

# Seasonal variations and annual fluxes of arsenic in the Garonne, Dordogne and Isle Rivers, France

Matthieu Masson, Jörg Schäfer\*, Gérard Blanc, Anschutz Pierre

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

Received 25 September 2006; received in revised form 19 October 2006; accepted 24 October 2006  
Available online 13 December 2006

## Abstract

Daily measurements of water discharges and suspended particulate matter (SPM) concentrations and monthly analyses for arsenic were conducted from 1999 to 2005 on the Garonne, Dordogne and Isle Rivers, the three main tributaries of the Gironde Estuary, France. Despite the known historical polymetallic pollution affecting the Lot–Garonne River system, the highest As concentration level was observed in the Isle River. This was explained by the geological context and various Au/As deposits in this watershed. In the three studied rivers, dissolved As concentrations showed important seasonal variations with maximum values in summer. The dissolved As concentrations were closely related to water temperature and their increase in spring/summer appeared to be induced by water temperatures above  $\sim 15$  °C, independently from discharge. The reduction of As(V) to more soluble As(III) and/or destruction of solid As carrier phases by micro-organisms could explain this observation, suggesting that temperature-dependent biogeochemical processes play an important role in controlling As partition and speciation in fluvial systems.

Water and SPM fluxes in the Garonne River mainly control arsenic inputs into the Gironde Estuary and the downstream coastal zones. Based on the present data, we propose an empirical model to roughly estimate the annual dissolved and particulate As fluxes in the Garonne, Dordogne and Isle Rivers from annual water and SPM fluxes. The comparison of observed As fluxes and those estimated from the empirical model suggests that resuspension of historical, polluted reservoir sediments during a major flood accounted for  $\sim 50\%$  of the annual As fluxes in 2003.

© 2006 Elsevier B.V. All rights reserved.

*Keywords:* Arsenic; River; Seasonal variations; Mass balance; Empirical model

## 1. Introduction

Arsenic is a ubiquitous element naturally present in all environmental compartments i.e. freshwater and seawater, soil, atmosphere, biosphere. Since several centuries, huge amounts of arsenic have been introduced into the environment by anthropogenic activities such as mining,

combustion of fossil fuels or agriculture (e.g. Smedley and Kinniburgh, 2002). Arsenic, by its high bioavailability and toxicity, has become a major environmental and human-health preoccupation. The Gironde Estuary and its tributaries, the Garonne, Dordogne and Isle Rivers, represent one of Europe's largest fluvial–estuarine systems. Although they drain one of the least industrialized regions of Europe (Abril et al., 2002), the Gironde watershed is affected by important polymetallic pollution attributed to former mining and ore-treatment activities in

\* Corresponding author. Tel.: +33 540002967; fax: +33 556880848.  
E-mail address: [j.schaefer@epoc.u-bordeaux1.fr](mailto:j.schaefer@epoc.u-bordeaux1.fr) (J. Schäfer).

the Lot watershed (e.g. Roux and Simonet, 1987; Jouanneau et al., 1993; Lapaquellerie et al., 1995; Blanc et al., 1999; Audry et al., 2004a,b; Schäfer et al., 2006; Fig. 1). Ore deposits and mining areas in the upper reaches of the Garonne, Dordogne and Isle watersheds (mainly Massif Central and Pyrenean Mountains) and intense agriculture in the downstream watersheds are major sources for metals (e.g. Cd, Zn, Pb, Cu) transported to the coast (Schäfer and Blanc, 2002; Masson et al., 2006). The Western Massif Central, mostly drained by the Garonne, Dordogne and Isle Rivers, presents various important As sources (mainly hydrothermal sources; Roussel et al., 2000; Smedley and Kinniburgh, 2002; Courtin-Nomade et al., 2005), suggesting large dissemination of this ecotoxic element (e.g. Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). Although As behaviour is well documented for the sources (e.g. mine areas in the Massif Central; Courtin-Nomade et al., 2003; Le Guern et al., 2003; Bodéan et al., 2004) and for the Gironde Estuary/ocean interface (Seyler and Martin, 1990; Michel et al., 1998, 2000), little is known on arsenic concentrations and transport in the Gironde's tributary river systems.

This study presents data obtained during a seven-year (1999–2005) observation in the Garonne River and during a four-year (1999–2002) observation in the Dordogne and Isle Rivers. Daily measurements of water discharge and suspended particulate matter (SPM) concentrations were combined with monthly measured

dissolved and particulate As concentrations. The objective of the present work is to determine and compare As concentrations and fluxes in the three studied watersheds, probably affected by various As sources. Gross As fluxes into the Gironde Estuary are reported and the role of microbially driven redox processes for seasonal variations of dissolved As concentrations is discussed.

## 2. Methodology

### 2.1. Sampling area

The Gironde Estuary (southwest France) drains a basin surface of  $\sim 79,000 \text{ km}^2$  (e.g. Schäfer et al., 2002; Fig. 1) composed by three main river systems: the Garonne River ( $\sim 51,500 \text{ km}^2$ ), the Dordogne River ( $\sim 15,000 \text{ km}^2$ ) and the Isle River ( $\sim 6600 \text{ km}^2$ ). For each river, the sampling sites have been chosen upstream of the dynamic tidal zone to exclude disturbances by estuarine influences (e.g. alternating flow direction), but as far downstream as possible to integrate a maximum area of the drainage basin (Schäfer and Blanc, 2002). The selected sites namely Pessac (Dordogne River), Guitres (Isle River) and La Réole (Garonne River) represent the three main entries of the Gironde Estuary (Fig. 1; Schäfer et al., 2002). National and regional offices (Port Autonome de Bordeaux;

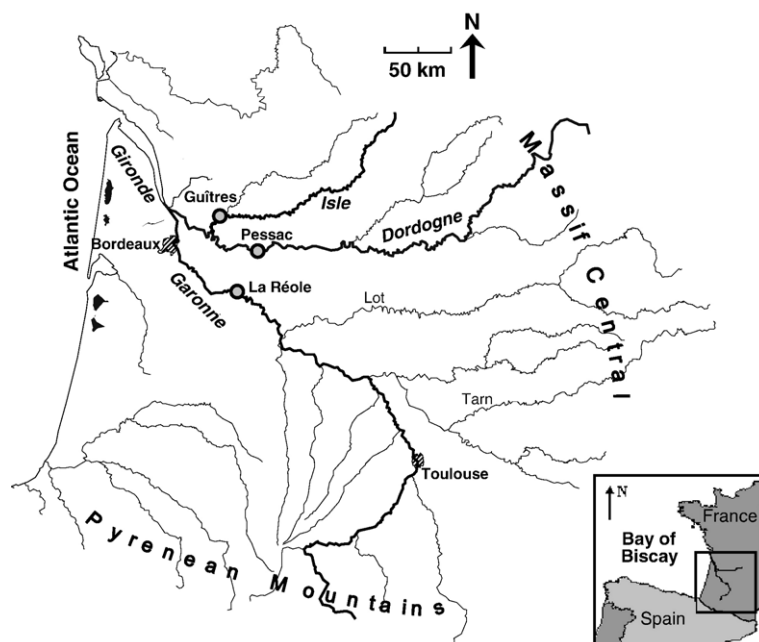


Fig. 1. Map of the Gironde Estuary and its major tributaries: the Garonne, Dordogne and Isle Rivers. Circles show the three permanent observation sites.

DIREN) responsible for the observation of river discharge have provided the daily discharge data for the Garonne, Dordogne and Isle Rivers for the observation period (1999 to 2005; Fig. 2).

## 2.2. In-situ measurements and sample collection

Physical parameters were measured monthly in-situ at ~1 m from the riverbank and at 0.2 m depth. 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 redox potential (Eh) were performed using a Sentix® 41 probe (PROFILINE, WTW).

