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A cadmium budget for the Lot-Garonne fluvial system (France)

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Abstract

Routine measurements of river discharge and total suspended sediment concentration (TSS) are combined with regular analyses for particulate and dissolved cadmium to produce a box model that allows us to propose a cadmium mass balance for the Lot-Garonne man-influenced river system (8400 km^2). Nearly half the cadmium in the Garonne river is supplied by the tributary Lot river. Cadmium input onto the Lot river comprises wet deposition from the atmosphere, molecular diffusion at the sediment-water interface, surface-water runoff and discharge from the leaching of waste at a zinc refining plant. Approximately 85% of the cadmium in the Lot river is derived from anthropogenic origin. Cadmium in the industrial discharge is 80% dissolved and 20% in the particulate phase (4.2 and 1.1 t yr^{-1}, respectively). Total inputs are estimated at 4.81 t yr^{-1} and 1.54 t yr^{-1} for the dissolved cadmium and for the particulate phase, respectively. Budgeting estimates an output onto the Garonne river of 0.54 t yr^{-1} for the dissolved cadmium (about 8%) and 6.13 t yr^{-1} for the particulate cadmium (about 92%) indicating that downstream sediment-associated cadmium fluxes are enhanced by the 4.27 t yr^{-1} removed from solution and the 0.32 t yr^{-1} remobilized by the erosion of sediment blanketing the Lot river bed. These figures are found to be comparable with those generated by a dilution model which suggests that 97% of dissolved cadmium is taken up by the particulate phase over 0.5 km downstream from the primary anthropogenic source.

Introduction

Although the Aquitaine basin is one of the least industrialised regions in France, the Lot-Garonne-Gironde fluvial system can be considered as a natural model for pollution in non-ferrous metals such as Cd, Zn, Ba, As (Roux & Simonet, 1987). Historically, chronic pollution has resulted from industrial and mining activities that started to develop in the late nineteenth century and in particular, cadmium, which has a high toxicity for biota, is considered as the major polluting metal of this fluvial system. Cadmium pollution was first recognised in 1979 within the framework of the 'National Observation Network' (Latouche, 1988) which documented the high cadmium content in the flesh of the Gironde oysters (up to 100 μg g^{-1} of dry matter). These concentrations are 10 times higher than those typically found in oysters from French non-industrial areas (Boutier, 1981) and reflect the high kinetics accumulation in oysters. As oysters are very sensitive to this pollution, the Marennes-Oleron oyster farming located ca. 30 km to the north of the mouth of the Gironde estuary is considered at risk (Jouanneau et al., 1993).

The primary source for present day cadmium pollution is probably attributed to leaching from the waste area of a now abandoned zinc ore manufacturing facility (Latouche, 1992). This plant was founded in 1840 and is located near Decazeville, a town on the Riou-Mort that tributes to the Lot river ca. 200 km upstream from the Lot-Garonne confluence. However, several large hydroelectric dams which were built from 1945 to 1960 in the upper reaches of the Lot valley, together with the 62 smaller storage structures located downstream from the Riou-Mort confluence, decrease the magnitude of winter and spring floods (Massio, 1976). This has resulted in significant sediment and cadmium accumulation in the lower reaches of the Lot river. Lapaquellerie et al. (1995) estimated that 0.47 $\pm$ 0.9 $\times$ 10^6 m^3 of sediment and about 200 tons of cadmium accumulated in the Lot valley between the Riou-Mort and Garonne river in 1991.

This paper aims to establish a macroscopic description of cadmium behaviour in the Lot-Garonne fluvial system (8400 km^2) by using the annual (1996) flux of both the particulate and dissolved phases. By quantifying the contributions from the primary source (i.e. the Riou-Mort river) and the secondary source (i.e. the sediment-associated cadmium in the Lot river), together with internal transfert processes and the overall output, we propose a tentative cadmium budget for the Lot-Garonne study basin.

Sampling and methods

Because the Lot river is the major polluting tributary of the Garonne, and then of the Gironde, it was necessary to obtain a representative estimation of its total suspended sediment (TSS) fluxes. This was accomplished using a total of six sampling sites (Figure 1). Samples from Temple (Lot) were collected automatically using a Buhler PB-MOS sampler, whilst samples from the five remaining sites were collected manually. The automatic sampler collects a daily cumulative 1 l sample consisting of 16 elementary samples. The frequency of TSS measurements and analyses for particulate and dissolved cadmium is reported in Table 1. Transverse and depth profiling was undertaken to test the representativeness of our local sampling at Temple and La Reole sites (cf. Lapaquellerie et al., 1996). At both sites, these tests showed that variations in TSS concentrations due to depth and distance from the bank did not exceed 6% and 2.3% during flood and base flows, respectively. TSS concentrations were determined using filtration (Whatmann GF/F, 0.70 μm filters) and each sample set typically showed a standard deviation of 1.5% about the mean. The annual mean values of the TSS concentrations for each site are reported in Table 2.

