Biogeochemistry (2013) 114:341–358
DOI 10.1007/s10533-012-9815-z

MMHg production and export from intertidal sediments to the water column of a tidal lagoon (Arcachon Bay, France)

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Received: 24 February 2012 / Accepted: 26 November 2012 / Published online: 7 February 2013

Abstract Hg cycling in biologically productive coastal areas is of special importance given the potential for bioaccumulation of monomethylmercury (MMHg) into aquatic organisms. Field experiments were performed during three different seasons in Arcachon Bay, a mesotidal lagoon (SW France), to assess the variability of the water column concentrations, sediment–water exchanges and potential formation and degradation of MMHg. The objectives were to evaluate the contribution of intertidal mudflats to MMHg production and the various pathways of Hg species export. Dissolved and bulk concentrations of Hg species in the water column downstream of tidal flats were measured throughout several tidal cycles. The Hg benthic fluxes at the sediment–water interface were determined by means of benthic chambers for three different stations. Hg methylation and demethylation potentials were determined in surficial sediments and the water column using isotopic tracers. The tidal surveys demonstrated that benthic remobilization of Hg occurs primarily in association with sediment erosion and advection during ebb tide. However, elevated dissolved Hg concentrations observed at low tide were found to be caused by a combination of pore-waters seeping, benthic fluxes and methylation in the water column. Benthic fluxes were more intense during late winter conditions (median MMHg and inorganic Hg (IHg) fluxes: 64 and 179 pmol m^{-2} h^{-1}, respectively) and subsequently decreased in spring (median 0.7 and −5 pmol m^{-2} h^{-1}, respectively) and fall (median −0.4 and −1.3 pmol m^{-2} h^{-1}, respectively). The trends in methylation and demethylation potentials were at the opposite of the fluxes, two times lower during winter than for spring or fall conditions. In this tidal environment, MMHg production in surface sediments and its subsequent release is estimated to be the major source of MMHg to the water

Electronic supplementary material The online version of this article (doi:10.1007/s10533-012-9815-z) contains supplementary material, which is available to authorized users.

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column during winter and spring time. However, during the more productive summer period, the Hg methylation extent in the water column may be very significant and equivalent to the sediment contribution.

Keywords Mercury species · Coastal ecosystem · Tidal cycling · Benthic reactivity

Introduction

Coastal ecosystems are among the most productive ecosystems on Earth due to important continental inputs, including organic matter and nutrients. Besides the relatively well documented effects of on-going eutrophication (Castel et al. 1996, De Wit et al. 2001), they are also under the constant pressure of contaminant inputs. In shallow tidal ecosystems, extended intertidal sediments support intense biogeochemical transformations, especially organic matter mineralization. Consequently, strong solute exchanges are established between intertidal sediment and the water column during immersion (e.g. Mortimer et al. 1999) and tidal pumping has been demonstrated to favor nutrient release from tidal flat sediments to the water column during low tide (Deborde et al. 2008a). Furthermore, the specific redox regime induced by tides has been demonstrated to affect the Hg species transformations and partitioning in sediments (Bouchet et al. 2011a) but overall Hg cycling in tidal environments remains poorly characterized.

Sediments act primarily as a sink for contaminants such as heavy metals (Gagnon et al. 1997, Ramalhosa et al. 2006a) but under various conditions, sediments may also act as a source of contaminants to the water column. Some previous studies have already demonstrated that the water column concentrations can be significantly influenced by benthic fluxes in Hg-impacted ecosystems (see detailed references below). However, the benthic exchanges of trace metals, especially Hg, are not yet well understood in low-impacted coastal ecosystems, precluding an evaluation of their significance as a MMHg source compared to methylation occurring in the water column (Monperrus et al. 2007a; Cossa et al. 2009). The difficulty to acquire reliable data prevents the establishment of frequent observations of the exchange mechanisms involved. Indeed, the measurements of benthic fluxes remain difficult to achieve, especially in highly dynamic environment such as tidal bays.

One of the ideas emerging from the examination of pore water concentrations profiles is that the mineralization of organic matter and/or the reductive dissolution of Fe\Mn-oxyhydroxides release associated trace metals that may further diffuse to the water column if not trapped with sulfides or back again with Fe\Mn-oxyhydroxides (e.g. Gagnon et al. 1997; Bloom et al. 1999; Ramalhosa et al. 2006b). However, previous studies that investigated the benthic Hg cycling, either in polluted (Covelli et al. 1999, 2008; Gill et al. 1999) or moderately contaminated sites (Choe et al. 2004; Point et al. 2007), demonstrated the relative unimportance of diffusive fluxes compared to that of advective transport resulting from biological activities. Diffusive fluxes often underestimate real fluxes and may even predict opposite directions, strengthening the importance of direct flux assessment methods. Nowadays, benthic chambers appear as one of the most suitable methods to estimate benthic fluxes in situ (see Thouzeau et al. 2007 for review). The net fluxes measured by this method are the result of several components, such as the diffusive and advective fluxes driven by bioturbation (Boucher and Boucher-Radoni 1988), but they also encompass the chemistry that might occur at the sediment–water interface, e.g. methylation or demethylation and any reactions that can act as a sink or source for a given species (Point et al. 2007).

MMHg in the water column usually originates from methylation in the water column itself or production in sediments followed by remobilization through various pathways, i.e. diffusive fluxes, physically or biologically induced advective fluxes and desorption from eroded particles. However, in tidal environments, there is a strong physical stress at the sediment–water interface given the combined action of tides and waves and pore-waters from intertidal sediments are effectively flushed out and mixed by tidal pumping. We thus hypothesized that MMHg produced in intertidal mudflat sediments might then be efficiently exported to the water column through different processes and wanted to compare it to the methylation occurring in the water column itself.

Since both MMHg production and transfers are extremely dependent on biological activity, large seasonal variabilities were expected and experiments were therefore performed in late winter, spring and late summer at three different stations in the upper part of Arcachon Bay. This work presents, for the first time,

a simultaneous assessment of Hg species benthic exchanges through various pathways and sediment/water transformation extents among different sites and seasons in a tidal lagoon. Tidal cycle surveys combined with short-term benthic fluxes measurements and Hg species transformations potentials in waters and sediments were carried out in an attempt to evaluate the respective influence of the different processes as MMHg sources to the water column. Relevant biogeochemical reactions towards Hg species exchanges are also discussed including a tentative examination of the effects of macrophyte meadows present in the intertidal zone.

Materials and methods

Study area

Arcachon Bay is a 156 km^2 mesotidal lagoon located on the French Atlantic coast (44°40′ N, 1°10′ W). The tide is semi-diurnal and the tidal amplitude varies from 0.8 to 4.6 m. Surface water temperature fluctuates seasonally between 1 and 25 °C, and surface water salinity between 22 and 32 PSU. At low tide, large tidal flats (114 km^2), located at the back of the bay, are exposed to the atmosphere about 15 h per day. Up to 70 km^2 of these tidal flats are covered by Zostera noltii meadows, while Zostera marina occupies only 4 km^2 (Auby and Labourg 1996). Station 1 (Fig. 1) is located on the intertidal part of a sandy beach comprised of permeable sediments (mean grain size ~250 µm, porosity ~0.4). Two other stations are located in the inner part of the lagoon, on a tidal mudflat characterized by a Z. noltii meadow (Station 3) and an area free of macrophytes (Station 2). Station 4 is a subtidal station located in the channel draining waters from the tidal flats where stations 2 and 3 are located. Stations 2, 3 and 4 are covered by cohesive silty materials (15–50 µm, porosity ~0.8), homogeneously distributed over the stations investigated (Deborde et al. 2008b). The sampling sites are representative of the different hydro-sedimentary and biological conditions of the intertidal mudflats found in the upper part of the lagoon (Fenies and Faugères 1998, Blanchet et al. 2005). The landward part of the bay receives moderate river inputs and underground freshwater discharges (Canton et al. 2010) with only a small river (0.12–0.16 $m^3\ s^{-1}$ annual mean discharge) connected to the channel investigated in this study (St. 4).

Diurnal cycles

The dissolved and particulate Hg species concentrations in the water column of the channel draining the tidal flats were studied over a 24 h-cycle at the subtidal St. 4 in May 2006 and October 2007. Every two hours, 5 L of bulk water were sampled at 1 m depth in acid-cleaned

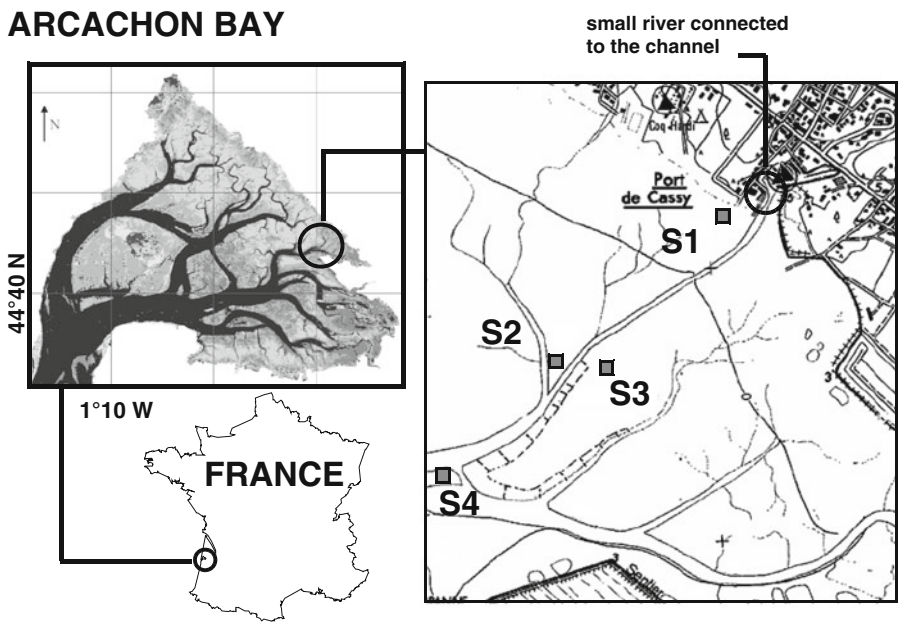

Fig. 1 Detailed map of the different study sites in Arcachon Bay. S1: sandy permeable sediments; S2: uncovered muddy sediments; S3: muddy sediments covered with Zostera Noltii; S4: subtidal station (scale 1:250)

polyethylene jars for the particulate fraction and another 1 L was collected in acid-cleaned polypropylene bottle (Nalgene) for the dissolved fraction (i.e. filter passing, 0.45 μm). After being transferred to the on-site laboratory, an appropriate amount of water (500 mL) was filtered for the dissolved fraction analyses and a variable amount of bulk water (between 1 and 4 L) was filtered to collect enough particles for Hg species analyses. The overall enrichments in dissolved Hg species over tidal cycles were averaged from the differences between the values recorded at low and high tide.

