediments could be a source of Hg. In contrast, the filter-passing Hg concentration was highest during low tide when there is minimal inflow of Hg-depleted Franks Tract water. Total and filter-passing MMHg concentrations were also highest during low tide and lowest during high tide. As the water level rose from low to high tide, Franks Tract water, with relatively low Hg and MMHg concentrations, flowed through the inlet, diluting Hg and MMHg concentrations in the marsh. Conversely, as the water level dropped from high to low tide, Hg- and MMHg-enriched Franks Tract marsh water was exported through the inlet to Franks Tract, increasing Hg and MMHg concentrations. These observations reflect not only that the sediment–water exchange flux of Hg and MMHg is significant enough to influence the overlying water column concentrations, but also that the marsh habitat could be a major source of MMHg to Franks Tract. However, it is not clear

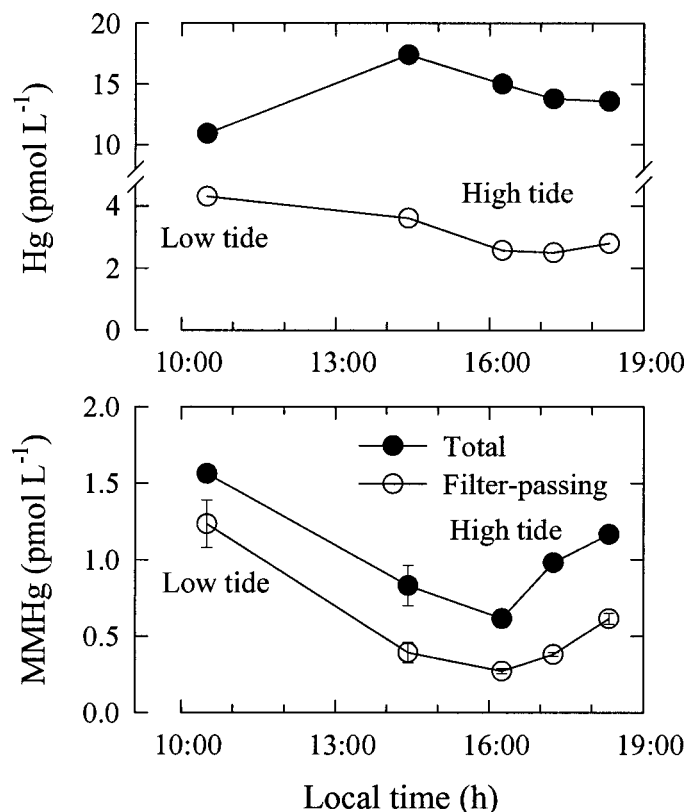


Fig. 11. Time series measurements of Hg and MMHg at the entrance to Franks Tract marsh on 19 May 2001.

whether input of MMHg from marsh sites, like Franks Tract marsh, influences MMHg concentration levels in the entire Delta.

*Comparison of benthic and riverine inputs*—An estimate of the sediment–water exchange of Hg and MMHg for the entire Delta region can be obtained by multiplying an average flux by the open-water area covering the sampling locations. The average Hg flux was  $630 \text{ pmol m}^{-2} \text{ d}^{-1}$ , and the surface area of open water, estimated by a Geographic Information System (GIS) program, was  $\sim 200 \text{ km}^2$ . The integrated sediment–water exchange flux obtained is  $\sim 130 \text{ pmol m}^{-2} \text{ d}^{-1}$ , which is equivalent to  $\sim 26 \text{ g d}^{-1}$ . For comparison, riverine flux estimates of Hg were made (C. Foe pers. comm.) between March 2000 and October 2001. Filter-passing ( $<0.45 \mu\text{m}$ ) Hg concentrations were measured monthly along with water flows from all the major freshwater sources to the Bay-Delta (Sacramento, San Joaquin, Mokelumne, Cosumnes Rivers, and Prospect Slough) and from all its major export sites. A direct comparison between riverine and sediment–water exchange fluxes is possible for the time period of May 2000 through October 2001. Riverine Hg import into the Delta averaged  $110 \text{ g d}^{-1}$  during wet months (January–March) and  $29 \text{ g d}^{-1}$  during dry months. The Hg exported out of the Delta averaged  $74 \text{ g d}^{-1}$  during wet months and  $23 \text{ g d}^{-1}$  during dry months. This flux comparison demonstrates that the sediment–water exchange flux is as important as riverine transport in the Delta’s Hg budget, especially during low-flow seasons.

For MMHg, sediment–water exchange fluxes averaged  $30 \text{ pmol m}^{-2} \text{ d}^{-1}$ , excluding the abnormally high value of  $850 \text{ pmol m}^{-2} \text{ d}^{-1}$  measured at Franks Tract marsh in October 2001. The resultant benthic MMHg flux estimate for the entire Delta is  $6 \text{ mmol d}^{-1}$ , which is equivalent to  $1.2 \text{ g d}^{-1}$  of MMHg. It should be noted that this is a minimum estimate and could increase substantially when the MMHg imported from marsh or seasonally flooded areas (e.g., Yolo Bypass) are included. Estimates of riverine MMHg flux were also made (C. Foe pers. comm.). Unfortunately, MMHg in the filter-passing fraction was not directly measured; it was assumed that 50% of the total MMHg was associated with the filter-passing phase. This approximation seems reasonable because the fraction of filter-passing MMHg in unfiltered water does not vary significantly within the San Francisco Bay estuary, averaging  $\sim 50\%$  of the total MMHg (Choe and Gill 2003). On average,  $5.6 \text{ g d}^{-1}$  of the filter-passing MMHg entered the Delta from all riverine sources during wet months and  $2.6 \text{ g d}^{-1}$  during dry months. Export from the Delta averaged  $3.4 \text{ g d}^{-1}$  during wet months and  $1.1 \text{ g d}^{-1}$  during dry months. These results suggest that the benthic input of MMHg within the Delta could be an important transport vector in the Bay-Delta, especially during dry seasons.

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