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Speciation of Mercury in Sediments of the Seine Estuary (France)

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Although the parameters regulating mercury methylation in sediments are fairly well known, conditions controlling the formation and mobilization of methylmercury in aquatic sediments are still poorly understood. In this work the environmental factors governing the distribution and behaviour of total mercury and methylmercury within the Seine estuary have been assessed through the analysis of sediment cores. Box-cores taken at coastal, estuarine and riverine locations in the period 1994–1997 were analysed for bulk sediment and porewater total mercury and methylmercury concentrations, as well as a number of other chemical variables. Levels of total mercury in sediment (300–1000 ng g^{-1}) were found to be uniform all over the estuary and did not show significant temporal or spatial variations. On the contrary, the distribution of methylmercury was distinct from that of its inorganic form since it displayed seasonal and spatial variability. Maximum methylmercury concentrations (up to 6 ng g^{-1}) and percentages (up to 2%) were obtained at the estuarine location with peak loading just below the sediment surface and a decreasing level in the deeper layers. As total mercury and methylmercury were nor correlated, the temporal and spatial behaviour of methylmercury appeared to reflect variations in salinity, redox potential and the sulphate reduction rate. Low concentrations of reactive mercury, but very high total mercury levels, were measured in the porewaters (10–400 ng l^{-1}), with maximum values at the sediment/water interface. In spite of a high proportion of organically complexed dissolved mercury, methylmercury in porewaters was mainly below the detection limit of the method (2 ng l^{-1}). From mercury speciation in the solid phase and dependence of its dissolved fraction on iron and manganese in porewater, the source and distribution of mercury in porewaters are discussed. Copyright © 1999 John Wiley & Sons, Ltd.

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INTRODUCTION

Mercury (Hg) species can undergo a variety of transformations in the environment. One of the most important processes is methylation of mercury in aquatic systems. Methylmercury (MeHg) is the mercury species that is most toxic and that bioaccumulates most efficiently, resulting in mercury biomagnification in the aquatic food chain.[1] Diverse bacteria are known to methylate Hg in culture, but some evidence from natural sediments[2–4] and waters[5] suggests that sulphate reducers are the principal mercury methylators. The rate of methylation is a function of both the activity of methylating bacteria and the total mercury concentration. Since a number of parameters (pH, redox potential, salinity, sulphide level or organic matter content) control the methylation/demethylation process,[6] the concentration of total Hg is not a good predictor of methylmercury concentration in aquatic systems.[7] Principal sites for MeHg production inside a water body are suboxic zones in both the water column and sediments.[5,8] Although

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numerous studies have been published on mercury distribution and methylation in aquatic sediments, there are only few where key geochemical parameters such as the distribution and speciation of Hg in both the dissolved and solid phases were measured simultaneously.[9] In addition, conditions regulating diagenetic behaviour and diffusion of Hg and MeHg from sediment to overlying water are still poorly characterized.[10]

The Seine estuary is a macro-tidal estuary significantly affected by anthropogenic inputs. A study of Hg speciation in estuarine water revealed that the estuary was highly contaminated by mercury,[11] with similar concentrations to those found in the Scheldt[12] and Elbe estuaries.[13] In such environments, enriched both with Hg and organic loading, favourable conditions for Hg methylation should exist, as has been already demonstrated in the Scheldt[12,14] and Elbe estuaries.[13,15] However, except for a few data on dimethylmercury (Me_2Hg) in the water of the Baie de la Seine,[11] data on MeHg formation and distribution in different compartments of the Seine estuary are absent from the literature.

In this work speciation of Hg in both solid and dissolved sediment phases was performed with the aim of assessing environmental factors governing the distribution and behaviour of total mercury and methylmercury in sediments of the Seine estuary. Mobility of Hg in sediment and its release from sediment to overlying water was also evaluated in order to estimate the importance of Hg input from sediment in comparison with other sources.

MATERIALS AND METHODS

Study area

The Seine river discharges into the North Sea via the English Channel. The hydrographic basin of the Seine river (75 000 km^2) includes 30% of the French population and 30–40% of the total economic activity (industrial and agricultural) in France.[16] As a consequence the Seine river is highly contaminated by domestic and industrial wastes, the impact of industrial activities also being important in the estuarine zone. The mean river discharge is 450 m^3 s^{-1}, varying between 60 m^3 s^{-1} during low flow and 2000 m^3 s^{-1} during flood. The salinity intrusion may extend up to 50 km upstream of Le Havre during low flow and up to 20 km during high flow.[16] The Seine estuary can be classified as a partially mixed macro-tidal estuary in which tidal range and depths are of the same order of magnitude. The suspended particulate matter (SPM) concentration in the river varies between 5 and 220 mg l^{-1}. In the mid-estuary a high-turbidity zone occurs (with SPM up to several grams per litre), whose extension and location depend on hydrodynamic conditions. The morphology of the estuarine part of the river bed is entirely artificial, as since the 19th century it has been progressively modified to create a single navigation channel. The estuary is a dynamic hydrosedimentary system with intensive sedimentation in the flood periods, and significant perturbation and erosion of the sediment surface.[16]

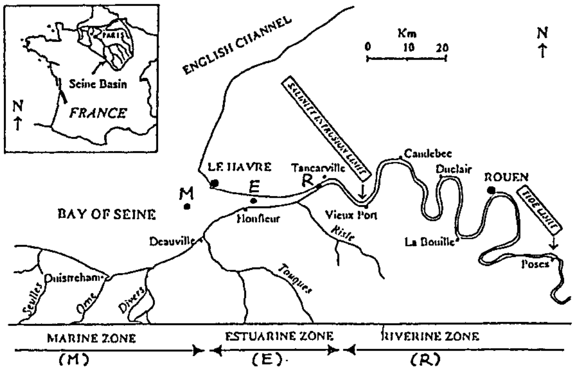

Figure 1 Map of the Seine estuary showing sampling stations.

