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Spatial and Habitat-Based Variations in Total and Methyl Mercury Concentrations in Surficial Sediments in the San Francisco Bay-Delta

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Recent studies indicate significant amounts of mercury (Hg) are annually transported into the San Francisco Bay-Delta (Bay-Delta) as a result of historic gold and Hg mining activities. We examined temporal and spatial variation in concentrations of total Hg (Hg_T) and monomethylmercury (MMHg) in surficial sediments of various ecosystem types in the Bay-Delta. We sampled surficial sediments across the Bay-Delta system and found Hg_T sediment concentrations in the central Delta were generally 100−200 ng g^{-1} and increased westward through Suisun Bay to 250−350 ng g^{-1}. MMHg concentrations in the central Delta were between 1 and 3 ng g^{-1}, while those in sediments in the perimeter waterways and adjacent bays were less than 1 ng g^{-1}. Six sites were monitored monthly for over a year to identify seasonal changes in Hg sediment concentrations. Hg_T sediment concentrations ranged from 48 to 382 ng g^{-1} and varied as a function of location not season. However, MMHg concentrations varied seasonally, increasing from 1 ng g^{-1} during winter months to 6 ng g^{-1} during spring and summer. Transects conducted at three marshes in the central Delta revealed MMHg sediment concentrations of 4−8 ng g^{-1}at the interior and 2 ng g^{-1} at the exterior of the marshes. Habitat type was a major factor controlling MMHg concentration and the MMHg to Hg_T ratio in sediments of the Bay-Delta. MMHg was significantly correlated to Hg_T (r^2 = 0.49) in marsh sediments.

Introduction

California, the leading producer of mercury (Hg) in the United States between 1850 and 1980, contributed ∼100 million kilograms to the world market. The California Coast Range has extensive natural deposits of cinnabar, a highly insoluble Hg sulfide mineral. During the California Gold Rush (1848 to the early 20th century) cinnabar mined in the Coast Range was processed and refined to elemental Hg on site and transported across the Central Valley to the Sierra Nevada where it was extensively utilized in gold mining activities. The legacy of historic mining activities in California is the introduction of millions of kilograms of Hg into the Coast Range and Sierra Nevada watersheds. Recent studies have determined that large amounts of Hg are annually transported into the San Francisco Bay and Sacramento-San Joaquin Delta (Bay-Delta) from both the Coastal Range and the Sierra Nevada (*1*−*4*). The result is widespread contamination of both sediments and biota (*5*−*7*). At this writing, Hg concentrations in large striped bass and other game fish residing in the Bay-Delta exceed the California Environmental Protection Agency safety guidelines for human consumption (0.23 μg g^{-1} ww). In response to Hg contamination of fish in the Bay-Delta and the potential risks to humans, health advisories have been posted throughout the estuary (*7*). Elevated concentrations of Hg in fish tissue may also represent a hazard to piscivorous wildlife in the Bay-Delta including rare and endangered bird species (*8*).

The Hg species of greatest concern to human and wildlife health in the Bay-Delta is monomethylmercury (MMHg). Human exposure to MMHg occurs primarily through the consumption of contaminated fish (*9*, *10*). Bloom (*11*) concluded that for all fish species studied, virtually all (>95%) of the Hg present is as MMHg. In aquatic systems it is generally accepted that MMHg production is mediated by microbial activities including those of sulfate-reducing bacteria (*12*−*15*). The primary site of methylation occurs in sediments at the oxic/anoxic interface which is often near the surface of marsh sediments (*16*, *17*). MMHg production is a function of both the activity of methylating bacteria and the availability of Hg for methylation (*18*). Thus, environments which favor increased bacterial activity with a readily available source of inorganic Hg for methylation generally favor the production of MMHg.

This study was conducted as part of California and Federal agencies (CALFED) Bay-Delta Hg project. We report here on the distribution of total Hg (Hg_T) and MMHg across the Bay-Delta system resulting from an extensive synoptic areal study of five major ecosystem types. Identifying ecosystem types which favor the production of MMHg is an important component for restoration and Hg remediation of the Bay-Delta. In addition, Hg speciation was studied on a broad temporal scale and the data presented illustrate dynamic changes in surficial sediment Hg cycling over time. Finally, this paper discusses the control of Hg_T on MMHg in Bay-Delta marshes.

