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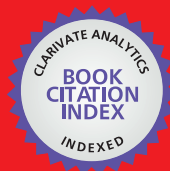
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# Spatial Cadmium Distribution in the Charente Watershed and Potential Risk Assessment for the Marennes Oleron Bay (Southwest France)

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## 1. Introduction

In recent years, high levels of pollutants in coastal ocean waters and in the marine food chain have been attributed to inputs either via the atmosphere (Nriagu, 1989) or by direct inputs from rivers and estuaries (e.g. Millward et al., 1996; Baeyens et al., 1997; Chiffolleau et al., 1999). In fact, rivers are considered as a major pathway for the organic and inorganic contaminant transfers from the continent to the ocean, especially during flood events (e.g. Coynel et al., 2007).

The Marennes Oleron Bay (MOB) is the first oyster-producing area in France providing nearly half of the oysters commercialised (Gouletquer & Héral, 1997; Soletchnik et al., 1999, 2002; Bry & Hoflack, 2004). The MOB and its biological compartments are subject to chronic pollution by some metals, especially Cd, representing a potential risk for shellfish cultivation (Pigeot et al., 2006; Strady et al., 2011). The latest estimates suggest that legal restrictions of oyster production in the MOB would result in a shortfall of between 50% and 70% of oysters on the market in the next years. Given that oyster is one of the top ten seafoods consumed in France, the economic consequences would be catastrophic for this region.

The Gironde Estuary, located ~30 km southward of the MOB, is affected by historic metal (e.g. Cd, Zn, Hg, Ag; Blanc et al., 1999; Schäfer et al., 2006; Castelle et al., 2009; Larrose et al., 2010; Lanceleur et al., 2011) contamination due to former Zn ore treatment in the industrial Decazeville basin, that was stopped after a major pollution accident in 1986. In this watershed drained by the Riou Mort River, anthropogenic contributions to particulate element fluxes were estimated to ~90-95% for Cd, Zn and Hg (Coynel et al., 2009). Despite decreasing Cd emissions in the Decazeville area due to ongoing remediation efforts since the early 1990s, the Lot-Garonne River system still contributes up to 80% to the annual Cd gross fluxes into the Gironde Estuary (Schäfer et al., 2002; Audry et al., 2004). Additionally, intensive agriculture and ongoing urbanization also considerably contribute to metal (e.g. Zn, Cu, Ag) gross fluxes into the Gironde Estuary (e.g. Masson et al., 2006; Lanceleur et al., 2011). In contrast to the well-studied Garonne-Gironde system, the Charente fluvial-

estuarine system remains poorly studied in spite of its great hydrological influence on the MOB. The Charente River is the major river discharging directly into the MOB. During summer, 90% of the freshwater inputs into the Bay come from the Charente River (Ravail-Legrand, 1993), which drains an area of 10,549 km<sup>2</sup> dominated by farming (Bry & Hoflack, 2004). Only few studies have previously assessed the importance of the Charente Estuary to the overall metal contamination of the MOB (Gonzalez et al., 1991; Boutier et al., 2000; Dabrin, 2009). Recently, Dabrin (2009) showed that dissolved and particulate Cd concentrations the outlet of the Charente watershed, i.e. at the entry of the Charente Estuary were similar to those in the Garonne River and contributed up to 60% to total Cd inputs into the MOB, highlighting the need to precisely identify the origin(s).

In this context, the objective of this study is to (i) characterize the Cd content in water (<0.2 µm; dissolved phase) and in particles (SPM and stream sediments) exported by the Charente sub-watersheds; (ii) assess their level of contamination by comparison with world references and ecotoxicological indices and (iii) identify point sources and/or diffuse sources in the Charente watershed. This first assessment of the sub-watershed contributions to the fluvial Cd export is essential to the control and reduction of Cd contamination in oysters, i.e. to successful environmental management in this vulnerable region.

## 2. Presentation of the study area

The Charente watershed (surface area = 10,549 km<sup>2</sup>; ~500,000 inhabitants) is surrounded by the Massif Central to the East, the Paris sedimentary basin to the North, the Aquitaine sedimentary basin to the South and by the Armorican Massif to the Northwest (Figure 1). It is essentially composed of limestone formations dating from the Secondary: (i) in the North, the Jurassic formations are composed of large limestone beds in various facies and, (ii) in the South, the Cretaceous formations are formed by clay, sand, chalk and decalcification clays. The Primary formations crop out in the most upstream catchment areas of the Charente watershed, represented by plutonic and metamorphic rocks (BRGM, 2003).



Fig. 1. Location of sampling sites

The Charente watershed can be divided into three main domains (Figure 1):

- The upstream Charente watershed features metamorphic rocks to the East. Two large reservoir dams, the Lavaud reservoir (400 ha; 10 Mm<sup>3</sup>) on the Charente River and the

Mas-Chaban reservoir (176 ha; 14.2 Mm<sup>3</sup>) on the Moulde River, were built in 1989-1990. In this section, the Tardoire River is considered the main tributary of the Charente System.

- The downstream Charente River system is located between Angouleme and Saintes, and represented by Quaternary formations. The main tributaries of the Charente River in this section are the Ne and the Seugne Rivers.
- The Charente Estuary, downstream of Saintes, is located in areas where sedimentary rocks and limestone prevail. Two dams have been set up within the estuarine reaches submitted to tidal influence: one at Saint Savinien on the Charente River and the second on the Trezence River, the main tributary of the Boutonne River.

The Charente watershed is considered predominantly as a rural sedimentary basin. Agriculture activities cover about 60% of this area and about 11% of the cultivated area is irrigated. However, 52% of the water bodies in this river system are at risk of failing the European Water Framework Directive objectives to achieve good ecological and chemical status, due to diffuse pollution (nitrates, turbidity, and pesticides) attributed to agricultural activities and practices (EPTB-Charente, 2007; Vernier et al., 2010).