At the Guitres site, river water samples for suspended particulate matter (SPM) measurements were collected automatically every 90 min using an automatic sampling device (integrated pumping, rinsing and sample distribution system; model: Bühler PB-MOS), which integrated 16 discrete samples into a 1 l daily composite sample. At the La Réole and Pessac sites, daily water samples for SPM determination were collected by hand. Both automatic and manual SPM samplings were realised in the mainstream at ~2 m from the riverbank and at 1 m depth.

Water and suspended particulate matter (SPM) for the chemical analysis were sampled monthly as previously described in detail in Audry et al. (2004a). Water samples were filtered immediately after sampling through 0.2 µm and 0.02 µm Nucleopore® polycarbonate filters in a glove box (laboratory van) and filtrates were collected in acid-washed PP bottles, acidified (HNO<sub>3</sub> suprapur 0.1%) and stored in the dark at 4 °C until analysis. Particulate matter for trace element analyses was collected with a PP-pump with PP-tubing followed by centrifugation (Westfalia; 12,000 g). This technique is considered a practicable and reliable method for representative SPM sampling in all hydrologic situations (Lapaquellerie et al., 2000; Schäfer and Blanc, 2002).

## 2.3. Sample analyses

Determination of SPM concentrations was performed by filtration of precise volumes of river water through dry pre-weighed filters (Whatman GF/F, 0.7 µm). Filters were dried to constant weight at 45 °C and re-weighed.

Representative sub-samples (30 mg of dry, powdered and homogenized material) were digested in closed Teflon reactors (Savillex®) using 750 µl HCl (12 M, suprapur), 250 µl HNO<sub>3</sub> (14 M, suprapur) and 2 ml HF

(26 M, suprapur). The reactors were then heated at 110 °C for 2 h. After complete cooling, the digested solution was evaporated to dryness. Each sample was brought to 10 ml using 150 µl HNO<sub>3</sub> (suprapur) and double deionized (Milli-Q®) water (Blanc et al., 1999).

Soluble reactive phosphate was determined colorimetrically from the molybdenum blue complex (Murphy and Riley, 1962). Dissolved and particulate As concentrations were measured using ICP-MS (Elan 5000, Perkin-Elmer and X7, Thermo) with external calibration. The analytical methods employed were continuously quality checked by analysis of certified international reference materials (PACS-1) and waters (SLRS-4). Accuracy was within 5% of the certified values and the analytical error (relative standard deviation) generally better than 5% for concentrations 10 times higher than detection limits (for ELAN 5000: 50 ng l<sup>-1</sup>; X7: 25 ng l<sup>-1</sup>). Furthermore, randomly selected samples were also analysed by flow injection-hydride generation Atomic Absorption Spectrometry (FIAS 400; AA 300, Perkin-Elmer) and Atomic Fluorescence Spectrometry (Merlin Millenium, PSA) after pre-reduction of As(V) by KI/ascorbic acid (0.1 M/0.06 M) in 2.4 M HCl, using commonly applied protocols (e.g. Yamamoto et al., 1985; Chaillou et al., 2003). The analytical results obtained from these independent analytical methods were similar (differences generally <7%).

## 2.4. Flux estimation

National and regional offices (Port Autonome de Bordeaux; DIREN) provided the daily discharge data for the Garonne (1999–2005; Fig. 2), Dordogne and Isle Rivers (1999–2002; Fig. 2). Annual dissolved and particulate As fluxes into the Gironde Estuary via the Garonne, Dordogne and Isle Rivers were estimated from daily discharge and SPM data and monthly measured metalloid concentrations using commonly applied equations (Walling and Webb, 1985; Meybeck and Ragu, 1996; Schäfer et al., 2002).

## 3. Results

### 3.1. Water discharges and SPM concentrations

From 1999 to 2005, daily discharges of the Garonne River varied by a factor ~90 (54–4740 m<sup>3</sup> s<sup>-1</sup>; Fig. 2). The annual mean water discharges ranged from 346 to 635 m<sup>3</sup> s<sup>-1</sup> (Fig. 2). During 1999–2002, daily discharges varied by a factor ~30 (51–1530 m<sup>3</sup> s<sup>-1</sup>) for the Dordogne River and ~70 (8–565 m<sup>3</sup> s<sup>-1</sup>) for the Isle

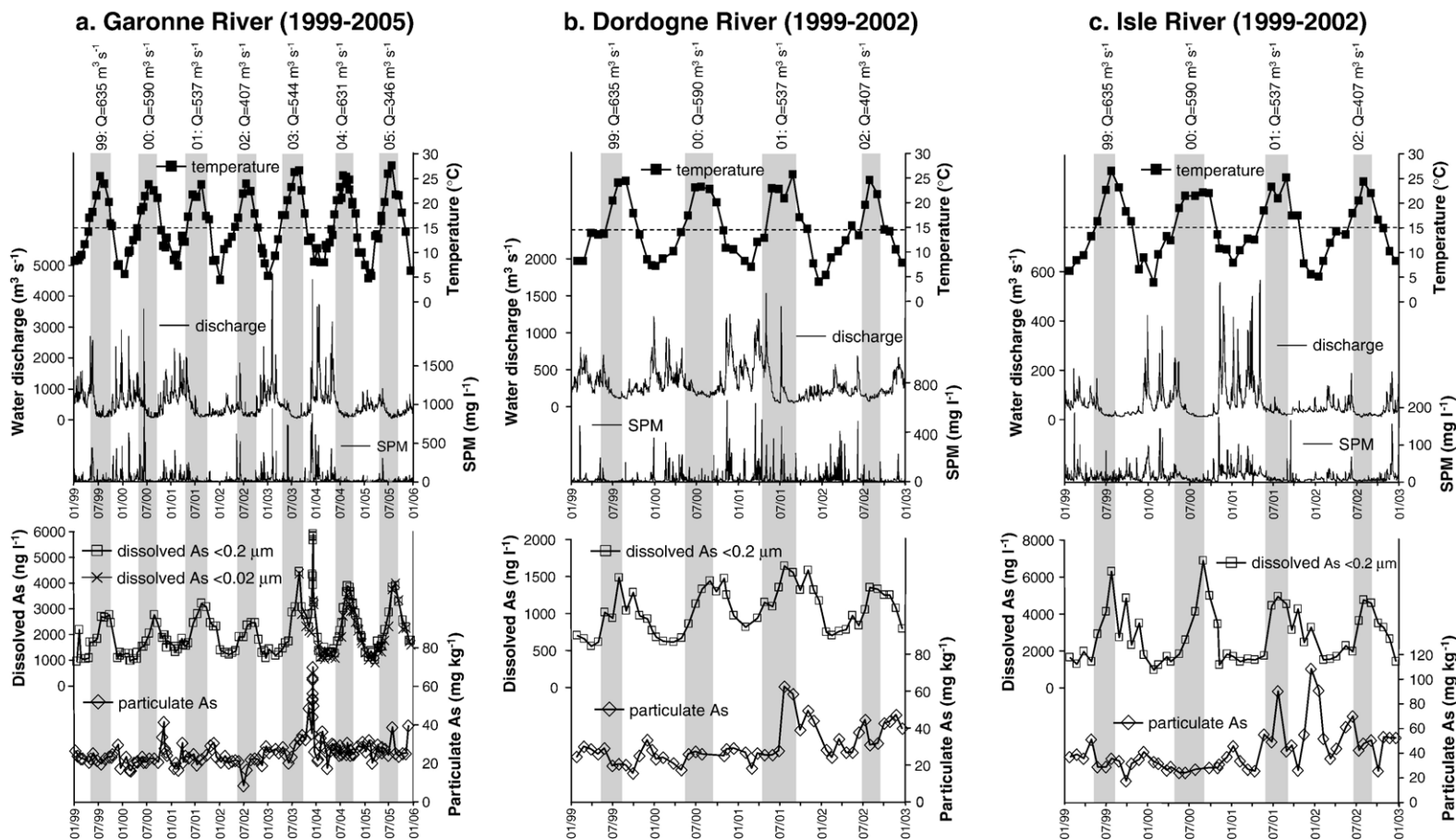


Fig. 2. Water discharges ( $\text{m}^3 \text{s}^{-1}$ ), SPM concentrations ( $\text{mg l}^{-1}$ ), temperature ( $^{\circ}\text{C}$ ), dissolved  $<0.02 \mu\text{m}$  and  $<0.2 \mu\text{m}$  As ( $\text{ng l}^{-1}$ ) concentrations and particulate As ( $\text{mg kg}^{-1}$ ) concentrations in the Garonne (1999–2005; a), Dordogne (1999–2002; b) and Isle (1999–2002; c) Rivers. The grey areas represent periods when the dissolved As concentrations increased and the dashed lines represent “activation” temperature.