Experimental Section

Environmental Setting. The Bay-Delta is the largest estuary on the west coast of the United States. The Bay-Delta receives the runoff from 40% of California's land and covers 300 000 ha with thousands of km of waterways within its boundaries. These waterways, originally formed from the natural meandering of rivers through the marshland, are now mostly restrained by rip-rap armor and extensive dikes. Historically, seasonal wetlands and marshes were the predominant habitat features in the Bay-Delta (*19*). Today, the majority of these seasonal wetlands and marshes have been reclaimed for agricultural uses (*20*, *21*). Within the Bay-Delta, diverse habitats of open water channels, flooded farm tracts, and marshes provide essential habitat for fish and wildlife,

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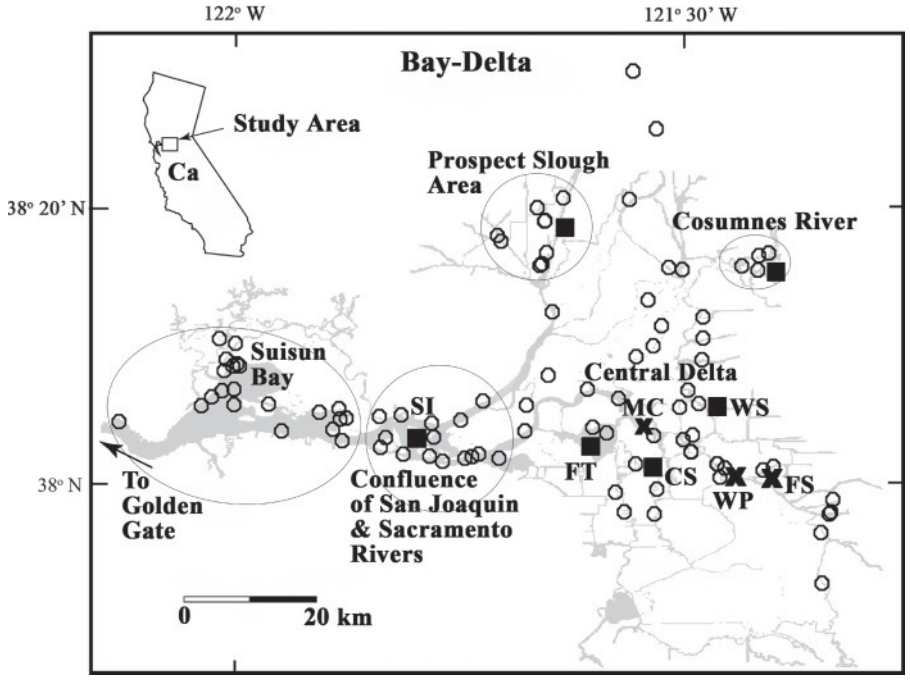

FIGURE 1. San Francisco Bay-Delta and locations sampled for the synoptic areal study (○), seasonal study (■), and marsh study (X).

supporting vegetation, as well as agriculture, and recreation (see Supporting Information).

Sampling. Samples were collected during winter of 1999 as part of a synoptic areal study of Bay-Delta sediments (Figure 1). Sampling locations were selected using GIS base maps to generate a random sampling of the following five major ecosystem types found in the Bay-Delta: mudflats, open water, seasonal wetlands, farmed wetlands, and marsh. Once in the field, problems with access necessitated modification of site locations (11.5% of randomly chosen sites), resulting in semi-random site selection. Additionally, at six sites, samples were collected monthly for eighteen months to investigate temporal variation in Hg cycling (Figure 1 and Table S1). Finally, samples were collected May 2001 from three marshes within the central Delta to investigate changes in Hg_T and MMHg concentrations (Figure 1 and Table S2).

