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Long-term records of cadmium and silver contamination in sediments and oysters from the Gironde fluvial–estuarine continuum – Evidence of changing silver sources

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Abstract:

The Gironde fluvial estuarine system is impacted by historic metal pollution (e.g. Cd, Zn, Hg) and oysters (*Crassostrea gigas*) from the estuary mouth have shown extremely high Cd concentrations for decades. Based on recent work (Chiffoleau et al., 2005) revealing anomalously high Ag concentrations (up to 65 mg kg^{-1}; dry weight) in Gironde oysters, we compared long-term (~1955–2001) records of Ag and Cd concentrations in reservoir sediment with the respective concentrations in oysters collected between 1979 and 2010 to identify the origin and historical trend of the recently discovered Ag anomaly. Sediment cores from two reservoirs upstream and downstream from the main metal pollution source provided information on (i) geochemical background (upstream; Ag: ~0.3 mg kg^{-1}; Cd: ~0.8 mg kg^{-1}) and (ii) historical trends in Ag and Cd pollution. The results showed parallel concentration-depth profiles of Ag and Cd supporting a common source and transport. Decreasing concentrations since 1986 (Cd: from 300 to 11 mg kg^{-1}; Ag: from 6.7 to 0.43 mg kg^{-1}) reflected the termination of Zn ore treatment in the Decazeville basin followed by remediation actions. Accordingly, Cd concentrations in oysters decreased after 1988 (from 109 to 26 mg kg^{-1}, dry weight (dw)), while Ag bioaccumulation increased from 38 up to 116 mg kg^{-1}, dw after 1993. Based on the Cd/Ag ratio (Cd/Ag ~2) in oysters sampled before the termination of zinc ore treatment (1981–1985) and assuming that nearly all Cd in oysters originated from the metal point source, we estimated the respective contribution of Ag from this source to Ag concentrations in oysters. The evolution over the past 30 years clearly suggested that the recent, unexplained Ag concentrations in oysters are due to increasing contributions (>70% after 1999) by other sources, such as photography, electronics and emerging Ag applications/materials.

Highlights

► Ag and Cd records in river sediment support common release by former ore-treatment. ► Cd levels in oysters reflect Cd decrease in sedimentary records after 1988. ► Ag levels in oysters reach maximum values between 1993 and 2003. ► Ag accumulation in oysters was attributed to additional sources.

Keywords: Silver ; Cadmium ; Estuary ; Oyster ; Biomonitoring

1. Introduction

The Gironde Estuary (Fig. 1) is known for its metal pollution since high Cd accumulation (> 100 µg g-1, dry weight) in oysters (*Crassotreas gigas*) was discovered in the end of 1970s (e.g. Claisse, 1989) resulting in prohibition of consumption, production and purification of oysters since 1996 (e.g. Audry et al., 2004a). The main source of metal pollution was coal mining and Zn-ore treatment in the Decazeville watershed. Since the cessation of this metallurgical industry (1986), remediation and pollution management have clearly reduced Cd emission (Audry et al., 2004a). In the Gironde watershed, suspended particles are major vectors for Cd, Ag and other metals (e.g. Audry et al., 2004a; Lanceleur et al. 2011,). Part of these particles accumulate in hydroelectric reservoirs, where the pollutants may be recycled (e.g. released to porewaters; Roulier et al., 2010) or stored over decades, providing sedimentary records of past pollutions (Audry et al., 2004b; Castelle et al., 2007; Valette-Silver, 1993). The hydroelectric reservoirs on the Lot River downstream from the Decazeville watershed contain huge sediment stocks with high metal loads ($9.47 \pm 0.9\ 10^6\ m^3$ of sediment containing approximately 200 t of Cd), that may be remobilized by floods, dredging and construction work (Audry et al., 2004a; Coynel et al., 2007). Although Cd has long been considered as the major pollutant, many other metals derived from the same source also show important anomalies in both sediment and water (e.g. Hg, Cu, Zn; Castelle et al., 2007; Schäfer et al., 2006). Furthermore, the regional geology and agricultural activities also contribute (e.g. As, Cu, Zn) to the metal/metalloid loads in the Gironde watershed (Masson et al., 2006, 2007). Recent work has revealed remarkably high Ag concentrations (up to 60 mg kg^{-1} in 2003/2004) in wild oysters at the mouth of the Gironde Estuary (Fig. 1A; i.e. the highest measured in oysters and mussels along the French coast; Chiffoleau et al., 2005), indicating the fluvial-estuarine system is also contaminated by Ag. Both Ag and Cd are highly toxic to aquatic organisms and may be easily bioaccumulated (Eisler, 1996; US EPA, 2001; Vijayavel et al., 2007), especially by oysters (e.g. Gunther et al., 1999; Ivanina et al., 2011; Reinfelder et al., 1997). The measured concentrations in the Gironde oysters clearly exceed safety limits for human consumption for Cd (5 mg kg^{-1}; dw; EC No 466/2001) and although there is no legal threshold for Ag, consumption of oysters from several sites along the French coast (Chiffoleau et al., 2005) may be incompatible with human maximum Ag daily intake recommended by the EPA (0.005 mg kg^{-1} day^{-1}; www.epa.gov/iris/subst/0099.htm).