Sample collection

Sediment cores were collected on several occasions in the period 1994–1997 at marine (M), estuarine (E) and riverine (R) locations (Fig. 1) under different flow regimes (Table 1). Undisturbed sediments were collected with a box-corer from which cores were taken with a Perspex tube 30 cm long. Redox potential and pH were measured immediately upon sampling in the parallel cores taken at the same time as samples for chemical analyses. Cores were subsampled, on board, at various depth intervals in a nitrogen-filled glove bag and placed in polycarbonate centrifuge tubes with sealing caps. In the laboratory, porewater from each sub-sample was separated by centrifugation, filtered through precombusted Whatman GF/F filters (0.7 μm) for mercury analysis and through cellulose nitrate filters (0.45 μm) for the analysis of other parameters (Cl^-, SO_4^{2-}, Mn, Fe). Upon

Table 1 Sampling dates, locations and hydrodynamic conditions in the Seine estuary

Sample	Date of sampling	Location	River discharge ($m^3\ s^{-1}$)	Observation
E-5/94	16 May 1994	Estuarine	544	Mean flow
R-2/95	04 Feb. 1995	Riverine	2147	Flood
M-4/95	06 Apr. 1995	Marine	1189	Flood
R-9/96, E-9/96, M-9/96	19 Sept. 1996	Riverine, Estuarine, Marine	175	Low flow
R-3/97, E-3/97 M-3/97	17 Mar. 1997	Riverine, Estuarine, Marine	523	Mean flow

filtration porewater was acidified with 1% HNO_3 for mercury (Hg) and other analyses and with 0.1% HCl for methylmercury (MeHg) analysis.

Standard solutions and chemicals

Acids used were of analytical quality (HNO_3, HCl, Merck) or suprapure grade (HCl, s.p., Merck). The mercury standard was prepared from stock standard solution ($HgCl_2$, 1 g l^{-1}, Merck). The standard solution was prepared weekly in 10% HNO_3 and 0.01% of $K_2Cr_2O_7$ whereas reference standard solutions were prepared daily in 1% HNO_3. Stock standard solution of MeHgCl (Alfa Ventron) was prepared by dissolving MeHgCl in acetone. Diluted standard solutions were prepared weekly by dissolving acetone stock solution in MQ water. A reductant solution (5% $SnCl_2$ in 10% HCl) was prepared by dissolving $SnCl_2$ (Prolabo or Merck) in concentrated HCl (p.a., Merck) and diluting with MQ water. Hg from the reductant solution was eliminated by purging overnight with mercury-free argon or nitrogen. All glassware was soaked in 10% HNO_3, with addition of a few drops of bromine monochloride (BrCl) solution, and rinsed several times with tap or MQ water before use. Teflon vials were cleaned by heating at 140 °C in concentrated HNO_3 for 12 h, kept in 10% HNO_3 and rinsed several times with tap or MQ water before use.

The standard reference material used for total Hg ($4.57 \pm 0.16\ \mu g\ g^{-1}$) and MeHg ($8.47 \pm 0.63\ ng\ g^{-1}$; Ref. 17) verifications was marine sediment PACS-1 (NRCC).

Instruments

For Hg detection a cold-vapour atomic fluorescence spectroscopy (CV AFS) method was used. Configuration includes a vapour generator (PSA 10.003), a gold–platinum trap (PSA 10.501, Galahad) and fluorescence detector (PSA 10.023, Merlin) and is described in detail elsewhere. (N. Mikac, S. Gressier and M. Wartel, Determination of mercury traces in products of TiO_2 manufacturing, *Analusis*, in press).

Procedures

Total Hg in the solid phase was determined after acid digestion of air-dried sediment with HNO_3 assisted by conventional or microwave heating.[18] Digestion by conventional heating was performed in closed Teflon FEP vials by heating 0.1–0.2 g of sediment in 5 ml of HNO_3 for 4 h at 150 °C. Open-vessel microwave digestion was performed in a Microdigest 300 (Prolabo, France) focused microwave system with a maximum power of 300 W. Sediment samples were soaked in 5 ml of HNO_3 and irradiated for 5 min at 10% power (30 W) in special glass digestion vessels. After cooling, the sample was diluted and Hg determined by CV AFS. Reactive Hg in porewater (Hg obtained after $SnCl_2$ reduction of an acidified sample) was measured within a few days of sampling. Total dissolved Hg was measured after cold oxidation of organic mercury compounds by 0.5% BrCl solution overnight[19] or in the microwave oven at 30 W for 3 min.[18] The detection limit of the method was 2 ng l^{-1}.

MeHg in the form of MeHgCl was isolated from sediment by distillation.[17] Dry or wet sediment (0.2–0.5 g) was distilled in glass vials under a nitrogen stream (80 ml min^{-1}) after addition of 8.5 ml of MQ water, 1 ml of 10% NaCl and 0.5 ml of 50% H_2SO_4. The distillate (8–8.5 ml) was diluted to 20 ml and an aliquot was checked for any inorganic Hg present. In the rest of the sample MeHg was decomposed by BrCl oxidation[20] (0.25 ml BrCl per 10 ml of sample) overnight, or by microwave-assisted BrCl oxidation (0.05 ml BrCl per 10 ml of sample) during 3 min at a power of 30 W,[18] and detected by CV AFS as inorganic

Hg after $SnCl_2$ reduction. The recovery of the method (verified by spiking the sediment with MeHg before destillation) was 80–90% and the detection limit 0.1 ng g^{-1}. The distillation was also used to separate MeHg from the total Hg in porewater. To 8 ml of porewater, NaCl and H_2SO_4 were added, followed by the distillation and detection performed in the same way as for sediment samples. The recovery of the method (verified by spiking 10–30 ng l^{-1} of MeHg into porewater before distillation) was 90–97% and the detection limit was 2 ng l^{-1}.

