

Chemical and physical speciation of mercury in Offatts Bayou: A seasonally anoxic bayou in Galveston Bay

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Abstract

A chemical equilibrium model was used to predict the solution speciation of dissolved mercury (Hg) in the stratified water column of Offatts Bayou, a subestuary in Galveston Bay, Texas, which undergoes seasonal anoxia in bottom waters. Chemical equilibrium modeling was conducted using conditional stability constants and concentrations of Hg-complexing organic ligands experimentally determined by competitive ligand equilibration methods. Dissolved Hg complexation was dominated by interactions with sulfide and dissolved organic matter (DOM) (HOHgHS^0 , $\text{HOHgHS}(\text{DOM})$, HgSHS^- , and HgS_2^{2-}) at all depths. Sulfide and glutathione competed for methylmercury (MeHg) complexation in oxic layers; in anoxic waters, sulfide complexation dominated MeHg speciation. The particle–water distribution coefficient (K_d) of Hg decreased in the anoxic layer of the water column, where the dissolved sulfide concentration increased, providing evidence that sulfide complexation influences the solubility of Hg. The solubility of MeHg was elevated in the anoxic as compared to the oxic layers, and this distributional feature was coincident with a change in the solution speciation of dissolved MeHg from glutathione/sulfide complexation in the oxic layers to a predominantly sulfide complexation in the anoxic layers. Maximum enrichment of Hg, MeHg, and iron (Fe) in suspended particulate matter was observed in the lower layer of the pycnocline, most likely resulting from formation of insoluble Fe oxide, which scavenged dissolved Hg-sulfide and MeHg-sulfide species. The concomitant decrease in dissolved inorganic Hg, Fe, and sulfide in the anoxic layers is suggested to result from scavenging of inorganic Hg by FeS, which is in accordance with the Hg speciation model. Overall, Hg cycling in the water column of Offatts Bayou was associated with sulfide and DOM complexation, Fe dissolution/precipitation, water column production of MeHg, and/or efflux of MeHg from anoxic sediment.

Determining the aqueous chemical speciation of mercury (Hg) under various redox conditions is important for understanding the methylmercury (MeHg) production process, which occurs in redox transition zones, mainly via sulfate-reducing bacteria (King et al. 1999). Neutral monosulfide (HOHgHS^0) and polysulfide species (HgS_2) are predicted to be bioavailable to sulfate-reducing bacteria (Benoit et al. 1999a,b; Jay et al. 2000). Thermodynamic equilibrium modeling calculations predict that the HOHgHS^0 concentration decreases with increasing sulfide concentration. This prediction is consistent with observed patterns of MeHg production in estuarine and freshwater sediments (Benoit et al. 1999a,b). While the solution speciation of dissolved Hg is critical for understanding MeHg production, most experimental studies of Hg speciation in redox transition zones have been limited to

the determination of MeHg and total Hg in sediment pore water.

The presence of dissolved sulfide and dissolved organic matter (DOM) in anoxic water is known to increase the solubility of particulate Hg and to drive competition between dissolution and adsorption/precipitation. Morel et al. (1998) showed that the solubility of Hg increased from 3 pmol L⁻¹ to 3 nmol L⁻¹ when dissolved sulfide increased from 1 μmol L⁻¹ to 1 mmol L⁻¹ because of sulfide complexation. This increase was amplified when Hg–polysulfide complexes were produced. Evidence of DOM causing increased Hg solubility has been provided by the inhibition of the nucleation of metacinnabar by DOM and by the enhanced dissolution of cinnabar in the presence of DOM (Ravichandran et al. 1999). Conditional stability constants between Hg and the Hg binding site in the DOM indicate that thiolates are a possible Hg-binding group in DOM and that Hg–DOM complexation dominates chloride complexation in surface oxic waters (Han et al. 2006). Sulfide, however, another strong Hg-binding ligand, has often been ignored in solution speciation calculations.

Studies of the competition between sulfide and DOM for Hg complexation in anoxic sediment pore water have concluded that sulfide complexation exceeds the DOM complexation even at sulfide concentrations of 1 nmol L⁻¹ (Benoit et al. 2001). These calculations are consistent with those of recent studies by Zhang et al. (2004) regarding Hg speciation in anoxic pore waters, using conditional stability constants between dissolved Hg and low-molecular-weight

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thiols. In the modeling of Zhang et al. (2004), pore-water Hg speciation was dominated by sulfide complexation, while thiol complexation competed with sulfide complexation in MeHg speciation. However, the conditional stability constants and concentrations of Hg-complexing ligands associated with DOM have not been experimentally determined in anoxic pore waters or estuarine waters. DOM in anoxic water may have different characteristics from that in surface water in terms of Hg-binding ability, as pointed out by Haitzer et al. (2003).

The goal of this study was to predict the solution speciation of dissolved Hg in an oxic–anoxic transition water column using experimentally determined concentrations and conditional stability constants of Hg-binding ligands associated with DOM. Offatts Bayou, a subestuary in Galveston Bay, Texas, was chosen for this purpose because it develops a highly sulfidic bottom layer every summer as a result of intense oxidation of organic matter and limited water circulation. Despite its proximity to many industrial complexes, Galveston Bay, with the exception of the San Jacinto River and the upper Houston Ship Channel, has low concentrations of Hg and other trace metals, similar to levels observed in pristine estuaries along the Texas coast (Stordal et al. 1996; Wen et al. 1999). As a shallow (average depth, 2 m) and turbid estuary, Galveston Bay has a high sedimentary flux of nutrients and trace metals (Santschi 1995). During the early 1900s, the Offatts Bayou area was used as a borrow pit for major construction, resulting in an artificial basin measuring 1 km × 2 km. The basin is two to five times deeper than the surrounding waters, resulting in restricted water exchange between Offatts Bayou and the adjacent waters of Galveston Bay (Cooper and Morse 1996). Furthermore, significant seasonal variation in surface-water temperature drives a seasonal thermohaline stratification of the water column. While water column stratification blocks the vertical mixing, the surface waters of Offatts Bayou are able to be mixed with nearby surface waters of Galveston Bay, mainly by tide-driven flows.

Materials and methods

Sample collection—Samples were collected on 09 September 2003 and 26 September 2004 at the eastern end of Offatts Bayou in a basin of about 7 m in depth. Dissolved oxygen concentrations, measured at 0.5-m depth intervals, were used to decide sample collection depths. In September 2003, Teflon-coated Go-Flo bottles, cleaned with weak hydrochloric acid, were used to collect water samples from four different depths. Go-Flo bottles were deployed twice at each depth. The first bottles were used for the in situ measurements of dissolved oxygen, salinity, temperature, and pH. The second Go-Flo bottles were moved to the laboratory immediately, where filtrations (using a peristaltic pump) were carried out. In September 2004, unfiltered water samples were collected at 1-m depth intervals using Teflon tubing connected to a peristaltic pump. Filtered samples were collected at the same depth intervals using a polyethersulfone membrane filter (0.45 μm) on the exit tubing.

Sample analyses—The concentration of suspended particulate matter (SPM) was determined from the dry weight of particles after vacuum filtration using polycarbonate filters (0.45 μm). A catalytic high-temperature organic carbon analyzer (Shimadzu TOC 5000) was used to determine organic carbon concentrations in filtered water samples.

Dissolved sulfide concentrations were analyzed by the methylene blue spectrophotometric method (Okumura et al. 1999), modified from the Cline method. The preparation of reagents and standard sulfide solutions is described in Okumura et al. (1999). About 100 mL of the sample was filtered into two graduated syringes (50 mL) connected to other syringes, each containing 4 mL mixed diamine solutions (0.08 g *N,N*-dimethyl-*p*-phenylenediamine sulfate, 0.6 g iron [III] chloride, and 4 g magnesium chloride in 100 mL of 6 mol L⁻¹ hydrochloric acid). The solutions were mixed through the tubing between the two syringes, and after 20 min the colored solution generated was passed through Sep-Pak[®] C18 cartridges (Waters). The absorbed methylene blue complex was re-eluted with 4 mL of methanol in 0.01 mol L⁻¹ hydrochloric acid solution. The absorbance of the elute was measured at 659 nm. The preconcentration step using a Sep-Pak[®] C18 cartridge was not applied to bottom-layer samples that showed high sulfide concentrations (>200 $\mu\text{mol L}^{-1}$). The detection limit, estimated as three times the standard deviation of the method blank, was 10 nmol L⁻¹.

Dissolved and total copper (Cu), iron (Fe), and manganese (Mn) concentrations were measured by graphite furnace atomic absorption spectrometry with Zeeman background correction. After acidification using high-purity nitric acid, trace-metal samples were ultraviolet-irradiated (Wen et al. 1999). Each set of samples was analyzed in triplicate, and the mean values were reported.