The mean annual discharge (1996) for the Lot and Garonne rivers was calculated using the daily measurements undertaken by the autonomous port of Bordeaux and the hydrological office of Toulouse (see Table 2). The precision is generally about 5% for water flows higher than 40 $m^3\ s^{-1}$.

Sediment-associated cadmium concentrations were determined from bulk suspended sediment samples retrieved by centrifuging between 500 and 1000 l of water using a Wesfalia separator. The cadmium contamination from this equipment is much less than the analytical error which is about 5% (Etcheber & Jouanneau, 1980).

The water samples were collected and filtered for cadmium analyses using a clean technique. Surface-water samples were taken from a small rubber dinghy, by immersing a teflon sampler specially designed to avoid any contact with the atmosphere. This sampler holds a 100 cm^3 acid-cleaned polypropylene vial. The water samples were immediately filtered through acid-cleaned (Ø 47 mm diameter, 0.45 μm pore-size) Nuclepore polycarbonate membranes.

Triplicate analyses for the particulate and dissolved cadmium concentrations of individual samples were undertaken using a graphite furnace atomic absorption spectrometer. Particulate cadmium analyses required the complete dissolution of individual dried solid samples. The total digestion used by this study involved the dissolution of 30 mg of each sample in 750 μl HCl (12N), 2 ml HF (26N) and 250 μl HNO_3 (14N) in small Teflon bombs. The bomb were then heated at 110 °C for 2 h, and after cooling, the digested solution was evaporated to dryness and the residue dissolved in 150 μl concentrated HNO_3. Each sample was left on a hotplate until the residue was completely dissolved and then brought to 5 ml in a volumetric flask using double-deionized water. Prior to the determination of dissolved cadmium content, the samples were preconcentrated in a class 100 clean room by complexating with ammonium pyrrolidine dithiocarbamate/ diethylammonium diethyl dithiocarbamate (APDC/DDDC), extracting into freon and back extracting with HNO_3 into deionized water (Danielsson et al., 1982). In the Riou-Mort tributary, dissolved concentrations were high enough to be analyzed directly, without preconcentration. Accuracy of the analyses was determined by comparisons to river sediment (CRM320) and water (SLRS3) international standards, and was within 5% for cadmium. The precision of the analyses, as determined from duplicate samples was generally 5% for cadmium at concentrations 10 times higher than the detection limit. The content of cadmium in solid phases is given in milligrams per kg, whereas the dissolved cadmium content is given in nanograms per l. The results of the cadmium analysis for 79 suspended sediment and 99 water samples collected during year 1996 are reported in Tables 3 and 4.

Results

River discharge, total suspended sediment (TSS) and cadmium concentrations are the major parameters for

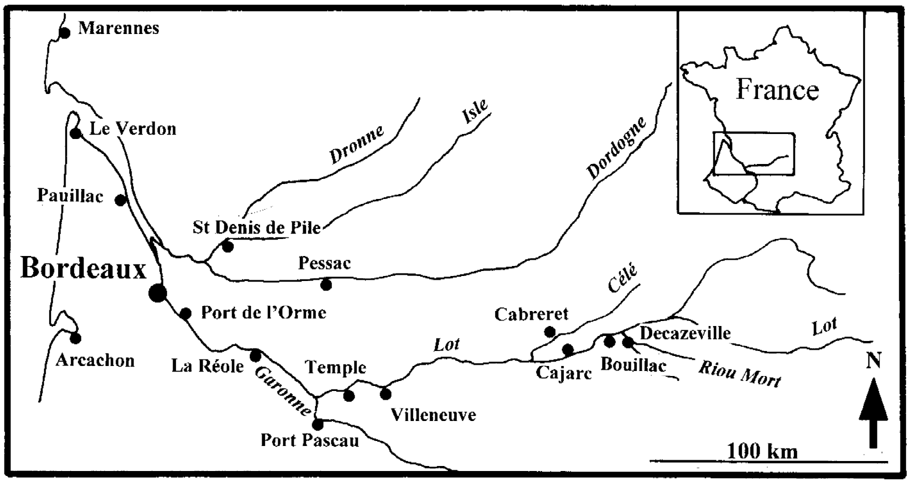

Figure 1. Sampling locations in the Garonne river, Lot river, and its tributaries (Riou-Mort, Célé), and also at the Verdon (estuary mouth).

Table 1. Location and sampling frequencies for the study sites, x and y are the coordinates in Lambert III projection, South Area