The upper portions of the sediment column are important in terms of trophic transfer and sediment/water flux of Hg (*22*−*24*). In Bay-Delta sediments, the oxic/anoxic transition boundary usually occurs within the first few mm (unpublished data, G. A. Gill, Battelle Marine Sciences Laboratory, Sequim, Washington). Maximum rates of Hg methylation have been observed to occur within the redoxcline in other studies (*14*, *25*, *26*). With the understanding that MMHg concentration in certain environments such as marshes may be elevated at depth (1−2 cm) as observed by Choe et al. (*22*), the 0−0.5 cm of sediment was chosen as the desired depth interval to sample across habitat types due to the shallow redoxcline observed in Bay-Delta sediments. There are, however, no commercially available samplers capable of reliably sampling this portion of the sediment column. A sampler was therefore designed and built, at Moss Landing Marine Laboratories (*27*), to cleanly capture the top 0−0.5 cm of sediment (see Supporting Information, Figure S1). Sediment samples were transferred into 60 mL wide-mouth borosilicate glass jars, with Teflon lined polyethylene caps, using established ultraclean handling protocols (*28*). Samples were placed on dry ice for transport back to the laboratory and kept frozen prior to analysis.

Hg_T Analysis. Sediment samples were digested by adding 4.0 mL of concentrated HCl to 1.0 g of wet sediment and swirling. Next, 1.0 mL of concentrated HNO_3 was added, the sample was swirled, and then the container was loosely capped and digested in a fume hood at room temperature for at least 4 h. After complete digestion, samples were diluted up to 40 ± 0.5 mL with high-purity deionized water (DI, 18 megaohm), capped tightly, shaken vigorously, and allowed to settle until the supernatant was clear. Hg_T was measured by aqueous-phase reduction with stannous chloride solution followed by atomic absorbance detection using an automated Perkin-Elmer flow injection mercury system (*27*). Precision, as indicated by the relative percent difference (RPD) of duplicate measurements averaged 9.9% for Hg_T in solids (n = 20 pairs). Accuracy, as determined by recoveries of spiked samples and the certified reference material (NIST 1944, 3.4 μg Hg g^{-1} dw sediment), averaged 115 ± 15% (n = 40) and 114 ± 7% (n = 20) respectively. The method detection limit (MDL), defined as three times the standard deviation of nine determinations of sand (known to be low in Hg and spiked with 60 ng Hg g^{-1} dw sediment), was 10.5 ng Hg g^{-1} dw sediment.

MMHg Analysis. Sediment samples for MMHg analysis were processed by the KBr and CH_2Cl_2 extraction procedure described by Bloom et al. (*29*). Briefly, 0.5−1.0 g of wet sediment was digested with acidic KBr solution and extracted into 10 mL of CH_2Cl_2 in a 35 mL Teflon centrifuge tube. A 2.0 mL aliquout of CH_2Cl_2 was then back extracted into DI water by purging out CH_2Cl_2 with high-purity nitrogen gas. Extracts were analyzed for MMHg by aqueous-phase ethylation, trapping on a Carbotrap column, gas chromatography separation, thermal decomposition to elemental Hg, and detection by cold vapor atomic fluorescence spectroscopy (*30*). Analytical recovery was checked regularly with the certified reference material DORM-1 (dogfish muscle, 731 ± 60 ng MMHg g^{-1} dw tissue, 99.4 ± 0.1% recovery (n = 28)) or DORM-2 (dogfish muscle, 4470 ± 320 ng MMHg g^{-1} dw tissue, 100.2 ± 0.5% recovery (n = 18)), purchased from the National Research Council of Canada. The MDL, defined as three times the standard deviation of nine determinations of low MMHg content sand, spiked with 0.06 ng MMHg g^{-1} dw sediment, was 0.019 ng MMHg g^{-1} dw sediment. Precision (RPD of duplicate measurements) averaged 10.6% for MMHg in solids (n = 46 pairs). Accuracy (spike recoveries) averaged 96.6 ± 20% (n = 92).