Dissolved glutathione (GSH) concentrations were determined by high-performance liquid chromatography using a SBD-F (ammonium 7-fluorobenzo-2-oxa-1,3-diazole-4-sulfonate) derivatization technique (Tang et al. 2000). Briefly, 500 μL of acidified sample (0.1% with methanesulfonic acid) was mixed with 30 μL of 10% tri-*n*-butylphosphine in *n,n*-dimethylformamide, and a 10-min period was allowed for reduction. Then, a 200- μL borate buffer (0.1 mol L⁻¹) containing 2.0 mmol L⁻¹ ethylenediaminetetraacetic acid, 40 μL of SBD-F solution (0.25 mg mL⁻¹), and 20 μL of 1 mol L⁻¹ NaOH were added for a SBD-F derivatization. The reaction was allowed to proceed in a 60°C water bath for 60 min and was stopped by addition of 100 μL of 1 mol L⁻¹ methanesulfonic acid. The GSH–SBD-F adducts were separated using a reversed-phase C18 column (Waters system, 250 × 4.6 mm) after passage through a C18 guard column. A gradient elution was performed with a mobile phase A containing 0.1% trifluoroacetic acid in water and a mobile phase B of acetonitrile by a flow rate of 1.0 mL min⁻¹. The elution profile and detailed detector conditions are described in Tang et al. (2000).

Mercury concentrations were analyzed by cold vapor atomic fluorescence spectrometry (CVAFS) following NaBH₄ reduction and gas-phase stripping onto gold (Choe

et al. 2003). Analytical reproducibility was generally better than 4% (coefficient of variation), and the detection limit (defined as three times the standard deviation of the method blank) was 0.1 pmol L⁻¹. Recovery tests using a sediment standard (PACS2, National Research Council Canada) averaged 105% ($n = 20$).

Methylmercury measurements were conducted using aqueous phase distillation (for purification), ethylation to gaseous phase methylethyl mercury using 1% sodium tetraethylborate solution, trapping on a Tenax TA column, gas chromatography separation, thermal (ca. 700°C) decomposition and reduction to Hg⁰ on a heated quartz wool column, and detection by CVAFS. Typically, a distillation volume of 150 mL was used for surface and mid-depth water samples. For the bottom waters, ca. 10 mL was diluted to 45 mL with acidified Milli-Q[®] water prior to distillation. Sample dilution for the bottom waters was necessary to minimize inhibition of MeHg recovery during the distillation step with samples that had extremely high sulfide concentrations. The detection limit, estimated as three times the standard deviation of the method blank, was 0.02 pmol L⁻¹. Matrix spike recoveries averaged 97% ± 7% ($n = 11$), and the analytical recoveries, checked on a daily basis with dogfish muscle certified by the National Research Council of Canada, NRCC-DORM-2 (4,470 ± 320 ng g⁻¹), averaged 4,240 ± 170 ng g⁻¹ ($n = 20$).

Determination of Hg-complexing ligands—The concentrations of Hg-complexing organic ligands (Lig) and stability constants of Hg–Lig complexes were determined by Hg titrations using the competitive ligand equilibration–solvent solvent extraction method described in Han and Gill (2005). A conditional stability constant (K_{cond}') with respect to free Hg²⁺ is defined in (1). [Lig'] is the concentration of organic ligand that is not bound by Hg.

$$K_{\text{cond}}' = \frac{[\text{HgLig}]}{[\text{Hg}^{2+}][\text{Lig}']} \quad (1)$$

$$[\text{Lig}'] = [\text{Lig}]_t - [\text{HgLig}] \quad (2)$$

Linearization of titration data, as described in van den Berg (1984), permits the calculation of a conditional stability constant and total ligand concentration ([Lig]_t) from the experimental determinations of [Hg²⁺] and [HgLig], using a linear least squares regression.

$$\frac{[\text{Hg}^{2+}]}{[\text{HgLig}]} = \frac{[\text{Hg}^{2+}]}{[\text{Lig}]_t} + \frac{1}{K_{\text{cond}}'[\text{Lig}]_t} \quad (3)$$

Mercury titrations were carried out by adding increasing amounts of inorganic Hg spike additions into a series of separatory funnels. In each separatory funnel, a buffer solution (2-amino-2-methyl-1,3-propanediol, 0.01 mol L⁻¹), competing ligand (thiosalicylic acid [TSA], 2 nmol L⁻¹), and Hg standard solution (generally 0.01–0.15 nmol L⁻¹) were added to 100 mL of natural sample water, after which 10 mL of toluene was added. The mixture was allowed to equilibrate for 20 to 24 h, with intermittent

shaking, after which the water phase was drained from the funnel. Thirty-milliliter aliquots of the water phase were acidified for the measurement of total Hg, and the rest of the water was used for the measurement of pH.

The potential interference of dissolved sulfide in the Hg titrations was investigated by comparing titration slopes obtained with oxic Galveston Bay and oxic/anoxic Offatts Bayou samples. The titrations of Offatts Bayou samples were performed under oxic conditions. The titration slope is determined by the concentration ratio between aqueous Hg and total Hg, where the abundance of aqueous Hg is the concentration of the hydrophilic Hg–TSA species. If sulfide interferes with the Hg–TSA speciation through competition, then there will be a shift in the titration slope. There was no significant indication that Hg–sulfide complexation interfered with Hg–TSA speciation. The average titration slope of the Galveston Bay titration curves was 0.47 ± 0.07 ($n = 12$), and that observed for the water column in Offatts Bayou was 0.44, 0.46, 0.47, and 0.39 for sample depths of 0.5, 3.5, 4.5, and 6.5 m, respectively.

The complexation coefficient determined between Hg and TSA, $\alpha_{\text{HgTSA}} (=K_1[\text{TSA}^{2-}] + \beta_2[\text{TSA}^{2-}]^2)$ in this study ranged between 16.0 and 16.1. A single titration was performed for each depth layer. The coefficient of variation determined from triplicate measurements of the Galveston surface-water samples was 5%, and the uncertainty associated with the linear least squares regression was ±20%. Additional analytical details of the method can be found in Han and Gill (2005).

Results and discussion

Water column chemistry—The water column was stratified with significant oxygen depletion (<50 μmol L⁻¹) in the near-bottom waters during both sampling years (Fig. 1). In September 2003, the upper 0–5 m was oxic (131 μmol L⁻¹ < [O₂] < 413 μmol L⁻¹) and from 6–7 m was hypoxic ([O₂] = 31 μmol L⁻¹); in September 2004, the upper 0–2, 3–5, and 6–7 m were oxic (210 μmol L⁻¹ < [O₂] < 320 μmol L⁻¹), hypoxic (2.0 μmol L⁻¹ < [O₂] < 63 μmol L⁻¹), and anoxic ([O₂] = 0 μmol L⁻¹), respectively. The persistence of a thermohaline structure during the summer, shifting to a mixed water column structure in the winter, is a common seasonal feature of this system (Cooper and Morse 1996). The pH decreased with the water depth, from 8.5 to 7.5 in 2003 and from 8.4 to 7.6 in 2004, probably varying with increases in total CO₂ content with the depth.

Total dissolved sulfide concentrations ranged from 35 nmol L⁻¹ to 234 μmol L⁻¹ in September 2003 and from 42 nmol L⁻¹ to 152 μmol L⁻¹ in September 2004 (Fig. 1), in agreement with the observations made by Cooper and Morse (1996) in the same area. Dissolved sulfide measured in the nearby Galveston Bay surface waters ranged from 2.1 to 4.7 nmol L⁻¹ (Tang and Santschi 2000). This range was 5 to 10 times lower than the levels found in the surface waters of Offatts Bayou, indicating that enhanced dissolved sulfide levels in the anoxic layers influences surface concentrations in the water