The Charente watershed meteorology is characterized by the Atlantic Ocean disturbances. The mean annual water discharge of the Charente River is ~74 m<sup>3</sup>/s, corresponding to a specific discharge (average discharge/watershed area) of ~0.007 m<sup>3</sup>/s/km<sup>2</sup>, i.e. 3 times less than that of the adjacent Dordogne watershed (Regional Environment Agency- DIREN; BanqueHydro®; Schäfer et al., 2002). Two major factors contribute to this low specific discharge: on the one hand, relatively low supply from its major tributaries (the Tardoire and Bandiat Rivers) flowing over a karst formation and, on the other hand, intense agricultural irrigation throughout the basin. During our sampling campaign, the estimated Charente River water discharge at the watershed was ~100 m<sup>3</sup>/s (Charente River at Chaniers [CHA10; Figure 1] + Boutonne River; data from DIREN), implying that the studied situation is representative of a moderate to a high hydrological situation.

### 3. Material and methods

#### 3.1 Sampling campaign

A sampling campaign was conducted from April 6 to April 8 2010. Strategic sites were selected by Geographical Information System (GIS, ArcView ®) for testing different environmental characteristics (e.g. geology, land-use) and evaluating their impacts on Cd concentrations. In total, 20 strategic sites were selected on the Charente River (n=10 sites; notified by CHA; Figure 1; Table 1) and its tributaries (n=10 sites; notified by a letter; Figure 1; Table 1) characterized by contrasting geology, industrial and agricultural activities. An additional site was chosen on a small drain near Riou Mort River (former mining area; "c", Figure 1) for collecting a stream sediment deposit. Note that this Riou Mort River in the Charente watershed is not identical with the well-studied Riou Mort River draining the polluted Decazeville basin, responsible for important historical polymetallic (mainly Cd, Zn, Cu, Pb, Hg, Ag) pollution in the Lot-Garonne river continuum (e.g. Blanc et al., 1999; Schäfer et al., 2002; Audry et al., 2004; Coynel et al., 2009).

Item	River	Area km <sup>2</sup>	Q m <sup>3</sup> /s	Cond. µS/cm	pH	eH mV	O <sub>2</sub> %	SPM mg/l	Nitrate µmol/l	Dissolved Cd µg/l	Part. Cd SPM mg/kg	Part. Cd (<63µm) mg/kg		
CHA1	Saint Gervais	Charente	40	0.14	X	86.4	7.3	101	98.4	15	112	0.030	3.78	1.69
CHA2	Sansac	Charente	44	1.1	X	96.6	7.4	95	92.5	4	170	0.010	2.11	0.73
CHA3	Pont de Suris	Charente	110	2.1	Diren	110	7.6	120	91.6	12	163	0.010	4.36	0.70
CHA4	Chez Paire	Charente	230	4.5	X	115	7.6	165	90.8	10	162	0.031	8.16	3.06
CHA5	Charroux	Charente	346	6.4	Diren	207	7.5	166	86.2	9	223	0.020	4.86	2.63
CHA6	Saint-Saviol	Charente	492	8.2	Diren	226	7.6	171	92.6	13	259	0.022	3.51	2.29
CHA7	Aunac	Charente	1090	22	X	373	7.8	153	93.6	13	415	0.011	3.07	1.39
CHA8	Vindelle	Charente	3750	47	Diren	374	8.0	227	89.7	11	425	0.009	2.33	0.90
CHA9	Sireuil	Charente	4070	82	X	378	8.0	205	91.0	12	381	0.008	2.96	2.18
CHA10	Chaniers	Charente	7412	91	Diren	461	8.0	197	90.3	9	410	0.010	4.97	2.11
a	Massignac	Upstream Moulde	52	0.46	X	98.3	7.4	85	101	6	114	0.009	1.20	0.82
b	Chez Boige	Downstream Moulde	54	0.96	X	103	7.5	135	99.8	2	134	0.008	2.72	0.76
c	Riou Mort	-	-	-	-	-	-	-	-	n.d	n.d	n.d	n.d	37.7
d	Poursac	Argentor	108	2.9	Diren	426	8.0	175	102	7	335	0.010	3.57	1.20
e	Mouton	Son-Sonnette	226	2.7	X	425	8.3	162	115	8	319	0.009	3.95	1.14
f	Saint Ciers/Bonnieure	Bonnieure	203	2.7	Diren	262	8.1	224	103	11	218	0.011	2.30	0.89
g	Montbron	Upstream Tardoire	389	9.4	Diren	87.5	7.6	94	89.4	9	93	0.013	4.59	1.78
h	Feuillade	Bandiat	333	5.2	Diren	176	7.8	189	90.0	9	100	0.009	6.17	1.70
i	Coulgens	Downstream Tardoire	1200	8.2	Diren	128	7.2	199	98.1	23	108	0.011	3.59	1.31
j	Les Perceptiers	Ne	602	7.4	Diren	651	8.1	202	110	11	477	0.009	1.80	0.72
k	La Lijardière	Seugne	902	9.9	Diren	654	7.9	212	97.0	12	470	0.009	2.13	0.72
Charente - CHA10 (2006-2007; Dabrin, 2009)										mean	0.024	4.89		
										min	0.011	1.21		
										max	0.048	9.86		

Table 1. Description of sampling sites, water discharge obtained by the Regional Environment Agency-DIREN or measured in this study (X), physical and chemical parameter values (conductivity, Eh, pH, dissolved oxygen saturation) and SPM, nitrate, dissolved and particulate Cd (in SPM and stream sediments < 63µm) concentrations

### 3.2 Discharge measurements

This sampling strategy, aiming at estimating instantaneous fluxes, required reliable discharge data for each of the selected observation sites. However, only 12 sites are equipped with permanent gauging stations maintained by the Regional Environment Agency-DIREN (BanqueHydro®). Therefore, for this study, 8 additional river gauging measurements were performed at the other sampling sites (Table 1). Standard instantaneous discharge measurements were made by measuring flow velocities at different depths along vertical profiles, each of them representing a segment of the river cross-section. The cross-sectional area of each segment was then multiplied by the corresponding integrated measured velocities to estimate water discharge in the segment. The sum of river discharges in all segments represents the estimated instantaneous water discharge of the river section. The uncertainty on the measurements was estimated between 5 and 10% (Regional Environment Agency- DIREN).

