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Arsenic and antimony release from sediments in a Mediterranean estuary

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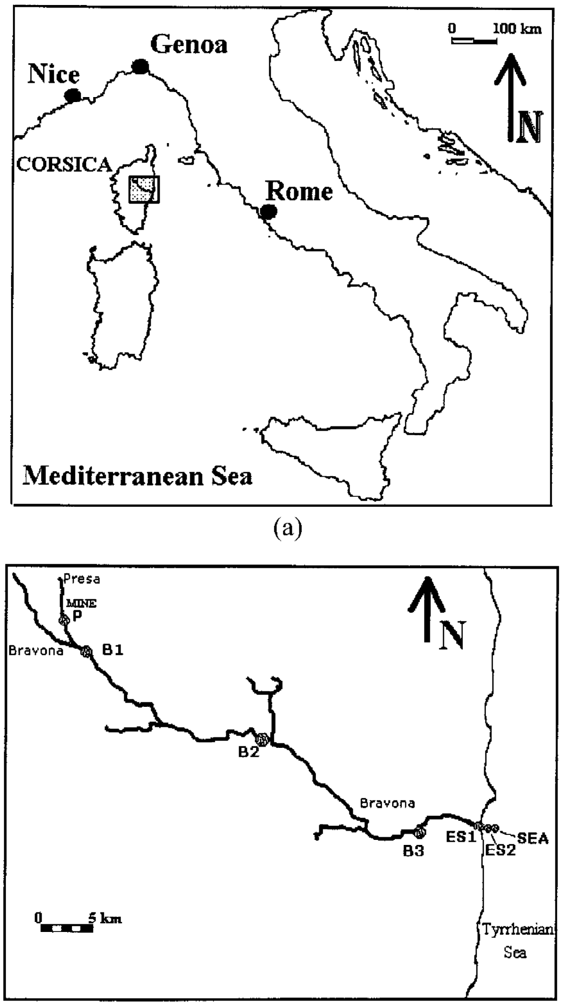
Abstract

An ancient realgar mine is responsible for the contamination of a riverine system in central Corsica. Nearby the mine, high As and Sb concentrations are found (up to 2–3 mg l^{-1} and 2–3 μg l^{-1} respectively). A significant increase of the As and Sb concentrations in water is found in the water of the mixing zone of river and sea (Bravona estuary; chlorinity 7000–7800). In the same area, a decrease of As and Sb concentrations in sediments is observed. Fe and Mn exhibit the same behaviour. The possible involvement of redox processes is discussed. However, owing to insufficient reducing capacity and insignificant variation of redox potential values along the various estuarine sites (from 320 down to 280 mV), this scenario is rather doubtful. Desorption from FeOOH particles is the most likely process in the Bravona estuary. The impact of these contaminated waters on the marine environment is discussed. Owing to decrease by dilution, as well as the reduced water flow of the estuary, the net supply of As and Sb to the Tyrrhenian Sea is approximately 5 and 1.5 t y^{-1} for As and Sb respectively. The possible harmful influence of the Bravona river should be of local concern only, and the emphasis of this study is, therefore, on a better knowledge of *in situ* processes.

Introduction

Mining activities are responsible for high concentrations of heavy metals in natural waters (Johnson & Thornton, 1987; Duzzin et al. 1988; Mok & Wai, 1990; Caboi et al., 1993; Migon et al., 1995), which can cause severe environmental harm. Many studies have been undertaken in order to determine the toxicity, the chemical speciation (and thus the bioavailability) and the possible removal mechanisms of heavy metals in freshwaters. In estuaries, which have specific physical and chemical characteristics, various metal transfers occur between dissolved and particulate phases, as well as uptake by phytoplankton (Windom et al., 1988; Dorten et al., 1991; Gadd, 1991; Martin et al., 1993; Migon, 1993). Many authors have discussed the impact of metals on natural ecosystems: e.g., Burrows & Whitton (1983) have observed that high concentrations of Cd, Pb and Zn in water and sediment generally lead to high metal concentrations in animals; Romeo (1991) reviewed physiological sublethal effects (respiration, growth, reproduction, behaviour) of Cd, Cu, Hg, Pb and Sn on marine organisms; Mori et al. (1999) studied the bioaccumulation of As and Sb and its effects on freshwater macroinvertebrate populations.

