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ScienceDirect
Applied Geochemistry 22 (2007) 1359–1370
Applied Geochemistry
www.elsevier.com/locate/apgeochem

50-year record and solid state speciation of mercury in natural and contaminated reservoir sediment

Sabine Castelle, Jörg Schäfer *, Gérard Blanc, Stéphane Audry, Henri Etcheber, Jean-Pierre Lissalde

Traceurs Géochimiques et Minéralogiques (TGM), UMR CNRS 5805 EPOC, Université Bordeaux I, Av. d. Facultés, F.33405 Talence Cedex, France

Received 14 March 2006; accepted 1 March 2007
Editorial handling by R. Fuge
Available online 20 March 2007

Abstract

Contaminated fluvial sediments represent both temporary sinks for river-borne pollutants and potential sources in case of natural and/or anthropogenic resuspension. Reservoir lakes play a very important role in sediment dynamics of watersheds and may offer great opportunities to study historical records of river-borne particles and associated elements transported in the past. The fate and potential environmental impact of Hg depends on its abundance, its carrier phases and its chemical speciation. Historical Hg records and solid state Hg speciation were compared in sediments from two contrasting reservoirs of the Lot River (France) upstream and downstream from a major polymetallic pollution (e.g. Cd, Zn) source. Natural (geochemical background) and anthropogenic Hg concentrations and their relationships with predominant carrier phases were determined. The results reveal important historical Hg contamination (up to 35 mg kg^{-1}) of the downstream sediment, reflecting the historical evolution of industrial activity at the point source, i.e. former coal mining, Zn ore treatment and post-industrial remediation work. Single chemical extractions (ascorbate, H_2O_2, KOH) suggest that at both sites most (~75%) of the Hg is bound to organic and/or reactive sulphide phases. Organo-chelated (KOH-extracted) Hg, representing an important fraction in the uncontaminated sediment, shows similar concentrations (~0.02 mg kg^{-1}) at both sites and may be mainly attributed to natural inputs and/or processes. Although, total Hg concentrations in recent surface sediments at both sites are still very different, similar mono-methylmercury concentrations (up to 4 μg kg^{-1}) and vertical distributions were observed, suggesting comparable methylation-demethylation processes. High mono-methylmercury concentrations (4–15 μg kg^{-1}) in 10–40 a-old, sulphide-rich, contaminated sediment suggest long-term persistence of mono-methylmercury. Beyond historical records of total concentrations, the studied reservoir sediments provided new insights in solid state speciation and carrier phases of natural and anthropogenic Hg. In case of sediment resuspension, the major part of the Hg historically stored in the Lot River sediments will be accessible to biogeochemical recycling in the downstream fluvial-estuarine environment.

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* Corresponding author. Fax: +33 5 56840848.
E-mail address: j.schaefer@epoc.u-bordeaux1.fr (J. Schäfer).

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doi:10.1016/j.apgeochem.2007.03.025

1. Introduction

At a regional scale, multiple terrestrial sources of natural (erosion, leaching) and anthropogenic origin (e.g. mining and smelting waste) lead to the presence of high levels of Hg in aqueous environments (Fitzgerald et al., 1991; Salomons, 1995). Particulate Hg may account for more than 90% of total Hg in freshwater systems, estuaries or coastal zones (Fitzgerald and Mason, 1997; Balcom et al., 2004; Schäfer et al., 2006) and sediment may represent both a sink for Hg (Gagnon et al., 1997; Mercone et al., 1999) or a source (remobilisation by dredging/works or flood events, gas releases, and/or mineralization by benthic biological activity; e.g. Gagnon et al., 1997; Covelli et al., 1999; Mikac et al., 1999; Birkett et al., 2001; Amouroux et al., 2004). Sedimentation under favourable hydraulic conditions in natural and reservoir lakes may allow historical recording of fluvial trace metal inputs and evaluating long-term trends of particulate metals transport in the system (e.g. Von Gunten et al., 1997; Müller et al., 2000; Audry et al., 2004a). Speciation analyses and characterization of transport phases in the sediment may provide information on (i) metal behaviour in sediments after deposition and (ii) reactivity, toxicity and bioavailability of metal after potential resuspension. Selective extractions are commonly applied to study metal distributions between the different operationally-defined carrier phases in suspended particulate matter (SPM) and sediments (Tessier et al., 1979; Gleyzes et al., 2002 and references therein; Audry et al., 2006), but relatively few studies concern Hg components (e.g. Bloom et al., 2003; Laurier et al., 2003; Sahuquillo et al., 2003).

The Riou Mort-Lot-Garonne-Gironde fluvial-estuarine system is known for historical polymetallic (mainly Cd, Zn, Cu and Pb) pollution derived from a former coal-fired Zn ore treatment facility in the Riou Mort watershed (e.g. Blanc et al., 1999; Audry et al., 2004b). Recent work on Hg concentrations in suspended particulate matter (SPM) and fluxes in the Lot River showed for the first time that the Riou Mort watershed is also an important Hg source to the downstream aquatic environment (Schäfer et al., 2006). However, recent estimates of Hg fluxes from the Riou Mort River cannot explain the elevated Hg concentrations and fluxes at the outlet of the Lot River during the last decade (1993–2003; 35–530 kg a^{-1}), highlighting the importance of sediment resuspension during floods and/or riverbed dredging for the Hg budget of polluted river system (Schäfer et al., 2006).

The present work aims to assess historical (~50 a) Hg records and particulate Hg speciation in sediment cores from two contrasted reservoir lakes on the Lot River, upstream and downstream of the Riou Mort River confluence. For this, particulate Hg concentrations are compared to geochemical background values of the studied system and Hg partitioning in different operationally-defined carrier phases (e.g. Fe- and Mn-oxy-hydroxydes, organic matter and sulphides, organo-chelated Hg) are determined using selective extractions. The impact of industrial activity and remediation work on the long-term evolution of total Hg concentrations, the solid state partitioning and speciation (mono-methylmercury) of Hg are addressed. Finally, the potential behaviour of different Hg carrier phases after sediment resuspension is discussed.