### 3.3 Water sampling

The general physical and chemical parameters (pH, conductivity, Eh and O<sub>2</sub>) were measured in-situ at each site. Temperature and conductivity were measured using a TetraCon 96® probe (PROFILINE, WTW). Oxygen saturation was determined by an ISY 52® probe. Determinations of pH and Eh were performed using a Sentix® 41 probe (PROFILINE, WTW). At each site, water was sampled manually for SPM, nitrate and Cd concentrations using clean techniques: all materials in contact with the water samples were made of polypropylene (PP), carefully decontaminated as previously detailed in Canton et al. (2012) for nitrate and in Audry et al. (2004) for Cd.



Back in the laboratory, river water samples were homogenized and precise volumes (~500 ml) were filtered through pre-weighed 0.7  $\mu\text{m}$  filters (Durieu®). Then the filters were dried to constant weight (45°C; 12 h) and re-weighed in order to obtain SPM concentrations. For dissolved nitrate and Cd, all river water samples were immediately filtered on-site through 0.2  $\mu\text{m}$  Sartorius® polycarbonate filters. For nitrate, filtrates were collected in 14 ml polypropylene tubes and stored at -80°C until analysis; for dissolved Cd, filtrates were collected in pre-cleaned 30 ml polypropylene bottles, acidified (1/1000; HNO<sub>3</sub> suprapur grade) and stored at 4°C awaiting analysis.

Suspended particulate matter for Cd analyses was retrieved by pumping up to 80 L of river water (~50 cm from the bank at 10-20 cm depth) using a peristaltic pump with PP-tubing followed by centrifugation (Westfalia, Germany; 12,000 g). This technique is considered a practicable and reliable method for SPM sampling in all hydrological situations (e.g. Schäfer & Blanc, 2002).

### 3.4 Stream sediment sampling

Stream sediments are commonly used for geochemical prospecting. Collected just after a strong hydrological event, the geochemical composition of these samples corresponds to the maximum particulate transfer to the estuary and coastal zone. Unlike SPM, whose composition can rapidly fluctuate, stream sediments integrate metal contamination (Coynel et al., 2009).

The coordinates of the sampling locations were recorded with a differential GPS. At each site, representative samples, consisting of the uppermost 1 cm of sediment from several recent depositional pockets were collected with a plastic spatula within a distance of 5-10 meters to enhance representativeness. The preferential accumulation of metals, either of natural or anthropogenic origin, in the fine-grained sediment fractions may induce grain size effects and reduced sample representativeness (Förstner & Wittmann, 1981; Horowitz, 1991; Benoit & Rozan, 1998). Therefore, stream sediment samples were sieved (<63  $\mu\text{m}$ ; nylon sieves) to remove coarse material which was obviously not representative of typical grain size of suspended sediment (Coynel et al., 2009).

### 3.5 Nutrient analysis

The dissolved inorganic compounds were colorimetrically analyzed according to standardized techniques. Dissolved nitrates ( $\Sigma\text{NO}_3 = \text{NO}_3^- + \text{NO}_2^-$ ) were analyzed by Flow Injection Analysis (FIA) according to Canton et al. (2012). Precision was  $\pm 10\%$  for  $\Sigma\text{NO}_3^-$ .

### 3.6 Particulate Cd extraction in SPM and stream sediment

Representative subsamples (~30 mg of dry, powdered and homogenized material) of SPM or sediment were digested in acid-cleaned closed reactors using 1.5 ml HCl s.p. (12 M), 2 ml HF s.p. (22 M) and 0.75  $\mu\text{l}$  HNO<sub>3</sub> s.p. (14 M) at 110°C for 2 h using a temperature-controlled digestion system (DigiPREP MS®, SCP SCIENCE). After evaporation to dryness (10 h at 110°C), the residues were completely re-dissolved in 0.25 ml HNO<sub>3</sub> s.p. (14 M) and 5 ml Milli-Q® water on a heating plate (15 min at 60°C) and after cooling brought to 10 ml in volumetric flasks using Milli-Q® water.

### 3.7 Dissolved and particulate Cd analysis

Dissolved and particulate Cd concentrations were measured using ICP-MS (X7, THERMO) with external calibration under standard conditions. The applied analytical methods were continuously quality checked by analysis of international certified reference sediments (PACS-1, BCR 320, SL-1, SLRS-4). Accuracy was within 5% and 7% of the certified values in the dissolved and particulate fractions, respectively. The analytical error (relative standard deviation) was better than 5% (rsd) for both phases. The detection limit estimated as 3 sigma of method blanks was 2 ng/l for the dissolved phase and 0.04 mg/kg for the particulate phase.

## 4. Results and discussion

### 4.1 Physical and chemical parameters

Conductivity, redox potentials (Eh) and pH (to a lesser extent) in the Charente River and its tributaries tended to increase from upstream to downstream, probably reflecting local geological characteristics (metamorphic rocks in the upstream sections; limestone formations in the downstream watershed) and land use (vineyards). The dissolved oxygen saturation values were rather similar whatever the sites (Table 1).

### 4.2 Discharge monitoring

The spatial variability of the Charente River water discharge is linearly related to its drainage basin area for the section between CHA1 and CHA9, except for CHA8 (Figure 2).