In certain cases, processes of metal remobilization from sediment to the overlying water may occur, which may increase the significance of the pollutant threat. Such a behaviour can be due to (i) the formation of soluble chloro-metal complexes (e.g., cadmium; Elbaz-Poulichet et al., 1987); (ii) regeneration or recycling from degrading organic matter (Church, 1986; Windom et al., 1988); (iii) ionic exchange during the transfer from freshwater to saltwater; (iv) reducing conditions, which may favour the dissolution of reduced forms and the release of free ionic species. Among potentially harmful elements, As and Sb are known to be highly toxic. A realgar (As_4 S_4) deposit was found in central Corsica, close to the village of Matra, between 1880 and 1890. In 1913, the ore production reached its highest value, more than 4000 tonnes per year. After a production of 30,000 tonnes of ore at 30% of As, the mine was abandoned in 1945. A minor river (Presa) crosses the ancient mine and then runs into the Bravona river, which reaches the



(a)

(b)

Figure 1. (a) Location of the contaminated rivers; (b) Location of the sampling sites.

Tyrrhenian Sea, nearby Aleria, on the eastern coast of Corsica (see Figure 1a). The Presa river is highly contaminated by the waste of this ancient mine, and high concentrations of As and Sb are found in water and in sediment. Significant concentrations of As and Sb remain in water and suspended matter until the river mouth, changing specific physical and chemical characteristics cause a different chemical behaviour.

2. Materials and methods

2.1. Sampling sites

Figure 1b indicates the sampling stations. The site P, on the Presa river, downstream from the ancient mine, was chosen in order to provide concentration values nearby the emission source. 10 km away from the mine, the Presa river runs into the Bravona river. Sites located on the Bravona river are called B1, B2 and B3. Estuarine samples were collected at sites ES1 and ES2. Marine samples were also collected (SEA). The flow of the river influences the deposition mode of the river suspended matter and thus 7 sampling campaigns were carried out at different seasons, i.e. with a mean river flow ranging between 0.2 (August) and 1.7 m^3 s^{-1} (February).

2.2. Sample collection

Sampling equipment was soaked with HNO_3 (suprapur), ultrasonically rinsed with deionised water and kept filled for a week with suprapur HNO_3 and rinsed again several times with deionised water. Sampling campaigns were carried out in 1992 and 1993 and included various seasons.

Samples in shallow waters were taken by hand and no vertical gradient was studied. The surface microlayer was avoided. For each site, 2 water samples were collected: the first one, using a plastic bottle, was used for measurement of pH and turbidity. The second one was used for the measurement of metal and metalloid concentrations (Teflon bottles, FEP). These latter samples were divided into two sub-samples: one was centrifuged in order to analyse dissolved material and the other used for the analysis of the total element concentrations. This separation was carried out immediately after sampling, in order to prevent any exchange. One sub-sample was acidified to pH 2 with HNO_3 (ultrapur, 0.5%) in order to avoid any adsorption phenomenon on the bottle surface during storage. In order to destroy organic matter, an acidic mineralization was carried out with HNO_3, H_2SO_4 and H_2O_2, followed by a prereduction in HCl with a KI/ascorbic acid solution. Surface sediment (0–6 cm) samples were collected with a box corer.

2.3. Chemical analysis

The pH was measured with a pH-meter with a combined electrode. Cl^- were measured with a colorimetric method, using an autoanalyser.

