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Early Contamination by Heavy Metals of the Guadalquivir Estuary After the Aznalcóllar Mining Spill (SW Spain)

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The Guadalquivir estuary was impacted by the accidental release of 5 million cubic meters of acid waste from the processing of pyrite ore (25 April 1998). The waste entered ecologically sensitive and protected areas such as the National Park of Doñana. Here are presented the results obtained from a time sequence of different sampling sites in the estuary and in the surrounding areas from May to September 1998. Water, suspended solids and sediments were analysed for six different metals (Fe, Mn, Zn, Cd, Pb, Cu). Also, the concentration of the metals in the different geochemical sediment fractions was determined as a means of assessing bioavailability. The results obtained during the first weeks after the incident show high concentrations of Zn. At the end of June a 10 000 m^3 temporary water-treatment plant was constructed on site for depuration of the toxic waters. The results obtained in August and September show a decrease in the metal concentrations measured in the estuary. Only concentrations of Zn were higher than sediment quality values proposed by various authors. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: National Park of Doñana; Guadalquivir estuary; heavy metals; Aznalcóllar acid mine waste; sediments; pollution.

Introduction

On 25 April 1998, part of the tailings pond dike of the ‘Los Frailes’ zinc mine, situated in Aznalcóllar (Andalucía, Spain), collapsed, releasing an estimated 5 million cubic meters of acid wastewater rich in toxic metals over the next 5 days, killing most of the wildlife in its path and posing a long-term threat to the Guadalquivir ecosystem which encompasses the World Heritage site of the Doñana National Park and other protected areas. Following the accident, the acid water moved into the Guadiamar river (across much of the floodplain, covering agricultural land) and through it to the Guadalquivir river reaching the edges of the Doñana Parks (Fig. 1).

Trace metal concentrations in riverine, estuarine and coastal environments are subject to large temporal and spatial variations as a result of variability in the extent of run-off, erosion and pollution. Transient variations, point sources and trends in biogeochemical cycles of trace metals can only be detected by frequent and detailed measurements, including: water, suspended particulate matter (SPM) and sediments. In order to obtain such information, we have combined the initial results of four different studies: trace metal concentrations in both dissolved and particulate forms in the water column, including suspended solids and their form and distribution in sediments.

This paper presents the early results of the monitoring of contamination originated by the mining spill, in the Guadalquivir estuary and at the borders of the National Park of Doñana. It shows the distribution and metal concentration of Fe, Mn, Zn, Cd, Pb and Cu in the mentioned areas for water, SPM and sediments, evaluating their geochemical behaviour and their potential adverse effect in the area.

Material and Methods

Approach

At Aznalcóllar, Zn, Pb, Cu and Mn-rich pyrite deposits are mined and the Agrio river receives the drainage water from open-cast-worked polymetal sulphide deposits and old mine spoil heaps (Cabrera *et al.*, 1984). The Agrio then joins the Guadiamar, which is a major tributary of the southern Guadalquivir river. The threat posed to the Doñana Park through inputs of metals by mining activities from the Guadiamar and Guadalquivir rivers has been previously studied (Cabrera, 1984; Albaiges *et al.*, 1987; Arambarri, 1996; DelValls *et al.*, 1999).

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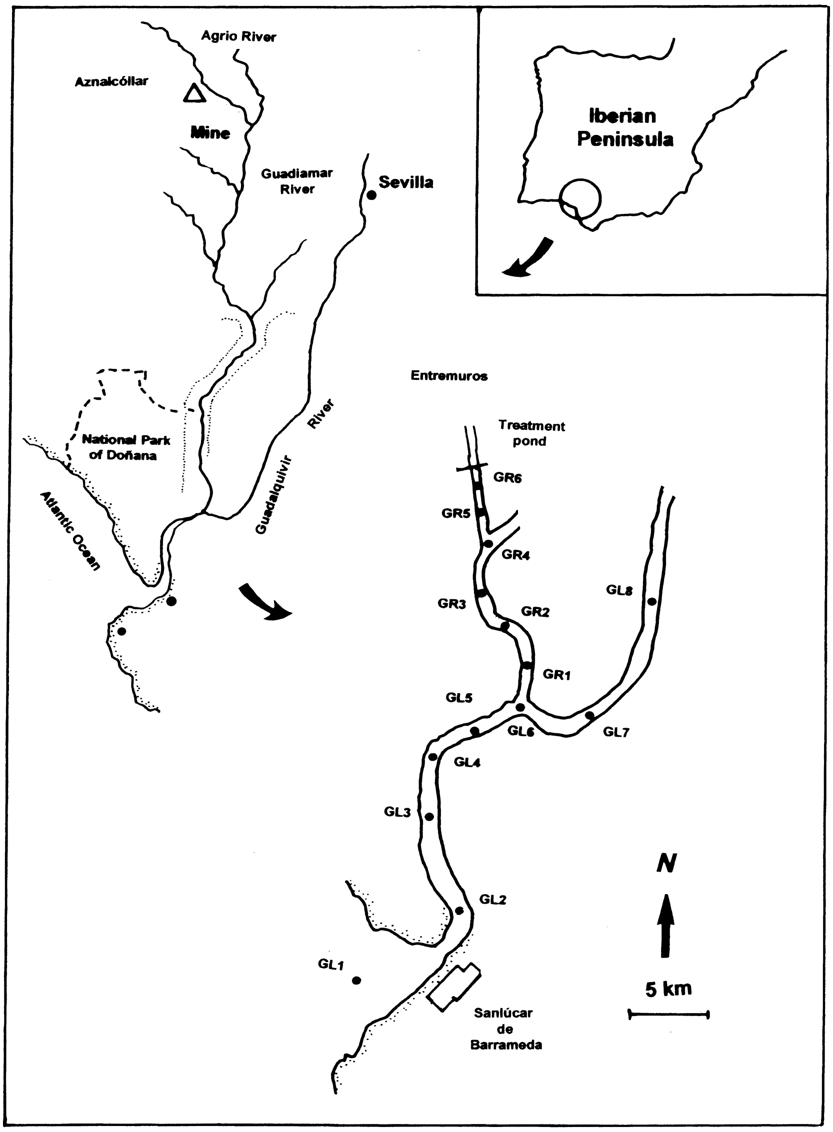