River (Fig. 2). The annual mean water discharges of the Dordogne and Isle Rivers were maximum in 2000 ( $364$  and  $79 \text{ m}^3 \text{ s}^{-1}$ , respectively; Fig. 2) and minimum in 2002 ( $244$  and  $43 \text{ m}^3 \text{ s}^{-1}$ ; Fig. 2). Flood events generally occurred in winter and spring (Fig. 2), except in 2002 for the three studied rivers and 2005 for the Garonne River, where discharges remained low throughout the whole year, resulting in very low annual mean discharge values. With respect to long-term discharge data (Nagy-Breitenstein, 1993; Probst and Tardy, 1985), the study period covered five average years (1999–2001 and 2003–2004) and two very dry years (2002 and 2005). For the Garonne River, the 2005-year was the third driest year since 1959.

Suspended particulate matter concentrations were highly variable and closely related to discharge (Fig. 2). Indeed, SPM concentrations varied by a factor of  $\sim 1500$  in the Garonne River ( $1\text{--}1550 \text{ mg l}^{-1}$ ) and by a factor of  $\sim 600$  in the Dordogne River ( $1\text{--}656 \text{ mg l}^{-1}$ ). In the Isle River, SPM concentrations were much less variable, showing a factor of only  $\sim 200$  between the lowest ( $1 \text{ mg l}^{-1}$ ) and the highest values ( $189 \text{ mg l}^{-1}$ ). In the Garonne River, a major flood was sampled between the 5th and the 9th December 2003. The flood peak occurred on the 5th December with water discharge of

$\sim 4550 \text{ m}^3 \text{ s}^{-1}$  and SPM concentrations of  $\sim 880 \text{ mg l}^{-1}$  (Fig. 2).

### 3.2. Physical and chemical parameters

In the surface water of the Garonne, Dordogne and Isle Rivers, temperatures, dissolved oxygen saturation and redox potentials (Eh) showed rather similar values and variations during the observation period (Table 1). The pH values were similar in the Garonne and Isle Rivers, whereas in the Dordogne River, they tended to be slightly lower (Table 1). Average conductivity showed the following order: Isle River ( $\sim 334 \text{ }\mu\text{S cm}^{-1}$ ) > Garonne River ( $\sim 286 \text{ }\mu\text{S cm}^{-1}$ ) > Dordogne River ( $\sim 179 \text{ }\mu\text{S cm}^{-1}$ ). In the Garonne, Dordogne and Isle Rivers, pH, redox potential and oxygen saturation did not show distinct seasonal or discharge-related variations, whereas conductivity tended to decrease with increasing discharge. Water temperature showed strong seasonal variations (Fig. 2) in the studied rivers with minimum values in winter ( $\sim 4 \text{ }^\circ\text{C}$ ) and maximum values in summer ( $\sim 27 \text{ }^\circ\text{C}$ ).

Average phosphate concentrations (Table 1) were higher in the Garonne River ( $0.12 \text{ mg l}^{-1}$ ) than those in

Table 1

Statistical values (mean, min: minimum, max: maximum, Q1: first quartile, med: median, Q3: third quartile) for the dissolved ( $<0.2 \text{ }\mu\text{m}$  and  $<0.02 \text{ }\mu\text{m}$ ;  $\text{ng l}^{-1}$ ) and particulate ( $\text{mg kg}^{-1}$ ) As concentrations, phosphate concentrations ( $\text{mg l}^{-1}$ ) and physical parameters (temp: temperature,  $^\circ\text{C}$ ; pH; Eh: redox potential, mV; sat  $\text{O}_2$ : dissolved oxygen saturation, %; cond: conductivity,  $\mu\text{S cm}^{-1}$ ) in the Garonne, Dordogne and Isle Rivers; n.m.: not measured

	As part $\text{mg kg}^{-1}$	As $<0.2$ $\mu\text{m ng l}^{-1}$	As $<0.02 \text{ }\mu\text{m}$ $\text{ng l}^{-1}$	$\text{PO}_4^{3-}$ $\text{mg l}^{-1}$	temp $^\circ\text{C}$	pH	Eh mV	sat $\text{O}_2$ %	cond $\mu\text{S cm}^{-1}$
<i>Garonne</i>									
mean	27.3	2140	2130	0.12	15.0	7.9	187	96	286
min	16.5	970	936	0.01	4.4	7.0	75	62	169
max	70.2	5950	4400	0.27	27.7	8.7	389	137	446
Q1	22.5	1330	1320	0.08	10.0	7.8	147	90	265
med	25.3	1820	2000	0.11	14.1	7.9	179	96	290
Q3	29.4	2700	2900	0.15	20.5	8.1	217	101	308
<i>Dordogne</i>									
mean	30.6	1050	n.m.	0.07	14.6	7.6	187	96	179
min	15.8	567	n.m.	0.01	4.0	6.3	105	72	114
max	62.4	1650	n.m.	0.14	26.0	8.3	318	148	250
Q1	24.8	784	n.m.	0.04	8.9	7.4	145	88	149
med	27.6	1030	n.m.	0.07	13.8	7.6	176	96	183
Q3	33.9	1310	n.m.	0.10	20.2	7.8	214	102	203
<i>Isle</i>									
mean	42.8	2820	n.m.	0.09	14.8	7.9	172	95	334
min	18.2	990	n.m.	0.01	3.9	6.6	84	79	200
max	109	6860	n.m.	0.32	26.7	8.6	290	118	437
Q1	29.7	1640	n.m.	0.04	9.6	7.6	135	86	308
med	37.1	2410	n.m.	0.08	13.7	8.0	157	95	343
Q3	51.5	3750	n.m.	0.10	20.6	8.2	209	102	369

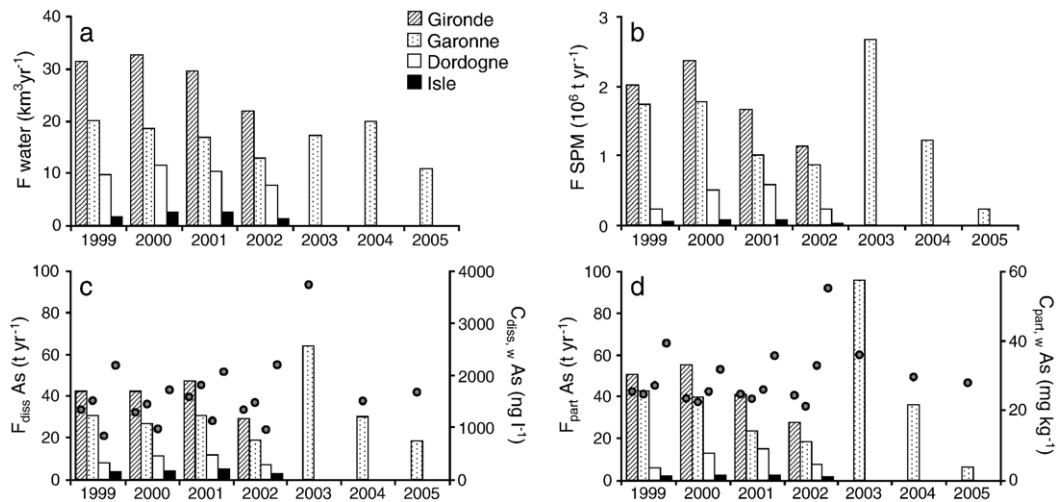


Fig. 3. Annual water (a;  $\text{km}^3 \text{yr}^{-1}$ ), SPM (b;  $10^6 \text{ t yr}^{-1}$ ) and dissolved (c;  $F_{\text{diss}}$ ;  $\text{t yr}^{-1}$ ) and particulate (d;  $F_{\text{part}}$ ;  $\text{t yr}^{-1}$ ) arsenic fluxes into the Gironde Estuary via the Garonne (1999–2005), Dordogne (1999–2002) and Isle (1999–2002) Rivers. Circles represent the mean annual discharge-weighted dissolved (c;  $C_{\text{diss, w}}$ ;  $\text{ng l}^{-1}$ ) and weighted (by SPM fluxes) particulate (d;  $C_{\text{part, w}}$ ;  $\text{mg kg}^{-1}$ ) As concentrations.