Table 1. Analysis of certified reference materials provided by the National Research Council, Canada. SLRS-3 is a riverine water reference material, and NASS-4 is a seawater sample. Concentrations are expressed in μg l^{-1}. MESS-2 is an estuarine sediment sample from the Gulf of Saint Laurent. Concentrations (conc.) are expressed in μg g^{-1}. For As and Sb, preconcentration techniques have been used (only for certified reference materials). s.d. are standard deviations

	SLRS-3		NASS-4		MESS-2	
	Conc.	s.d.	Conc.	s.d.	Conc.	s.d.
As (reference)	0.72	0.05	1.26	0.09	20.7	0.8
As (measured)	0.68		1.12		23.0	
Sb (reference)	0.12	0.01			1.09	0.13
Sb (measured)	0.10				1.18	
Fe (reference)	100	2	0.105	0.016	43504	2168
Fe (measured)	98				42300	
Mn (reference)	3.9	0.3	0.380	0.023	365	21
Mn (measured)	4				338	

Sediment was mineralized in a closed Teflon bottle and heated in a micro-wave oven. Ultrapur acids were used (HNO_3, H_2SO_4 and HF), with a solubilisation in boric acid 6%. Tot-Fe was measured by flame atomic absorption spectrophotometry (Perkin-Elmer 3030 B) and Tot-Mn by graphite furnace atomic absorption spectrophotometry (GFAAS). As and Sb were measured by GFAAS, using the hydride generation technique (Perkin Elmer 3100 and FIAS 200). Rinsing solution was HCl 0.4 M and the reducing solution was $NaBH_4$0.2% in NaOH 0.05%. The vector gas was argon (flow: 100 ml mn^{-1}).

Matrix modifiers were used for Mn ($Mg(NO_3)_2$), and As and Sb ($Ni(NO_3)_2$). Standard solutions were provided by Merck. Relative standard deviations were 0.5 to 5% and 1 to 10% for As and Sb respectively. Detection limits were 1 and 10 μg l^{-1} for Mn and Fe respectively. Quality assurance for analyses is given in Table 1.

3. Results

After crossing the mining spoils, the Presa water becomes enriched in As and Sb, and high concentrations are found (up to 2–3 mg l^{-1} for As and 175 to 330 μg l^{-1} for Sb), decreasing rapidly downstream. After the confluence with the Bravona river (site B1), the As and Sb concentrations decrease by dilution. The values range here from 15 to 63 for As and from 2 to 26 μg

Table 2. Elemental concentrations (expressed in μg l^{-1}) at the different sampling stations

	P	B1	B2	B3	ES1	ES2	SEA
September 1992							
Turbidity	0.7	0.8	1	1	0.7	0.5	
pH	7.8	7.4	7.4	7.5	7.3	7.3	7.9
Cl	5	4.5	8.5	86	2180	7838	22400
Tot–As	3042	355	172	40	19	165	10
diss–As (%)	95	86	81	87.5	84	88	80
Tot–Sb	193	41	32	17	9	70	9
diss–Sb (%)	98	98	84	82	89	71	78
Fe	77	43	74	80	165	682	190
Mn	91	78	85	80	143	190	5
November 1992							
pH	7.8	7.6	7.6	7.6	7.7	7.5	8
Cl	6	4	4	336	2320	7550	21800
Tot–As	3200	190	150	40	22	150	8
diss–As (%)	100	95	80	95	68	80	75
Tot–Sb	199	23	26	15	9	60	7
diss–Sb (%)	90	78	92	87	78	58	71
Fe	80	72	60	99	178	655	205
Mn	36	20	44	56	95	118	4
January 1993							
pH	8.5	7.7	7.6	7.8	7.8	7.3	8
Cl	8	8	15	282	1980	7795	22800
Tot–As	2350	600	110	15	33	220	10
diss–As (%)	98	83	91	100	85	91	90
Tot–Sb	330	106	36	26	18	100	16
diss–Sb (%)	99	77	83	69	883	75	81
Fe	75	75	70	88	148	495	220
Mn	53	30	62	64	106	123	2
March 1993							
pH	7.9	7.8	7.7	7.8	7.7	7.6	8
Cl	8	7	12	354	765	6945	22555
Tot–As	3040	20	153	46	45	215	6
Tot–Sb	250	1	32	2	5	30	10
Fe	82	76	80	141	188	361	195
Mn	33	25	45	75	77	100	2
April 1993							
pH	7.8	7.5	7.6	7.6	7.6	7.5	8.1
Cl		7	13	326	2535	7640	23500
Tot–As	2080	17	153	41	27	185	4
Tot–Sb	175	2	38	3	8	55	16
May 1993							
pH	7.8	7.4	7.4	7.6	7.4	7.4	7.9
Cl		4	4	75	1520	7305	20000
Tot–As	3010	20	148	63	39	220	1
To–Sb	249	3	31	10	2	15	1