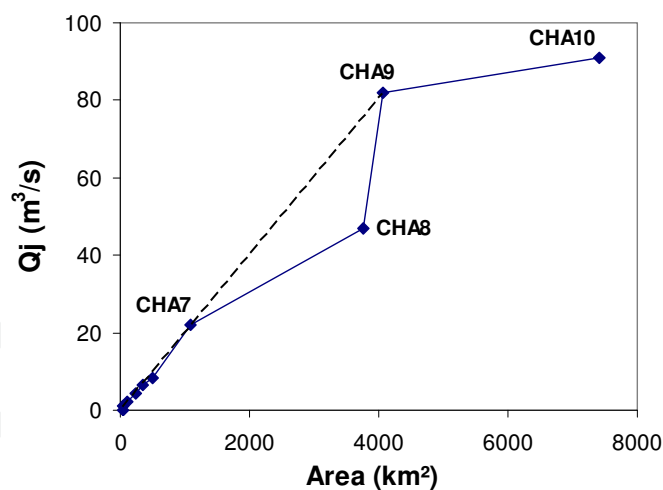


Fig. 2. Relationship between daily water discharges measured at different sites of the Charente River and the corresponding surface areas

The permanence of shoal sedimentation during the Middle and Upper Jurassic is a local feature which explains the development of the La Rochefoucauld karstic system, close to Angouleme city (Figure 1) and the relatively low water discharge measured at CHA8. The Bandiat and the Tardoire Rivers flow over the La Rochefoucauld karst accounting for more than 50% of the outlet discharges (Kurtulus & Razack, 2007). The La Touvre spring, located near of Angouleme city, constitutes an important discharge system of the aquifer varying

between 2 m<sup>3</sup>/s and 40 m<sup>3</sup>/s. During our water monitoring campaign, the La Touvre water discharge was ~19.3 m<sup>3</sup>/s. The apparent water discharge deficit at CHA10 compared to the general relation between discharge and area drained may reflect the intense agricultural irrigation (Figure 2).

### 4.3 SPM measurements

The SPM concentrations ranged from 2 mg/l in the Moulde River, just after the Mas-Chaban Reservoir to 23 mg/l in the Tardoire River (Table 1). The lowest value can be explained because of hard to erode rock sills combined with the settling of SPM due to the presence of the Mas-Chaban Reservoir. Based on the world river classification of SPM concentration proposed by Meybeck et al. (2003), these values can be considered as either “very low” (<20 mg/l), generally observed for watersheds located downstream of major or numerous lakes (e.g. Alpine Rhone River), or in very flat and humid regions with wetland predominating (e.g. the Central Amazon watershed) or “low” (20-100 mg/l) characteristic of plain watersheds. However, even if our sampling campaign is representative of a moderate to high discharge hydrological situation ( $Q \sim 100$  m<sup>3</sup>/s), SPM concentrations probably are much higher during flood events as previously observed by Dabrin (2009), during 2006-2007, at the outlet of the Charente watershed (Chaniers site; SPM = 200 mg/l during a flood event with  $Q = 350$  m<sup>3</sup>/s)

### 4.4 Nitrate concentrations

The nitrate concentrations were 93-477 μM/l with an average ~246 μM/l (Table 1). Nitrate concentrations measured in the main hydrological section of the Charente River increased from upstream (~100 μM/l) to downstream (up to 425 μM/l at CHA8) and were positively correlated to water discharge at the watershed scale (Figure 3). This clear nitrate increase

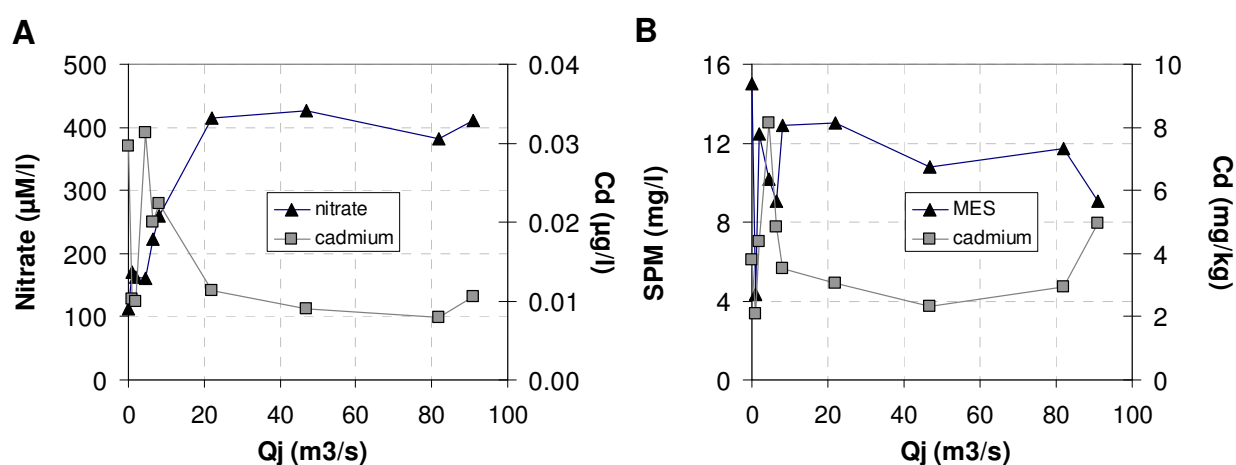


Fig. 3. (A) Nitrate and dissolved Cd concentrations versus daily water discharge in the Charente River; (B) Suspended Particulate Matter (SPM) and particulate Cd concentrations versus daily water discharge in the Charente River.



starts at the CHA5 site, i.e. where the Charente River drains maize areas. Based on this observation, we have determined typical nitrate concentrations for each land use in the Charente System: the mean nitrate concentrations are  $\sim 140 \mu\text{M}/\text{l}$  in the areas mainly occupied by pasture,  $\sim 350 \mu\text{M}/\text{l}$  for corn/maize production and  $\sim 430 \mu\text{M}/\text{l}$  in vineyard areas.