the Isle River ( $0.09 \text{ mg l}^{-1}$ ) and in the Dordogne River ( $0.07 \text{ mg l}^{-1}$ ). In the three studied rivers, phosphate did not show seasonal or discharge-related variations and was not correlated with any of the measured parameters.

### 3.3. Dissolved and particulate arsenic concentrations

The dissolved As concentrations ( $<0.2 \mu\text{m}$ ) varied by a factor  $\sim 6$  in the Garonne River, by a factor  $\sim 3$  in the Dordogne River and by a factor  $\sim 7$  in the Isle River (Table 1). The dissolved As concentrations showed strong seasonal variations in the three studied rivers (Fig. 2). Generally, the minimum dissolved As values occurred in January–March whereas the dissolved As concentrations were maximum in July–October (Fig. 2). During the sampled flood in the Garonne River (December 2003), the dissolved As concentrations strongly increased from 2800 (before the flood, 28th November 2003) to 5950  $\text{ng l}^{-1}$  (6th December 2003). The As concentration of the “truly” dissolved ( $<0.02 \mu\text{m}$ ) fraction was only measured in the Garonne River between August 2003 and December 2005. These concentrations varied from 940  $\text{ng l}^{-1}$  to 4400  $\text{ng l}^{-1}$  (Fig. 3). The  $<0.02 \mu\text{m}$  dissolved As concentrations generally represented 70–100% of the total dissolved ( $<0.2 \mu\text{m}$ ) As concentrations (Fig. 2). There was no relationship between the contribution of the  $<0.02 \mu\text{m}$  dissolved As fraction to the total dissolved As ( $<0.2 \mu\text{m}$ ) concentration and discharge, SPM concentration or physical parameters.

In the Garonne River, particulate As concentrations typically varied by a factor 2.5 ( $16.5\text{--}41.6 \text{ mg kg}^{-1}$ ; Fig. 2; Table 1). However, during the flood in December

2003, particulate As concentrations reached exceptionally high values of up to  $63.9 \text{ mg kg}^{-1}$ . From January 1999 to June 2001, particulate As concentrations varied by a factor 2 ( $15.8\text{--}33.8 \text{ mg kg}^{-1}$ ; Fig. 2) in the Dordogne River and by a factor 3 ( $18.2\text{--}56.1 \text{ mg kg}^{-1}$ ; Fig. 2) in the Isle River. During the second half-year of 2001, As concentrations were higher and more variable than during the previous period, showing values of up to  $62.4 \text{ mg kg}^{-1}$  in the Dordogne River and up to  $109 \text{ mg kg}^{-1}$  in the Isle River (Fig. 2).

## 4. Discussion

### 4.1. Spatial variations of the arsenic concentrations

During 1999–2002, the dissolved and particulate As concentrations showed the following order: Isle River > Garonne River > Dordogne River (Fig. 2; Table 1). The discharge-weighted dissolved As concentrations followed the same order (Fig. 3c). In contrast, the weighted (by SPM fluxes) particulate As concentrations were slightly higher in the Dordogne River than those in the Garonne River (Fig. 3d). The relatively low As concentrations of the Garonne River compared to the Dordogne and Isle Rivers were somewhat unexpected, with regard to the historical polymetallic pollution of the Lot–Garonne river system (e.g. As, Cd, Zn, Ba; Roux and Simonet, 1987). The generally high dissolved and particulate As concentrations observed in the Isle River may be attributed to various Au/As ore deposits and mining areas localized in the upper reaches of the Isle watershed (BRGM, 1984; Schäfer and Blanc, 2002;

Bodéan et al., 2004). Moreover, the geochemical background level of As in the upper reaches of the Isle watershed is considered as relatively high with natural average As concentration in the soils of  $120 \text{ mg kg}^{-1}$  (Chéry and Gateau, 1998). The lowest dissolved As concentrations observed in the Dordogne Rivers may be due to the presence of large hydroelectric reservoirs along the Dordogne River (Maneux et al., 2001). These reservoirs favor water-column stability and particle sedimentation, increasing light penetration into the water-column and stimulating phytoplankton growth (Sullivan et al., 2001). Phytoplankton, exclusively present in the particulate phase (Thurman, 1985), may adsorb dissolved As (e.g. Seyler and Martin, 1989; Knauer and Hemond, 2000) and decrease the dissolved As concentrations in the water. This process could also explain why the highest weighted (by SPM fluxes) particulate As concentrations were observed in the Dordogne River (Fig. 3d). However, rapid sedimentation of particles in the Dordogne reservoirs (Maneux et al., 2001) may efficiently remove As from the water column. Most of the total dissolved ( $<0.2 \mu\text{m}$ ) As in the Garonne River belongs to the “truly dissolved” ( $<0.02 \mu\text{m}$ ) As fraction (Fig. 2a), suggesting that in this river system the  $0.02\text{--}0.2 \mu\text{m}$  colloidal fraction does not play an important role in As transport.

In the Garonne, Dordogne and Isle watersheds, the drinking water resources mainly derived from surface water ( $\sim 70\%$ ; e.g. riverbank filtration; Agence de l'Eau Adour-Garonne, 2006) and consequently river water quality is an essential issue for water resources management. All dissolved As concentrations measured in the Garonne, Dordogne and Isle Rivers were lower than the maximum permissible limit for drinking water ( $10 \mu\text{g l}^{-1}$ ; European Community Water Framework Directive 1998/83/CE; Fig. 2). Nevertheless, all dissolved As concentrations were higher than world average value ( $620 \text{ ng l}^{-1}$ ; Gaillardet et al., 2003), except for 4 samples from the Dordogne River (Fig. 2). The particulate As concentrations measured in the Garonne, Dordogne and Isle watersheds were 3–20 fold higher than the world average values ( $5 \text{ mg kg}^{-1}$ ; Martin and Whitfield, 1983; Fig. 2) emphasizing the influence of the local geological context. Indeed, arsenic is a major element in different types of ore deposits present in numerous mining areas localized in the upper reaches of the studied watersheds (e.g. Zn, Pb, W, Au; BRGM, 1979, 1984, 1985; Schäfer and Blanc, 2002; Courtin-Nomade et al., 2003).

In the Garonne River, the dissolved and particulate As concentrations were maximum during the December flood in 2003 (Fig. 2). This exceptionally intense flood

event was caused by heavy rainfalls, mainly in the upper Lot River watershed (Coynel, 2005). This area is known for important potential As point sources such as the tailings of the Engualès mine ( $100\text{--}300 \text{ mg kg}^{-1}$ ; Courtin-Nomade et al., 2003), waste areas in the Riou Mort watershed (Coynel, 2005) or contaminated sediments (up to  $0.1\text{--}2 \text{ wt.}\%$  of As; Audry, personal communication). In contrast, the February 2003 flood (maximum discharge:  $4740 \text{ m}^3 \text{ s}^{-1}$ ) was generated by heavy rainfalls in the headwater reaches of the Garonne watershed (Languedoc Roussillon region), where As sources may probably be less abundant and/or important than in the Massif Central (Coynel, 2005). This may explain the relatively low As concentrations and fluxes observed during the February 2003 flood (Fig. 2).