The present work aimed at documenting for the first time the historical Ag records in reservoir sediments upstream and downstream from the Decazeville watershed to (i) establish geochemical background for Ag in the upper Lot River watershed and (ii) quantify the extent of historical Ag contamination by the metal point source (Fig. 1B). Furthermore, we compare and discuss the chronologies of Cd and Ag accumulation in reservoir sediments and oysters from the Gironde watershed to understand (i) their relationships and (ii) changes over time in both concentrations and potential sources.

2. Materials and Methods

2.1. Study area

The Gironde Estuary (~170 km length; Fig. 1), draining a 80,000 km² watershed, is a major European estuary. Its mean annual freshwater discharge varies between 800 and 1000 m^3 s^{-1}, with typical water and particle residence times of ~20–90 days and ~1–2 years, respectively (Sottolichio and Castaing, 1999). Suspended Particulate Matter (SPM) concentrations in its well developed Maximum Turbidity Zone (MTZ) frequently exceed 1 g L^{-1}, making the Gironde Estuary one of the most turbid estuaries in Europe. A high number of studies on physical, hydrological and geochemical characteristics of the Gironde Estuary and its watershed (e.g. metal pollution) make it a model estuary, especially for understanding trace element transport and reactivity in impacted watersheds and macrotidal estuaries (e.g. Schäfer et al., 2002; Sottolichio and Castaing, 1999).

The main source of the historical metal pollution is located in the upper Lot River watershed, where a small tributary (i.e. the Riou Mort River) drains a waste area of a former zinc ore manufacturing facility (1842 to 1987) in the Decazeville basin (Fig. 1B). The metallurgical activity ended after a major pollution accident in 1986 followed by ongoing remediation efforts such as the treatment of drainage water and the confinement of a part of the waste deposits in storage basins (1987). However, the major part of the metallurgical waste is still exposed to atmospheric agents, i.e. leaching and erosion continue (e.g. Audry et al., 2004b).

2.2. Core retrieval and sampling

Reservoir sediments usually accumulate at high rates (typically > 2 cm y^{-1}; e.g. Müller et al., 2000, Audry et al., 2004b) and consequently are considered as being little affected by early diagenesis processes, i.e. providing preserved records of historical inputs (Callender, 2000). In June 2001, sediment cores (0–140 cm depth) were collected in two hydroelectric reservoirs on the Lot River, upstream (Marcenac) and downstream (Cajarc) from the pollution source (Fig. 1B) as described elsewhere (Audry et al., 2004b). Briefly, horizontal sections of the cores were sliced, dried at 50°C to constant weight, powdered and homogenized with an agate mortar and stored in the dark awaiting analyses.

2.3. Bioindicator sampling

As suspension-feeding bivalves, oysters are exposed to both dissolved metals and metals bound to mineral particles, phytoplankton and organic matter. Their capacity to accumulate both Ag and Cd from their environment (e.g. Baudrimont et al., 2005; Gunther et al., 1999) makes them good bioaccumulators for monitoring studies. Within the National Network for the Observation of Marine Environment Quality (RNO/ ROCCH; i.e. the French Mussel-Watch; http://www.ifremer.fr/deltn/pages/rno.htm), 2-year old wild-growing Japanese oysters (*Crassostrea gigas*) were collected according to the guidelines for monitoring contaminants in biota defined by the OSPAR commission (http://www.ospar.org). Three sites at the mouth of the Gironde Estuary (Fig. 1A) have been sampled four times a year during 1979-2002, twice a year from 2003 to 2007 (February and November) and annually (February) since 2008. The sampling sites are located in the downstream part of the Gironde Estuary dominated by marine sand and gravel with some shell fragments (Larrose et al., 2010). Wild oyster banks at the Bonne Anse and La Fosse sites are surrounded by silty/sandy sediment, whereas at Pontaillac they are close to rocky outcrops (calcareous cliffs). The three sites are representative of different salinity ranges with typical salinity ranges being 25 to 30 at the Bonne Anse site, 20 to 25 at the Pontaillac site and 15 to 20 at the La Fosse site.

2.4. Analyses

All the labware used was acid cleaned (HNO_3 analytical grade; 10%; 72 h), thoroughly rinsed with Milli-Q water, dried under a laminar flow hood and stored in double sealed polyethylene bags prior to use. For the determination of total trace element concentrations in reservoir sediments, representative sub-samples (30 mg of dry, powdered and homogenized material) were digested in acid-cleaned PP-tubes (DigiTUBEs®, SCP SCIENCE) using 1.5 mL HCl (12 M, Plasmapur), 0.5 mL HNO_3 (14 M, Plasmapur) and 2 mL HF (26 M, Plasmapur) at 110°C for 2 h in a temperature-controlled digestion system (DigiPREP MS®, SCP SCIENCE). After complete cooling, the digestate was evaporated to dryness, then the residue was dissolved using 150 µL HNO_3 (12 M, Plasmapur), brought to 10 mL with double deionized Milli-Q water and stored in the dark at 4°C awaiting analysis (adapted from Audry et al., 2004a and Schäfer and Blanc, 2002). The Cajarc core was ^{137}Cs-dated using a low background noise γ-ray spectrometer with Ge detector (Intertechnique EGSP 2200–25; Audry et al., 2004b). Cadmium and Ag bioaccumulation in oysters was measured from aliquots (200 mg) of freeze-dried samples digested at 90°C with HNO_3 for Cd and a mixture of HNO_3 and HCl for Ag as described elsewhere (Chiffoleau et al., 2005).

