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Sediment−Water Fluxes of Mercury in Lavaca Bay, Texas

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The aqueous flux of inorganic Hg and monomethyl Hg from sediments to the water column was determined at several sites in Lavaca Bay, an estuary along the Texas Coast, historically impacted by Hg discharges. Diffusive fluxes were calculated at 15 sites using interstitial pore water gradients and compared to direct flux measurements obtained at two sites using benthic flux chambers. The diffusive flux of monomethyl mercury (MMHg), when modeled as a chloride species, varied over 3 orders of magnitude from 0.2 to 1500 ng m^{-2} day^{-1}. Diffusive fluxes determined at a single site revealed that MMHg fluxes varied seasonally; maximal fluxes occurred in late winter to early spring. Flux chamber deployments at an impacted site revealed that MMHg was the Hg species entering the water column from sediments and the flux was not in steady-state; there was a strong diurnal signal with most of the MMHg flux occurring during dark periods. The flux of inorganic Hg was smaller and not as easily discernible by this method. The MMHg flux during the dark period (830 ng m^{-2} day^{-1}) was about 6 times greater than the estimated diffusional flux (140 ng m^{-2} day^{-1}) for MMHgCl, suggesting that biological and/or chemical processes near the sediment−water interface were strongly mediating the sediment−water exchange of MMHg.

Introduction

Texas estuaries are typically shallow and broad as compared to estuaries in other coastal environments. Hence, one would anticipate that water column concentrations in Texas estuaries are characterized by exchange processes with sediments to a greater degree than in other estuaries. Indeed, our recent work has provided indirect evidence showing that sediments play an important role in controlling or mediating the concentration of several trace elements and nutrients in Galveston Bay (*1*−*3*).

Two approaches are usually used to obtain information on the sediment−water exchange of interstitial pore fluids with the overlying water column. An indirect assessment can be made from measurements of the vertical distribution of the constituent of interest in interstitial pore fluids using diffusion modeling approaches (*4*). A more direct approach is to enclose a portion of the bottom sediments with a chamber and monitor the change in concentration of the constituent of interest over time (*5*, *6*). The gradient approach provides only steady-state flux information, while the chamber method has the potential to provide information on the temporal scales for which sampling is conducted.

While there have been numerous studies of the Hg content of sediments in a variety of aquatic systems, our understanding of diagenetic reactions, redox cycling, and the sediment−water exchange of Hg in aquatic systems is limited. To date, there have been a limited number of studies of the interstitial pore fluid content of Hg in sediments and related studies on the exchange flux of Hg between sediments and the water column (*7*−*10*). Such information is a vital component of mass balance studies and geochemical modeling efforts.

In this work, the sediment−water exchange flux of total dissolved Hg (THg), dissolved inorganic Hg (IHg), and dissolved monomethyl mercury (MMHg) were obtained by two approaches: interstitial pore water gradients and benthic flux chamber deployments. This study was part of a larger research effort to characterize and describe Hg cycling in an Hg-impacted embayment site in Lavaca Bay, TX. Related reports to appear in this Journal include studies on the cycling, diagenetic behavior, depositional history, and migration of Hg in sediments (*11*, *12*) and information of sediment pore water sampling methodology for Hg (*13*).

Methods

Site Description and Sample Collections. Lavaca Bay is a secondary bay of the Matagorda Bay system on the Texas Gulf Coast that has been impacted by Hg discharges from a chlor-alkali facility between 1966 and 1979. The site was placed on the EPA Superfund list in March 1994, and a series of investigations were begun in April 1996 to elucidate factors contributing to elevating Hg in fish and shell fish. As part of a reconnaissance program, observations were obtained at 15 locations within and near the impacted region to obtain information on Hg cycling in or in close proximity to five different habitats: intertidal mudflats (IM), oyster reefs (OR), grass flats or fringe wetlands containing emergent *Spartina* (GF), open water sites (OW), and within the ship channel (SC) (Figure 1). In addition, site GF-2 was monitored periodically for approximately 1 year to investigate seasonal trends. Replicate sediment cores, biota, and water column samples were obtained at all locations.

Interstitial pore water concentrations of IHg and MMHg concentrations were obtained for depth intervals of 0 (water column), 0−1, 1−2, 3−5, and 5−7 cm at the 15 study sites in the spring of 1996. Samples were also collected over a 1-year time period (at site GF-2) to monitor seasonal changes in interstitial pore water conditions and associated flux estimates. Interstitial pore fluids were extracted from intact