Benthic chamber deployment

Measurements of benthic fluxes were carried out in situ using large-sized scuba diver-operated benthic chambers that proved to be reliable tools for measuring benthic fluxes, when compared to core incubation techniques (Dedieu et al. 2007, Thouzeau et al. 2007). The benthic chambers' surface area is 0.2 m^2 with an internal volume ranging from 55 to 75 L depending on how deep the base was inserted into the sediment (from 10 to 15 cm). The chamber setup was carefully designed to minimize the biases due to enclosures on hydrodynamics (bottom current and turbulence) and on biological activities driving the solute exchanges between the compartments (Tengberg et al. 2004, 2005). Pump stirrers with diffusers were used since they give a more even distribution of bottom currents and diffusive boundary layer (DBL) thicknesses than paddle wheel-type stirrers (Tengberg et al. 2005). Homogenization of water inside the enclosure was provided by adjustable submersible pumps connected to waterproof batteries (closed-circuit water circulation). As metabolic responses depend on hydrodynamics (Patterson et al. 1991; Forja and Gomez-Parra 1998), water flow in each enclosure was adjusted to the minimum value (2 L min^{-1}), allowing stable continuous measurements of oxygen concentration, temperature, salinity and pressure to be recorded by YSI 6920 probes (Table 1). Short-time incubations were performed to avoid hypoxic conditions to develop within the chambers. Incident irradiance was also measured continuously in one of the chambers during light incubations, using a LI-192SA quantum sensor connected to a LI-1000 data logger. For each incubation series, three benthic chambers (separated by a distance of about 2 m) were deployed simultaneously at each site. For the intertidal stations (2 and 3), the chambers were installed at flood tide and when the water height was at least of 0.8 m. The incubations roughly started 2 h before high tide and ended 1 h after. The chamber setup, equilibration (1 h 15 min) and operating conditions appropriate for trace metal flux measurements are described in Point et al. (2007), as well as the flux calculations and uncertainties while trace metal analyses (other than Hg) are described in the supplementary information. The chambers were re-opened for 20 min between dark and light incubations to restore ambient conditions. The incubations were performed in March 2005, May 2006 and October 2007 in daylight (21 incubations) and dark conditions (24 incubations) for short periods (from 1 h 50 min to 5 h) to minimize the disturbance at the sediment–water interface. The data statistical treatment and error-weighted least squares linear regressions were performed with Origin® software. Six data points out

Table 1 Summary of environmental parameters measured during the field campaigns in Arcachon Bay

		March 2005	May 2006	October 2007
Tide range (m)		2.2–4.1	2.1–3.2	1.5–3.3
Air temperature (°C)[a]		−2–10	14–29	8–25
Bottom water temperature (°C)		5.7–8.6	17.2–20.6	17.6–19.3
Bottom water salinity (PSU)		26.0–27.5	26.0–28.9	31.3–32.1
Bottom water oxygenation (%)		114 ± 7	86 ± 7	98 ± 4
Bottom Photosynthetic	S2	166 (78)	nd	420–920
Active Radiation (μmol m^{-2} s^{-1})[b]	S3	8 (9)	45 (54)	60–310
	S4	nd	~0	54–20

[a] Range of data recorded by the closest National Meteorological Survey station

[b] Mean value (±SD) or range recorded during benthic chamber incubations under light conditions

nd: not determined

of 45 were removed due to experimental problems or because they were outliers.

The O_2 level in the chambers did not vary by more than 10 % and decreased smoothly over time, which is indicative of a steady benthic respiration regime. The sediment–water interface consisted in the sediment surface; no nepheloïd layer was visually observed. At the end of the incubation, 3–5 sediment cores placed randomly in each chamber were collected manually by divers to determine macrofaunal abundance and biomass (described in the supplementary information). In addition, 2–3 sediment cores were also carefully collected in each chamber, subsequently sliced every cm or half cm in the top first two cm and down to 13–17 cm and analyzed for ancillary data (supplementary information) while an aliquot of the top two centimeters was kept frozen for solid Hg species analysis.

Hg species transformation assessments

The methylation/demethylation potentials were periodically assessed in the water column in May 2006 and October 2007 and in surficial sediments (0–2 cm) in October 2007 and January 2008 (St. 2 solely). The transformation experiments consisted of 24 h-incubations with isotopic-enriched tracers (^{199}IHg and ^{201}MMHg) as described in Monperrus et al. (2007a, b). The amount of tracer added was carefully evaluated to maintain the ambient species concentrations (typical range: 20–150 % although IHg and MMHg reached up to 500 and 1100 % in one water incubation). For the sediment incubations, 5 mL of percolating pore-waters were added to a few grams of wet sediments, collected at low tide at St. 1, 2 and 3, to ensure a better homogenization of the slurries and the isotopic tracers were added after equilibration for 15 min with pore-waters, under suboxic conditions. The sediment incubations were carried out as slurries in 30 mL glass vials sealed with Teflon caps, stored in double zip-bags and immersed in water to maintain a constant temperature. The incubations were carried out either as dark controls or under natural diurnal cycle conditions and the temperature variations were moderated with periodic on-site water renewal.

The water incubations were carried out with water sampled at high tide at the subtidal St. 4. The influence of dark and light conditions was evaluated on both bulk and filtered waters. The incubations were done with 500 mL transparent PFA bottles, avoiding any headspace. The bottles were stored in double zip-bags and incubated for 24 h in near-shore waters, again either as dark controls or under natural diurnal cycle conditions. Given that UV light transmission across PFA is not complete, species transformations and especially demethylation might be underestimated under light conditions (Lehnherr and Louis 2009) but transformation rates were not corrected for, due to large uncertainties in this potential artifact.

Sample treatments

All samples for trace metal and Hg species determinations were treated according to clean procedures and using acid cleaned material. All water samples were filtered within a few hours after collection under a class 100 portable laminar flow hood (ADS Laminaire, France) using 500 mL Polysulfone filtering units (Sartorius) fitted with 0.45 μm acid cleaned Durapore PVDF filters (47 mm diameter, Millipore). For trace metals other than Hg, the dissolved fractions were collected in 125 mL (LDPE) Nalgene bottles and stabilized with 1 % HNO3 (J.T. Baker, Ultrex). For Hg species, the dissolved fractions were poured in 250 mL PFA Nalgene bottles and stabilized at pH 2 with HCl (J.T. Baker, Ultrex). The samples were then stored in double Ziploc plastic bags at 4 °C in the dark. Blanks were regularly performed, using the same protocol with 18.2 MΩ MQ water (Millipore). The sediments were kept at −20 °C before being freeze-dried and subsequently extracted for analyzes. The filters were kept in the same conditions as well as blank filters to correct for Hg contamination and dried under a laminar flow hood for 48 h before extraction.

Hg speciation analyses

Hg speciation analyses were carried out by species-specific isotope dilution and GC-ICPMS (Focus GC Thermo-Finnigan, X7 II ICPMS Thermo Elemental) detection according to Monperrus et al. (2005), allowing species interconversion to be corrected. Potential dimethylmercury (DMHg) degradation in MMHg after acidification couldn't be corrected by this methodology; however DMHg was demonstrated to be negligible in underlying sediments (Bouchet et al. 2011a) and in the water column for all seasons investigated (unpublished results). Briefly, 100 mL of the water sample were spiked with ^{199}IHg and

^{201}MMHg of known isotopic composition and concentrations, buffered with 5 ml of 0.1 M sodium acetate buffer (pH 4). After a pH adjustment (pH 4), proper volumes of isooctane and of 1 % (w/v) sodium tetrapropylborate were added. The flask was immediately capped and vigorously manually shaken for 5 min. The organic phase was then transferred to a 2 mL vial and injected in triplicate into the GC-ICPMS using an autosampler. Solid phase Hg species were analyzed according to the same protocol after a microwave acidic extraction (HNO_3, Hg < 5 ppb, Fluka Analytical) (Monperrus et al. 2007b). The typical detection limits reached during the sample analyses were 10^{-2} pmol L^{-1} for the dissolved species and 0.15 pmol g^{-1} for the solid species.

Results

Biogeochemistry of the superficial sediments

Solid phase

The carbon and sulfur contents ranged from 2.1 to 4.9 % and 0.9 to 2.0 %, respectively and were lower in October (late summer) 2007 (Table 2). The concentrations of reactive Fe-oxyhydroxides were slightly higher for St. 2 (120–135 μmol g^{-1}) than for the two other sites (73–94 μmol g^{-1}) and spatial and temporal variations were limited. The Mn-oxyhydroxides levels were the lowest at St. 3 (≤DL to 0.3 μmol g^{-1}) and similar for St. 2 and 4 (4.2–5.3 μmol g^{-1}) in winter and spring conditions while rather equivalent in late summer (0.3–0.7 μmol g^{-1}). The concentrations of P associated with Fe-oxyhydroxides ranged from 4.6 to 9.8 μmol g^{-1} and appeared lowest in October 2007. The macrofauna biomasses were equivalent for the late winter and spring conditions (Table 2). Higher biomasses were observed for St. 3 (20–38 g AFDW m^{-2}), compared to St. 2 or 4 (1–19 g AFDW m^{-2}), due to the structural role of the seagrass meadows present at St. 3 (Deborde et al. 2008b).