Other metals in sediment and porewater were determined by inductively coupled plasma atomic emission spectrometry (ICP AES) after wet digestion by a mixture of acids ($HCl + HNO_3 + HF$) of sediment samples.[21] The concentrations of Cl^- and SO_4^{2-} were measured by ion chromatography (Dionex DX 500). Organic carbon (C_{org}) was estimated from the difference between the carbon value (determined by elementary LECO CHNS 932 analyser) before and after heating a dry sediment at a temperature of 430 °C for 24 h.

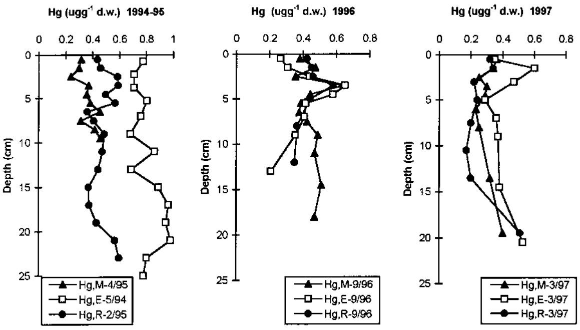

Figure 2 Depth distribution of total Hg concentrations in sediments.

RESULTS AND DISCUSSION

Sediment characteristics

Sediment of the Seine estuary can be characterized as a fine anoxic mud (3–10% of clay and 70–90% of silt). The granulometric compositions of sediment vary little with depth and with the sampling location. The sediments are anoxic in nature, with more oxic conditions only in the surface layer. They are rich in organic matter (2–6% of C_{org}) whose values vary more with granulometric composition than with the position in the estuary. The percentage of organic matter in sediment is comparable with that in the suspended matter (3–5%; Refs 11, 22).

Distribution of total Hg in sediment

Total Hg concentrations in the unfractionated sediments (Fig. 2) varied between 300 and 1000 ng g^{-1} (460 ± 140 ng g^{-1}). Spatial Hg distribution was uniform with respect to space and time (380 ± 80 ng g^{-1} at location M; 580 ± 200 ng g^{-1} at location E; and 406 ± 98 ng g^{-1} at location R), indicating a constant contamination imput during the period investigated and efficient sediment transport from the inner (locations R and E) to the outer (location M) estuary. The mercury concentration in the core E-4/95 is somewhat higher (700–900 ng g^{-1}) than in other cores (the average at location E without this core is 410 ± 95 ng g^{-1}), but this core was taken by hand (at the low-water level) at the location closest to the river bank, and probably reflects some local situation. The level of Hg in sediment is about half of that found in the suspended matter in the period 1991–1992 (1.1 ± 0.5 μg g^{-1}; Ref. 11). The particulate Hg measured in September 1996 at five locations in the estuary gave practically the same mean value (1.0 ± 0.2 μg g^{-1}), confirming that the pollution level did not change with time. A much lower concentration of Hg in sediment than in the particulate matter suggests a release of mercury from particles upon sedimentation and degradation of labile organic matter at the sediment–water interface. The mercury levels obtained are a few times higher than the accepted background value of about 0.1 μg g^{-1}, and are typical for rivers impacted by anthropogenic activity. A study of the Hg distribution in the water column of the estuary had already indicated that River Seine is highly contaminated with respect to mercury.[11]

Vertical distribution within the sediment cores does not show great variability, or consistent gradient with depth (Fig. 2). Highly significant positive correlations between total Hg and organic matter (OM), aluminium, iron and manganese have been found in most of the cores ($r = 0.7–0.95$, $P < 0.05$). This indicates that organic matter and granulometric composition control the level of total Hg in sediments of the Seine estuary. Because total Hg was significantly correlated with OM it was revealing to normalize them with respect to OM and to study the remaining variations. Normalized

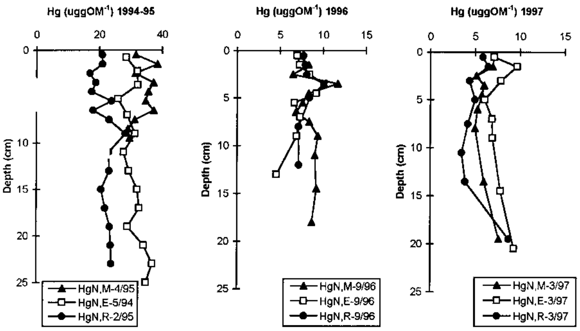

Figure 3 Depth distribution of total Hg concentrations normalized to organic matter (OM) content.

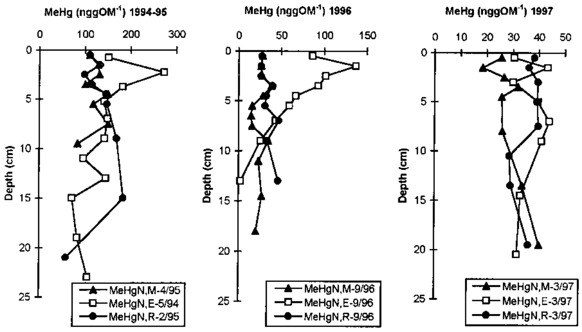

Figure 5 Depth distribution of MeHg concentrations normalized to organic matter (OM) content.