The Charente River faces high nitrate levels (Bry & Hoflack, 2004; EPTB-Charente, 2007). These high levels probably reflect the intensification of agriculture in the central and lower systems and increase the risk of eutrophication. The intensification of crops, particularly corn production, was accompanied by a high water demand for irrigation over the last thirty years. Vineyards are also located in the basin and can generate diffuse water pollution by nitrates. To assess whether the concentrations obtained on the Charente River are comparable to other systems, we compared our results with those recently published for rivers draining the Arcachon basin (SW France), which is affected by eutrophication due to nitrogen transfer from agricultural areas to the river system (Canton et al., 2012). These authors demonstrated that low concentrations (20 to  $45 \mu\text{M}/\text{l}$ ) occur in watersheds dominated by forest, whereas nitrate concentrations were considered as high in watersheds draining agricultural areas with an average of  $140 \mu\text{M}/\text{l}$  (Canton et al., 2012). For these agricultural watersheds, nitrate concentrations increased from 200 to  $500 \mu\text{M}/\text{l}$  in winter during high water discharges. Accordingly, our results obtained for the Charente River are similar to those in the rivers studied by Canton et al. (2012) supporting that the high nitrate concentrations may be attributed to agriculture as suggested previously (Bry & Hoflack, 2004; Vernier et al., 2010) and probably result in significant nitrate export to the Marennes-Oleron Bay and the adjacent coastal area.

#### 4.5 Dissolved Cd concentrations

The dissolved Cd concentrations ( $\text{Cd}_\text{D}$ ) in the Charente watershed ranged from 8 to  $31 \text{ ng}/\text{l}$ , with an average of  $\sim 17 \text{ ng}/\text{l}$  (Table 1). Unlike the spatial nitrate evolution, the dissolved Cd concentrations in the mainstream decreased from upstream to downstream until CHA9; then a slight  $\text{Cd}_\text{D}$  increase occurred at CHA10 (Figure 3). Based on the  $\text{Cd}_\text{D}$  levels, a  $\text{Cd}_\text{D}$  distribution map aims at visualizing the spatial variation in the Charente watershed (Figure 4). The color classes were determined using the detection limit ( $2 \text{ ng}/\text{l}$ ), the  $\text{Cd}_\text{D}$  level ( $10 \text{ ng}/\text{l}$ ) representing “good status” of water quality as proposed by the Ministry of Environment and Sustainable Development and the Water Agencies quality guideline (SEQ-eau; MEDD and Agences de l’Eau, 2003) and the average  $\text{Cd}_\text{D}$  in world rivers proposed by Martin & Meybeck (1979) marked MA in Figure 4 ( $\text{MA}=50 \text{ ng}/\text{l}$ ).

In the downstream Charente watershed, the Seugne, Né, Sonnette and Bandiat Rivers showed  $\text{Cd}_\text{D}$  typical of good water quality ( $<10 \text{ ng}/\text{l}$ ), as well as the upstream sections of the Moulde, the Argentor and the Son-Sonnette Rivers. In contrast, the  $\text{Cd}_\text{D}$  concentrations in the upstream section of the Charente River (CHA1; CHA4-CHA6) suggested lower water quality ( $20\text{-}30 \text{ ng}/\text{l}$ ; Table 1). However, even the highest  $\text{Cd}_\text{D}$  measured in this study were lower than the  $\text{Cd}_\text{D}$  level defined for the world's major rivers ( $\text{MA}=50 \text{ ng}/\text{l}$ ; Figure 4), with low human influences (e.g. Amazon and Congo Rivers; Martin & Meybeck, 1979).

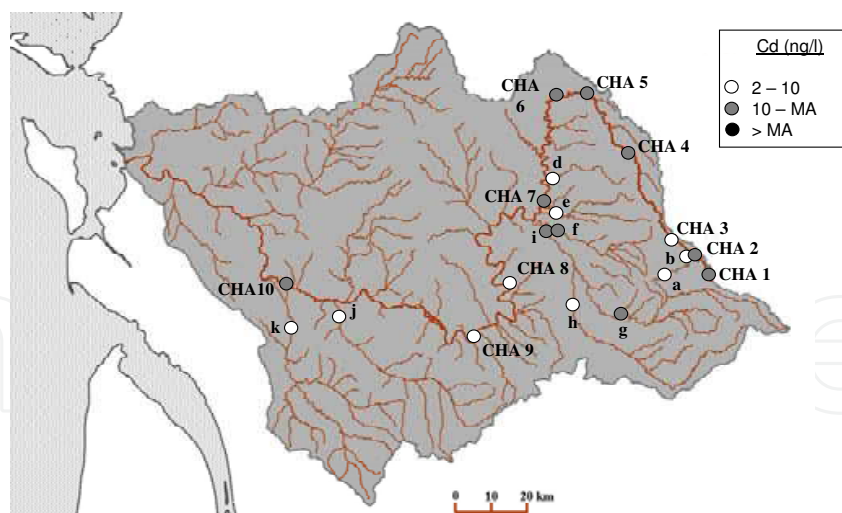


Fig. 4. Spatial distribution of dissolved Cd concentrations

#### 4.6 Particulate Cd concentrations in SPM

The particulate Cd concentrations ( $Cd_P$ ) were variable from one site to another with values comprised between 1.20 mg/kg and 8.16 mg/kg (Table 1). Most of these values were clearly higher than the average concentration measured in the SPM defined for World Rivers (MA=1.55 mg/kg; Viers et al., 2009), except for the Upstream Moulde River (Table 1). As observed for  $Cd_P$  in the main hydrological section of the Charente watershed, the  $Cd_P$  concentrations in SPM decreased from upstream to downstream until CHA9; then a significant Cd increase occurred at CHA10 (Figure 3). The spatial evolution of the particulate Cd concentration is not correlated with that of the Charente SPM concentrations (Figure 3). We compared particulate Cd concentrations with consensus-based sediment quality guidelines proposed for freshwater sediments (MacDonald et al., 2000), i.e. concentration classes supporting the assessment of ecotoxicological risk potential (Figure 5).

