
Mercury in the Lot–Garonne River system (France): Sources, fluxes and anthropogenic component

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Abstract: Dissolved and particulate Hg fluxes in the Lot–Garonne–Gironde fluvial-estuarine system were obtained from observation of daily discharge and suspended particulate matter (SPM) concentrations. In addition to the measurements of the total dissolved (<0.45 µm) and particulate Hg (>0.45 µm), called HgTD and HgTP respectively, the dissolved inorganic Hg species (HgRD) were determined monthly. Geochemical background values for HgTP in sediments and SPM were similar to crustal values and to typical concentrations in SPM of non-contaminated river systems, respectively. The Riou Mort watershed already known as the origin of important historical polymetallic (e.g., Cd, Zn) pollution was identified as an important Hg point source. In the downstream Lot River, Hg concentrations were clearly higher than those in other moderately contaminated systems. The mean relative contribution of HgRD to HgTD in the Lot River and in the Garonne River was close to 25% and 50%, respectively, and showed no correlation with water discharge or SPM concentration. Depending on the origin and nature of SPM, HgTP concentrations were correlated or not with particulate organic C (POC). Maximum HgTP concentrations were measured in samples containing low POC concentrations and were attributed to sediment resuspension. In contrast, high POC concentrations (6–17%) during algal blooms were associated with low/moderate HgTP concentrations (<0.5 mg kg⁻¹) at different sites, suggesting that Hg concentrations in fluvial phytoplankton may be limited by bioavailability of dissolved Hg and/or physiologically controlled Hg accumulation. Mercury was mostly (up to 98%) transported in the particulate phase with estimated annual Hg fluxes at the outlet of the Lot River system ranging from 35 to 530 kg a⁻¹ for the past decade. The minimum anthropogenic component (58–84% of total Hg fluxes) could not be explained by present Riou Mort point source contributions, suggesting important Hg release from contaminated sediment as a major source and from downstream point sources (e.g., coal-fired power plants and/or metal processing industries). HgTP concentrations and fluxes were strongly related to hydrologic variations and were clearly increased by riverbed dredging during lock construction. Therefore, the estimated Hg stocks in the Lot River sediment (5–13 tons) represent an important potential Hg source for the downstream fluvial-estuarine system.

Keywords: mercury, organic matter, river, SPM, Garonne, Lot

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Abstract

Dissolved and particulate mercury fluxes in the Lot-Garonne-Gironde fluvial-estuarine system were obtained from observation of daily discharge and suspended particulate matter (SPM) concentrations. In addition to the measurements of the total dissolved ($< 0.45 \mu\text{m}$) and particulate mercury ($> 0.45 \mu\text{m}$), called HgT_D and HgT_P respectively, the dissolved inorganic mercury species (HgR_D) were determined monthly. Geochemical background values for HgT_P in sediments and SPM were similar to crustal values and to typical concentrations in SPM of non-contaminated river systems, respectively. The Riou Mort watershed already known as origin of important historical polymetallic (e.g., Cd, Zn) pollution was identified as an important Hg point source. In the downstream Lot River, mercury concentrations were clearly higher than those in other moderately contaminated systems. The mean relative contribution of HgR_D to HgT_D in the Lot River and in the Garonne River was close to 25% and 50% respectively, and showed no correlation with water discharge or SPM concentration. Depending on the origin and nature of SPM, HgT_P concentrations were correlated or not with particulate organic carbon (POC). Maximum HgT_P concentrations were measured in samples

with low POC concentrations and were attributed to sediment resuspension. In contrast, high POC concentrations (6-17%) during algal blooms were associated with low/moderate Hg_{TP} concentrations (<0.5 mg.kg⁻¹) at different sites, suggesting that Hg concentrations in fluvial phytoplankton may be limited by bioavailability of dissolved Hg and/or physiologically controlled mercury accumulation. Mercury was mostly (up to 98 %) transported in the particulate phase with estimated annual Hg fluxes at the outlet of the Lot River system ranging from 35-530 kg.a⁻¹ for the past decade. The minimum anthropogenic component (58-84 % of total Hg fluxes) could not be explained by present Riou Mort point source contributions, suggesting important mercury release from contaminated sediment as a major source and from downstream point sources (e.g., coal-fired power plants and/or metal processing industries). Hg_{TP} concentrations and fluxes were strongly related to hydrologic variations and were clearly increased by riverbed dredging during lock construction. Therefore, the estimated mercury stocks in the Lot River sediment (5-13 tons) represent an important potential mercury source for the downstream fluvial-estuarine system.

Keywords: *mercury, organic matter, river, SPM, Garonne, Lot*

Introduction

Atmospheric transport and deposition are important components in global Hg cycling (Fitzgerald et al., 1991; Vandal et al., 1993; Shotyk et al., 2003). However, on a regional scale, rivers transport important amounts of Hg, derived from: (i) atmospheric deposition onto the whole catchment and (ii) terrestrial sources of natural and anthropogenic origin (Cordeiro et al., 2002; Lawson and Mason, 2001; Ganguli et al., 2000). In aqueous environments, Hg is

an important pollutant due to possible methylation, enhancing its toxicity for aquatic organisms and bioaccumulation in the food chain (Miles and Tome, 1997; Murata et al., 1999; Samson and Shenker, 2000). Various processes may induce important Hg transformation and recycling with significant changes in Hg speciation and transport phases (Cossa et al., 2001; Tseng et al., 2001; Laurier et al., 2003) and, thus, even sediments may represent either sinks (Mercone et al., 1999) or secondary sources (Covelli et al., 1999). The potential impact of trace metals such as Hg, Cd, Zn and Cu on the coastal environments and related seafood production depends on pollutant concentrations, species and renewable input (Miles and Tome, 1997). However, Hg fluxes in rivers are generally poorly documented and are often based on relatively short observation periods and/or low sampling frequencies that are not adapted to hydrological variations (Coynel et al., 2004a).

In this paper, we present data on concentrations and fluxes of dissolved and particulate Hg in the Lot-Garonne river system, a well documented pathway of a historical poly-metallic pollution (Cd, Zn, Pb, Cu; Blanc et al., 1999; Schäfer and Blanc, 2002; Audry et al., 2004a) of the Gironde estuary (Figure 1). The objective is to characterize the distribution and transport of dissolved and particulate mercury using long-term data covering a wide range of hydrologic conditions. Mercury concentrations in water, sediment and suspended particulate matter (SPM) and Hg fluxes are compared to those of other fluvial systems. Background values for particulate Hg in SPM and the anthropogenic contribution to Hg fluxes in the Lot River are estimated. Finally, the role of sediment remobilisation during riverbed dredging as a potential Hg source for the Gironde estuary is discussed.

2 Material and methods

2.1 Sampling sites

The most upstream site on the Lot River represents the part of the watershed that is not affected by the polymetallic pollution from the Riou Mort watershed: Boisse Penchot (BP; Figure 1; Audry et al., 2004b). The sampling site at the outlet of the Riou Mort (RM) watershed integrates fluxes from natural, urban and heavily polluted areas (e.g., uncovered tailings) due to former open-cast coal mining, coal-fired power production (until 2001) and coal-fired Zn-ore treatment (until 1987; Audry et al., 2004a). The site Cajarc (C) represents the first reservoir on the Lot River downstream from the Riou Mort River/Lot River confluence (Figure 1). Additional permanent sampling sites are located at Temple (T) on the Lot River and at Port Ste Marie (PSM) on the Garonne River, each upstream of the confluence (Figure 1). The most downstream sampling site on the Garonne River, La Réole (LR), integrates fluxes from the Lot-Garonne watershed that represents the major fluvial pathway of river water and SPM transported into the Gironde estuary (Schäfer et al., 2002). The site is located upstream of the tidal reaches (neither inversion of flow direction nor intrusion of brackish water) to ensure well-defined discharge conditions, but as far downstream as possible to represent a maximum portion of the drainage basin (Schäfer and Blanc, 2002).