2. Materials and methods

2.1. Study area

The Lot river watershed (11,840 km^2) is known for historic polymetallic (Cd, Zn, Cu, Pb and Ba) contamination of water and sediments due to former coal-fired sulphide Zn ore treatment (1842–1987) in the industrial basin of the Riou Mort Creek (e.g. Blanc et al., 1999; Schäfer et al., 2002; Audry et al., 2004b). After an episode of accidental and drastic pollution (leakage of a waste drain tube in 1986), ore treatment was stopped and remediation work was done at the industrial site. Nevertheless, the Riou Mort watershed still represents an important potential Hg source due to an open-cast coal mine (abandoned in 2001), various uncovered tailings and ore treatment residues. Additionally, until 2002, there was a coal-fired power plant close to the outlet of the Riou Mort watershed. Recent Hg fluxes determined for the Riou Mort River still represent 2–7% of total fluvial Hg inputs into the Gironde estuary for a water contribution of only 0.2% (Schäfer et al., 2006). The two sampling sites, Marcenac and Cajarc represent the first reservoir lakes on the Lot River upstream and downstream from the Riou Mort confluence (Fig. 1). The sediment at Marcenac represents the material derived from the upstream Lot River basin and the sediments at Cajarc integrate particles from the upstream Lot River and the Riou Mort River (Fig. 1; Audry et al., 2004a).

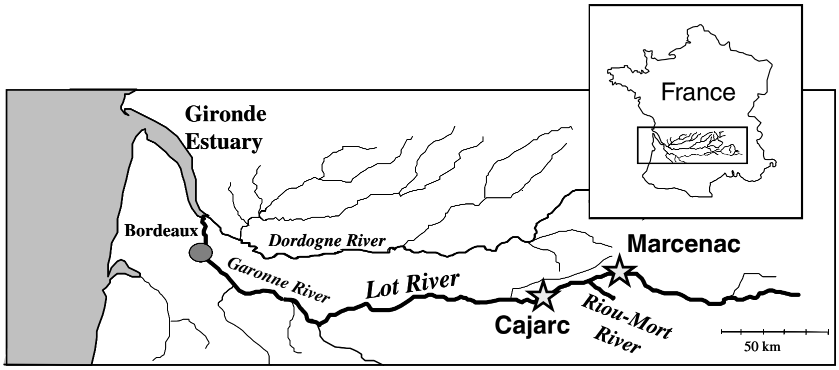

Fig. 1. Map of the study area with location of the sampling sites shown as open stars.

2.2. Sampling methods

In June 2001, sediment cores (0–140 cm depth) were retrieved in the reservoirs Marcenac and Cajarc (Fig. 1) using a 10 × 10 cm plexiglas corer (Audry et al., 2004a). The sediment cores were sliced in thin horizontal sections with a plastic cutter at 1 cm resolution from the surface to 25 cm. The lower part of the 2 cores was sampled with a 5 cm resolution. Sediment samples were dried at 50 °C to constant weight, powdered and homogenized with an agate mortar and stored in the dark.

2.3. Analytical methods

All the labware was acid cleaned (HCl analytical grade; 10%, 72 h), thoroughly rinsed with MilliQ water and dried under a laminar flow hood prior to being in contact with the samples. The Cajarc sediment core was dated by ^{137}Cs measurements using a low background noise γ-ray spectrometer with Ge detector (Intertechnique EGSP 2200–25). Details on grain size distribution and radiocesium measurements are given in Audry et al. (2004a).

Particulate organic C (POC) and total S (S_{tot}) concentrations were measured directly from the dry, powdered and homogenized material using a carbon/sulphur analyzer (LECO, CS–125) according to Cauwet et al. (1990). Quality was checked by measuring certified reference materials (e.g. LECO 501–503). Accuracy was within 5% of the certified values and the analytical error (RSD) generally better than 5%.

2.3.1. Total particulate mercury

Total Hg concentration (HgT_p) was determined directly on ~30–100 mg of dry sediment by cold vapour atomic absorption spectrometry after incineration (O_2 stream) and amalgamation, using a Direct Mercury Analyzer (MILESTONE, DMA 80). The results were expressed in mg kg^{-1} (dry weight) and detection limits (3 sd of the blank values, determined daily) were 0.001–0.002 mg kg^{-1} (Schäfer et al., 2006). The analytical results were quality checked analyzing international certified reference materials (CRM 320, PACS-1, SL-1) after each set of 4 samples. Precision was better than 3% (r.s.d.) and results were consistently within the certified ranges.

2.3.2. Selective extractions

Selective extractions are commonly applied to assess trace metal distribution between different solid phases by extracting different operationally-defined fractions. Most of the methods described in the scientific literature are based on sequential extraction procedures (Gleyzes et al., 2002 and references therein) and often refer to the sequential extraction scheme according to Tessier et al. (1979). However, in the present study, Hg distribution was assessed using 3 single chemical extractions (i.e. using a separate aliquot of the same sample for each reagent) in order to avoid some limitations of sequential extractions (Audry et al., 2006).

The reducing single extraction aimed to extract Mn oxides and to separate the most reactive Fe oxide fraction (i.e. amorphous oxides) from crystalline Fe oxides using an 0.11 M ascorbate reagent consisting of a 5:5:2 sodium citrate/sodium-bicarbonate/ascorbic-acid mixture (J.T. Baker, baker analyzed/J.T. Baker, baker analyzed/Acrôs Organics); (Kostka and Luther, 1994; Anschutz et al., 1998, 2000; Audry et al., 2006). For this, 12.5 ml of ascorbate solution were added to 200 mg of dry sediment in 50 ml HCl-cleaned Teflon® centrifuge tubes (Nalgene, Oak-Ridge) for 24 h with end-over-end tumbling at 12 rpm. Tubes were then centrifuged at 3000 rpm for 20 min, the residual sediment was rinsed with MilliQ® water, and dried at 50 °C. The remaining particulate Hg concentration was measured as described above and subtracted from HgT_p to determine the ascorbate extracted Hg fraction (Hg_{asc}).

