Mercury (Hg) speciation and partitioning have been investigated in a fluid mud profile collected in the high turbidity zone of the Gironde estuary. The formation of the fluid lens generates local and transient oxic—anoxic oscillations following the sedimentation-resuspension tidal cycles under a specific hydrodynamic regime. The total Hg concentration, ranging from 5 to 190 nM, increases with SPM concentration (4–174 g L⁻¹) to a maximum at bottom. Particulate Hg averages 99% of total Hg. Particulate inorganic Hg (I(Hg(II))) and monomethyl Hg (MMHg) exhibit a similar trend: the maximum concentration is observed within the upper layer above the depth of 7 m and the minimum at the bottom layers of the fluid mud. Significant levels of “dissolved” (i.e. filter passing) Hg species (I(Hg(II)), Hg⁰, MMHg, DMHg) are observed within the redox transition interface. In the sub/anoxic fluid mud layer, increasing concentrations of I(Hg(II)) and MMHg coincide with decreasing concentrations of I(Hg(II)) and MMHg, respectively. The distribution coefficient (log Kd) between the “dissolved” and particulate fraction for I(Hg(II)) averages 4.5 ± 0.2. A Kd minimum for I(Hg(II)) is observed in the surface layer and at the bottom of the fluid mud and coincides with the maximum levels of dissolved Mn and Fe. Log Kd for MMHg averages 3.3 ± 0.9 and presents the highest values (4.3–4.6) in the surface and the lowest (~2.2) at bottom, corresponding to the particulate carbon profile. These results demonstrate that the fate of I(Hg(II)) and MMHg in the fluid mud system is influenced by the redox cycling of major species such as carbon, Fe, and Mn. It is therefore suggested that the redox oscillations generated by fluid mud formation in the high turbidity zone affect the distribution and transfer of Hg species in macrotidal estuaries.

Introduction

Maximum turbidity zones (MTZs) are common features in macrotidal estuaries found in the northern hemisphere (1–4). In these estuarine environments, hyperconcentrated benthic layers, referred to as “fluid mud” (5), are commonly found during summer and neap tides. These MTZs undergo a series of oxic–anoxic oscillations following the alternate cycling of sedimentation (neap tides) and resuspension (spring tides) (6, 7). These environments directly affect the speciation and partitioning of metals under these extreme conditions (1, 6).

The occurrence of Hg species such as elemental Hg (Hg⁰), inorganic Hg (I(Hg(II))), monomethyl Hg (MMHg), and dimethyl Hg (DMHg) in the water column of European turbid macrotidal estuarine systems (e.g., the Loire, the Seine) has been studied (8). Nevertheless, complete Hg speciation and partitioning in the fluid mud of these systems has not yet been systematically investigated. Fluid mud is an environment characterized by strong chemical gradients, especially redox potential. The processes that influence the behavior of Hg in such an environment are supposed to be similar to those occurring in surface sediments. Several investigations (9–11) have shown that the fate of Hg can be affected by redox change during early diagenesis in sediments. The distribution of Hg species (i.e. I(Hg(II)), MMHg) in pore waters and solid sediments were found to be related to those of iron (Fe) and manganese (Mn). It indicates that Fe and Mn oxides play a critical role in the cycling of Hg in sediment (9, 10). Hg can be remobilized into porewater through the dissolution of Fe and Mn, induced by the microbial degradation of organic matter under sub/anoxic conditions. On the other hand, Fe and Mn oxides can also act as geochemical barriers at the water—sediment interface which to prevent Hg diffusion in the overlying water column. In consequence, in examining Hg biogeochemistry in the fluid mud system and its relation to the redox cycling of Fe and Mn, it is important to investigate the interactions between the early diagenesis processes and Hg speciation.

This study presents results obtained on the detailed speciation of Hg in a fluid mud profile in the MTZ of the Gironde estuary. The sampling was performed on a well established fluid mud lens in the Gironde with a high vertical resolution. Early diagenesis processes affecting the behavior of Hg within the oxic/anoxic transition zone were studied in detail. The results have allowed us to assess the impact of the transient sedimentary cycle (sedimentation/resuspension) on Hg cycling in the fluid mud and the adjacent water column. They indicate that fluid mud systems influence both phase rearrangement and chemical transformations of Hg in turbid macrotidal estuaries.