From June 2001 to December 2002, the particulate As concentrations of the Dordogne and Isle Rivers, were higher and more variable than during the previous period. Similar observations were also observed in the Lot River (data not shown) suggesting a common supplementary particulate As source in these neighbored three watersheds. The construction of a new N–S highway in the Massif Central affecting the upper Dordogne, Isle and Lot watersheds (Demmerle et al., 2004) may account for this perturbation. Indeed, important amounts of local, naturally As-rich rock material were crushed and used for the banking up probably intensifying rock weathering and leaching processes.

#### 4.2. Seasonal variations of the As concentrations

In the Garonne, Dordogne and Isle Rivers, the dissolved As concentrations showed strong seasonal variations (Fig. 2), the minimum and maximum As concentrations occurring in winter and summer, respectively. Such cyclic variations were reported for other rivers (e.g. Seine River, Elbaz-Poulichet et al., 2006; Waikato River, McLaren and Kim, 1995; Po River, Pettine et al., 1997), but their amplitudes were clearly lower than those observed in the studied system. In the Gironde's tributaries, the dissolved As concentrations clearly decrease with increasing water discharges (Fig. 4a, b,c), suggesting that dissolved As concentrations may be affected by dilution. Nevertheless, dissolved As concentrations reached low values during the winter 2001–2002 in the Garonne, Dordogne and Isle Rivers and during the winter 2004–2005 in the Garonne River, although no clear changes in discharge (winter floods) were observed (Fig. 2). These results suggest that dilution processes cannot entirely explain the seasonal dissolved As variations. Except for discharge, water temperature was the only measured parameter related with the dissolved As

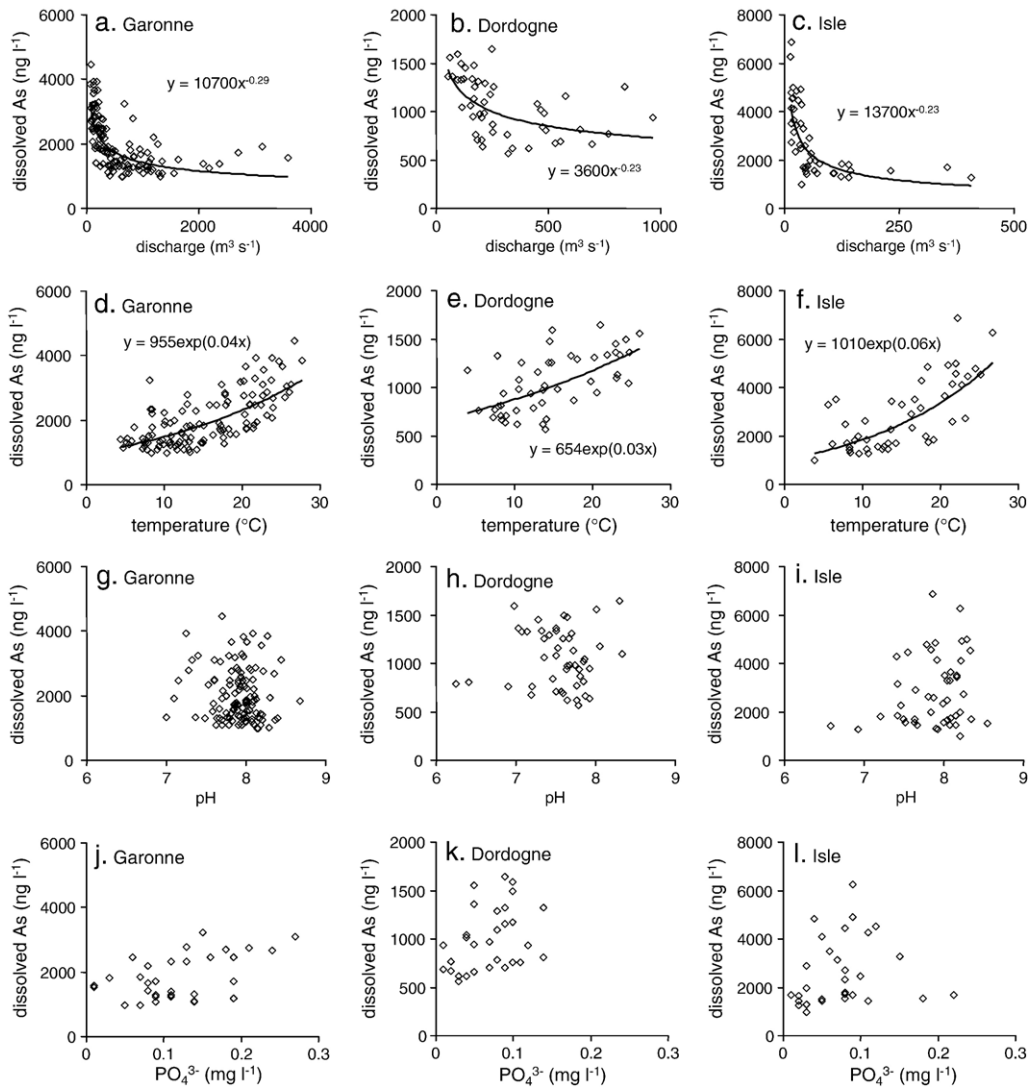


Fig. 4. Relationship between dissolved As concentrations and discharge (a, b and c;  $\text{m}^3 \text{s}^{-1}$ ), temperature (d, e and f; °C), pH (g, h and i) and phosphate concentrations (j, k and l;  $\text{mg l}^{-1}$ ) in the Garonne River (1999–2005, excepted during the December flood), Dordogne (1999–2002) and Isle (1999–2002) Rivers.

concentrations in the Garonne, Dordogne and Isle Rivers (Fig. 4d,e,f). Some bacteria are capable of reducing As (V) species to As(III) species (e.g. McLaren and Kim, 1995; Pettine et al., 1997; Knauer and Hemond, 2000; Oremland et al., 2000). As the As(III) species are less particle reactive and, thus, more mobile than the As(V) species (e.g. Aurillo et al., 1994; Ahmann et al., 1997; Elbaz-Poulichet et al., 1997), bacterial As reduction may increase the dissolved As concentrations in water (Sanders and Windom, 1980; McLaren and Kim, 1995). These processes generally depend on microbial activity and typically occur when water temperature is high (e.g. above 12 °C; Howard et al., 1984; Pettine et al., 1997). In

the Garonne, Dordogne and Isle Rivers, the increase of dissolved As concentrations appeared to be initiated when temperature reached  $\sim 15$  °C (Fig. 2), suggesting that in the studied rivers water temperature may partly control As distribution and speciation.

Several studies showed that pH may also influence trace element mobility in rivers by controlling sorption process (e.g. Fuller and Davis, 1989; Bourg et al., 2000). However, in the Garonne, Dordogne and Isle Rivers, neither seasonal pH trends nor clear relationships between dissolved As concentrations and pH were observed (Fig. 4g,h,i), suggesting that pH cannot explain the seasonal As variations in the studied rivers.



Based on the good correlation between dissolved As and phosphate concentrations in the Marne and Seine Rivers, Elbaz-Poulichet et al. (2006) suggest arsenate assimilation by phytoplankton in spring as a substitute for phosphate (similar molecular structure; e.g. Pettine et al., 1997), and release by organic matter mineralization during summer. Although similar processes cannot be excluded, no relationship between dissolved As and phosphate concentrations nor seasonal phosphate variations were observed in the Garonne (Probst, 1983; this study), Dordogne and Isle Rivers (Fig. 4j,k,l).

