

# A comparative study of mercury distribution and methylation in mudflats from two macrotidal estuaries: The Seine (France) and the Medway (United Kingdom)

B. Ouddane<sup>a,\*</sup>, N. Mikac<sup>b</sup>, A.B. Cundy<sup>c</sup>, L. Quillet<sup>d</sup>, J.C. Fischer<sup>a</sup>

<sup>a</sup> *Université des Sciences et Technologies de Lille, UMR CNRS Geosystemes 8157, Equipe Chimie Analytique et Marine Bat C8, 59655 Villeneuve d'Ascq Cedex, France*

<sup>b</sup> *Center for Marine and Environmental Research, Rudjer Boskovic Institute, Zagreb, Croatia*

<sup>c</sup> *University of Brighton, School of the Environment, United Kingdom*

<sup>d</sup> *Université de Rouen, UMR CNRS 6143, Morphodynamique Continentale et Côtière (M2C), Groupe de Microbiologie, 78821 Mont Saint Aignan Cedex, France*

Received 1 February 2007; accepted 9 November 2007

Editorial handling by J.E. Gray

Available online 19 November 2007

---

## Abstract

Mercury is a contaminant of great concern in the marine environment, particularly in coastal environments where the formation of methylmercury (MeHg) in aquatic sediment, and its subsequent bioaccumulation in edible aquatic organisms (mainly fish), presents a major pathway for human exposure to MeHg. Consequently, it is important to determine the factors controlling MeHg production in sediment, especially in contaminated environments. This study investigates some geochemical factors affecting the speciation and distribution of Hg in estuarine sediment from two highly industrialized macrotidal salt marsh/mudflat systems in the Seine estuary, France, and in the Medway estuary, UK. Obtained data revealed that the entire sediment core from a rapidly accreting mudflat in the Seine estuary (170 cm vertical accretion over the last 10–50 a) was contaminated with Hg at concentrations which are 10–50 times higher than the Hg background for sediments of the Seine basin. In the Medway mudflat, characterized by a slow sedimentation rate (400 cm over approximately the last 800 a), near-surface sediment was significantly more contaminated (10–40 times) than sediment at greater depths, which were characterized by pre-industrial Hg concentrations. Geochemical conditions in the surface sediment of the Medway mudflat are characterized by stable anoxic redox conditions (about –200 mV), which are generally favourable for Hg methylation, whereas near-surface sediment of the Seine mudflat is characterized by more oxidizing redox conditions (about +100 mV), which are generally less conducive to Hg methylation. Consequently, MeHg concentration in the upper 10 cm of the sediment column was about four times higher in the Medway than in the Seine mudflat, in spite of similar total Hg concentrations. In surface sediment, where Hg is actively methylated, MeHg variability was associated with the activity of  $\text{SO}_4^{2-}$ -reducing microorganisms (SRM) and the presence of acid volatile sulphides (AVS). A strong

---

\* Corresponding author. Tel.: +33 3 20 43 44 81; fax: +33 3 20 43 48 22.

E-mail address: [baghdad.ouddane@univ-lille1.fr](mailto:baghdad.ouddane@univ-lille1.fr) (B. Ouddane).

correlation was observed between MeHg and AVS in sediments from these mudflats, which may be a consequence of the common origin of AVS and MeHg (both produced by microorganism activity), but also can be derived from the ability of Fe monosulfides to adsorb, and thus stabilize, solid phase MeHg.

© 2007 Elsevier Ltd. All rights reserved.

## 1. Introduction

Mercury is present in the environment in a wide variety of compounds, amongst which the most toxic is monomethylmercury ( $\text{CH}_3\text{Hg}^+$ ), which has the ability to cross cell membranes, accumulate in biological tissues, and biomagnify throughout the food chain (Bodaly et al., 1997; Mason and Benoit, 2003). Even when present in small quantities in estuarine water or sediment, MeHg shows a marked tendency to bioaccumulate in organisms, particularly fish. Transformation of inorganic Hg to MeHg is most common in the sediment column, where MeHg is formed by microbial methylation, dominantly by SRM (Compeau and Bartha, 1985). Consequently, increased  $\text{SO}_4^{2-}$  reduction may potentially lead to an increase in MeHg production, provided that inorganic Hg is bioavailable (Ullrich et al., 2001, 2007). Through the effect of diffusion, and particularly through the remobilisation of surface sediment, a fraction of MeHg is periodically transferred into the water column (Heyes et al., 2004; Mason et al., 2006; Hammerschmidt and Fitzgerald, 2006; Castelle et al., 2007). Such processes may be important in the bioaccumulation of MeHg in estuarine ecosystems.

A number of environmental factors may affect the rate of MeHg formation by influencing the supply of bioavailable Hg and/or the activity of the microbial community. In addition to Hg concentration, effective proxy indicators for MeHg production and accumulation identified by previous research include sulphide concentration, total organic C, and redox potential (Baeyens et al., 1998; Benoit et al., 1999, 2001; Mason and Lawrence, 1999; Stoichev et al., 2004; Hines et al., 2006). In some environments, typically in coastal and marine sediment, organic matter has been shown to be the main factor regulating MeHg concentration (Hammerschmidt et al., 2004; Hammerschmidt and Fitzgerald, 2006; Mason and Lawrence, 1999; Lambertsson and Nilsson, 2006). In other systems, Hg methylation is more regulated by sulphide concentration in sediment porewater, which influences speciation of dissolved inorganic Hg, and thus

may limit the pool of Hg available for Hg methylating organisms (Benoit et al., 1999, 2001). In estuarine environments, which are not  $\text{SO}_4$ -limited systems, sulphide enrichment can vary with organic matter enrichment resulting in increased Hg methylation at higher sulphide concentration (Sunderland et al., 2006).

This study investigates the relative importance of geochemical factors, which may affect the speciation and distribution of Hg in estuarine sediment, using sediment samples from two contrasting macrotidal salt marsh/mudflat systems – a rapidly prograding, relatively young marsh system in the Seine estuary, France, and a more mature, less extensive marsh system in the Medway estuary, UK. Both estuaries are affected by industrial contamination, and the long-term accumulation of Hg in sediment and its temporal variability is compared via analysis of dated sediment cores. Solid phase MeHg concentrations were determined along with organic C content ( $C_{\text{org}}$ ), the activity of SRM, and the concentration of AVS and chromium reducible sulphides (CRS) to examine geochemical conditions that are most important for regulating Hg methylation.

## 2. Material and methods

### 2.1. Study areas and sediment sampling

The Seine (Fig. 1a) is one of the most polluted estuaries in Europe with respect to potentially harmful elements (Miramand et al., 2001), receiving effluents from the upstream Paris urban area, and also local inputs from the heavily-industrialised Rouen and Le Havre regions. For Hg, the Seine was one of the most contaminated catchments in the world in the 1970s with a maximum content recorded in sediment of  $26 \text{ mg kg}^{-1}$  Hg. Today the average content for Hg ( $1.08 \text{ mg kg}^{-1}$ ) is much lower but still in the upper 90% of the global scale distribution and well above the natural background value determined in pre-historical deposits (Meybeck et al., 2007). In addition, the estuary is contaminated by wastes derived from agricultural sources and domestic sewage: 30–40% of the French

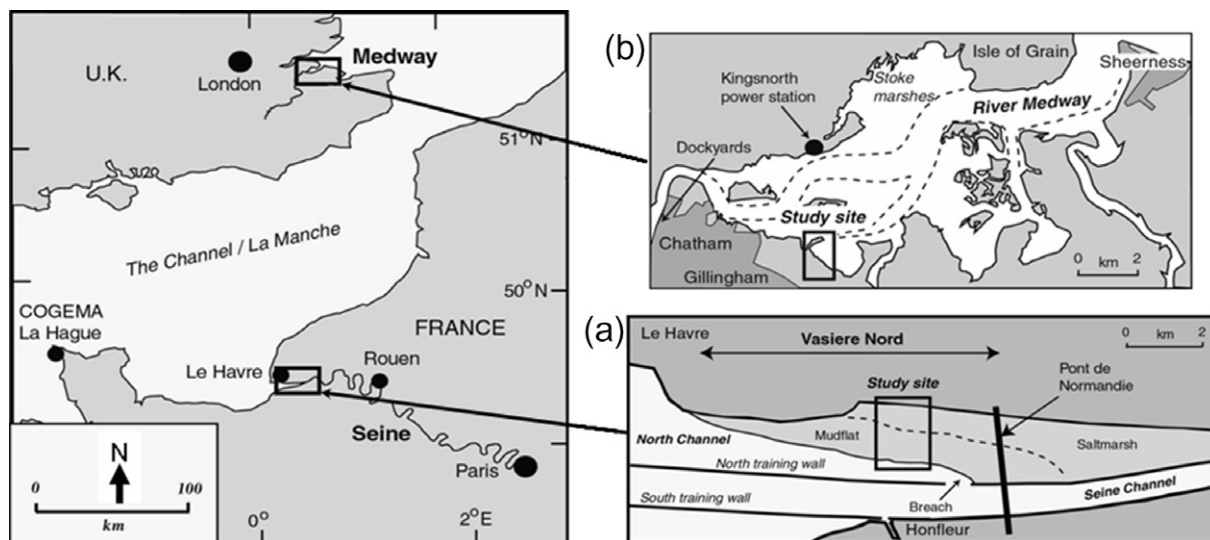


Fig. 1. Study areas and sample sites.

industrial activity is located in the 75,000 km<sup>2</sup> drainage basin, in which 30% of the French population lives (Chiffolleau et al., 2001).