Sites	Map	Location x / y	Sampling Type	Sampling strategy TSS	dis.Cd	part.CD
Riou-Mort	IGN 2238 W	560.05 / 3241.09	manual	8 yr^{-1}	8 yr^{-1}	8 yr^{-1}
Bouillac	IGN 2338	589.00 / 3253.45	manual	8 yr^{-1}	6 yr^{-1}	5 yr^{-1}
Cajarc	IGN 2238 W	560.05 / 3241.09	manual	5 yr^{-1}	39 yr^{-1}	5 yr^{-1}
Temple sur Lot	IGN 1839 W	453.55 / 3234.00	Automatic sampler	365 yr^{-1}	18 yr^{-1}	18 yr^{-1}
Port Pascau	IGN 1739 E	439.07 / 3323.00	manual	365 yr^{-1}	18 yr^{-1}	18 yr^{-1}
La Réole	IGN XV-37 (3–4)	374.22 / 280.20	manual	365 yr^{-1}	18 yr^{-1}	18 yr^{-1}
Le Verdon	IGN XIV-33 (1–2)	334.62 / 62.18	manual	4 yr^{-1}	5 yr^{-1}	6 yr^{-1}

the estimation of dissolved and particulate matter fluxes. The river discharge can vary by factors of about 45 and 30 for the Garonne and Lot rivers, respectively. At the beginning of a flood such maximum changes in river discharge can usually be observed during a single day. In addition, the TSS concentrations change by a factor greater than one thousand between the flood and the lowest water level periods. At La Réole, the TSS concentration reached up to 1300 mg l^{-1} in December, whereas it fell down to 0.3 mg l^{-1} in September (Table 2). The annual mean value of TSS concentration varies spatially, increasing from 25 mg l^{-1} the Riou-Mort to 110 mg l^{-1} Cajarc. Conversely, the TSS concentration at Temple shows an annual mean value of 98 mg l^{-1}. This lower value probably results from the settling of the suspended sediment into the numerous reservoirs. In 1996, the TSS concentration at Port-Pascau (Garonne) was approximately twice that of the downstream Lot. The changes in concentration of the particulate and dissolved cadmium show a temporal variability less than that of TSS concentration. Thus, it was not necessary to collect a sample every day, although the floods were sampled.

In 1996, the mean particulate cadmium concentrations decreased progressively from 460 mg kg^{-1} at the Riou-Mort to 12.5 mg kg^{-1} at Temple (Table 3). They were 10 times lower at Port-Pascau, and, consequently, a mean cadmium concentration of 2.6 mg kg^{-1} was determined at La Réole, downstream of the junction of the Lot and Garonne rivers. Because of the chlorinity increases in the Gironde estuary, the particulate cadmium concentrations reach a minimum mean value of 0.43 mg kg^{-1} at Le Verdon. The mean particulate cadmium concentration of 2.59 mg kg^{-1}, determined in 1996 at La Réole, is comparable to that given by Elbaz-Poulichet (1988) for the Rhône river, and that given by Chiffoleau et al. (1997) for the Seine river (i.e. 2.8 mg kg^{-1}), but much lower the

Table 2. 1996 mean, maximum and minimum values for river discharge ($m^3.s^{-1}$) and TSS concentration ($mg.l^{-1}$) at each sampling site

		Riou-Mort	Bouillac	Cajarc	Temple	Port Pascau	La Réole	Le Verdon
River discharge (m^3 s^{-1})	mean	3	80	89	171	637	808	1200
	max	35	431	480	922	3523	3928	4748
	min	8	18	22	30	32	85	170
TSS (mg l^{-1})	mean	25.4	99.9	110.4	98.5	207.4	182.9	151.9
	max	81	196	205	390	1105	1297	313
	min	13	45	10	6	0.2	0.3	35

Table 3. Particulate cadmium concentrations determined at each site in 1996

	Riou Mort (mg kg^{-1})	Bouillac (mg kg^{-1})	Cajarc (mg kg^{-1})	Temple (mg kg^{-1})	Port Pascau (mg kg^{-1})	La Réole (mg kg^{-1})	Le Verdon (mg kg^{-1})
Jan 04				11.3	0.69	2.53	
Jan 12				15.2	0.34	2.34	
Jan 24				16.1	0.33	1.91	
Jan 28							0.56
Feb 5				15.9	0.74	1.47	
Feb 28				12.3	1.32	1.58	
Mar 28				10.4	1.24	2.34	
Apr 17	484	17.3	23.1				
Apr 29				16.0	1.2	3.6	
May 16							0.94
May 23				10.8	1.31	3.52	
May 24	504	29.3	17.1				
Jun 10							0.48
Jun 28	767			7.7	1.59	2.34	
Jul 10	350	22.5	26.7				
Jul 18				8.1	1.69	2.45	
Aug 28				13.6	1.39	2.33	
Sep 02	244						
Sep 06							0.21
Sep 10	689	29.9	21.7				
Sep 26				16.9	1.67	3.02	
Oct 08				16.9	2.29	3.8	
Oct 15							0.18
Oct 28	286			10.2	2.56	2.22	
Nov 07				7.4	1.15	3.3	
Nov 22				12.1	1.86	2.01	0.21
Dec 04	386	33.1	14.5				
Dec 10				14.6	2.44	3.1	
Dec 19				9.4	2.13	2.17	
Dec 23	432						
Mean value	460	26.4	20.6	12.5	1.44	2.59	0.43