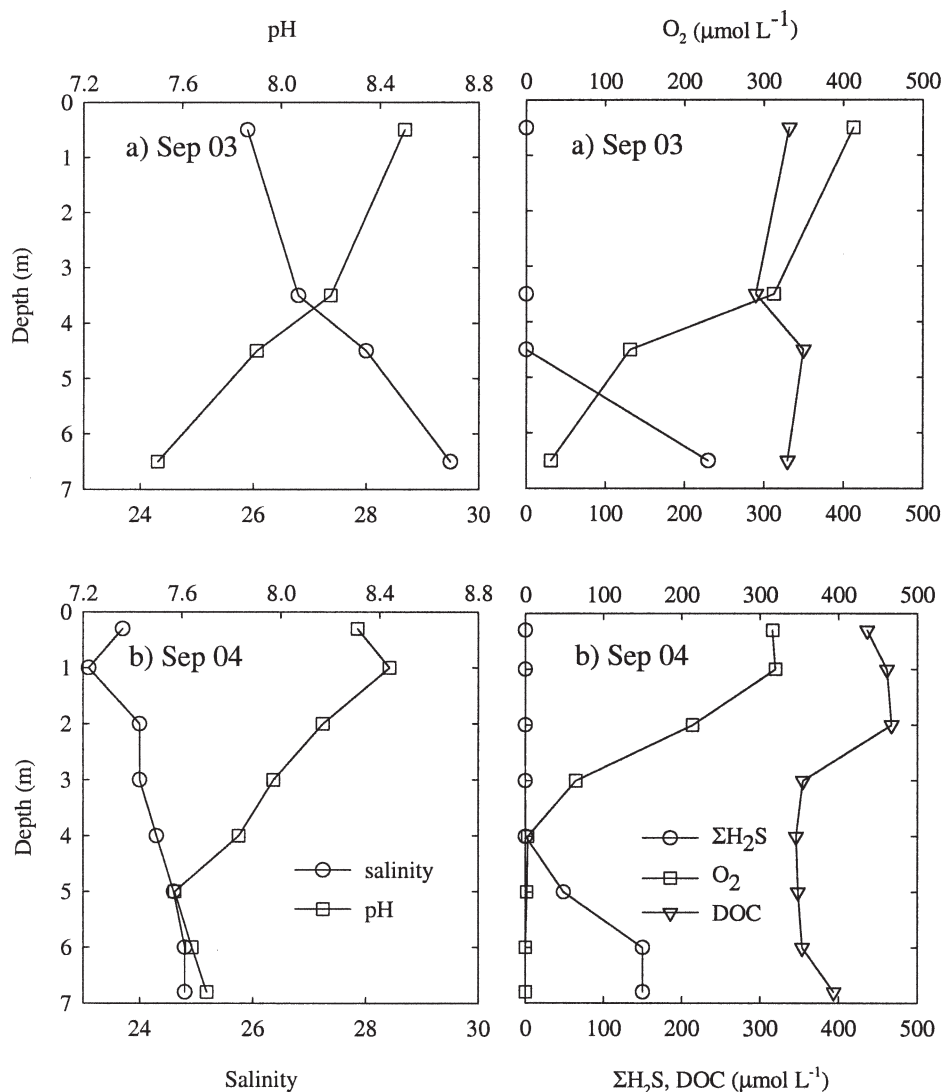


Fig. 1. Vertical profiles of salinity, pH, dissolved oxygen, dissolved sulfide, and dissolved organic carbon (DOC) in Offatts Bayou in (a) September 2003 and (b) September 2004.

column. Complexation of sulfide by metals (e.g., Cu, Fe, and zinc [Zn]) could account for some of the elevated levels of dissolved sulfide observed in the oxic layers of Offatts Bayou, as compared to the nearby Galveston Bay surface waters (Al-Farawati and van den Berg 1999). Dissolved Cu concentrations ranged from 4.1 to 12 nmol L⁻¹ and Fe from 11 to 28 nmol L⁻¹, respectively. While these combined metal concentrations are only a small portion of the maximum observed sulfide levels, they are sufficient to complex a majority of the observed sulfide in the oxic layers. Resistance of sulfide oxidation in oxic surface water through metal complexation has been reported for both freshwater and marine systems (Rozaan et al. 2000). Sulfide clusters of Fe, Cu, Zn, lead (Pb), and silver (Ag) have been found in environmental samples from the oxic ocean, river, and lake waters, as well as in samples from the sulfidic waters (Rozaan et al. 2000; Luther and Rickard 2005). Rozaan et al. (2000) reported that Ag replaced Zn in

a laboratory solution of Zn-sulfide clusters, indicating that sulfide clusters are more likely to occur for class-B metals, such as Hg.

Concentrations of dissolved Mn and Fe ranged from 0 to 19 μmol L⁻¹ and from 0 to 490 nmol L⁻¹, respectively, in 2004 (Fig. 2). The highest dissolved Mn and Fe concentrations occurred in the anoxic bottom layers (6–7 m) and are attributed to the dissolution of Mn (IV) and Fe (III) oxide as a consequence of the microbial degradation of organic matter. The slight reduction in dissolved Fe at a depth of 7 m may be attributed to FeS precipitation. The parallel depth profile of dissolved sulfide supports this possibility (Fig. 2). A large enrichment of particulate Fe and Mn was observed in the lower layers of the pycnocline ([Fe]_p = 62 μmol g⁻¹ in the 0–2-m samples; =176 μmol g⁻¹ in the 3–5-m samples; and =45 μmol g⁻¹ in the 6–7-m samples; [Mn]_p = 115 μmol g⁻¹ in the 0–2-m samples and 846 μmol g⁻¹ in the 3–5-m samples), indicating that while

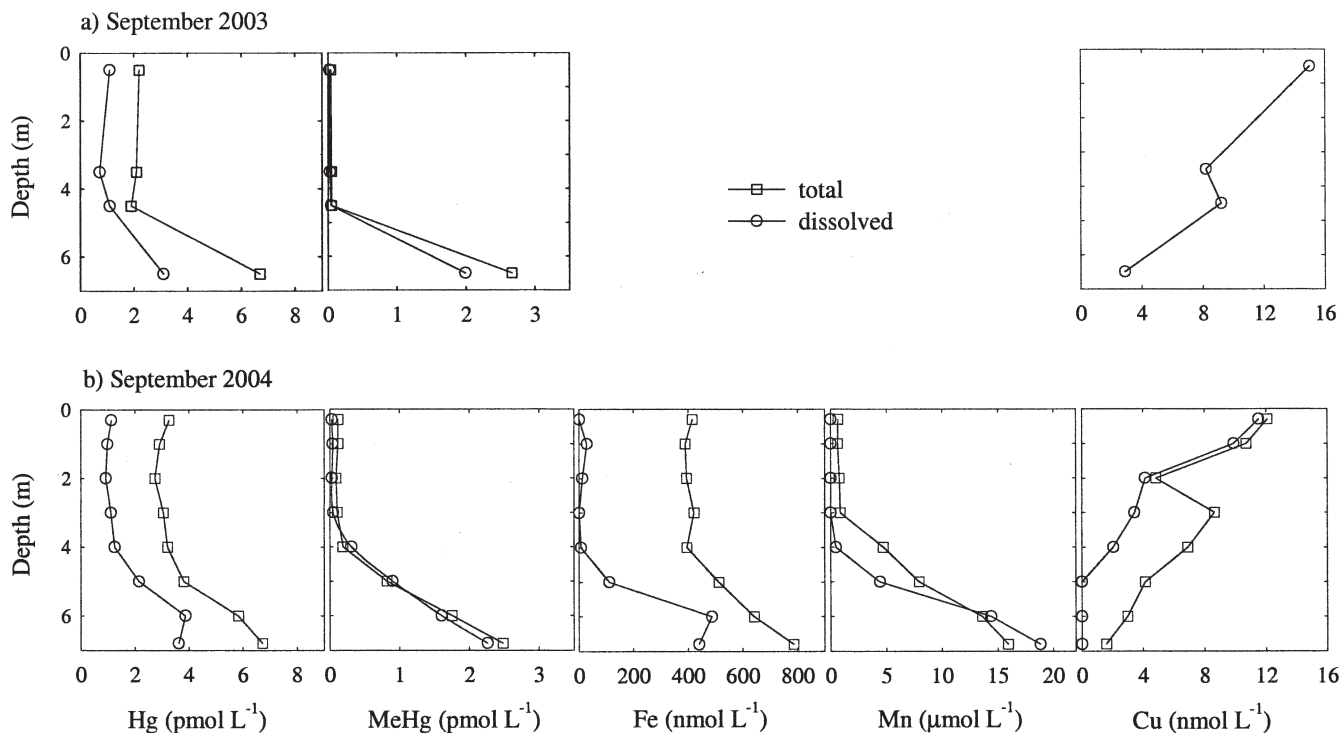


Fig. 2. Vertical profiles of Hg, MeHg, Fe, Mn, and Cu in Offatts Bayou in (a) September 2003 and (b) September 2004.

dissolved Fe (II) and Mn (II) diffuse upward into the oxic zone, highly insoluble phases such as MnO_2 and $\text{Fe}(\text{OH})_3$ are formed and resettle downward into the anoxic zone.