Continued on p. 84

Table 2. contd.

June 1993							
Turbidity	0.3	1.6	0.8	30	31	0.4	
pH	8	7.9	7.6	7.8	7.9	7.7	8
Cl	25	16	16	45	2100	7620	20500
Tot–As	2860	180	130	35	25	175	12
Tot–Sb	240	38	28	20	13	80	10
Fe	75	76	59	78	154	672	170
Mn	15	17	12	17	31	46	2

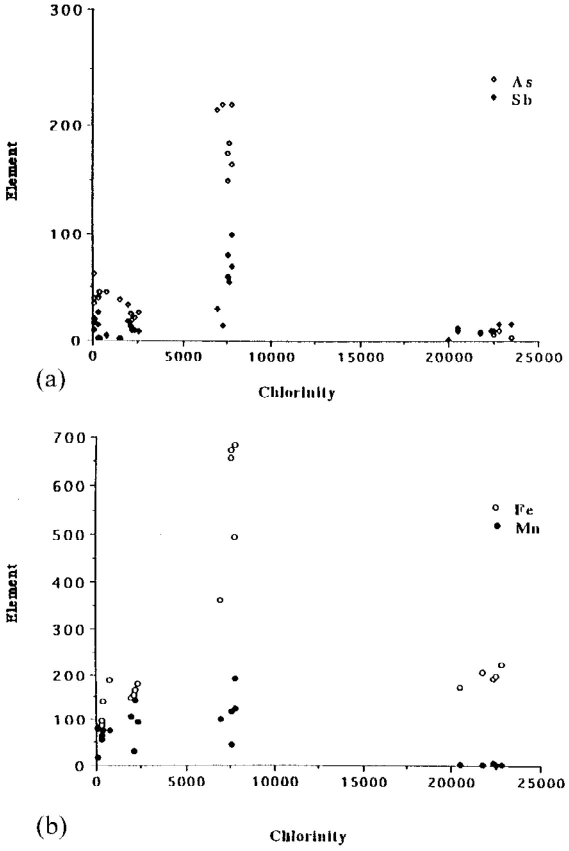


Figure 2. (a) Variation of As and Sb concentrations in water (expressed in μg l^{-1}) with chlorinity; (b) Variation of Fe and Mn concentrations in water (expressed in μg l^{-1}) with chlorinity.

l^{-1} for Sb at B3, i.e. upstream the mixing zone (Table 2).

In the river mouth (in sites ES1 and ES2), diss-As and diss-Sb concentrations significantly increase. Although As and Sb concentrations strongly vary in estuarine and coastal waters, particularly because of the seasonal phytoplanktonic activity (Michel, 1993), As is generally removed in such zones (Angelidis & Grimanis, 1987; Johnston & Thornton, 1987). In contrast, As and Sb concentrations significantly increase in the Bravona mixing zone (Figure 2).