Hg concentrations (HgN) were less variable, both in the surface layer and with depth (Fig. 3). It was especially visible in samples collected during 1994–1995, when cores were not taken simultaneously and a significant difference in the percentage of C_{org} existed between cores (M, 1–2%; E, 2–4%; R, 2–4%). Vertical profiles of HgN values were very similar at all three sampling sites when sampled at the same time (September 1996 and March 1997), indicating homogeneous sedimentation all over the estuary. A strong correlation has been reported between organic matter and Hg in numerous types of sediments: estuarine,[23,24] lake[25] or riverine.[15] A significant positive correlation has also been observed between particulate Hg and particulate organic carbon (POC) in the Seine estuary.[26] Such distribution is consistent with removal of dissolved Hg from the water column via scavenging onto organic particles, the mechanism responsible for Hg deposition in a number of estuaries.[9,27]

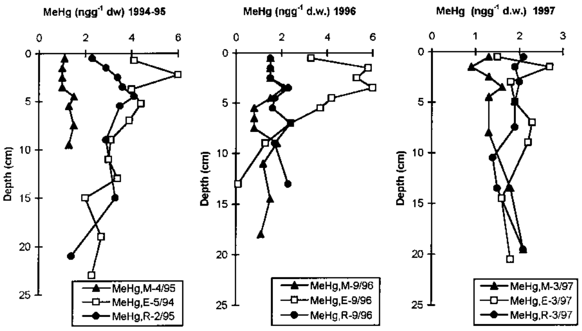

Figure 4 Depth distribution of MeHg concentrations in sediments.

Distribution of MeHg in sediment

The MeHg level in sediment (Fig. 4) was in the range 0.1–6 ng g^{-1} (2.3 ± 1.0 ng g^{-1}). This a typical concentration ($<$10 ng g^{-1}) for uncontaminated or slightly contaminated estuarine sediments.[9,14,23,24] Only in environments highly contaminated with mercury such as the River Elbe[13] or River Yare,[28] are concentrations higher than 20 ng g^{-1} (up to 100 ng g^{-1}) observed. High rates of MeHg production could also be driven by high organic matter inputs, as in reservoirs[7] or wetlands.[29]

Contrary to the total Hg distribution, that MeHg shows a clear spatial pattern, demonstrating lower concentrations at marine (1.3 ± 0.2 ng g^{-1}) than at estuarine (3.1 ± 1.2 ng g^{-1}) and riverine (2.3 ± 0.6 ng g^{-1}) locations (Fig. 4). Vertical MeHg profiles at marine (M) and riverine (R) locations do not show a significant change with depth up to 25 cm, whereas at estuarine locations (E) a pronounced subsurface maximum just below the sediment/water interface appeared in all sampling seasons. Deeper maxima could also be seen in cores R-2/95 and E-9/96, but these disappeared when concentrations of MeHg were normalized to the organic matter (OM) content in sediment (Fig. 5). A weak correlation ($r = 0.5$–0.6, $p > 0.05$) between MeHg and OM exist in most of the cores (seven out of nine), suggesting that MeHg is in some way related to organic carbon. Indeed, organic matter may promote both the affinity of MeHg for sediment particles and bacterial methylation, but since many other parameters influence the methylation process the relationship between OM and MeHg was not always found in aquatic sediments.[23,24,27] Generally, MeHg was not related

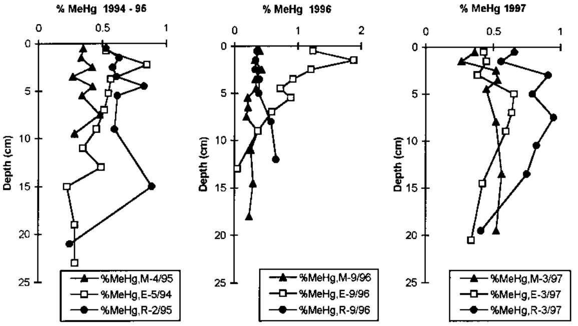

Figure 6 Depth distribution of MeHg percentage in sediments.

to total Hg, as in only five out of nine cores was a weak correlation ($r = 0.5$–0.6, $p > 0.05$) observed. When taking into account all samples (not particularly sediment cores) there was no correlation between MeHg and Hg ($r = 0.410$), indicating that factors other than total Hg loading control the MeHg level in sediments of the Seine estuary. Environmental studies revealed that lakes[7] and rivers[13] are frequently characterized with a lack of correlation between Hg and MeHg. Therefore, it was concluded[7] that, except for the systems where inorganic Hg was increased above background by over an order of magnitude, the concentration of total Hg was not a good predictor of MeHg concentration in aquatic systems.

The percentage of MeHg (Fig. 6) varied between 0.1 and 2% ($0.5 \pm 0.2\%$). As for the MeHg concentration, the percentage of MeHg was lower at marine ($0.4 \pm 0.1\%$) than at estuarine ($0.6 \pm 0.3\%$) and riverine ($0.6 \pm 0.1\%$) locations. Relative to many lakes and wetlands, where the percentage of MeHg can reach 10%,[4,24] in marine and estuarine sediments it is generally low, <0.5%.[23,27] The Seine samples follow this trend with 0.5% MeHg on average. The subsurface maximum of MeHg concentration observed in core E-3/97 (Fig. 3) disappears when expressed as a percentage of MeHg, indicating that some features of MeHg profiles could be explained by variations of total Hg content.