The Seine estuary can be classified as a macrotidal estuary (3 m tidal range at neap tides, 7.5 m tidal range at spring tides, based on data for Le Havre city), with an annual (land-derived) suspended sediment flux of about  $6 \times 10^5 \text{ t a}^{-1}$  (Lesourd et al., 2001) and is characterized by a high turbidity zone (suspended loads up to several  $\text{g L}^{-1}$ ). This turbidity maximum is dynamic, but is typically found between Tancarville (9 km upstream of the Pont de Normandie) and Le Havre (Fig. 1a).

The River Medway (Fig. 1b) is a major tributary of the River Thames, joining it at Sheerness, Isle of Sheppey. The River Medway drains a catchment area of 1761 km<sup>2</sup> (Pethick, 1993), and opens in its estuarine reaches into a flat-floored valley up to 8 km across. The estuary is macrotidal with mean tidal ranges of 5.6 m for spring tides and 4.0 m for neap tides (Pethick, 1993). The intertidal zone comprises fragmented fringing and island salt marshes and extensive tidal mudflats dominated by fine sediment. Historically, the Medway estuary has received pollution from many sources. Halfway through the 19th century, extensive dockyards were built at Chatham and Rochester, housing a variety of industries, and by the late 1800s three large Naval basins had also been excavated (Spencer et al., 2003). More recently, a range of industrial facilities have been established in the lower reaches of the estuary including a power station at Kingsnorth

and an oil refinery on the Isle of Grain (Fig. 1b). The estuary also receives contamination from further upstream, with discharges from a large pesticide plant at Yalding (approximately 25 km upstream from the study site), paper (which used phenylmercuric acetate as a slimicide) and chemical industries, timber treatment plants, and a number of private and public sewage works (National Rivers Authority, 1991).

The intertidal mudflat areas chosen for study were selected (a) on the basis of their proximity to historical and current contaminant sources (for the Seine, the major industrial region east of Le Havre, and for the Medway, historical dockyards and recent sewage waste inputs), and (b) to provide contrasting geomorphological settings (i.e., a rapidly prograding and extensive young marsh in the Seine estuary versus a more mature and less extensive marsh system in the Medway estuary). The study site in the Seine estuary (the Vasiere Nord) is located west of the Pont de Normandie (Fig. 1a), close to Le Havre, on the north bank of the Seine. The marsh system and fronting intertidal mudflat is approximately 2 km wide. This mudflat is characterized by a high sedimentation rate ( $15\text{--}18 \text{ cm a}^{-1}$ ) and a unique pattern of sedimentation (Deloffre et al., 2006, 2007). Sedimentation rhythms are discontinuous and deposition occurs only during the highest spring tides, whereas wind-induced erosion (up to 5 cm) occurs in periods between sedimentation (about 10 times per year, Deloffre et al., 2007). Sediment of the Seine mudflat is generally

fine-grained mud with 5–15% sand. The study site in the Medway estuary is located at Horrid Hill (Fig. 1b) behind an artificial spit used to supply a former cement works. The marsh itself is approximately 100 m wide. The sediment starved Medway estuary (sedimentation rate is about  $4 \text{ mm a}^{-1}$ , Cundy et al., 2005; Deloffre et al., 2007) is characterized by the stable sediment surface on the mudflat and reworking of the fine particles inside the estuary. Sediment is composed of very fine particles lacking sand.

Sediment samples were collected in July 2003 in the Seine estuary and in September 2003 in the Medway estuary. Sediment cores were taken from the low marsh/mudflat boundary at each site. At each site cores collected included (a) one long core used for Hg speciation,  $C_{\text{org}}$ , and SRM analyses and, (b) one short core that was used for porewater extraction and AVS and CRS analysis. The long sediment cores were sampled using a closed barrel vibrocorer. In the Medway mudflat, a core of about 400 cm was collected, but in the Seine estuary the core was only about 200 cm due to presence of a sand bank at a depth of 2 m, which lies over a gravel bed and prevented sampling of a longer core at this site. Short cores (30 cm) were collected using a hand-driven gouge corer. The surface sections of the long cores (to 30 cm depth) were sliced into 2 cm increments and the remaining sections of the cores were sliced into 25–30 cm layers. Because of the length of the cores, the long cores had to be cut under an open atmosphere. The short cores for AVS and CRS analyses were transported intact to the laboratory, and immediately sectioned into 2 cm layers under a  $\text{N}_2$  atmosphere in order to prevent change in redox conditions and oxidation of reduced S species. Sectioned cores were kept frozen in plastic bags until analysed.

Clean techniques were used for the preparation of material and for sample collection. All lab ware and material for sampling were cleaned in 10%  $\text{HNO}_3$ , rinsed thoroughly with ultrapure water, and dried in a laminar flow hood.

## 2.2. Determination of mercury and methylmercury

Total Hg was measured in dry sediment samples (without any pre-treatment) by means of atomic absorption spectroscopy (AAS) using an AMA 254 solid phase Hg-analyzer (Altec Ltd., Prague, Czech Republic). After thermal combustion of 50–100 mg of dried sediment, released Hg gas is

collected on a Au trap. The Hg–Au amalgam is subsequently heated to  $700^\circ\text{C}$ , and Hg is released and detected by AAS. A detailed description of the method is given by Hall and Pelchat (1997). The detection limit is  $0.1 \mu\text{g kg}^{-1}$  of Hg in sediment for analysis of 100 mg of sample.

Analysis of MeHg was by isothermal GC–CVAFS (Gas Chromatography–Cold Vapour Atomic Fluorescence Spectrometry) after MeHg extraction from sediment into dichloromethane and reextraction into the water phase by dichloromethane evaporation. The extracted MeHg was ethylated, and purged with Ar onto Tenax columns (Liang et al., 1994). Ethylated Hg species were separated by isothermal gas chromatography, combusted to  $\text{Hg}^0$ , and measured using an AFS detector (PSA Analytical, UK). Full experimental details and analytical conditions for MeHg analysis are described in Foucher (2002). The lower reporting limit for MeHg analysis in sediment was  $0.02 \mu\text{g kg}^{-1}$  for the analysis of 1 g of sample (method limit is  $1 \text{ ng L}^{-1}$  in the final solution). All samples for Hg and most of the samples for MeHg were analysed in duplicate. The precision (expressed as relative standard deviation) was better than 5% for total Hg and 10% for MeHg. Results are reported on a dry weight basis.

Three certified reference materials were used to check the accuracy of the method for total Hg and MeHg: marine sediment PACS (NRC, Canada), estuarine sediment IAEA-405 and marine sediment IAEA-433 (IAEA, Vienna, Austria). Mean recoveries for total Hg were: 108% for PACS, 96% for IAEA-405, and 92% for IAEA-433, and for MeHg: 102% for IAEA-405 and 106% for IAEA-433.

## 2.3. Determination of organic carbon and reduced sulphur species

Water content was determined by weight loss at  $105^\circ\text{C}$ . The  $C_{\text{org}}$  was determined using an elemental carbon–hydrogen–nitrogen–sulfur (CHNS) analyzer (LECO CHNS932); a first measurement allows the determination of the total C (organic and mineral) and a second one (after calcination at  $430^\circ\text{C}$  over 24 h) provides the mineral C. The difference between these two results is the  $C_{\text{org}}$  concentration.