Cadmium and Ag concentrations in the sediment digestates were measured by ICP-MS (X7, Thermo-Fisher) at EPOC, Bordeaux 1 University. Precision, evaluated from parallel analyses of international certified reference materials (NCS-DC-70317, NCS-DC-70311), was < 5% (rsd) and results were consistently within the certified ranges (Table 1; Audry et al., 2004b; Lanceleur et al., 2011).

Cadmium and Ag concentrations in oyster digestates were determined at Ifremer, Centre de Nantes by graphite furnace atomic absorption spectrometry (AA800, Varian) using the Zeeman background correction for non-specific absorption. Quality control was satisfactorily performed by analyses of CRM (CRM TORT-2, CRM DOLT-2, SRM 1566b; Table 1; Chiffoleau et al., 2005) and through regularly successful participations in QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) intercalibration excercises.

Flux estimates of particulate Cd and Ag gross fluxes (fluvial fluxes into the estuary) at the La Réole site, i.e. the main fluvial entry of the Gironde Estuary were performed from daily discharge and SPM (suspended particulate matter) data and monthly measured metal concentrations using commonly applied methods described in detail elsewhere (e.g. Audry et al., 2004a; Masson et al., 2007; Schäfer et al. 2002). The particulate Ag fluxes for the 1990-1998 period (no Ag data available) were estimated from the SPM fluxes (Schäfer et al., 2002) and using a particulate Ag concentration of 1.0 mg kg^{-1}, i.e. the mean particulate Ag concentration measured during the last decade at the La Réole site (Lanceleur et al., 2011).

3. Results

3.1. Ag and Cd concentrations in sediment cores

At the Marcenac site, which served as a reference site for the geochemical background of the upper Lot River watershed (Audry et al., 2004b), concentrations (mean ± SD) were low and rather constant, i.e. 0.31 ± 0.06 mg kg^{-1}for Ag and 0.77 ± 0.22 mg kg^{-1}for Cd (Fig. 2). In the Cajarc sediment, directly affected by the former industrial activity in the Decazeville watershed (e.g. Audry et al., 2004b; Castelle et al., 2007), Ag concentrations ranged from 0.43 to 6.96 mg kg^{-1} and were correlated with Cd concentrations ($R_{Spearman} = 0.90$; $n = 43$; $p < 0.01$). Concentrations of both Ag and Cd decreased from the 42 cm depth to the surface (Cd: from 300 to 11 mg kg^{-1}; Ag: from 6.7 to 0.43 mg kg^{-1}), corresponding to the 1986-2001 period according to ^{137}Cs records (Fig. 2). Normalization of metal concentrations by Sc presented in previous work showed that grain size variations had a negligible impact on the historical metal record (Audry et al., 2004b).

3.2. Ag and Cd concentrations in oysters

Total metal concentrations in oysters, expressed as mg kg^{-1} dry weight (dw) of oyster tissue, undergo seasonal variations due to weight gains and losses during the reproduction cycle (Figs. 3A and 3B; Páez-Osuna et al., 1995). In order to (1) limit scattering induced by seasonal environmental parameters on oyster life cycles and (ii) account for different sampling frequencies (see sampling section) we used only the February data obtained during the whole observation period for the comparison of historical data with recent values (Figs. 3C to 3G).

Oysters from the La Fosse site (the most upstream site) showed systematically higher concentrations in both Cd and Ag, while the lowest concentrations occurred at the Bonne Anse site (Figs. 3C and 3D). Cadmium concentrations in oysters at the La Fosse site decreased after 1988 from 109 to 26 mg kg^{-1}, dw, while Ag bioaccumulation increased from 38 to 116 mg kg^{-1}, dw, after 1993 (Figs. 3C and 3D). Although being clearly lower, the Cd and Ag concentrations at the other sites showed similar trends. Compared to the La Fosse site, the Cd and Ag concentrations at the Pontaillac and the Bonne Anse sites were respectively equivalent to 54 ± 11% for Cd and 78 ± 18% for Ag and 31 ± 10% for Cd and 38 ± 16% for Ag.