The use of inorganic and/or organic arsenical pesticides (e.g. Yokel and Delistraty, 2003; Jones and Huang, 2003; Sarkar et al., 2005) could also contribute to the observed seasonal variations in dissolved As. However, the use of inorganic As pesticides has largely decreased during the last decades in favor of organo-arsenical compounds (e.g. Sarkar et al., 2005). The FI-HG-AAS method only detects the organic As compounds (Michel et al., 1998), whereas both the organic and inorganic As compounds are detected by the ICP-MS. As we did not observe systematic differences between the results obtained from these independent techniques, we assume that organic As compounds are negligible for the dissolved As transport in the studied rivers. Although we cannot entirely exclude mobilization of formerly applied pesticides from agricultural areas to rivers, recently applied As-based pesticides do not seem to influence dissolved As concentrations. Therefore, we suggest that bacterial reduction of As(V) to more soluble species As(III) may be a main process controlling the seasonal variations of dissolved As concentrations in the Garonne, Dordogne and Isle Rivers. However, no seasonal variation was observed for the particulate As concentrations (Fig. 2). Assuming an increase in dissolved As concentration of  $\sim 3000 \text{ ng l}^{-1}$  and a SPM concentration of  $\sim 20 \text{ mg l}^{-1}$  for a given situation in summer, the As concentration in SPM should decrease by  $\sim 150 \text{ mg kg}^{-1}$ , i.e.  $\sim 3\text{--}5$  fold the observed particulate As concentrations. These results suggest that As mobilization via reduction processes probably occurs in the sediment and/or in the riverbank aquifers rather than in the water column and that these compartments may contain important stocks of releasable As. Further work including sediment/riverbank sampling during summer and As speciation measurements will help to better understand and quantify these processes.

#### 4.3. Annual arsenic fluxes and transport

During 1999–2002, the annual dissolved As fluxes in the Garonne River ( $19\text{--}64 \text{ t yr}^{-1}$ ; Fig. 3c) were clearly higher

than those in the Dordogne ( $7.3\text{--}11.6 \text{ t yr}^{-1}$ ; Fig. 3c) and Isle Rivers ( $3\text{--}5 \text{ t yr}^{-1}$ ; Fig. 3c) and controlled the gross dissolved As fluxes into the Gironde Estuary (Fig. 3c). The relative contributions of the three rivers to the annual dissolved As fluxes into the Gironde Estuary (gross fluxes) were relatively constant during 1999–2002 ( $\sim 65\%$  for the Garonne River,  $\sim 25\%$  for the Dordogne River and  $\sim 10\%$  for the Isle River; Fig. 3c). The mean annual specific dissolved As fluxes were similar in the Garonne, Dordogne and Isle Rivers ( $0.52\text{--}0.64 \text{ kg km}^{-2} \text{ yr}^{-1}$ ) and lower than those of the heavily polluted Humber River ( $0.88 \text{ kg km}^{-2} \text{ yr}^{-1}$ ; Neal and Davies, 2003).

Although the particulate As concentrations in the Garonne River were lower than those of the Dordogne and Isle Rivers, the annual particulate As fluxes of the Garonne River ( $6.4\text{--}96 \text{ t yr}^{-1}$ ; Fig. 3d) controlled the particulate As fluxes entering into the Gironde Estuary. The high contribution of the Garonne River ( $\sim 57\text{--}84\%$ ; Fig. 3d) to the annual particulate As gross fluxes is attributed to the relatively high annual SPM fluxes in the Garonne River ( $0.87$  to  $1.8 \cdot 10^6 \text{ t yr}^{-1}$ ; Fig. 3b) compared to those in the Dordogne and Isle Rivers (respectively  $0.22\text{--}0.58 \cdot 10^6 \text{ t yr}^{-1}$  and  $0.03\text{--}0.08 \cdot 10^6 \text{ t yr}^{-1}$ ; Fig. 3b; Masson et al., 2006). The contribution of the Dordogne and Isle Rivers to the annual particulate As gross fluxes ranged from 12 to 37% for the Dordogne River ( $6\text{--}15 \text{ t yr}^{-1}$ ; Fig. 3d) and was  $\sim 5\%$  for the Isle River ( $1.6\text{--}2.5 \text{ t yr}^{-1}$ ; Fig. 3d). The mean annual specific particulate As fluxes of the Garonne ( $0.60 \text{ kg km}^{-2} \text{ yr}^{-1}$ ) and Dordogne ( $0.69 \text{ kg km}^{-2} \text{ yr}^{-1}$ ) Rivers were similar and clearly higher than those of the Isle ( $0.33 \text{ kg km}^{-2} \text{ yr}^{-1}$ ) and Humber Rivers ( $0.22 \text{ kg km}^{-2} \text{ yr}^{-1}$ ; Neal and Davies, 2003), suggesting that particulate As transport (e.g. by erosion) in the Garonne and Dordogne watersheds is intense.

In the Garonne River, the estimated dissolved ( $64 \text{ t yr}^{-1}$ ; Fig. 3c) and particulate ( $96 \text{ t yr}^{-1}$ ; Fig. 3d) As fluxes in 2003 were the highest of the studied period, mainly due to the December flood (see below). In the Garonne and Dordogne Rivers As transport in the particulate and dissolved phases were quite equivalent (Fig. 3c,d), whereas in the Isle River As was mainly transported in the dissolved fraction ( $\sim 65\%$ ; Fig. 3c,d).

#### 4.4. Empirical model

In the Garonne, Dordogne and Isle Rivers, the mean annual discharge-weighted dissolved and weighted (by SPM fluxes) particulate As concentrations were relatively constant during 1999–2002 (Fig. 3c,d). Moreover, the variations of discharge and SPM concentrations were clearly higher than those of As concentrations (Fig. 2),

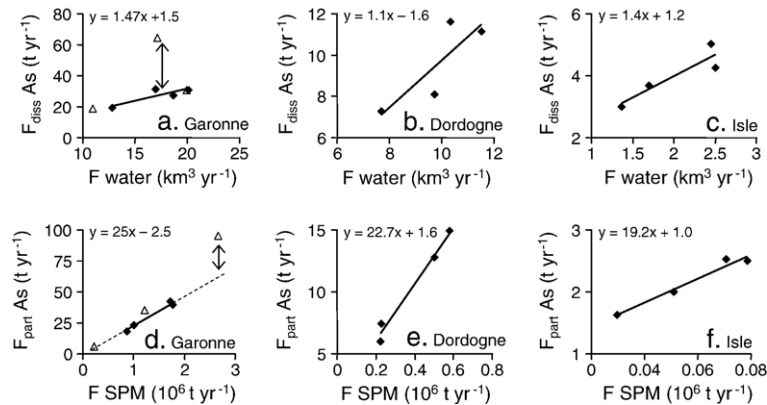


Fig. 5. Relationship between the annual dissolved As fluxes ( $F_{\text{diss}} \text{ As}$ ) and the annual water fluxes ( $F_{\text{water}}$ ) and between the annual particulate As fluxes ( $F_{\text{part}} \text{ As}$ ) and the annual SPM fluxes ( $F_{\text{SPM}}$ ) in the Garonne (a and d), Dordogne (b and e) and Isle (c and f) Rivers (for 1999–2002; black diamonds). The open triangles represent fluxes in 2003 (strongly impacted by the December floods), 2004 and 2005 which are not considered for the linear regression.