Methods

Study Site. The Gironde estuary is the largest French estuary, with a length of 170 km covering 625 km² at high tide (Figure 1). The mean annual freshwater discharge varies between 800 and 1000 m³ s⁻¹. A stable turbidity maximum forms at the upstream limit of the salinity intrusion and extends along a longitudinal spread of 50–100 Km (12). In this MTZ, the concentration of the suspension (mainly silt and clay) ranges from 0.1 to 10 g L⁻¹ and between 100 and 500 g L⁻¹ for the established fluid mud lenses (7). The Gironde is a macrotidal estuary and has a long residence time for water (3 months) and suspended matter (1–2 years) (12). It is a heterotrophic system, where 50% of the continental particulate organic carbon (POC) is mineralized, the dissolved organic carbon (DOC) is conservative (13), and photosynthesis is strongly limited by turbidity (14). The heterotrophic activity is concentrated in the MTZ and occurs both in oxic (water column) and anoxic (fluid mud) conditions. This activity results in the oxygen depletion of its surface waters (60% saturation) (7).
Sample Collection and Processing. Sampling of fluid mud was performed in the MTZ (PK 12), at neap tide and low tide slack, in June 1997, as part of the BIOGEST project (Biogas transfer in estuaries). During this period, a MTZ was well developed in the low salinity zone (river flow = 410 m$^3$/s$^{-1}$). A 2-m vertical profile (from top 6 m depth to bottom 8 m) was collected with a 20-cm vertical resolution using a sampler specially designed for this purpose and depicted in ref 15. Briefly, the sampler consists of a 2-m cylinder divided into 10 boxes. At slack tide, the closed sampler, filled with nitrogen gas (N$_2$), was sent down gently into the fluid mud until the ballast touched bottom. After a few minutes for stabilization, the sampler was opened remotely from the ship. At least 2 min were allowed for the boxes to be filled and stabilized, before reclosing. Once on board, the samples were extruded from the sampler using N$_2$ pressure. Dissolved O$_2$ (O$_2$D) and pH were measured immediately on the subsamples (15). The rest was poured into 250 mL centrifuge flasks also under N$_2$ atmosphere and then centrifuged at 3500 rpm. Under He gas pressure (2 bar), the supernatant was poured into precleaned 0.45-$\mu$m nylon filters (90 mm i.d., Magma membrane) (Bioblock Scientific). The centrifuged solids were freeze-dried in order to analyze particulate total carbon (PTC), POC, Fe, Mn, and Hg species. Filtered water subsamples were acidified with a 1% solution of sub-boiling distilled nitric acid in order to measure DOC, Fe, Mn, and Hg species. Others were frozen to measure inorganic nitrogen species.

Hg Species Determination. The different Hg species determined in this study in the aqueous and particulate samples were as follows: (a) for the operationally defined "dissolved phase" (>0.45-$\mu$m): dissolved inorganic Hg ([Hg(II)]$_D$), elemental Hg (Hg$^{0}$), monomethyl Hg (MMHg$_D$) and dimethyl Hg (DMHg$_D$) and (b) for the particulate phase (>0.45-$\mu$m): particulate total Hg ([Hg(II)]$_P$), acid leachable inorganic Hg ([Hg(II)]$_L$), subscript L denotes Hg obtained from an acid leach) and monomethyl Hg (MMHg$_P$).

All determinations of Hg species were performed with a cryogenic trapping (CT) technique hyphenated to quartz furnace atomic absorption spectrometry (QFAAS) if in particulate phase or ICP-mass spectrometry (MS) if in dissolved phase, after hydride generation (HG) and ethylation (EtH) derivatization. As mentioned, "dissolved" Hg species ([Hg(II)]$_D$, MMHg$_D$, DMHg$_D$) are operationally defined measurements of filter-passing Hg (>0.45-$\mu$m filter), including truly dissolved and colloidal Hg fractions, that can easily be reduced by the addition of NaBH$_4$ in an acidic medium (16, 17). This fraction of the Hg, operationally defined as the "reducible form", include Hg that is readily released from inorganic and organic complexes. The determination of dissolved gaseous Hg species ([Hg(II)]$_D$ and MMHg$_D$) was analyzed by purging the unperturbed sample (volume 250 mL) (18). Particulate mercury species ([Hg(II)]$_P$, MMHg$_P$) and total mercury ([Hg$_P$]) were determined after microwave-assisted extraction with 6 M HNO$_3$ and HCl/HNO$_3$ 1:1, respectively (16, 19). ([Hg(II)]$_L$) was operationally defined as an acid leachable fraction. This fraction, extracted by 6 M HNO$_3$, mainly corresponds to the phases where [Hg(II)] is associated with carbonate, hydroxides and organic matter. Experimental data showed that about 90% of the total in Hg(II) in certified reference sediments (BCR S19 and CRM 580, polluted river and estuarine sediments) was extracted by this method (20). Complete digestion of all Hg species (e.g., organically bound Hg, mineral Hg) was made by aqua regia acid digestion using a microwave-assisted technique (Tseng, unpublished results). No potential artifact for MMHg measurements was found during the analytical procedure according to the QA/QC procedures proposed by Tseng et al. (20).