4. Discussion

4.1. Geochemical background and historical record of Cd and Ag in river sediment

The historical metal records in the Cajarc sediments closely reflect the evolution of the industrial activity in the source area from the 1950's to present, including termination of the Zn extraction in 1986 and subsequent remediation (Audry et al., 2004b; Castelle et al. 2007). The geochemical background values of the upstream Lot River watershed estimated from the Marcenac values (Cd: 0.77 mg kg^{-1}; and Ag: 0.30 mg kg^{-1}) were 15 to 384 and 1.4 to 23 times lower, respectively, than Cd and Ag concentrations at the contaminated Cajarc site. Co-evolution of Cd and Ag concentration-depth profiles supports common source and transport, suggesting that the Decazeville basin formerly was an important Ag source to the Lot-Garonne-Gironde fluvial estuarine continuum (Fig. 2). The observed Ag concentrations in the Lot River sediments were of similar magnitude as those reported for polluted English estuaries (up to 5 mg kg^{-1} with 0.1 mg kg^{-1} as the background concentration; Bryan, 1984). As in many industrially affected aquatic systems at the global scale, metal stocks in the contaminated Lot River sediments are of great concern for the Gironde fluvio-estuarine system due to their possible remobilisation during floods (e.g. Coynel et al., 2007), dredging (e.g. Audry et al., 2004a), passive diffusion at the water–sediment interface, (e.g. Rivera-Duarte and Flegal, 1997; Van Den Berg et al., 1999) or bioturbation (e.g. Zoumis et al., 2001).

4.2. Bioavailability of Cd and Ag to oysters

The concentration gradient of Cd and Ag in oysters from the La Fosse site to the Bonne Anse site, i.e. decreasing concentrations from upstream to downstream, could be explained by differences in exposure. Exposure of oysters to dissolved metals results in direct uptake (direct pathway) and is considered the major contamination pathway for both Cd (e.g. Ettajani et al., 2001) and Ag (e.g. Abbe and Sanders, 1990). In estuarine salinity gradients, both dissolved Cd and Ag typically show highest concentrations in the 15-20 salinity range (e.g. Dabrin et al., 2009; Tappin et al., 2010) due to desorption from the particulate phase by chloride-complexation (e.g. Luoma et al., 1995; Turner et al., 1993). Fluvial Cd and Ag transport into the Gironde Estuary mainly occurs in the particulate phase (respectively ~80% and ~96%; Lanceleur et al., 2011; Schäfer et al., 2002). Their addition to the dissolved phase results in the typical ‘bell-shaped’ distribution of dissolved Cd (e.g. Dabrin et al., 2009) and Ag (Lanceleur et al., unpublished; Tappin et al., 2010) along the estuarine salinity gradient. In the Gironde Estuary, dissolved Cd and Ag concentrations decrease from respectively 150-170 ng L^{-1} and 6-8 ng L^{-1} in the 15-20 salinity range towards the seaward end due to dilution by oceanic water (Atlantic Ocean: Cd_D= 4 ± 3 ng L^{-1}; Kremling, 1985; North Atlantic Ocean: Ag_D=0.39 ng L^{-1}; Rivera-Duarte et al., 1999). This may induce systematic spatial differences in oyster exposure with decreasing concentrations from the La Fosse to the Bonne Anse site (Figs. 1 and 3). During the whole observed period, concentrations in oysters from the Pontaillac site were lower than those in La Fosse oysters, i.e. by 46 ± 11% for Cd and 22 ± 18% for Ag (with metal concentrations at La Fosse being set equal to 100%). Accordingly, relative (compared to the La Fosse site) metal accumulation at the Pontaillac site (i.e. at higher salinity) appeared significantly higher for Ag than for Cd ($p < 0.001$; Log transformation of data followed by a one-way ANOVA). Similarly, but to a lesser extent, the relative metal accumulation at Bonne Anse was significantly higher ($p < 0.001$) for Ag

(38 ± 16%) than for Cd (31 ± 10%). Further work is necessary to understand if these differences are due to (i) differences in the slopes of dissolved Cd and Ag distribution in the high salinity range, i.e. the fact that maximum Ag release from particles occurs at higher salinities than for Cd as it was shown experimentally (Ciffroy et al., 2003) and/or (ii) different assimilation efficiencies for Cd and Ag species. In fact, compared to Cd, data on dissolved Ag distribution and speciation along estuarine salinity gradients are extremely scarce, i.e. inexistent for most estuaries. From recent maximum dissolved Cd (170 ng L^{-1}) and Ag (8 ng L^{-1}) concentrations in the Gironde Estuary salinity gradient (S=15-20; Dabrin et al., 2009; Lanceleur et al., unpublished) and the respective concentrations in oysters from the La Fosse site (Cd: ~30 mg kg^{-1}, dw; Ag: ~80 mg kg^{-1}, dw), we estimated minimum bioaccumulation factors (concentration in oysters/concentration in water) at 0.18 10^6 for Cd and 10 10^6 for Ag. This suggests that in the Gironde Estuary oysters bioaccumulation factors are ~55 times higher for Ag than for Cd. These results are consistent with previous experimental work showing that even if assimilation efficiency by trophic transfer in oysters is higher for Cd (*C. virginica*) than for Ag (Reinfelder et al., 1997), Ag-chlorocomplexes play an important role in Ag accumulation via the direct pathway by oysters compared to Cd (Engel et al., 1981), making Ag the strongest accumulated trace metal for certain marine bivalves (e.g. Luoma et al., 1995).