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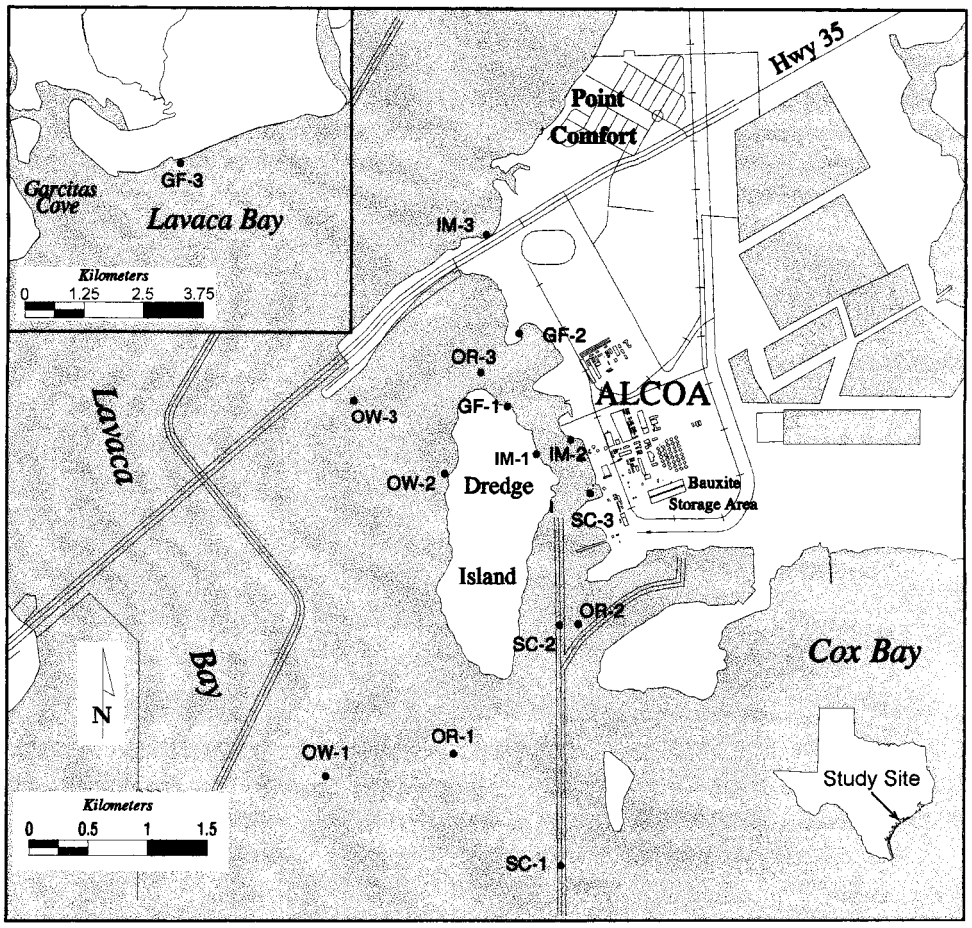

FIGURE 1. Location of sampling sites in Lavaca Bay. Sampling was conducted at three stations in each of five habitat types designated as OW, open water; GF, grass flats; SC, ship channel; OR, oyster reef; and IM, intertidal mudflat.

cores using centrifugation under nitrogen following ultraclean protocols (*13*).

The benthic flux chambers employed are similar to those used to study remineralization of organic matter on continental margin sediments (*6*). The chamber has a total volume of 8.08 L and a surface area of 0.0962 m^2. Precise internal volume is maintained by pushing the chamber into the sediments until it rests against a collar fastened to the outside of the chambers. Water within the box is inductively stirred with an external battery-operated motor and a Teflon-coated stir bar. The benthic flux chambers are constructed from polycarbonate (Lexan) materials that we have verified to be noncontaminating and suitable for trace element studies once properly cleaned. They are fitted with Teflon sampling ports for sample withdrawal into a polyethylene syringe. The stirring motor and sampling paraphernalia are battery-operated. Sampling is performed by SCUBA at increasingly longer intervals (from ca. 1 h up to 24 h) until dissolved oxygen has decreased by ca. 40% so that the diffusive barrier (*14*) remains exposed to approximately ambient conditions under low turbulence. To compensate for volume loss during sampling, ambient external water is drawn in through an open port fitted with a Teflon needle. Considerable testing of this chamber design for benthic flux studies have been undertaken (*6*). For example, diffusive sublayer thickness studies in the chamber have been conducted using alabaster plates (*15*). Flux determinations made with chambers include diffusive and bio-irrigational sediment−water exchanges but not wave-induced flows.

Analytical Methods. Mercury measurements were conducted following well-documented and established protocols (*13, 16, 17*). In this paper, IHg concentration is operationally defined as the difference between THg and MMHg measurement. As defined, organic mercury complexes and associations with dissolved organic carbon will be included in the IHg fraction. Dissolved oxygen was determined by a hand-held probe on aliquots withdrawn by syringe within a few minutes of collection. Nutrient measurements were determined by standard spectrophotometric methods (*18*). Analytical reproducibility for THg and MMHg measurements of interstitial pore waters and chamber samples averaged 6.6% and 8.5%, respectively (*11, 13*).