Using QFAAS detection, the method detection limits (DL), depending on the sample size used, have been estimated at 0.5 pM, 0.5 pmol g$^{-1}$ in aqueous samples and dry sediments (16, 19). It was also calculated at 0.025 pM in aqueous samples when using ICP/MS as detector (17). The mean overall precision, referring to the relative standard deviation (RSD) of duplicate analysis, was obtained under 10%. Accuracy, as measured by spike recoveries and standard reference materials, of the analytical procedures was estimated to be 90–110%. Other analytical performance of the methods is described in detail elsewhere (16, 17, 19).

Dissolved and particulate Fe and Mn were determined by inductively coupled plasma-optical emission spectrometry. The mineralization of particulate Fe and Mn was treated by an open focused microwave system (Prolabo) with a mixture of HCl/HNO$_3$ 1:1. The pretreatment supposed that all Fe and Mn fractions (including oxides), except refractory silicate mineral fraction, were digested. Other biogeochemical parameters such as DOC, POC, PTC, pH$_D$, and inorganic N species were determined following the procedures described by ref 7.

Results and Discussion

Main Biogeochemical Parameters. The general geochemical profiles of the different parameters in the fluid mud system can be briefly illustrated in Figure 2. First, the oxic section between the top of the fluid mud lens and 6.8 m with a decrease in pH was identified. Second, the suboxic zone (i.e., without O$_2$ but with NO$_3$) existed between 6.8 and 7.5 m. The third zone from 7.6 m down to the consolidated substrate was anoxic with intense denitrification conditions. Other diagenetic properties of the freshly deposited fluid mud were described in detail by refs 7 and 15.

The major observations show that oxygen rapidly decreased to zero below 6.5 m in the fluid mud profile. The pH also decreased with depth with a sharp gradient between 6.5 and 7 m. A decreasing gradient in particulate inorganic carbon (PIC) between 6.5 and 7 m depth was also observed at these depths. In the bottom, anoxic conditions, decreasing NO$_3$ concentrations result from significant denitrification as...
confirmed by the peak of NO$_2$ (15). Under these conditions, Mn and Fe reduction also takes place, resulting in increasing levels of dissolved Mn and Fe down to the bottom of the profile, close to the consolidated sediment. Fe$_D$ and Mn$_D$ concentrations ranged from 780 to 910 mol g$^{-1}$ and from 12.7 to 15.3 mol g$^{-1}$, respectively, and Fe$_P$ and Mn$_P$ concentrations ranged from 1.7 to 8.4 mol g$^{-1}$ and from 0.7 to 3.9 $\mu$M, respectively.

**Hg Distribution in the Profile.** Total Hg and Suspended Particulate Matter (SPM). It is already well-known that Hg is strongly bound to the SPM in freshwater and estuarine environments (8, 21). The vertical total Hg concentrations, obtained by the sum of dissolved and particulate Hg, increased with the SPM concentrations in the fluid mud, ranging from 5 to 190 ng g$^{-1}$ with a mean concentration of 110 $\pm$ 65 nM (Figure 2). Results presented in Table 1 illustrate that more than 99% of total Hg is associated with particles (regression coefficient ($r^2$) = 0.96, confidence level (P) > 99%). This relationship (Hg$_p$ versus SPM) has also been observed during various seasonal cruises in the same estuary (21).

**Particulate Hg(II) and MMHg.** The distribution of the different Hg species associated with particles along the profile is presented in Figure 3. For the total particulate Hg (Hg$_P$), the concentration varied from 0.9 to 1.5 nmol g$^{-1}$ with a mean of 1.2 $\pm$ 0.1 nmol g$^{-1}$. The concentration of the acid leachable Hg(II) fraction, ([Hg(II)]$_P$), in the fluid mud (Figure 3 and Table 1) ranged from 0.9 to 1.2 nmol g$^{-1}$ with an average of 1.0 $\pm$ 0.1 nmol g$^{-1}$ (dry weight). This chemically extractable fraction represented approximately 88 $\pm$ 5% of Hg$_P$. Both distributions along the core presented the same trends with two maximums taking place at respective depths of 6.4 and 6.8 m. These concentrations decreased slightly to a minimum close to the sediment. The two Hg$_P$ peaks coincided with the peaks in PIC, PTC, Fe$_P$, and Mn$_P$, whereas the correlation with POC was insignificant. Under suboxic conditions (at depths 7–7.8 m), the decrease of particulate Hg followed that of the POC and PTC. The overall distribution of Hg$_P$ could be closely related to variations of PTC, POC, Fe$_P$, and Mn$_P$ as indicated by the good correlation coefficients displayed in Table 2. On the other hand, the relationships among the parameters with [Hg(II)]$_P$ were better than those of [Hg$_P$] in terms of correlation coefficients (Table 2). This result suggested that the acid leachable Hg content in particles reflect more accurately the change in Hg biogeochemical cycling with respect to environmental conditions.