Table 4. Dissolved cadmium concentrations determined at each site in 1996

	Riou-Mort (ng l^{-1})	**Bouillac** (ng l^{-1})	**Cajarc** (ng l^{-1})	**Temple** (ng l^{-1})	**Port Pascau** (ng l^{-1})	**La Réole** (ng l^{-1})	**Le Verdon** (ng l^{-1})
Jan 04			340	65	16	29	
Jan 12			134	48	48	33	
Jan 24			420	72	48	28	
Jan 28							385
Feb 5			532	97	49	64	
Feb 28			158	105	54	42	
Mar 28			245	64	58	95	
Apr 17	25 000	139	593				
Apr 29			169	43	32	88	
May 23			433	15	24	59	
May 24	25 600	975	150				
Jun 03			176				
Jun 04			134				
Jun 10							481
Jun 28	49 800	810		255	56	200	
Jul 10	34 300		346				
Jul 18			628	230	120	185	
Aug 26			245				
Aug 27			284				
Aug 28			179	110	110	315	
Sep 02			534				
Sep 03			157				
Sep 04			608				
Sep 06							
Sep 10	80 300	1860					467
Sep 26			303	20	64	52	
Oct 08			252	210	83	32	
Oct 15							320
Oct 28	16 500		128	240	45	41	
Nov 07			640	35	87	34	
Nov 14			635	94	19	38	
Nov 22							245
Dec 04	67 280	1135	325				
Dec 10			436	110	70	44	
Dec 19				87	99	32	
Dec 23	53 600	1230					
Mean value	44 048	1025	340	106	60	78	380

32 mg kg^{-1} given by Van der Weijden et al. (1989) for the Rhine. However, Idlafkih et al. (1995) gave a value of 4.9 mg kg^{-1} for the Seine river.

The dissolved cadmium concentration in 1996 averaged 44 000 ng l^{-1}in the Riou-Mort (Table 4). This high content rapidly decreased downstream and reached a value of 106 ng l^{-1} at Temple. The mean dissolved cadmium concentrations at the Garonne river sites in 1996 were slightly lower, and thereafter increased by a factor of four (i.e. 380 ng l^{-1}) at Le Verdon, where the salinity ranged from 14 to 24 ‰. An average value of 400 ng l^{-1} was previously determined for a comparable salinity range (Jouanneau et al., 1990), although Kraepiel et al. (1997) meas-

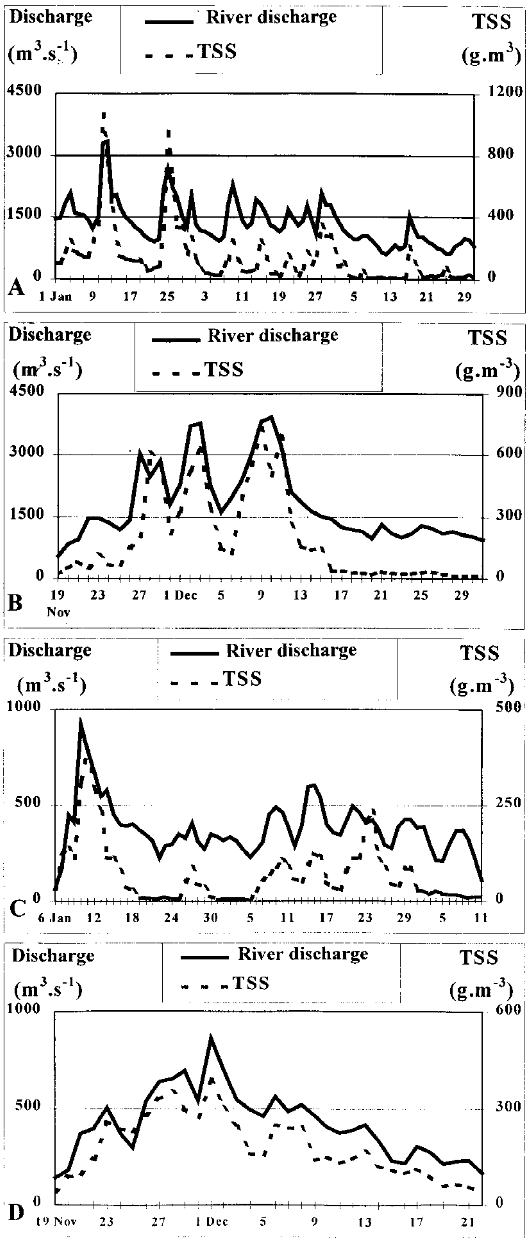

Figure 2. Temporal variations in 1996 peak discharge and TSS concentrations for the Garonne (A–B) and Lot (C–D) rivers.

ured values three times lower in February 1994 when high floods occurred. The mean concentration of the dissolved cadmium at La Réole, endpoint of the fresh water before the Gironde estuary, was 78 ng l^{-1}. This value is higher than the world average (i.e. 20 ng l^{-1}) estimated for river water (Martin & Whitfield, 1983), and is comparable to that of the Mississippi river (i.e. 90 ng l^{-1}) (Trefry & Presley,1976). The Cd concentration of 78 ng l^{-1} for the Garonne is, however, higher than values measured in other major French rivers. In the Seine, Idlafkih et al. (1995) and Chiffoleau et al. (1997) gave values of 27 ng l^{-1} and 26 ng l^{-1}, respectively. These values for the Seine are similar to those in the Rhine river (Elbaz-Poulichet, 1988), whereas a value of 48 ng l^{-1} was given by Valenta et al. (1984) for the Rhône river.