Modeling the Diffusive Flux of Ions and Molecules from Sediment−Pore Water. The diffusion of ions or molecules in interstitial pore fluids, in the absence of biological irrigation, is usually modeled based on a modification of Fick's first law. For diffusion in a sediment−pore water mixture, a generally accepted form of Fick's first law is

$$\text{diffusive flux } (F) = -\left(\frac{\varphi D_w}{\theta^2}\right)\frac{\partial C}{\partial x} \qquad (1)$$

where F is the flux of a solute with concentration C at depth x, θ is the tortuosity (dimensionless), φ is the sediment porosity, and D_w is the diffusion coefficient of the solute of interest in water without the presence of the sediment matrix. Tortuosity is a parameter that is not readily measured, but fortunately it has been shown that it is related to porosity, a parameter that is readily determined. Numerous studies have been conducted to relate tortuosity to sediment porosity. A relationship between tortuosity and porosity has recently been proposed (*4*) and will be used for all flux calculations made herein:

TABLE 1. Sediment−Water Diffusive Fluxes[a] of Inorganic Mercury and Monomethyl Mercury Assuming Different Solution Forms and %MMHg in Interstitial Pore Fluids at 15 Sites in Lavaca Bay

site	MMHgCl flux (ng m^{-2} day^{-1})	MMHg−MOM[b] flux (ng m^{-2} day^{-1})	$HgCl_4$ flux (ng m^{-2} day^{-1})	IHg−MOM[b] flux (ng m^{-2} day^{-1})	% MMHg in pore water[c]
GF1	270 ± 50	41 ± 7	47 ± 8	10 ± 2	80
GF2	140 ± 80	22 ±12	30 ± 16	6.3 ± 3.5	74
GF3	0.21 ± 0.04	0.03 ±0.01	10 ± 2	2.1 ± 0.4	2
IM1	1500 ± 1100	230 ±170	77 ± 55	16 ± 12	48
IM2	63 ± 46	10 ± 7	23 ± 17	4.8 ± 3.5	50
IM3	1.7 ± 1.6	0.3 ± 0.0	11 ± 11	2.4 ± 2.2	9
OR1	0.9 ± 1.4	0.1 ± 0.0	4.7 ± 7.1	1.0 ± 1.5	4
OR2	40 ± 26	6.2 ± 4.0	7.0 ± 4.5	1.5 ± 1.0	70
OR3	26 ± 11	4.0 ± 1.7	12 ± 5	2.5 ± 1.1	53
OW1	12 ± 9	1.9 ± 1.4	1.7 ± 1.3	0.4 ± 0.3	44
OW2	10 ± 12	1.5 ± 1.9	6.8 ± 8.4	1.4 ± 1.8	39
OW3	16 ± 25	2.4 ± 3.8	8.4 ± 13	1.8 ± 2.8	40
SC1	0.4 ± 0.3	0.1 ± 0.0	15 ± 10	3.3 ± 2.2	3
SC2	2.9 ± 1.4	0.5 ± 0.2	15 ± 7	3.2 ± 1.5	8
SC3	9.1 ± 6.6	1.4 ± 1.0	81 ± 59	17 ± 12	6

[a] Flux determinations based on average pore water Hg concentration in the top 1 cm sediment layer obtained from 3−4 separate cores. Flux calculations for each Hg fraction (IHg and MMHg) are modeled assuming that the solution forms exist either as inorganic complexes ($HgCl_4^{2-}$ and $MMHgCl^0$) or are associated with MOM. [b] MOM, macromolecular organic matter with a molecular mass of 5000 Da. [c] Top 1 cm layer only.

$$\theta^2 = 1 - \ln(\varphi^2) \quad (2)$$

Limitations in this type of flux estimation come from averaging over the large sediment collection intervals and also in the choice of diffusion constants (see below). To improve this estimation method, a finer resolution of interstitial pore water measurements must be obtained to more accurately characterize the interfacial Hg gradient.

Estimation of a Diffusion Coefficient. A rigorous determination of the diffusion of Hg out of pore fluids necessitates an understanding of the major solution forms of Hg present and an assessment of the diffusion coefficient for each Hg species. Such a treatment is currently not possible because of the paucity of information on the solution speciation of Hg in seawater. To provide reasonable constraints on the flux estimate, we will assume two cases. A maximal flux can be estimated by assuming that IHg and MMHg in pore fluids exist as the anionic tetrachloro complex ($HgCl_4^{2-}$) and the neutrally charged chloride species (CH_3HgCl^0), respectively. A lower bound to the diffusional flux estimate can be made by assuming that all of the IHg and MMHg are bound in association with organic macromolecules in the colloidal size range. This latter treatment is supported by recent observations on the phase speciation of Hg (II) in Texas estuaries where an average of 57 ± 20% of the filter-passing (>0.45 μm) Hg existed in colloidal organic forms of molecular mass >1 kDa (*3*).

We have not been able to find direct determinations of diffusion coefficients for these species appropriate for flux calculations. An estimate (of 9.5×10^{-6} cm^2 s^{-1}) for the inorganic form can be made by assuming that it behaves similar to other doubly charged anionic species, particularly those of comparable mass. Diffusion coefficients at 25 °C and infinite dilution for several doubly charged anionic species (e.g., WO_4^{2-}, 9.23×10^{-6}; MoO_4^{2-}, 9.91×10^{-6}; CrO_4^{2-}, 11.2×10^{-6}; SeO_4^{2-}, 9.46×10^{-6}; and SO_4^{2-}, 10.7×10^{-6} cm^2 s^{-1}) have been reported that fall within a fairly narrow range (*19*).