The particulate MMHg profile in the fluid mud exhibited higher MMHg values (2.6–5.8 pmol g$^{-1}$) in the upper part of the fluid mud (between 6 and 6.8 m depth). A sharp drop in concentration to a minimum of approximately 0.6 pmol g$^{-1}$ occurred just below the 7.0 m depth following the oxygen depletion pattern. Again, the respective amount of MMHg$_P$ to total particulate Hg was the highest (0.4–0.5% of [Hg$_P$]) in the surface layer and decreased between 6.8 and 7 m to a minimum of about 0.05–0.07% of [Hg$_P$]. Similar MMHg distributions have been reported by Bloom et al. (22) in coastal sediment profiles. Significant correlation between MMHg$_P$ and both POC (r = 0.72) and Fe$_P$ (r = 0.73) were obtained. A negative correlation was also found with DOC (r = −0.87) (Table 2).

**Dissolved Hg(II) and MMHg.** The vertical distribution of the dissolved Hg species was presented in Figure 3. Dissolved Hg(II) concentrations were 52 and 68 pm in the upper two samples. Down 6.2 m, the concentrations dropped to a minimum value (19 pm at 6.4 m) and then increased smoothly 40 pm and then abruptly up to 84 pm (above the consolidated sediments). These distributional trends closely followed that of Mn$_P$ (r = 0.90) and Fe$_P$ (r = 0.60), suggesting that the Hg(II)$_P$ distribution could be directly related to the processes affecting the dissolution of Fe/M mineral oxides.

An increase of MMHg$_P$ from the values below the detection limit up to 4.6 pm occurred under suboxic/anoxic conditions and corresponded to the minimum of MMHg$_P$. The MMHg$_P$ distribution of [Hg$_P$]$_D$ ranged from 0.88 down to 0.05 pm (above the consolidated sediments). These distributional trends closely followed that of Mn$_P$ (r = 0.90) and Fe$_P$ (r = 0.60), suggesting that the Hg(II)$_P$ distribution could be directly related to the processes affecting the dissolution of Fe/M mineral oxides.

**Gaseous DMHg and Hg.** Dissolved gaseous Hg species presented a similar trend along the whole profile. Highest variations were observed in the upper layer of the fluid mud. The highest DMHg$_D$ concentration (1.5 pm) was indeed recorded just above the oxic/anoxic transition zone. The lowest DMHg$_D$ concentrations were close to or below the D.L. and were found at the bottom of the profile with O$_2$ depletion. The concentrations recorded were in general much higher than those reported in open marine environments such as the equatorial Pacific Ocean (n.d. ~ 0.67 pm) (23) or the Alboran Sea (n.d. ~ 0.29 pm) (24), but lower than those found in mangrove sediments (0.2–1.4 nM g$^{-1}$) (25). An inverse relationship between MMHg$_D$ and DMHg$_D$ can be noticed with a negative correlation coefficient of −0.50.

Dissolved elemental Hg (Hg$_D$) decreased steadily with increasing SPM concentration from 0.88 down to 0.05 pm (near detection limit) at the bottom of the profile. Its distribution closely followed that of O$_2$ (r = 0.75) and was inversely related to that of DOC (r = −0.80). The contribution of the gaseous Hg species (DMHg and Hg$_D$) represented less than 5% of total dissolved Hg ([Hg$_D$] as shown in Table 1).

**Hg Species Partitioning in the Profile.** The partition coefficient ($K_p = [M]_P/[M]_D$, L kg$^{-1}$) between particulate and “dissolved” (including truly dissolved and colloidal fraction)
fraction. c Percentage of [HgT]D in IHg(II), MMHg, DMHg, and Hg2+ in this study, the log bioavailability of toxic elements in aquatic environments. In (Bassens, June 12, 1997).

particulate Hg species in a fluid mud profile of the Gironde estuary.