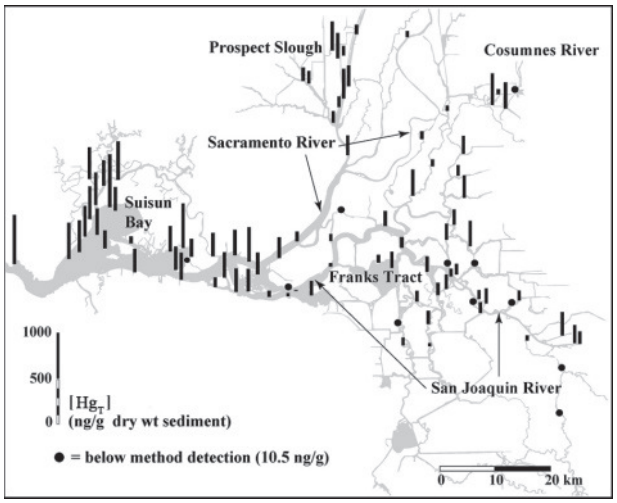

FIGURE 2. Total mercury (Hg_T) surficial sediment concentrations as scale bars in ng Hg g^{-1} dw sediment. Locations with Hg_T values less than the method detection limit of 10.5 ng g^{-1} are represented by solid black circles.

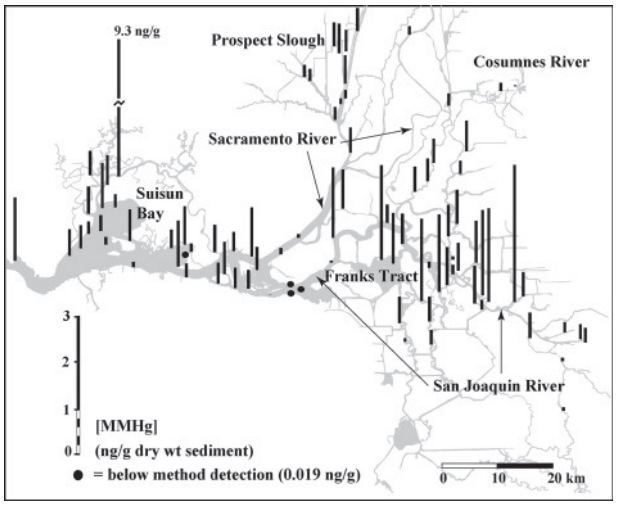

FIGURE 3. Monomethylmercury (MMHg) surficial sediment concentrations as scale bars in ng MMHg g^{-1} dw sediment except when value is given. Solid black circles represent locations with MMHg concentrations less than the method detection limit of 0.019 ng g^{-1}.

Results and Discussion

Synoptic Areal Study. Hg_T concentrations in Bay-Delta surficial sediments averaged 195 ng g^{-1} (Table S3; all sediment concentrations are based on dry weight) and are consistent with measurements of Hg_T in San Francisco Bay sediments by others (*22*, *31*). Surficial sediment Hg_T concentrations across the Bay-Delta were highly variable ranging from below detection level (10.5 ng g^{-1}) to 570 ng g^{-1} (Figure 2). Although the distribution of Hg_T was variable, sediment concentrations decreased, from 305 ± 131 ng g^{-1} (uncertainties = SD) in Suisun Bay, moving east through the convergence of the Sacramento and San Joaquin River (170 ± 114 ng g^{-1}) into the central Delta (110 ± 78 ng g^{-1}). Prospect Slough and Cosumnes River areas averaged 181 ± 84 and 169 ± 166 ng g^{-1} respectively. Sediment Hg_T concentrations in the Bay-Delta are comparable to values reported for sediments in Long Island Sound, an area significantly perturbed by current and historic pollution, including sewage (*32*). San Francisco Bay natural background Hg concentration in sediments was estimated to be 60 ± 10 ng g^{-1} (*5*). Sites sampled in this study had Hg_T concentrations typically 2−5 times higher than background, indicating that most of the Bay-Delta experiences non-point source Hg contamination.