Dissolved phase

A previous study demonstrated that the presence of solid oxidized compounds in these muddy sediments was always limited to the upper 2–3 mm of sediments (Deborde et al. 2008b). Early diagenesis recycled products, such as ΣCO_2, NH_4^+, DIP, Fe(II) and Mn(II) increased directly below the surface (Figure SI-1), demonstrating that sub-oxic and anoxic processes of organic matter mineralization occurred as already shown (Deborde et al. 2008b). ΣCO_2 and NH_4^+ concentrations exceeded 3 mM and 200 μM below 2 cm depth, respectively, and gradually increased below. Over the first 10 cm, Fe(II), Mn(II) and H_2S generally leveled off at 30, 80 and 360 μM, although some higher levels have been rarely observed for Fe (up to 645 μM) and H_2S (820 μM). It is important to note that H_2S always remained low (<15 μM) over the first 3 cm, the important load of Fe to Arcachon Bay is

Table 2 Hg species concentrations and main biogeochemical parameters in surficial sediments collected in the benthic chambers

			IHg pmol g^{-1}	MMHg pmol g^{-1}	C-tot %	S-tot (%)	Fe-asc μmol g^{-1}	Mn-asc μmol g^{-1}	PO_4-asc μmol g^{-1}	Macrofauna g m^{-2} (AFDW)
2005	Intertidal	S2	1108 ± 156	4.4 ± 0.4	4.2 ± 0.5	1.8 ± 0.1	120 ± 10	4.2 ± 0.7	7.2 ± 1.1	5 ± 5
	Zostera	S3	957 ± 129	3.5 ± 1.0	4.9 ± 0.4	1.9 ± 0.1	93 ± 16	0.3 ± 0.1	3.8 ± 0.3	35 ± 31
2006	Intertidal	S2	972 ± 13	4.6 ± 0.1	4.4 ± 0.6	2.0 ± 0.3	126 ± 8	5.3 ± 4.8	9.6 ± 0.4	5 ± 6
	Zostera	S3	840 ± 40	6.7 ± 0.3	4.3 ± 0.8	1.7 ± 0.4	94 ± 1	≤DL	8.0 ± 0.2	38 ± 25
	Subtidal	S4	1022 ± 25	8.5 ± 6.5	2.8 ± 0.5	1.1 ± 0.3	93 ± 13	5.0 ± 0.3	9.8 ± 1.4	3 ± 2
2007	Intertidal	S2	1225 ± 65	6.4 ± 1.6	3.4 ± 0.4	1.5 ± 0.8	135 ± 2	0.3 ± 0.4	6.9 ± 0.8	19 ± 11
	Zostera	S3	992 ± 224	5.3 ± 1.5	2.1 ± 1.1	0.9 ± 0.8	73 ± 19	0.7 ± 0.6	4.6 ± 1.7	20 ± 12
	Subtidal	S4	754 ± 173	4.2 ± 1.6	2.3 ± 0.1	1.1 ± 0.6	73 ± 10	nd	4.7 ± 0.1	1 ± 1

Hg species concentrations (mean ± SD) were generally averaged from three surficial subsamples (2 cm depth) from sediment cores collected inside the benthic chamber (min 2 and max 6 subsamples). Geochemical parameters were averaged from two or three surficial subsamples from sediments cores collected at the same location (Fe/Mn/PO_4-asc: reactive phases extracted by an ascorbic reagent, see SI). Macrofauna biomasses were averaged from five sediment cores collected in each benthic chambers

nd not determined

known to be an efficient mechanism against the buildup of high dissolved sulfide concentrations (Stal et al. 1996).

The O_2 benthic fluxes measured in each benthic chamber represent the net balance between the O_2 produced by the photosynthetic activity and the O_2 consumed by the heterotrophic activity, located mainly in the sediment. The mean O_2 benthic fluxes ranged from −7.9 to 2.4 mmol m^{-2} h^{-1} over the three years and averaged −1.6 mmol m^{-2} h^{-1}, emphasizing that heterotrophic consumption generally dominated production (Supplementary Table 1).

Diurnal and tidal variability of Hg species

Time–series measurements were conducted at the subtidal St. 4 to examine the variability of the Hg species concentrations in the water column of the channel draining the tidal flats during tidal events (Fig. 2). Turbidity varied between 5–28 NTU in May 2006 versus 4–18 NTU in October 2007, and was the highest during ebb tide. The bulk MMHg concentrations ranged from 0.12 to 0.67 pmol L^{-1} and the bulk IHg concentrations from 9 to 88 pmol L^{-1}. They both exhibited clear and similar patterns related to the tidal level with maxima recorded during ebb tide and strongly associated with turbidity peaks while minima were observed at high tide. The dissolved concentrations of MMHg displayed significant variations with tide in 2006, from 0.07 pmol L^{-1} during flood tide to maxima at low tide of 0.18 and 0.22 pmol L^{-1}, i.e. an averaged 0.13 pmol L^{-1} enrichment following tidal flats immersion. In 2007, the dissolved MMHg varied from a minimum of 0.07 pmol L^{-1} to maxima of 0.09 and 0.10 pmol L^{-1}, i.e. a lower averaged enrichment (0.02 pmol L^{-1}) compared to 2006. The dissolved IHg concentrations ranged from 4.8 to 8.2 pmol L^{-1} in 2006, showing enrichment at high tide. They ranged from 2.9 to 4.3 pmol L^{-1} in 2007 with slight enrichments of about 0.9 pmol L^{-1} observed at low tide, in opposition with the previous observations.

The dissolved and particulate concentrations of Hg species are displayed in Fig. 3 according to the salinity level. The MMHg particulate concentrations (5–15 pmol g^{-1}) were similar to the sediment concentrations (2–16 pmol g^{-1}) while IHg particulate concentrations (903–3708 pmol g^{-1}) were higher than the sediments values (523–1305 pmol g^{-1}). This latter is explained by a more important resuspension of finer particles, relatively enriched in IHg, during the tidal cycles. Significant negative correlations exist between both dissolved and particulate concentrations and the salinity level over the two years (given in the caption of Fig. 3). They demonstrate that the channel investigated (where St. 4 is located) behaves as a small-scale estuary with a mixing of upstream inputs and oceanic waters. Unfortunately, the salinity range is too narrow and the data too scattered to fully discuss the conservative nature of the Hg behavior and related sorption/desorption processes (cf. first discussion paragraph). The small river connected to the channel does not represent a significant Hg upstream source, considering its low discharge and low dissolved concentrations. For example, dissolved MMHg and IHg concentrations were 0.55 and 0.90 pmol L^{-1} in October 2007, respectively, in this small river. As well, Hg species concentrations are lower in the coastal marine waters off the Bay compared to the inner waters. For example, dissolved MMHg varied between 0.12 and 0.18 pmol L^{-1} and IHg between 1.8 and 4.1 pmol L^{-1} in surface coastal waters collected in April 2007 in the Bay of Biscay. It is to be noted that the ambient Hg species concentrations recorded in benthic chambers were higher than concentrations measured in the channel and were in the upper part of the mixing line for the two seasons studied (hatched boxes, Fig. 3).

Hg species concentrations at the sediment–water interface

The mean solid IHg concentrations in surficial sediments, collected in the benthic chambers, ranged between 754 ± 173 and 1225 ± 65 pmol g^{-1} and exhibited little differences between the stations and among seasons, as observed for the major geochemical parameters (Table 2). The spatial heterogeneity, assessed by three measurements per chamber was also limited, between 1 and 23 % (RSD). The mean solid MMHg concentrations (3.5 ± 1.0–8.5 ± 6.5 pmol g^{-1}) exhibited much larger spatial variations among and within stations (2–76 %). A seasonal pattern was also observed with MMHg maxima recorded in May 2006 (7 ± 4 pmol g^{-1} compared to 4 ± 1 and 5 ± 2 pmol g^{-1} in March 2005 and October 2007, respectively), even if the results were not significantly different due to large spatial variations.

The distributions of the bottom water concentrations of Hg species (initial samples collected in the

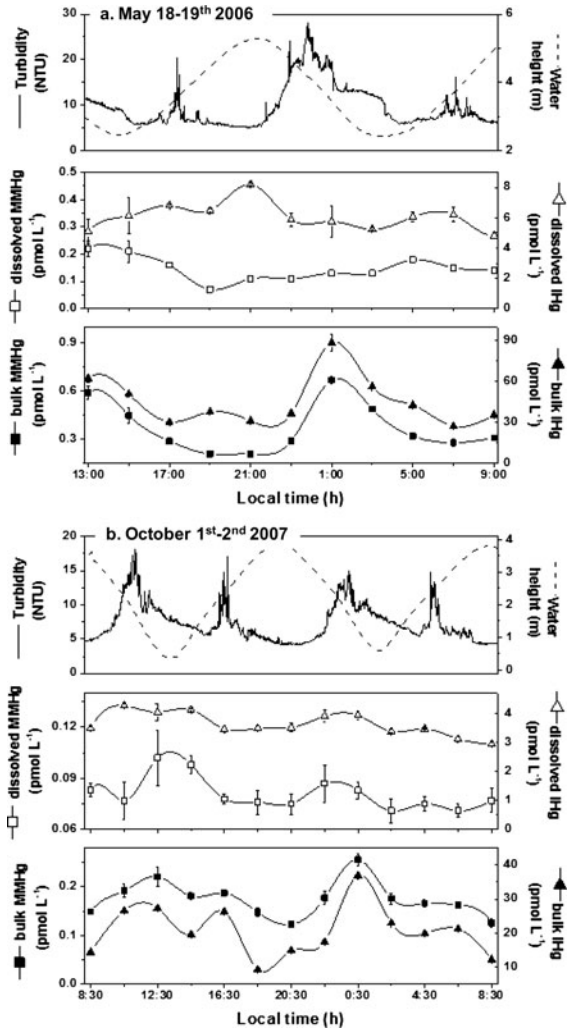

Fig. 2 Hg species remobilization during tidal cycles. The dissolved species were measured in the filter-passing fraction (0.45 μm) while the bulk concentrations were recalculated from dissolved and particulate fractions