2.2 Sampling

At La Réole and Temple, a permanent high resolution observation of river water, SPM and Cd fluxes had been realized since 1990 (Audry et al., 2004a; Schäfer et al., 2002). Suspended particulate matter concentrations were measured daily at all sites. In 1999-2003 dissolved reactive mercury (HgR_D), total dissolved mercury (HgT_D) and particulate mercury (HgT_P) concentrations were measured monthly at the sites RM, T, PSM and LR, with additional sampling during floods. The reference site for the upper Lot River at Boisse Penchot was sampled twice-monthly in 2000-2003. Before 1998, HgT_P was measured only in SPM from the Lot River at Temple. Most of the pre-1998 samples analyzed were recovered

during floods, as samples collected during drought and mean discharge often did not provide enough material for HgT_P analysis. However, particulate Hg fluxes estimated from these data were considered representative, as particulate trace metal transport in the Lot-Garonne River system is controlled by floods (Audry et al., 2004a; Schäfer et al., 2002). During the exceptional flood event in December 2003, additional samples for SPM and HgT_P measurements were retrieved every three hours at the Temple site throughout six days and daily at the Boisse Penchot site.

Water samples were collected with acid-cleaned (HCl, Baker instra-analyzed, 10 %) 500 ml Teflon bottles, thoroughly rinsed with river water of the site. The samples were immediately filtered through 0.45 µm Teflon filters (LCR Membranes, Millipore®) in a glove box (laboratory van) under an inert N₂ atmosphere (N₂ purified by a gold trap). The filtrates were collected in acid-cleaned (HCl; Baker instra-analyzed, 10 %) 125 ml Teflon (FEP) bottles, previously rinsed with an aliquot of the filtrate, acidified (1% HCl; ultrapure, Baker) and stored in double polyethylene bags at 4-6° C in the dark until analysis. SPM for HgT_P analysis was sampled by pumping and centrifugation (12,000g; Westfalia) of up to 1000 l of river water (Schäfer and Blanc, 2002). Discharge, SPM load and HgT_P concentrations in the torrential Riou Mort watershed were highly variable. Therefore, additional samples retrieved by automated systems (SIGMA 900, Bühler-Montech) were analyzed for HgT_P. For this, aliquots (120 ml) of river water were sampled every 3 hours, and stored in acid-cleaned (HNO₃, 10%) 1 liter polypropylene bottles, each representing one day. Particulate matter was separated by centrifugation. Consecutive samples representing periods of similar discharge were composited (4-6 days), dried, homogenized and analyzed for HgT_P. Flood samples were analyzed separately. These high frequency HgP data were combined with the respective SPM concentrations to increase reliability of flux estimates (Coynel et al., 2004), but were not used for partition coefficients.

In June 2001, sediment (0-140 cm depth) was sampled in reservoirs at Boisse Penchot, Cajarc and Temple (Figure 1) using a 10x10 cm polypropylene corer (Audry et al., 2004c). The sediment at Boisse Penchot 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. Sediment at the Temple site, near the outlet of the Lot River, integrates material from the whole watershed (Audry et al., 2004c).

2.3 Determination of SPM and POC concentrations

The daily SPM-concentrations were determined by filtering defined volumes of river water through pre-combusted (500° C; 6 h), pre-weighed filters (Whatman GF/F, 0.7 µm). The filters were dried to constant weight (36-48 h, 45° C) and re-weighed. The ratio of particle mass and filtered volume represents SPM concentrations. The filtered SPM were acidified by HCl (37%) to remove carbonates and POC was analysed using a carbon/sulphur analyser (LECO, CS-125) as described in (Cauwet et al., 1990). Quality control was maintained by measuring certified reference materials (e.g., LECO 501-503). Accuracy was generally better than 5 % deviation from certified values and precision was better than 5 % (r.s.d).

2.4 Mercury analyses

Dissolved reactive Hg (HgR_D) also called easily reducible mercury, an operationally defined fraction containing labile species, and total dissolved Hg (HgT_D), composed of all the dissolved mercury species, were measured by cold vapour atomic fluorescence spectrometry (AFS-Merlin, PSA analytical) after $Hg(0)$ generation using $SnCl_2$ as a reductant and gold trap amalgamation (Bloom and Creclius, 1983). According to the same authors, for HgR_D the reduction was performed directly on an unamended filtered water sample, while for HgT_D the reduction was performed after $BrCl$ oxidation of the sample (destruction of non-labile, mainly

organic Hg species; Bisinoti and Jardim, 2003). Calibration was done by injection of variable amounts of gaseous Hg(0). The detection limit (3 times the standard deviation of 5 blank values) was determined daily and varied from 0.06 to 0.1 ng.l⁻¹. The reproducibility (coefficient of variation of 5 replicate samples) was below 10 % for both HgR_D and HgT_D. Particulate Hg (HgT_P) was analyzed from the dry, homogenized material (SPM and sediment) by cold vapour atomic absorption spectrometry after calcination under an oxygen stream and amalgamation on a gold trap using automated mercury analyzers (ALTEC-AMA-254 and MILESTONE-DMA-80). The results were expressed in mg.kg⁻¹ (dry weight) and the detection limit (3 times the standard deviation of 5 blank values) varied daily from 0.001 to 0.002 mg.kg⁻¹. The accuracy of the analytical results was checked by analyzing certified reference materials (CRM 320, PACS-1, SL-1) after each set of four samples. Precision (coefficient of variation of 5 replicate samples) was better than 5% and results were consistently within the certified concentration intervals. Protocols and quality assurance measurements are detailed in Cossa et al. (2002 and 2003a).

Comparing our results to data of other recent studies necessitated calculation of “total Hg” concentrations, as these authors measured Hg in unfiltered samples (Tseng et al., 2001; Lawson et al., 2001; Kwokal et al., 2002). Therefore, total Hg_{unfiltered} concentrations, were calculated from SPM, HgT_P and HgT_D concentrations ($Hg_{unfiltered} = SPM * HgT_P + HgT_D$) and were considered similar to what would have been obtained by analysis of unfiltered samples.

2.5 Flux estimates

Dissolved and particulate Hg fluxes at the sites Temple, Port Ste Marie and La Réole were estimated from daily discharge and SPM concentrations combined with monthly measured dissolved and particulate Hg concentrations using adapted, commonly applied algorithms (*e.g.*, Walling and Webb, 1985; Meybeck et al., 1996; Schäfer et al., 2002; Audry

et al., 2004a). At the Riou Mort site, where SPM and HgP concentrations are highly variable, reliable HgP fluxes were obtained by using additional HgP concentrations with up to daily resolution measured in samples retrieved every 3 hours by an automated sampling device (see sampling section).