We now consider the MeHg distribution obtained in sediments of the Seine estuary. There are number of factors which affect methylation and demethylation of Hg in sediments, e.g. total Hg level, organic matter content, oxygen, temperature, pH, salinity, chloride, sulphate and sulphide.[6,30] Results presented here show that MeHg distribution in the Seine sediments cannot be explained solely by variations in inorganic mercury loading or organic matter content; therefore some other parameters are responsible for the distribution obtained. It is now generally accepted that sulphate-reducing bacteria (SRB) are important mediators of mercury methylation in sediment.[2,3] As the sulphate concentrations are much lower in lakes or rivers (0.01–0.2 mmol l^{-1}) than in seawater (28 mmol l^{-1}), the activity of SRB is significantly lower in freshwater than in marine sediment.[6] However, high concentrations of the resulting sulphide produced could prevent mercury methylation.[6] Therefore, it was postulated that an optimal sulphate concentration exists (0.2–0.5 mmol l^{-1}), above which sulphide would inhibit methylation, while at lower sulphate levels sulphate reduction and hence methylation would be limited by available sulphate. Extensive studies of parameters regulating MeHg concentration in estuarine sediment[23] showed that maximum MeHg production could be expected at a redox potential of 0 to -100 mV, where the sediment is anaerobic but not too high in sulphide, and where aerobic demethylating bacteria are not active. In a similar study[24] MeHg concentration in sediment increased with salinity, until sulphide levels reached a critical level (2–6 mg g^{-1}, depending on the area) above which they decreased with increasing salinity. Recent studies[27,31] demonstrated also that dissolved sulphides in porewaters affect the speciation and therefore the biovailability of dissolved and/or solid-phase Hg for methylation.

The vertical distribution of MeHg in sediment was also shown to be dependent on the sulphate reduction rate (SRR). For freshwater sediment[4] it was found that sediment depth profiles of bacterial sulphate reduction and Hg methylation rate were similar, and in-situ MeHg concentrations, like the SRR, were highest near the sediment water interface. In spite of feedback inhibition by sulphide formation in saline sediments, connections between the MeHg concentration and the SRR were also found in high-salinity estuarine sediments,[32] as the highest MeHg concentration was associated with the sediment layer where the highest SRR have been observed.

The salinity of the Seine sediment porewater (calculated from Cl^-) was 30–32‰ at marine locations and variable at estuarine (10–20‰) and riverine (<1–10‰) locations, depending on the river flow. Accordingly, various concentrations (values normalized to Cl^-) of sulphates in porewaters, are presented in the depth profiles in Fig. 7.

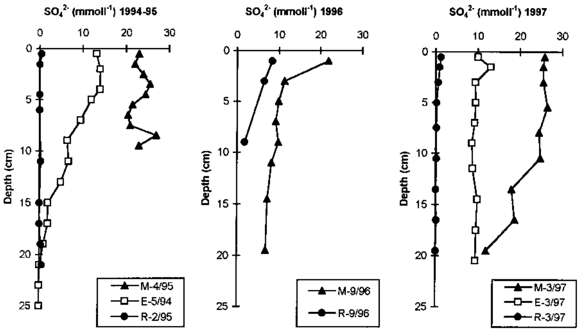

Figure 7 Depth distribution of sulphate (concentrations normalized to chloride) in porewaters.

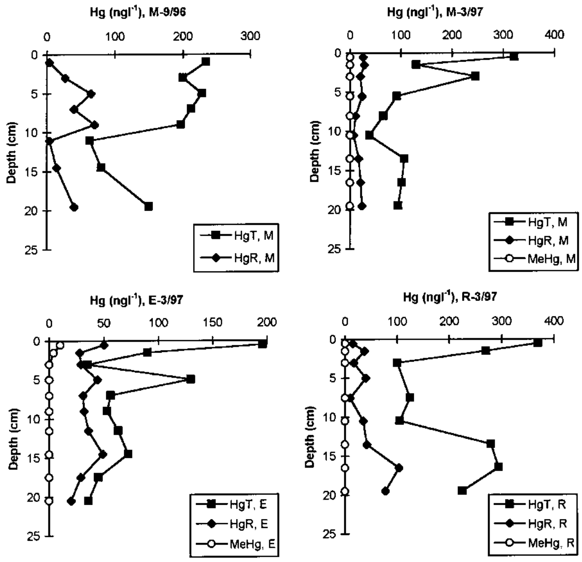

Figure 8 Depth distribution of dissolved reactive (HgR) and total (HgT) mercury and MeHg in porewaters.

The lowest MeHg concentration and percentage at marine location could therefore be explained by a negative effect of a high salinity/sulphate level on the methylation potential. From Fig. 7. it can be seen that sulphate profiles are not the same in different marine cores. A constant profile in the core M-4/95 suggests a low SRR, whereas a significant decrease in sulphate with depth in cores M-9/96 and M-3/97 suggests a high SRR. However, a difference between the MeHg concentration and percentage in these cores was not observed (Figs 4, 6). Due to the paradox that SRB mediate Hg methylation, while the sulphide they produce inhibits the process, both sulphate and sulphide should be determined to elucidate the role of the sulphur cycle on the MeHg level in sediment. The same low MeHg level could be on one hand a consequence of low SRB activity (as in core M-4/95, where a very low level of reduced sulphur in the sediment indicated that sulphate reduction has not yet been started[33]), and on the other hand a consequence of a negative effect of sulphides (as is probably the case in cores M-9/96 and M-3/97). The last hypothesis could not be confirmed, as reduced sulphur species in these cores were measured neither in sediment nor in porewater.