**TABLE 1: Results of Mercury Speciation in a Fluid Mud Profile of the Gironde Estuary (Bassens, June 12, 1997)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth, m</th>
<th>[HgL]p, nmol/g</th>
<th>[Hg(II)]p, nmol/g</th>
<th>M/M Hg</th>
<th>pH</th>
<th>[HgL]b, pmol/g</th>
<th>M/M Hgb</th>
<th>[Hg(II)]b, pmol/g</th>
<th>M/M Hggb</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>6.0</td>
<td>1.16</td>
<td>1.04</td>
<td>89.9</td>
<td>4.86</td>
<td>0.4</td>
<td>52</td>
<td>0.53</td>
<td>1.0</td>
</tr>
<tr>
<td>B2</td>
<td>6.2</td>
<td>1.13</td>
<td>1.06</td>
<td>94.0</td>
<td>5.78</td>
<td>0.5</td>
<td>68</td>
<td>0.57</td>
<td>0.85</td>
</tr>
<tr>
<td>B3</td>
<td>6.4</td>
<td>1.45</td>
<td>1.19</td>
<td>82.1</td>
<td>2.57</td>
<td>0.2</td>
<td>19</td>
<td>0.60</td>
<td>1.2</td>
</tr>
<tr>
<td>B4</td>
<td>6.6</td>
<td>1.10</td>
<td>1.04</td>
<td>94.5</td>
<td>3.19</td>
<td>0.3</td>
<td>24</td>
<td>0.00</td>
<td>1.3</td>
</tr>
<tr>
<td>B5</td>
<td>6.8</td>
<td>1.37</td>
<td>1.17</td>
<td>86.1</td>
<td>4.12</td>
<td>0.5</td>
<td>44</td>
<td>0.21</td>
<td>0.18</td>
</tr>
<tr>
<td>B6</td>
<td>7.0</td>
<td>1.16</td>
<td>1.03</td>
<td>88.4</td>
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<td>0.1</td>
<td>30</td>
<td>0.88</td>
<td>0.18</td>
</tr>
<tr>
<td>B7</td>
<td>7.2</td>
<td>1.19</td>
<td>1.01</td>
<td>85.1</td>
<td>0.57</td>
<td>0.1</td>
<td>30</td>
<td>0.71</td>
<td>0.19</td>
</tr>
<tr>
<td>B8</td>
<td>7.4</td>
<td>1.14</td>
<td>0.93</td>
<td>81.6</td>
<td>0.65</td>
<td>0.1</td>
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<td>0.12</td>
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</tr>
<tr>
<td>B9</td>
<td>7.6</td>
<td>1.11</td>
<td>0.92</td>
<td>82.9</td>
<td>0.61</td>
<td>0.1</td>
<td>40</td>
<td>0.32</td>
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</tr>
<tr>
<td>B10</td>
<td>7.8</td>
<td>0.93</td>
<td>0.88</td>
<td>95.2</td>
<td>0.67</td>
<td>0.1</td>
<td>84</td>
<td>0.46</td>
<td>0.01</td>
</tr>
</tbody>
</table>

**FIGURE 3.** Concentration and distribution of dissolved and particulate Hg species in a fluid mud profile of the Gironde estuary (Bassens, June 12, 1997).

phases is often used to evaluate and model the fate and bioavailability of toxic elements in aquatic environments. In this study, the log Kd values for IHg(II) calculated from the acid extractable Hg (4.4 ± 0.2) were comparable with those from the total Hg (4.5 ± 0.2) along the profile (Figure 4 and Table 1). Minimum Kd values were recorded at the subsurface and bottom fluid mud layers. They closely followed the concentration maximum of dissolved Mn and Fe. These values are similar to those (ranging between 4.4 and 5.0) reported in coastal sediment profiles (22). But they are lower than the averaged values of 5.0–6.0 in log Kd reported in the surface waters of different riverine, estuarine, and coastal systems such as Lena, Ob, and Yenisei (26); Loire and Seine (8); Elbe and North Sea (27); and British estuaries (28). The reason for such lower Kd values is first related to important desorption processes taking place in the fluid mud. On the other hand, the so-called “colloidal effect” for Hg leading to lower Kd with increasing particle concentration takes place in fluid mud system (8). Colloidal–associated Hg in water increases with increasing particle concentration as well as increasing DOC.