Phase speciation of Hg—Total Hg (Hg in unfiltered water) concentrations in the surface layers (Table 1) of Offatts Bayou are comparable to those found in the Galveston Bay surface waters and other pristine estuarine waters along the Texas coast (Stordal et al. 1996; Han and Gill 2005; Han et al. 2006). Interestingly, the total Hg concentrations did not covary with the SPM concentrations. This is in marked contrast to what is observed in Galveston Bay and most estuaries, where total Hg concentrations are strongly dependent on the abundance of SPM (Choe et al. 2003; Han et al. 2006). The dissolved Hg fraction averaged $47\% \pm 10\%$ and $44\% \pm 13\%$ of the total Hg in 2003 and 2004, respectively, increasing with the water depth (34%, 45%, and 60% in oxic, hypoxic, and anoxic layers, respectively, in 2004). The fraction of dissolved Hg in Offatts Bayou is higher than in the Galveston Bay surface waters ($29\% \pm 14\%$, Han et al. 2006) and most other estuarine surface waters. The higher dissolved Hg fraction in Offatts Bayou is similar to that from the stratified water column of the Pettaquamscutt Estuary in Rhode Island (Mason et al. 1993).

Particulate Hg concentrations (in nmol g^{-1}) were higher in 2004 than in 2003, while suspended particle concentrations were higher in 2003 (Table 1). This resulted in a higher particle–water distribution coefficient (K_d) in 2004 (Table 1). The particle–water distribution coefficient depends on several factors, including concentrations of dissolved and particulate organic matter, dissolved sulfide, and acid

volatile sulfide (Benoit et al. 1999a; Hammerschmidt and Fitzgerald 2004). Because dissolved organic carbon (DOC) concentrations were higher in 2004 ($395 \pm 53 \mu\text{mol L}^{-1}$) than in 2003 ($163 \pm 13 \mu\text{mol L}^{-1}$), it is reasonable to speculate that SPM was enriched in organic matter in 2004 and that this may be the reason for higher Hg_p levels in 2004. However, this variation in DOC content is not sufficient to explain an order of magnitude difference in $\log K_d$ (Hg).

One possible explanation for the difference in the particle–water partition coefficient between years is the “particle concentration effect” (Honeyman and Santschi 1988), a decrease in the particle–water partition coefficient with increasing SPM levels, resulting from an increase of colloidal ligands (Benoit and Rozan 1999). Colloidal Hg concentrations were not determined in this study, but colloidal Hg concentrations representing $57\% \pm 20\%$ of the dissolved Hg present have been reported in surface waters of three Texas estuaries, including Galveston Bay (Stordal et al. 1996). In fact, a particle concentration effect was observed in the Galveston Bay surface waters by Stordal et al. (1996).

The particle–water partition coefficient observed for surface waters in 2003 ($\log K_d = 4.0$) is lower than that observed by Stordal et al. (1996) for the surface waters in Galveston Bay estuary (i.e., $\log K_d = 5.1$ to 5.5 for $C_p = 10 \text{ mg L}^{-1}$, $\log K_d = 4.7$ to 5.1 for $C_p = 100 \text{ mg L}^{-1}$). However, the particle–water partition coefficient observed for surface waters in 2004 ($\log K_d = 5.5$) agrees well with the Galveston Bay data of Stordal et al. (1996). The lower-than-expected value for the particle–water partition coefficient in the 2003 surface waters could have resulted from

Table 1. Concentrations of dissolved (indicated by superscript letter d), total (indicated by superscript letter t), and particulate (total-dissolved) (indicated by superscript letter p) mercury (Hg) and methylmercury (MeHg) and particle-water distribution coefficients (K_d) of Hg and MeHg in Offatts Bayou.

Year	Depth (m)	SPM* (mg L ⁻¹)	Hg _d (pmol L ⁻¹)	Hg _t (pmol L ⁻¹)	Hg _p † (nmol g ⁻¹)	log K_d ‡ (Hg) (L kg ⁻¹)	MeHg _d (pmol L ⁻¹)	MeHg _t (pmol L ⁻¹)	MeHg _p (pmol g ⁻¹)	log K_d (MeHg) (L kg ⁻¹)
2003	0–1	90	1.1(1.1)§	2.2(2.2)§	0.012(0.012)§	4.0(4.0)§	0.021	0.043	0.24	4.1
	3–4	28	0.73(0.70)	2.1(2.1)	0.050(0.049)	4.8(4.8)	0.030	0.054	0.86	4.5
	4–5	29	1.1(1.1)	1.9(1.8)	0.028(0.027)	4.4(4.4)	0.046	0.053	0.24	3.7
	6–7	18	3.1(1.1)	6.7(4.0)	0.20(0.16)	4.8(5.2)	2.0	2.7	37	4.3
2004	0.3	6.4	1.1(1.1)	3.2(3.1)	0.33(0.31)	5.5(5.5)	0.032	0.12	14	5.6
	1	6.5	0.98(0.94)	2.9(2.8)	0.29(0.28)	5.5(5.5)	0.041	0.12	12	5.5
	2	5.7	0.92(0.89)	2.7(2.6)	0.32(0.31)	5.5(5.5)	0.029	0.090	11	5.6
	3	1.3	1.1(1.1)	3.0(2.9)	1.5(1.4)	6.1(6.1)	0.050	0.11	46	6.0
	4	5.6	1.3(0.99)	3.3	0.36	5.5	0.31	0.19	—	—
	5	3.2	2.2(1.3)	3.8	0.50	5.4	0.90	0.82	—	—
	6	5.6	3.9(2.3)	5.9(4.2)	0.36(0.33)	5.0(5.2)	1.6	1.8	27	4.2
	6.8	5.6	3.6(1.3)	6.7(4.2)	0.55(0.51)	5.2(5.6)	2.3	2.5	39	4.2

* SPM, suspended particulate matter.

† $Hg_p = (Hg_t - Hg_d)/SPM$.

‡ K_d (L kg⁻¹) = [particulate Hg] (mol kg⁻¹)/[dissolved Hg] (mol L⁻¹).

§ Values in parentheses are inorganic Hg (Hg–MeHg).

an enhancement in the abundance of colloidal Fe oxide and FeS with concomitant increases in colloidal Hg.

Particulate Hg was enriched and, correspondingly, the particle-water partition coefficient for Hg was highest in the lower layers of the pycnocline (6–7 m in 2003 and 3 m in 2004) in both years. These increases at depth could be due to the scavenging of dissolved Hg by insoluble Mn and Fe oxides, which form when soluble forms of the metals diffuse into the oxic layers from the bottom waters (Mason et al. 1993). DOM coated on Fe and Mn oxides may provide strong binding sites for dissolved Hg (Chin et al. 1998; Chadwick et al. 2006). Evidence of DOM coating on Fe oxides is given by a strong correlation between dissolved Fe (II) and DOM released during the Fe oxide reduction in pore waters of a freshwater wetland (Chin et al. 1998).

Dissolved Hg concentrations in the surface layers of Offatts Bayou (Table 1) were comparable to concentrations found previously in the Galveston Bay surface waters: 1.1–1.2 pmol L⁻¹ at salinities between 23 and 27 (Han et al. 2006). In September 2003, dissolved Hg concentrations in Offatts Bayou ranged from 0.73 to 1.1 pmol L⁻¹ in the oxic layers and increased to 3.1 pmol L⁻¹ in the hypoxic layer. In September 2004, dissolved Hg concentrations ranged from 0.92 to 1.1 pmol L⁻¹ in the oxic layers, increasing to 2.2 pmol L⁻¹ in the hypoxic layer, and reaching 3.6–3.9 pmol L⁻¹ in the anoxic bottom layer. The increase in dissolved Hg in the hypoxic and anoxic layers resulted primarily from increases in MeHg in both years. However, dissolved inorganic Hg (operationally defined as Hg–MeHg) increased in the anoxic layers, with a peak at 6 m (2.3 pmol L⁻¹) in 2004 (Table 1). Dissolved Hg, Fe, and sulfide concentrations were all slightly lower in the bottom layer, with peak concentrations at 6 m, indicating the adsorption of Hg on solid FeS. Particulate FeS has been thought to control dissolved trace-metal concentrations in

anoxic environments through the scavenging of metal sulfide complexes (Dyrssen and Kremling 1990).

Chemical equilibrium modeling of Hg—The Hg-complexing organic ligand concentrations ranged from 68 to 162 pmol L⁻¹ (Table 2), and were two- to eightfold higher than the concentration levels (19–37 pmol L⁻¹) found by Han et al. (2006) in the nearby Galveston Bay surface waters of the same salinity range. The increase in Hg-complexing ligand concentration with depth indicates a significant sediment flux of these ligands, possibly related to degradation of sedimentary organic matter. However, it has been reported that 3-mercaptopropionic acid, a strong Hg-complexing ligand, in coastal marine sediments is formed by an abiotic reaction between hydrogen sulfide and activated unsaturated bonds in organic molecules, such as acrylic acid (Vairavamurthy and Mopper 1987). A mechanism of this type, possibly involving in situ water column production, may also be responsible for the increase of Hg-complexing organic ligands with depth.