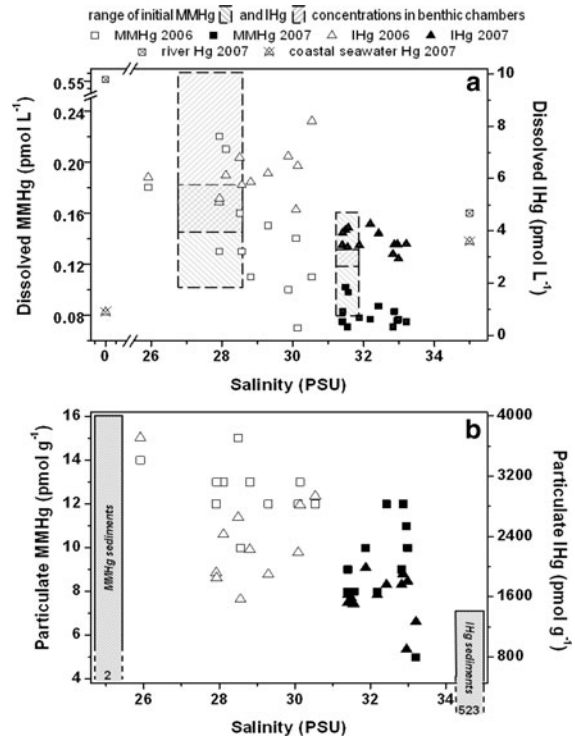

Fig. 3 Hg species dissolved (**a**) and particulate (**b**) concentrations as a function of salinity recorded during tidal surveys in the channel over the St. 4. Concentrations measured in the small river connected to the channel (salinity 0) and measured in coastal waters during a cruise in the Bay of Biscay in April 2007 (salinity 35) are also indicated. The *hatched boxes* indicate the ranges of species concentrations measured initially in the benthic chambers for the two seasons investigated. The equations for the significant negative correlations (p-values < 0.001) between the concentrations and the salinity (S) are: dissolved MMHg: $y = -0.02S + 0.66$, $R^2 = 0.67$; dissolved IHg: $y = -0.5S + 20.6$, $R^2 = 0.49$; particulate MMHg: $y = -0.8S + 35$, $R^2 = 0.42$; particulate IHg: $y = -193S + 7850$, $R^2 = 0.39$

benthic chambers) over the three campaigns are shown in the supplementary section (Figure SI-2). In the case of MMHg (Figure SI-2a), 50 % of the values measured were between 0.11 and 0.26 pmol L^{-1} while the mean (0.5 ± 0.8 pmol L^{-1}) was strongly influenced by the data recorded in 2005. The highest MMHg concentrations in bottom waters were recorded in March 2005, ranging from 1.0 to 2.1 pmol L^{-1} (Table 3). The mean MMHg concentrations (averaged from the three benthic chambers) ranged from 0.09 to 0.19 pmol L^{-1} and from 0.08 to 0.20 pmol L^{-1} in May 2006 and October 2007, respectively. The individual IHg concentrations (Figure SI-2b) revealed a more homogeneous distribution than MMHg, with 50 % of the values between 3 and 6 pmol L^{-1} and less than a threefold difference between the mean and extreme values. The mean IHg bottom-water concentrations (Table 3) were also highest in March 2005 (4.8–9.5 pmol L^{-1}) and May 2006 (4.1–9.8 pmol L^{-1}) compared to October 2007 (2.8–3.8 pmol L^{-1}, Mann–Whitney test, p-values $= 1.9 \times 10^{-4}$ and 1.6×10^{-6}).

Hg species fluxes at the sediment–water interface

The distribution of the individual MMHg benthic fluxes values over the three seasons is displayed in

Table 3 Bottom water concentrations and benthic fluxes of Hg species recorded over the different seasons and sites under light (L) and dark (D) conditions

			MMHg				IHg			
			Bottom water	Fluxes (pmol m^{-2} h^{-1})			Bottom water	Fluxes (pmol m^{-2} h^{-1})		
			(pmol L^{-1})	Mean	Precision[a] (%)	Variability[b] (%)	(pmol L^{-1})	Mean	Precision[a] (%)	Variability[b] (%)
2005	Intertidal	S2-L	2.11 ± 1.40	−63	13	257	4.8 ± 1.4	552	12	63
		S2-D	1.33±0.58	157	11	173	5.2 ± 2.4	304	27	148
	Zostera	S3-L	1.04 ± 0.31	38	13	155	9.5 ± 4.2	−306	12	171
		S3-D	1.84 ± 1.73	71	23	304	7.2 ± 6.8	−182	21	188
2006	Intertidal	S2-D	0.11 ± 0.01	2.9	41	69	4.1 ± 0.6	283	9	47
	Zostera	S3-L	0.17 ± 0.01	−2.3	39	24	4.8 ± 1.1	0.8	24	11,687
		S3-D	0.19 ± 0.07	−1.5	17	458	9.8 ± 4.4	−281	3,212	143
	Subtidal	S4-L	0.09 ± 0.02	3.8	13	19	4.6 ± 0.8	40	84	113
		S4-D	0.15 ± 0.04	−0.6	44	403	9.7 ± 7.0	−243	17	140
2007	Intertidal	S2-L	0.11 ± 0.02	1.5	89	75	3.2 ± 0.2	−9	784	367
		S2-D	0.11 ± 0.02	−0.2	1,640	633	3.0 ± 0.3	7	52	509
	Zostera	S3-L	0.14 ± 0.02	−2.3	37	67	2.9 ± 0.5	−43	74	104
		S3-D	0.20 ± 0.04	27.5	–	–	3.8 ± 0.5	90	55	73
	Subtidal	S4-L	0.11 ± 0.01	−1.2	51	7	3.1 ± 0.2	2.2	239	487
		S4-D	0.08 ± 0.02	0.0	77	6,108	2.8 ± 0.2	7	87	316

[a] Averaged analytical error for the three fluxes

[b] spatial variability expressed as % of the averaged flux

Figure SI-3a. Half of the fluxes measured were between −2.9 and 4.6 pmol m^{-2} h^{-1}, while the mean flux was higher (16 pmol m^{-2} h^{-1}) because of the high values recorded in 2005. The most intense MMHg exchanges were observed in March 2005 (Table 3, Fig. 4), leading to a median flux of 64 pmol m^{-2} h^{-1}. The spatial variability, calculated as the relative standard variability of the three chambers deployed at the same site, ranged from 155 to 304 %, while the analytical precision on individual fluxes remained satisfactory, from 11 to 23 %. The flux intensities recorded in May 2006 and October 2007 were usually 1–2 orders of magnitude below the March 2005 values and so were the median fluxes (0.7 and −0.4 pmol m^{-2} h^{-1}, respectively) but the spatial variability remained generally similar to that of March 2005, within 19–458 % in May and 7–633 % in October. The trends for the IHg fluxes were consistent to those of MMHg but exhibited order of magnitude higher values (Figure SI-3b). Half of the fluxes measured over the three years were between −56 and 137 pmol m^{-2} h^{-1}, with a mean positive value of 8 pmol m^{-2} h^{-1}. As for MMHg, the flux intensities recorded in May 2006 and October 2007 (median −16 and −1 pmol m^{-2} h^{-1}, respectively) were lower compared to March 2005 (median 178 pmol m^{-2} h^{-1}) while the spatial variability was also comparable over the three periods and among the stations, ranging from 63 to 509 % for significant flux values (Table 3, Fig. 4).

Hg species transformations in waters and sediments

The methylation and demethylation potentials were assessed in the water column in May 2006 and October 2007 (Table 4). Overall, methylation was found to be very low in water, often under the detection limits (0.02 %). In May 2006, significant methylation potentials were found in bulk water exposed to light (0.8 % d^{-1}) and in filtered water kept in the dark (1.1 % d^{-1}). The maximum methylation potential recorded reached up 1.5 % d^{-1}. At the opposite, demethylation was found significant in all the