Fig. 1 General areas sampled and locations of sampling stations. GR indicates stations located in the 'Brazo de la Torre' of the Guadiamar river and GL indicates the Guadalquivir river and estuary.

To assess the influence of early contamination from the Aznalcóllar incident, in the Guadalquivir estuary and the surrounding areas, as well as to evaluate the efficiency of the emergency treatment pond in cleaning-up the acid water from the spill, 14 sampling stations were sited: eight in the Guadalquivir river and six through the Guadiamar artificial channel (Brazo de la Torre). The location of sampling sites and stations selected are showed in Fig. 1. Stations were sited following the gradient of contamination in the Guadiamar river (GR6 to GR1) and in the estuary (GL8 to GL1).

Sampling schedule, collection and treatments

Sampling for water and SPM was conducted during May, July, August and September 1998. During May and July, three different depths were selected in the Guadalquivir estuary (surface, medium and deep samples) for water and SPM analyses, during both high-tide and low-tide, otherwise only surface water was sampled. In May and September, sediments were also sampled.

Water samples were collected in acid-washed ruttner bottles made of polycarbonate, and rapidly transfered to 5 l polyethylene vessels and transported to the laboratory to be stored in the dark at 4°C until analyses. Due to this transportation conditions the metal measured in this aqueous phase could incorporate amounts of labile heavy metals from the particulate matter.

The amount of suspended solids was calculated by filtration through Millipore AP40 filters. Heavy metals in SPM were measured using the methodology of Loring and Rantala (1992): SPM was obtained by filtration using Nuclepore 0.4 μm polycarbonate

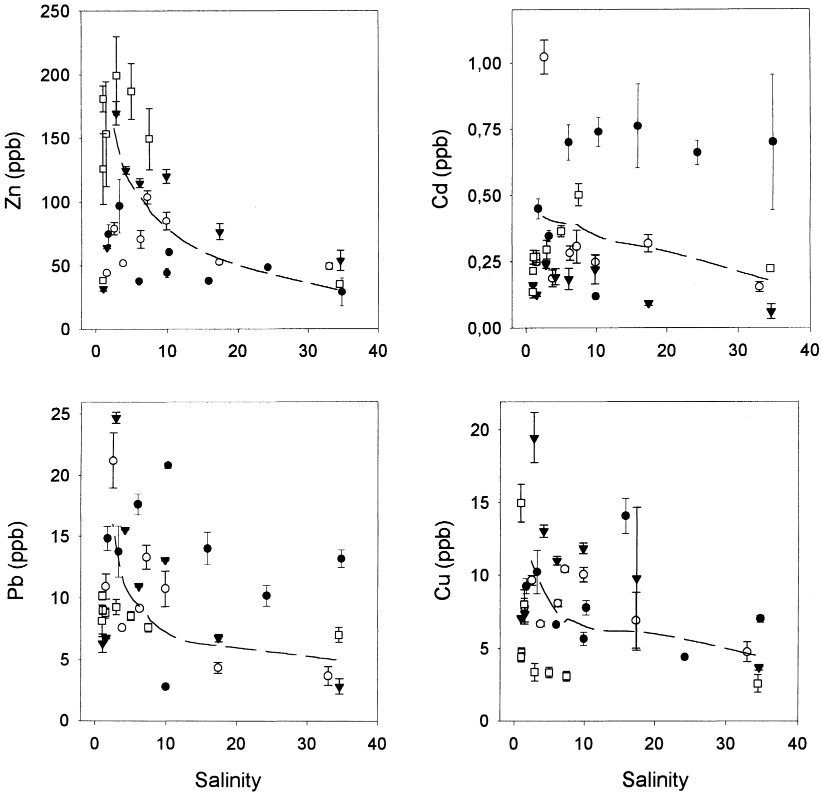

Fig. 2 Summarized heavy metal concentrations (Zn, Cd, Pb and Cu; µg l^{-1}) in water compared to salinity values during the four different sampling periods: squares – 05/1998; filled circles – 07/1998; empty circles – 08/1998; inverse filled triangles – 09/1998.

filter membranes, dried, then decomposed in teflon bombs using aqua regia:HF, 1:1 v/v mixtures (Merck, Suprapur).