The log conditional stability constants determined between Hg and organic ligands at pH 9.6 ranged from 26.8 to 27.3. For modeling purposes, we converted the conditional constant range to pH-independent values ($K_{HgL} = 10^{27.9}–10^{28.3}$) using an acidity constant (K_a) typical of most thiols: $pK_a = 10$ (Benoit et al. 2001). The range in conditional stability constants we observed for the Hg-organic ligand complexes in Offatts Bayou was comparable to that determined by Haitzer et al. (2003) using DOM isolated from the Florida Everglades ($10^{28.7±0.1}$, [Lig] = 5 nmol mg⁻¹ DOM) and by Han et al. (2006) in the surface waters of Galveston Bay ($10^{28.6±0.3}$, [Lig] = 19–93 pmol L⁻¹). The good agreement between these conditional stability constants determined in different aqueous systems indicates a consistency in the Hg–

Table 2. Concentrations of mercury (Hg)-complexing organic ligands (Lig), conditional stability constants between Hg and ligands determined at pH = 9.6 (K'), pH-corrected conditional stability constants (K), and glutathione (GSH) concentrations.

Depth (m)	α_{HgTSA}^*	[Lig] (pmol L ⁻¹)	log $K'\dagger$	log $K\ddagger$	[GSH] (nmol L ⁻¹)
0–1	16.1	68 ± 3§	27.3 ± 0.1§	28.3	47
3–4	16.1	81 ± 4	27.3 ± 0.1	28.3	42
4–5	16.0	121 ± 5	27.0 ± 0.1	28.0	44
6–7	16.0	162 ± 7	26.8 ± 0.1	27.9	61

* $\alpha_{\text{HgTSA}} = K_1[\text{TSA}^{2-}] + \beta_2[\text{TSA}^{2-}]^2$; TSA: thiosalicylic acid; α_{HgTSA} , the complexation coefficient determined between Hg and TSA,

† $K' = [\text{HgLig}]/([\text{Hg}^{2+}][\text{Lig}'])$, $[\text{Lig}'] = [\text{Lig}]_t - [\text{HgLig}]$.

‡ $K = [\text{HgLig}^+]/([\text{Hg}^{2+}][\text{Lig}^-])$, corrected for $I = 0$.

§ Errors were calculated from three separate titrations with Galveston Bay surface waters.

DOM binding strength at different compositions of bulk DOM.

The chemical speciation of dissolved inorganic Hg was determined using the equilibria described in Table 3; the experimentally determined concentrations of inorganic Hg, GSH, Hg-complexing organic ligands, DOM, Cu, and sulfide; and the chemical equilibrium program MINEQL+. The concentrations of Fe and Mn were obtained from 2004 data of the same dissolved oxygen level. The formation constants between Hg and dissolved sulfide shown in Table 3 were obtained from Benoit et al. (1999a,b), who reported average literature values. The formation constants between DOM and neutral Hg-sulfide species [HOHgHS^0 and $\text{Hg}(\text{HS})_2^0$] were obtained from Miller (2006). All other stability constants not mentioned in Table 3 were directly obtained from the MINEQL+ database. The solubility constraint of cinnabar (HgS) was not exceeded in all depths, while covellite (CuS) and chalcopyrite (CuFeS_2) were precipitated at 0–5 m and 6–7 m, respectively.

Several caveats must be recognized when assessing this modeling exercise. First, reported conditional stability constants between Hg and sulfide species vary over several orders of magnitude, depending on the source literature; hence, the results in Table 4 should be considered as approximations rather than absolutes. Second, the traditional methylene blue methodology for sulfide determinations was used in this study, and this measures H_2S , HS^- , S^{2-} , FeS , ZnS , CdS , and MnS , but not CuS and organic sulfur compounds (Mylon and Benoit 2001). In addition, the authors of previous studies have suggested that sulfide in the oxic zone is stabilized as metal-sulfide complexes and clusters, possibly as FeS , ZnS , and CuS (Rozan et al. 2000; Luther and Rickard 2005). However, metal-sulfide clusters were not included in the speciation modeling because of the lack of stoichiometry and conditional stability constant information. We assessed the effects of the metal-sulfide cluster formation on the dissolved Hg speciation using the conditional stability constants for the ZnS cluster (Luther et al. 1999) and a dissolved Zn concentration found in the surface waters of Galveston Bay (3 nM; Wen et al. 1999). The equilibrium modeling results showed that dissolved Hg speciation was not changed significantly as a result of the much higher binding strength between Hg and sulfide. Finally, the replacement of Cu, Fe, and Zn in metal-sulfide clusters by Hg ions is a possibility. This equilibrium was not considered because the stoichiometry and conditional

stability constants of Hg-sulfide clusters have not been reported.

The equilibrium modeling results, shown in Table 4, predict that dissolved Hg is dominated by sulfide complexation at all depths. When the association of neutral Hg species with DOM was excluded, HOHgHS^0 is predicted to dominate in the upper waters (0–5 m), where sulfides are lower in concentration ($[\text{total sulfide}] < 178 \text{ nmol L}^{-1}$). In the bottom waters (6–7 m), where sulfide is highest in concentration, the speciation shifts and HgS_2^{2-} and $\text{HgS}(\text{HS})^-$ are predicted to dominate the solution speciation of inorganic Hg. This trend is consistent with thermodynamic calculations that include the interaction of Hg with solids containing one or two sulfide groups (Benoit et al. 1999a). Similar concentration ranges were obtained between HgGS^- and HgLig , indicating that Hg-complexing organic ligands (Lig) are comparable to organic thiols in terms of the Hg complexation coefficient, α . However, both Lig and GSH played negligible roles in the dissolved Hg complexation.

Recently it was suggested that neutral Hg-sulfide species interact with DOM as a result of the partitioning of the neutral Hg-sulfide into the hydrophobic portion of the DOM (Miller 2006). When this interaction is also considered (stability constants taken from Miller [2006]), the concentration of the neutral Hg-sulfide species HOHgHS^0 decreases but still remains dominant, and the $\text{HOHgHS}(\text{DOM})$ species becomes important in the upper water column, where lower dissolved sulfide levels occur (Table 4).

Making the assumption that the $\text{pK}_a = 10$ for thiols that complex Hg does not significantly affect the solution speciation calculations. For example, if the pK_a of Lig were 8 rather than 10, then the concentration of the HgLig^+ species would be increased only by an order of magnitude, and it would still be insignificant compared to the Hg-sulfide species.

The presence of elemental sulfur is known to increase the solubility of cinnabar through complexation by polysulfide ligands, such as $\text{Hg}(\text{S}_n)\text{HS}^-$, $\text{Hg}(\text{S}_n)_2^{2-}$, HOHgS_n^- , and HgS_5 (Jay et al. 2000). Equilibrium calculations indicate that in the presence of elemental sulfur, HgOHS^0 concentrations in the bottom waters would decrease in favor of dissolved Hg species such as $\text{HOHg}(\text{S}_n)$ and $\text{Hg}(\text{S}_n)_2^{2-}$. Similarly, in the upper layers, HOHgHS^0 would decrease to <1% of the total dissolved Hg by the formation of HOHgS_n^- .

Table 3. Formation constants used in the chemical equilibrium modeling of dissolved mercury (Hg) and dissolved methylmercury (MeHg) in Offatts Bayou (I = 0).