Reduced S species were determined only in the short cores because it was not possible to cut long cores under a  $\text{N}_2$  atmosphere (due to glove bag size limitations) and preserve AVS and CRS in these cores. The inorganic S was divided into AVS and

CRS fractions and their extraction was performed in two steps following sequential extraction procedures described by Cornwell and Morse (1987), and optimized by Billon et al. (2001). The first extraction was performed by addition of HCl  $6 \text{ mol dm}^{-3}$  at ambient temperature over one hour. This procedure extracts AVS, which is present in sediment mainly in the form of amorphous Fe monosulphide. The CRS extraction was done on the residue of the AVS step by the addition of  $\text{Cr}^{2+}$  which reduces the residual S compounds present in sediment. This fraction, often qualified as CRS, contains pyrite ( $\text{FeS}_2$ ) and elemental S ( $\text{S}^0$ ). The concentration of  $\text{H}_2\text{S}$  gas liberated upon extractions was measured after conversion to sulphide by means of a sulphide specific membrane electrode. The accuracy of these two methods was estimated to be <8% and the lower limit of determination of this method (1 g of sediment) was about  $20 \text{ mg kg}^{-1}$  of S in the sediment. The optimisation of this method and the artefact related to sampling and determination was discussed by Billon et al. (2001) and the results of optimisation are in agreement with the conclusion of Rickard and Morse (2005).

#### 2.4. Molecular quantification of the *dsrAB* genes and Sulphate-reducing microorganisms (SRM)

One of the methods to estimate microbial  $\text{SO}_4^{2-}$ -reducing communities consists of molecular detection and qualification of a functional gene present in every SRM – the *dsrAB* gene (dissimilatory sulfite reductase), which encodes for the key enzyme involved in dissimilatory sulphate respiration. Using competitive PCR (cPCR) the abundance of SRM (carrying the *dsrAB* gene) in the total microbial community of anoxic sediments can thus be determined (Leloup et al., 2004). Briefly, total DNA was extracted from 0.5 g sediment samples (wet weight) using a Bio-101 FastDNA Spin kit in combination with a FastPrep FP120 bead beating system (Bio-101, Inc., Ca, USA) according to the manufacturer's instructions. Total crude DNA was purified by elution through Elutip-D columns (Schleicher & Schuell, Dassel, Germany). The concentration of the resulting DNA was estimated by UV transillumination of samples spotted on ethidium bromide agarose plates. The *dsrAB* genes present in DNA extracted from sediment samples were quantified by competitive PCR (Leloup et al., 2004). The cPCR principle is based on a co-amplification of the target and a competitor sequence with

the same primer set: 150 fg of competitor sequence carried by pKSAII was added to serial dilutions (25–250 fg) of the target sequence carried by pAS44. Similarly, 150 fg of competitor DNA was added to 4 ng of DNA extracted from estuary sediments. The PCR products (20  $\mu\text{L}$ ) were analysed by electrophoresis in an agarose gel (1% (w/v), 0.5X TAE), stained with ethidium bromide and viewed under UV light. PCR products were quantified from digitised gel images (Alpha-Imager™ 1220, Alpha Innotech Corporation, Ca, USA). A standard curve was constructed by plotting the log intensity of DNA amplified from the serial dilution against the intensity of the competitor DNA amplification ( $\log[\text{pdsr}/\text{pdsr-c}]$ ). The amount of target was then determined from the log intensity ratio of *dsr-s/dsr-c* DNA. The results are expressed as the number of gene copies per ng of extracted DNA, and are thus independent of the DNA extraction yield. The detection limit was 45 copies of the *dsrAB* genes per ng of DNA.

#### 2.5. Determination of other auxiliary parameters

Redox potential (Eh) and pH were determined immediately after sampling using a Pt/Pt–Ag/AgCl combined electrode and glass microelectrode, respectively. The electrodes were inserted at different levels into the sediment column by holes drilled in the wall of the plastic tubes and capped with rubber during the sampling. The values of electrodes potentials were corrected to the normal hydrogen electrode potential. Sodium concentration in pore-water was determined via inductively coupled plasma atomic emission spectroscopy (ICP AES, axial, Liberty Series II; Varian) and  $\text{SO}_4^{2-}$  was determined by the nephelometric method at 650 nm after acidification and its precipitation/resuspension with  $\text{BaCl}_2$  in the presence of polyoxyethylene sorbitan monolaureate. Precision, expressed as relative standard deviation (RSD) of four replicate samples, was better than 2% for Na and 5% for  $\text{SO}_4^{2-}$ .

### 3. Results

#### 3.1. Total and methyl mercury distribution

The concentration of total Hg in long cores shows distinct differences between the two estuaries (Fig. 2). In the Seine core, total Hg concentration gradually increases with depth from an average in the first 20 cm of  $0.31 \pm 0.12 \text{ mg kg}^{-1}$  up to  $1.5 \text{ mg kg}^{-1}$  at



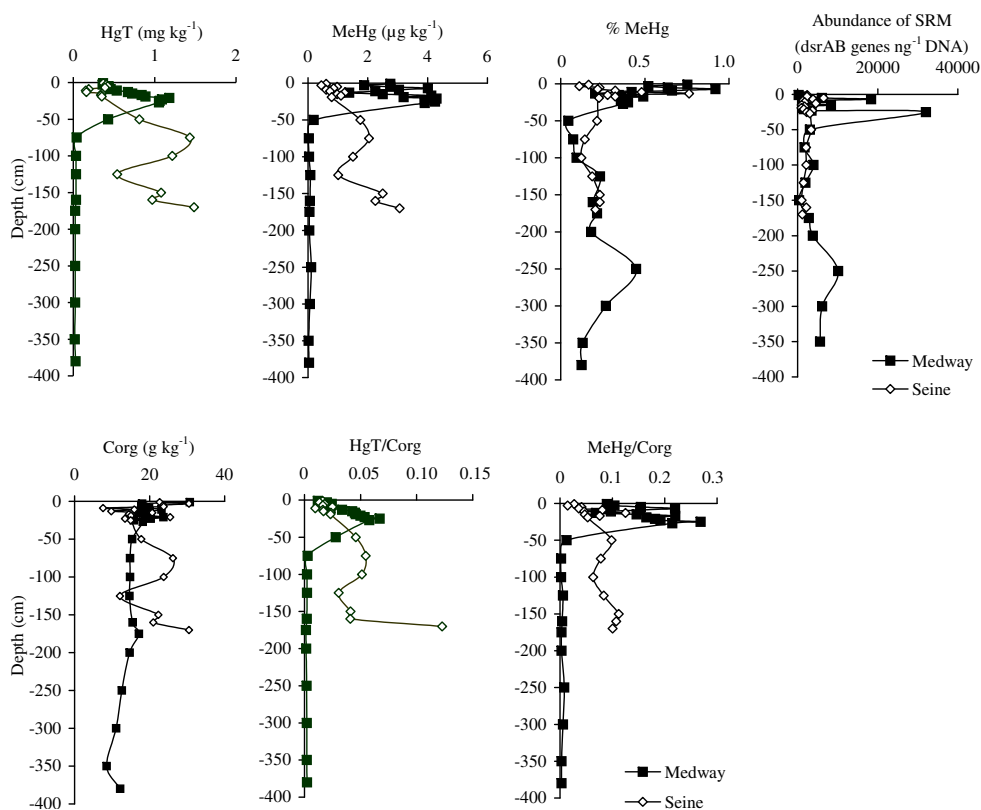


Fig. 2. Total Hg, MeHg, %MeHg,  $C_{org}$  and abundance of SRM versus depth in sediment of the long cores from the Seine and the Medway mudflats.

70 cm depth and remain elevated ( $0.5\text{--}1.5\text{ mg kg}^{-1}$ ) to the bottom of the core (175 cm). Conversely, in the Medway core, total Hg gradually increases from the surface ( $0.3\text{ mg kg}^{-1}$ ) to a maximum at about 22 cm depth ( $1.2\text{ mg kg}^{-1}$ ) and then rapidly decreases with depth. In the deeper parts of the Medway core (75–380 cm), Hg concentrations are low with little variation (average concentration of  $0.03 \pm 0.01\text{ mg kg}^{-1}$ ). Smaller differences in total Hg were found in the top 20 cm of the cores from the Seine and Medway mudflats (Fig. 3), where Hg concentrations are less variable ( $0.31 \pm 0.12\text{ mg kg}^{-1}$  in the Seine versus  $0.57 \pm 0.19\text{ mg kg}^{-1}$  in the Medway). In the Seine core, the lowest total Hg and  $C_{org}$  concentrations generally were found between 10 and 15 cm depth, which corresponds with the presence of a sand layer.