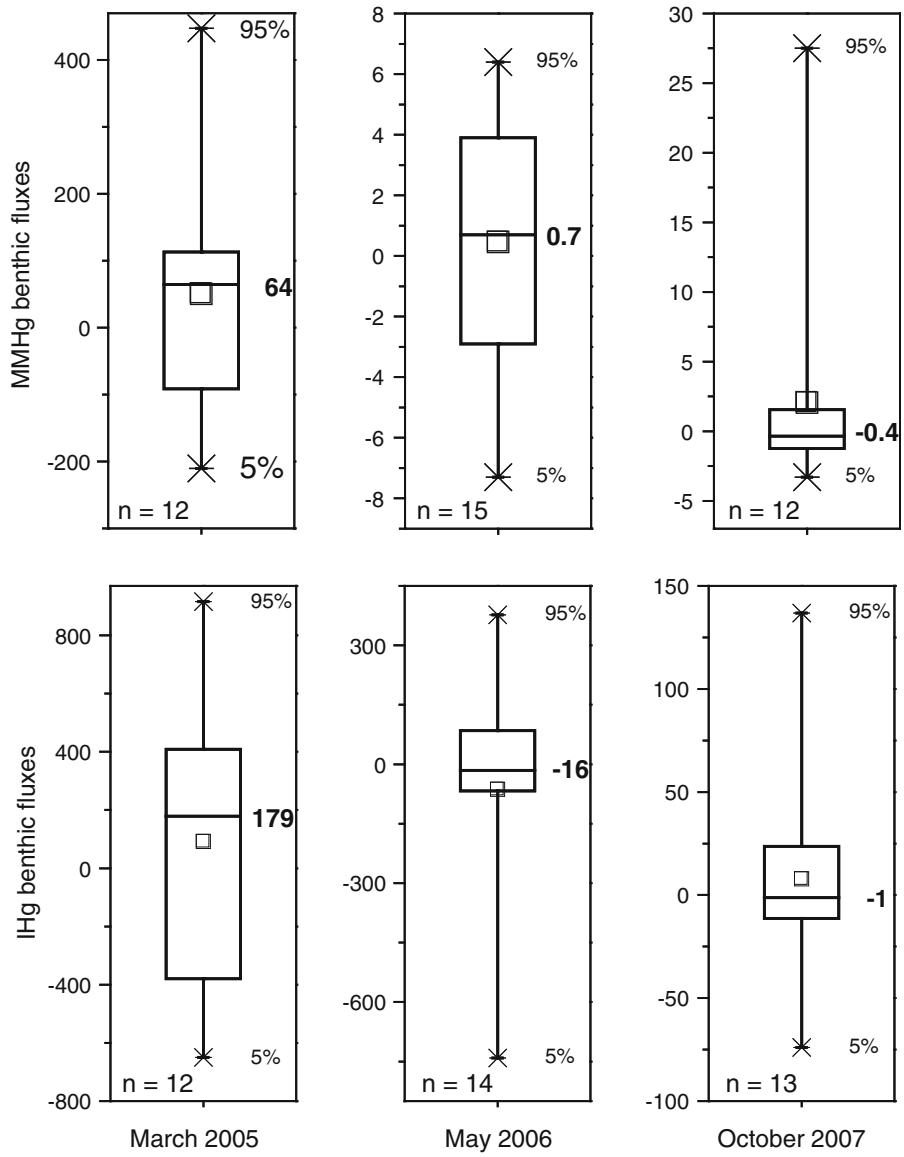

Fig. 4 Distribution of the individual Hg species benthic fluxes (pmol m^{-2} h^{-1}) measured each season (median value at the *right of the box*, one outlier discarded for MMHg in 2007 and one for IHg in 2006, lower and upper limits of the *box* represent the percentiles 25 and 75)

conditions tested and for both seasons. The demethylation potentials ranged from 1.3 to 11.9 % d^{-1} and were always higher for light than for dark conditions and higher for bulk than for filtered waters.

Significant methylation was always measured in sediments, from 0.3 % d^{-1} at St. 2 in January 2008 to 3.2 % d^{-1} at St 1 in October 2007 (Table 4). Basically, the methylation potentials were the lowest in January when the temperature was low (5.7–8.6 °C). The highest methylation potentials were found in St. 1 (2.8–3.2 % d^{-1}) and the lowest in St. 3 (0.4–0.6 % d^{-1}). The demethylation exhibited an opposite trend with the lowest potentials recorded at St. 1 (37–47 % d^{-1}) and the highest at St. 3 (69–72 % d^{-1}). Potentials at St. 2 were in all case intermediate between St. 1 and 3. The lowest demethylation potentials were also recorded in January 2008 (21–32 % d^{-1}).

Table 4 Hg species transformations (% per 24 h) in the water column sampled at Station 4 and in the sediments of the different stations

Water		Bulk		Filtered	
		Dark	Light	Dark	Light
Methylation	May 2006	≤0.02	0.8 ± 0.2	1.1 ± 0.6	≤0.02
	October 2007	≤0.02	≤0.02	≤0.02	≤0.02
Demethylation	May 2006	3.9 ± 1.2	6.2 ± 2.3	1.5 ± 1.3	1.8 ± 1.6
	October 2007	9.0 ± 2.1	11.9 ± 1.4	1.3 ± 0.4	8.2 ± 1.2

Sediments		Station 1		Station 2		Station 3	
		Dark	Light	Dark	Light	Dark	Light
Methylation	October 2007	2.8 ± 0.6	3.2 ± 0.2	0.8 ± 0.2	1.1 ± 0.2	0.6 ± 0.03	0.4 ± 0.04
	January 08			0.3 ± 0.1	0.3 ± 0.1		
Demethylation	October 2007	37 ± 5	47 ± 8	65 ± 7	60 ± 7	69 ± 1	72 ± 4
	January 08			32 ± 12	21 ± 9		

Results are mean (±SD) of 3 replicate conditions. The methylation detection limit in the water incubations is 0.02 %

Table 5 Comparison of benthic fluxes, transformations potentials and pore-waters seeping as sources and sinks for MMHg in the water column and surficial sediments over a 6-hours tidal cycle

		Methylation	Demethylation	MMHg fluxes	Pore-waters seeping[c]
Water column[a]	Mean/median	+0.003	−0.005	+0.11/+0.004	+0.02/+0.13
(pmol L^{-1})	Max	+0.02	−0.04	+2.7	
Surface sediment[b]	Mean/median	+2.9	−0.7	NA	NA
(pmol g^{-1})	Max	+7.9	−0.9	+0.5	

Only the mean value is given for species transformation

NA not applicable in this case

[a] Calculations were performed assuming a water column of 1 m depth average and well-mixed, leading to homogeneous species distributions and transformations. The averaged IHg and MMHg aqueous concentrations were considered as available substrates for reactions

[b] Calculations were performed over the first 0.5 cm, assuming a sediment density of 0.5 g cm^{-3} and averaged IHg and MMHg solid concentrations

[c] Only the values found in 2006 (spring) and 2007 (late summer) are given as a range

Discussion

Respective influence of pore-waters seeping, benthic fluxes and methylation for MMHg accumulation and removal in waters and sediments

The tidal cycle surveys demonstrated that the channel investigated behave as a small-scale estuary with a dilution of an enriched upstream source and coastal waters. However, as explained above ("Diurnal and tidal variability of Hg species"), the small river connected to the channel does not represent a significant source of Hg, leading to the conclusion that tidal mudflats effectively export Hg. Particulate Hg is remobilized through sediment particles erosion and advection during ebb tide. As stated above, it is not really possible to discuss the influence of sorption processes on Hg dissolved concentrations, although the IHg enrichment at high tide observed in 2006 suggests that desorption may occur under large salinity variations. Conversely, Hg species were not affected by the low salinity variations observed in 2007.

On the other side, the mudflats may directly influence dissolved Hg concentrations through three

mechanisms: benthic fluxes and species transformations at high tide and pore-waters seeping at low tide. Their respective influence can be only evaluated from the data collected in spring and late summer conditions. The MMHg enrichment observed in the water masses following mudflats immersion were 0.13 and 0.02 pmol L^{-1}, respectively. The median benthic fluxes were 0.7 and −0.4 pmol m^{-2} h^{-1}, representing 3 and −12 % of the enrichment in spring and late summer, respectively. Over these two periods, benthic exchanges may not contribute at all to the enrichment (negative fluxes) but on the other side, may contribute from 18 to 48 % when considering the 3rd quartile of the flux distributions and 28–83 % when considering the maximum flux values. Unfortunately, no data have been acquired during a tidal cycle in late winter conditions (March 2005) when the exchanges were the most intense but the median flux (64 pmol m^{-2} h^{-1}) represents a 0.38 pmol L^{-1} enrichment, i.e. three times higher than the one observed in spring. The averaged methylation recorded in the water column accounts for 2 and 15 % of the enrichment in spring and late summer, respectively while maximum methylation represents 15 and 95 %, respectively. Therefore, pore-waters seeping appears as the main contribution to the enrichment in spring (95 %) while benthic fluxes and methylation in the water column likely account for only 15 % of it in late summer but a larger contribution, up to 100 %, remains possible.

The comparison of benthic fluxes and transformation potentials towards MMHg accumulation or removal for both the water column and surface sediments is possible for the three seasons investigated (Table 5). The averaged methylation potential and the median benthic flux were found to be equivalent for increasing the MMHg concentrations in the water column (0.003 vs. 0.004 pmol L^{-1}). A 0.3 % d^{-1} methylation extent is equivalent to the median spring benthic fluxes and therefore methylation is likely to outcompete benthic fluxes during spring and late summer. However, given the important variability in Hg benthic exchanges, it should be noted that the maximum MMHg efflux (2.7 pmol L^{-1}) was two orders of magnitude higher than the maximum methylation (0.02 pmol L^{-1}). Demethylation is the most likely sink of MMHg in the water column (0.005 pmol L^{-1}) given that the median MMHg flux is positive. In superficial sediments, the solid MMHg concentrations were found to be controlled by the methylation/demethylation processes, even if the maximum demethylation and benthic fluxes were roughly equivalent.

Finally, Hg methylation in sediments followed by MMHg export through pore-waters seeping and benthic fluxes appear as the major source of MMHg in the water column in such background intertidal ecosystem under winter and spring conditions. Conversely, methylation in the water column has to be considered during late summer when sediment MMHg release is minimal as it can be equally significant. It demonstrates that different approaches must be conducted to better constrain the main pathways involved in the dynamic MMHg cycling.

Spatial and temporal variability associated with benthic fluxes

Data on Hg species benthic fluxes measured in situ in low-impacted coastal ecosystems are scarce and even not reported in intertidal areas. However, the flux intensities reported here are in agreement with previous studies where solid Hg concentrations were similar (Choe et al. 2004, Point et al. 2007, Hammerschmidt and Fitzgerald 2008). However, the spatial variability of benthic fluxes observed in Arcachon Bay was largely higher than when reported elsewhere. In the microtidal Thau lagoon (Point et al. 2007), the spatial variability for Hg species fluxes ranged from 20 to 65 % for the two seasons considered, while a maximum of 181 % was reported for Pb. In the present study, the mean spatial variability recorded for other trace metals varied from 106 to 612 % when considering the three seasons, reaching up to 8,000 % for Mo in 2005 (Table SI-1) and 285 % for gaseous Hg (Bouchet et al. 2011b). Specific methodological biases in Hg fluxes determination were ruled out given that the spatial variability of Hg species was similar to those of other trace metals fluxes (data not shown) and Hg fluxes were overall evenly distributed (Fig. 4 and SI-3). Therefore, the observed variability of the Hg species exchanges can be firmly ascribed to heterogeneous environmental conditions. The variability observed was evenly distributed between stations and seasons and may be well explained by the biological activity (Benoit et al. 2009) considering the macrofauna, which was heterogeneous (19–173 % RSD between the three benthic chambers, mean 95 ± 46 %) as well as the macrophytic biomass

distribution (42–61 % RSD, St. 3, October 2007, data not shown).