Hg_T concentration was significantly correlated to percent fine-grained sediment collected from Suisun Bay ($r^2 = 0.28$, $p = 0.01$, $n = 21$), the confluence of the Sacramento and San Joaquin Rivers ($r^2 = 0.67$, $p < 0.01$, $n = 15$), and the central Delta ($r^2 = 0.33$, $p < 0.01$, $n = 43$). This finding is in agreement with observations of Conaway et al. (*31*) that Hg_T correlated very well with percent clay for the entire estuary. Many studies have also observed Hg_T concentrations to be linked with organic content associated with fine-grained sediment (*31*−*33*). However, we found no significant correlation between Hg_T concentration and percent loss on ignition (LOI), which was used as a proxy for total organic content.

There was large spatial variability in surficial MMHg sediment concentrations in the Bay-Delta (Figure 3; Table S3). In contrast to Hg_T distribution, MMHg concentrations in the central delta were higher than those in adjacent waterways and bays. The central Delta average MMHg concentration was 0.72 ± 0.68 ng g^{-1}. Prospect Slough and Cosumnes River MMHg concentrations averaged 0.39 ± 0.19 and 0.10 ± 0.10 ng g^{-1}, respectively. MMHg concentrations were very low or nondetectable in the Sacramento and San Joaquin River channels moving west, out of the central Delta, but increased to an average of 0.40 ± 0.31 ng g^{-1} at the Sacramento and San Joaquin Rivers convergence. Suisun Bay MMHg averaged 0.53 ± 0.36 ng g^{-1} and was the location (Joyce Island) of the highest MMHg concentration (9.3 ng g^{-1}) observed during the survey.

MMHg covaried with LOI in the central Delta ($r^2 = 0.29$, $p < 0.01$, $n = 37$) and Prospect Slough ($r^2 = 0.72$, $p < 0.01$, $n = 10$). A significant relationship between organic matter content and MMHg concentration in sediments has been reported for other areas (*32*, *34*, *35*). MMHg was shown to have a significant positive relationship with percent clay in the northern reach of San Francisco Bay (*31*). A significant positive relationship was also observed between MMHg and percent fine-grained sediment ($r^2 = 0.13$, $p = 0.03$, $n = 38$) in the central Delta.

The degree to which inorganic Hg is transformed to MMHg has been termed (net) methylation efficiency and it has been estimated in aquatic sediments using the concentration ratio of MMHg to Hg_T as a proxy (*36*). Methylation efficiency may be used to gauge an ecosystem's potential production of MMHg. Furthermore, the rate of *in situ* MMHg production is a key factor in MMHg bioaccumulation and subsequent biomagnification in the food web (*36*, *37*).

The central Delta had the greatest methylation efficiency; many sites in the central Delta had greater than 2% of the Hg_T as MMHg (Figure S2). Franks Tract had the largest percentage MMHg (2.6%). In addition, four sites within the central Delta had Hg_T concentrations that were below the detection limit and a relatively high percent MMHg. Tributaries surrounding the central Delta had very low percent MMHg. Suisun Bay had a relatively low percent MMHg with the exception of Joyce Island (2.3%). A comparison of percent MMHg between the open water and other ecosystem types found a significant difference (Mann−Whitney: $p < 0.01$) only between MMHg/Hg_T ratios measured in the marshes versus open water areas.

The distribution of Hg across the Bay-Delta identified in the synoptic areal study enables a broad look at the region and identification of locations impacted by pollution. Distribution of MMHg across the Bay-Delta is spatially variable with major tributaries having lower concentrations than the central Delta (Figure 3). The central Delta has environmental conditions favorable for the methylation of Hg while the tributaries surrounding the Delta appear less favorable (Figure S2). Although central Delta sediments had a higher percent MMHg compared to tributaries, concurrent