suggesting that dissolved and particulate As transport mainly depend on water and SPM transport. The annual dissolved and particulate As fluxes of the three studied rivers can be roughly estimated from the annual water and SPM fluxes (Fig. 3a,b) using the following equations:

$$F_{\text{diss}}^* (\text{As}) = a^* F_w + b$$

$$F_{\text{part}}^* (\text{As}) = c^* F_{\text{SPM}} + d$$

where  $F_{\text{diss}}^* (\text{As})$  and  $F_{\text{part}}^* (\text{As})$  represent the annual dissolved and particulate As fluxes,  $F_w$  represents the annual water flux and  $F_{\text{SPM}}$  represents the annual SPM flux. The coefficients  $a$ ,  $b$ ,  $c$  and  $d$  were determined from the equations of the linear regressions (Fig. 5). In 2004 and 2005, the annual dissolved and particulate As fluxes of the Garonne River estimated by this simple empirical model are very close to the fluxes estimated from field observation (Fig. 5). For example, in 2004, the differences were  $\sim 22\%$  and  $4\%$  for the particulate and the dissolved As fluxes, respectively. In contrast, the empirical model does not reproduce the fluxes observed in 2003 (Fig. 5a,d). The important difference between the fluxes estimated from field observation and those obtained from the model may probably be attributed to the flood event. Accordingly, we estimate that the flood contributed  $\sim 58\%$  and  $\sim 34\%$  to the annual dissolved and particulate As fluxes, respectively, in the Garonne River. This result is coherent with observations made for a number of trace elements (e.g. Cd, Zn, Cu, Pb, Hg, Sb etc.; Coynel, 2005), emphasizing the importance of major flood events and flood management for trace element transport in regulated river systems.

## 5. Conclusions

During the 7-year monitoring on the Garonne River and 4-year monitoring on the Dordogne and Isle Rivers, the dissolved and particulate As concentrations measured in the three studied rivers were higher than world average values reflecting the high geochemical background values and various anthropogenic (mining, ore treatment) sources of the Massif Central. In the Isle River, As concentrations were generally higher than those in the Garonne River, despite the historical polymetallic pollution of the Lot–Garonne River system. The relatively high dissolved and particulate concentrations in the Isle River may be explained by a large number of Au/As mining areas and ore deposits localized in this watershed. In the Dordogne River, the low dissolved As concentrations and relatively high particulate As concentrations may be due to the adsorption onto phytoplankton in the large reservoirs along this river, followed by scavenging to the sediment. Nevertheless, all dissolved As concentrations measured in the studied rivers were lower than the permissible limit for drinking water. The dissolved As was mainly transported in the  $< 0.02 \mu\text{m}$  fraction suggesting low affinity for the  $0.02\text{--}0.2 \mu\text{m}$  colloidal fraction.

In contrast to other rivers, the strong seasonal variations in dissolved As concentrations observed in the Garonne, Dordogne and Isle Rivers seem to be controlled by water temperature. This was attributed to microbial reduction of As(V) to less particle active As (III) species at water temperatures above  $\sim 15^\circ \text{C}$ .

The As budget of the Gironde Estuary and the adjacent coastal environment depends mainly on inputs via the Garonne River and may be roughly estimated from an empirical model based on annual water and

SPM fluxes without measuring As concentrations. However, this empirical model does not take into account exceptional flood events, such as the December 2003 flood that contributed ~50% to the annual As fluxes in the Garonne River.

## Acknowledgements

This study is a scientific contribution of the 'GIS-ECOBAG' (Groupement d'Intérêt Scientifique: Environnement, Ecologie et Economie du Bassin Adour-Garonne). This work was supported by grants from 'l'Agence de l'Eau Adour-Garonne', 'la Région Aquitaine', 'le Ministère de la Recherche' and 'le FEDER-Région Aquitaine'. The authors greatly acknowledge S. Audry, C. Bossy, A. Coynel, Y. Lapaquellerie, G. Lavaux, J.P. Lissalde and N. Maillet for their important contributions to field and laboratory works.

## References

- Abril G, Nogueira M, Etcheber H, Cabeçadas G, Lemaire E, Brogueira MJ. Behaviour of organic carbon in nine contrasting European estuaries. *Estuar Coast Shelf Sci* 2002;54:241–62.
- Agence de l'Eau Adour-Garonne. <http://www.eau-adour-garonne.fr>; September 2006.
- Ahmann D, Krumholz LR, Hemond HF, Lovley DR, Morel FMM. Microbial mobilization of arsenic from sediments of the Aberjona watershed. *Environ Sci Technol* 1997;31:2923–30.
- Audry S, Schäfer J, Blanc G, Bossy C, Lavaux G. Anthropogenic components of heavy metal (Cd, Zn, Cu, Pb) budgets in the Lot–Garonne fluvial system (France). *Appl Geochem* 2004a;19:769–86.
- Audry S, Schäfer J, Blanc G, Jouanneau JM. Fifty-year sedimentary record of heavy metal pollution (Cd, Zn, Cu, Pb) in the Lot River reservoirs (France). *Environ Pollut* 2004b;132:413–26.
- Aurillo AC, Mason RP, Hemond HF. Speciation and fate of arsenic in three lakes of the Aberjona watershed. *Environ Sci Technol* 1994;28:577–85.
- Blanc G, Lapaquellerie Y, Maillet N, Anschutz P. A cadmium budget for the Lot–Garonne fluvial system (France). *Hydrobiologia* 1999;410:331–41.
- Bodénan F, Baranger P, Piantone P, Lassin A, Azaroual M, Gaucher E, et al. Arsenic behaviour in gold-ore mill tailings, Massif Central, France: hydrogeochemical study and investigation of in situ redox signatures. *Appl Geochem* 2004;19:1785–800.
- Bourg ACM, Kedziorek MAM, Crouzet C. Seasonal cycles of dissolved Cd, Mn and Zn in River Water caused by variations in pH induced by biological activity. *Aquat Geochem* 2000;6:461–71.
- BRGM—Bureau de Recherches Géologiques et Minières. Cartes des gîtes minéraux de la France 1/500 000, feuille Lyon. Service Géologique National; 1979.
- BRGM—Bureau de Recherches Géologiques et Minières. Cartes des gîtes minéraux de la France 1/500 000, feuille Bordeaux. Service Géologique National; 1984.
- BRGM—Bureau de Recherches Géologiques et Minières. Cartes des gîtes minéraux de la France 1/500 000, feuille Toulouse. Service Géologique National; 1985.
- Chaillou G, Schäfer J, Anschutz P, Lavaux G, Blanc G. The behaviour of arsenic in muddy sediments of the Bay of Biscay (France). *Geochim Cosmochim Acta* 2003;67:2993–3003.
- Chéry L, Gateau C. Mise à disposition de l'inventaire géochimique sur le territoire national (pour identifier les zones à risques de teneurs naturelles élevées en métaux lourds dans les eaux destinées à l'AEP). BRGM Report R40207; 1998.
- Courtin-Nomade A, Bril H, Neel C, Lenain J-F. Arsenic in iron cements developed within tailings of a former metalliferous mine — Enguialès, Aveyron, France. *Appl Geochem* 2003;18:395–408.
- Courtin-Nomade A, Grosbois C, Bril H, Roussel C. Spatial variability of arsenic in some iron-rich deposits generated by acid mine drainage. *Appl Geochem* 2005;20:383–96.
- Coynel A. Erosion mécanique des sols et transferts géochimiques dans le bassin Adour-Garonne. PhD Thesis. Université Bordeaux 1 (France) 2005.
- Demmerle D, Sauvaget P, Giroussens M, Riondy G. Crossing of the Isle and Dordogne Valleys by the A89 motorway near Libourne. *Houille Blanche* 2004;4:52–8.
- Elbaz-Poulitchet F, Nagy A, Csemey T. The distribution of redox sensitive elements (U, As, Sb, V and Mo) along a river–wetland–lake system (Balaton region, Hungary). *Aquat Geochem* 1997;3:267–82.
- Elbaz-Poulitchet F, Seidel J-L, Casiot C, Tusseau-Vuillemin M-H. Short-term variability of dissolved trace element concentrations in the Marne and Seine Rivers near Paris. *Sci Total Environ* 2006;367:278–87.
- Fuller CC, Davis JA. Influence of coupling of sorption and photosynthetic processes on trace element cycles in natural waters. *Nature* 1989;340:52–7.
- Gaillardet J, Viers J, Dupré B. Trace elements in river waters. In: Drever JI, editor. *Surface and Ground Water. Weathering, and Soils*. Oxford: Elsevier; 2003. p. 1–47.
- Howard AG, Arbab-Zavar MH, Apte S. The behaviour of dissolved arsenic in the estuary of the River Beaulieu. *Estuar Coast Shelf Sci* 1984;19:493–504.
- Jones KD, Huang W-H. Evaluation of toxicity of the pesticides, chlorpyrifos and arsenic, in the presence of compost humic substances in aqueous systems. *J Hazard Mater* 2003;103:93–105.
- Jouanneau JM, Lapaquellerie Y, Latouche C. Origin and pathways of Cd contamination in the Gironde Estuary, Garonne River and tributaries. In: Vernet JP, editor. *Environment Contamination*. Amsterdam: Elsevier; 1993. p. 373–89.
- Knauer K, Hemond H. Accumulation and reduction of arsenate by the freshwater green alga *Chlorella* sp. (Chlorophyta). *J Phycol* 2000;36:506–9.
- Lapaquellerie Y, Jouanneau JM, Maillet N, Latouche C. Cadmium pollution in sediments of the Lot River (France), estimate of the mass of cadmium. *Environ Technol* 1995;16:1145–54.
- Lapaquellerie Y, Maillet N, Schäfer J, Blanc G. Etude comparative de deux méthodes de récupération des MES : Pièges à particules et pompage-centrifugation. Technical report. Toulouse, France: Agence de l'Eau Adour-Garonne; 2000.
- Le Guern C, Baranger P, Crouzet C, Bodénan F, Conil P. Arsenic trapping by iron oxyhydroxides and carbonates at hydrothermal spring outlets. *Appl Geochem* 2003;18:1313–23.
- Mandal BK, Suzuki KT. Arsenic round the world: a review. *Talanta* 2002;58:201–35.
- Maneux E, Probst J-L, Veysy E, Etcheber H. Assessment of dam trapping efficiency from water residence time: application to fluvial sediment transport in the Adour, Dordogne and Garonne River basins (France). *Water Resour Res* 2001;37:801–11.