The concentration of MeHg (Fig. 3;  $3.2 \pm 0.95\text{ µg kg}^{-1}$ ) in surface sediment of the Medway mudflat was, on average, about four times higher than MeHg of the Seine mudflat ( $0.83 \pm 0.24\text{ µg kg}^{-1}$ ). Conversely, in the deep cores at  $>50\text{ cm}$  depth, the inverse applies where MeHg con-

centrations average  $0.06 \pm 0.05\text{ µg kg}^{-1}$  in the Medway core, compared with an average of  $2.0 \pm 0.67\text{ µg kg}^{-1}$  in the Seine. However, the general shape of the concentration profiles for total Hg and MeHg are similar in both the Medway and Seine cores (Fig. 2 and Fig. 3). While total Hg is rather constant in the top 30 cm of the cores (Fig. 3), the concentration of MeHg shows several peaks, which are especially pronounced in the Medway core.

Concentrations of both total Hg and MeHg found in the Medway and Seine estuaries are similar to those observed in other European estuaries (Table 1), which have also experienced contamination (e.g., the Scheldt (Baeyens et al., 1998), Krka (Kwokal et al., 2002), and Adour estuaries (Stoichev et al., 2004)). Higher concentrations of Hg and MeHg have only been detected in estuaries where a local industrial source of Hg (e.g., a chloralkali plant) are found, such as in the Tagus estuary, Portugal (Canário et al., 2005). The range of total and MeHg concentrations found in this work are also in good agreement with previous measurements in the

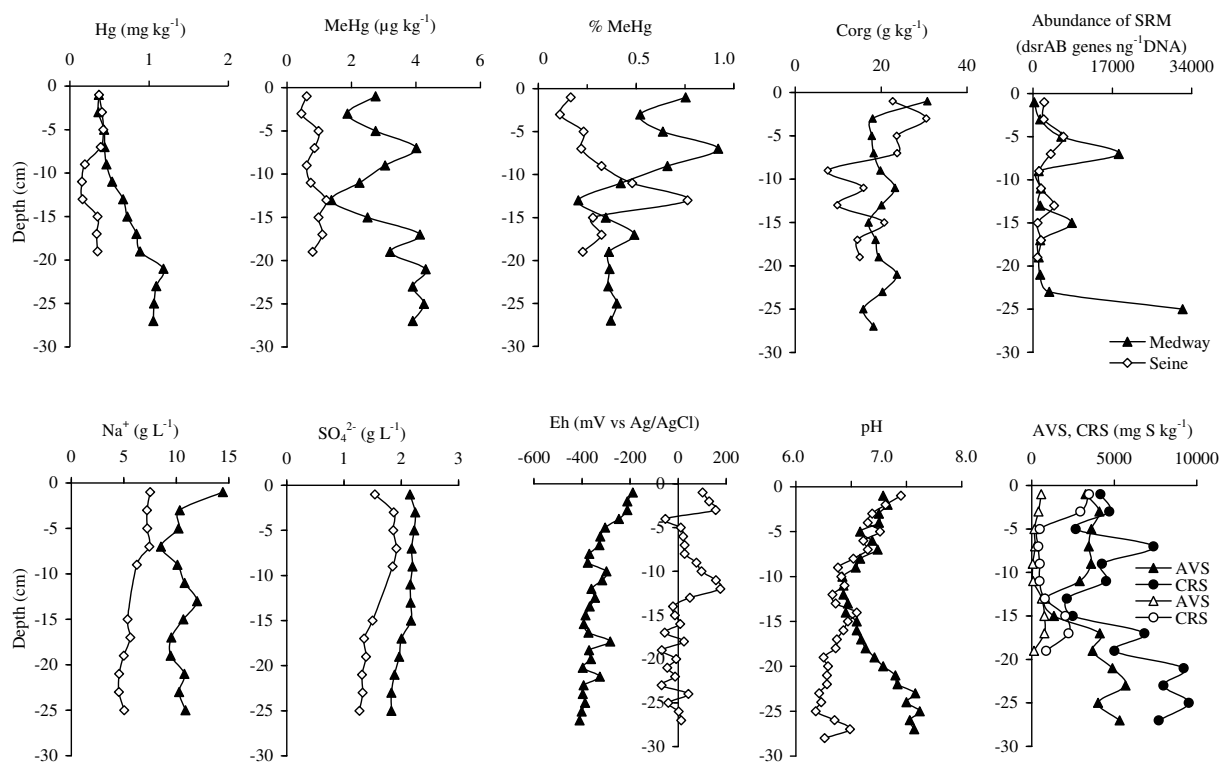


Fig. 3. Detailed depth profiles of total Hg, MeHg, %MeHg,  $C_{org}$  and abundance of SRM in the upper 30 cm of sediment of the long cores and depth profiles of Eh, AVS and CRS and some porewater parameters ( $Na$ , pH,  $SO_4^{2-}$ ) measured in short cores from the Seine and the Medway mudflat. Open symbols represents the Seine mudflat and filled symbols represent the Medway mudflat.

Table 1

Comparison of total Hg and MeHg concentrations in sediment collected from the Medway, Seine, and other European estuaries

Estuary	Hg ( $mg\ kg^{-1}$ )	MeHg ( $\mu g\ kg^{-1}$ )	Reference
Scheldt (Belgium)	0.14–1.80	0.8–6	Baeyens et al. (1998)
Ore (Sweden)	0.03–0.12	0.01–1.00	Kwokal et al. (2002)
Krka (Croatia)	0.10–1.42	0.01–1.40	Kwokal et al. (2002)
Tagus (Portugal)	0.01–66.7	0.3–43	Canário et al. (2005, 2007)
British estuaries (UK)	0.05–4.46	0.1–4.0	Craig and Moreton (1986)
Medway (UK)	0.02–1.30	–	Spencer et al. (2006)
Loire (France)	0.04–0.23	<0.03–0.3	Coquery (1994)
Lot-Garonne (France)	0.06–0.5	–	Schafer et al. (2006)
Adour (France)	0.004–1.46	0.1–1.6	Stoichev et al. (2004)
Seine (France)	0.3–1.0	0.1–6.0	Mikac et al. (1999)
Seine – Vasière Nord (France)	0.33–0.97	0.37–1.08	Foucher (2002)
Seine – Vasière Oissel (France)	0.39–2.15	0.29–1.55	Foucher (2002)
Seine – Vasière Nord (France)	0.15–1.5	0.6–3.0	This work
Medway – Horrid Hill (UK)	0.02–1.2	0.02–4.3	This work

Medway and Seine estuaries (Table 1; Spencer et al., 2006; Mikac et al., 1999; Foucher, 2002; Niessen et al., 2003).

Despite differences in MeHg concentration between the Medway and Seine cores, when MeHg is considered as a percentage of total Hg (Fig. 2), the general shape of the %MeHg plots for both

cores are similar. Overall %MeHg varies between 0.1% and 0.92% and in both cores is about twice as high in the first 30 cm ( $0.48 \pm 0.19\%$  in Medway and  $0.31 \pm 0.19\%$  in Seine; Fig. 3) than in deeper sediment layers ( $0.18 \pm 0.1\%$  in Medway and  $0.19 \pm 0.04\%$  in Seine; Fig. 2). However, in the Seine core, the %MeHg is low (<0.2%) in the first

10 cm with a maximum (0.75%) at a depth of about 15 cm, whereas in the Medway core the maximum % of MeHg was found in the first 10 cm (up to 0.92%), which then decreases below 15 cm depth. The %MeHg in these sediments is similar to that found at other estuarine sites (Baeyens et al., 1998; Heyes et al., 2004; Sunderland et al., 2004; Lambertsson and Nilsson, 2006) and comparable with previous data from the Seine estuary (Foucher, 2002; Niessen et al., 2003).