3 Results

In the upstream Lot River, at site Boisse Penchot, HgT_D concentrations ranged from 0.6-1.5 ng.l⁻¹ (Table 1) and HgR_D represented 7-53% (mean ~18%) of HgT_D. In contrast, in the Riou Mort River HgT_D showed the highest and most variable values (0.1-2.8 ng.l⁻¹; Table 1), HgR_D representing 6-90% of HgT_D with a mean of ~35%. Mean and minimum HgT_D and HgR_D concentrations in the downstream Lot River at Temple were similar to those at Boisse Penchot (Table 1). However, maximum HgT_D concentrations were almost 3-fold higher at Temple than at Boisse Penchot. Relative contributions of HgR_D to HgT_D ranged from <3-95%, with a mean of 25%. The lowest mean HgT_D concentrations occurred in the Garonne River at both sites (LR and PSM), whereas mean HgR_D concentrations were higher than in the Lot River (Table 1). The relative contribution of HgR_D to HgT_D ranged from 12-90% at LR and from 29-72% at PSM, with similar means of 48% and 52%, respectively. Consequently, mean relative contributions of HgR_D to HgT_D were 2-fold higher in the Garonne River than in the Lot River. Dissolved mercury speciation (HgR_D/HgT_D-ratio) showed no correlation with discharge or SPM concentration. However, the relatively low mean contribution of HgR_D to HgT_D in the Lot River suggests dominance of non labile (i.e. mainly organically bound; Bisinoti and Jardim, 2003) dissolved mercury species. This and the highly variable HgR_D/HgT_D-ratio in the Lot River probably reflect the high and highly variable dissolved organic carbon (DOC) concentrations in the Lot River (e.g., 4.23±2.33 mg.l⁻¹ in 2003). In 2003, DOC concentrations in the Garonne River at PSM

($3.03 \pm 1.39 \text{ mg.l}^{-1}$) and at LR ($2.95 \pm 1.37 \text{ mg.l}^{-1}$) were about 1.5-fold lower and less variable than those in the Lot River at Temple (e.g., Lemaire et al., in press).

In the upper Lot River at Boisse Penchot, mean HgT_P concentrations were clearly lower and less variable than those in both, the Riou Mort River and the downstream Lot River at Temple (Table 1). Indeed, the highest and most variable HgT_P concentrations occurred in the Riou Mort River. In the Lot River, downstream from the Riou Mort/Lot River confluence, mean HgT_P concentrations in SPM from Cajarc (2000) and Temple (1998-2003) were comparable and ranged from $0.35\text{-}0.45 \text{ mg.kg}^{-1}$. However, in 2000, average HgT_P concentration at Temple was clearly higher than in the other years (Table 1). There was no clear trend of mean annual HgT_P concentrations at Temple in 1992-2003.

Particulate mercury concentrations in SPM from the Garonne River were similar at both sites (LR and PSM) and clearly lower and less variable than in the Lot River (Table 1). In the Riou Mort, Lot and Garonne Rivers, HgT_P concentrations were not correlated with discharge, SPM or POC concentrations. In the Lot River, maximum HgT_P concentrations occurred in samples with relatively low POC concentrations (see discussion). In both rivers maximum POC concentrations were associated with moderate to low HgT_P concentrations, i.e. samples with high POC (>8 %) always showed HgT_P concentrations lower than 0.45 mg.kg^{-1} .

Partition coefficients (K_d value = ratio $\text{HgT}_P/\text{HgT}_D$; kg.l^{-1}) were quite similar at the different sites (Table 1). However, maximum annual mean log K_d values (6.2) were observed in the Riou Mort River and minimum annual mean log K_d (5.2) occurred in the upper Lot River at Boisse Penchot site. At these two upstream sites, K_d was more variable than at the other three sites (T, PSM and LR). Although K_d was systematically higher in the Lot River than in the Garonne River, K_d was not related to discharge, POC, $\text{HgR}_D/\text{HgT}_D$ -ratio or SPM concentrations in the whole Lot-Garonne River system.

The sedimentary record in the upper sediment (0-15 cm depth, representing ~3-5 years; Audry et al., 2004c; Table 2) of the Lot-River reservoirs suggests minor/negligible variability of Hg concentrations in settling particles for the period ~1996 to 2001. This is consistent with the observation that episodically (mainly during floods) measured Hg_{TP} concentrations in SPM from the Lot River did not show important variations in 1992-1997 and were similar to those obtained monthly in 1998-2003 (Table 1). From the Cd stock in the Lot River sediments (~200 tons; Lapaquellerie et al., 1995) and the Cd/Hg concentration ratio of 15-40 (Schäfer et al. 2004) in reservoir sediment at Cajarc and Temple we estimate that the present day Hg stock in the Lot River sediment is 5-13 tons, of which >80% are considered anthropogenic (Schäfer et al. 2004).

4 Discussion

4.1 Particulate Hg concentrations and organic matter

In the Riou Mort River, samples with high POC concentrations covering the whole range of Hg_{TP} concentrations (Figure 2a) were attributed to erosion of carboniferous rocks (open-cast coal mine), uncovered tailings and residues of former Zn ore treatment and/or urban sources because chlorophyll *a* was generally low (<1000 mg kg⁻¹; Lemaire et al. in press). Additionally, until 2002, there was a coal-fired power plant a few hundred meters downstream from the Riou Mort sampling site.

At the Temple site, samples with high POC concentrations (>8%) and high chlorophyll *a* (4800-7900 mg kg⁻¹; Lemaire et al., in press), probably due to important phytoplankton activity, typically showed intermediate Hg_{TP} values (0.2-0.48 mg.kg⁻¹; Figure 2a). Indeed, these samples showed chlorophyll *a*/POC ratios from 10 to 30 mg.g⁻¹, similar to those typically observed in phytoplankton cultures (Harris, 1986). This reflects

intense algal blooms, where phytoplankton is the main constituent of SPM (Harris, 1986; Sullivan et al., 2001). This suggests that in this environment, Hg uptake by phytoplankton is limited, resulting in maximum HgT_P concentrations below 0.5 mg kg⁻¹. In contrast, high HgT_P concentrations (>0.5 mg.kg⁻¹) at Temple were generally measured in samples with (for this site) low POC concentrations. Highest HgT_P concentrations occurred during situations with high SPM concentrations like the dredging period in 2000/2001 (Audry et al., 2004b; Figure 2a) and the major flood in December 2003, when HgT_P concentrations ranged from 0.5 to 1 mg.kg⁻¹ (n=15) during 2 days of maximum sediment load. Therefore, high HgT_P concentrations at the Temple site were attributed to sediment resuspension by dredging and/or riverbed erosion during intense floods.

Although there was no statistically significant correlation between HgT_P and POC concentrations, the data suggest a general increase of HgT_P with increasing POC for the Garonne River sites (La Réole and Port Ste Marie, Figure 2b), especially in the “usual” POC range for these sites (2-5%), when particulate organic matter is mainly derived from topsoil and litter (Veyssy et al., 1999). Therefore, the associated Hg could be derived mainly from deposition of atmospheric Hg in the catchment and transported into rivers together with organic matter by erosion. In contrast, during algal blooms both Garonne River sites showed high POC concentrations (6-17%) associated with low/moderate HgT_P concentrations (Figure 2) similar to what was observed at Temple site. Therefore, we suggest that Hg concentrations in fluvial phytoplankton typically are clearly below 0.5 mg.kg⁻¹, whatever the site. This is probably due to limited bioavailability of dissolved Hg and/or physiologically limited Hg uptake. Biologically mediated reduction of ionic Hg to elemental Hg (Hg⁰) may occur in both seawater and freshwater (e.g., Vandal et al, 1995). Moreover, high phytoplankton activity needs light and is thus coupled to low SPM concentrations. During these high irradiation periods, abiotic Hg photoreduction is at maximum, probably intensified

by the presence of fulvic and humic acids (Alberts et al., 1974; Amyot et al., 1994). Both processes may result in important production of Hg^0 and subsequent evasion. As in many aquatic systems Hg^0 production is limited by the supply rate of reactive Hg (Amyot et al., 1994; Fitzgerald and Mason, 1997), we suggest that it may itself limit Hg bioavailability and/or accumulation in phytoplankton of the Lot-Garonne fluvial system.