Maximum fluxes were generally recorded in late winter conditions in the few annual surveys that have been conducted and our results are overall consistent with previous works in their seasonal patterns. We also recorded the maximum flux intensities during late winter conditions, when the tidal range and the water oxygenation were the highest (Table 1) and sulfide production supposedly the lowest. Although some other biogeochemical parameters were not measured, this is consistent with previous works demonstrating that Hg exchanges are strongly influenced by bioturbation (Riedel et al. 1997; Point et al. 2007; Benoit et al. 2009), which is dependent of dissolved O_2 saturation (Hammerschmidt and Fitzgerald 2008) but also by bottom shear stress (Guédron et al. 2012). On the other hand, the much lower flux intensities we observed in late summer are coherent with Covelli et al. (1999), who suggested that the production of sulfides in summer reduces the Hg mobility. Although the sulfide data recorded during this study never revealed sulfide accumulation (for the reason explained "Biogeochemistry of the superficial sediments"), sulfate reduction is still expected to be higher during summer (Stal et al. 1996) and sub-products (sulfides or FeS minerals) could explain the reduced Hg mobility observed.

Biogeochemical pathways affecting Hg species exchange

Even if benthic fluxes are not the main pathway for Hg export to the water column, data collected in the benthic chambers are somehow helpful to speculate about the biogeochemical drivers of Hg remobilization. For each season, specific relationships were found between the Hg species benthic fluxes and different relevant parameters (Fig. 5). It demonstrates that the respective influence of the various factors controlling Hg exchanges, through sediment–water partitioning and transport, evolves along seasons, as suggested from the seasonal variability in the fluxes intensities. In late summer conditions (October 2007), no relationship was found for MMHg but the flux intensities were really low during that period.

Hg species release from organic matter mineralization

In late winter conditions, when the water column is well oxygenated and sulfide accumulation is lower, a significant relationship is found between the averaged MMHg benthic fluxes and O_2 consumption (Fig. 5a). It was also found true for IHg in late summer conditions and the relationship is also apparent but not significant in March 2005 if data from St 2 under light conditions (net O_2 production) are discarded (Fig. 5d). The benthic fluxes are thus partly controlled by the heterotrophic aerobic mineralization of organic matter through the release of Hg species from sediments to pore-waters. It is consistent with the strong Hg-OM affinity established both in the water column and sediments (e.g. Lamborg et al. 2003; Sanei and Goodarzi 2006) and has been previously suggested (Mikac et al. 1999; Cossa and Gobeil 2000). However, there are striking differences between the slopes and x-intercepts obtained for MMHg and IHg. First, the x-intercept between IHg and O_2 was low (-2.6 mmol m^{-2} h^{-1}) compared to MMHg (0.1 mmol m^{-2} h^{-1}), demonstrating that higher OM mineralization is required to support an IHg efflux to the water column compared to MMHg. Second, the MMHg/O_2 slope is only seven times lower than the IHg/O_2 slope, while MMHg roughly represents 1 % of Hg_T in superficial sediments. It overall demonstrates that MMHg has a higher mobility and is more efficiently released to the water column than IHg, which is consistent with highest Kds for IHg, usually observed either in water column or in pore waters (Bloom et al. 1999; Hammerschmidt et al. 2004; Hammerschmidt and Fitzgerald 2006).

It is also important to note that the benthic Hg fluxes were generally poorly correlated with the Mn benthic fluxes (except IHg fluxes in 2007, see below), which suggests that the release of Hg species resulting from the reductive dissolution of oxyhydroxides was negligible (Hammerschmidt et al. 2004; Mason et al. 2006) in this environment. This result is in agreement with previous data from specific extractions showing only small proportions of Hg associated with these reactive minerals when the sediment organic content is high (Hammerschmidt et al. 2004; Belzile et al. 2008).

Hg species release regulated by diffusion and sulfur chemistry

In May 2006 (spring), the fluxes recorded for MMHg were relatively low and in agreement with the magnitude of diffusive fluxes presented in some other studies (Choe et al. 2004; Muresan et al. 2007). During

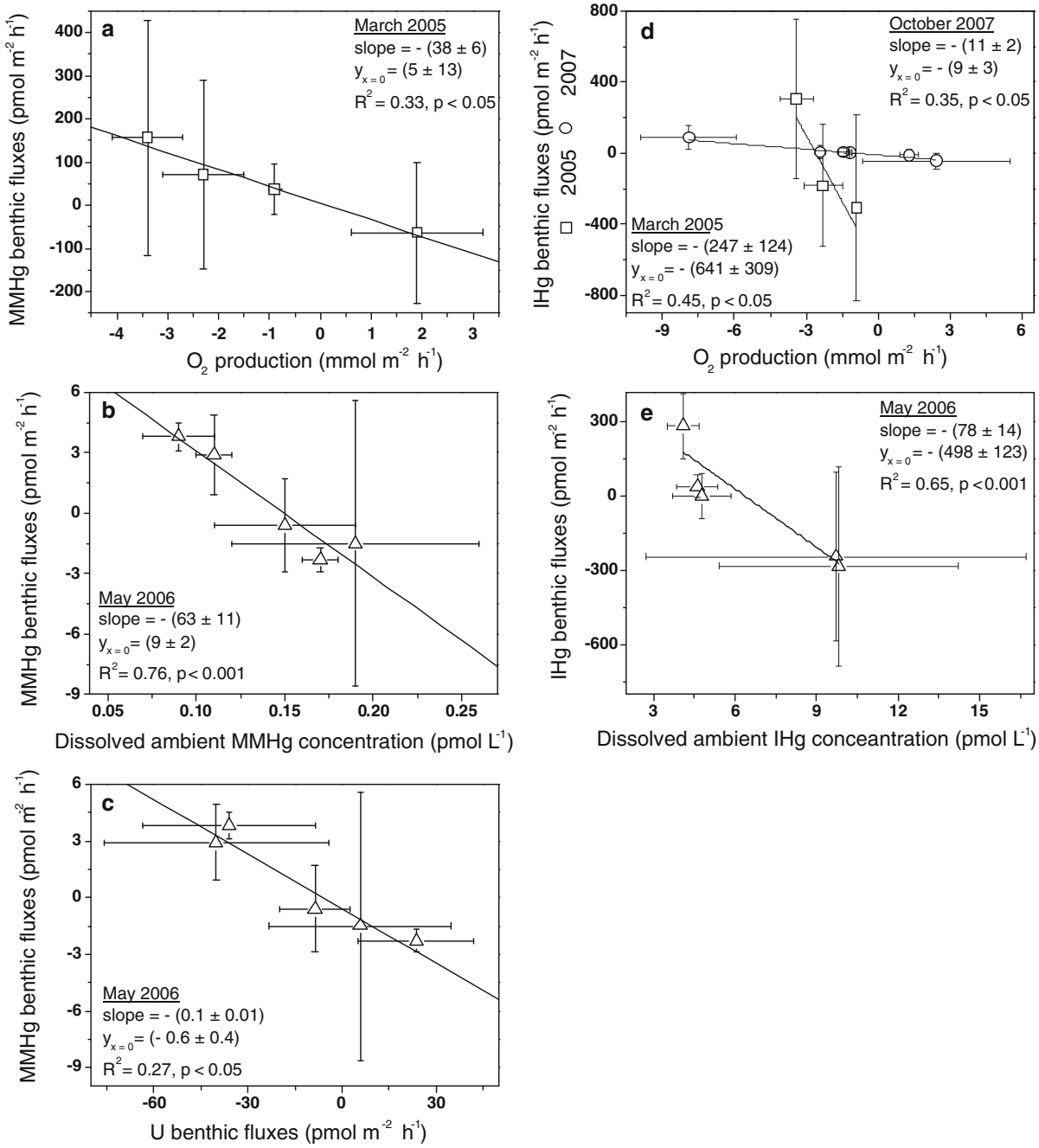

Fig. 5 Relationships between MMHg and IHg benthic fluxes and **a** and **e** O_2 production, **b** and **d** dissolved ambient MMHg concentration and **c** U benthic fluxes for the three seasons considered. *Error bars* represent one standard deviation of the three measurements performed at each site

this period, both Hg species fluxes were negatively correlated to their dissolved ambient concentration in overlying waters (Fig. 5b, e) with closely similar slopes between MMHg and IHg. It demonstrates the diffusive nature of the exchanges, which were regulated by a chemical gradient between pore and overlaying waters in line with the conclusions of Hammerschmidt and Fitzgerald (2008) for their