Reaction	log K _f	Reference
Hg ²⁺ + Lig ⁻ * = HgLig ⁺	27.9–28.3	This study
Lig ⁻ + H ⁺ = LigH	10.0	This study
Hg ²⁺ + 2Cl ⁻ = HgCl ₂	14.0	Zhang et al. 2004
Hg ²⁺ + 3Cl ⁻ = HgCl ₃ ⁻	15.0	Zhang et al. 2004
Hg ²⁺ + 4Cl ⁻ = HgCl ₄ ²⁻	15.6	Zhang et al. 2004
Hg ²⁺ + H ₂ O + Cl ⁻ = HOHgCl + H ⁺	4.3	Zhang et al. 2004
Hg ²⁺ + H ₂ O = HgOH ⁺ + H ⁺	-3.4	Zhang et al. 2004
Hg ²⁺ + 2H ₂ O = Hg(OH) ₂ + 2H ⁺	-6.17	Zhang et al. 2004
Hg ²⁺ + HS ⁻ + H ₂ O = HOHgHS ⁰ + H ⁺	26.7	Benoit et al. 1999a
Hg ²⁺ + HS ⁻ + H ₂ O + DOM = HOHgHS(DOM) + H ⁺	25.7†	Miller 2006
Hg ²⁺ + HS ⁻ = HgS (s) + H ⁺	36.5	Benoit et al. 1999a
Hg ²⁺ + HS ⁻ = HgHS ⁺	30.5	Benoit et al. 1999a
Hg ²⁺ + 2HS ⁻ = Hg(HS) ₂ ⁰	37.5	Benoit et al. 1999a
Hg ²⁺ + 2HS ⁻ + DOM = Hg(HS) ₂ DOM	36.7†	Miller 2006
Hg ²⁺ + 2HS ⁻ = HgS ₂ H ⁻ + H ⁺	32.0	Benoit et al. 1999a
Hg ²⁺ + 2HS ⁻ = HgS ₂ ²⁻ + 2H ⁺	23.5	Benoit et al. 1999a
H ⁺ + HS ⁻ = H ₂ S	7.02	Zhang et al. 2004
Hg ²⁺ + GS ³⁻ ‡ = HgGS ⁻	27.3	Zhang et al. 2004
Hg ²⁺ + GS ³⁻ + H ⁺ = HgHGS	34.0	Zhang et al. 2004
Hg ²⁺ + GS ³⁻ + 2H ⁺ = HgH ₂ GS ⁺	37.2	Zhang et al. 2004
Hg ²⁺ + GS ³⁻ + OH ⁻ = HOHgGS ²⁻	16.7	Zhang et al. 2004
GS ³⁻ + H ⁺ = HGS ²⁻	10.2	Zhang et al. 2004
GS ³⁻ + 2H ⁺ = H ₂ GS ⁻	19.3	Zhang et al. 2004
GS ³⁻ + 3H ⁺ = H ₃ GS	23.0	Zhang et al. 2004
GS ³⁻ + 4H ⁺ = H ₄ GS ⁺	25.0	Zhang et al. 2004
CH ₃ Hg ⁺ + GS ³⁻ = CH ₃ HgGS ²⁻	16.7	Zhang et al. 2004
CH ₃ Hg ⁺ + GS ³⁻ + H ⁺ = CH ₃ HgHGS ⁻	26.4	Zhang et al. 2004
CH ₃ Hg ⁺ + GS ³⁻ + 2H ⁺ = CH ₃ HgH ₂ GS	30.0	Zhang et al. 2004
CH ₃ Hg ²⁺ + H ₂ O = (CH ₃ Hg)OH + H ⁺	-4.53	Zhang et al. 2004
2CH ₃ Hg ²⁺ + H ₂ O = (CH ₃ Hg) ₂ OH ⁺ + H ⁺	-2.11	Zhang et al. 2004
CH ₃ Hg ⁺ + Cl ⁻ = CH ₃ HgCl	5.45	Zhang et al. 2004
CH ₃ Hg ⁺ + SH ⁻ = CH ₃ HgS ⁻ + H ⁺	7.0	Zhang et al. 2004
Fe ²⁺ + HS ⁻ = FeHS ⁺	6.1	Al-Farawati and Van den Berg 1999
2Fe ²⁺ + H ₂ S = [Fe ₂ (HS)] ³⁺ + H ⁺	10.2	Luther et al. 2003
3Fe ²⁺ + H ₂ S = [Fe ₃ (HS)] ⁵⁺ + H ⁺	16.8	Luther et al. 2003
Mn ²⁺ + HS ⁻ = MnHS ⁺	4.5	Al-Farawati and Van den Berg 1999
Mn ²⁺ + 2HS ⁻ = Mn(HS) ₂ ⁰	9.9	Al-Farawati and Van den Berg 1999

* Mercury-complexing organic ligand.

† In L mg carbon (C)⁻¹. DOM, dissolved organic matter.

‡ Glutathione.

Table 4. Mercury (Hg) and methylmercury (MeHg) speciation determined by MINEQL+ in Offatts Bayou in September 2003. Concentrations and conditional stability constants of Hg and other complexes are shown in Tables 1 through 3 and in Figs. 1 and 2.

	Depth (m)	HOHgHS ⁰ (mol L ⁻¹)	HOHgHS(DOM) (mol L ⁻¹)	HgS ₂ ²⁻ (mol L ⁻¹)	HgS(HS) ⁻ (mol L ⁻¹)	Hg(GS) ⁻ (mol L ⁻¹)	HgLig ⁺ (mol L ⁻¹)	MeHgS ⁻ (mol L ⁻¹)	MeHg(HGS) (mol L ⁻¹)
Excluding	0–1	1.1 × 10 ⁻¹²	—	1.7 × 10 ⁻¹⁴	4.9 × 10 ⁻¹⁵	1.3 × 10 ⁻²²	2.3 × 10 ⁻²³	8.1 × 10 ⁻¹⁵	1.1 × 10 ⁻¹⁴
HOHgHS ⁻	3–4	6.9 × 10 ⁻¹³	—	9.4 × 10 ⁻¹⁵	5.2 × 10 ⁻¹⁵	3.1 × 10 ⁻²³	1.1 × 10 ⁻²³	1.5 × 10 ⁻¹⁴	1.4 × 10 ⁻¹⁴
DOM*	4–5	1.0 × 10 ⁻¹²	—	3.0 × 10 ⁻¹⁴	3.3 × 10 ⁻¹⁴	6.9 × 10 ⁻²⁴	5.8 × 10 ⁻²⁴	3.6 × 10 ⁻¹⁴	9.9 × 10 ⁻¹⁵
association	6–7	4.6 × 10 ⁻¹⁵	—	5.3 × 10 ⁻¹³	5.7 × 10 ⁻¹³	2.7 × 10 ⁻²⁹	9.3 × 10 ⁻³⁰	2.0 × 10 ⁻¹²	3.1 × 10 ⁻¹⁶
Including	0–1	7.8 × 10 ⁻¹³	3.1 × 10 ⁻¹³	1.3 × 10 ⁻¹⁴	3.5 × 10 ⁻¹⁵	9.5 × 10 ⁻²³	1.7 × 10 ⁻²³	8.1 × 10 ⁻¹⁵	1.1 × 10 ⁻¹⁴
HOHgHS ⁻	3–4	5.1 × 10 ⁻¹³	1.8 × 10 ⁻¹³	7.0 × 10 ⁻¹⁵	3.9 × 10 ⁻¹⁵	2.3 × 10 ⁻²³	8.1 × 10 ⁻²⁴	1.5 × 10 ⁻¹⁴	1.4 × 10 ⁻¹⁴
DOM	4–5	7.4 × 10 ⁻¹³	3.1 × 10 ⁻¹³	2.2 × 10 ⁻¹⁴	2.4 × 10 ⁻¹⁴	4.9 × 10 ⁻²⁴	4.1 × 10 ⁻²⁴	3.6 × 10 ⁻¹⁴	9.9 × 10 ⁻¹⁵
association	6–7	4.5 × 10 ⁻¹⁵	2.9 × 10 ⁻¹⁵	5.2 × 10 ⁻¹³	5.7 × 10 ⁻¹³	2.7 × 10 ⁻²⁹	9.3 × 10 ⁻³⁰	2.0 × 10 ⁻¹²	3.1 × 10 ⁻¹⁶

* DOM, dissolved organic matter.

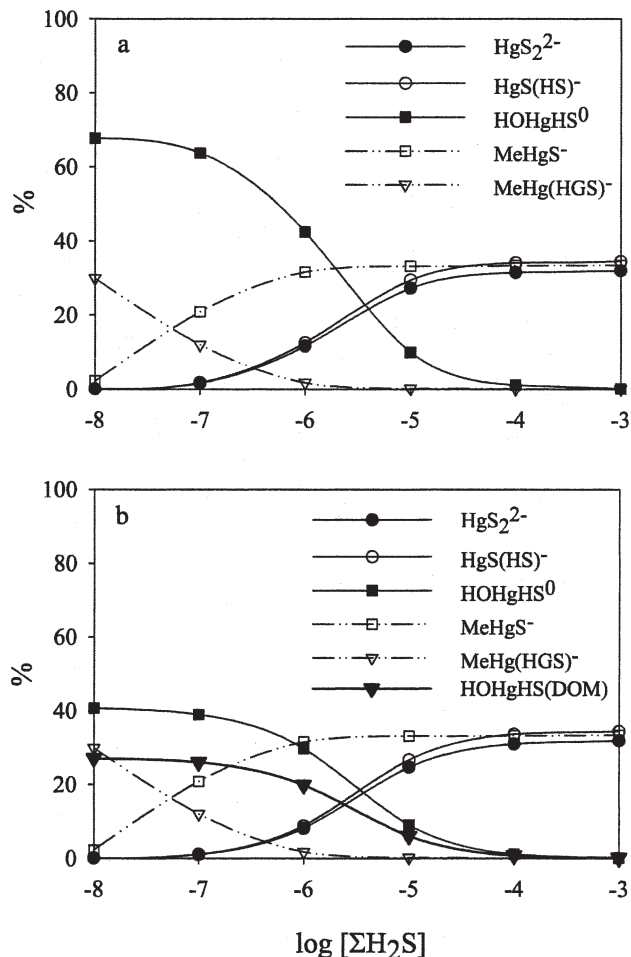


Fig. 3. Mercury speciation as a function of dissolved sulfide concentration under the following conditions: [inorganic Hg] = 2 pmol L⁻¹, [MeHg] = 1 pmol L⁻¹, [GSH] = 50 nmol L⁻¹, [DOM] = 4.2 mg L⁻¹, pH = 7.9, and $I = 0.6$. (a) Excluding HOHgHS-DOM association. (b) Including HOHgHS-DOM association.