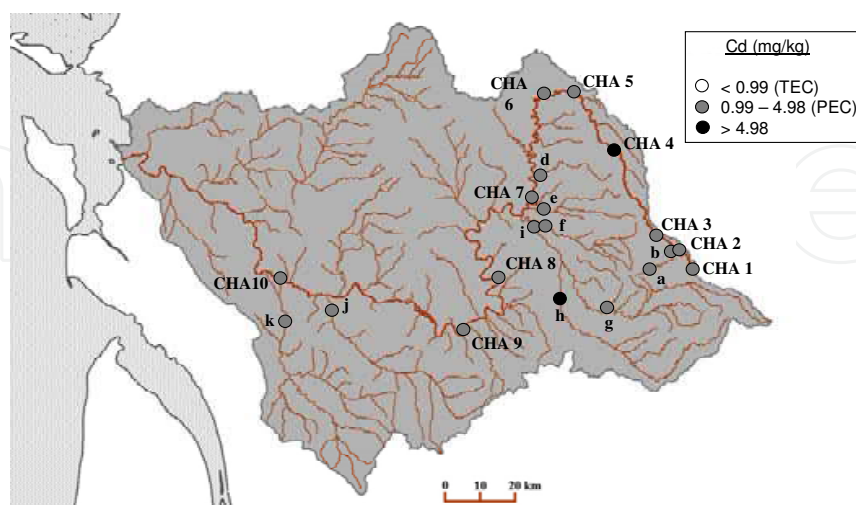


Fig. 5. Spatial distribution of particulate Cd concentrations in SPM

- The TEC (Threshold Effect Concentration;  $Cd_P=0.99$  mg/kg) is defined as the  $Cd_P$  concentration below which no effect on organisms is expected;

- The PEC (Probable Effect Concentration;  $Cd_P = 4.98$  mg/kg) is defined as the  $Cd_P$  concentration above which effects on organisms are expected.

Most of the  $Cd_P$  in the Charente River SPM were higher than the TEC and at two sites the measured values exceeded the PEC level ("b" and "CHA4" with  $Cd_P = 6.17$  and  $8.16$  mg/kg, respectively); two other sites (CHA10; CHA5) have values close to the PEC level (Figure 5). These results suggest that in the Charente River system toxic effects on aquatic organisms due to the presence of Cd (i) cannot be excluded at most of the sites studied and (ii) should be expected locally.

#### 4.7 Particulate Cd concentrations in stream sediments (<63 $\mu$ m)

Excluding the Riou Mort site "c" ( $Cd = 37.7$  mg/kg) which drains a former mineral resource deposit,  $Cd_P$  in sieved stream sediments ranged from 0.70 to 3.06 mg/kg (Table 1). The comparison with ecotoxicological indices showed that a majority of sites have  $Cd_P$  concentrations above the TEC, yet without exceeding the PEC level (Figure 6). This suggests that potential toxicity effects on water organisms in the Charente River due to the presence of Cd cannot be excluded.

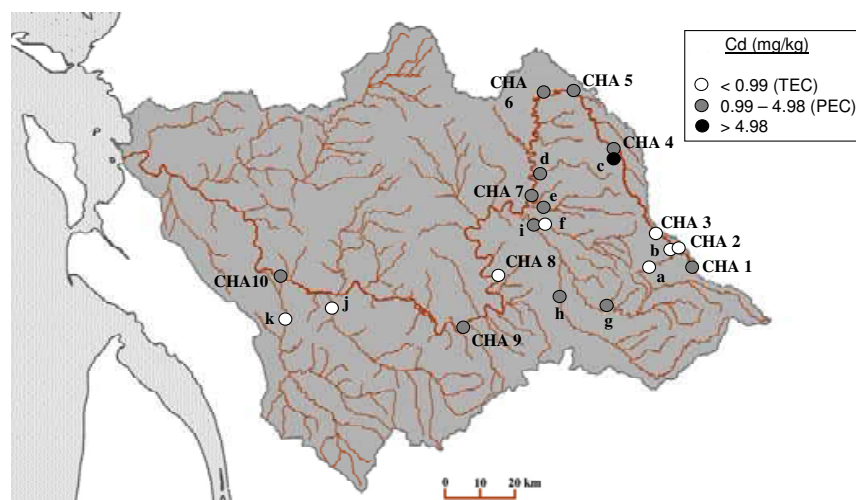


Fig. 6. Spatial distribution of particulate Cd concentrations in <63  $\mu$ m sediments

#### 4.8 Comparison with the geochemical monitoring performed during 2006-2007

The dissolved and particulate Cd concentrations measured at the Chaniers site (CHA10 site) in this study were compared with those obtained during the 2 year-geochemical monitoring achieved in the Inter-Regional project "Défi Cadmium" (Cadmium Challenge, Water Agency Adour-Garonne) performed during 2006 and 2007 (Dabrin, 2009; Table 1). The Chaniers site is considered as the outlet of the fluvial Charente watershed. The  $Cd_P$  in SPM from CHA10 measured in this study was similar to average  $Cd_P$  established during the "Défi Cadmium" project. In contrast, the  $Cd_P$  concentration was lower than the minimum  $Cd_P$  value measured by Dabrin (2009). It has been classically observed in river systems that the lowest metal concentrations in water and in SPM occurred during high flow rates. This phenomenon can be related to dilution by (i) rainwater for the dissolved phase and (ii) coarse particles (coarse silt to sand) with low metal adsorption capacity for the particulate

phase (e.g. Schleichert, 1975; Dawson & Macklin, 1998; Cobelo-Garcia et al., 2004). In the Charente River system, Dabrin (2009) showed that the dissolved concentrations of some metals such as Cd decreased with water discharges, highlighting the close link between hydrology and geochemistry. As our campaign is representative of “medium to high water” conditions in the Charente River, our evaluation of the SPM quality defined throughout the watershed does not represent the worst geochemical situation. We can therefore assume that  $Cd_P$  may frequently exceed critical thresholds (e.g. PEC) at many sites during low waters and we recommend specific water monitoring during this period in order to evaluate ecotoxicological risk at the watershed scale.