Minimum discharge values of 1500 and 500 m^3 s^{-1} were used to identify a total of 45 and 19 flood days during 1996 for the Garonne and Lot rivers, respectively. The maximum values for the river water flows and the TSS concentrations were observed in January–February and November–December (Figure 2). Note that the higher TSS concentrations correspond to the higher river water flows, as previously recorded for numerous rivers (Meybeck, 1992). The river water flow data were recorded for the 1973–1996 period at Temple (Lot) and for the 1959–1996 period at La Réole (Garonne), and gave mean respective values of 160 and 640 m^3 s^{-1}. These values are comparable to those determined in 1996: 170 m^3 s^{-1} and 810 m^3 s^{-1}, respectively. The mean discharge estimated for 1996 is, therefore, representative of the longer term hydrology of the study basin.

Discussion

As the frequency of TSS sampling is high, the quantification of the annual TSS fluxes (F_{TSS}) in the Lot-Garonne system is based on the assumption that the TSS concentration remained constant between two consecutive samples (i.e. day after day). Thus, the annual F_{TSS} are defined as the sum over 365 days of the following products (Meybeck, 1992):

$$F_{TSS} = \Sigma_1^{365} Q_{riv} \,.\, C_{TSS}, \tag{1}$$

where Q_{riv} is the daily mean river water discharge and C_{TSS} is the measured TSS concentration for each day. Considering the errors due to the sampling and analytical methods and those deriving from the Qriv determination, the precision is about 15% for the F_{TSS} at Temple (Lot), Port Pascau and La Reole (Garonne).

As the daily mean TSS fluxes are well known, the annual particulate cadmium fluxes (F_{partCd}) can be estimated from the assumption of the constant concentration given by Meybeck et al. (1994) as follows:

$$F_{\mathrm{partCd}} = \Sigma_1^{365} F_{\mathrm{TSS}} \,.\, C_{\mathrm{partCd}}, \tag{2}$$

where F_{TSS} is the daily mean TSS fluxes, C_{partCd} is the particulate Cd concentration which is considered as a constant between each sampling episode.

Table 5. 1996 river discharge and cadmium flux estimates for Temple (downstream Lot river), and percentage of cadmium delivered by the Lot to the Garonne river

	1996
River discharge (m^3 s^{-1})	171
TSS flux (10^6 t yr^{-1})	0.531
Dis. Cd flux (t yr^{-1})	0.54
Part. Cd flux (t yr^{-1})	6.13
Total Cd flux (t yr^{-1})	6.67
Lot river contribution (%)	48

Because the annual variability of the river discharge is well established, the mean annual dissolved cadmium flux (F_{disCd}) was calculated using the weighted volume concentrations (Meybeck et al., 1994) as follows:

$$F_{\mathrm{disCd}} = Q'.(\Sigma Qi.Ci/\Sigma Qi),$$

where Q' is the annual water discharge, Ci is the dissolved cadmium concentration in a sample (i), and Qi is the instantaneous river water flow measured at the time when the sample (i) was collected.

The total cadmium fluxes given in t yr^{-1} is obtained by the summation of the F_{partCd} and F_{disCd}. These calculated fluxes are reported in Table 5. The results calculated for 1996 show that about 48% of cadmium flux through the Garonne is contributed by the Lot river. This result is comparable to others obtained since 1990 (Lapaquellerie et al., 1996). Our results also show that 90% of the cadmium output from the Lot is in the particulate phase. In order to define roughly the internal reactivity in the Lot river, it is useful to compare the cadmium output with the input onto this fluvial system.

Sources of cadmium

The annual atmospheric cadmium flux (1994) was estimated by determining the cadmium concentration of rain water collected by two rain gauges installed at Temple (downstream Lot) and at Castelnau Lassout (upstream Lot) (Figure 1). These measurements gave values averaging 37 ng l^{-1} at Castelnau Lassout and 39 ng l^{-1} at Temple for the cadmium concentrations, and 3.5 and 2 ng cm^{-2} yr^{-1} for the cadmium fluxes. Maneux et al. (1998) reported annual cadmium fluxes of 9 ng cm^{-2} yr^{-1} in 1994 from the rain deposition to the Arcachon Lagoon, which is a coastal zone in southwestern France, 60 km from Bordeaux. A maximum annual cadmium flux of 0.3 t yr^{-1} was then calculated for the entire Lot catchment (i.e. 8400. 10^{10} cm^2). Because 1994 was the most humid year since 1996, the magnitude of the atmospheric cadmium flux probably leads to a small error in the atmospheric cadmium input for 1996. However, the annual water height at Castelnau Lassout was two times higher than that at Temple in 1994, while the cadmium concentrations were comparable in both sites.