Estimates of the molecular diffusion coefficient of neutral molecules (such as CH_3HgCl^0) in water can be made using the observed linear relationship between the molar volume (V) of the molecule and its molecular diffusion coefficient (Figure 9.7 in ref *20*):

$$D_w = \left(\frac{2.7 \times 10^{-4}}{(V)^{0.71}}\right) \quad (3)$$

where D_w is the molecular diffusion coefficient in water at 25 °C (cm^2 s^{-1}) and V is the molar volume (cm^3 mol^{-1}) of the neutral molecule. For CH_3HgCl^0, a diffusion coefficient of 1.3×10^{-5} cm^2 s^{-1} is obtained using an estimated molar volume for CH_3HgCl^0 of 56.41 cm^3 mol^{-1}. An estimate for the diffusion coefficient of IHg and MMHg associated with macromolecular organic matter (MOM) can be made by assuming that diffusivity is solely controlled by the diffusion of the organic substrate. The free diffusion of organic molecules has been shown to be related to molecular weight (M_w) (*21*). A diffusion coefficient for MOM of 2×10^{-6} cm^2 s^{-1} is obtained using the relationship between M_w and D_w given by Alperin et al. (*22*):

$$D_w = 3.3 \times 10^{-5} (1/M_w)^{1/3} \quad (4)$$

and an average molecular mass for DOC in coastal marine sediments of 5000 Da. Temperature corrections to the diffusion coefficients at 25 °C were made when necessary using the relationship (*23*)

$$D_{T1} = D_{T2}(1 + 0.048\Delta t) \quad (5)$$

where Δt is the temperature difference in degrees Centigrade.

Results and Discussion

Mercury Fluxes Estimated from Pore Water Gradients. Given in Table 1 are sediment−water diffusive flux estimates for MMHg and IHg. Sediment−water diffusional fluxes were determined based on the concentration gradient between an average Hg concentration in the top 1 cm of interstitial fluid obtained from 3−4 separate cores at each site (*11*) and the overlying water column Hg concentration. This gradient was chosen because maximum MMHg pore water concentrations were observed in the top 1 cm layer in almost all cases. Maximal fluxes at each site result when the solutions forms of MMHg and IHg are modeled as $MMHgCl^0$ and $HgCl_4^{2-}$, respectively. Minimal fluxes occur when the solution forms of both MMHg and IHg are treated as associated with MOM, having an average molecular mass of 5000 Da. The true solution speciation and flux can thereby be constrained by these end-member treatments.

It was not possible to provide tight constraints on the diffusional flux estimates; most have considerable error associated with them (Table 1). The inability to provide a precise flux estimate at each site arises from the large

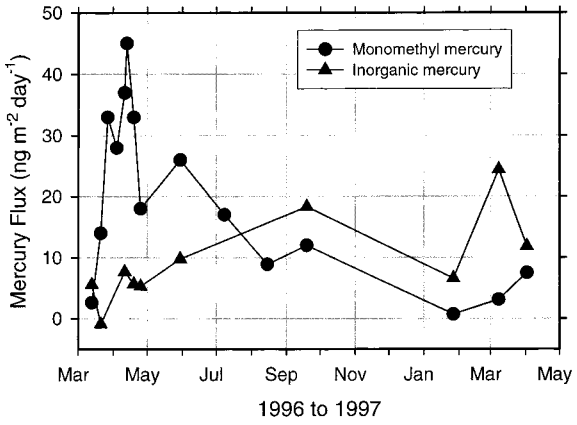

FIGURE 2. Seasonal estimates of the sediment−water exchange fluxes of MMHg and IHg at the time series site GF-2 determined from diffusional flux approaches. The flux calculations were made assuming that the diffusional species were MMHgCl and $HgCl_4^{2-}$. Binding of MMHg and IHg with molecular organic matter would reduce these fluxes by about 80%.

variability in Hg concentrations observed in surficial interstitial water at each site. For example, the relative standard deviation (RSD) of replicate determinations of interstitial MMHg concentrations in the top 1 cm of sediments, based on 3−4 core collections at each site, varied between ±25% and ±177% and averaged ±72% for the 15 study sites. Similarly, the reproducibility for IHg varied between ±12% and ±122% and averaged ±52% for the 15 study sites. This variability suggests that considerable heterogeneity exists for Hg in surface sediments of Lavaca Bay on relatively small spatial scales.