The log Kd for MMHg, ranging between 2.2 and 4.7 with an averaged 3.3 ± 0.9, presented a different profile. The Kd values for MMHg and MMHgP are similar to those reported in the anoxic coastal porewater-sediment system by Bloom et al. (22). Average log Kd for MMHg is 1 order of magnitude lower than for IHg(II), indicating that MMHg is less strongly bound to the solid phase than IHg(II). Such behavior has been observed in abiotic laboratory adsorption experiments on iron oxides (α-FeOOH) and clay (kaolin) particles (29, 30). The overall good correlation observed between log Kd of MMHg and some biogeochemical parameters, such as POC (r = 0.65), PTC (r = 0.81), FeT (r = 0.83), and MnT (r = 0.70), suggests that the partitioning of MMHg between solid and aqueous phases is controlled by both Fe and Mn redox cycles and carbon transformation.

**Biogeochemistry of Hg in the Fluid Mud.** Under a stable regime, the fluid mud lens typically evolves from suboxic to anoxic conditions and is the location of various bio- or chemically driven reactions. Different chemical processes, such as CaCO3 dissolution resulting from a pH decrease, occur. The pH decrease is in turn mediated by aerobic respiration and important denitrification processes (6, 7). These conditions may directly affect the production of methylated Hg species in the fluid mud and their partitioning between gaseous, dissolved, and particulate phases. Previous studies have shown that methylated Hg species (MMHg, DMHg) can be formed in the water column (23, 31) as well as in sediment (32, 33). Our results indicate that the maximum concentration of methylated species in either particulate or dissolved form can be found in the upper suboxic part of the fluid mud. These findings are consistent with those of other authors who have reported the occurrence of methylated species in the oxygen depleted areas of aquatic systems such as oceans (23, 24), lakes (34, 35), and estuaries (36).

Several processes may account for this enhanced methylated Hg concentration in the upper part of the fluid mud. Passive processes such as desorption of MMHg from the particles must be negligible since the log Kd of MMHg is higher in this part of the profile. On the other hand, in-situ production by microorganisms (e.g. methylcobalamin-utilizing bacteria) could be a significant pathway (24). This hypothesis is supported by the observation that the highest ratios of MMHg/([Hg]p) and MMHg/([Hg]D) (0.5 and 3.4%) were found in the upper part of the fluid mud (Table 1). In addition, the good correlation between the [Hg(II)]p, [Hg(II)]b, MMHg, and DMHg concentrations (Table 2) allows us to suggest that “labile” inorganic Hg could be the main substrate for the initial production of methyl-Hg (23). Moreover, the availability of the uncharged HgS0 species, suggested as a methylation substrate, could play a role in
MMHg formation in the fluid mud system (37). Bacteria and MMHg formation have indeed already been observed in various aquatic environments such as the Wisconsin lakes (34, 38) and the Pettaquamscutt estuary (36).

It is worth mentioning that the maximum level of DMHg was located just below the maximum level of MMHg and that both their concentrations displayed a negative correlation (Figure 3 and Table 2). This relationship could indicate that MMHg is a precursor to DMHg (or vice versa) under specific conditions found in the fluid mud profile. Formation of methylated Hg species may take place along different routes such as methylation via a methyl-donor, enzymatic methylation (39, 40), or transmethylation (25).

This upper part of the fluid mud displays intense biogeochemical activity under low oxygen conditions. These processes (e.g., microbial reduction) may also account for the observed distribution of dissolved Hg in the profile. The Hg concentration observed in the upper part of the profile is approximately 20 times greater than those in the bottom sediment. Here their values are near 45 fM expected at equilibrium (i.e., with water temperature at 22.5 °C and gaseous elemental mercury in the air at 2.5 ng/m³). Low Hg concentrations in anoxic conditions may be related to the increasing DOC as shown by the negative correlation between the two parameters. DOC may diminish the reduction of IHg(II) after its complexation by organic ligands. It may also act to remove Hg from the solution by the formation of hydrophobic complexes. These results indicate that IHg(II) reduction processes are mostly taking place in oxic surface waters through biotic (e.g., microbial reduction) (41, 42) or abiotic processes (e.g., photochemical reduction) (43).

In the anoxic part of the fluid mud, significant desorption takes place, especially at the bottom of the profile where important denitrification takes place. The significant increase of dissolved MMHg at the bottom of the profile could, in this case, result from several indirect processes such as active decomposition of the organic matter and intense denitrification. First, abiotic desorption due to the decrease of pH from the solid substrate is more likely to lead to the decrease of log Kd (MMHg). Second, this release from the particulate substrate can also be related to the increasing dissolution of Mn and Fe from the solid phase after the mineralization of POC.