Composite sediment samples (3–4 grabs per sample) were collected at each of the 14 selected stations (Fig. 1) with a 0.025 m^2 Van Veen grab. Only grabs that had achieved adequate penetration (2/3 of total volume) and that showed no evidence of leakage or surface disturbance were retained and the top 5 cm removed and transferred to a cooler. The contents of the cooler were homogenized with a teflon spoon until no color or textural differences could be detected. Then the coolers, chilled with ice, were transported to the laboratory. Sediment samples were maintained in the cooler at 4°C in the dark until processing and analysis, when the sediments were dried at 60°C and again gently homogenized. Sediment samples were totally digested following the method described by Loring and Rantala (1992): aqua regia:HF, 1:6 v/v mixtures (Merck, Suprapur).

To measure contamination in areas surrounding the Guadalquivir river, stations were selected in wetland areas along both left and right river margins, and water samples were collected as described above.

Prior to sample collection and between uses, all containers for the collection and storage of water, suspended solids and sediment samples were thoroughly cleaned with acid (10% HNO_3), and then rinsed in ultrapure water (Milli-Q).

Analytical methods

Concentrations of Zn, Cd, Pb and Cu in water, SPM and sediment were determined by differential pulse anodic stripping voltametry (DPASV). Measurements were taken with a hanging mercury drop electrode (HMDE), using a Methrom 693 processor. The quantification of the metal concentration was performed using the standard addition procedure by means of standard solutions for each metal (Titrisol, Merck). Concentrations of Fe and Mn were determined by flame AAS. The analytical procedure for dissolved metals was checked using reference material CASS3 with an accuracy of ±10%. The analytical procedure for solid extracts was checked using reference material (MESS-1 NRC and CRM 277 BCR) and allow agreement with the certified values higher than 90%.

Speciation of metals in sediments was determined following the method proposed by Tessier *et al.* (1979). According to this method, five sequential extractions are carried out (F1, F2, F3, F4 and F5). The F1 includes metals associated with sediment in the most easily changeable. The F2 extract metals united mainly with carbonates and is highly sensible to changes in the pH. In the F3 extraction we obtain the metals bonded to Mn and Fe oxides. The F4 fraction the metals associated with the organic material and sulfides are released. Finally, in the F5 fraction we obtain the 'residual' or 'lithogenic' fraction, a portion of metals that are

TABLE 1

Summarized values of dissolved and particulate heavy metals concentrations (Zn, Cd, Pb and Cu; μg l^{-1}) measured at the stations selected along the Guadiamar river; salinity is also provided.

	GR1	GR2	GR3	GR4	GR5	GR6
Dissolved (06/1998)						
Salinity	3.024	2.279	2.447	2.895	1.860	1.324
Zn	212.9	109.1	142.6	166.5	125.2	8.3
Cd	6.502	1.084	1.113	0.845	0.911	0.180
Pb	59.44	22.05	19.73	27.82	8.66	0.36
Cu	10.70	4.11	4.79	5.05	2.70	1.14
Dissolved (09/1998)						
Salinity	2.302	2.058	2.257	2.475	2.497	1.392
Zn	53.24	63.40	218.41	75.30	52.28	50.47
Cd	0.3045	0.3111	0.9086	0.4280	0.3487	0.2806
Pb	4.07	3.98	12.86	6.92	5.78	9.03
Cu	3.75	3.86	7.89	4.39	2.71	3.24
Particulate (09/1998)						
Zn	34.744	32.555	24.000	18.703	22.210	25.175
Cd	0.0078	0.0569	0.0132	0.0407	0.0261	0.0325
Pb	3.203	3.3331	3.1298	2.4947	2.3655	4.2094
Cu	8.4467	7.2244	10.1778	5.4671	4.4569	9.8527

strongly bonded to the lithogenic minerals of the sediments. We have modified the exchangeable fraction (F1) according to Kestern and Förstner (1986) and the residual or lithogenic fraction (total) according to Loring and Rantala (1992). The F1 (exchangeable), F2 (carbonates) and F3 (Fe and Mn oxyhydroxides) fractions were acidified to avoid re-adsorption (Belzile *et al.*, 1989). Also and separately for each station, the homogenized sediments were totally digested as described by Loring and Rantala (1992). Results are expressed as milligram per kilogram dry sediment for total analysis and as percentages for the speciation study. Percentage recovery was between 85% and 115% depending on the metal evaluated.