4.3. Comparison of particulate Cd and Ag fluvial gross fluxes to the Gironde Estuary with Cd and Ag accumulation in oysters

The Garonne River (the La Réole site; Fig. 1) is the main fluvial entry of particles and associated metals transported to the Gironde Estuary with > 80% (Cd; Schäfer et al., 2002) and ~96% (Ag; Lanceleur et al., 2011) of the fluvial gross fluxes (i.e. fluvial fluxes to the estuary) occurring in the particulate phase. The evolution over time of Cd and Ag annual gross fluxes to the Gironde Estuary reflects (i) decreasing emissions in the historic source area (i.e. the Decazeville watershed) and (ii) the hydrological variability (e.g. Schäfer et al., 2002). Accordingly, Cd particulate gross fluxes at the La Réole site globally decreased by a factor of ~4 over the last two decades and may explain the parallel decrease in Cd concentrations in La Fosse oysters (from 95 to 25 mg kg^{-1}, dw; Fig. 3E). Similar to Cd, the estimated particulate Ag gross fluxes also tended to decrease during 1992-2009 by a factor of ~4 (Fig. 3F). In contrast to Cd, Ag concentrations in oysters were at maximum during 1998-2003 and their evolution over time did not reflect that of the estimated Ag gross fluxes (Fig. 3F). This shows that after 1993 the fluvial Ag gross fluxes cannot explain the evolution of Ag bioaccumulation in oysters.

4.4. Historical trend of Ag and Cd pollution

Based on the observation that the Cd/Ag ratio in oysters from the La Fosse site was constant before the termination of Zn ore treatment in the Decazeville basin (Cd/Ag=2 ± 0.4; 1981-1985) and assuming that during the whole observation period nearly all Cd in oysters was derived from the metal point source, we estimated the respective (theoretical) Ag concentrations in oysters over time (Fig. 3G). The latter assumption is based on mass balances at the watershed scale, showing that even 13 to 16 years after the termination of Zinc ore treatment (i.e. 1999 to 2002), the Decazeville basin contributed more than 61 to 92% of total Cd fluxes into the Gironde Estuary (Masson et al., 2006). This is further supported by (i) historical records of Cd in estuarine freshwater sediments, reflecting the industrial activity in the Decazeville watershed (Grousset et al. 1999) and (ii) mass balances at the estuary scale, suggesting that intra-estuarine sources (e.g. the Bordeaux agglomeration) are negligible, compared to the main source (e.g. Audry et al., 2007; Dabrin et al., 2009; Schäfer et al., 2002).

Comparing the estimated theoretical Ag concentrations to the measured data suggests that before ~1993, Ag in the oysters from La Fosse was mostly derived from the Decazeville basin (Fig. 3G). In contrast, increasing Ag concentrations after 1993 were attributed to increasing contributions (> 70% after 1999) by other sources. While soil erosion is the main natural Ag source to rivers, there are various anthropogenic Ag sources such as coal combustion, smelting, photography manufacturing and development, urban runoff, sewage treatment plants, cloud seeding and electrical supplies, etc. (e.g. Lanceleur et al., 2011; Purcell and Peters, 1998; US PHS, 1990). In 1986, photography accounted for 45% of Ag demand in the United States (US PHS 1990) and greatly contributed to the Ag contamination of San Francisco Bay sediment, water and biota until the mid 1980s (Flegal et al., 2007). In France, photographic film sales increased from 103 to 136 million in 1995-2001 and decreased to 24 million in 2007 and 9 million in 2009, due to the development of numeric photography (Fig. 3G; data from the French Observatory for Imaging Professions OPI, 2010). Even if Ag load in oysters from the La Fosse site apparently followed this trend during 1995-2005, concentrations tended to increase after 2005 (Fig. 3G). Future work should aim at quantifying the contribution of recent increases in silver-containing paper sales (+21% between 2006 and 2007; OPI, 2010), electronic products and emerging sources, e.g. growing use of Ag nanoparticles (e.g. Blaser et al., 2008).

Conclusion

Anomalously high Cd and Ag concentrations, up to 384 and 23 times higher than the respective regional background concentrations of 0.77 mg kg^{-1} (Cd) and 0.30 mg kg^{-1} (Ag) in the Lot River sediments downstream from the Decazeville watershed showed that Ag is a historical pollutant in the Gironde fluvial-estuarine system. The decreasing Cd concentrations in sediments since the end of the metallurgical activity in 1986 and the evolution of fluvial particulate Cd gross fluxes, fully explain the decreasing Cd concentrations in oysters from the estuary mouth. In contrast, neither the historical Ag record in river sediments nor the fluvial Ag gross fluxes can explain the recent increase in Ag concentrations in oysters, clearly suggesting increasing contributions (> 70% after 1999) by other, probably intra-estuarine sources. The observed gradients in Cd and Ag concentrations in oysters from the three sites near the estuary mouth probably reflect exposure to dissolved Cd and Ag concentrations, i.e. their typical distribution along the estuarine salinity gradient. Further work is necessary to identify these recent Ag sources and to understand their role in the estuarine Ag cycle and in Ag contamination of aquatic organisms.