4.2 Mercury contamination of the Lot River

High and highly variable dissolved and particulate Hg concentrations in the Riou Mort River indicate that this small watershed is an important Hg source for the Lot River. This variability and the observed concentration ranges suggest coexistence and variable dominance of natural and heavily contaminated material. The role of the Riou Mort watershed as an important historical Hg source is confirmed by the important differences in HgT_p concentrations in SPM and sediment from the upstream site Boisse Penchot and the downstream site Cajarc (Table 2). Therefore, we reasonably assume that the Hg contamination of the Lot-Garonne River system is mainly associated with the historical polymetallic pollution (e.g., Cd, Zn, Cu, Pb; Audry et al., 2004b) due to former coal-fired Zn ore treatment.

Particulate Hg concentrations in SPM from site Boisse Penchot that were considered as reference values for the upstream Lot River watershed are higher than usually reported continental crust concentrations ($\sim 0.012\text{-}0.06 \text{ mg kg}^{-1}$; e.g., Wedepohl, 1995; Gao et al., 1998; Rudnik and Gao, 2003). However, natural Hg concentrations in sedimentary rocks and soils are often higher than crustal values, mainly attributed to organic matter (Fitzgerald and Lamborg, 2004). Accordingly, HgT_p concentrations in SPM from the upstream Lot River are similar to typical values of non-contaminated systems (e.g., Rémy et al., 2003, Fitzgerald and Lamborg, 2004) suggesting that despite potential sources in the upper Lot watershed (e.g., ore bearing rocks or mining; BRGM, 1978) the main Hg sources for the Lot River must be

located downstream from Boisse Penchot. Accordingly, HgT_p concentrations in surface sediments (0-15 cm depth) of the reservoir at site Boisse Penchot are close to average crustal values ($\sim 0.05 \text{ mg.kg}^{-1}$; Rudnick and Gao, 2003) and, thus, even lower than in SPM from the same site (Table 2). This observation suggests separation of dense or coarse, settling material with relatively low Hg concentrations from light or fine-grained suspended particles with higher Hg content, reflecting differences in i) grain size or ii) particle nature. Particulate organic matter, clay-size particles and Mn-oxides (to a lesser extent) are known as important carrier phases for Hg (e.g., Gagnon et al., 1996; Quémerais et al., 1998; Laurier et al., 2003) and could explain this observation. However, the relation between POC and HgT_p at the different sites appears to be complex (Figure 2).

HgT_p concentrations in SPM (Table 1) and in the upper sediment (0-15 cm depth) of the downstream Lot River (Cajarc and Temple sites; Table 2) were similar or up to 2-fold higher than those reported for some well industrialized fluvial systems (Mason and Sullivan, 1998; Quémerais et al., 1999) and also systematically higher than 0.15 mg.kg^{-1} , Hg concentration that, according to the U.S. Environmental Protection Agency (US EPA, 1999), should not be exceeded to avoid negative effects on aquatic wildlife. However, they were one or two orders of magnitude lower than those in SPM and sediment from the most heavily polluted river systems (e.g., Ganguli et al., 2000; Cossa et al., 2001; Gray et al., 2002; Berzas Nevado et al., 2003).

The HgT_D concentrations in the Lot-Garonne River system were generally comparable to typical freshwater values (Mason and Sullivan, 1998) and clearly lower than those in the Seine River (Cossa et al., 2003b) or the heavily polluted San Carlos Creek ($< 1.5\text{-}140 \text{ ng.l}^{-1}$; Ganguli et al., 2000). Total (“unfiltered”) $Hg_{unfiltered}$ concentrations were mainly controlled by SPM and HgT_p concentrations and ranged from $2.2\text{-}336 \text{ ng.l}^{-1}$ in the Lot River and from $0.3\text{-}120 \text{ ng.l}^{-1}$ in the Garonne River. In the Riou Mort River, $Hg_{unfiltered}$ concentrations were up to

880 ng.l⁻¹. These concentrations were much lower than the 2400 ng.l⁻¹ standard recommended by the US Environmental Protection Agency (US EPA, 1999) to protect against acute effects to aquatic wildlife. However, at Temple, ~40% of the samples showed higher Hg_{unfiltered} concentrations than the 50 ng.l⁻¹ standard recommended to protect against chronic effects to aquatic wildlife (US EPA, 1999). Concentrations below 50 ng.l⁻¹ occurred during low to intermediate discharge, when SPM concentrations were low. Although using Hg_{unfiltered} concentrations may be helpful for establishing guidelines (e.g., US EPA, 1999) and comparing different systems, they reflect SPM concentration rather than Hg behaviour in rivers. It seems therefore essential to separately consider the dissolved and particulate phases in threshold recommendations and management guidelines.

Distribution coefficients (K_d; Table 1) were in the upper range of typical values for rivers and estuaries (Whyte and Kirchner, 2000) and were similar to those reported for the maximum turbidity zone of the Gironde estuary (Tseng et al., 2001), Californian creeks draining former Hg mines (Ganguli et al., 2000) and the Croatian Kastela Bay, where up to “almost 100%” of total Hg was retained by 0.45 µm filters (Kwokal et al., 2002). In the Lot-Garonne system, particulate Hg fluxes generally accounted for more than 90% of total Hg fluxes (Table 1), which may be considered as typical, especially for river systems draining areas with mine tailings. In contrast to the Anacostia River, an urban watershed in Washington D.C. (Mason and Sullivan, 1998), K_d in the Lot-Garonne system was not related with POC.

4.3 Mercury fluxes in the Lot-Garonne-Gironde fluvial-estuarine system

From 1998 to 2003, Hg fluxes in the Lot-Garonne fluvial system were highly variable and ranged from 32 kg.a⁻¹ to 424 kg.a⁻¹ at Temple and from 176 kg.a⁻¹ to 428 kg.a⁻¹ at La Réole (Table 1). During this period, the upstream Garonne River at site PSM contributed 116-185 kg.a⁻¹. In 1999, 2002 and 2003 mass balances between these three sites were equilibrated,

whereas in 2000/2001 the sum of fluxes at Temple and PSM clearly exceeded those at La Réole (Table 1; see discussion). Mercury fluxes in the Riou Mort River were 5.5 to 35 kg.a⁻¹. In 1999 and 2002 the Riou Mort contributed ~15% to total Hg fluxes at Temple (Table 1), whereas it typically contributes only ~1% of discharge (Audry et al., 2004a). Mercury fluxes in the Riou Mort River represented 2-7% of total fluvial Hg inputs into the Gironde estuary, although its freshwater contribution generally was below 0.2%. As Hg fluxes were mainly due to SPM transport, the contribution of the Lot River to Hg fluxes at La Réole varied with hydrology (Table 1) and reached a minimum in 2002, a very dry year (Schäfer et al., 2002). In wet/average years, the Lot River was the main fluvial transport path for Hg into the Garonne River and the Gironde estuary (Table 1).

As Hg is essentially transported in the particulate fraction, we can reasonably estimate Hg fluxes at Temple from 1992-2003 annual mean HgT_P concentrations and well-established SPM fluxes (Schäfer et al., 2002; Audry et al., 2004a), without considering HgT_D fluxes. Accordingly, estimated annual Hg fluxes at the outlet of the Lot River system for the past decade ranged from 35-530 kg.a⁻¹ (Figure 3).