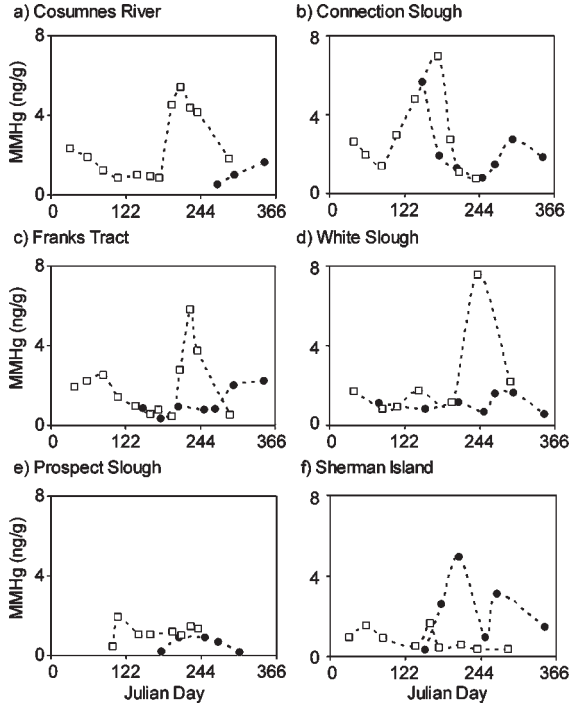

FIGURE 4. MMHg concentration (reported as dry weight sediment) in surficial sediment collected from six locations over a year and a half period (shown as Julian day), within the Bay-Delta. The data shown as solid circles (●) are year 2000 and open squares (□) are year 2001.

studies of Hg levels in fish found significantly lower Hg concentrations in biota collected in the central Delta than tributaries (*38*). Recent studies have demonstrated Hg accumulation in zooplankton and higher trophic levels can be strongly influenced by MMHg dilution at the base of the food web due to algal abundance (*39*, *40*). Biodilution remains to be demonstrated as an explanation for this apparent paradox in fish Hg concentration in the Bay-Delta. A second postulate is that MMHg in sediment within the central Delta is not the source of MMHg to fish in the Bay-Delta. This has not been clearly demonstrated and would set Hg cycling in the Bay-Delta apart from other locations extensively studied such as Chesapeake Bay, Maryland (*41*) and the Florida Everglades (*16*) where a strong correlation between MMHg sediment concentration and MMHg in biota has been demonstrated.

Seasonal Study. A time series of sediment collections was made at six sites between May 2000 and October 2001 representing the first seasonal study of Hg_T and MMHg in Bay-Delta sediments. Total Hg concentration showed no apparent seasonal trend (Figure S3). Cosumnes River had the highest Hg concentration (382 ng g^{-1}). The central Delta sites (Connection Slough, Franks Tract, and White Slough) had similar Hg concentrations (160 ng g^{-1}) and less variability than Cosumnes River, Prospect Slough, and Sherman Island. This may be explained by the central Delta sites being lower-flow, depositional environments compared to the Cosumnes River, Sherman Island, and Prospect Slough which experience high flows and bottom scouring. Sherman Island had the lowest Hg_T concentration (48 ng g^{-1}) with concentrations at this site generally higher during the first half of the study.

MMHg concentration increased by a factor of 3 during late spring and summer at Cosumnes River, Connection Slough, Franks Tract, and White Slough (Figure 4, panels a−d). A second feature, lesser in magnitude (factor of 2) than the late spring/summer peak, was observed during winter months. The winter MMHg peak, although lesser in magnitude (2 ng g^{-1}), was generally a longer lasting feature (3−4 months), while the spring/summer peak was larger in magnitude (6 ng g^{-1}) but shorter in duration (1−2 months). MMHg in the sediments at Prospect Slough remained constant (1 ng g^{-1}) over the length of the study (Figure 4, panel e). Sherman Island had an extended period of elevated MMHg concentration in summer and fall of 2000, followed by a decrease in concentration throughout the remainder of the study (Figure 4, panel f). At Sherman Island, MMHg concentration appears to be coupled with Hg_T concentration. This is discussed in greater detail below.

The absence of an increase in MMHg during the summer of 2000 at Franks Tract and White Slough is conspicuous. While it is possible that no increase in MMHg concentration occurred at Franks Tract and White Slough, it is also possible that any short duration incrases may have gone undetected because of the frequency of sampling: once per month at Franks Tract and White Slough during the summer of 2000. This possibility is supported by the 2001 summer peak at Franks Tract which occurred very rapidly; it was necessary to increase the sampling frequency to twice per month to observe the event. A similar observation was made in Lavaca Bay, Texas by Gill et al. (*23*) who reported a rapid seasonal increase of MMHg which necessitated frequent sampling.