According to the already-mentioned suggestion[4,6] on the optimum sulphate concentration for Hg methylation, one would expect lower MeHg levels in estuarine than in riverine sediments of the Seine estuary. However, a high SRR does not necessarily mean high sulphide levels in porewater, as they could be removed from the dissolved phase by precipitation as FeS and FeS_2.[34] Recent experiments on the conversion of Hg species in saltmarsh sediments have shown that interaction between Hg and sulphur chemistry is more complicated than previously thought.[35] Thus, optimum conditions promoting *in-situ* methylation will be found in anoxic sediments having sulphide-poor porewaters and enriched with biodegradable organic carbon and nutrients.[10] In the Seine sediments such optimum conditions for Hg methylation could be fulfilled in the estuarine and not in the riverine part of the estuary. From two estuarine cores in which porewater sulphates were determined one was characterized by a high (E-5/94) and other by a low (E-3/97) SRR (Fig. 7). A more prominent subsurface maximum (up to 6 ng g^{-1}) has been found in core E-5/94 at a depth which corresponded to the layer where the highest SRR could be expected, thus confirming an association between MeHg concentration and SRB activity.

Distribution of Hg in porewater

Dissolved Hg concentrations in porewater were determined in sediment cores sampled in 1996 and 1997 (Fig. 8). Obtained concentrations were highly variable, ranging from 4 to 100 ng l^{-1} for reactive Hg (HgR) and from 35 to 370 ng l^{-1} for total Hg (HgT). The percentage of Hg in labile complexes available for $SnCl_2$ reduction (HgR) varied between 2 and 70% on average constituting 15–40% of the total dissolved Hg. Recent data

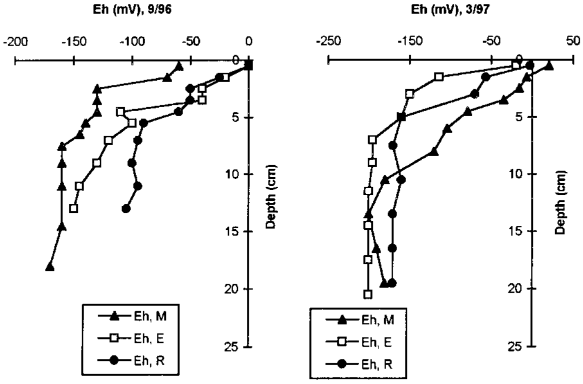

Figure 9 Depth distribution of redox potential E_h in sediments.

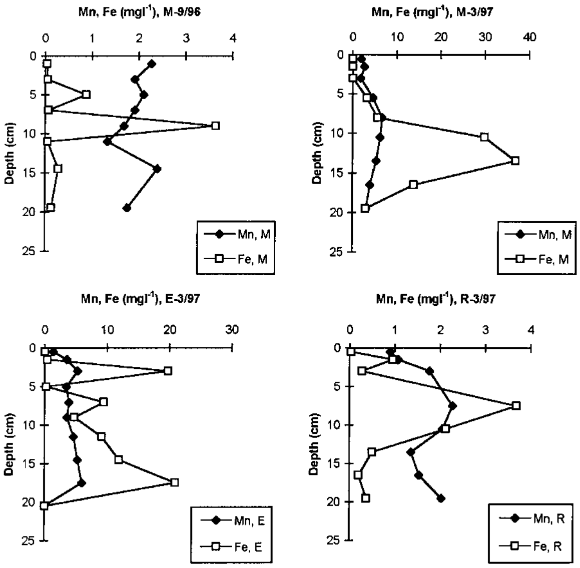

Figure 10 Depth distribution of dissolved iron and manganese in porewaters.

for mercury in porewater are still scarce. Concentrations observed in this study are similar to those reported for marine sediments (up to 500 ng l^{-1}; Ref. 9) and lake sediment (up to 800 ng l^{-1}; Ref. 36), but roughly one order of magnitude higher than those reported for coastal sediment (up to 12 ng l^{-1}; Ref. 37), estuarine sediment (up to 10 ng l^{-1}; Ref. 27) and freshwater sediment (up to 15 ng l^{-1}; Ref. 31). Data for speciation of dissolved inorganic Hg (determination of both HgR and HgT) in porewater are virtually absent from the literature.

Hg porewater distributions from all the sites exhibited similar profiles: high concentrations near the surface, a zone of low concentration below this, then higher concentrations again at depth in some cores (Fig. 8). The Hg porewater profiles were not related to sediment Hg content (Figs 8 and 2), suggesting that porewater concentrations were not simply controlled by an exchange equilibrium between these two phases. The depth distribution of dissolved Hg may depend more on the solid speciation of mercury in sediment (affinity for specific sediment components) than its total concentration.[36] Three principal pathways for the release of dissolved chemical species from sediments are proposed.[38] They include the release from easily degradable organic matter at the sediment/water interface, the release from manganese and ferrous oxyhydroxides in the suboxic zone, and the release of soluble metal–sulphide complexes in the anoxic zone. To elucidate which of these processes are responsible for Hg dissolution from sediments of the Seine estuary, redox zones in the sediments investigated should be defined. According to the sequence of the redox potential (Fig. 9) and dissolved iron and manganese profiles (Fig. 10), most of the cores (except M-3/97 where $E_h > 0$ at the surface) are already suboxic from the first centimetre. Direct measurement of dissolved oxygen in sediment cores sampled in 1994–1995 showed that the oxygen penetration depth was limited to first few millimetres of the sediment.[33] We can also suppose that at the bottom of cores M-9/96 and R-3/97, where iron was no longer present in porewater, an anoxic zone containing sulphides (which eliminate iron from the dissolved phase by precipitating FeS) had developed.

Therefore, the observed Hg profiles may be explained in the following way. The high concentration at the sediment/water interface could be a consequence of microbial solubilization and degradation of the organic carbon which releases bound mercury. The highest percentage of mercury in the form of strong organic complexes (HgT − HgR) at the sediment surface supports this idea. Results from sequential extraction indicate that most of the mercury (especially in the surficial layer) is associated with base-soluble (humic and fulvic acids) organic matter.[36] The association of mercury with iron and mangenese oxyhydroxides does not seem to be important in the Seine sediment, as their dissolution was not generally followed by Hg release (compare Figs 8 and 10).