Mean annual Hg fluxes (1998-2003) in the Riou Mort River clearly exceeded those in the San Carlos Creek (California), draining the New Idria mine, formerly the 2nd largest Hg mine in North America. Indeed, Hg fluxes in the San Carlos Creek were estimated ~7.3 g.day⁻¹, i.e. <1.5 kg.a⁻¹ (Ganguli et al., 2000), but the authors suggest that real fluxes might possibly be one order of magnitude higher. In this case, the San Carlos Creek Hg fluxes would still be lower than those in the Riou Mort River (Table 1), although Hg has never been exploited in this watershed. The observed Hg anomaly in the Riou Mort watershed is probably due to impurities of the formerly processed sulphide ores, coal fired industrial processes and/or the open pit coal mine. Despite the low industrialisation/urbanisation of the region drained by the Lot-Garonne-Gironde fluvial-estuarine system, its Hg fluxes are relatively high, compared to

flux data reported for other river systems. Mercury fluxes into the Gironde estuary (200-560 kg.a⁻¹) are similar to the lower limit of Hg fluxes into the Seine estuary (500-1,500 kg.a⁻¹; Cossa et al., 2003b), both draining watersheds of comparable size. However, the Seine River drains one of the most industrialized and urbanized watersheds in Europe. The Gironde fluvial Hg fluxes in 1999-2003 were also similar to those i) in the polluted Mersey estuary (300-500 kg.a⁻¹ in 1995-1997; Harland et al., 2000) and ii) in a creek at the outlet of a former Californian cinnabar mine, where annual Hg fluxes can reasonably be supposed to be lower than ~400 kg.a⁻¹ (Whyte and Kirchner, 2000). An important part of fluvial Hg fluxes into the Gironde estuary was transported in the Lot-Garonne River system representing a temporary reservoir and the main transport path for the polymetallic contamination caused by former industrial activities in the Riou Mort watershed.

4.4 Anthropogenic contribution to Hg fluxes

Our results show that HgT_P concentrations in the upper Lot River watershed which is dominated by igneous and metamorphic rocks are low, compared to maximum values proposed for uncontaminated and moderately urbanized areas (up to 0.2 mg.kg⁻¹; Förstner and Wittmann, 1983; Coquery et al., 1997; Rémy et al., 2003). The central and downstream part of the Lot River watershed is covered by Jurassic, Cretaceous and Quaternary sediments (mainly carbonates; BRGM, 1978). Therefore, according to Fitzgerald and Lamborg (2004), we assumed that geological Hg contents in bedrock of the whole watershed range from 0.03-0.09 mg.kg⁻¹, which is clearly lower than measured HgT_P concentrations in SPM at the remote site Boisse Penchot. The difference is probably attributed to organic matter, but the complex relations between Hg and organic matter of variable origin make it difficult to estimate natural HgT_P background concentrations in fluvial SPM. Assuming that natural atmospheric Hg inputs are similar within the whole catchment area and that rocks (e.g., Carboniferous rocks) potentially rich in Hg are mainly present in the upstream part of the Lot River catchment, we

propose the mean HgT_p concentration (0.15 mg.kg^{-1}) observed at the upstream site Boisse Penchot as background HgT_p concentration for the Lot River SPM. This approximate background value also includes anthropogenic Hg (atmospheric and dispersed) inputs and thus may slightly overestimate natural background. Consequently, we consider 0.15 mg.kg^{-1} as the maximum natural HgT_p concentration in SPM from the Lot River. We used this maximum natural HgT_p concentration and annual SPM fluxes at the Temple site (Table 1) to roughly estimate the maximum non-anthropogenic component of Hg fluxes in the Lot River. The difference between total and maximum non-anthropogenic Hg fluxes was considered as minimum anthropogenic Hg fluxes. Accordingly, in 1992-2003, the mean estimated anthropogenic Hg flux at the outlet of the Lot River was $\sim 200 \text{ kg.a}^{-1}$ representing a minimum anthropogenic contribution of 58-84% to total Hg fluxes (Figure 3).

The specific Hg output fluxes of the Lot River basin ($3\text{-}45 \text{ g.km}^2.\text{a}^{-1}$) were variable and much higher than typical values ($1\text{-}5 \text{ g.km}^2.\text{a}^{-1}$) observed for various watersheds in Northern Europe and North America, with different types of land use (forest, agricultural, wetland; Hurley et al., 1995; Porvari and Verta, 2003). The potential impact of atmospheric Hg inputs at the watershed scale was estimated as follows: Using typical atmospheric Hg deposition values of $10\text{-}20 \text{ }\mu\text{g.m}^2.\text{a}^{-1}$ (Shotyk et al., 2003; Lawson and Mason, 2001; Seigneur et al., 2003), atmospheric input into the Lot River watershed ($11,800 \text{ km}^2$) was estimated $118\text{-}236 \text{ kg.a}^{-1}$. As Hg retention in watersheds typically ranges from 80-98% (Lawson and Mason, 2001; Lorey and Driscoll, 1999; Quémerais et al., 1999; Kamman and Engstrom, 2002), atmospheric deposition would contribute $2.4\text{-}47.2 \text{ kg.a}^{-1}$ to fluvial Hg fluxes at Temple site. Given the low industrialisation/urbanisation and the important forest cover of the catchment, we suggest that atmospheric Hg deposition was clearly lower than $20 \text{ }\mu\text{g.m}^2.\text{a}^{-1}$ and/or Hg retention in the Lot River watershed was much higher than 80%. Therefore, at the watershed

scale atmospheric Hg inputs are considered to contribute less than 10% to fluvial Hg transport in the Lot River.

In 2000, the sum of particulate Hg fluxes at Temple and Port Ste Marie was higher than fluxes at La Reole (Table 1). Similar results have been reported for Cd fluxes (Audry et al., 2004b). Indeed, river bed dredging related to lock constructions in the Lot River induced remobilisation of heavily contaminated sediment from September 2000 to June 2001, clearly increasing local SPM concentrations (Figure 4) and fluxes (Audry et al., 2004b). As a consequence, SPM and Hg_{Tp} concentrations were systematically higher during the dredging period (2000/2001), than in 1999, 2002 or 2003 and clearly increased Hg_{unfiltered} concentrations (Figure 4). The average Hg_{Tp} concentration in the sediment at Temple (~1 mg.kg⁻¹ within the 0-60 cm depth range; Schäfer et al., 2004) and the estimated dredging-related, additional SPM flux (38,000-113,000 t; Audry et al., 2004b), suggest an additional anthropogenic Hg flux of 38-110 kg in 2000. Accordingly, we estimate that in 2001 the dredging-related fluxes were 180,000-280,000 t for SPM (Bossy et al., 2002) and 180-280 kg for Hg. These estimates are coherent with our estimated minimum anthropogenic Hg fluxes (Figure 3).

Mass balances suggest settling of heavy Hg-rich particulate matter upstream from La Réole in 2002/2001 (Audry et al., 2004b), steady state in 2002 (very dry year) and important sediment resuspension during a major flood event in December 2003 (Coynel et al., 2004b; Table 1). Indeed, in anticipation of this centenary flood, reservoirs had been systematically opened, strongly decreasing water levels in reservoirs. Consequently, historically contaminated reservoir sediments (e.g., Audry et al., 2004b) were exposed to unusually high current velocities and exceptionally strong sediment erosion. In contrast to Hg_{Tp}, Hg_{Td} and Hg_{Rd} concentrations did not increase during the dredging period or the flood event. From high resolution SPM and trace metal data we estimate that the flood-related sediment erosion

in the downstream Lot River during the December 2003 event mobilized about 240,000 t of sediment (Coynel et al., 2004b) and 120-380 kg of Hg. During the same event, estimated Hg fluxes were 25-30 kg at Boisse Penchot and ~10 kg at Riou Mort site. Again, these estimates are widely coherent with estimated minimum anthropogenic Hg fluxes (Figure 3). Consequently, the major part of anthropogenic Hg fluxes at the Temple site was attributed to sediment erosion due to dredging in 2000/2001 and flood management in December 2003. Therefore, the polluted Lot River sediments must be considered as an important potential Hg source for the downstream fluvial-estuarine system.