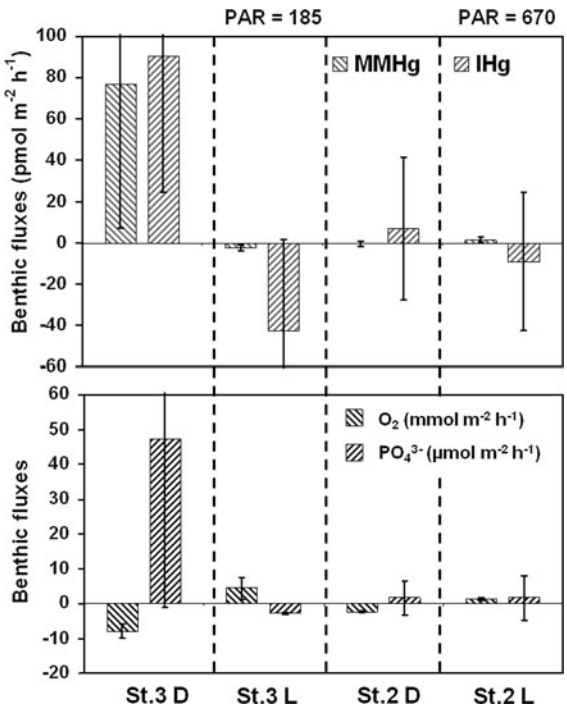

Fig. 6 Effects of light (L) and dark (D) conditions on mean (±1 SD) Hg fluxes measured in benthic chambers at St. 2 and 3 in October 2007. Light levels (PAR values) are in µmol m^{-2} s^{-1}

summer measurements. Furthermore, MMHg fluxes were also negatively correlated with U fluxes (Fig. 5c). U removal from the water column is known to be a relevant proxy of anoxic conditions and sulfide accumulation at the sediment–water interface (Point et al. 2007); it was sometimes even directly correlated with sulfate reduction activity (Barnes and Cochran 1993). Therefore, MMHg effluxes could be directly proportional to the sulfate reduction rates and/or sulfide production rates. Two hypotheses follow: (1) the fluxes are linked to the MMHg production in the upper sediments that we assume to be roughly proportional to the sulfate reduction rate (Devereux et al. 1996, King et al. 1999, 2001, Monperrus et al. 2007b) and/or (2) the increased production of sulfides is competing with solid phase MMHg to form dissolved MMHg-sulfur complexes (Paquette and Helz 1997; Benoit et al. 1998; Merritt and Amirbahman 2007) which further diffuse upward. This issue is difficult to sort out because pore-waters sulfide concentrations, ranging roughly from 2 to 15 µM in the first 3 cm, support an increase of Hg availability (Benoit et al. 1999) but also probably MMHg solubility even if the latter is more difficult to infer (Skyllberg 2008). These results reinforce previous findings (Emili et al. 2011) on the dual effect of sulfides, promoting evasion at low concentrations and immobilization at high concentrations (Hammerschmidt and Fitzgerald 2008; Covelli et al. 1999).

Concerning IHg, a positive relationship would be expected with U benthic fluxes, due to its strong affinity for sulfur. However, the general trend was negative (data not shown) if significant. The production of dissolved sulfides and/or solid reduced sulfur was not sufficient to remove IHg from pore waters by precipitation or adsorption and led instead to an increased IHg evasion probably through the sulfide effect on solubility (Benoit et al. 1999). Given the strong control of sulfides by Fe (Stal et al. 1996), the IHg behavior may be rather controlled by adsorption onto FeS (Jeong et al. 2007) or by organic sulfur (Canario et al. 2008) rather than by direct precipitation of cinnabar.

Macrophytic influence on Hg species exchange

Figure 6 exemplifies the flux reversibility according to light conditions, observed in late summer conditions when the macrophytic cover was well developed (St. 3). The mean fluxes measured in the dark were positive at 70 and 90 pmol m^{-2} h^{-1} for MMHg and IHg, respectively, while negative fluxes occurred under light conditions, −2.3 and −43 pmol m^{-2} h^{-1} respectively. The *Zostera* biomass measured inside the benthic chambers averaged 2.9 ± 1.8 g m^{-2} and 3.8 ± 1.6 g m^{-2} (dry weight) for dark and light conditions, respectively. The same pattern was observed on St. 2 for IHg, although with a lower amplitude which can be related to the absence of *Zostera*. The mean fluxes were −0.2 and 7 pmol m^{-2} h^{-1} for MMHg and IHg, respectively under dark conditions and 1.5 and -9 pmol m^{-2} h^{-1} for MMHg and IHg, respectively under light conditions. The microphytic benthic biomass (estimated by Chl a measurement) averaged 126 ± 19 mg m^{-2} on St. 2 and 205 ± 22 mg m^{-2} on St. 3 (dw, A. Migné, personal communication).

It is coherent with previous studies on diurnal variations of Hg (Gill et al. 1999; Point et al. 2007; Covelli et al. 2008). Gill et al. (1999) measured a decrease in dissolved Hg concentrations inside the

benthic chambers during the daylight period that coincided with a reversal of nutrients fluxes. These authors suggested a downward migration of the oxic-anoxic transition zone due to photosynthetic production of O_2 at the water–sediment interface that would affect the redox cycling of Fe and associated metals. In the present study, the IHg fluxes were correlated with the fluxes of PO_4^{3-} ($R = 0.96, p = 0.04$) and Mn ($R = 0.99, p = 0.004$) at the two stations (Figure SI-4). The *P* cycling is known to be closely associated to Fe (Anschutz et al. 1998). Deborde et al. (2008b) demonstrated the effect of the annual development of the *Zostera noltii* meadows on the Fe and P cycles in the same investigated area of Arcachon Bay. The Hg species release appeared thus indirectly inhibited by the macro- and to a minor extent microphytic activities through their local influence on Fe and Mn biogeochemistry, re-oxidized under dominant photosynthetic conditions. This calls for further investigations because the *Zostera* biomass could reach up to 370 g (dry weight) m^{-2} at the end of the growth period, i.e. late summer (Deborde et al. 2008b).

Acknowledgments This work is a contribution to the PROTIDAL project (ANR Blanc program) and Littoral Atlantic project (PNEC program). The authors would like to thank the municipality of Lanton (Arcachon Bay, France) for the logistic organization of the field campaigns. The authors greatly appreciate technical assistance from R. Marc, A. Masson and C. Robineau (LEMAR IUEM, CNRS/UBO/IRD, Plouzané, France) and R. Bridou, P. Pinel-Raffaitin and D. Point (IPREM-LCABIE) during field campaigns. The authors also thank A. Mouret and Dr. B. Deflandre (EPOC, University of Bordeaux, France) for providing us with some major geochemical measurements and Dr. A Migné (University of Paris 6, Roscoff, France) for the microphytobenthos biomass data. One anonymous reviewer and Dr. Carl Lamborg (WHOI) are greatly acknowledged for constructive comments during the review process and a revision of the manuscript at its final stage, respectively. S. Bouchet and P. Rodriguez-Gonzalez acknowledge respectively the French and the Spanish Ministers of Education and Research for their respective PhD and Postdoctoral fellowships.

References

Anschutz P, Zhong S, Sundby B, Mucci A, Gobeil C (1998) Burial efficiency of phosphorus and the geochemistry of iron in continental margin sediments. Limnol Oceanogr 43:53–64

Auby I, Labourg PJ (1996) Seasonal dynamics of *Zostera noltii* Hornem. in the Bay of Arcachon (France). J Sea Res 35:269–277

Barnes CE, Cochran JK (1993) Uranium geochemistry in estuarine sediments: controls on removal and release processes. Geochim Cosmochim Acta 57:555–569

Belzile N, Lang CY, Chen YW, Wang M (2008) The competitive role of organic carbon and dissolved sulfide in controlling the distribution of mercury in freshwater lake sediments. Sci Total Environ 405:226–238

Benoit JM, Gilmour CC, Mason RP, Riedel GS, Riedel GF (1998) Behavior of mercury in the Patuxent river estuary. Biogeochemistry 40:249–265

Benoit JM, Gilmour CC, Mason RP, Heyes A (1999) Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. Environ Sci Technol 33:951–957

Benoit JM, Shull DH, Harvey RM, Beal SA (2009) Effect of bioirrigation on sediment–water exchange of methylmercury in Boston Harbor, Massachusetts. Environ Sci Technol 43:3669–3674

Blanchet H, De Montaudouin X, Chardy P, Bachelet G (2005) Structuring factors and recent changes in subtidal macrozoobenthic communities of a coastal lagoon, Arcachon Bay (France). Estuar Coast Shelf Sci 64:561–576

Bloom NS, Gill GA, Cappellino S, Dobbs C, McShea L, Driscoll C, Mason R, Rudd J (1999) Speciation and cycling of mercury in Lavaca Bay, Texas, sediments. Environ Sci Technol 33:7–13

Boucher G, Boucher-Radoni R (1988) In situ measurements of respiratory metabolism and nitrogen fluxes at the interface with oyster beds. Mar Ecol Prog Ser 44:229–238

Bouchet S, Bridou R, Tessier E, Rodriguez-Gonzalez P, Monperrus M, Abril G, Amouroux D (2011a) An experimental approach to investigate mercury species transformations under redox oscillations in coastal sediments. Mar Environ Res 71:1–9

Bouchet S, Tessier E, Monperrus M, Bridou R, Clavier J, Thouzeau G, Amouroux D (2011b) Measurements of gaseous mercury exchanges at the sediment–water, water–atmosphere and sediment–atmosphere interfaces of a tidal environment (Arcachon Bay, France). J Environ Monitor 13:1351

Canario J, Poissant L, O'Driscoll N, Ridal J, Delongchamp T, Pilote M, Constant P, Blais J, Lean D (2008) Mercury partitioning in surface sediments of the Upper St. Lawrence River (Canada): evidence of the importance of the sulphur chemistry. Water Air Soil Pollut 187:219–231

Canton M, Anschutz P, Coynel A, Polsenaere P, Auby I, Poirier D (2010) Nutrient export to an Eastern Atlantic coastal zone: first modeling and nitrogen mass balance. Biogeochemistry. doi:10.1007/s10533-010-9558-7

Castel J, Caumette P, Herbert R (1996) Eutrophication gradients in coastal lagoons as exemplified by the Bassin d'Arcachon and the etang du Prevost. Hydrobiologia 329:ix–xxviii

Choe KY, Gill GA, Lehman RD, Han S, Heim WA, Coale KH (2004) Sediment-water exchange of total mercury and monomethyl mercury in the San Francisco Bay-Delta. Limnol Oceanogr 49:1512–1527

Cossa D, Gobeil C (2000) Mercury speciation in the lower St. Lawrence estuary. Can J Fish Aquat Sci 57:138–147

Cossa D, Averty B, Pirrone N (2009) The origin of methylmercury in open mediterranean waters. Limnol Oceanogr 54:837–844