Table 3. Elemental concentrations in sediment (expressed in μg g^{-1}; d.l. = detection limit)

	P	B1	B2	B3	ES1	ES2	SEA
January 1993							
As	9450	3297	354	207	92	41	36
Sb	1108	300	40	35	20	5	8
Fe	57000	61000	45000	47000	44000	17500	45000
Mn	500	550	470	370	240	< d.l.	10
March 1993							
As	8820	3005	298	203	104	63	47
Sb	1005	315	50	35	18	6	10
Fe	60000	52000	44000	40000	38000	16000	39000
Mn	650	510	450	390	220	50	10
April 1993							
As				252	98	66	33
Sb				30	15	4	6
Fe				37000	34000	13500	29000
Mn				360	190	20	5
June 1993							
As				205	85	44	40
Sb				24	15	8	12
Fe				42000	36000	12500	25000
Mn				260	110	6	4

A decrease of As and Sb concentration is also observed in sediment (Table 3), from site P (9 and 1 mg g^{-1} for As and Sb respectively) to site SEA (40 and 5 μg g^{-1} for As and Sb respectively). The concentration of As in marine sediments generally ranges between 5 and 20 μg g^{-1} (Michel, 1993). However, much higher levels can be found in estuarine or coastal areas (e.g., Angelidis & Grimanis, 1987). Sb concentration was always lower in ES2 than in SEA, while As concentration decrease was regular. Fe and Mn concentrations exhibit the same tendency. The apparent depletion in ES2 is particularly marked for Fe, but it is observed only in January 1993 for Mn.

The size of sediment particles also exhibits a shift from 250–2000 μm at ES1 to < 63–163 μm at ES2 (Table 4).

Table 4. Size of sediment particles from P to ES2

Particle size	P	B1	B2	B3	ES1	ES2
$>$ 2 mm	38	29		25.5	1	7
2000–600 μm	85.5	50		54	24	2
600–250 μm	13	33		31	64	3
250–163 μm	1	8		7	7	7
163–63 μm	0.5	6		6	4	35
$<$ 63 μm	0.5	3		3	2	53

4. Discussion

4.1. Exchange between sediment and overlying water in the mixing zone

Because of their similar chemistry, and literature data being scarse for Sb, we assume for the moment that this element behaves like isostructural As.

The separation between dissolved and total As and Sb was made only for samples 1 to 3, because the ratio of diss-As and diss-Sb over Tot-As and Tot-Sb concentrations remained approximately constant from upstream down to the mixing zone (Table 2). This ratio varied from 83–95% (B1) to 68–85% (ES1) for As and from 77–97% (B1) to 78–89% (ES1). In ES2, the ratio was 80–91% for As, while it slightly decreased for Sb: 58–75%. This is particularly marked for the sample 2 (diss-Sb/Tot-Sb = 58%). The Bravona estuary has a neutral pH, which does not alter the As and Sb solubility: only low and high pH values will increase the solubility of these elements (Mok & Wai, 1990).

A specific behaviour occurred in the mixing zone: the dissolved concentrations increased considerably and the concentrations in the sediment decreased concomitantly. Increased diss-As and diss-Sb concentrations may be caused by two chemical processes:

(a) sorption processes

The adsorption of As onto particles, supposedly FeOOH (Angelidis & Grimanis, 1987; Sadiq, 1990), can be written as the following chemical equilibrium (De Vitre et al., 1991; see also Golterman (1995), considering the chemical similarity between As and P):

$$\mathrm{FeOOH} + \mathrm{H_3AsO_4} <==> \mathrm{Fe(OOH)\text{-}AsO_3} + \mathrm{H_2O}$$