Conclusions

The Lot-Garonne-Gironde fluvial-estuarine system is impacted by historical Hg pollution due to former coal mining and Zn ore treatment in the Riou Mort River basin. This has led to contamination of reservoir sediments, suggesting that many other river systems affected by mining and ore treatment may also present important and yet undiscovered Hg contaminations. Mercury fluxes in the Lot-Garonne river system are closely related to SPM transport and mainly of anthropogenic origin (58-84 %). Recent mercury fluxes derived from the upstream watershed, the point sources (e.g., former coal mines, tailings, power plant) in the contaminated Riou Mort watershed and atmospheric inputs cannot explain the important fluxes at the outlet of the Lot watershed. Indeed, remobilisation of historically contaminated sediment due to riverbed dredging and flood-related sediment erosion accounts for the major part of recent Hg fluxes. The present monitoring highlights the complex relationship between mercury transport in river SPM and spatial and temporal source variations on the one hand and organic matter of variable origin on the other hand.

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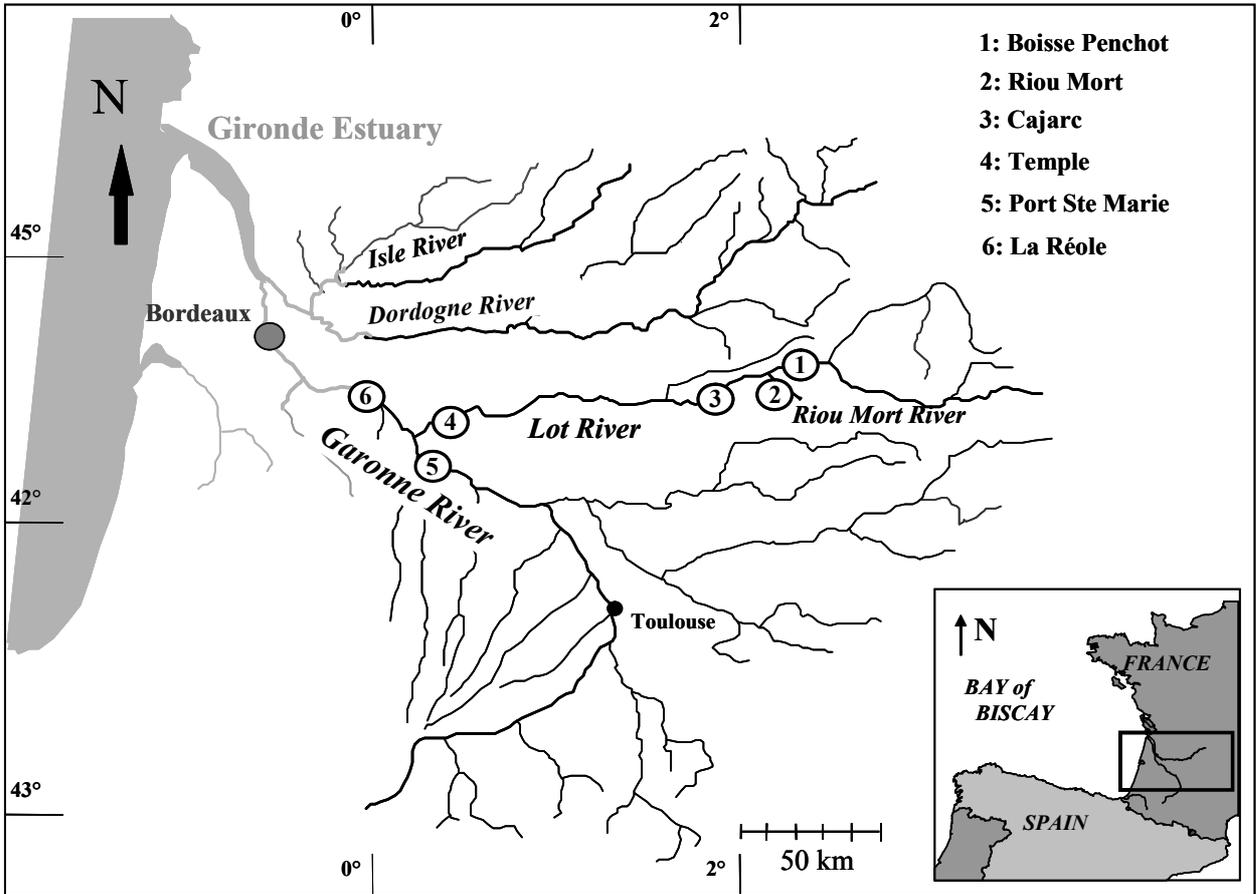


Figure 1

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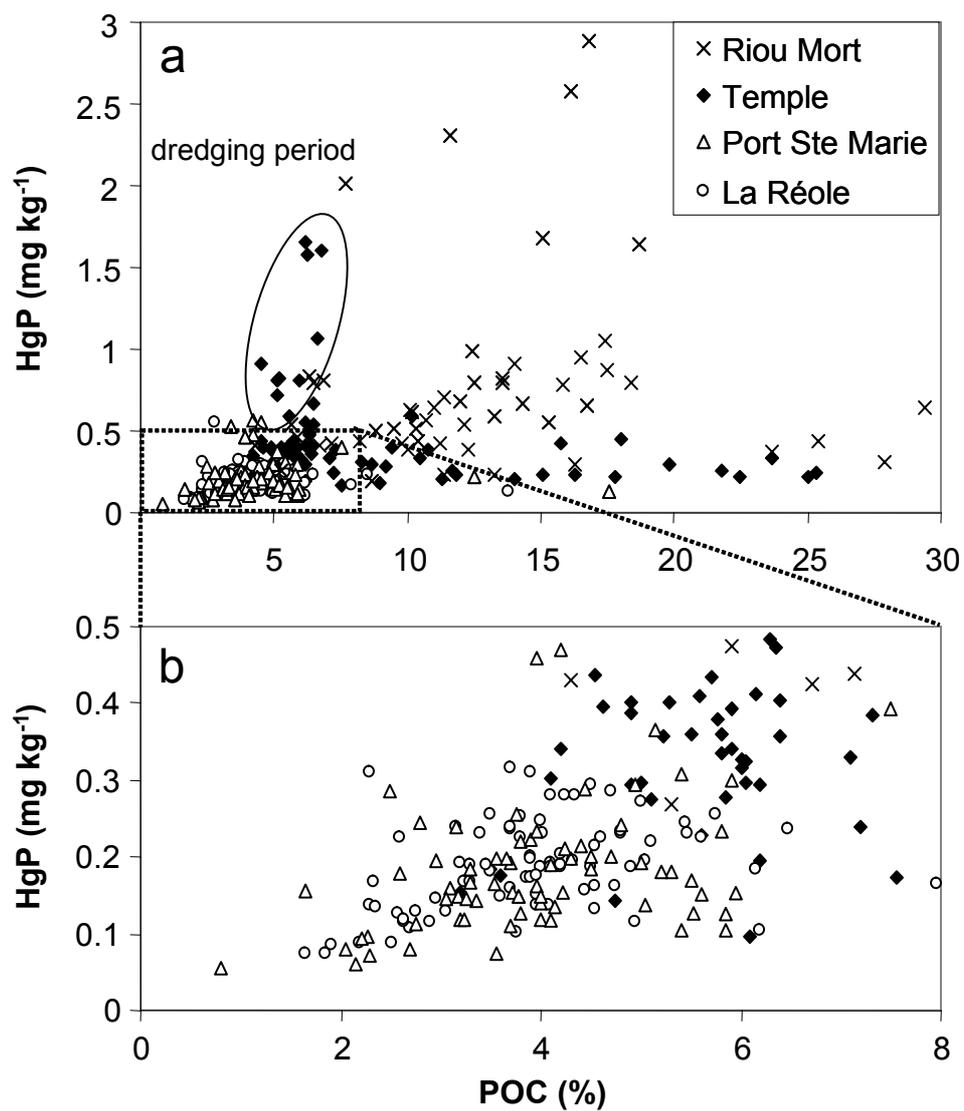


Figure 2

Schäfer et al.