### 3.2. Geochemical characteristic of the sediment column

Concentrations of  $C_{\text{org}}$  in the Seine and the Medway mudflats are similar, ranging from 10–30 g kg<sup>-1</sup> (Fig. 2, Fig. 3). In the Seine mudflat,  $C_{\text{org}}$  shows little variation in the top 20 cm (except for a minimum at 15–20 cm caused by a sand layer) and the highest  $C_{\text{org}}$  concentrations were 25 g kg<sup>-1</sup> at 80 cm and 30 g kg<sup>-1</sup> at 170 cm depth (Fig. 2). These variations in the deeper part of the core are generally controlled by variations in sediment composition (Cundy et al., 2005). The range of measured  $C_{\text{org}}$  concentrations is comparable with previous measurements from the Seine mudflat (10–30 g kg<sup>-1</sup>, Foucher, 2002), but are lower than concentrations found in the benthic sediment (20–60 g kg<sup>-1</sup>, Mikac et al., 1999). In the Medway estuary,  $C_{\text{org}}$  is highest in the top 25 cm (18–30 g kg<sup>-1</sup>; Fig. 3) and then decreases to a constant concentration (15–18 g kg<sup>-1</sup>; Fig. 2) in deeper parts of the core.

The concentration of Na measured in porewater (Fig. 3) illustrates the different salinities of the Seine and Medway mudflats. At the Seine mudflat, salinity is lower ranging from 5 to 7 g L<sup>-1</sup>, whereas in the Medway mudflat Na concentrations range from 8 to 14 g L<sup>-1</sup> and correspond to the salinity of seawater. Accordingly, the concentration of SO<sub>4</sub><sup>2-</sup> in porewater (Fig. 3) is lower in the Seine mudflat than in the Medway mudflat. In both sediment cores, no decrease of SO<sub>4</sub><sup>2-</sup> concentration was found with depth, which would indicate its reduction by SRM. However, SO<sub>4</sub><sup>2-</sup> reduction rate (which was not measured in this study) is a better indicator of SO<sub>4</sub><sup>2-</sup> reduction than the change of the SO<sub>4</sub><sup>2-</sup> concentration in porewater (Leloup et al., 2005). Porewater pH was similar in the top 10 cm of sediment in both mudflats (varying from 7.5 to 7), but pH then decreased in the deeper part of the Seine core, whereas it increased deeper in the Medway core (Fig. 3).

The redox profiles in the Seine and Medway cores show considerable variation (Fig. 3). In the Seine mudflat, the top 15 cm of the sediment column is oxic and the lower part of the column is generally anoxic, whereas in the Medway core the entire sediment column is anoxic. These measured redox potentials fit well with the distribution of reduced S species in the two mudflats. In the Seine core, AVS and CRS are low in the top 15 cm and increase slightly at a depth where sediment is more anoxic. This indicates instability of AVS and partly CRS in the surface sediment layers, which are characterized by unstable redox conditions. Elevated CRS in the top 5 cm suggests reoxidation of less stable Fe monosulfides and preservation of pyrite in this surface layer. These AVS and CRS profiles are typical for the Seine mudflat and similar profiles were obtained in previous studies (Billon et al., 2002; Niessen et al., 2003). In the Medway mudflat, AVS and CRS are higher than in the Seine mudflat, a consequence of more stable, anoxic redox conditions and higher SO<sub>4</sub><sup>2-</sup>, which is consistent with higher SRM abundance in the Medway mudflat.

### 3.3. Sulfate-reducing microorganism quantification

The abundance of the *dsrAB* genes corresponds to the proportion of SRM in the total microbial community. Abundance of SRM is higher in the Medway than in the Seine mudflat sediment (Fig. 2 and Fig. 3) and the highest SRM activity was found in the upper 30 cm of the cores. The integrated abundance of SRM in the top 30 cm of the sediment (number of *dsrAB* microorganisms/cm<sup>2</sup>) is about six times higher in the Medway (19.6E+9) than in the Seine sediments (3.2E+09; data not shown). In both mudflats, several pronounced SRM peaks were found between depths of 5 and 25 cm, with the most pronounced peak at a depth of 25 cm in the Medway core. In the Medway core, an SRM peak was also found in a deeper part of the core (250 cm, Fig. 2) suggesting that sediment SRM activity is not only limited to the surface layers. Previously published data on the abundance and activity of SRM in sediment of the Seine mudflat sampled from 2001 to 2002 (Leloup et al., 2005) showed similar SRM results; the value was highest in June (5000–7000 *dsrAB* genes ng<sup>-1</sup> DNA) and comparable with the present data from July 2003 (Fig. 3) versus other seasons with lower SRM (<3000 *dsrAB* genes ng<sup>-1</sup> DNA).



## 4. Discussion

### 4.1. Mercury pollution history

Vertical profiles of metals in dated sediment can give an insight into temporal trends of pollution if sediment characteristics and sedimentation rates are known. Dating of the sediment cores shown here was performed by Cundy et al. (2005) using  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  radionuclides where they concluded that the sediment accumulation rates in the Seine mudflat were at least  $3\text{ cm a}^{-1}$ . More precise dating of the sediment in this core was not possible due to erratic radionuclide profiles in this rapidly accumulated and disturbed mudflat. A much lower accumulation rate ( $4\text{--}5\text{ mm a}^{-1}$ ) was estimated for the Medway mudflat from the radionuclide data (Cundy et al., 2005). The depth profiles of  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  indicate that the upper part of the core shows a continuous record of sediment accumulation, whereas the earlier (pre-1880) record of industrial activity may have been disturbed by clay extraction (Cundy et al., 2005). Additional measurements of the Seine estuary (25/07/01–04/05/03, Deloffre et al., 2007) showed that sedimentation rates were about  $15\text{--}18\text{ cm a}^{-1}$ . The sedimentation rates for the Seine mudflat suggest that the 175 cm sediment core sampled in this study was probably deposited in the last 10 a, and certainly deposited in the period

of  $<50$  a. The 380 cm sediment core sampled in this study from the Medway estuary may cover about the past 800 a, indicating that sediment deeper than 70 cm corresponds to the pre-industrial period.

Total Hg concentration is constant in the upper 20 cm of the Seine core (Fig. 3), which is probably a consequence of sediment deposition in a short time period. Deloffre et al. (2006, 2007) indicated that Seine mudflat deposition was discontinuous, occurring only during the highest spring tides. For example, in May 2003, after a high flow period of Seine River, a 27 cm layer was deposited on the mudflat (Deloffre et al., 2006). Increase of Hg concentration with depth (Fig. 2) in the Seine core may be a consequence of a higher anthropogenic load of Hg in the recent past, but may also reflect variation of the sediment characteristics with depth. The pattern of  $C_{\text{org}}$  (Fig. 2) in the Seine core is similar to that of Hg, and Hg and  $C_{\text{org}}$  are significantly correlated (Table 2) indicating that Hg is associated with particular organic matter. However, when total Hg concentration is normalized on  $C_{\text{org}}$  (Fig. 2) an increase with depth was found suggesting higher anthropogenic input of Hg into the Seine estuary in the past. Previous studies of metal contamination in the Seine River basin (Meybeck et al., 2004, 2007; Thevenot et al., 2007) have indicated that anthropogenic input of metals (including Hg) has decreased significantly in the last 20 a. These authors also

Table 2

Correlation matrix for Hg, MeHg,  $C_{\text{org}}$ , SRM, AVS and CRS in long and short cores from the Seine ( $n = 17$ ) and the Medway mudflats ( $n = 25$ )

Medway long core (0–380 cm)	MeHg	$C_{\text{org}}$	SRM	AVS	CRS
HgT	<b>0.871**</b>	<b>0.518</b>	0.203	–	–
MeHg		<b>0.606*</b>	0.291	–	–
$C_{\text{org}}$			–0.261	–	–
Medway short core (0–28 cm)	MeHg	$C_{\text{org}}$	SRM	AVS	CRS
HgT	<b>0.606</b>	–0.173	0.215	0.394	<b>0.657</b>
MeHg		–0.106	0.436	<b>0.695*</b>	<b>0.868**</b>
$C_{\text{org}}$			–0.498	0.053	–0.066
SRM				0.036	0.473
AVS					<b>0.745*</b>
Seine long core (0–175 cm)	MeHg	$C_{\text{org}}$	SRM	AVS	CRS
HgT	<b>0.865**</b>	<b>0.593</b>	–0.219	–	–
MeHg		0.379	–0.185	–	–
$C_{\text{org}}$			0.058	–	–
Seine short core (0–20 cm)	MeHg	$C_{\text{org}}$	SRM	AVS	CRS
HgT	–0.156	<b>0.793*</b>	0.202	0.162	0.432
MeHg		–0.392	0.377	0.438	–0.326
$C_{\text{org}}$			0.238	0.079	0.478
SRM				–0.130	–0.307
AVS					<b>0.662</b>

Bold:  $p < 0.05$ ; bold+\*  $p < 0.01$ ; bold+\*\*  $p < 0.001$ .

showed that from about 2000 to the present day, Hg contamination of Seine sediment was still high. Enrichment factors (EF, ratio of sediment metal concentration to that in the natural background) have been calculated as a measure of Hg contamination. The background concentration of Hg in sediment of the Seine basin determined from pre-historical deposits (Thevenot et al., 2007; Meybeck et al., 2007) was  $0.03 \text{ mg kg}^{-1}$ . The EF for the sediment in the Seine core varies between 10 in the top layer to a maximum 50 in the deeper layers. Therefore, although it is not possible to reconstruct the recent pollution history of the Seine mudflat using vertical Hg profiles from this highly disturbed sedimentary environment, these EFs suggest that the entire sediment core is contaminated with Hg.