The calculated diffusive flux of MMHgCl from pore water gradients for the 15 stations in Lavaca Bay varied over 3 orders of magnitude from 0.2 to 1500 ng m^{-2} day^{-1}, while the $HgCl_4^{2-}$ flux had a much smaller range from 1.7 to 77 ng m^{-2} day^{-1}. Treating these Hg forms as 100% associated with MOM reduced the diffusive flux of MMHg by 85% and of IHg by 79% (Table 1). MMHg was the dominant Hg species entering the water column from sediments at 9 out of the 15 sites, reflecting its abundance over IHg in interstitial pore water in surficial sediments at these sites (Table 1). Not surprisingly, those sites located outside the zone of historical Hg impact (OW1, IM3, OR1, SC1, and GF3) tended to have the lowest IHg and MMHg fluxes. Within the impacted region, higher MMHg fluxes were observed in intertidal mudflats and nearby grass flats as compared to the other habitat types, again primarily reflecting the abundance of MMHg over IHg in interstitial pore water at these sites.

The sediment−water flux of MMHg at site GF-2 also had a marked seasonal pattern (Figure 2). MMHg fluxes were maximal in late winter to early spring (~40 ng m^{-2} day^{-1}) and then steadily decreased over the remainder of the year, reaching minimal values (~1 ng m^{-2} day^{-1}) in winter. This seasonal MMHg flux cycle appears to be driven by seasonal variations in the production of MMHg and in seasonal changes in the particle−water partition coefficient (K_d) for MMHg (*11*). This is consistent with previous studies, which have shown that MMHg is produced principally in surficial sediments by sulfate-reducing bacteria that methylate IHg (*24*−*26*). The seasonal pattern for K_d is inverse that of MMHg production, showing minimal values during high production periods (*11*). Interestingly, the large peak in MMHg flux observed in the spring of 1996 was much smaller in the spring of 1997. Production of MMHg was apparently not as intense in spring 1997. While the reason for this apparent difference is not known, one factor that may be responsible is interannual differences in freshwater inflow. 1996 was a much dryer year than 1997, and there was extensive freshwater influence at GF-2 during the spring of 1997 that did not occur in 1996 that may have influenced microbial communities and MMHg production.

In contrast, seasonal IHg fluxes tended to be less variable and were opposite in trend to the seasonal pattern of the MMHg fluxes. Interstitial IHg levels were less than overlying water column concentrations during one spring 1996 sampling event, suggesting that the direction of the IHg flux was actually from water to sediment (i.e., −0.9 ng m^{-2} yr^{-1}). IHg fluxes reached a mid-summer peak of ~17 ng m^{-2} yr^{-1} as the MMHg fluxes were in steady decline. The maximal IHg flux (23 ng m^{-2} yr^{-1}) was observed in March 1997 when production of MMHg did not occur as intensely as in the previous year.

Benthic Flux Chamber Deployments. Two dual benthic flux chambers were deployed at an open water site (OW-1) outside of the area of highest Hg-impacted sediments on April 9, 1996, for approximately an 8-h daylight period. Mercury, oxygen, and nutrient data obtained for these deployments are illustrated in Figure 3, panels A−E. A small increase in MMHg concentration but no significant increase in IHg was evident with time if the results from all chambers are collectively considered (see regression line, Figure 3, panels A and B). However, results from individual chambers varied considerably, making it hard to derive definitive conclusions.

The inability to resolve an IHg flux and the large variability between chambers at this site is not entirely unexpected. Of the 15 sites for which sediment−water flux calculations were made based on interstitial pore water gradients, the OW-1 site had the lowest predicted IHg flux (Table 1). Moreover, the ability to detect an IHg flux is hampered by the fact that overlying ambient water has a higher IHg/MMHg concentration ratio (1.37/0.01 ng/L) as compared to the IHg/MMHg concentration ratio (1.61/1.21 ng/L) in interstitial pore waters of surficial sediments. This makes it easier to detect small changes in MMHg in the chamber as compared to IHg because a large background signal is not present. This same feature also impacts interstitial pore water concentration gradients markedly favoring the flux of MMHg out of sediments. The concentration gradient for MMHg at OW-1 is 5-fold higher than that for IHg at site OW-1. The large variability in interstitial pore water Hg concentrations in surface sediments noted previously most likely accounts for some of the variability observed between chambers.

Time course concentrations of nutrients and oxygen in the chambers show clear evidence of microbial respiration of organic matter that utilizes oxygen and releases nutrients to solution (Figure 3, panels C−E). However, concentration trends with time were not comparable in both chambers, despite the fact that the chambers were deployed only a few meters apart. Chamber 1 had marked increases with time in ammonia and phosphate as compared to chamber 2, and it had concomitantly lower oxygen levels than chamber 2. There is also evidence that benthic photosynthesis may be present and that photosynthetic activity varied temporally and spatially as well. Oxygen concentrations initially dropped in all four chambers during the first hours of deployment. Subsequently, conditions differed in the two chambers. Oxygen levels remained slightly lower than starting conditions in chamber 1 and increased above starting conditions in chamber 2 during midday when light intensity is generally maximal. These features further support earlier suggestions that sediment and biological conditions are highly heterogeneous; sediments underlying chamber 1 were more active microbially, and benthic photosynthesis may also be temporally impacting sediment−water exchange processes.