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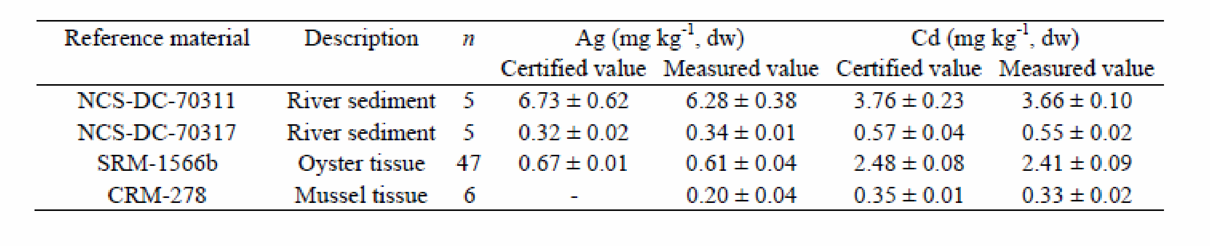
Table 1. Results obtained from analyses of Certified Reference Materials. *n*: number of independent analyses.



Reference material	Description	*n*	Ag (mg kg^{-1}, dw)		Cd (mg kg^{-1}, dw)	
			Certified value	Measured value	Certified value	Measured value
NCS-DC-70311	River sediment	5	6.73 ± 0.62	6.28 ± 0.38	3.76 ± 0.23	3.66 ± 0.10
NCS-DC-70317	River sediment	5	0.32 ± 0.02	0.34 ± 0.01	0.57 ± 0.04	0.55 ± 0.02
SRM-1566b	Oyster tissue	47	0.67 ± 0.01	0.61 ± 0.04	2.48 ± 0.08	2.41 ± 0.09
CRM-278	Mussel tissue	6	-	0.20 ± 0.04	0.35 ± 0.01	0.33 ± 0.02

Figure 1: The Gironde Estuary (SW France) with sampling locations of A) oysters and B) sediment cores. The La Réole site, located at the upstream limit of tidal dynamics, is a permanent observation site for trace element concentrations and fluxes at the main entry of the Gironde Estuary (for details see Schäfer et al., 2002).

Figure 2: Cadmium concentrations, Ag concentrations and ^{137}Cs activity vs depth for the sediment cores from the Marcenac (geochemical background; empty symbols) and the Cajarc (historical record of metallurgical pollution; filled symbols) sites. Cadmium and ^{137}Cs profiles are from Audry et al. (2004b).

Figure 3: Concentrations of Cd (A, C and E) and Ag (B, D, F and G) in oysters from the La Fosse (A, B, C, D, E and F), Pontaillac (C and D) and Bonne Anse (C and D) sites during 1979-2010. Oysters have been sampled four times a year during 1979-2002, twice a year from 2003 to 2007 (February and November) and annually (February) since 2008 (A and B). February data are represented for Cd (C and E) and Ag (D, F and G) concentrations in oysters. Particulate Cd (E; white bars) and Ag (F; white and grey bars) gross fluxes at the La Réole site over time. (E): Particulate Cd gross fluxes in 1990-1999 are from Schäfer et al. (2002), Audry et al. (2004a) for 2000, Masson et al. (2006) for 2001-2002, from Dabrin et al. (2009) for 2003-2007 and unpublished data for 2008-2009. (F): The grey bars represent estimated particulate Ag gross fluxes at the La Réole site in 1990-1998. Particulate Ag fluxes in 1999-2009 are from Lanceleur et al. (2011). (G): Ag concentrations in oysters and photographic film sales in France vs time. Ag levels were measured (full circles) and estimated (open squares) from pre-1986 Cd/Ag ratio and from Cd concentrations in oysters.