The speciation change of Hg as a function of dissolved sulfide concentration is presented in Fig. 3 for the conditions in which [inorganic Hg] = 2 pmol L⁻¹, [MeHg] = 1 pmol L⁻¹, [DOM] = 4.2 mg L⁻¹, [GSH] = 50 nmol L⁻¹, and pH = 7.9. These and other solution conditions are the same as for the anoxic layer (6–7 m) in 2003. Figure 3 demonstrates that Hg-Lig and Hg-GSH complexes are negligible in anoxic estuarine waters. In particular, HOHgHS⁰ is dominant when $\Sigma H_2S < \sim 5 \mu\text{mol L}^{-1}$, while HgS_2^{2-} and $HgS(HS)^-$ are dominant when $\Sigma H_2S > 5 \mu\text{mol L}^{-1}$. Applying the conditional stability constants between HOHgHS⁰ and DOM to the speciation calculation, it was demonstrated that about 35% of HOHgHS⁰ is associated with DOM (Fig. 3b). The concentrations of $Hg(HS)_2^0$ and $Hg(HS)_2(DOM)$ were negligible in the sulfide range from 10^{-8} to 10^{-4} mol L⁻¹ and, when sulfide > 1 mmol L⁻¹, the concentrations were comparable to [HOHgHS⁰] and [HOHgHS⁰(DOM)]. The association between neutral Hg-sulfide and DOM not only explains the positive correlations between dissolved Hg and

the DOM often found in estuarine surface waters (Stordal et al. 1996; Choe et al. 2003), but it also supports previous reports that a major fraction ($57\% \pm 20\%$) of dissolved Hg in the Galveston Bay surface water exists as colloids (Stordal et al. 1996; Choe et al. 2003).

The enrichment of particulate-phase Hg in the lower pycnocline may be due to the scavenging of Hg-sulfide species by Fe and Mn oxides. It was shown that adsorption of Hg to hydrous ferric oxide (HFO) decreased with increasing DOM concentration in experimental solutions containing hydrophilic DOM (Miller 2006). Miller (2006) also suggested that the complexation of Hg with HFO is controlled by a ternary complex, with the interaction between DOM and HFO driving the association of Hg to HFO. We investigated the importance of an HFO-DOM-Hg interaction in the lower pycnocline, where dissolved Fe is undergoing oxidation and precipitation, using equilibrium modeling with the following conditions: (1) The maximum adsorbed density of DOM to Fe oxide minerals (hematite and goethite) at near-neutral pH is $0.17\text{--}0.29$ mg carbon (C) m⁻² (Gu et al. 1994, 1995; Zhou et al. 2001); (2) The surface area of HFO is 600 m² g⁻¹ Fe (Dzombak and Morel 1990); (3) Particulate Fe concentration was $23.5 \mu\text{g L}^{-1}$ (3 m in 2004); (4) log K for the equilibrium $RS^- + Hg^{2+} \leftrightarrow RSHg^+$ is 27.3 (Miller 2006); and (5) The pK_a for a typical organic thiol (RSH) is 10.0 (Benoit et al. 2001). The predicted concentration for the HFO-DOM-Hg interaction ranged from 1.0×10^{-14} to 1.7×10^{-14} mol L⁻¹. This range corresponds to a log K_d (Hg) of 5.7 to 5.9, when the particulate Fe and dissolved inorganic Hg concentrations are $23.5 \mu\text{g L}^{-1}$ and 1.1 pmol L⁻¹, respectively. The range of log K_d obtained for this modeling exercise is similar to the value determined experimentally, log K_d = 6.1. This indicates that the surface complexation of dissolved Hg by sites on DOM (which is, in turn, adsorbed to Fe oxide) may control the particle-water partitioning of inorganic Hg in that portion of the lower pycnocline where Fe precipitation is occurring.

Thermodynamic calculations do not predict precipitation of HgS in anoxic bottom water. Enrichment of particulate Hg in the bottom water is possibly due to adsorption of dissolved Hg-sulfide species onto solid CuFeS₂ and FeS. We tested this possibility by modeling the interaction with the following conditions: (1) A neutral surface site abundance for solid FeS of 1.2 mmol g⁻¹ FeS (Wolthers et al. 2003); (2) A particulate Fe concentration of 346 nmol L⁻¹ (6.8 m in 2004); (3) The log K for the equilibrium of surface adsorption sites by protons ($\equiv FeSH^0 \leftrightarrow \equiv FeS^- + H^+$) is -6.5 (Wolthers et al. 2003); (4) The log K for the adsorption of inorganic Hg ($\equiv FeS^- + Hg^{2+} \leftrightarrow \equiv FeSHg^+$) is 36.1 (Miller 2006); (5) The % organic C in SPM ranges from 2% to 10% (Warnken and Santschi 2004); (6) The % reduced sulfur (S) in organic matter is 0.4% (Ravichandran 2004); (7) An SPM concentration of 5.6 mg L⁻¹; (8) The pK_a for a typical organic thiol (RSH) is 10.0 (Benoit et al. 2001); and (9) The interaction between inorganic Hg and organic thiols is given by $RS^- + Hg^{2+} \leftrightarrow RSHg^+$, log K = 27.3 (Miller 2006). Equilibrium modeling predicts that the ratio of [$\equiv FeSHg^+$] to [Hg^{2+}] is 3.2×10^{28} . The predicted ratio of [$\equiv FeSHg^+$] to [Hg^{2+}] is 11 to 12

orders of magnitude higher than the concentration ratio observed for the Hg associated with particulate organic matter (the ratio of [Hg-POM] to [Hg²⁺]). This modeling prediction indicates that solid FeS may be an important sorption site for dissolved Hg in anoxic waters. Additional support for this mechanism comes from Cooper and Morse (1996), who showed that the total reactive (HCl plus HNO₃ extractable) Hg fraction in Offatts Bayou sediments was predominantly associated with pyrite (FeS₂) produced from precursor FeS, excess sulfide, and elemental sulfur.

Phase speciation of MeHg—Total MeHg (MeHg in unfiltered water) concentrations ranged from 0.043 to 2.7 pmol L⁻¹ in September 2003 and from 0.090 to 2.5 pmol L⁻¹ in September 2004 (Table 1). Higher MeHg concentrations were observed in the hypoxic and anoxic bottom layers. Enhanced MeHg levels in anoxic hypolimnion has been reported for several stratified freshwater systems (Chadwick et al. 2006; Eckley and Hintelmann 2006), but there have been fewer reports of this phenomenon occurring in marine systems (Lu et al. 1986; Pempkowiak et al. 1998). Dissolved MeHg concentrations ranged from 0.021 to 2.0 pmol L⁻¹ in September 2003 and from 0.029 to 2.3 pmol L⁻¹ in September 2004, also increasing in the hypoxic and anoxic layers.

The particle-water partition coefficients determined for MeHg in the upper oxic water column in 2004 were higher than the values observed in 2003 (Table 1). A similar trend was also observed for inorganic Hg (discussed previously), which we speculated arose from a “particle concentration effect.” We hypothesize that a particle concentration effect is also responsible for the increase in the particle-water partition coefficient of MeHg observed in 2004. The particle-water partition coefficient for MeHg in oxic waters in 2004 ranged from 5.5 to 5.6. This observation agrees well with the observations of Choe and Gill (2003) for surface waters in San Francisco Bay at similar particle concentration levels. In contrast, the particle-water partition coefficient for MeHg in 2003 is lower than would be predicted from the comparison with San Francisco Bay values at comparable particle concentrations (log K_d = 5.5 to 6.0 when C_p = 6 mg L⁻¹; log K_d = 5.1 to 5.6 when C_p = 90 mg L⁻¹; Choe and Gill 2003). An enhanced particle concentration effect in 2003, arising from enhancement in the abundance of colloidal MeHg, is suggested as a reason for the smaller K_d (MeHg) in 2003.