The annual cadmium flux deriving from the natural run-off was estimated from a 1991–1996 database. Concentrations of dissolved and particulate cadmium were determined at Boisse Penchot, located 1 km upstream from the junction of the Riou-Mort and Lot rivers, and at Cabreret located 5 km from the junction of the Célé tributary and the Lot river (Figure 1). At Boisse Penchot, the mean concentrations of the dissolved and particulate cadmium were 65 ng l^{-1}, and 1.2 mg kg^{-1}, respectively. These values are comparable to those measured since 1990 at Port Pascau for the Garonne basin (i.e. 51 ng l^{-1} and 1.4 mg kg^{-1}) (Lapaquellerie et al. , 1996). Taking a mean river water flow of 77 m^3 s^{-1} in 1996, the dissolved cadmium flux was 0.16 t yr^{-1}. Because the variability of the TSS concentrations is poorly documented at Boisse Penchot, we assume that the TSS flux at this site is equal to the difference between the TSS flux determined at Bouillac located 2 km downstream (i.e. 0.252 10^6 t yr^{-1}) and that of the Riou-Mort river (i.e. 0.0024 10^6 t yr^{-1}). Thus, our estimation of 0.28 t yr^{-1} for the particulate cadmium flux must be considered as an approximate average value. At Cabreret, the concentrations show mean values of 98 ng l^{-1} for dissolved cadmium, 18.5 mg kg^{-1} for particulate cadmium, and 49 mg l^{-1} for TSS, leading to the calculated fluxes of 9 kt yr^{-1} for TSS, 0.16 t $yr^{-1}$for particulate and 0.02 t yr^{-1} for dissolved cadmium. Thus, the dissolved and the particulate run-off discharges from the Lot catchment are 0.18 t yr^{-1} and 0.44 t yr^{-1}, respectively.

The next point is the estimation of the main cadmium source: the Riou-Mort. In 1996, two surveys of 24 d each were carried out using an automatic sampler. In addition to the values given in Tables 3 and 4, we calculated annual fluxes for TSS, dissolved and particulate cadmium of 2.4 kt yr^{-1}, 4.17 t yr^{-1} and 1.10 t yr^{-1}, respectively. Although the temporal variability

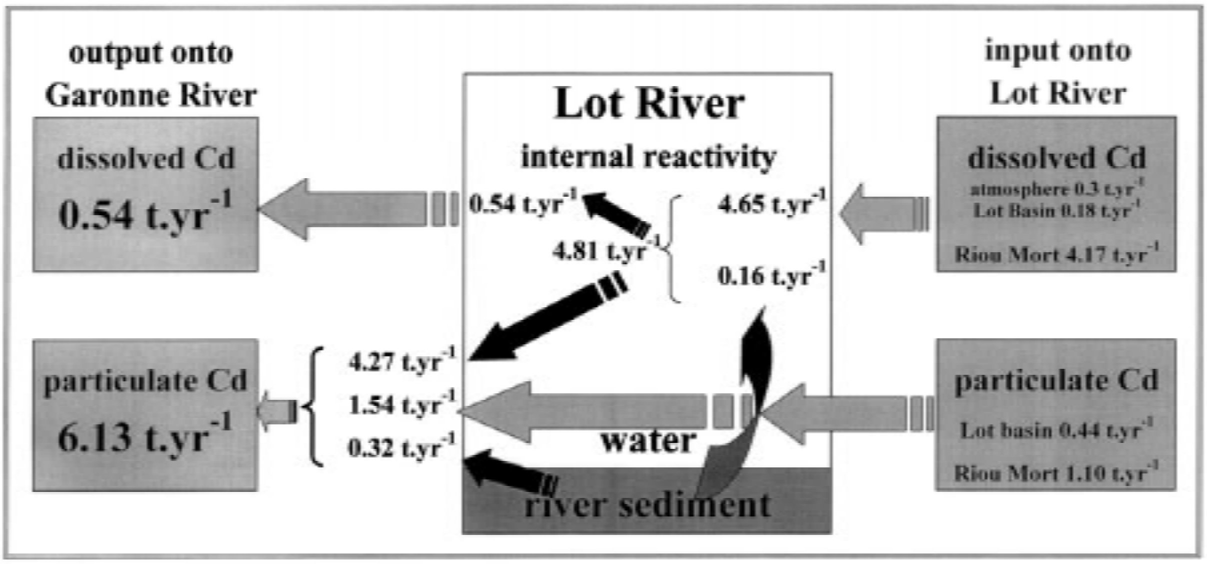

Figure 3. Box model of the cadmium budget for the Lot-Garonne study basin.