Only in the core M-9/96 do peaks of HgR correspond to iron peaks, which indicates that remobilization of iron oxides could play a role in the diagenetic remobilization of mercury. The correlation between HCl-extractable Hg, manganese and iron provides more supporting evidence for the role played by iron and managanese oxides, which were found to be significant in some coastal sediments.[9,37] Therefore, such an extraction should be performed in Seine sediments to judge whether Hg is partly recycled with manganese and iron oxides. Finally, the increase in dissolved Hg in cores M-9/96 and R-3/97 (Fig. 8) could be ascribed to the formation of highly soluble Hg polysulphides.[9,27] The formation of such complexes has been suggested to explain the presence of porewater metal concentrations largely exceeding values predicted from the solubility of metal sulphides such as HgS.[39]

Dissolved MeHg was determined in porewaters of three cores sampled in March 1997 (Fig. 8). In most of the samples MeHg was below the detection limit of the method (2 ng l^{-1}). Only in the surface layers of the core E-3/97 was a low level of MeHg (4–10 ng l^{-1}) detected, making about 5% of the total dissolved Hg. The few data existing in the literature show that MeHg levels in porewater are frequently below 1 ng l^{-1},[27–31] but could reach 10 ng l^{-1} (making up 10–20% of total porewater Hg).[10] It was suggested that anoxic but weakly sulphidic conditions were conducive to MeHg accumulation in porewater, as it was not detected in surficial oxic sediments.[10] As indicated by E_h and iron profiles (Figs 9 and 10), core E-3/97, where MeHg in porewater was detected, already showed a rapid development of highly anoxic conditions from the surface. This supports the idea that MeHg persists under suboxic conditions, whereas in oxic sediment it is rapidly decomposed by aerobic demethylating bacteria.

Hg flux from sediment

Sediments provide a potential source of Hg and MeHg for the water column through the diffusive flux of dissolved species as well as bioaccumulation through the benthic food web or porewater advection. The porewaters of the Seine sediments are 10–100 times richer in Hg than the overlying water (1–5 ng l^{-1} in the estuary).[11] From the concentration gradient between porewater and river water the total Hg diffusive flux at the sediment/water interface was estimated according to Fick's first law of diffusion (Eqn [1]):

$$J = -\Phi D_s(\partial C/\partial z) \qquad [1]$$

where Φ is porosity (a value of 0.8 was used),[33] D_s is the bulk sediment diffusion coefficient and ($\partial C/\partial z$) is the concentration gradient across the sediment/water interface. The value D_s was assumed to be equal to $\Phi^2 D_o$[40] where D_o is the molecular diffusion coefficient. We have adopted $D_o = 5 \times 10^{-6}$ cm^2 s^{-1}, after Bothner.[41] The concentration gradient was calculated from the Hg concentration in porewaters collected from the first sediment sampling interval (i.e. 0–1 cm; thus $\Delta z = 0.5$ cm). Calculated fluxes ranged from 38 to 58 ng cm^{-2} y^{-1} and are comparable with the ones obtained in the Saguenay Fjord[9] for sites where more reducing conditions in sediments prevailed (26–36 ng cm^{-2} y^{-1}). Much lower fluxes (1–20 ng cm^{-2} y^{-1}) are found in more oxic sediments[37] where the presence of oxidized surface sediments inhibits transfer of Hg to the overlying water.

We estimated the integrated flux of Hg for the entire estuary by multiplying the mean flux value (50 ng cm^{-2}y^{-1}) by the approximate surface area of the estuary (30 km^2; Ref. 33). The value obtained (15 kg y^{-1}) was compared with the amount of Hg transported by the river, to estimate the importance of Hg input from sediment. The average riverine input of dissolved Hg (calculated from the mean river discharge of 500 m^3 s^{-1} and mean Hg concentration of 2.3 ng l^{-1}; Ref. 11) was 35 kg y^{-1}. Therefore, diffusive sediment flux could be quite important, representing about 40% of the dissolved riverine input. However, both fluxes are negligible in comparison with particulate riverine input, which is higher by one order of magnitude (about 500 kg y^{-1}; Ref. 11) than input of dissolved mercury from both sources.

CONCLUSIONS

The percentage of MeHg in sediments of the Seine estuary is typical for estuarine sediments (<1% MeHg). As in most other sediments, the highest methylation occurs near the surface of sediment and appears to be mediated by sulphate-reducing bacteria. In coastal marine sediments methylation seems to be suppressed by high salinity, but the higher MeHg levels found in estuarine sediments as compared with riverine ones cannot be fully explained. The influence of reduced sulphur species on its speciation and methylation in both dissolved and solid sediment phases should be studied to understand better the MeHg distribution obtained.[27,31]

The results of this study demonstrated that the interstitial water of Seine sediments is enriched in mercury relative to the overlying water. The release of mercury to porewater is regulated by the degradation of organic matter in the oxic and suboxic zones and by the formation of soluble metal–sulphide complexes in the anoxic zone. The role of iron and manganese oxyhydroxides in Hg remobilization (dissolution and precipitation) is not unequivocal and should be further studied by using partial sediment extraction.[9,37]

The calculated diffusive flux of mercury from sediments of the Seine estuary is of the same order of magnitude as dissolved riverine input, but it is negligible compared with the riverine input of particulate Hg.[11]