An estimate of the MMHg flux at site OW-1 can be obtained by regressing the average MMHg concentration at each sampling interval against time (Figure 3A). This approach

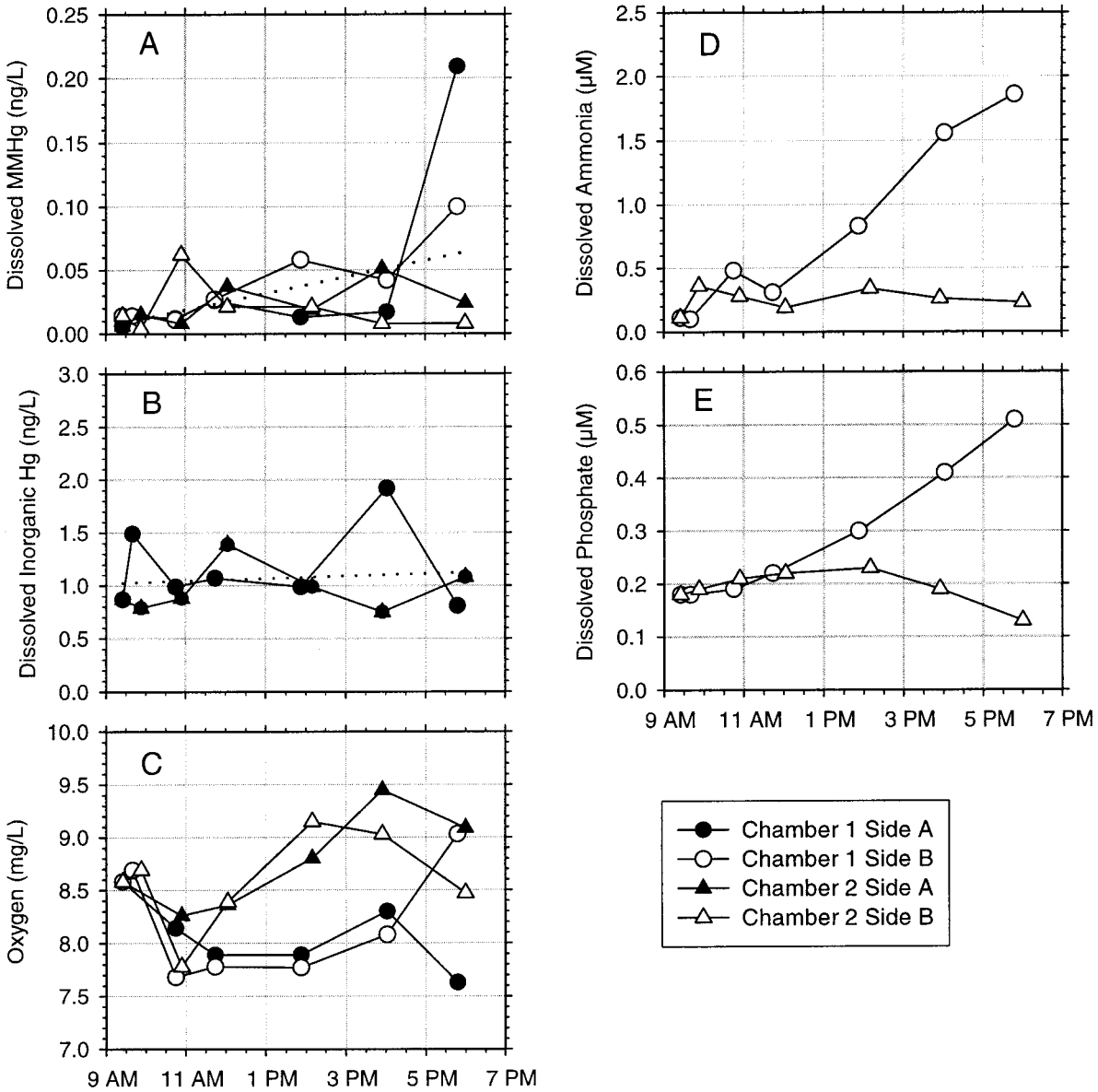

FIGURE 3. Dual flux chamber deployments at site OW-1 on April 9, 1996. Shown are time course concentrations over approximately 8 h of dissolved concentrations of monomethyl Hg (A), inorganic Hg (B), oxygen (C), ammonia (D), and phosphate (E) obtained from each side of each of two individual benthic flux chambers (four chambers total). Dotted lines in panels A and B are linear regression lines drawn through all the data.

yields a MMHg flux of 0.6 ng m^{-2} h^{-1} (15 ng m^{-2} day^{-1}). If the one high point is excluded from consideration, the MMHg flux reduces to 0.3 ng m^{-2} h^{-1} (7 ng m^{-2} day^{-1}). This direct estimate of MMHg flux agrees surprisingly well with that obtained for $MMHgCl^0$ by diffusive calculations (15 vs 12 ng m^{-2} day^{-1}, respectively). A similar approach for estimating the IHg flux is not appropriate since the correlation coefficient obtained for the linear regression between IHg concentration and time is very weak ($r = 0.21$).