As noted above, the phase partitioning of both inorganic Hg and MeHg onto suspended particles showed similar distributional characteristics with depth (Table 1). This similarity indicates that a common process controls the adsorption and desorption of inorganic Hg and MeHg. In 2004, the lowest K_d occurred in the anoxic layers, indicating that the dissolution of Fe releases MeHg from the particulate phase and/or the sulfide complexation increases the solubility of MeHg. The K_d (MeHg) did not increase in the bottom anoxic layer, in contrast to that for inorganic Hg, indicating that adsorption of MeHg onto FeS(s) does not occur. Indeed, the estimated ratio of [≡FeSMeHg] to [MeHg⁺] (8.1 × 10⁴) corresponds to the lower limit of the ratio of [POM-MeHg] to [MeHg⁺] (1.4 ×

10⁴ to 2.8 × 10⁷). Each ratio was calculated with the complexation constants (log K of ≡FeS⁻ + MeHg⁺ ↔ ≡FeSMeHg: 12.5; log K of RS⁻ + MeHg⁺ ↔ RSMHg: 14.5–17.1; Miller 2006) and concentrations of each binding sites determined in the previous section.

Dissolved Mn and Fe may be reoxidized in the oxic-anoxic transition zone and scavenge dissolved MeHg. This process is apparent from the observed MeHg enrichment in SPM at the lower pycnocline, at 6–6.8 m in 2003 and at 3 m in 2004. However, biogenic particulate matter can be a reason for the MeHg enrichment in this zone, as well as in the anoxic layers. Several studies have reported an enrichment of particulate MeHg in the lower pycnocline coincident with a peak of bacteriochlorophyll abundance (Hurley et al. 1991; Mason et al. 1993). Coexisting sulfate reducers were suggested as a cause of the enrichment of particulate MeHg. Hurley et al. (1991) reported that MeHg concentration in anoxic water declined during winter, while dissolved Fe concentrations remained constant, demonstrating the role of biogenic particles.

Chemical equilibrium modeling of MeHg—The solution speciation of MeHg in Offatts Bayou is shown in Table 4, using stability constants taken from Table 3. Analytical methodologies currently do not exist to determine conditional stability constants and concentrations of MeHg-complexing organic ligands in natural waters using competitive ligand approaches. In addition, interaction between MeHg-sulfide and DOM could not be considered because of the lack of stability constants. Therefore, the solution speciation of MeHg was assumed to be dominated by interaction with GSH and sulfide complexation. In the oxic layers, GSH played an important role in MeHg speciation; this is in marked contrast to GSH's role in inorganic Hg speciation (Table 4). The sulfide species (MeHg)S⁻ outcompeted the GSH species (MeHg)HGS⁻ when [ΣH₂S] > 80 nmol L⁻¹ (Fig. 3). The competition between thiol and sulfide ligands for MeHg complexation has been reported by Zhang et al. (2004) to occur near the sediment-water interface (pH = 6.5, [ΣH₂S] = 500 nmol L⁻¹, [cysteine] = 60 nmol L⁻¹). The dominance of the GSH complexation of MeHg when sulfide concentrations are low is supported by the positive correlation observed in the surface estuarine waters between the distributions of MeHg and DOM (Choe and Gill 2003).

The particle-water partition coefficients of MeHg were much lower in the anoxic layers of Offatts Bayou than in the oxic layers in 2004 (Table 1). This shift in particle-water partition coefficients is coincident with a shift in speciation from complexation by glutathione, (MeHg)HGS⁻, to a MeHg-sulfide complex, indicating that high sulfide concentrations in the anoxic layer increased the solubility of MeHg. Mobilization of dissolved MeHg from sediment pore water and/or dissolution of Fe oxide may enhance this shift of K_d.

We can offer two possible explanations for the increase in MeHg concentration in the hypoxic and anoxic layers. One possibility is in situ production of MeHg associated with the pycnocline. Mason et al. (1993) reported that the peak of bacteriochlorophyll occurred at the pycnocline

coincident with the peak of dissolved MeHg, indicating that methylation by sulfate-reducing bacteria occurred *in situ* at the boundary between the oxic and anoxic waters. Because pigmented sulfur bacteria oxidize sulfide, they are often found to be associated with sulfate-reducing bacteria. Alternatively, the linear increase with depth of dissolved and particulate MeHg can be attributed to the diffusion and advection of MeHg from sediment pore waters and subsequent particle scavenging in the oxic layers. The flux of dissolved MeHg from sediment pore water to overlying water has been determined in freshwater and estuarine sediments (Choe et al. 2004). A thin oxic layer in surface sediments may function as a MeHg diffusion barrier (Gagnon et al. 1997; Gill et al. 1999). The absence of this oxygen barrier at our sampling site, due to the anoxic condition of the bottom layers, could result in a rapid transfer of dissolved MeHg from sediment pore waters. To ascertain where MeHg is produced and how the profile develops will require detailed microbial and water column measurements, as well as sediment-water exchange flux measurements. Diffusion of MeHg would be limited to the suboxic layers because of the rescavenging of MeHg-sulfide species by Fe and Mn precipitates. In the mixed layer, MeHg may also be destroyed by photodegradation and microbial demethylation.

The solution speciation modeling results obtained in this study indicate that inorganic sulfide is the primary complexing ligand for Hg in oxic surface waters as well as in anoxic waters. Sulfide complexation generally results in increasing the solubility of inorganic Hg, which offers one explanation for increased dissolved Hg concentrations in the deep anoxic waters of Offatts Bayou, as compared to the Galveston Bay surface waters. The decrease of bioavailable Hg species (HOHgSH^0) in anoxic waters may explain why MeHg production generally occurs in oxic/anoxic transition layers, rather than in stable anoxic layers in sediment pore waters and hypoxic water columns (Mason et al. 1993; Gilmour et al. 1998). The limitations in sulfate-reducing bacterial activity and bioavailable Hg species would inhibit MeHg production in the oxic and stable anoxic layers, respectively. The predominant sulfide complexation of MeHg in anoxic waters offers an explanation for why MeHg levels are able to remain enhanced in anoxic zones as compared to oxic waters. The changes in modeled solution speciation and experimentally derived phase speciation between oxic and anoxic waters are geochemically consistent.

The changes in phase speciation of inorganic Hg and MeHg in the water column most likely involve the dissolution/precipitation cycling of Fe. Where Fe oxide precipitates, Hg-sulfide and MeHg-sulfide complexes are scavenged, resulting in increases in K_d of inorganic Hg and MeHg in the lower pycnocline. The role of Fe oxide in the transport and cycling of Hg and MeHg was also reported in the hypolimnion of a freshwater lake (Chadwick et al. 2006). In anoxic and high-sulfidic layers, the Hg speciation model provides evidence that a FeS-Hg association is more important than that for a POM-Hg association. A decrease of Hg solubility by forming an FeS-Hg association would restrict MeHg production in dissolved Hg-limited systems

such as organic and sulfate-rich estuarine and coastal sediment pore waters (Hammerschmidt and Fitzgerald 2004). However, the increase of MeHg observed in the bottom anoxic layer of Offatts Bayou indicates that this solubility restriction was not a main factor controlling the distribution of MeHg in Offatts Bayou.

Thermodynamic modeling conducted without consideration of Hg-sulfide-DOM associations predicted that Hg-sulfide complexes dominate the solution speciation of Hg even at nmol L^{-1} sulfide concentrations. This modeling prediction does not explain the role of DOM as a carrier of Hg in stratified water columns (Chadwick et al. 2006), nor does it explain the role of DOM in surface oxic waters (Ravichandran 2004). In addition, determinations of the octanol-water partition coefficient were lower than would be predicted with the presence of Hg-sulfide species (Miller 2006). It may be that there is an association between DOM and Hg-sulfide species that was not considered in the thermodynamic modeling. Miller (2006) suggested that the possible association between DOM and Hg-sulfide is a partitioning of hydrophobic Hg-sulfide complexes into hydrophobic components of DOM based on the observed interaction between neutral Hg-sulfide complexes and DOM in the laboratory-prepared solutions. Similar conclusions were drawn for natural Hg complexes in wastewater effluent (Hsu-Kim and Sedlak 2005). Extremely strong HgL complexes ($\log K > 10^{30}$) were stable over weeks in the presence of oxygen, and the combination of sulfide and humic acid resulted in the formation of Hg complexes that show characteristics similar to natural Hg complexes (Hsu-Kim and Sedlak 2005). Studies involving qualitative and quantitative assessments of Hg-sulfide-DOM associations in natural waters are required in order to more clearly understand the Hg bioavailability and methylation processes.

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