Salinity was measured by means of an induction salinometer (Beckman, RS-10). Quality assurance/quality control (QA/QC) procedures used in all the processes from the field to the final data followed those outlined by Kratochvil and Taylor (1981) and Taylor (1981).

Results and Discussion

Waters

Dissolved metal concentrations in the stations selected in the Guadalquivir estuary (GL1 to GL8) vs the salinity measured, during the four sampling times for high-tide and low-tide situations, are shown in Fig. 2. The estuary can be considered vertically homogeneous, showing little variation in salinity. Maximum concentrations of all metals were associated with low salinity (within the estuary). This non-conservative behaviour of metals has been reported in other estuaries and in general is related to precipitation or adsorption processes on the SPM of both organic and inorganic origin (see e.g., Benoit *et al.*, 1994). Summarized mean values for the metals were: at low salinity – Zn 125 μg l^{-1}, Cd 0.40 μg l^{-1}, Pb 15 μg l^{-1}, Cu 10 μg l^{-1}; at high salinity – Zn 50 μg l^{-1}, Cd 0.20 μg l^{-1}, Pb 7 μg l^{-1}, Cu 5 μg l^{-1}. These heavy metal concentration results agree with those obtained by Cordón *et al.* (1986) and Cabrera *et al.* (1987) in nearby stations in the Guadalquivir estuary except for the Zn concentrations, which are higher by a factor of four.

Table 1 provides summarized results for metal concentrations in water from the Guadiamar river at two different times. Higher values are for water sampled from station GR1 located close to the confluence with

TABLE 2

Summarized results for the concentration (average values expressed in mg of SPM per liter of water) of SPM along the Guadalquivir river (GL) and the Guadiamar river (GR).

Stations		Average SPM ($mg \cdot l^{-1}$)
Guadalquivir river		
GL1	(surface)	13.45
	(bottom)	17.14
GL2	(surface)	55.42
	(bottom)	113.21
GL3	(surface)	146.17
	(bottom)	167.87
GL4	(surface)	147.18
	(bottom)	275.17
GL5	(surface)	247.99
	(bottom)	310.96
GL6	(surface)	466.32
	(bottom)	609.41
GL7	(surface)	127.32
	(bottom)	888.90
GL8	(surface)	130.37
	(bottom)	279.82
Guadiamar river		
GR1		96.75
GR2		116.20
GR3		131.65
GR4		127.85
GR5		107.00
GR6		117.65

the Guadalquivir. Lower values for all metals were determined at station GR6. Particularly high values were measured for Zn at station GR1 during June. Metal levels measured in the river were lower than levels obtained in the Guadalquivir estuary, except for Zn and Cd in June. Levels of Cd were high at the confluence of the two rivers, with a maximum of 6.5 μg l^{-1}. September values were lower than those obtained in June, probably related to the effectiveness of the emergency treatment plant installed after the June sampling.

Suspended solids

Summarized results for SPM are shown in Table 2. These data were used to calculate metal concentrations in SPM per liter of water. Figure 3 shows the summarized results of metal (Zn, Cd, Pb, Cu, Fe and Mn) concentrations in SPM vs salinity. All metal concentrations showed a similar pattern to the results obtained in water; the highest levels of all metals and for all depths were at low salinity, inside the estuary. This pattern is related to the progressive dilution process associated with the tides. Summarized average values for metals were: at low salinity – Zn 50 μg l^{-1}, Cd 0.15 μg l^{-1}, Pb 5 μg l^{-1}, Cu 11 μg l^{-1}, Fe 10 mg l^{-1}, Mn 0.05 mg l^{-1}; at high salinity – Zn 5 μg l^{-1}, Cd 0.01 μg l^{-1}, Pb 0.5 μg l^{-1}, Cu 2 μg l^{-1}, Fe 5 mg l^{-1}, Mn 0.01 mg l^{-1}. These values of the heavy metal concentrations are, except for Fe, similar than those obtained by Cordón *et al.* (1986) in the Guadalquivir estuary. Metal concentrations in