- Martin JM, Whitfield M. The significance of the river input of chemical elements to the oceans. In: Wong CS, Boyle E, Bruland KW, Burton JD, Goldberg ED, editors. Trace metals in Sea Water. New York: Plenum; 1983. p. 265–96.
- Masson M, Blanc G, Schäfer J. Geochemical signals and source contributions to heavy metal (Cd, Zn, Pb, Cu) fluxes into the Gironde Estuary via its major tributaries. *Sci Total Environ* 2006;370:133–46.
- McLaren SJ, Kim ND. Evidence for a seasonal fluctuation of arsenic in New Zealand's longest river and the effect of treatment on concentrations in drinking water. *Environ Pollut* 1995;90:67–73.
- Meybeck M, Ragu A. River discharges to the Oceans. An assessment of suspended solids, major ions and nutrients. Nairobi: Environment Information and Assessment Rpt. UNEP; 1996. 250 pp.
- Michel P, Boutier B, Herbland A, Averty B, Artigas LF, Auger D, et al. Behaviour of arsenic on the continental shelf off the Gironde estuary: role of phytoplankton in vertical fluxes during spring bloom conditions. *Oceanol Acta* 1998;21:325–33.
- Michel P, Boutier B, Chiffolleau J-F. Net fluxes of dissolved arsenic, cadmium, copper, zinc, nitrogen and phosphorus from the Gironde Estuary (France): seasonal variations and trends. *Estuar Coast Shelf Sci* 2000;51:451–62.
- Murphy J, Riley JP. A modified single solution method for the determination of phosphate in natural waters. *Anal Chim Acta* 1962;27:31–6.
- Nagy-Breitenstein G. Analyse quantifiée de l'évolution hydromorphologique séculaire de l'estuaire amont de la Gironde. PhD Thesis. Université Bordeaux I (France) 1993.
- Neal C, Davies H. Water quality fluxes for eastern UK rivers entering the North Sea: a summary of information from the Land Ocean Interaction Study (LOIS). *Sci Total Environ* 2003;314–316: 821–82.
- Oremland RS, Dowdle PR, Hoefl S, Sharp JO, Schaefer JK, Miller LG, et al. Bacterial dissimilatory reduction of arsenate and sulfate in meromictic Mono Lake, California. *Geochim Cosmochim Acta* 2000;64:3073–84.
- Pettine M, Mastroianni D, Camusso M, Guzzi L, Martinotti W. Distribution of As, Cr and V species in the Po–Adriatic mixing area, (Italy). *Mar Chem* 1997;58:335–49.
- Probst J-L. Hydrologie du bassin de la Garonne. PhD Thesis. Université Paul Sabatier Toulouse (France) 1983.
- Probst J-L, Tardy I. Fluctuations hydroclimatiques du Bassin d'Aquitaine lors des 70 dernières années. *Rev Geol Dyn Geogr Phys* 1985;26:59–76.
- Roussel C, Neel C, Bril H. Minerals controlling arsenic and lead solubility in an abandoned gold mine tailings. *Sci Total Environ* 2000;263:209–19.
- Roux M, Simonet M. Pollutions accidentelles du Lot: flux polluant. *Revue de l'Agence de l'Eau Adour-Garonne*, Toulouse, France, vol. 34.; 1987. p. 7–9.
- Sanders JG, Windom HL. The uptake and reduction of arsenic species by marine algae. *Estuar Coast Mar Sci* 1980;10:555–67.
- Sarkar D, Datta R, Sharma S. Fate and bioavailability of arsenic in organo-arsenical pesticide-applied soils. Part-I: Incubation study. *Chemosphere* 2005;60:188–95.
- Schäfer J, Blanc G. Relationship between ore deposits in river catchments and geochemistry of suspended particulate matter from six rivers in southwest France. *Sci Total Environ* 2002;298: 103–18.
- Schäfer J, Blanc G, Lapaquellerie Y, Maillet N, Maneux E, Etcheber H. Ten-year observation of the Gironde tributary fluvial system: fluxes of suspended matter, particulate organic carbon and cadmium. *Mar Chem* 2002;79:229–42.
- Schäfer J, Blanc G, Audry S, Cossa D, Bossy C. Mercury in the Lot–Garonne River system (France): sources, fluxes and anthropogenic component. *Appl Geochem* 2006;21:515–27.
- Seyler P, Martin J-M. Biogeochemical processes affecting arsenic species distribution in a permanently stratified lake. *Environ Sci Technol* 1989;23:1258–68.
- Seyler P, Martin J-M. Distribution of arsenite and total dissolved arsenic in major French estuaries: dependence on biogeochemical processes and anthropogenic inputs. *Mar Chem* 1990;29:277–94.
- Smedley PL, Kinniburgh DG. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl Geochem* 2002;17: 517–68.
- Sullivan BE, Prahl FG, Small LF, Covert PA. Seasonality of phytoplankton production in the Columbia River: a natural or anthropogenic pattern? *Geochim Cosmochim Acta* 2001;65: 1125–39.
- Thurman EM. Organic geochemistry of natural waters. Nijhoff M, Junk W, Dordrecht 1985, 497 pp.
- Walling DE, Webb BW. Estimating the discharge of contaminants to coastal waters by rivers: some cautionary comments. *Mar Pollut Bull* 1985;16:488–92.
- Yamamoto M, Yasuda M, Yamamoto Y. Hydride-generation atomic absorption spectrometry coupled with flow injection analysis. *Anal Chem* 1985;57:1382–5.
- Yokel J, Delistraty DA. Arsenic, lead, and other trace elements in soils contaminated with pesticide residues at the Hanford site (USA). *Environ Toxicol* 2003;18:104–14.