The oxidizing single extraction (H_2O_2) typically extracts organic matter, but sulphides are also partially oxidized during this step (e.g. Tessier et al., 1979). A modified Tessier protocol previously validated by Ma and Uren (1995) was used (Audry et al., 2006). For this, 8 ml of 30% H_2O_2 (J.T. Baker, baker analyzed), buffered to pH 5 with NaOH (J.T. Baker, baker analyzed), were added to 200 mg of dry sediment in 50 ml Teflon® centrifuge tubes (Nalgene, Oak-Ridge). The tubes were then placed in an oven at 80 °C for 5 h with manual agitation every 10 min and 3 ml of 30% H_2O_2 and 5 ml of 5 M ammonium acetate (complexing agent, J.T. Baker, baker analyzed) were added after 3 h. Then, the tubes were shaken for 30 min, centrifuged (3000 rpm; 20 min) and the remaining sediment was recovered and dried. The residual particulate Hg concentration was then determined with the Direct Mercury Analyzer and subtracted from HgT_p to determine the H_2O_2 extracted Hg fraction ($Hg_{H_2O_2}$) as described by Sahuquillo et al. (2003).

The single extraction using KOH was described by Bloom et al. (2003) and aims to extract the (operationally-defined) organo-chelated Hg fraction (Hg_{KOH}). For this, 40 ml of 1 M KOH (J.T. Baker, baker analyzed) were added to 400 mg of sediment in 50 ml Teflon® centrifuge tubes for 18 h with end-over-end tumbling. The tubes were then centrifuged at 3000 rpm for 20 min, and the supernatants filtered through 0.45 μm nitrocellulose membranes. Aliquots (16 ml) of the supernatant were placed into 40 ml borosilicate glass bottles with Teflon®-lined-caps (RESTEK, VOA), oxidized with 4 ml of 0.2 M BrCl solution and diluted to 40 ml with MilliQ water. Dissolved Hg was measured as described in Schäfer et al. (2006) by cold vapour atomic fluorescence spectrometry (AFS-Merlin, PS Analytical) with $SnCl_2$ reduction (Bloom and Crecelius, 1983).

2.3.3. Mono-methylmercury determination

Particulate mono-methylmercury (MMHg) concentrations were determined using a modified version of the protocol described in Rodriguez Martin-Doimeadios et al. (2003). Sediment aliquots (0.5 g) were extracted in 10 ml HNO_3 (6 M, Merck, suprapur) for 12 h with end-over-end tumbling at 12 rpm. After centrifugation (3000 rpm; 30 min), aliquots (2 ml) of the supernatant were placed into 20 ml borosilicate glass bottles with Teflon®-lined-caps (RESTEK). Then 1.5 ml of iso-octane (J.T. Baker, baker HPLC-analyzed) and 100 μl of concentrated HCl (J.T. Baker, baker INSTRA-analyzed) were added and the tubes were vigorously shaken by hand (10 min). The addition of HCl at this step aims to keep inorganic Hg in the aqueous phase, avoiding/limiting methylation artefacts during the ethylation step (Rodriguez Martin-Doimeadios et al., 2003). After separation of the organic and aqueous phases, 1 ml of the iso-octane was transferred into borosilicate (20 ml) glass bottles for ethylation at pH 3.9 (5 ml sodium acetate/acid acetic buffer 0.1 M, Sigma-Aldrich/Merck Suprapur) by 1 ml of sodium tetra-ethylborate (Strem Chemicals, 1% (w/v) in KOH 2%) and vigorously shaken (5 min). After separation of the organic and aqueous phases, the organic phase was analyzed by Gas Chromatography (Focus; Thermo Electron) coupled with ICP-MS (X7; Thermo Electron) as described in Rodriguez Martin-Doimeadios et al. (2003). Calibration was done by standard addition of CH_3HgCl solution (100 ng (Hg) ml^{-1}) to the 2 ml aliquots recovered from acid extraction of the solid sample. The method detection limit of the system is 5 pg. The analytical results were quality checked analyzing international certified reference materials (BCR 580, IAEA 356, IAEA 405). Accuracy was 96 ± 8% and precision (RSD) better than 5% at the 0.005 mg kg^{-1} level.

3. Results

The general description of the sediment cores, the interpretation of the ^{137}Cs data and the relationship of the sedimentary metal record (Cd, Zn, Pb and Cu) with the evolution of industrial activities and manufacturing procedures at the former ore treatment plant are described elsewhere (Audry et al., 2004a).

3.1. Total particulate Hg concentrations

The Marcenac site shows low total particulate Hg concentrations (HgT_p; 0.05 ± 0.02 mg kg^{-1}; $n = 42$) within the whole core (Fig. 2a). The minimum and maximum HgT_p concentrations are

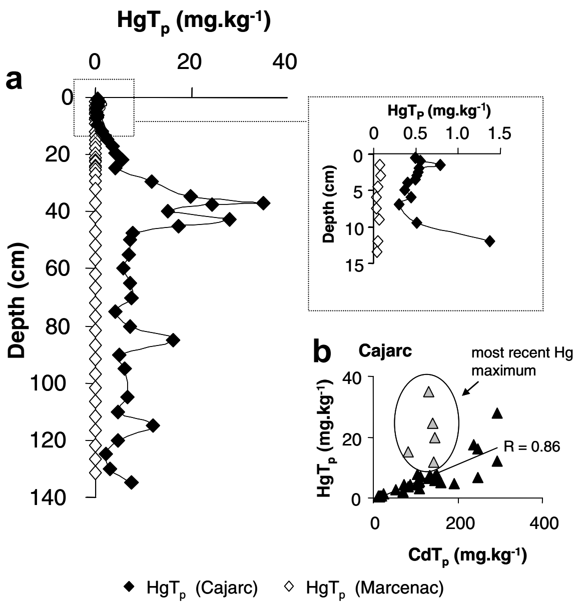

Fig. 2. (a) Depth-concentration profiles for total particulate Hg (HgT_P). (b) Relationship between total particulate Cd (CdT_P) and HgT_P. Open symbols represent the Marcenac site and filled symbols represent the Cajarc site.