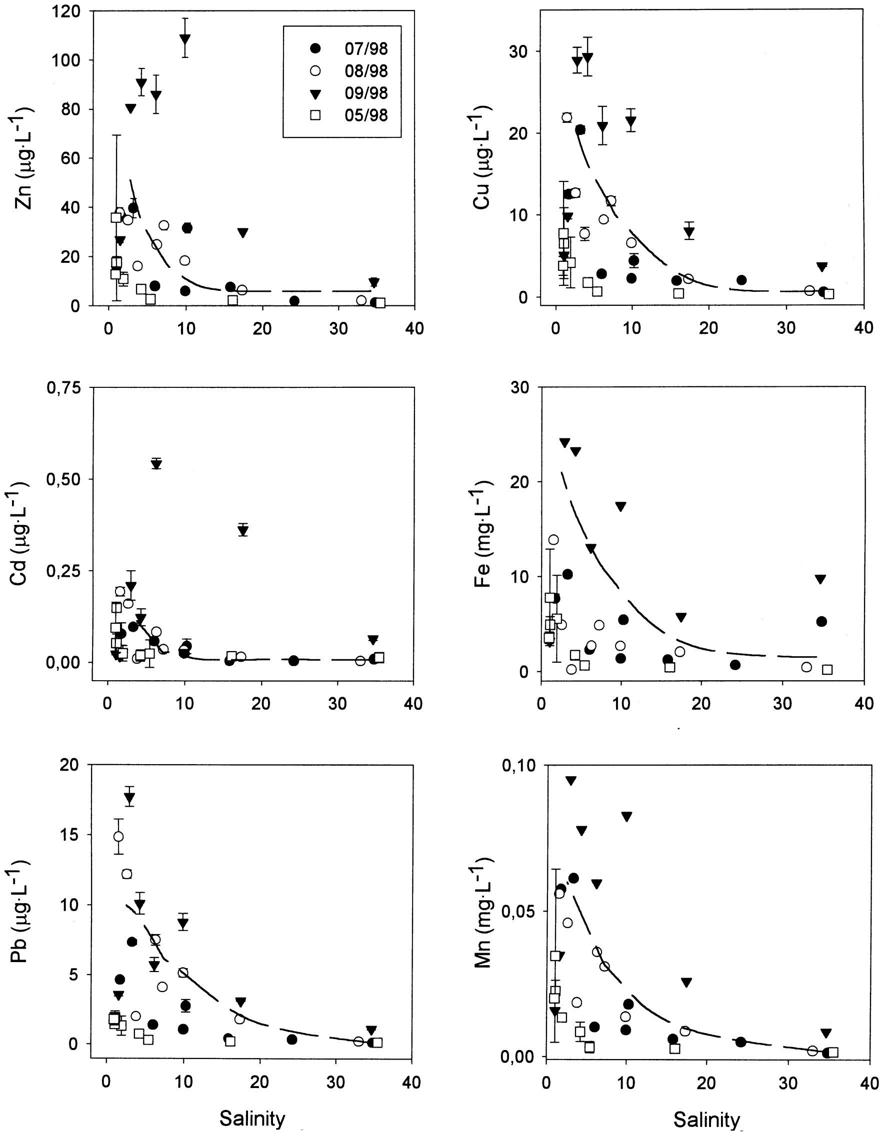

Fig. 3 Summarized metal concentrations (Zn, Cd, Pb, Cu, Fe and Mn) in SPM per liter of water compared to salinity values the during four different sampling periods: squares – 05/1998; filled circles – 07/1998; empty circles – 08/1998; inverse filled triangles – 09/1998. The concentration of Zn, Cd, Pb and Cu is expressed in μg l^{-1}. The concentration of Fe and Mn is expressed in mg l^{-1}.

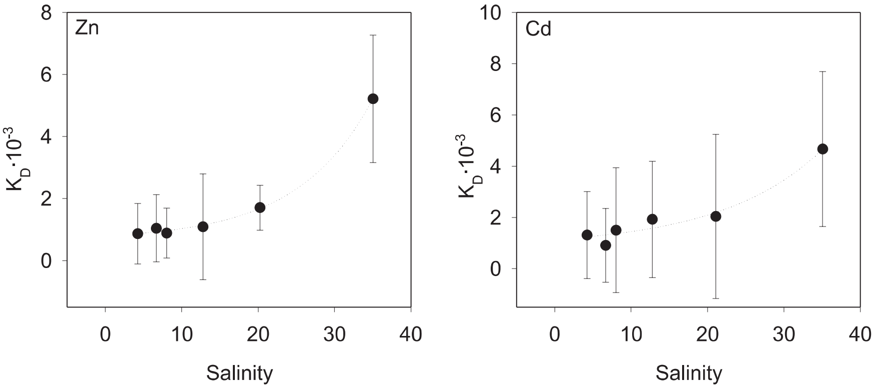

Fig. 4 Averaged partitioning coefficient between the concentration of heavy metals (Zn and Cd) in SPM and that in water (K_D) as a function of the salinity.

SPM from the Guadiamar river showed the same pattern as those for waters (Table 2).

The adsorption capacity of the SPM produces high values of the averaged partition coefficient (K_D). This K_D is defined as the ratio between the concentration of the heavy metal in SPM and that dissolved in the water. In Fig. 4 are shown the average K_D values obtained for the stations located in the Guadalquivir estuary vs the salinity values.

Sediments

Total sediment concentrations. Table 3 shows, as an extracted example, the summarized results of total metal concentrations in sediment from stations GL2 and GL6 for May and September. For both sampling dates, the concentrations of heavy metals in sediments from station GL6 near the Guadiamar river confluence were higher than those from station GL2, except for Cu, Fe and Mn in May. Zn and Cd concentrations at station GL6 in May were more than twice as high as those measured at station GL2. In general and for all metals, sediment concentrations were higher in May than in September. These data are similar to the results by Cordón *et al.* (1986) for the Guadalquivir estuary, except for Zn at station GL6 during May. These data appear to be related to an input of Zn from the incident in May, while decreased concentrations measured in September appear to be due to the clean-up efforts and associated with the strong hydrodynamics of the estuary.