Realizing the constant ratio dissolved/total upstream, we assume that As (or Sb) on the particles is in equilibrium with the diss-As (or diss-Sb). When the sediments are settled downstream, the increase of diss-As and diss-Sb concentrations in the water may be due to desorption from these particles. The partitioning between dissolved and adsorbed or particulate concentrations in estuaries may in principle be controlled by salinity and particle concentration. Turner (1996) showed that the dissolved fraction increases with salinity and with suspended matter concentration. Salinity increased at ES2, as indeed the diss-As and diss-Sb concentrations. However, the estuarine zone where As and Sb are released (ES2) is characterised by increased sediment concentration and the relative abundance of small grained sediments (Table 4). Under these conditions, hydrodynamic processes may be responsible for a more efficient resuspension of sediment particles and thus increase the suspended matter concentration. As a consequence, As and Sb desorption from FeOOH particles should be enhanced. It is likely that, in addition to the increase of diss-As and diss-Sb (as well as diss-Fe) concentrations, the increased efficiency of hydrodynamical particle resuspension in ES2 also leads to the increase of part-As and part-Sb concentrations. The result may be the apparent conservation of the ratio dissolved/particulate along the different sampling sites.

On the contrary, the following zone (SEA) exhibits sediments essentially made of large particles ($>$ 600 μm). In addition to the dilution effect, this may explain the fall of As and Sb concentrations downward ES2.

The hypothesis of sorptive processes is consistent with the increase of water concentrations and the depletion of sediment in ES2 as well.

(b) redox processes

Figure 2 shows that, although the involvement of Fe and Mn oxyhydroxides in controlling the As solubility cannot be denied, Fe and Mn concentrations in the waters entering the Bravona mixing zone are insufficient to induce coprecipitations with As or Sb, or to adsorb As and Sb onto the oxides.

However, a significant increase of Fe and Mn concentration in water is also observed at sampling points ES1 and ES2. The As and Sb release is combined with relatively high Fe and Mn concentrations in water, and no precipitation process occurs. This situation may be an indication of a reducing environment: reducing conditions can prevent the precipitation of Fe and Mn oxyhydroxides.

The accumulation of As and Sb is favoured by rich organic environments (Jenner & Browner, 1990).

Migon et al. (1995) have shown that detritivorous animals which live on small organic debris in sediments exhibit high As and Sb accumulation. One of them, *Caenis luctuosa*, is more abundant in ES2 (approximately 6% of the total benthic fauna) than upstream ES1 (approximately 0.09%). High concentrations of degrading organic matter are found in the Bravona mixing zone, although data such on O_2 or organic matter concentration are not available as yet. The estuary water is stagnant, which may create an anoxic environment, exhibiting reducing conditions. This point is partly sustained by the decrease of the ratio NO_3^-/NH_4^+ previously observed (Mori, 1992) from the upstream river (50) down to the estuary (7).

Redox conditions strongly affect the solubility of As minerals. In particular, arsenates should control As solubility in oxic sediments, while As concentrations should decrease in anoxic sediments (Lindsay & Sadiq, 1983; Sadiq, 1990). As and Sb adsorbed onto Fe hydroxide may be released after reduction. In the sampling site ES2, i.e. where the highest As and Sb concentrations are observed in estuarine waters, the As and Sb levels are the lowest in sediment (Table 3). Fe and Mn concentrations also decrease in the sediment, while they are relatively high in water. In anoxic zones, arsenates are reduced to arsenites. However, such environments also reduce Fe^{3+} to species which are soluble and are released into the water. This may indicate that As and Sb are released from sediment to water with reductive processes. In particular, As and Sb could be released from biogenic particles during organic matter decomposition, which consumes O_2. Such a process was already observed in a coastal marine environment (Gaillard et al., 1986). Golterman (1995) observed, for the case of chemically similar phosphorus, that phosphate was partly desorbed with reduction of Fe hydroxides to FeS, but that a large excess of reducing capacity was needed.

In the case of redox process involvement, the release observed at ES2 would require on the one hand the reduction of As and Sb and, on the other hand, the reduction of FeOOH as Fe^{2+}. However, according to the chemical similarity of P and As, natural conditions do not permit the reduction of Fe-bound As, owing to insufficient reducing capacity (Golterman, 1984). Even the reduction of only FeOOH on which As and Sb are presumably trapped is not possible, taking into account the large amounts of FeOOH found in sediment. Moreover, a redox shift is counterbalanced in nature by a concomitant pH decrease (Golterman, 1984), and no significant decrease is observed in the Bravona estuary, where pH values are stable.