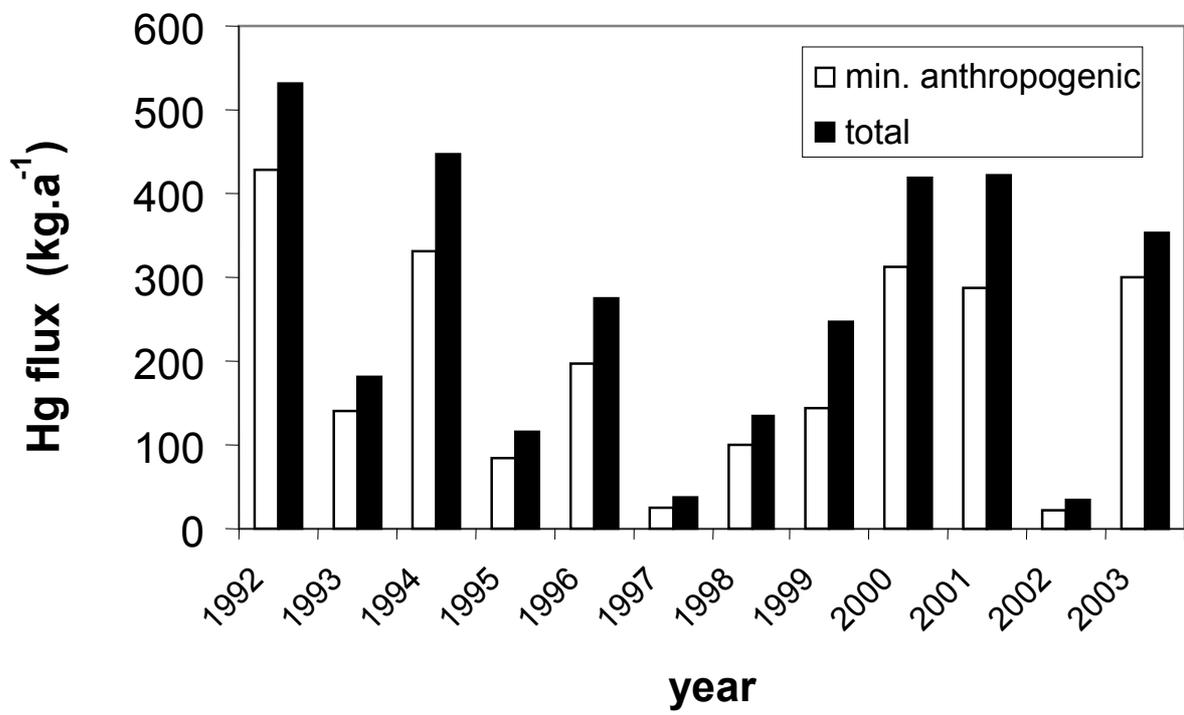


Figure 3

Schäfer et al.

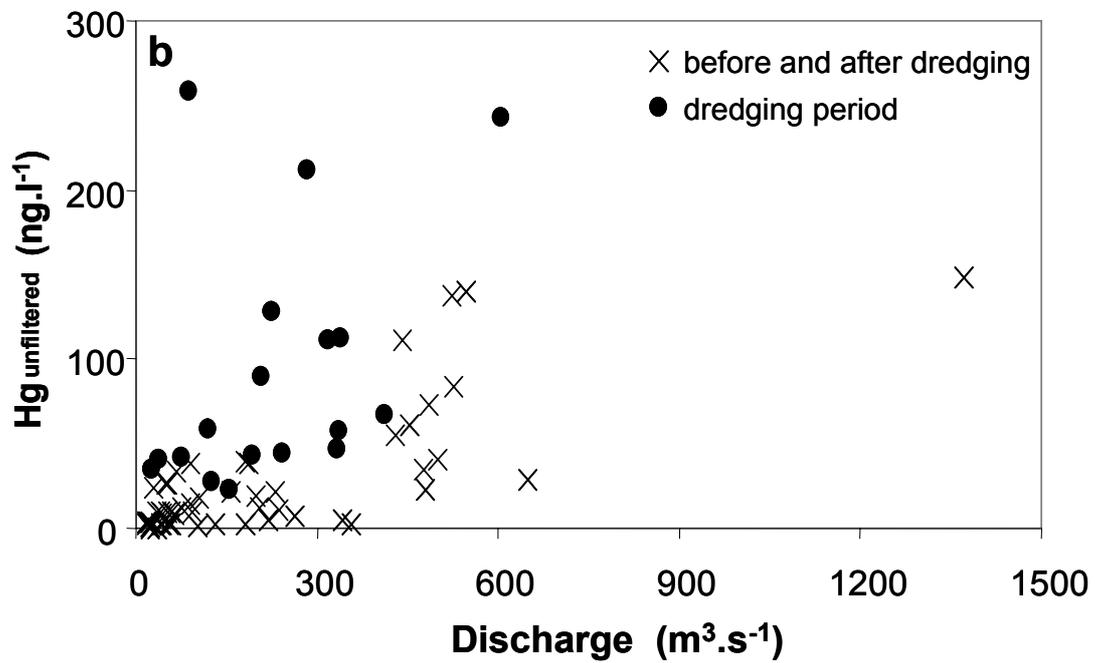
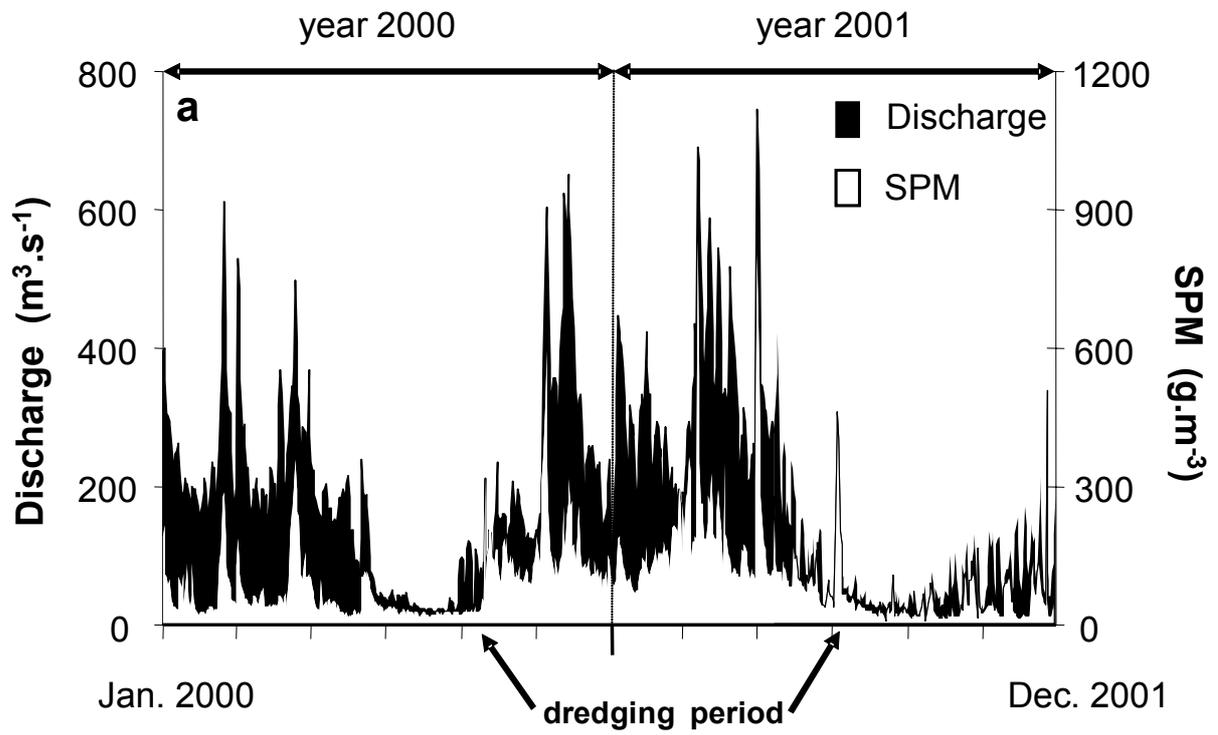


Figure 4

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Figure Captions

FIGURE 1: Map of the study area and the sampling sites

FIGURE 2: Relationship between HgT_P and POC concentrations (dry weight) at the different sites (1999-2003) showing the total range of measured concentrations (a) and a zoom of the lower concentration range (b). POC concentrations are expressed in weight %, i.e. 10^4 mg.kg^{-1} .