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REFERENCES

1. W. Fitzgerald and T. Clarkson, *Environ. Health. Perspect.* **96**, 159 (1991).
2. G. C. Compeau and R. Bartha, *Appl. Environ. Microbiol.* **50**, 498 (1985).
3. G. C. Compeau and R. Bartha, *Appl. Environ. Microbiol.* **53**, 261 (1987).
4. C. H. Gilmour, E. A. Henry and R. Mitchell, *Environ. Sci. Technol.* **26**, 2281 (1992).
5. C. J. Watras, N. S. Bloom, S. A. Claas, K. A. Morrison, C. C. Gilmour and S. R. Craig, *Water Air Soil Pollut.* **80**, 735 (1995).
6. C. H. Gilmour and E. A. Henry, *Environ. Pollut.* **71**, 131 (1991).
7. C. A. Kelly, J. W. M. Rudd, V. L. St. Louis and A. Heyes, *Water Air Soil Pollut.* **89**, 715 (1995).
8. J. W. M. Rudd, *Water Air Soil Pollut.* **80**, 697 (1995).
9. C. Gagnon, E. Pelletier and A. Mucci, *Mar. Chem.* **59**, 159 (1997).
10. C. Gagnon, E. Pelletier, A. Mucci and W. Fitzgerald, *Limnol. Oceanogr.* **41**, 428 (1996).
11. M. Coquery, D. Cossa D. and J. Sanjuan, *Mar. Chem.* **58**, 213 (1997).
12. M. Leemakers, C. Meuleman and W. Baeyens, *Water Air Soil Pollut.* **80**, 641 (1995).
13. R. D. Wilken and D. Wallschlager, The Elbe river: a special example for a European river contaminated heavily with mercury. In: *Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances*, W. Baeyens *et al.* (eds), Kluwer Academic, Dordrecht 1996, pp. 317–328.
14. B. B. M. Muhaya, M. Leemakers and W. Baeyens, *Water Air Soil Pollut.* **94**, 109 (1997).
15. H. Hintelmann and R. D. Wilken, *Sci. Tot. Environ.* **166**, 1 (1995).
16. J. Avoine, D. Boust and J. F. Guillaud, *Rapp. P.V. Reun. Cons. Int. Explor. Mer.* **186**, 392 (1986).
17. M. Horvat, N. S. Bloom and L. Liang, *Anal. Chim. Acta.* **281**, 135 (1993).
18. N. Mikac, S. Niessen and M. Wartel, Microwave-assisted determination and speciation of mercury in sediments. Paper presented at International Forum *Intelligent Analytical Solutions*, 24–29 Sept. 1998, Juelich, Germany.
19. N. S. Bloom and E. A. Crecelius, *Mar. Chem.* **14**, 49 (1983).
20. O. Szakacs, A. Lasztity and Z. S. Horvath, *Anal. Chim. Acta* **121**, 219 (1980).
21. B. Ouddane, E. Martin, A. Boughriet, J. C. Ficher and M. Wartel, *Mar. Chem.* **58**, 189 (1997).
22. G. Thoumelin, L. Bodineau and M. Wartel, *Mar. Chem.* **58**, 59 (1997).
23. P. D. Bartlett and P. J. Craig, *Water Res.* **15**, 37 (1981).
24. P. J. Craig and P. A. Moreton, *Water Res.* **20**, 1111 (1986).
25. O. Regnell and G. Ewald, *Limnol. Oceanogr.* **42**, 1784 (1997).
26. M. Coquery, Biogéochimie du mercure en milieu estuarien et cotier. Thesis, Université de P. et M. Curie, Paris, France, 1994.
27. J. M. Benoit, C. H. Gilmour, R. P. Mason, G. S. Riedel and G. F. Riedel, *Biogeochemistry* **40**, 249 (1998).
28. N. J. Croston, J. M. Bubb and J. N. Lester, *Hydrobiology* **321**, 35 (1996).
29. V. L. St Louis, J. W. M. Rudd, C. A. Kelly, K. G. Beaty, N. S. Bloom and R. J. Flett, *Can. J. Fish. Aquat. Sci.* **51**, 1065 (1994).
30. J. E. Blum and R. Bartha, *Bull. Environ. Contam. Toxicol.* **25**, 404 (1980).
31. C. H. Gilmour, G. S. Riedel, M. C. Ederington, J. T. Bell, J. M. Benoit, G. A. Gill and M. C. Strodal, *Biogeochemistry* **40**, 327 (1998).
32. D. Cossa, M. Coquery, C. Gobeil and J.-M. Martin, Mercury fluxes at the ocean margins. In: *Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances*, W. Baeyens *et al.* (eds), Kluwer Academic, Dordrecht 1996, pp. 229–247.
33. E. Martin, Reactivité du fer et du manganese au cours de la diagénèse précose de sediments de l'estuarie de la Seine. Thesis, Université de Lille 1, France, 1996.
34. C. Gagnon, A. Mucci and E. Pelletier, *Mar. Chem.* **52**, 195 (1996).
35. J. H. Weber, R. Evans, S. H. Jones and M. E. Hines, *Chemosphere* **36**, 1669 (1998).
36. J. M. Matty and D. T. Long, *J. Great. Lakes Res.* **21**, 574 (1995).

37. C. Gobeil and D. Cossa, *Can. J. Fish. Aquat. Sci.* **50**, 1794 (1993).
38. I. Rivera-Duarte and R. Flegal, *Croat. Chem. Acta* **70**, 389 (1997).
39. W. Stumm and J. J. Morgan, *Aquatic Chemistry*, Wiley, New York, 1981.
40. W. J. Ullman and R. C. Aller, *Limnol. Oceanogr.* **27**, 552 (1982).
41. M. H. Bothner, R. A. Jahnke, M. L. Peterson and R. Carpenter, *Geochim. Cosmochim. Acta* **44**, 273 (1980).