Evidence for a Diurnal MMHg Efflux. Note that at site OW-1 the very last collection period for two of the chambers showed a substantial increase in MMHg concentration while the other two did not (Figure 3A). These latter collections were obtained near sunset, suggesting the possibility of an enhanced flux associated with light levels. Preliminary evidence for a diurnal change in Hg efflux noted at OW-1 was verified in a subsequent 22-h deployment at site GF-2 on May 22, 1996 (Figure 4). This deployment was initiated at sunset to specifically observe any impacts associated with the absence of light. Clearly, the sediment−water flux of Hg varies diurnally as does nutrient fluxes. Moreover, the predominate Hg form that was fluxing out of the sediments was MMHg. The IHg flux was much smaller and is more difficult to quantify due to the background level of IHg present as compared to MMHg (see previous discussion). The predominance of the MMHg flux is consistent with the observation that MMHg accounts for ~80% of the Hg in interstitial water of surface sediments during this period of the year (*11*).

This observation stands in marked contrast to the current paradigm, which treats sediment−water exchange as a steady-state process. This is partly a result of the fact that the preponderance of studies have been based on pore water gradient approaches. There are far fewer studies with chamber deployments. Observation of diurnal variations with chamber deployments have probably also been limited because deployments are usually made only during daylight hours and also in water depths where light penetration to the bottom is minimal. Some dark/light chamber studies have been conducted in Gulf Coast waters to examine respiration activity on carbon and nutrient budgets (Gil Rowe and co-workers, personal communication), but we have not

TABLE 2. Sediment−Water Mercury Fluxes at Sites OW-1 and GF-2 in Lavaca Bay

site	date	method	Hg flux (ng m^{-2} day^{-1}) IHg	MMHg	collection time interval
OW-1	4/11/96	pore gradient	1.7/0.4[a]	12/1.9[b]	
OW-1	4/9/96	flux chamber		15	8 h (light period)
OW-1		burial flux estimate	~4000	~2	
GF-2	4/11/96	pore gradient	30/6.3[a]	140/22[b]	
GF-2	5/22/96	flux chamber	~1	154	22 h integrated
GF-2	5/22/96	flux chamber	115	830	9 h (dark period)
GF-2	5/22/96	flux chamber	−82	−330	12 h (light period)
GF-2		burial flux estimate	~13 000	~10	
atmospheric deposition[c]	11/96 to 11/97	wet + dry	16 ± 12 (n = 48)		2 weeks

[a] IHg form used to determine exchange flux: $HgCl_4$/IHg associated with macromolecular organic matter (IHg−MOM). [b] MMHG form used for to determine exchange flux: MMHgCl/MMHg associated with macromolecular organic matter (MMHg−MOM). [c] Gill and Lehman (unpublished data).

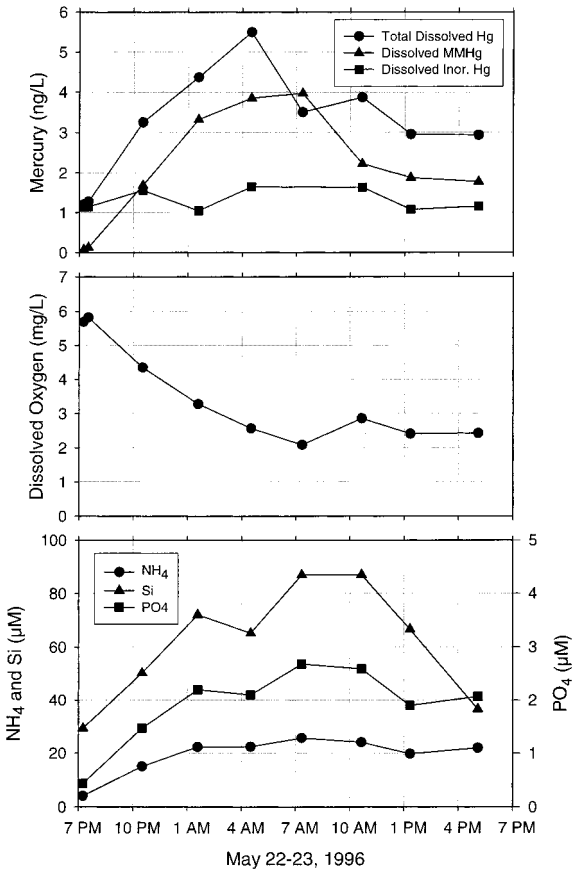

FIGURE 4. Flux chamber deployment at site GF-2 on May 22−23, 1996. Shown are time course concentrations over a 22-h period of dissolved concentrations of total dissolved Hg, monomethyl Hg, and inorganic Hg (top panel); dissolved oxygen (middle panel); and ammonia, silicate, and phosphate concentrations (bottom panel).

been able to find any literature information of diurnal variations for other components. If this phenomenon is widespread in Texas estuaries, it will revolutionize our understanding of the relative importance and treatment of sediment efflux processes and its impact on controlling water column concentrations of many potentially important parameters.