FIGURE 3: Estimates of minimum anthropogenic and total mercury fluxes in the Lot River at Temple in 1992-2002. White bars represent minimum anthropogenic Hg fluxes obtained from annual SPM fluxes and HgT_P concentration of 0.15 mg.kg^{-1} .

FIGURE 4: Impact of riverbed dredging on SPM (a) and $Hg_{unfiltered}$ (b) concentrations at Temple.

TABLE 1: Mercury concentrations (mean, range, number of samples) and fluxes of water, SPM and mercury in the Lot-Garonne River system

Site	Year	River water flux	SPM flux	HgR _D	HgT _D	HgT _P	log Kd	HgT _D flux	HgT _P flux
		(10 ⁹ m ³ .a ⁻¹)	(10 ⁶ t.a ⁻¹)	(ng.l ⁻¹)	(ng.l ⁻¹)	(mg.kg ⁻¹)		(kg.a ⁻¹)	(kg.a ⁻¹)
Riou Mort River	1999	0.082	0.0351	n.m.	0.92 (0.1-2.8) n=8	1.3 (0.253-2.89) n=13	6.2	0.1	35
	2000	0.059	0.0335	0.5 (<0.1-1.1) n=8	1.3 (0.3-3.0) n=8	0.60 (0.185-0.847) n=14	5.7	0.1	18
	2001	0.058	0.0342	0.5 (0.1-1.5) n=14	1.8 (0.9-4.1) n=14	0.55 (0.107-1.12) n=33	5.5	0.1	15
	2002	0.033	0.0116	1.0 (0.1-2.4) n=12	2.3 (0.8-4.6) n=12	0.68 (0.187-3.04) n=59	5.5	0.06	5.4
	2003	0.050	0.0256	0.9 (0.5-1.3) n=13	1.7 (0.9-2.3) n=13	0.54 (0.113-1.91) n=61	5.5	0.08	12
Lot River Temple	1992	6.24	0.670	n.m.	n.m.	0.75 (0.358-0.950) n=9	n.m.	n.m.	530
	1993	4.04	0.280	n.m.	n.m.	0.62 (0.411-0.784) n=3	n.m.	n.m.	182
	1994	7.66	0.773	n.m.	n.m.	0.54 (0.245-0.764) n=5	n.m.	n.m.	446
	1995	4.44	0.216	n.m.	n.m.	0.61 (0.214-0.811) n=4	n.m.	n.m.	116
	1996	5.40	0.531	n.m.	n.m.	0.52 (0.121-0.975) n=8	n.m.	n.m.	276
	1997	3.43	0.080	n.m.	n.m.	0.46 (0.295-0.622) n=2	n.m.	n.m.	36
	1998	4.69	0.223	n.m.	n.m.	0.87 (0.216-2.10) n=15	n.m.	n.m.	134
	1999	5.02	0.706	n.m.	n.m.	0.34 (0.079-0.590) n=13	n.m.	n.m.	245
	2000	5.85	0.710	0.3 (<0.1-0.6) n=14	1.1 (0.6-2.4) n=14	0.68 (0.204-1.65) n=18	5.8	4	420
	2001	5.17	0.831	0.2 (<0.1-0.3) n=14	0.7 (0.4-1.4) n=14	0.41 (0.213-0.806) n=14	5.8	4	416
	2002	2.95	0.106	0.4 (0.1-1.7) n=14	1.2 (0.5-3.2) n=14	0.31 (0.203-0.398) n=14	5.4	4	32
2003	4.29	0.367	0.3 (<0.1-1.6) n=12	0.9 (0.4-2.4) n=12	0.33 (0.153-1.03*) n=15	5.9	4	354	
Garonne River P. Ste Marie	1998	10.6	0.578	n.m.	n.m.	0.37 (0.213-0.611) n=13	n.m.	n.m.	176
	1999	15.1	0.907	n.m.	n.m.	0.29 (0.137-0.563) n=13	n.m.	n.m.	206
	2000	13.4	1.10	n.m.	n.m.	0.17 (0.072-0.238) n=18	n.m.	n.m.	185
	2001	11.8	0.539	0.2 (<0.1-0.6) n=14	0.7 (0.3-2.1) n=14	0.16 (0.061-0.530) n=14	5.4	9	116
	2002	10.4	0.687	0.5 (0.2-0.9) n=14	0.9 (0.7-1.5) n=14	0.20 (0.105-0.393) n=14	5.4	9	130
	2003	12.1	1.07	0.7 (0.3-1.2) n=12	1.2 (0.7-2.1) n=12	0.12 (0.074-0.193) n=15	5.0	15	134
Garonne River La Réole	1998	15.3	0.84	n.m.	n.m.	0.31 (0.172-0.496) n=20	n.m.	n.m.	291
	1999	20.1	1.73	n.m.	0.7 (0.3-1.6) n=7	0.26 (0.182-0.777) n=15	5.6	22	406
	2000	18.7	1.77	n.m.	0.9 (0.2-1.6) n=15	0.19 (0.089-0.315) n=18	5.4	22	383
	2001	16.9	0.986	0.2 (<0.1-0.3) n=14	0.6 (0.4-0.9) n=14	0.17 (0.088-0.236) n=14	5.4	14	170
	2002	12.8	0.868	0.6 (0.2-1.0) n=14	1.2 (0.7-1.1) n=14	0.20 (0.116-0.255) n=14	5.2	15	161
	2003	17.2	2.56	0.6 (0.2-1.1) n=12	1.0 (0.7-2.6) n=12	0.26 (0.074-0.570) n=15	5.4	29	559

* maximum daily HgT_P concentration during the December 2003 flood, was also used to calculate the mean annual HgT_P concentration.

TABLE 2: Overview on HgT_D and HgT_P concentrations in river water, SPM and upper sediment at the three studied reservoir sites Boisse Penchot, Cajarc and Temple (from upstream to downstream).

site	Boisse Penchot	Cajarc	Temple
	average (range) n= number of samples	average (range) n= number of samples	average (range) n= number of samples
HgT_D (ng.l⁻¹)	1.2 (0.6-1.5) n=22	n.m.*	1.0 (0.4-3.2) n=54
year	(2000-2003)		(2000-2003)
HgT_P (mg.kg⁻¹)	0.15 (0.059-0.228) n=22	0.36 (0.150-0.489) n=12	0.42 (0.097-1.65) n=120
year	(2000-2003)	(2000)	(1992-2003)
Log Kd	5.2	n.m.*	5.5
Sediment (0-15 cm)	0.058±0.019 n=13	0.50±0.12 n=12	0.39±0.037 n=13

* n.m. = not measured. Values in parentheses represent the range of measured concentrations.
n= number of samples analyzed