0.017 mg kg^{-1} and 0.107 mg kg^{-1}, respectively. At Cajarc (Fig. 2a), HgT_p concentrations in the first 10 cm are 0.49 ± 0.11 mg kg^{-1} ($n = 12$) and increase continuously in the 10–25 cm depth range reaching up to 5.46 mg kg^{-1}, i.e. 100-fold the concentration measured at the Marcenac site. Between 25 and 42.5 cm, HgT_p concentrations strongly increase showing a double-peak (35 mg kg^{-1} at 37 cm and 28 mg kg^{-1} at 42.5 cm) with concentrations ~700-fold higher than Marcenac values. In the 42.5–135 cm depth range HgT_p concentrations remain high around 6 mg kg^{-1} and show two moderate peaks at 85 cm (16 mg kg^{-1}) and at 115 cm depth (12 mg kg^{-1}; Fig. 2a).

3.2. Particulate organic carbon (POC) and sulphur (S)

At both sites POC concentrations in surface sediment range from 65 to 80 g kg^{-1} and show a 30–60% decrease in the first 10 cm likely due to microbial mineralization of organic matter (Fig. 3a and c). In contrast to Marcenac, where POC variations below 10 cm seem to be controlled by grain size variations (Audry, 2003), POC at Cajarc tends to increase with depth, reaching up to 100 g kg^{-1} at 95 cm (Fig. 3c). This may reflect inputs of refractory organic matter, probably due to erosion of coal-bearing Carboniferous rocks and/or coal detritus from the open-pit coal mine (closed in 2002) and related stocks in the Riou Mort watershed. Particulate S concentrations in the Marcenac sediments range from 0.2 to 1.3 g kg^{-1} and are closely related with POC concentrations ($r = 0.88$; data not shown), probably reflecting a non-perturbed site. Particulate S concentrations in surface sediments at Cajarc (1.6 g kg^{-1}) are clearly higher than those at Marcenac and increase with depth (Fig. 2c). Sulphur concentrations at Cajarc are not correlated with POC. Indeed, the S/POC ratio at Cajarc is

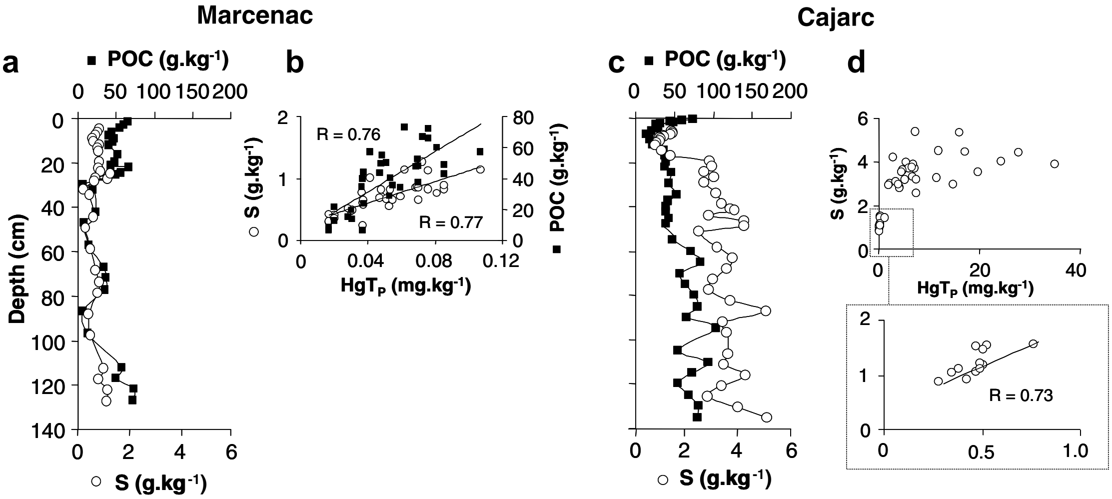

Fig. 3. (a–c) Sulphur and particulate organic C concentrations expressed in weight percent at the Marcenac and Cajarc sites as a function of depth. (b) Relationship of HgT_p to S and POC at the Marcenac site. (d) Relationship of HgT_p to S at the Cajarc site.

clearly higher (0.058 ± 0.021; $n = 42$) than that at Marcenac (0.022 ± 0.011; $n = 34$). This suggests additional S inputs from the Riou Mort watershed via sedimentation of coal detritus and sulphide ore particles and/or authigenic sulphide precipitation by SO_4^{2-} reduction (Audry et al., 2005).

3.3. Ascorbate extracted fraction

At Marcenac, particulate Hg extracted by ascorbate (Hg_{asc}) is not detectable. Indeed, the residual Hg concentrations are not significantly different from HgT_p, suggesting that Hg_{asc} represents <3% of HgT_p within the whole Marcenac core. In contrast, at the Cajarc site, the 0–10 cm section shows Hg_{asc} concentrations of 0.18 ± 0.13 mg kg^{-1} ($n = 8$) (Fig. 4a). Deeper in the sediment Hg_{asc} increases steadily to 0.97 mg kg^{-1} at 25 cm and then shows an important peak of 8.9 mg kg^{-1} at 37 cm. Below this depth Hg_{asc} remains low (0.80 ± 0.67 mg kg^{-1}; $n = 11$), except for small peaks at 42.5 and 50 cm (2.8 mg kg^{-1} and 2.0 mg kg^{-1}; Fig. 4a).