Interestingly, during the daylight period the concentrations of MMHg and THg decreased substantially; IHg did as well, but not to the same degree, suggesting that a Hg removal process was in operation in the water column during sunlight periods. The drop off in MMHg during the daylight period also coincided with a reversal in the release of nutrients and a halting in oxygen utilization from microbial degradation of organic matter.

The 9-h dark interval integrated flux of MMHg was 830 ng m^{-2} day^{-1} (35 ng m^{-2} h^{-1}). This is more than an order of magnitude larger than that predicted from pore water gradients at this site during the seasonal observations (Figure 2). The 12-h light period integrated flux (loss) was −330 ng m^{-2} day^{-1} (−14 ng m^{-2} h^{-1}). The net 22-h light and dark period flux was 150 ng m^{-2} day^{-1} (6.4 ng m^{-2} h^{-1}). For IHg, the 9-h dark interval flux was 110 ng m^{-2} day^{-1} (4.7 ng m^{-2} h^{-1}), and the 12-h light period flux was −79 ng m^{-2} day^{-1} (−3.3 ng m^{-2} h^{-1}). There was no net flux of IHg for the 22-h light and dark period.

This preliminary evidence leads us to hypothesize that sediment−water exchange processes in Lavaca Bay are highly dynamic and variable on a spatial and diurnal basis, most likely responding to the magnitude of microbial activity in sediments and the abundance and respiration activity of benthic photosynthetic organisms. As benthic organisms photosynthesize during light periods, they facilitate the migration of the oxic−anoxic (redox) boundary deeper into the sediments, in essence slowing down the transfer of elements that have high concentrations in anoxic solution. This process in turn affects the sediment−water transfer of many other nonredox-sensitive trace components.

The element that would respond most markedly to this daily redox zone shift is Fe(II), which rapidly oxidizes to Fe(III) in oxygenated seawater in a matter of minutes (*27*). Fe(III)/Fe(II) redox cycling is well-known to be very important in the marine environment, varying considerably on seasonal time scales (*28*−*30*). Whether the redox cycling of Fe is important on even shorter times scales and influences other trace metals in surface sediments remains an open question. A scenario could be envisioned where Fe(II) is transferred from dissolved to particulate phases on a diurnal basis as the redox zone migrates diurnally. Trace constituents with high particulate reactive behavior, such as Hg, are probably showing similar diurnal flux behavior due to adsorption onto the surfaces of the iron(III) oxide phases during oxic periods and are subsequently released back into solution during anoxic periods. These arguments are supported by the seasonal variations of MMHg and IHg concentrations in pore waters in relation to seasonal Fe cycling at site GF-2 (*11*). These authors argue that seasonal Fe cycling controls the mobility of MMHg but not IHg. Moreover, preliminary modeling studies using MINEQL also predict that absorption of MMHg to iron oxides is significant in estuarine sediment but is minor for IHg (*31*).

Comparison of Flux Estimation Methods. A summary of the Hg flux information obtained by pore water gradients and benthic flux chamber deployments for sites OW-1 and GF-2 is given in Table 2. Included are measurements of background atmospheric Hg deposition rates obtained along the Texas Coast (Gill and Lehman, unpublished data) and an estimate of the THg and MMHg burial in sediments. The burial flux estimate is based on observed near-shore and off-shore sedimentation rates of ~1 and 0.7 cm yr^{-1}, respectively (*12*); THg concentrations in surface sediments (*11*); and a porosity and density for surficial sediments of 0.7 and 2.5 ng cm^{-3}, respectively. Both methods of estimating sediment−water fluxes for IHg and MMHg produced reasonably consistent results given the limitations associated with the estimation approaches. The chamber results are in best agreement with the diffusional flux estimates when the IHg fraction is modeled as the $HgCl_4^{2-}$ complex and the MMHg fraction is treated as $MMHgCl^0$ (Table 2). Sediment−water exchange fluxes for IHg are comparable to atmospheric deposition but trivial by comparison to the IHg being buried on an annual basis due to sedimentation processes. This simple comparison suggests that the sediment efflux of MMHg is a major factor in the cycling of MMHg in near-surface sediments of Lavaca Bay Estuary. While no atmospheric MMHg deposition measurements were made, other studies have shown that MMHg in rain is small as compared to IHg (*32*).

Potential Impact of Benthic Hg Fluxes on Water Column Hg Concentrations. The influence of the sediment−water exchange fluxes given in Table 2 on water column Hg concentrations in Lavaca Bay can be estimated. Assuming that MMHg only enters the water column during dark periods (~9 h) at a flux rate of 830 ng m^{-2} day^{-1} (35 ng m^{-2} h^{-1}), the amount of MMHg introduced into the water column would be 320 ng m^{-2} each day. If the water depth is assumed to be 1 m, typical for shallow Texas estuaries, then the MMHg flux to the water column would be 0.32 ng of MMHg L^{-1} day^{-1}. Typical concentration levels of MMHg in the water column at GF-2 are <0.4 ng of MMHg/L for filtered water and <1.2 ng of MMHg/L for unfiltered samples. Thus, the sediment−pore water−water column flux of MMHg should have a marked influence on MMHg levels in the water column.

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