Implications for Hg Distribution and Transfer in Estuarine Waters. Fluvial Hg species loaded into the Gironde estuary are first trapped in the MTZ and further subject to many sedimentation-resuspension cycles. Abril et al. (7) reported that suspended particles in the Gironde estuary experience at least 12 neap-spring cycles and several hundred tidal cycles before being transported to the coast. The long residence time for particulate matter (several months to years), therefore, allows phase rearrangements and biogeochemical processes to occur. Figure 5 shows a conceptual model of the potential pathways involved in Hg cycling in the fluid mud system. Two major sedimentological processes, sedimentation and resuspension, control the cycling and transport of particles. Due to the fact that about 99% of Hg is associated with particles, these have a crucial effect on Hg cycling.

Table 3 shows the average results of particulate and dissolved Hg species in the fluid mud compared to those obtained in surface waters of the MTZ (salinity between 0 and 5). Surface waters sample (2–3 m depth) were collected during BIOGEST cruises for three different seasons (spring, summer, winter) (21). The total contents of particulate Hg species (IHg(II), MMHg) in the MTZ surface waters were always significantly higher than those found in the fluid mud samples. An inverse trend was observed for dissolved Hg species between the surface and fluid mud samples. Indeed, the average IHg(II) concentrations (ca. 42 ± 20 pM) in the fluid mud were much higher than those recorded (ca. 9 ± 5 pM) in the MTZ surface waters. This can be seen in the log Kd values for IHg(II) or MMHg in oxic surface waters, which

### TABLE 2: Correlation Coefficients for the Data Obtained for Hg Species and Biogeochemical Parameters in a Fluid Mud Profile of the Gironde Estuary (n = 10)

<table>
<thead>
<tr>
<th></th>
<th>[HgT]_P</th>
<th>[IHg(II)]_P</th>
<th>M M HgD</th>
<th>IHg(II)D</th>
<th>MMHgD</th>
<th>DMHgD</th>
<th>HgD *</th>
<th>PTC</th>
<th>POC</th>
<th>DOC</th>
<th>M nP</th>
<th>FeP</th>
<th>M nO</th>
<th>FeO</th>
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<tr>
<td>[HgT]_P</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[IHg(II)]_P</td>
<td>0.81</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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*Acid leachable fraction with 6 N HNO₃ (subscript L denotes Hg obtained from an acid leach). *Particulate total carbon.
The respective enrichments of \( \text{IHG(II)} \) and \( \text{MMHgD} \) in the fluid mud lens compared to overlaying waters (Table 3) suggest that effective transfers (i.e., resuspension, diffusion) of the dissolved or colloidal species between the two compartments are occurring during tidal cycles and contribute to the input of Hg-rich solutes in surface waters. Based on estimated volumes of the fluid mud and the MTZ (12) and average data presented in Table 3, the respective inventories of \( \text{IHG(II)} \) and \( \text{MMHgD} \) are approximately 15 and 0.5 mol in the fluid mud and 12 and 1 mol in the MTZ water column. Consequently, this suggests that the erosion of the fluid mud system may have a significant impact on Hg supply. \( \text{IHG(II)} \) and \( \text{MMHgD} \) concentrations in the surface waters of the MTZ can increase up to a factor of 2 (100%) and 1.5 (50%), respectively. This assumption is supported by the distribution of Hg species observed in the surface waters of the Gironde estuary during three seasons (21). On the other hand, the contribution of \( \text{IHG(II)} \) and \( \text{MMHgD} \) diffusion into the water column can be considered to be negligible, considering the lack of turbulence and the brief tide slacks (i.e., a few hours of fluid mud setting). This study demonstrates that the Gironde fluid mud system acts as a biochemically mediated fluidized bed reactor for both remobilizing and transforming Hg species in macrotidal estuaries.

### Acknowledgments
We are grateful to A. De Resseguié, who has designed and made the fluid mud sampler, for his kind help during sample handling. We thank all the captains and crews of the RVs Côte d’Aquitaine. We also sincerely acknowledge W. F. Fitzgerald, C. Lamborg, and S. Lyons from the University of Connecticut, U.S.A., for fruitful discussion and English correction. C. M. Tseng acknowledges the scholarship from Taiwan government for his Ph.D. study. This work is a contribution to the EU ELOISE program (ELOISE No. 219) in the framework of the BLEGES project (Contract ENV4-CT96-0213).