3.4. H_2O_2 extracted fraction

At both sites the $Hg_{H_2O_2}$ profile parallels that of total Hg concentrations (Figs. 2a and 4b). At Marcenac, the Hg fraction extracted by H_2O_2 ($Hg_{H_2O_2}$) is 0.046 ± 0.021 mg kg^{-1} ($n = 14$). At Cajarc, $Hg_{H_2O_2}$ is clearly higher and relatively constant (0.36 ± 0.09 mg kg^{-1}; $n = 10$) in the surface sediment (0–10 cm). In the 10–25 cm depth range $Hg_{H_2O_2}$ increases continuously to 3.8 mg kg^{-1} (25 cm) and shows two important peaks of 28.2 mg kg^{-1} (37 cm) and 18.1 mg kg^{-1} (42.5 cm; Fig. 4b). Below 47.5 cm, $Hg_{H_2O_2}$ is lower and less variable (4.27 ± 1.2 mg kg^{-1}; $n = 15$).

3.5. KOH extracted fraction

At Marcenac, Hg_{KOH} is 0.017 ± 0.006 mg kg^{-1} ($n = 17$) and the profile seems to parallel that of $Hg_{H_2O_2}$ (Fig. 4b and c). In contrast to the other selectively extracted fractions, Hg_{KOH} at Cajarc is similar to typical Marcenac values (0.021 ± 0.015 mg kg^{-1}; $n = 36$) including two relatively important peaks in the 25–45 cm section of 0.07 mg kg^{-1} (Fig. 4c).

3.6. Mono-methylmercury

The mono-methylmercury (MMHg) concentration profile at Marcenac shows two distinct zones. In the upper sediment, MMHg varies from 0.0012 to 0.0043 mg kg^{-1} ($n = 6$) with a maximum at the surface and a second, smaller peak at ~20 cm depth, whereas below 30 cm MMHg values are constant and low (~0.0003 mg kg^{-1}; Fig. 4d). At the Cajarc site, MMHg is 0.0015 ± 0.0008 mg kg^{-1} ($n = 6$,

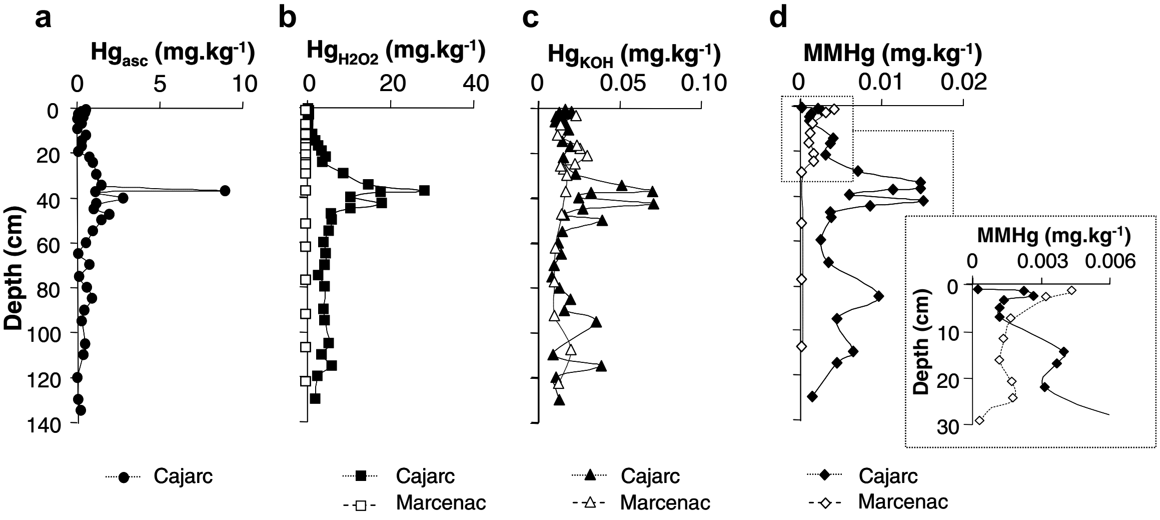

Fig. 4. (a) Ascorbate-extracted Hg (Hg_{asc}) depth-concentration profiles. (b) H_2O_2-extracted Hg ($Hg_{H_2O_2}$) depth-concentration profiles. (c) KOH-extracted Hg (Hg_{KOH}) depth-concentration profiles. (d) Mono-methylmercury (MMHg) depth-concentration profiles. Open symbols represent the Marcenac site and filled symbols represent the Cajarc site. (Hg_{asc} at the Marcenac site was not detectable).

Fig. 4d) in the 0–10 cm layer and shows a second, higher level (0.0036 ± 0.0004 mg kg^{-1}) in the 10–25 cm section. Below 25 cm MMHg is high and highly variable (0.074 ± 0.044 mg kg^{-1}) forming a double peak in the 34–43 cm depth range with values up to 0.015 mg kg^{-1} (Fig. 4d).