of the concentrations is underdocumented in comparison with that obtained at Temple, these results are comparable to those obtained from two short surveys in February and June 1994 made by the "Agence de l'Eau Adour-Garonne" (1995). Furthermore, we note that only about 20% of the cadmium is transported by the Riou-Mort river in particulate forms. Thus, the temporal variability of the TSS concentrations has a smaller influence on the estimation of the total cadmium input to the Lot river. From these results, we assume that the cadmium input is characterized by fluxes of 4.65 t yr^{-1} in dissolved form and 1.54 t yr^{-1} in particulate form. However, an additional source of dissolved cadmium needs to be evaluated: this is the molecular diffusion flux at the water-sediment interface. Two concentration-depth profiles for the dissolved cadmium were obtained from two sediment cores recovered in 1996 at Cajarc and Temple. If we assume that only vertical transport through interstitial waters is important, then the flux of a chemical constituent can be described by the Fick law. Using a corrected temperature diffusion coefficient of 3.3 10^{-6} cm^2 s^{-1} for cadmium (Lerman, 1979), dissolved cadmium diffusion fluxes of 25 10^{-6} and 9.2 10^{-6} ng cm^{-2} s^{-1} were computed from the concentration gradients obtained between the interstitial and the deep water at Cajarc and Temple, respectively. Two other cores recovered at the same sites in 1992 gave fluxes slightly higher, 41 10^{-6} and 16.2 10^{-6} ng cm^{-2} s^{-1}. The sediment surface within the Lot river channel between its confluences with the Riou-Mort and the Garonne was estimated at 22 km^2 (Lapaquellerie et al., 1995). Thus, we obtain a rough estimate of 0.16 t $yr^{-1}$for the annual cadmium flux associated with molecular diffusion. Consequently, the dissolved cadmium input could be 4.81 t yr^{-1}.

Since the dissolved cadmium output was 0.54 t yr^{-1}, the suspended material must act as a sink for dissolved cadmium, which is removed from the solution (Figure 3). The magnitude of this removal is 4.27 t yr^{-1}, which makes up about 70% of the particulate cadmium output. By adding 1.54 t of particulate cadmium transported by the Lot river in 1996, we obtain a deficit of 0.32 t yr^{-1} for the particulate cadmium output. Note that the cadmium input is approximately equal to the output in 1996. This small deficit can be interpreted, however, in terms of cadmium mobilization removed from the Lot river sediment by erosion.

Cadmium mass balance

This result can be tested by a simple model that shows the change of the cadmium concentrations as a function of dilution from the Riou-Mort to the Gironde estuary. The dissolved concentrations are diluted by the progressive downstream increase in the river discharge for the Lot, whereas the dilution of the particulate concentrations is related to the TSS fluxes. Thus, it is convenient to use a framework in which dissolved cadmium and particulate cadmium are con-

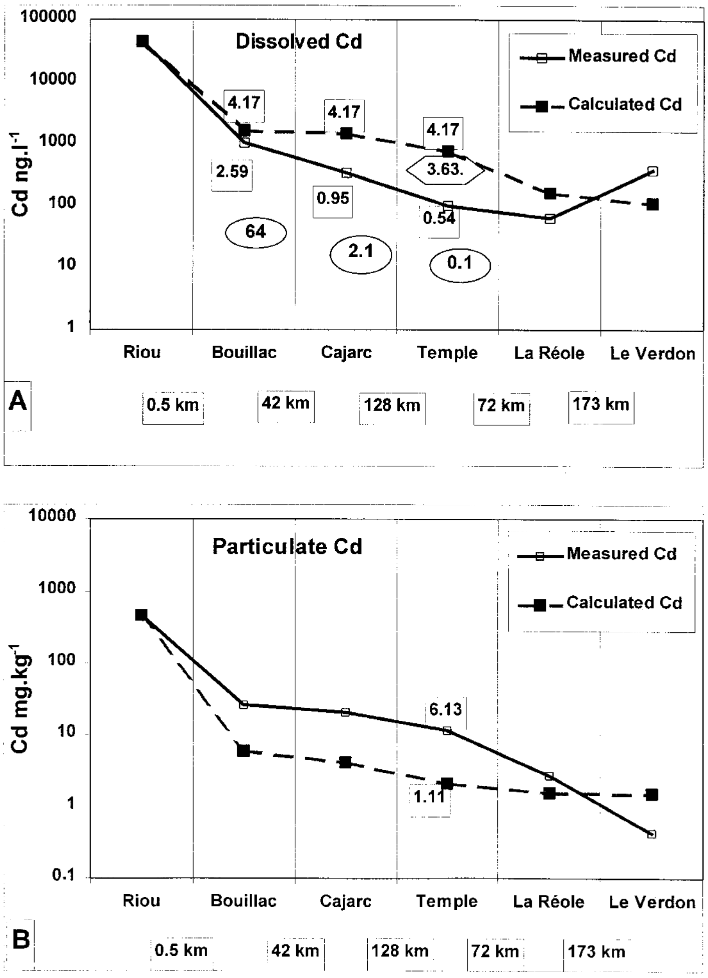

Figure 4. Dilution model for dissolved (A) and the particulate (B) cadmium concentrations. Numbers into open squares are in t yr^{-1}, numbers in open circles are in μg m^{-1} s^{-1}.