### Literature Cited

### TABLE 3: Comparison of Average Concentrations of Mercury Species in Surface Waters and in the Fluid Mud of the Gironde Estuary

<table>
<thead>
<tr>
<th>species</th>
<th>surface water (salinity 0–3, n = 10)</th>
<th>fluid mud (salinity 0, n = 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>concn (%)</td>
<td>concn (%)</td>
</tr>
<tr>
<td>( \text{Hg} ) (nM)</td>
<td>0.9 ± 0.5</td>
<td>110 ± 65</td>
</tr>
</tbody>
</table>
| \( \text{Hg} \) (pmol g
\( ^{-1} \) ) | 1.5 ± 0.9 (99.2 ± 0.7)          | 1.0 ± 0.1 (99.8 ± 0.2)          |
| \( \text{MMHgD} \) (nmol g
\( ^{-1} \) ) | 8.9 ± 7.3 (0.8 ± 0.7)          | 2.4 ± 1.9 (0.2 ± 0.2)          |
| \( \text{HgD} \) (\( \text{IHG(II)} \)) (nM) | 8.6 ± 5.0 (88.0 ± 11.8) | 42 ± 20 (94.9 ± 2.6) |
| \( \text{MMHgD} \) (pmol) | 0.7 ± 1.0 (8.0 ± 1.6)          | 1.6 ± 1.5 (3.3 ± 2.8)          |
| \( \text{DMHgD} \) (pmol) | 0.3 ± 0.3 (1.1 ± 2.0)          | 0.3 ± 0.2 (0.6 ± 0.6)          |
| \( \text{HgD} \) (\( \text{IHG(II)} \)) (pM) | 0.4 ± 0.3 (4.0 ± 2.8) | 0.3 ± 0.2 (0.6 ± 0.6) |
| \( \text{log K\(_{\text{Hg}}\)} \) (Hp) | 4.5 ± 0.2                     | 4.5 ± 0.2                       |
| \( \text{log K\(_{\text{Hg}}\)} \) (Hp) | 5.2 ± 0.2                     | 4.4 ± 0.2                       |
| \( \text{log K\(_{\text{Hg}}\)} \) (MMHgD) | 4.1 ± 0.6                     | 3.3 ± 0.3                       |

* \( \text{HgD} \) concentration for surface water was calculated by the sum of \( \text{IHG(II)} \) and \( \text{MMHgD} \) for the fluid mud was estimated from the sum of \( \text{IHG(II)} \) and \( \text{MMHgD} \). * No available data. * Percentage of \( \Sigma \text{Hg} \) \( \text{IHG(II)} \) and \( \text{MMHgD} \) in \( \text{IHG(II)} \) fraction. * Percentage of \( \Sigma \text{Hg} \) \( \text{IHG(II)} \) \( \text{IHG(II)} \) \( \text{MMHgD} \) \( \text{DMHgD} \) \( \text{HgD} \) \( \text{IHG(II)} \) fraction.

are approximately 1 order of magnitude higher than in the fluid mud layer. Similar results were reported by Coquery et al. (8). This is also true for the \( \text{MMHgD} \) concentrations, which always display higher values in the fluid mud (1.6 ± 1.5 pm) compared to that of MTZ surface waters (0.7 ± 0.1 pm). Slightly higher \( \text{HgD} \) levels (0.4 ± 0.3 pm) are found in oxic surface waters than in anoxic bottom waters (0.3 ± 0.2 pm). DMHgD was only found in the region of the dissolved oxygen depletion, but not in MTZ surface waters.

FIGURE 5. Conceptual model of the inorganic \( \text{Hg(II)} \) and \( \text{MMHgD} \) cycling in the fluid mud system. (Oxycline) represents the strong oxygen gradient boundary. (An up and down arrow) denotes dynamic oscillation controlled by the tidal regime during the neap-spring tide cycle. As the fluid mud settles, Hg bound to particles will be transported from the surface water to the deeper sediment. Sediment particles, once deposited, are rapidly subject to degradation/ mineralization under microbiologically mediated reducing conditions. Hg can also be easily released from the particulate phase through the dissolution of Fe/Mn oxides or carbonates and the mineralization of POC. At this stage, methylation of Hg may occur at the oxic/anoxic boundary layer. Resuspension, as a sediment–water exchange process, brings the deposited particles and interstitial waters to the oxic and pH increasing conditions of surface waters. The reduced materials, present in the fluid mud, are reoxidized and further result in a rapid precipitation through Fe/Mn oxides/hydroxides or coating. Hg species will be scavenged through the processes of adsorption/coprecipitation by freshly formed surfaces. Such processes will therefore transfer Hg species from dissolved to particulate phases.

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