Covelli S, Faganeli J, Horvat M, Brambati A (1999) Porewater distribution and benthic flux measurements of mercury and methylmercury in the Gulf of Trieste (Northern Adriatic Sea). Estuar Coast Shelf Sci 48:415–428

Covelli S, Faganeli J, De Vittor C, Predonzani S, Acquavita A, Horvat M (2008) Benthic fluxes of mercury species in a lagoon environment (Grado Lagoon, Northern Adriatic Sea, Italy). Appl Geochem 23:529–546

De Wit R, Stal LJ, Lomstein BA, Herbert RA, Van Gemerden H, Viaroli P, Cecherelli VU, Rodríguez-Valera F, Bartoli M, Giordani G, Azzoni R, Schaub B, Welsh DT, Donnelly A, Cifuentes A, Antón J, Finster K, Nielsen LB, Pedersen AGU, Neubauer AT, Colangelo MA, Heijs SK (2001) Robust: the role of buffering capacities in stabilising coastal lagoon ecosystems. Cont Shelf Res 21:2021–2041

Deborde J, Anschutz P, Auby I, Glé C, Commarieu MV, Maurer D, Lecroart P, Abril G (2008a) Role of tidal pumping on nutrient cycling in a temperate lagoon (Arcachon Bay, France). Mar Chem 109:98–114

Deborde J, Abril G, Mouret A, Jezequel D, Thouzeau G, Clavier J, Bachelet G, Anschutz P (2008b) Effects of seasonal dynamics in a *Zostera noltii* meadow on phosphorus and iron cycles in a tidal mudflat (Arcachon Bay, France). Mar Ecol Prog Ser 355:59–71

Dedieu K, Rabouille C, Thouzeau G, Jean F, Chauvaud L, Clavier J, Mesnage V, Ogier S (2007) Benthic O_2 distribution and dynamics in a Mediterranean lagoon (Thau, France): an in situ microelectrode study. Estuar Coast Shelf Sci 72:393–405

Devereux R, Winfrey MR, Winfrey J, Stahl DA (1996) Depth profile of sulfate-reducing bacterial ribosomal RNA and mercury methylation in an estuarine sediment. FEMS Microbiol Ecol 20:23–31

Emili A, Koron N, Covelli S, Faganeli J, Acquavita A, Predonzani S, Vittor CD (2011) Does anoxia affect mercury cycling at the sediment-water interface in the Gulf of Trieste (northern Adriatic Sea)? Incubation experiments using benthic flux chambers. Appl Geochem 26:194–204

Forja JM, Gomez-Parra A (1998) Measuring nutrient fluxes across the sediment-water interface using benthic chambers. Mar Ecol Progr Ser 164:95–105

Gagnon C, Pelletier É, Mucci A (1997) Behaviour of anthropogenic mercury in coastal marine sediments. Mar Chem 59:159–176

Gill GA, Bloom NS, Cappellino S, Driscoll CT, Dobbs C, McShea L, Mason R, Rudd JWM (1999) Sediment–water fluxes of mercury in Lavaca Bay, Texas. Environ Sci Technol 33:663–669

Guédron S, Huguet L, Vignati DAL, Liu B, Gimbert F, Ferrari BJD, Zonta R, Dominik J (2012) Tidal cycling of mercury and methylmercury between sediments and water column in the Venice Lagoon (Italy). Mar Chem 130–131:1–11

Hammerschmidt CR, Fitzgerald WF (2006) Methylmercury cycling in sediments on the continental shelf of southern New England. Geochim Cosmochim Acta 70:918–930

Hammerschmidt CR, Fitzgerald WF (2008) Sediment-water exchange of methylmercury determined from shipboard benthic flux chambers. Mar Chem 109:86–97

Hammerschmidt CR, Fitzgerald WF, Lamborg CH, Balcom PH, Visscher PT (2004) Biogeochemistry of methylmercury in sediments of Long Island Sound. Mar Chem 90:31–52

Jeong HY, Klaue B, Blum JD, Hayes KF (2007) Sorption of mercuric ion by synthetic nanocrystalline mackinawite (FeS). Environ Sci Technol 41:7699–7705

King JK, Saunders FM, Lee RF, Jahnke RA (1999) Coupling mercury methylation rates to sulfate reduction rates in marine sediments. Environ Toxicol Chem 18:1362–1369

King JK, Kostka JE, Frischer ME, Saunders FM, Jahnke RA (2001) A quantitative relationship that demonstrates mercury methylation rates in marine sediments are based on the community composition and activity of sulfate-reducing bacteria. Environ Sci Technol 35:2491–2496

Lamborg CH, Tseng CM, Fitzgerald WF, Balcom PH, Hammerschmidt CR (2003) Determination of the mercury complexation characteristics of dissolved organic matter in natural waters with "reducible Hg" titrations. Environ Sci Technol 37:3316–3322

Lehnherr I, Louis VL (2009) Importance of ultraviolet radiation in the photodemethylation of methylmercury in freshwater ecosystems. Environ Sci Technol 43:5692–5698

Mason RP, 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

Merritt KA, Amirbahman A (2007) Mercury dynamics in sulfide-rich sediments: geochemical influence on contaminant mobilization within the Penobscot River estuary, Maine, USA. Geochim Cosmochim Acta 71:929–941

Mikac N, Niessen S, Ouddane B, Wartel M (1999) Speciation of mercury in sediments of the Seine estuary (France). Appl Organomet Chem 13:715–725

Monperrus M, Tessier E, Veschambre S, Amouroux D, Donard O (2005) Simultaneous speciation of mercury and butyltin compounds in natural waters and snow by propylation and species-specific isotope dilution mass spectrometry analysis. Anal Bioanal Chem 381:854–862

Monperrus M, Tessier E, Amouroux D, Leynaert A, Huonnic P, Donard OFX (2007a) Mercury methylation, demethylation and reduction rates in coastal and marine surface waters of the Mediterranean Sea. Mar Chem 107:49–63

Monperrus M, Tessier E, Point D, Vidimova K, Amouroux D, Guyoneaud R, Leynaert A, Grall J, Chauvaud L, Thouzeau G, Donard OFX (2007b) The biogeochemistry of mercury at the sediment-water interface in the Thau Lagoon. 2. Evaluation of mercury methylation potential in both surface sediment and the water column. Estuar Coast Shelf Sci 72:485–496

Mortimer RJG, Krom MD, Watson PG, Frickers PE, Davey JT, Clifton RJ (1999) Sediment–water exchange of nutrients in the intertidal zone of the Humber Estuary, UK. Mar Poll Bull 37:261–279

Muresan B, Cossa D, Jezequel D, Prevot F, Kerbellec S (2007) The biogeochemistry of mercury at the sediment-water interface in the Thau lagoon. 1. Partition and speciation. Estuar Coast Shelf Sci 72:472–484

Paquette KE, Helz GR (1997) Inorganic speciation of mercury in sulfidic waters: the importance of zero-valent sulfur. Environ Sci Technol 31:2148–2153

Patterson DM, Sebens KP, Olson RR (1991) In situ measurements of flow effects on primary production and dark respiration in reef corals. Limnol Oceanogr 36:936–948

Point D, Monperrus M, Tessier E, Amouroux D, Chauvaud L, Thouzeau G, Jean F, Amice E, Grall J, Leynaert A, Clavier

J, Donard OFX (2007) Biological control of trace metal and organometal benthic fluxes in a eutrophic lagoon (Thau Lagoon, Mediterranean Sea, France). Estuar Coast Shelf Sci 72:457–471

Ramalhosa E, Pato P, Monterroso P, Pereira E, Vale C, Duarte AC (2006a) Accumulation versus remobilization of mercury in sediments of a contaminated lagoon. Mar Poll Bull 52:353–356

Ramalhosa E, Segade SR, Pereira E, Vale C, Duarte A (2006b) Mercury cycling between the water column and surface sediments in a contaminated area. Water Res 40:2893–2900

Riedel GF, Sanders JG, Osman RW (1997) Biogeochemical control on the flux of trace elements from estuarine sediments: water column oxygen concentrations and benthic infauna. Estuar Coast Shelf Sci 44:23–38

Sanei H, Goodarzi F (2006) Relationship between organic matter and mercury in recent lake sediment: the physical-geochemical aspects. Appl Geochem 21:1900–1912

Skyllberg U (2008) Competition among thiols and inorganic sulfides and polysulfides for Hg and MeHg in wetland soils and sediments under suboxic conditions: Illumination of controversies and implications for MeHg net production. J Geophys Res, [Biogeosciences] 113, G00C03. doi: 10.1029/2008JG000745

Stal LJ, Behrens SB, Villbrandt M, Van Bergeijk S, Kruyning F (1996) The biogeochemistry of two eutrophic marine lagoons and its effect on microphytobenthic communities. Hydrobiologia 329:185–198

Tengberg A, Stahl H, Gust G, Muller V, Arning U, Andersson H, Hall POJ (2004) Intercalibration of benthic flux chambers I. Accuracy of flux measurements and influence of chamber hydrodynamics. Progr Oceanogr 60:1–28

Tengberg A, Hall POJ, Andersson U, Linden B, Styrenius O, Boland G, de Bovee F, Carlsson B, Ceradini S, Devol A, Duineveld G, Friemann JU, Glud RN, Khripounoff A, Leather J, Linke P, Lund-Hansen L, Rowe G, Santschi P, de Wilde P, Witte U (2005) Intercalibration of benthic flux chambers: II. Hydrodynamic characterization and flux comparisons of 14 different designs. Mar Chem 94:147–173

Thouzeau G, Grall J, Clavier J, Chauvaud L, Jean F, Leynaert A, Longphuirt S ni, Amice E, Amouroux D (2007) Spatial and temporal variability of benthic biogeochemical fluxes associated with macrophytic and macrofaunal distributions in the Thau lagoon (France). Estuar Coast Shelf Sci 72:432–446