Methylation of Hg in sediments is generally accepted as a bacterially mediated process and has been linked to microbial sulfate reduction (*12*, *14*). Factors that increase sulfate reduction rates, such as availability of organic carbon, increased water temperature, and sufficient sulfate are likely to increase the production of MMHg (*12*, *14*). We observed no relationship between the seasonal increase in MMHg and changes in organic carbon (as measured by % LOI). A likely explanation is the insensitivity of the LOI determinations to the carbon pool utilized by microbes. Stimulation of microbial activity and any resultant production of MMHg are dependent in part on the availability of labile carbon; LOI is a description of the total amount of material lost on ignition, both labile and refractory. Sediments containing a large percentage of refractory material such as peat would have a high percent LOI and also a very high C:N ratio. The refractory carbon in these sediments probably is of little benefit in supplying substrate to the bacterial community. Water temperature in the Delta fluctuates annually following a sinusoidal curve with maximum summer water temperatures of 20 °C and winter minimum temperatures of 10 °C. Increased MMHg accumulation and presumably net Hg methylation occurred in Bay-Delta surficial sediments when water temperature increased. Gilmour et al. (*16*), in a study of the Florida Everglades, also found higher rates of net Hg methylation and MMHg accumulation during periods of elevated water temperatures.

Monthly measurements of chlorophyll a (Chl a), sulfate, and temperature in water collected at Cosumnes River from February to October 2001 are combined with MMHg sediment concentrations (Figure S4). MMHg sediment concentration is slightly elevated with high sulfate concentration, slightly elevated Chl a concentration, and low water temperature. With decreased sulfate and Chl a concentrations MMHg concentration is low as water temperature increases. Elevated water temperature, sulfate concentration, and Chl a concentration occurs with a concomitant increase in sediment MMHg accumulation. This observation illustrates the importance temperature plays in MMHg accumulation in Bay-Delta sediments.

The spring and summer increases in MMHg concentration observed in the Bay-Delta may have resulted from several processes: (a) increased *in situ* MMHg production within the sampling interval, (b) vertical migration of the zone of maximum MMHg production in relation to the sampling

interval, and/or (c) decreased MMHg degradation rate within the sampling interval.

Bubb et al. (*42*) reported seasonal changes in sediment MMHg, with maximum concentrations observed during summer in the River Yare, Norfolk, UK. In the River Yare, the MMHg peak tended to reside uppermost in the sediment profile in the summer and extended to greater depths in the winter and spring. This phenomenon was linked to variations in methylation and demethylation mechanisms as governed by oxygen availablility, temperature, and the nature of the bacterial communities (*42*). Choe et al. (*22*) measured MMHg sediment depth profiles at five of the seasonal sites concurrently with this study. The MMHg profiles generally show a maximum at the surface and do not support a seasonal migration of the MMHg peak. However, MMHg depth profiles were not measured at a frequency necessary to rule out this possibility. Sediment accumulation of MMHg is related to net MMHg production and a decrease in MMHg degradation may result in an increase in MMHg sediment concentrations. Marvin-DiPasquale and Agee (*43*) measured MMHg degradation in the 0−2 cm sediment interval, concurrently with this study, at Prospect Slough, Franks Tract, and Cosumnes River, winter and spring of 2001. MMHg degradation was elevated in May 2001 relative to February 2001 at all sites (*43*). This observation is opposite of what would be expected for changes in degradation processes to be driving increased MMHg sediment concentrations during spring and summer. This is evidence that spring and summer increases in sediment MMHg concentration were a result of Hg methylation processes rather than decreased MMHg degradation.

Fringe Marsh Study. Studies have shown wetlands to be areas of high MMHg production (*44*−*46*). We tested this hypothesis by conducting an investigation of Hg methylation efficiency, as measured by the MMHg:Hg_T ratio, in three central Delta marsh areas in May 2001 (Table S2 and Supporting Information).