sidered separately. The parameters for calculation are presented in Table 6, and the calculated concentrations are compared to those measured in Figure 4. This comparison shows that the calculated dissolved cadmium concentrations are higher than those measured from the Riou-Mort to La Réole, whereas the measured concentrations are higher than those calculated in the estuary. The pattern is reversed for the particulate cadmium. Qualitatively, Figure 4 shows that cadmium is removed from the solution between the Riou-Mort and La Réole, then the cadmium undergoes estuarine dissolved-particulate reactions which lead to its addition to the dissolved phase. The quantification of this addition cannot be assessed with accuracy because the cadmium output at the estuary mouth is not adequately documented in this study. Nevertheless, it is useful to look at the difference between the calculated and measured concentrations along the Lot river. From these concentrations, dissolved cadmium fluxes can be estimated for each sample site (Figure 4A). At Temple, the flux difference (e.g. 4.17 t yr^{-1} minus 0.54 t yr^{-1}) yields a value of 3.63 t yr^{-1} which corresponds to the annual removal of the Riou-Mort dissolved cadmium input. By adding the cadmium input not taken into account in the dilution model (i.e. atmosphere, run-off, and diffusion inputs), we find 4.27 t yr^{-1}, equal to the removal value determined in the box model. By considering the distance between each site along the Lot river, we deduced that the cadmium removal from solution decreases rapidly in the downstream direction, with a rate of 64 μg m^{-1} s^{-1}from the Riou-Mort junction to Bouillac (0.5 km), 2.1 μg m^{-1} s^{-1}from

Table 6. A comparison between measured and modelled cadmium concentrations for each sampling sites. Parameters used for the calculation of the dissolved and particulate concentrations resulting from the dilution of the Riou-Mort cadmium input. The calculated particulate cadmium concentrations are deduced from the dilution factor due to the additional TSS fluxes along the Lot river. The calculated dissolved cadmium concentrations are deduced from the dilution factor due to the additional river discharge along the Lot river

	TSS flux (10^6 t yr^{-1})	Dilution factor	measured part. Cd (mg kg^{-1})	calculated part. Cd (mg kg^{-1})	Discharge (m^3 s^{-1})	Dilution factor	measured dis. Cd (ng l^{-1})	calculated dis. Cd ng l^{-1})
Riou-Mort	0.0024		460	460	3		44 048	44 048
Bouillac	0.252	77	26.4	6	80	27	1025	1652
Cajarc	0.31	114	20.7	4.1	89	30	340	1485
Temple	0.531	221	11.6	2.1	171	57	101	773
La Réole	4.661	1942	2.69	1.53	808	269	64	164
Le Verdon	5.75	2395	0.43	1.5	1200	400	380	110

Bouillac to Cajarc (42 km) and 0.1 μg m^{-1} s^{-1} from Cajarc to Temple (128 km). Thus, 97% of dissolved cadmium input is absorbed by the suspended sediment within 0.5 km after the confluence of the Riou-Mort and the Lot. The magnitude of the removal from dissolved to particulate phases can also be estimated using the dilution model of the particulate cadmium (Figure 4B). The cadmium concentrations measured at Temple lead to a flux of 6.13 t yr^{-1}. This particulate cadmium flux included four discrete discharges. They are the natural cadmium delivered by the Lot catchment (i.e. 0.44 t yr^{-1}), the cadmium released from the sediment blanketing the Lot river bed (i.e. 0.32 t yr^{-1}), the Riou-Mort cadmium discharge which is the value given by the dilution model (1.11 t yr^{-1}), and the cadmium which is deduced to be removed from solution (4.26 t yr^{-1}). This value is clearly comparable to that determined using the box model. Thus, the budgeting approach developed in this study is efficient to describe the macroscpic behaviour of cadmium in the Lot-Garonne study basin.

Conclusion

The annual river discharge for the Lot-Garonne fluvial system during 1996 is representative of the longer-term mean. The flux estimates presented in this study are based upon regular high frequency measurement for a large study basin and algoritihms recommended by Meybeck et al. (1994). These algorithms are similar to those used for British rivers (Webb et al., 1997). Bearing this point in mind, the tentative budget produced by this study estimates that 48% of the cadmium flux in the Garonne river originates from the Lot river. The cadmium contribution from the Lot is about 90% particulate. This particulate flux comprises the particulate cadmium transported by the entire Lot catchment (∼25%), the particulate cadmium removed from solution by exchange from dissolved to particulate phases (∼70%), and the particulate cadmium mobilized from the sediment blanketing of the Lot bed (∼5%). The cadmium input into the Lot river is 75% dissolved. The dissolved cadmium input overall includes wet atmospheric deposition (∼6%), surface run-off of the Lot catchment (∼4%), molecular diffusion at the water-surface interface (∼3%), and the major anthropogenic source: the Riou-Mort tributary (∼87%). Within a distance of 0.5 km from this anthropogenic source, about 97% of dissolved cadmium input is taken up by the suspended solid phase.

This study indicates that two areas of the Lot-Garonne study basin should be targeted by any future investigations of change in metal speciations between the particulate, dissolved and colloidal phases. These are between the Riou-Mort and Bouillac on the Lot river, and from La Réole to Bordeaux at the Garonne-Gironde fresh/salt water interface.

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