Due to a lower sedimentation rate in the Medway estuary, the older sediments in the deeper part of the core ( $>70 \text{ cm}$ ) correspond to the pre-industrial times (pre-1880) and can be used to define a background concentration of Hg in sediment from this estuary. This background concentration ( $0.03 \text{ mg kg}^{-1}$ ) is the same as for the Seine River. The upper part of the Medway core shows enrichment of Hg compared to this background and the maximum of Hg ( $1.2 \text{ mg kg}^{-1}$ ) was found at 22 cm (Fig. 3). Although total Hg is significantly correlated with  $C_{\text{org}}$  over the entire core depth (Table 2), the profile of total Hg concentration normalized against  $C_{\text{org}}$  shows similar patterns to the Hg and  $C_{\text{org}}$  plots, indicating periods of increased Hg input into the estuary in the past. Using the sediment accumulation rate of  $4\text{--}5 \text{ mm a}^{-1}$ , the timing of historical inputs of Hg into the Medway estuary was calculated, indicating onset of Hg contamination at about 200 a ago, which reached a maximum between 1930 and 1970 after which it steadily decreased. According to Spencer et al. (2006) the source of this Hg contamination could be local paper mills, which used phenylmercuric acetate as a slimicide in wood storage piles until the middle of the 20th century and was an important industry in the Medway estuary from about 1700. The EF for Hg varies from 10 for the upper 10 cm of the Medway core to 42 at 26 cm. Due to different sedimentation rates in the Seine and the Medway mudflats direct comparison of the Hg contamination in the past is not possible.

#### 4.2. Factors affecting methylmercury distribution

In the Medway and Seine long cores, concentrations of MeHg and total Hg show similar patterns

(Fig. 2) and MeHg is significantly correlated ( $r > 0.8$ ,  $p < 0.001$ ) with total Hg (Table 2). Stepwise regression analysis was applied to identify the dominant variables (among Hg,  $C_{\text{org}}$ , SRM measured in the long cores) that explain the variability in MeHg concentration. This analysis indicates that 75% (Medway core) and 73% (Seine core) of the variability in MeHg concentration can be explained by variations in total Hg. Therefore, one factor influencing MeHg distribution in the long cores is the concentration of total Hg. Higher %MeHg in the surface ( $<30 \text{ cm}$ ) versus that in the deeper sediment layers suggests, however, that production of MeHg is mainly limited to surface sediment where microbial activity (SRM, Fig. 2) is high. High MeHg concentration in deeper Seine sediment suggests persistence of MeHg in older, buried sediment. The high sedimentation rate and discontinuous pattern of sedimentation on this mudflat (Deloffre et al., 2007) promote rapid burial of sediment resulting in anoxic conditions under which MeHg can be preserved; demethylation processes in this situation are probably minor as they are mostly driven by aerobic organisms (Ullrich et al., 2001). A peak of SRM abundance at a depth of 250 cm in the Medway core, which parallels maximum %MeHg at the same depth, indicates some MeHg formation in deep sediment.

In the upper part of the sediment cores, where total Hg concentrations were less variable (Fig. 3), correlation between MeHg and total Hg for the Medway core was found to be less significant than for the long core, and there was no correlation in the Seine short core (Table 2). In surface sediment where Hg methylation is active, production of MeHg is dependent on other parameters in addition to total Hg concentration. Although a correlation between MeHg and SRM was not found in any of the cores (Table 2), SRM activity peaks generally parallel those in MeHg concentration and %MeHg in depth profiles in the upper part of the cores (Fig. 3). Concentration of MeHg and SRM activity in the Medway and the Seine cores are good indicators of Hg methylation in these mudflats.

One of the principal differences between MeHg sediment data from the Medway and the Seine mudflats is the depth of maximum MeHg production. In the Medway sediments, the highest %MeHg is found just below sediment/water interface in the upper few cm of the sediment column, which is consistent with other studies of estuarine and marine sediment (Sunderland et al., 2004; Hammerschmidt

et al., 2004; Hammerschmidt and Fitzgerald, 2006). In the Seine sediment, the maximum %MeHg was found to be deeper (0.75% at 12 cm) and %MeHg in most of the remainder of the sediment column is lower (<0.2%, Fig. 3). The maximum %MeHg in the Seine core is coincident with the change from oxic to anoxic redox conditions and an increase in AVS and CRS concentrations (Fig. 3). Unstable redox and generally oxic conditions in the upper 15 cm of the Seine core are either unfavorable for Hg methylation or are favorable for Hg demethylation.

The patterns for MeHg, %MeHg, AVS, and anoxic Eh measurements in the Medway core (Fig. 3) all reflect conditions favourable for MeHg production, which have resulted in MeHg concentrations about four times higher in surface sediments compared to those of the Seine core. However, maximum SRM abundance and sediment MeHg at a depth of 25 cm in the Medway core is not followed with high %MeHg, which is probably attributed to less efficient Hg methylation in the presence of high sulphide concentration (demonstrated by increased AVS and CRS at this depth, Fig. 3).

#### 4.3. Relation between methylmercury and reduced sulphur species

In the upper part of the Medway core, MeHg correlates with AVS ( $r = 0.695$ ) and CRS ( $r = 0.868$ ) and total Hg correlates with CRS ( $r = 0.606$ , Table 2). However, in the upper part of the Seine core, these correlations were not found (Table 2). Conversely, when all samples from both cores are considered, MeHg is strongly correlated with AVS ( $r = 0.912$ ,  $p < 0.001$ ), CRS ( $r = 0.899$ ;  $p < 0.001$ ), and SRM ( $r = 0.431$ ,  $p < 0.05$ ) (Fig. 4). Stepwise regression analysis showed that, when all samples are taken into account, 88% of MeHg variation can be explained by combination of the AVS and SRM. Sediment samples from the Seine estuary are characterized by a much lower concentration of AVS (<1000 mg S kg<sup>-1</sup>, Fig. 4) than the Medway sediments (1000–6000 mg S kg<sup>-1</sup>), although the Seine data are more typical of other estuarine environments (e.g., Bay Autie and Bay Fresnay in Northern France, Billon et al., 2001). In addition to a strong correlation between MeHg and AVS in all Medway and Seine samples, a strong correlation was also found between total Hg and AVS ( $r = 0.706$ ,  $p < 0.001$ ) and total Hg and MeHg

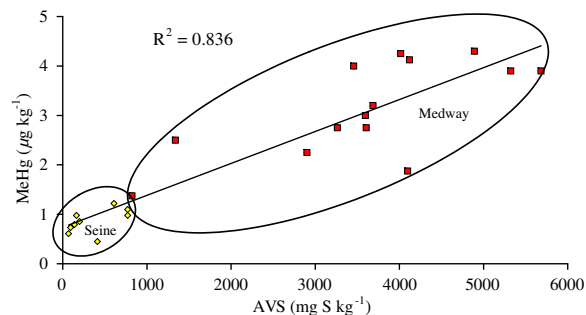


Fig. 4. Change in MeHg concentration as a function of AVS in samples from the Medway and the Seine mudflats.