FeOOH can oxidize arsenites to arsenates, which then may precipitate with iron hydroxides (Johnson, 1986; Angelidis & Grimanis, 1987; Johnson & Thornton, 1987; Andreae & Andreae, 1989; Sadiq, 1990; Kitts et al., 1994):

$$2\ \mathrm{FeOOH} + \mathrm{As\ (III)} \longrightarrow 2\ \mathrm{Fe}^{2+} + \mathrm{As\ (V)}$$

which leads to the conclusion that even As (III) can be adsorbed and, owing to the high amounts of FeOOH, it also means no reduction occurs.

The redox values measured in the sediment of the Bravona estuary are in agreement with this assumption: despite an effective decrease from ES1 to ES2 (from 320 to 280 mV), the difference between these values is too low to induce the reduction processes.

4.3. Water quality of the Presa-Bravona system

The As and Sb concentrations in the water may be compared with the directives formulated by French policies for drinking water, i.e. 50 and 10 μg l^{-1} for As and Sb (DDASS, 1995). The maximum concentrations admitted by the United States Public Health Service for drinking water is lower: 10 μg l^{-1} for As (Mok & Wai, 1990). Officially, the Bravona water is not used for drinking, but many camping places are pitched between B3 and ES1. At B2, the water is widely used for agricultural irrigation.

The concentrations found in the Presa-Bravona system are high if compared with those generally found in other natural waters. For example, in the Krka river (Croatia), which can be considered as an unpolluted river, As concentration is 0.08 μg l^{-1} (Elbaz-Poulichet et al., 1989); in the Coeur d'Alene river (Idaho, U.S.A.), which is contaminated by mining waste, the mean As and Sb concentrations reach 1.64 and 8.25 μg l^{-1} respectively (Mok & Wai, 1990). In contrast, in Canada, waters in Keg and Meg lakes have a mean As concentration of about 2 mg l^{-1}, the highest value being 3.4 mg l^{-1} (Moore et al., 1988). These values are comparable with those of the Presa environment, although, as a general rule, lakes presumably act as sinks for pollutants more efficiently than rivers. However, De Vitre et al. (1991) have suggested that Fe oxyhydroxides efficiently scavenge As from sediment pore waters and thus reduce its toxicity by oxidation, As (V) being less toxic than As (III) (Shannon and Strayer, 1989). In seawater, As and Sb concentration levels decrease again, owing principally to dilution effect. The Bravona river has a low mean flow (0.8 m^3 s^{-1}) and brings 5 t As y^{-1} and 1.5 t Sb y^{-1} to the Tyrrhenian Sea. The impact of its toxic discharges is of local concern only. On a local scale, the impact of As and Sb loadings on estuarine ecosystems may have dramatic effects. Four points should be considered: (i) the most toxic form of arsenic, As (III), is predominant in reducing environments (Sadiq, 1990). Although the reducing processes are limited and the presence of As (III) is unlikely, this toxic species may cause local harm; (ii) the degradation of organic matter presumably liberates As and Sb forms whose toxicity is higher than that of organic matter-complexed species (Bénaïm, 1990); (iii) the bioaccumulation of the inorganic forms is more significant than that of organic species (Spehar et al., 1980); and (iv) desorption processes increase the concentration of dissolved species, which are easily assimilable. The physical and chemical conditions of the Bravona estuary enable to define a release mechanism which may be of major implication in other estuaries as well. The As, Sb and Fe remobilization process discussion in the present paper will provide data for a better understanding of metal and metalloid behaviour in estuaries. This is particularly acute for Sb, for which our knowledge is poor.

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