#### 4.9 Dissolved and particulate Cd fluxes

The instantaneous (daily) dissolved and particulate Cd fluxes were calculated for each sampling site (Table 2). The  $Cd_D$  levels significantly increased between the CHA3 and the CHA4 sites, inducing a clear increase in  $Cd_D$  flux that was not proportional to water discharge, suggesting an additional point source within this section (Figure 7A). The additional Cd point source ( $\Delta 1 \sim 8g/d$ ; Figure 7A) may be linked to the presence of mineral deposits in the metamorphic formation areas and specifically, near the fault of Beaumont Confolent (BRGM, 2003). This is supported by high  $Cd_P$  measured in the sediment collected in the former mining area (site “c”; Figure 1). A second abnormal increase in  $Cd_D$  fluxes ( $\Delta 2 \sim 25g/d$ ; Figure 7A) can be observed between the CHA9 and the CHA10 sites and cannot be explained by the  $Cd_D$  supply via the Ne and Seugne Rivers alone (“j” and “k”; Table 2). Additional campaigns will be needed to identify the source in this section by performing a longitudinal profile along the Charente River. Note that in this geographical area, we have located a manufactory which produces batteries for all types of civil and military aircrafts.

Item	River	SPM Flux t/j	Part Cd flux g/j	Diss Cd flux g/j	Part Cd flux contribution	
<b>CHA1</b>	<i>Saint Gervais</i>	Charente	0.2	0.7	0.4	66%
<b>CHA2</b>	<i>Sansac</i>	Charente	0.4	0.8	0.9	47%
<b>CHA3</b>	<i>Pont de Suris</i>	Charente	2.2	10	1.8	85%
<b>CHA4</b>	<i>Chez Paire</i>	Charente	4.0	32	12	73%
<b>CHA5</b>	<i>Charroux</i>	Charente	5.0	24	11	69%
<b>CHA6</b>	<i>Saint-Saviol</i>	Charente	9.1	32	16	67%
<b>CHA7</b>	<i>Aunac</i>	Charente	25	76	21	78%
<b>CHA8</b>	<i>Vindelle</i>	Charente	44	102	36	74%
<b>CHA9</b>	<i>Sireuil</i>	Charente	83	245	56	81%
<b>CHA10</b>	<i>Chaniers</i>	Charente	71	353	82	81%
<b>a</b>	<i>Massignac</i>	Upstream Moulde	0.2	0.3	0.3	45%
<b>b</b>	<i>Chez Boige</i>	Downstream Moulde	0.2	0.5	0.7	40%
<b>c</b>	<i>Riou Mort</i>	-	-	-	-	-
<b>d</b>	<i>Poursac</i>	Argentor	1.8	6.3	2.4	72%
<b>e</b>	<i>Mouton</i>	Son-Sonnette	1.8	7.1	2.2	77%
<b>f</b>	<i>Saint Ciers/Bonnieure</i>	Bonnieure	2.5	5.9	2.6	69%
<b>g</b>	<i>Montbron</i>	Upstream Tardoire	7.2	33	11	76%
<b>h</b>	<i>Feuillade</i>	Bandiat	3.9	24	4.2	85%
<b>i</b>	<i>Coulgens</i>	Downstream Tardoire	16	59	8.1	88%
<b>j</b>	<i>Les Perceptiers</i>	Ne	7.3	13	5.7	70%
<b>k</b>	<i>La Lijardière</i>	Seugne	11	22	8.0	74%

Table 2. Daily SPM flux and dissolved and particulate Cd flux and particulate Cd flux contribution at strategic sites



The evolution of the daily  $Cd_P$  flux in the section of the Charente River was compared to that of the corresponding SPM flux. This comparison revealed a good statistical relationship between both parameters (Figure 7B). Based on this relationship, we can define a  $Cd_P$  average of  $\sim 2.90$  mg/kg, corresponding to the regression slope and, probably, to the  $Cd_P$  level in agricultural lands which are mechanically eroded during runoff. Based on this, we have detected a small increase in  $Cd_P$  that was not due to the contribution of SPM at the CHA4 site and a strong  $Cd_P$  anomaly at the CHA10 site. Like for  $Cd_D$ , the minor  $Cd_P$  anomaly in CHA4 probably results from the presence of formerly exploited mineral deposits (Ba-Pb-Zn mineralization). Between the CHA9 and CHA10 sites, we have observed a SPM decrease related to sedimentation inducing decreasing SPM fluxes ('loss') in this section. Based on the observed relationship between SPM flux and  $Cd_P$  flux in the Charente River, the expected  $Cd_P$  flux at the Chaniers site for an instantaneous SPM flux of 71 t/d would be  $\sim 200$  g/d (Figure 7B). The observed  $Cd_P$  flux of 353 g/d being  $\sim 1.8$  times higher (Table 2) clearly suggests a significant Cd enrichment in SPM due to anthropogenic sources and reflects observations made for  $Cd_D$ .