( $r = 0.776$ ,  $p < 0.001$ ). These multiple correlations suggest that the relationship between MeHg and AVS is a result of complex interactions between Hg, MeHg, and AVS. Correlation between Hg and AVS can be explained by the strong tendency of Hg (and other metals) to form insoluble sulphides (Morse and Luther, 1999) and AVS, which has been proposed as a principal phase for sorbing Hg in AVS-rich sediment (Gagnon et al., 1997). So, the correlation between MeHg and AVS could be partly driven by the interaction of Hg and MeHg. However, the much stronger correlation between MeHg and AVS, and also correlation between %MeHg and AVS ( $r = 0.447$ ,  $p < 0.05$ ) suggest that reduced S species affect Hg methylation. Data and correlations shown here indicate that Hg methylation in the Medway and Seine mudflats is dominantly driven by microbial activity and reduced S species.

The role of solid sulphides in Hg methylation in aquatic sediment has been less widely investigated than the role of dissolved sulphide (Gilmour et al., 1998; Benoit et al., 1999, 2001; Hammerschmidt and Fitzgerald, 2004). One of the first studies considering the role of sulphides in Hg methylation in surface sediment of the Mersey and Clyde estuaries showed that an increase in MeHg concentration resulted when an optimal sulphide concentration was reached, of approximately 5800 mg S kg<sup>-1</sup> (Bartlett and Craig, 1981). Subsequently, Craig and Moréton (1986) defined for several other estuaries a sulphide concentration ranging between 2000 and 3000 mg S kg<sup>-1</sup> as the general limit affecting Hg methylation. Hintelmann and Wilken (1995) showed that an increase in MeHg concentration followed increasing AVS in sediment cores from the Elbe River, and related this to the affinity of MeHg for sulphide binding sites in AVS. A study investigating

parameters influencing MeHg distribution in surface sediment of Baltimore Harbour (Mason and Lawrence, 1999) failed to demonstrate a relationship between AVS and MeHg; a lack of correlation between Hg, MeHg, and AVS was explained by a low sediment pyritization and an important role of organic matter on Hg methylation. Hammerschmidt and Fitzgerald (2004, 2006) and Hammerschmidt et al. (2004), studied coastal sediment from Long Island Sound and found that Hg methylation was reduced where AVS was increased, which was related to reduced availability of Hg to methylating bacteria. Stoichev et al. (2004) found a co-dependence of MeHg with total S concentrations of up to 3000 mg S kg<sup>-1</sup> in the macrotidal Adour estuary. Obviously, AVS can have an important influence on MeHg in sediment; it can promote binding of MeHg to the sulphide, and thus, prevent its demethylation or it can inhibit MeHg production by limiting available dissolved inorganic Hg. The much better correlation between MeHg and AVS than between %MeHg and AVS obtained in the present study suggests that in the mudflats studied here (especially in the Medway estuary) the role of AVS in binding and stabilizing MeHg is more important than its negative effect on the MeHg production.

## Acknowledgements

This work was supported by the SEINE AVAL national program, the Region Nord Pas-de-Calais, and the INTERREG III program. We appreciate the helpful advice of O. CLARISSE, J.F. BARTHE and S. EL MEDOUN in field and laboratory analysis. We would like to thank Dr. John GRAY for a number of helpful suggestions and for editorial assistance.

## References

- Baeyens, W., Meuleman, C., Muhaya, B., Leermakers, M., 1998. Behaviour and speciation of mercury in the Scheldt estuary (water, sediments and benthic organisms). *Hydrobiologia* 366, 63–79.
- Bartlett, P.D., Craig, P.J., 1981. Total mercury and methylmercury levels in British estuarine sediments – II. *Water Res.* 15, 37–47.
- Benoit, J.M., Gilmour, C.C., Mason, R.P., Heyes, A., 1999. Sulphide controls on mercury speciation and bioavailability to methylating bacteria in sediment porewaters. *Environ. Sci. Technol.* 33, 951–957.
- Benoit, J.M., Gilmour, C.C., Mason, R.P., 2001. The influence of sulphide on solid-phase mercury bioavailability for methylation by pure cultures of *Desulfobulbus propionicus* (1pr3). *Environ. Sci. Technol.* 35, 127–132.
- Billon, G., Ouddane, B., Boughriet, A., 2001. Artefacts in the speciation of sulfides in anoxic sediments. *Analyst* 126, 1805–1809.
- Billon, G., Ouddane, B., Gengembre, L., Boughriet, A., 2002. On the chemical properties of sedimentary sulphur in estuarine environments. *Phys. Chem. Chem. Phys.* 4, 751–756.
- Bodaly, R.A., St. Louis, V.L., Paterson, M.J., Fudge, R.J.P., Hall, B.D., Rosenberg, D.M., Rudd, J.W.M., 1997. Bioaccumulation of mercury in the aquatic food chain in newly flooded areas. In: Sigel, A., Sigel, H. (Eds.), *Metal Ions in Biological Systems, Mercury and its Effects on Environment and Biology*, vol. 34. Marcel Dekker Inc., NY, pp. 259–287.
- Canário, J., Vale, C., Caetano, M., 2005. Distribution of monomethylmercury and mercury in surface sediments of the Tagus estuary (Portugal). *Mar. Pollut. Bull.* 50, 1142–1145.
- Canário, J., Branco, V., Vale, C., 2007. Seasonal variation of monomethylmercury concentrations in surface sediments of the Tagus estuary (Portugal). *Environ. Pollut.* 148, 380–383.
- Castelle, S., Schäfer, J., Blanc, G., Audry, S., Etcheber, H., Lissalde, J.P., 2007. 50-year record and solid state speciation of mercury in natural and contaminated reservoir sediment. *Appl. Geochem.* 22, 1359–1370.
- Chiffolleau, J.F., Auger, D., Chartier, E., Mîche, I.P., Truquet, I., Ficht, A., Gonzalez, J.L., Romana, L.A., 2001. Spatiotemporal changes in cadmium concentration in the Seine estuary (France). *Estuaries* 24 (6B), 1029–1040.
- Compeau, G.C., Bartha, R., 1985. Sulphate-reducing bacteria: principal methylators of mercury in anoxic estuarine sediment. *Appl. Environ. Microbiol.* 50, 498–502.
- Coquery, M., 1994. Biogeochemistry of mercury in estuarine and coastal environments. Ph.D. thesis, Univ. Paris 06, France.
- Cornwell, J.C., Morse, J.W., 1987. The characterization of iron sulphide minerals in anoxic marine sediments. *Mar. Chem.* 22, 193–206.
- Craig, P.J., Moreton, P.A., 1986. Total mercury, methylmercury and sulphide levels in British Estuarine sediments – III. *Water Res.* 20, 1111–1118.
- Cundy, A.B., Hopkinson, L., Lafite, R., Spencer, K., Taylor, J.A., Ouddan, B., Heppell, C., Carey, P., Charman, R., Shell, D., Ulliyott, S., 2005. Heavy metal distribution and accumulation in two *Spartina* sp. – dominated macrotidal salt marshes from the Seine estuary (France) and the Medway estuary (UK). *Appl. Geochem.* 20, 1195–1208.
- Deloffre, J., Lafite, R., Lesueur, P., Verney, R., Lesourd, S., Cuvilliez, A., Taylor, J., 2006. Controlling factors of rhythmic sedimentation processes on an intertidal estuarine mudflat – role of the turbidity maximum in the macrotidal Seine estuary, France. *Mar. Geol.* 235, 151–164.
- Deloffre, J., Verney, R., Lafite, R., Lesueur, P., Lesourd, S., Cundy, A.B., 2007. Sedimentation on intertidal mudflats in the lower part of macrotidal estuaries: sedimentation rhythms and their preservation. *Mar. Geol.* 235, 151–164.
- Foucher, D., 2002. Geochemistry of mercury in estuarine and coastal sediments: case studies in the Seine estuary (France) and the Kaštela bay (Croatia). Ph.D. thesis, Univ. Lille1, France.
- Gagnon, C., Pelletier, E., Mucci, A., 1997. Behaviour of anthropogenic mercury in coastal marine sediments. *Mar. Chem.* 59, 159–176.