Apart from Zn and Cd, the other values are similar to those obtained in the Bay of Cádiz and Barbate river (Table 3). However, all the values except for Mn are very much lower than those monitored in the mining area of Huelva (Tinto and Odiel rivers), giving an interesting indication of the fundamental difference between the long-term effects of continuous heavy metal discharge over centuries and the effect of an isolated, albeit very large, single discharge.

Chemical speciation of metals in sediments. Chemical speciation of metals in sediments for stations GL2 and GL6 shows how the different metals associate with different geochemical sediment matrices. In general, the distribution for each metal could be described as: Cd – about 90% distributed between three different fractions (F2, F3, F5), predominantly associated with the carbonate (F2) fractions (39%); Cu – about 60% distributed between two principal fractions (F4 and F5), somewhat more associated with organic matter (F4) (31%); Pb – about 90% of the total was found in two different fractions (F3 and F2), more predominantly associated with Fe and Mn oxyhydroxides (F3) (55%); Mn: 90% distributed evenly between three different fractions (F2, F3, F5).

Figure 5 shows the distribution of Zn and Fe in different geochemical fractions for the two selected stations. About 90% of the total iron measured in sediments was in the residual or lithogenic fraction (F5) for both stations, with the carbonates fraction (F2) representing between 6% and 11%. For Zn, speciation was distributed in different fractions: at station GL2, the

TABLE 3

Summarized results for the metals Fe, Mn, Zn, Cd, Pb and Cu measured in sediments at the stations GL2 and GL6 in Guadalquivir river (mg kg^{-1} dry sediment)[a].

	Zn	Cd	Pb	Cu	Fe	Mn
(*05/1998*)						
Station 2	166	0.58	28.7	18.5	23697	535
Station 6	395	1.38	33.8	13.1	14660	412
(*09/1998*)						
Station 2	109	0.27	18.4	9.8	8769	173
Station 6	157	0.46	22.5	11.1	12828	351
Bay of Cadiz	135	0.71	55.5	44.2	31258	277
Barbate river	84	N.D.	33.1	36.6	28859	293
Tinto river	2810	15.60	2915.0	2403.0	10700	193
Odiel river	1558	4.40	928.0	1070.0	76000	305

[a] Mean values are also provided for the Bay of Cádiz, Barbate river, Tinto river and Odiel river (Ria of Huelva) (Cordón *et al.*, 1986, Pérez *et al.*, 1991; DelValls *et al.*, 1998).

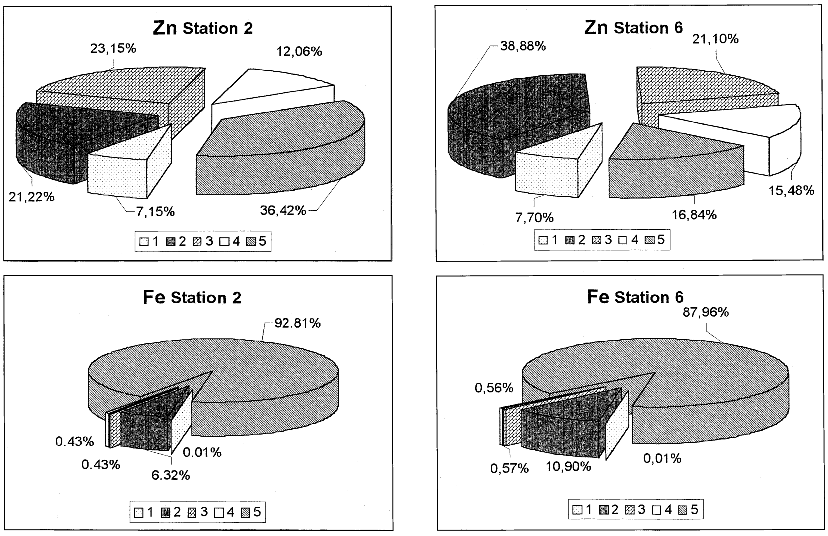

Fig. 5 Example of partitioning of Zn and Fe in the five geochemical fractions: F1 (exchangeables), F2 (carbonates), F3 (Fe and Mn hydroxides), F4 (organic matter), F5 (lithogenic or non-reactive fraction) in sediments from GL2 and GL6.

TABLE 4

Ratio of average Pb, Zn, Cu and Cd concentrations (mg kg^{-1} dry weight) in superficial sediments from the Guadalquivir estuary (GL#) and the Guadiamar river (GR#) to benchmark and site-specific sediment quality values (SQVs) proposed by different authors[a].