4. Discussion

4.1. Historical mercury record

The sedimentary record in the ^{137}Cs dated Cajarc sediments shows important historical Cd, Zn, Cu and Pb pollution and reflects the evolution in manufacturing procedures at the industrial site in the Riou Mort watershed since the 1950s (Audry et al., 2004a). The 1986 pollution event, followed by drastic emission reduction due to the cessation of the ore treatment and remediation work (from 1987 on ward) resulted in an important metal concentration peak at 43 cm, decreasing values from 37–10 cm (∼1987–1997) and constant values in the top 10 cm (Audry et al., 2004a). The HgT_p record in the Cajarc core shows a generally similar evolution (Fig. 2a). The measured HgT_p values are high and highly variable compared to those at Marcenac, which can be considered as the geochemical background of the upper Lot River watershed including inputs from natural and diffuse anthropogenic Hg sources (Fig. 2a; Schäfer et al., 2006). Consequently, the historical Hg contamination of sediments and SPM (Schäfer et al., 2006) of the Lot River downstream from the Riou Mort confluence is attributed to the polymetallic pollution known for other metals (e.g. Cd, Zn, Cu and Pb). Before 1986 (below 45 cm), HgT_p shows a constant level, ∼70-fold higher than geochemical background. The double HgT_p peak in the 25–45 cm zone, covering a period of approximately 7 a represents a period of major Hg contamination. The lower HgT_p peak at 43 cm depth corresponds to the ^{137}Cs activity peak of 1986 (Chernobyl accident) and was attributed to the 1986 accidental polymetallic pollution in the Riou Mort watershed (Audry et al., 2004a). Indeed, total particulate Hg and Cd concentrations are generally well correlated in the Cajarc core whatever the depth ($r = 0.9$; Fig. 2b), suggesting common sources and transport. However, in contrast to Cd (Audry et al., 2004a), the HgT_p profile shows a second major peak (∼700-fold the geochemical background, Fig. 2a and b) at 37 cm depth. This was attributed to important Hg release during ∼1988–1990, i.e. after the cessation of ore treatment and during the period of remediation work, when Cd emission drastically decreased (Fig. 2a; Audry et al., 2004a). Such separation of Hg from other less volatile metals (e.g. Cd), could be explained by coal-fired sulphide roasting, resulting in volatilization, atmospheric emission, condensation and settling of Hg as visible metallic droplets near the smelter (personal communication of former smelter workers). Indeed, during the smelting process up to almost 100% of Hg present in the ores and the coal may be emitted to the atmosphere as metallic Hg and then be partly oxidized by other waste gas constituents (e.g. HCl; Pacyna, 1980). In 1988–1990, removal of the ore treatment facilities and re-landscaping probably resulted in mobilization of Hg-contaminated soil, which could explain the most recent Hg peak in the Cajarc sediments. Moreover, low HgT_p levels in the Marcenac sediments, (<10 km from the smelting site; Fig. 1) suggest (i) rapid Hg condensation and deposition mainly near the smelter, and (ii) that direct atmospheric Hg deposition did not significantly affect sediment concentrations in the Lot River. In contrast, fluvial transport and sedimentation of fly ash, dust and contaminated soil probably contributed to Hg concentrations in Cajarc sediments. Despite remediation work, HgT_p concentrations in recent Cajarc sediments (0–10 cm ∼ 1997–2001) remain ∼10-fold higher than those at Marcenac (Fig. 2a), suggesting that the Riou Mort watershed is still an important Hg source for the Lot River. From the Cd/Hg concentration ratio (10–40; this study and unpublished data) generally observed in sediments downstream from the Riou Mort watershed and the estimated Cd stock in the Lot River sediments (200 ton; Lapaquellerie et al., 1995), the authors estimate that roughly 5–20 ton of Hg is temporarily stored in the Lot River sediments.

4.2. Mercury carrier phases and solid state speciation

4.2.1. Ascorbate fraction

At the Marcenac site, Hg_{asc}, i.e. the fraction attributed to reactive (easily reducible) Fe- and Mn-oxyhydroxides (Laurier et al., 2003) is negligible (<3% of HgT_p). In contrast, at Cajarc, Hg_{asc} partly reflects the high and highly variable HgT_p values and contributes 17 ± 11% (0–60 cm; $n = 22$) and 5.7 ± 3.1% (60–140 cm; $n = 13$), respectively, to HgT_p. The only Hg_{asc} peak (up to 8.9 mg kg^{-1}; Fig. 4a) coincides with the most recent HgT_p peak

(37 cm) supporting the interpretation that this maximum Hg input can be attributed to specific release mechanisms and transport phases, such as soil erosion in the watershed during remediation work (see above).

4.2.2. H_2O_2 fraction

At both sites $Hg_{H_2O_2}$ represents the most important operationally-defined carrier phase with relative contributions to HgT_p of $79 \pm 11\%$ ($n = 14$) and $72 \pm 10\%$ ($n = 38$), respectively. This result confirms the strong affinity of Hg for organic and/or S-rich phases (Davis et al., 1997). Sahuquillo et al. (2003) reported that 20–64% of Hg was extracted by H_2O_2 from certified reference sediments (BCR CRM 580 and BCR CRM 277). After subtraction of $Hg_{H_2O_2}$ from HgT_p in the Marcenac core, the residual Hg concentrations (probably reflecting refractory mineral Hg contents) are 0.012 ± 0.008 mg kg^{-1}. These values are consistent with geological Hg contents in various bedrocks reported by Fitzgerald and Lamborg (2004) and confirm the hypothesis that the major part of Hg in river SPM and uncontaminated surface sediment is associated with organic matter (Schäfer et al., 2006). Accordingly, HgT_p is correlated with both POC and S at Marcenac (Fig. 3b, $R = 0.76$ and 0.77, respectively), suggesting that in the uncontaminated sediment S is associated with natural organic matter. However, the similar relative contribution of $Hg_{H_2O_2}$ to HgT_p observed at both, the reference site and the polluted site is unexpected. Moreover, the close relationship between $Hg_{H_2O_2}$ and HgT_p throughout the whole Cajarc core ($R = 0.99$, data not shown) is not what would have been expected, given the highly contrasted HgT_p concentrations during the industrial activity and after remediation. There is no clear relationship between HgT_p and POC at Cajarc, whereas there seems to be a complex relationship between HgT_p and S (Fig. 3d), suggesting that HgTp and $Hg_{H_2O_2}$ are mainly associated with sulphide phases of different nature. Indeed, the upper sediment (0–10 cm) with low S concentrations shows a linear relationship between HgT_p and S (Fig. 3d). In contrast, deeper sediment (10–140 cm) shows high S contents without a clear relationship with HgT_p (Fig. 3d). Indeed, S content in the two depth ranges directly reflects the drastic reduction of industrial inputs after remediation (Audry et al., 2004a). Assuming that the H_2O_2 extraction mainly extracts organic matter and amorphous/reactive sulphides (Tessier et al., 1979; Ma and Uren, 1995; Audry et al., 2006), the major part of HgT_p in the Cajarc core is supposed to be mainly associated with reactive sulphide phases and organic matter throughout the whole core. Assuming that Hg_{KOH} represents the organo-chelated Hg fraction (see below), the difference $Hg_{H_2O_2}$–Hg_{KOH} should provide a rough estimate of the sulphide-bound fraction. Accordingly, it is estimated that the sulphide-bound Hg fraction contributes ~45% and 70% to HgT_p at Marcenac and in the polluted Cajarc sediments, respectively. The residual phase (HgT_p–$Hg_{H_2O_2}$) at Cajarc representing ~0.3 mg kg^{-1} and ~3–5 mg kg^{-1} in the upper and lower depth ranges, respectively, could mainly consist of Hg bound to non-reactive sulphides not extracted by H_2O_2. Such sulphides, probably pyrite or arsenopyrite, could be derived from ore treatment residues (Audry et al., 2005) and/or coal detritus (Yudovich and Keris, 2005). However, worldwide typical Hg concentrations in coal (~0.1–1 mg kg^{-1}; Yudovich and Keris, 2005) and some point measurements in the Riou Mort watershed (~0.3–0.5 mg kg^{-1}; $n = 5$) suggest that coal associated Hg may be negligible compared to Hg concentrations in sulphide ores. Indeed, HgS may account for up to 90% in furnace dust and 98% in calcine piles (Davis et al., 1997). The high amounts of $Hg_{H_2O_2}$ in the Cajarc sediments suggest potentially important Hg release to the water column in the case of resuspension and oxidation of these sediments.