Figure S5 shows MMHg and Hg_T sediment concentrations along transects moving from the interior to the edge of three marsh sites. The highest MMHg concentrations were at the interiors of each wetland and decreased at the edge. Within-marsh MMHg concentration ranged from 3.84 to 7.82 ng g^{-1} compared to 1.37−2.06 ng g^{-1} at the exterior. Hg_T concentration followed a similar but less dramatic trend having 170−256 ng g^{-1} at the interior compared to 108−246 ng g^{-1} at the exterior. The interior of the marshes had higher MMHg/Hg_T ratios (2−3%) than the edge (1%).

Marsh areas cover a small fraction of the Bay-Delta, yet may be important sites of MMHg production, export, and bioaccumulation by fish and wildlife (*47*, *48*). MMHg concentration and the MMHg/Hg_T ratios within the marshes were much higher than the open water locations sampled during the synoptic areal study (Figures 3 and S2). The marshes of the Bay-Delta may also have a disproportional influence on the uptake of Hg into the biota as it is within these habitats that fish and birds forage. Time spent foraging in or around the marshes would likely result in a higher body burden of Hg than similar foraging in the more modified open water areas.

MMHg/Hg_T Relationship and Ecosystem Types. The relationship between MMHg and Hg_T in surficial sediments was significant ($r^2 = 0.49$, $p < 0.01$, $n = 17$) within the three marsh habitats we studied (Figure S6). Additionally, MMHg and Hg_T were significantly correlated in sediment collected around Sherman Island at the convergence of the Sacramento and San Joaquin Rivers ($r^2 = 0.69$, $p < 0.01$, $n = 9$; Table S3) and during the temporal study ($r^2 = 0.40$, $p < 0.01$, $n = 15$)(Figures S3 and 4 panel f). Many studies have examined the relationship between MMHg and Hg_T in surface sediments and report contradictory results: some finding significant correlation (*33*, *49*, *50*) and others no significant relationship between MMHg and Hg_T in sediments (*22*, *34*). This apparent contradiction supports the arguments of Benoit et al. (*51*) who point out that Hg_T concentration is only one of several factors involved in controlling MMHg production and bioaccumulation in aquatic ecosystems. Additionally, for ecosystem types, the relationship between MMHg and Hg_T in sediments was significant for estuaries, lakes, and rivers, but not for wetlands (*51*). Furthermore, within single rivers or wetlands, or even clusters of similar ecosystems, significant relationships can exist, but lack predictive power due to the importance of other parameters. We found a correlation between MMHg and Hg_T in a cluster of similar marsh ecosystem types within the central Delta and downstream in the estuary at Sherman Island. In agreement with Benoit et al. (*51*), the relationship lacked predictive power and there was no correlation between MMHg and Hg_T in sediments of marsh habitat sampled during the synoptic study (Table S3). This suggests that other environmental factors, possibly temperature, superseded the importance of Hg_T concentrations on MMHg production during winter within Bay-Delta marshes.

Ecosystem type within the Bay-Delta was important with respect to MMHg sediment concentrations. Marsh habitat had higher MMHg/Hg_T ratios than open water habitat. Hg_T appears to be a key factor controlling MMHg sediment concentrations within marsh habitat, however other factors such as temperature may play an equal role in controlling Hg methylation. This may explain lower MMHg sediment concentrations found in the marsh habitats during the winter synoptic study compared to spring sampling. Hg_T was not a good predictor of MMHg sediment concentrations across all habitat types of the Bay-Delta. Furthermore, spring and summer increases in MMHg concentration occurred independent of changes in Hg_T concentration. However, the relationship between Hg_T and MMHg concentration observed within the marsh habitat indicates Hg_T is a key parameter influencing Hg methylation in this habitat type within the Bay-Delta. Remediation strategies aimed at lowering the Hg load to the marsh habitat may be beneficial in reducing Hg levels in fish. These specific habitats play an important role in the bioaccumulation of Hg into biota within the Bay-Delta as it is a preferred habitat of fish and birds. Additional research aimed at mechanisms of MMHg formation, degradation, fate, and transport is needed in the Bay-Delta to better understand the factors controlling the levels of MMHg in fish.

Acknowledgments

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Supporting Information Available

Tables, figures, and descriptions as mentioned in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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