	SQVs	GL1	GL2	GL4	GL5	GL6	GL7	GL8	GR1	GR4	GR6
Pb											
(a)	*60*	0.57	0.48	0.47	0.47	0.56	0.47	0.50	0.60	0.64	0.96
(b)	*250*	0.14	0.11	0.11	0.11	0.14	0.11	0.12	0.14	0.15	0.23
(c)	*110*	0.31	0.26	0.26	0.26	0.31	0.26	0.28	0.33	0.35	0.52
(d)	*450*	0.08	0.06	0.06	0.06	0.08	0.06	0.07	0.08	0.09	0.13
(e)	*84.6*	0.41	0.34	0.33	0.33	0.40	0.33	0.36	0.42	0.45	0.68
Zn											
(a)	*200*	0.72	0.83	_1.47_*	_1.69_*	_1.98_*	_1.26_*	_1.68_*	_3.72_*	0.89	_1.39_*
(b)	*800*	0.18	0.21	0.37	0.42	0.49	0.31	0.42	_0.93_*	0.22	0.35
(c)	*270*	0.53	0.62	_1.09_*	_1.25_*	_1.47_*	_0.93_*	_1.24_*	_2.75_*	0.66	_1.03_*
(d)	*410*	0.35	0.41	0.72	0.83	0.96	0.61	0.82	_1.81_*	0.43	0.68
(e)	*225*	0.64	0.74	_1.31_*	_1.51_*	_1.76_*	_1.12_*	_1.49_*	_3.30_*	0.79	_1.23_*
Cu											
(a)	*50*	_1.43_*	0.37	0.85	_1.08_*	0.26	0.30	0.33	0.84	_0.99_*	_1.05_*
(b)	*114*	0.63	0.16	0.37	0.47	0.12	0.13	0.15	0.37	0.43	0.46
(c)	*390*	0.18	0.05	0.11	0.14	0.03	0.04	0.04	0.11	0.13	0.13
(d)	*390*	0.18	0.05	0.11	0.14	0.03	0.04	0.04	0.11	0.13	0.13
(e)	*98*	0.73	0.19	0.43	0.55	0.13	0.15	0.17	0.43	0.50	0.54
Cd											
(a)	*6*	0.13	0.10	0.14	0.10	0.23	0.13	0.14	0.51	0.21	0.15
(b)	*9*	0.08	0.06	0.09	0.07	0.15	0.09	0.10	0.34	0.14	0.10
(c)	*10*	0.08	0.06	0.08	0.06	0.14	0.08	0.09	0.31	0.13	0.09
(d)	*5.1*	0.15	0.11	0.16	0.12	0.27	0.15	0.17	0.60	0.25	0.18

[a] (a) US Environmental Protection Agency (Army Corps of Engineers, 1977); (b) Ontario Ministry of Environment (Persaud *et al.*, 1989); (c) National Oceanic and Atmospheric Administration (Long *et al.*, 1995); (d) Washington State (Washington State Department of Ecology, 1991); (e) Gulf of Cádiz and San Francisco Bay (DelValls and Chapman, 1998).

lithogenic fraction (F5) was predominant, at 36%, with the Fe and Mn oxyhydroxides fraction (F3) and the carbonates fraction (F2) second and third in importance (with 23% and 21%, respectively); at station GL6, the Zn was more predominantly associated with the carbonates fraction (F2), at about 39% of the total, while 21% was associated with the Fe and Mn oxyhydroxide fraction (F3), none of the residual fractions comprising more than 17%. These two different fractionation behaviours in sediment are related to the distinct nature of the two metals, the zinc associating more with the exchangeables matrix in sediment and the iron more with the minerals.

In general, the heavy metals Pb, Cu, Fe and Mn associate to non-easily changeable fractions (F4 and F5) being more associated to reactive fractions in the station

GL6. On the other hand, metals Zn and Cd, which associate mainly with the reactive fractions (F1, F2 and F3), are notably higher in the station GL6. The concentration of metals in these fractions is related to a potential bioavailability because they represent the proportion of heavy metals that can be easily remobilized by changes in the environmental conditions such as pH, salinity, redox potential, etc. It demonstrates that sediments at station GL6 are more polluted with Zn and Cd than sediments at station GL2 and could be associated with a potential ecological risk.

Potential adverse effects associated with the levels of metals

The potential for adverse effects on biological organisms at the metal levels measured in the sediments was evaluated, based on comparisons with available sediment quality values (SQVs). In the absence of sediment values specific to the estuary studied, our results have been compared with values derived from other areas (Table 4).

In order to quantify the relative hazard to aquatic biota posed by the presence of the metals in superficial sediments, hazard indices (ratios) were calculated (Table 4) by dividing the average concentrations found at each station by the proposed SQVs. A ratio of 1.0 or higher was taken to indicate a sediment metal concentration potentially associated with an adverse effect on benthic biota. On this basis, Zn concentrations in superficial sediments are of concern for stations GL4, GL5, GL6, GL7 and GL8 in the Guadalquivir estuary and GR6 in the Guadiamar river. Of greatest concern is the Zn concentration (744 mg kg^{-1}) at station GR1 at the confluence of the two rivers, for which all the SQVs were exceeded and ratios higher than 3.5 were calculated. Integrative assessments including sediment toxicity evaluations should be conducted on these sediments to determine whether adverse biological effects are manifest.