4.2.3. KOH fraction

At Marcenac, Hg_{KOH}, representing organo-chelated Hg (Bloom et al., 2003), is ~2-fold lower than $Hg_{H_2O_2}$ and represents $\sim 37 \pm 17\%$ of HgT_p. These results suggest that Hg_{KOH} may be an important fraction of HgT_p in uncontaminated fluvial sediments. Moreover, at Marcenac organic matter and sulphides (deduced from the difference between $Hg_{H_2O_2}$ and Hg_{KOH}) may represent carrier phases of equal importance. However, in the case of incomplete leaching of organically-bound Hg by the KOH extraction used, the determined sulphide-bound fraction could be overestimated.

At the Cajarc site, Hg_{KOH} generally shows similar concentrations as at Marcenac (~0.02 mg kg^{-1}; except for the double peak at 37–42 cm; Fig. 4c), with Hg_{KOH} contributions to HgT_p of 3.3% in the upper sediment (0–10 cm) and ~0.26% in the deeper sediment. These results suggest that organo-chelated Hg (Hg_{KOH}) is a negligible fraction of $Hg_{H_2O_2}$ in the Cajarc core and that the major part of $Hg_{H_2O_2}$ is bound to reactive H_2O_2-extractable sulphide. The weak proportion of organo-chelated Hg in the contaminated sediment may reflect (i) initial partitioning of Hg during transport and sedimentation (e.g. relatively constant inputs of organo-chelated Hg and dominance of Hg-bearing sulphides) or (ii) in situ redistribution of Hg between organic matter and authigenic sulphide phases. The first hypothesis is supported by the observation that most of the Hg_{KOH} values at Cajarc in sediment deposited during and after the ore treatment period are similar to Marcenac values suggesting that organo-chelated Hg inputs are independent of industrial activities in the Riou Mort watershed and probably represent geochemical background (Fig. 4c). Accordingly, more or less reactive sulphide phases are supposed to be the major carriers during transport and sedimentation of Hg from the Riou Mort watershed. This is coherent with the generally parallel profiles of HgT_p and CdT_p in the Cajarc core (Fig. 2a and b). Comparing relative Hg_{KOH} contributions at Marcenac and at Cajarc, it is estimated that sulphide phases from ore residues and/or coal detritus may account for ~90% of recent (1997–2001) Hg inputs into the Cajarc sediments. The double Hg_{KOH} peak at 37–42 cm (Fig. 4c), attributed to the accidental pollution and to remediation work (1987–1990), suggests either increased inputs and/or in situ production of organo-chelated Hg from Hg transported as sulphides, oxides or metal. Assuming that the double Hg_{KOH} peak is attributed to two distinct mobilization processes with Hg transported in two different chemical forms (see above), it is proposed that the double Hg_{KOH} maximum that parallels that of particulate MMHg may result from in situ transformation processes also involved in methylation (see below).

4.2.4. Mono-methylmercury content

At the Marcenac site, the vertical MMHg distribution (Fig. 4d), and the close relationship between MMHg and POC concentrations ($R = 0.84$; Fig. 5a) suggests that production and/or deposition of MMHg occurs in the uppermost cm of the sediment, probably directly related with microbial degradation of fresh organic matter, followed by demethylation processes with burial (Hines et al., 2004; Benoit et al., 2006; Muresan et al., 2006). The observed MMHg concentrations and contributions to HgT_p (~0.001–0.004 mg kg^{-1}; 0.6–5.7%; Fig. 4d) are in the range of values typically observed in sediments (e.g. Davis et al., 1997; Fitzgerald and Mason, 1997; Hines et al., 2004; Benoit et al., 2006; Muresan et al., 2006). At Cajarc, the overall MMHg concentration profile seems to be strongly influenced by HgT_p (Figs. 2a and 4d), but relative MMHg contributions to HgT_p are clearly lower (0.5–0.04%) than at Marcenac. However, MMHg concentrations in the uppermost 20 cm are similar to those measured at Marcenac in the same depth