Figure 1

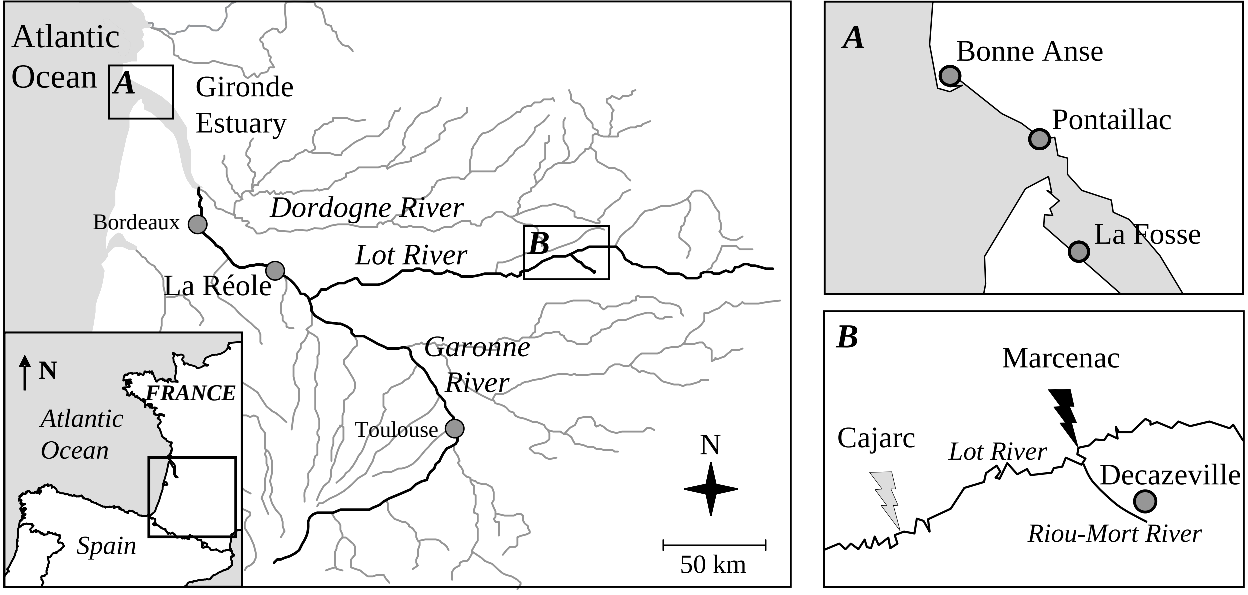

Atlantic
Ocean
A
Gironde
Estuary
Dordogne River
Bordeaux
La Réole
Lot River
B
Garonne
River
Toulouse
N
50 km
N
FRANCE
Atlantic
Ocean
Spain
A
Bonne Anse
Pontaillac
La Fosse
B
Marcenac
Cajarc
Lot River
Decazeville
Riou-Mort River