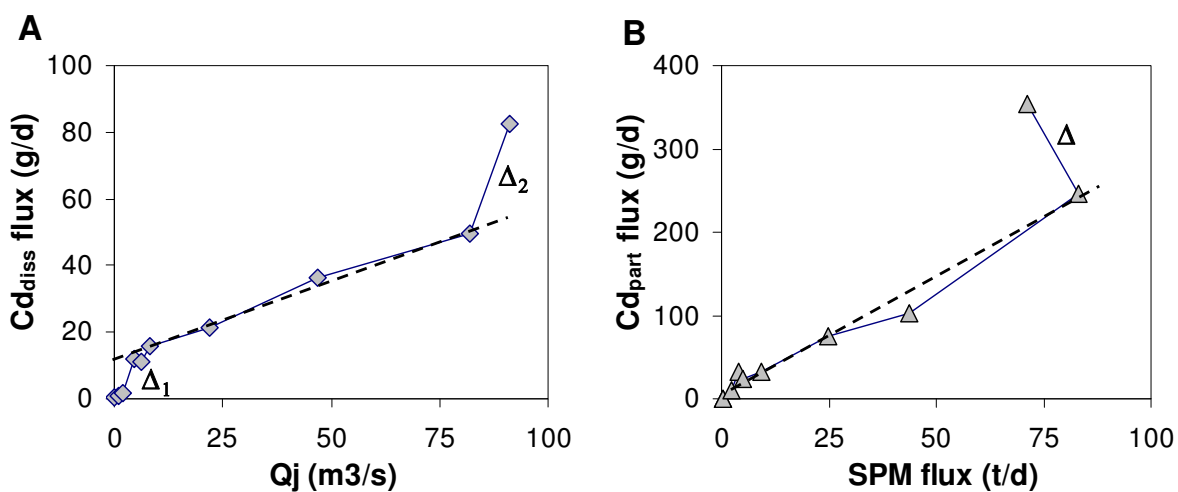


Fig. 7. Relationship between daily dissolved Cd flux and water discharge (A) and between daily particulate Cd flux and SPM flux (B) at strategic sites in the main channel of the Charente River

The dissolved and particulate flux estimates underline the Cd partitioning (i.e. chemical form) in the Charente River system. In the main section of the Charente River, the instantaneous Cd flux was mainly due to SPM transport (reaching 80% at CHA10), except at CHA2 (downstream from the Lavaud Reservoir) and in the Moulde River (upstream and downstream part), where the particulate transport contributed 47%, 45% and 40%, respectively, to total (dissolved + particulate) Cd ( $Cd_T$ ) fluxes. These results suggest that the particulate phase is the predominant Cd vector in the Charente River system and demonstrate that efficient reduction of Cd transport into the Marennes-Oleron Bay would imply limitation of mechanical erosion, mainly in the agricultural areas.

By extrapolating daily fluxes to the annual scale, we have obtained a first approximation of annual SPM and Cd exports to the Charente Estuary and in fine to the MOB. These estimates probably represent the orders of magnitude, although errors on flux estimates



related to inadequate sampling frequency may be very high and are likely to result in severe under-estimation of fluxes (Coynel et al., 2004). Based on this extrapolation, annual SPM flux and Cd<sub>T</sub> export at CHA10 were evaluated to ~26,000 t/yr and 159 kg/yr, respectively, corresponding to a specific sediment yield of ~2.45 t/km<sup>2</sup>/yr and a specific Cd<sub>T</sub> flux ~ 15 g/km<sup>2</sup>/yr. Accordingly, the specific (potentially under-estimated) Cd flux of the Charente watershed would be 2 times lower than that of the Cd-polluted Garonne watershed in 2006/2007 (39 g/km<sup>2</sup>/yr; Dabrin, 2009). However, as explained above, this Cd estimation for the Charente River system is probably highly underestimated. Indeed, based on a permanent observation sampling in 2006-2007 with high temporal resolution, the annual specific Cd<sub>T</sub> was evaluated to 54 g/km<sup>2</sup>/yr for the Charente River, i.e. higher of that reported for the Garonne River (Dabrin, 2009). Furthermore the totality of Cd exported from the Charente watershed via the Charente Estuary directly enters the MOB and may reach the oyster farms therein, whereas only part of the Cd exported from the Gironde system may reach the vulnerable zones of the MOB. Our work intends to demonstrate that the Charente River system should be further studied because of its significant impact on the MOB.

## 5. Conclusion

This study represents a major advance in the geochemical characterization of water and water-borne particles in the Charente River and contributes to a better understanding of the Cd transfer into the Marennes-Oleron Bay. The main results obtained have allowed to:

- develop a first spatially resolved geochemical database of dissolved and particulate Cd concentrations at the watershed scale, i.e. in three different compartments (water, sediment and SPM) at 21 strategic sites along the Charente River and its tributaries, taking into account the geology and land use characteristics;
- assess the quality of these three geochemical compartments using ecotoxicological criteria or world river references and locate sub-catchment with potential chemical risk;
- quantify the daily dissolved and particulate Cd fluxes representative of a moderate hydrological situation from the water discharge measurements provided by the Regional Environment Agency-DIREN and complemented by gauging measurements during this campaign;
- estimate the Cd contribution from subcatchments and identify major zones with point and/or diffuse Cd sources.

In terms of perspectives, further work should be carried out during low water because of the strong relationship between water quality and hydrology. It would also be necessary to determine more precisely the origins of the observed Cd anomaly, by taking samples from the former mining deposit and agricultural soils. This approach should be completed by a longitudinal sampling profile between CHA9 and CHA10, where significant additional dissolved and particulate Cd fluxes occurred. Our study includes the Charente River upstream from the Chaniers site, which is considered as the outlet of the fluvial system. Furthermore, a more complete mass balance should include fluxes via two other major tributaries, the Boutonne and Arnoult Rivers, entering the Charente Estuary in the tidal reaches.

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Edited by Dr. Yuzhou Luo

ISBN 978-953-51-0519-0

Hard cover, 344 pages

**Publisher** InTech

**Published online** 20, April, 2012

**Published in print edition** April, 2012

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Coyne Alexandra, Khoury Alaa, Dutruch Lionel, Blanc Gérard, Bossy Cécile, Derriennic Hervé and Schäfer Jörg (2012). Spatial Cadmium Distribution in the Charente Watershed and Potential Risk Assessment for the Marennes Oleron Bay (Southwest France), Novel Approaches and Their Applications in Risk Assessment, Dr. Yuzhou Luo (Ed.), ISBN: 978-953-51-0519-0, InTech, Available from: <http://www.intechopen.com/books/novel-approaches-and-their-applications-in-risk-assessment/spatial-cadmium-distribution-in-the-charente-watershed-and-potential-risk-assessment-for-the-marenne>

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