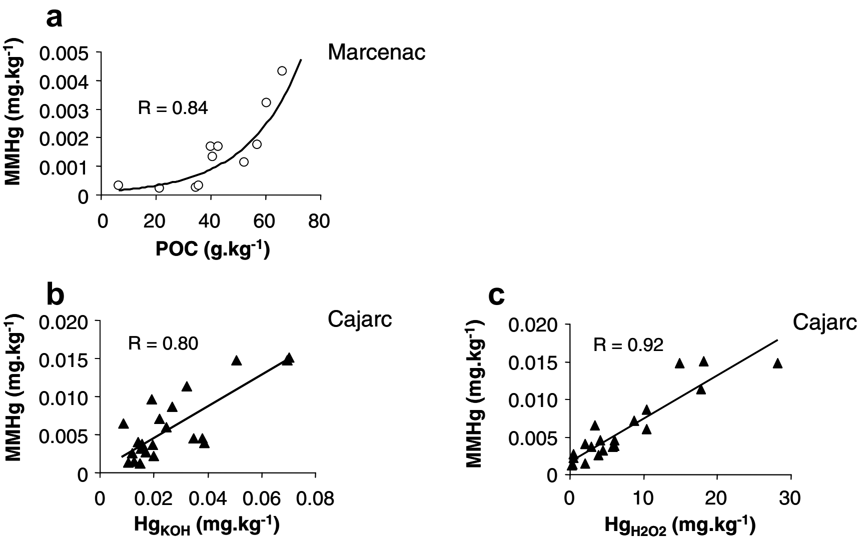

Fig. 5. (a) Relationship between particulate mono-methylmercury and particulate organic C at the Marcenac site. (b) Relationship between particulate mono-methylmercury and KOH-extracted Hg at the Cajarc site. (c) relationship between particulate mono-methylmercury and H_2O_2-extracted Hg at the Cajarc site.

range and at both sites show a zone of maximum MMHg close to the water sediment interface (Fig. 4d). This observation suggests similar in situ methylation/demethylation in surface sediment of the uncontaminated reference site and in the recent (after 1990) Cajarc sediment. In contrast to the reference site, MMHg concentrations are highest deeper in the Cajarc sediment (Fig. 4d), suggesting persistence of MMHg in 10–40 a-old contaminated, sulphide-rich sediment, probably due to slow biodegradation (Davis et al., 1997; Hintelmann et al., 2000; Rodríguez Martín-Doimeadios et al., 2004). However, the relatively low contribution of MMHg to HgT_p may be due to limited methylation in the presence of high sulphide concentrations (e.g. Craig and Moreton, 1983; Berman and Bartha, 1986; Benoit et al., 1999; Rodriguez Martin-Doimeadios et al., 2000). In the depth range, where maximum HgT_p concentrations occur (37–42 cm), MMHg represents ~25% of Hg_{KOH} and shows a parallel profile. Although, the methylation potential of a sediment is correlated with Hg_{KOH} (Bloom et al., 2003), MMHg in the polluted Cajarc sediment seems to be more closely correlated with $Hg_{H_2O_2}$ ($R = 0.92$; Fig. 5b) than with Hg_{KOH} ($R = 0.80$; Fig. 5c). This is coherent with the fact that methylation of Hg in sediments is often attributed to microbially driven SO_4 reduction (Gilmour et al., 1992), being expected to go along with production of authigenic, reactive sulphides on the one hand and degradation of reactive organic matter on the other hand.

4.3. Potential Hg release by sediment resuspension

Remobilisation of heavily polluted Lot River sediments during dredging periods and/or intense floods may release important amounts of metals into the aquatic environment and significantly change the annual metal budget of the downstream system, including the Gironde estuary (e.g. Birkett et al., 2001; Audry et al., 2004b; Coynel, 2005; Schäfer et al., 2006). The present results suggest that most of the Hg temporarily stored in contaminated fluvial sediments, is associated with more or less reactive carrier phases and thus may be mobilized and transformed by various biogeochemical processes in the estuary (e.g. organic matter degradation, sulphide oxidation, SO_4 reduction; Tseng et al., 2001; Laurier et al., 2003; Audry et al., 2005). Methylation in the estuarine turbidity zone, enhanced by sedimentation and resuspension cycles (e.g. Tseng et al., 2001), increases Hg bio-availability and may contribute to the observed accumulation in some estuarine fish species (e.g. estuarine shad; Durrieu et al., 2005).

5. Conclusions

1. The present sedimentary record clearly shows that the Lot River sediments downstream from the Riou Mort confluence are affected by important historical Hg pollution, suggesting that monitoring of metal concentrations realized in many other aquatic systems affected by mining and/or ore treatment should integrate Hg measurements.
2. More than a decade after the end of the industrial activity and despite intense remediation work, contamination of the downstream reaches goes on. Moreover, remediation work itself probably resulted in important Hg release.
3. Mercury extracted by H_2O_2 represents the major part of HgT_p at both the polluted and the uncontaminated site and shows similar relative contributions (~70–75%). Therefore, organic matter and/or more or less reactive sulphides are the major carrier phases of Hg in both contrasting sediments.
4. Organo-chelated Hg represents an important fraction in the uncontaminated sediment, whereas its contribution at the contaminated site is negligible. Similar Hg_{KOH} concentrations at both sites suggest that organo-chelated Hg is mainly of natural origin and that Hg at Cajarc is mainly associated with sulphides.
5. Methylmercury concentrations and profiles are almost similar in the upper sediment of both sites, suggesting that the recent contamination level at the polluted site does not significantly modify methylation/demethylation. Although methylation may be limited by the presence of high sulphide concentrations deeper in the contaminated sediment, high MMHg in more than 10 a-old sediment suggests slow MMHg degradation in this environment.
6. Resuspension of reservoir sediments during dredging or intense floods may remobilize important quantities of Hg, mainly bound to reactive carrier phases. This Hg will be exposed to biogeochemical processes (e.g. oxidation-reduction cycles and estuarine methylation) in the downstream environments probably increasing its bioavailability and eco-toxicological potential.

Acknowledgement

This study is a scientific contribution of the 'GIS-ECOBAG' (Groupement d'Intérêt Scientifique: Ecologie du Bassin Adour-Garonne). This work was supported by Grants from 'l'Agence de l'Eau Adour-Garonne', 'la Région Aquitaine', 'le Ministère de la Recherche' and 'le FEDER-Région Aquitaine'.

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