Contamination of surrounding areas

The results obtained for Zn, Cd, Pb and Cu measured in waters sampled in different wetland areas surrounding the Guadiamar and the Guadalquivir rivers, including areas inside the National Park of Doñana, are shown in Fig. 6. Values for Zn ranged between 1195 and 25; for Pb, between 10 and 0.4; for Cd, up to 4.5; for Cu, between 11.8 and 2.3 μg l^{-1}.

High concentrations of Zn and Cd are especially notable on the left margin of the river, being higher than those obtained in wet areas located to the right margin of the river. Concentrations of metals were especially high in two different samples at stations E (Zn 689.9 μg l^{-1}; Cd 0.78 μg l^{-1}) and B (Zn 1195.8 μg l^{-1}; Cd 4.53 μg l^{-1}). Station E was located in a wastewater channel running from rice-fields close to the emergency treatment plant. Station B was located in one of the channels leading from the Guadalquivir river to the National Park of Doñana. These values compared to those obtained by Cabrera *et al.* (1987) in the same area are notably higher (by a factor of about 10). The Zn concentrations were higher than two orders of magnitude than the usual maximum concentration obtained in coastal areas (e.g., for UK estuaries: Zn 10–25 μg l^{-1}; Cd 0.01–0.17 μg l^{-1}; Pb 0.01–0.13 μg l^{-1}; Cu 2–3 μg l^{-1}, Bryan and Langston, 1992).

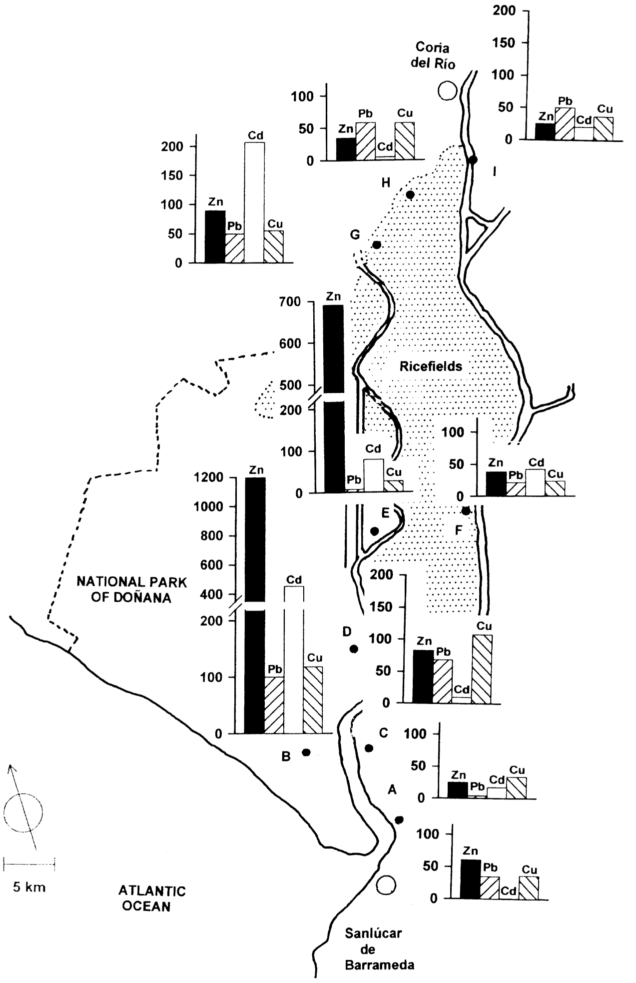

Fig. 6 Map of the wetlands associated with the Guadalquivir river and the Doñana Park showing the Zn, Pb, Cd and Cu concentrations. The concentration of metals was expressed as: Zn, μg l^{-1}, Pb and Cu × 10 μg l^{-1} and Cd × 100 μg l^{-1}.

Elevated concentrations of metals were also measured in samples collected close to the rice-fields. These values need to be confirmed and their potential adverse biological effects evaluated.

Conclusions

The heavy metals in the estuary show a non-conservative behaviour, which has been reported before for other areas around the world. This kind of pattern is mainly due to the incorporation of metals to the suspended solid phases in the estuary. However, the global transport of the heavy metals seaward of the estuary is carried out in the dissolved phase.

High measured concentrations of Zn and Cd in the estuarine environmental compartments (water, suspended solids and sediments) are due to the accident at the mine in Aznalcóllar. There is an enrichment of Zn in sediments sampled at the confluence of the Guadiamar and Guadalquivir rivers. This metal is predominantly associated with the more exchangeable geochemical fractions in sediments. Only the Zn concentrations are of concern when compared with national and international SQVs.

High concentrations of Zn and Cd measured in wetlands associated with both rivers and associated with the National Park of Doñana areas indicate that the contamination reached the Park.

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