Figure 2

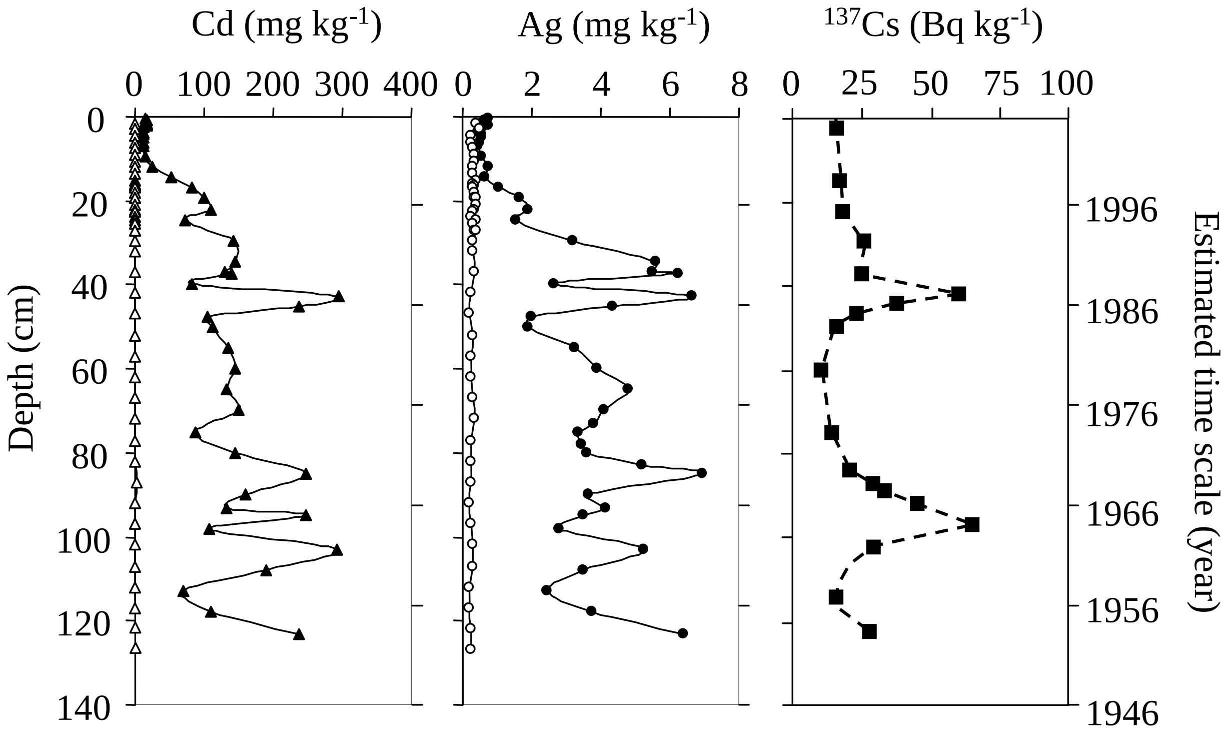
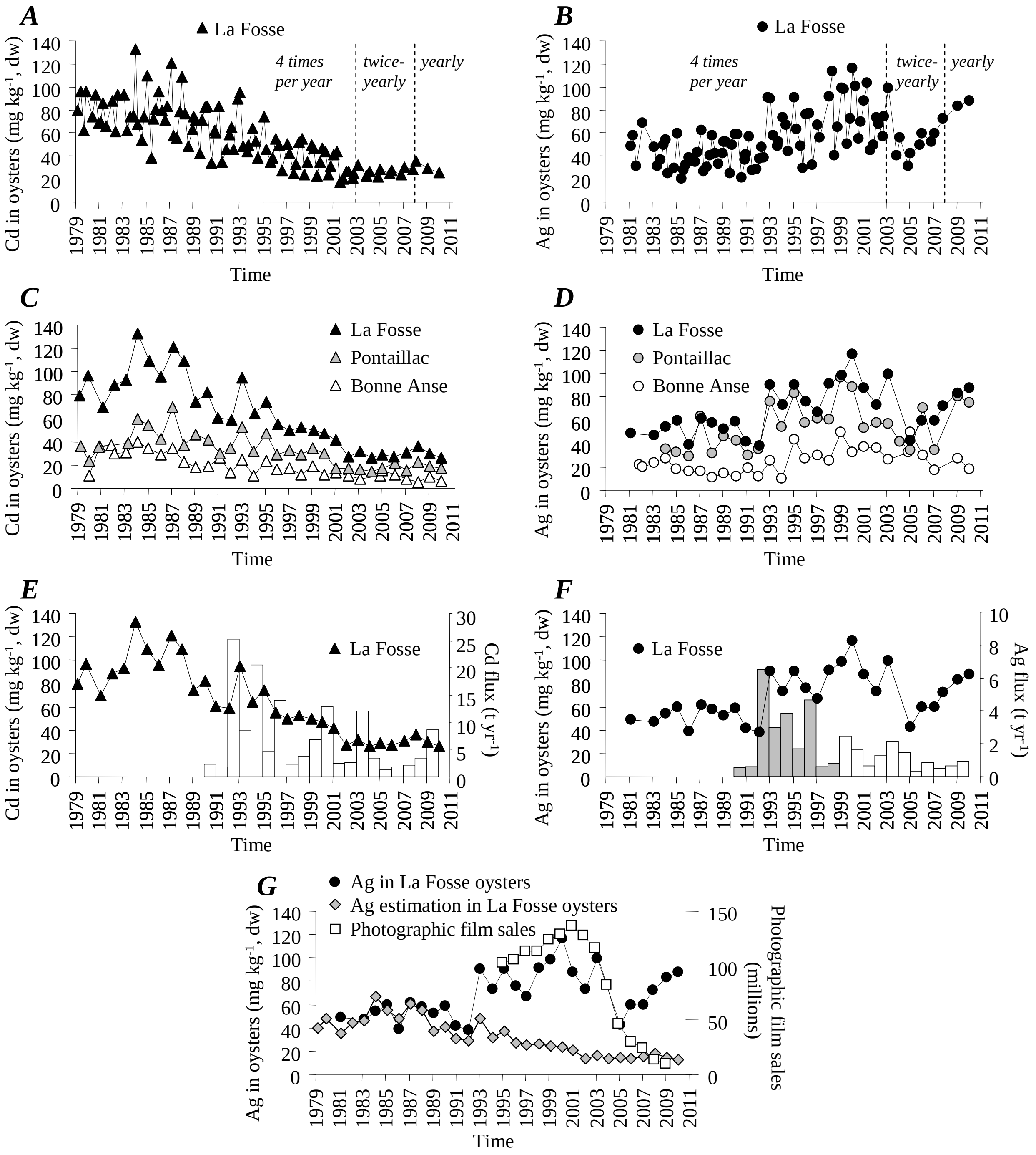

Cd (mg kg-1)
Ag (mg kg-1)
137Cs (Bq kg-1)
0
100
200
300
400
0
2
4
6
8
0
25
50
75
100
Depth (cm)
0
20
40
60
80
100
120
140
Estimated time scale (year)
1996
1986
1976
1966
1956
1946

Figure 3


A
La Fosse
4 times per year
twice-yearly
yearly
Cd in oysters (mg kg-1, dw)
Time
B
La Fosse
4 times per year
twice-yearly
yearly
Ag in oysters (mg kg-1, dw)
Time
C
La Fosse
Pontaillac
Bonne Anse
Cd in oysters (mg kg-1, dw)
Time
D
La Fosse
Pontaillac
Bonne Anse
Ag in oysters (mg kg-1, dw)
Time
E
La Fosse
Cd in oysters (mg kg-1, dw)
Cd flux (t yr-1)
Time
F
La Fosse
Ag in oysters (mg kg-1, dw)
Ag flux (t yr-1)
Time
G
Ag in La Fosse oysters
Ag estimation in La Fosse oysters
Photographic film sales
Ag in oysters (mg kg-1, dw)
Photographic film sales (millions)
Time
0
20
40
60
80
100
120
140
1979
1981
1983
1985
1987
1989
1991
1993
1995
1997
1999
2001
2003
2005
2007
2009
2011