- Gilmour, C.C., Riedel, G.S., Ederington, M.C., Bell, J.T., Benoit, J.M., Gill, G.A., Stordal, M.C., 1998. Methylmercury concentrations and production rates across a trophic gradient in the Northern Everglades. *Biogeochemistry* 40, 327–345.
- Hall, G.E.M., Pelchat, P., 1997. Evaluation of a direct solid sampling atomic absorption spectrometer for the trace determination of mercury in geological samples. *Analyst* 122, 924.
- Hammerschmidt, C.R., Fitzgerald, W.F., 2004. Geochemical controls on the production and distribution of methylmercury in near-shore marine sediments. *Environ. Sci. Technol.* 38, 1487–1495.
- Hammerschmidt, C.R., Fitzgerald, W.F., 2006. Methylmercury cycling in sediments on the continental shelf of southern New England. *Geochim. Cosmochim. Acta* 70, 918–930.
- Hammerschmidt, C.R., Fitzgerald, W.F., Lamborg, C.H., Balcom, P.H., Visscher, P.T., 2004. Biogeochemistry of methylmercury in sediments of Long Island Sound. *Mar. Chem.* 90, 31–52.
- Heyes, A., Miller, C., Mason, R.P., 2004. Mercury and methylmercury in Hudson River sediment: impact of tidal resuspension on partitioning and methylation. *Mar. Chem.* 90, 75–89.
- Hines, M.E., Faganeli, J., Adatto, I., Horvat, M., 2006. Microbial mercury transformations in marine, estuarine and freshwater sediment downstream of the Idrija Mercury Mine, Slovenia. *Appl. Geochem.* 21, 1924–1939.
- Hintelmann, H., Wilken, R.D., 1995. Levels of total mercury and methylmercury compounds in sediments of the polluted Elbe river: influence of seasonally and spatially varying factors. *Sci. Total Environ.* 166, 1–8.
- Kwokal, Z., Franciskovic-Bilinski, S., Bilinski, H., Branica, M., 2002. A comparison of anthropogenic mercury pollution in Kastela Bay (Croatia) with pristine estuaries in Ore (Sweden) and Krka (Croatia). *Mar. Pollut. Bull.* 44, 1150–1155.
- Lambertsson, L., Nilsson, M., 2006. Organic material: the primary control on mercury methylation and ambient methylmercury concentrations in estuarine sediments. *Environ. Sci. Technol.* 40, 1822–1829.
- Leloup, J., Quillet, L., Oger, C., Boust, D., Petit, F., 2004. Molecular quantification of sulphate-reducing microorganisms (carrying *dsrAB* genes) by competitive PCR in estuarine sediments. *FEMS Microbiol. Ecol.* 47, 207–214.
- Leloup, J., Petit, F., Boust, D., Deloffre, J., Bally, G., Clarisse, O., Quillet, L., 2005. Dynamic of sulphate-reducing microorganisms (*dsrAB* genes) in two contrasting mudflats of the Seine estuary (France). *Microbiol. Ecol.* 59, 307–314.
- Lesourd, S., Lesueur, P., Brun-Cottan, J.C., Auffret, J.P., Poupinet, N., Laignel, B., 2001. Morphosedimentary evolution of the macrotidal Seine estuary subjected to human impact. *Estuaries* 24 (6B), 940–949.
- Liang, L., Horvat, M., Bloom, N.S., 1994. An improved speciation method for mercury by GC/CVAFS after aqueous phase ethylation and room temperature precollection. *Talanta* 41, 371–379.
- Mason, R.P., Benoit, J.M., 2003. Organomercury compounds in the environment. In: Craig, P.J. (Ed.), *Organometallic Compounds in the Environment*. John Wiley & Sons, pp. 57–100.
- Mason, R.P., Lawrence, A.L., 1999. Concentration distribution and bioavailability of mercury and methylmercury in sediments of Baltimore Harbour and Chesapeake Bay, Maryland, USA. *Environ. Toxicol. Chem.* 18, 2438–2447.
- Mason, R.P., Kim, E.H., Cornwell, J., Heyes, D., 2006. An examination of the factors influencing the flux of mercury, methylmercury and other constituents from estuarine sediment. *Mar. Chem.* 102, 96–110.
- Meybeck, M., Horowitz, A.J., Grosbois, C., 2004. The geochemistry of Seine river basin particulate matter: distribution of an integrated metal pollution index. *Sci. Total Environ.* 328, 219–236.
- Meybeck, M., Lestel, L., Bonte, P., Moilleron, R., Colin, J-L., Rousselot, D., de Ponteves, C., Grosbois, C., Thevenot, D.R., 2007. Historical perspective of heavy metals contamination (Cd, Cr, Cu, Hg, Pb, Zn) in the Seine River basin (France) following a DPSIR approach (1050–2005). *Sci. Total Environ.* 375, 204–231.
- Mikac, N., Niessen, S., Ouddane, B., Wartel, M., 1999. Speciation of mercury in sediments of the Seine estuary (France). *Appl. Organometal. Chem.* 13, 715–725.
- Miramand, P., Guyot, T., Rybarczyk, H., Elkaim, B., Mouny, P., Dauvin, J.C., Bessineton, C., 2001. Contamination of the biological compartment in the Seine estuary by Cd, Cu, Pb and Zn. *Estuaries* 24 (6B), 1056–1065.
- Morse, J.W., Luther III, G.W., 1999. Chemical influences on trace metal-sulphide interactions in anoxic sediments. *Geochim. Cosmochim. Acta* 63, 3373–3378.
- National Rivers Authority, 1991. River Medway Catchment Management Plan Phase 1. NRA, Southern Region, Worthing, Sussex.
- Niessen, S., Foucher, D., Clarisse, O., Fischer, J.C., Mikac, N., Kwokal, Z., Fajon, V., Horvat, M., 2003. Influence of sulphur cycle on mercury methylation in estuarine sediment (Seine estuary, France). *J. Phys. IV France* 107, 953–956.
- Pethick, J.S., 1993. The Medway estuary; Coastal Processes and Conservation. Institute of Coastal and Estuarine Studies, University of Hull, Hull.
- Rickard, D., Morse, J.W., 2005. Acid volatile sulphide (AVS). *Mar. Chem.* 97, 141–197.
- Schafer, J., Blanc, G., Cossa, D., Audry, S., Bossy, C., 2006. Mercury in the Lot-Garonne river system (France): sources, fluxes and anthropogenic component. *Appl. Geochem.* 21, 515–527.
- Spencer, K., Cundy, A.B., Croudace, I.W., 2003. Heavy metal distribution and early-diagenesis in salt marsh sediments from the Medway estuary, Kent, UK. *Estuar. Coast. Shelf Sci.* 56, 1–12.
- Spencer, K.L., MacLeod, C.L., Tuckett, A., Johnson, S.M., 2006. Source and distribution of trace metals in the Medway and Swale estuaries, Kent, UK. *Mar. Pollut. Bull.* 52, 226–230.
- Stoichev, T., Amouroux, D., Wasserman, J.C., Point, D., De Diego, A., Bareille, G., Donard, O.F.X., 2004. Dynamic of mercury species in surface sediments of a macrotidal Estuarine-Coastal system (Adour River, Bay of Biscay). *Estuar. Coast. Shelf Sci.* 59, 5111.
- Sunderland, E.M., Gobas, F.A.P.C., Heyes, A., Branfireun, B.A., Bayer, A.K., Cranston, R.E., Parsons, M.B., 2004. Speciation of mercury in well mixed estuarine sediments. *Mar. Chem.* 90, 91–105.
- Sunderland, E.M., Gobas, F.A.P.C., Branfireun, B.A., Heyes, A., 2006. Environmental controls on the speciation and distribution of mercury in coastal sediments. *Mar. Chem.* 102, 111–123.



- Thevenot, D.R., Moilleron, L., Gromaire, M.-C., Rocher, V., Cambier, P., Bonte, P., Colin, J.L., de Ponteves, C., Meybeck, M., 2007. Critical budget of metal sources and pathways in the Seine River basin (1994–2003) for Cd, Cr, Cu, Hg, Ni, Pb and Zn. *Sci. Total Environ.* 375, 180–203.
- Ullrich, S.M., Tanton, T.W., Abrdashitova, S.A., 2001. Mercury in the aquatic environment: a review of factors affecting methylation. *Crit. Rev. Environ. Sci. Technol.* 31, 241–293.
- Ullrich, S.M., Ilyushchenko, M.A., Kamberov, I.M., Tanton, T.W., 2007. Mercury contamination in the vicinity of a derelict chlor-alkali plant Part I: Sediment and water contamination of lake Balkyldak and the river Irtysh. *Sci. Total Environ.* 381, 1–16.