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Influence of the Aznalcóllar mining spill on the vertical distribution of heavy metals in sediments from the Guadalquivir estuary (SW Spain)

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Abstract

The Natural Park of Doñana and the Guadalquivir estuary were impacted by the release of 6 million cubic meters of acid waste after the mine-tailing spill in Aznalcóllar (Andalusia, SW, Spain). Here is presented the monitoring of the accidental spill on vertical distribution of heavy metals in the estuarine sediments. The total concentration of six metals (Fe, Mn, Zn, Cd, Pb, Cu), their chemical speciation and the organic carbon concentration were analyzed in sediment vertical profiles. The results obtained determine background levels similar to previously reported in the area. The analysis catalogues the impact of the accident on the estuary as acute and mainly associated with high concentrations of Zn and Cd. The recent enrichment in Zn and Cd and their geochemical association with the more mobile fractions of the sediment determine an environmental risk associated with the acute impact and detected in some of the areas of the estuary. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Doñana; Guadalquivir estuary; Heavy metals; Aznalcóllar acid mine waste; Sediment pollution; Chemical speciation

1. Introduction

On 25th April 1998 part of the tailings pond dike of the "Los Frailes" zinc mine, situated in Aznalcóllar collapsed, releasing an estimated 4 million cubic meters of acidic water and 2 million cubic meters of toxic mud rich in toxic metals over the next 5 days. The Aznalcóllar accident is one of the worst disasters related to acute pollution ever recorded in Spanish history. It damaged about 4328 ha situated at both shores of the Guadiamar river. It occurred in the vicinity of the Doñana National Parks and affected the Doñana Natural Park. Doñana National Park is the major marsh protected area in Europe which harbors 70% of all European bird species (Grimalt and Macpherson, 1999). Because of its international importance 120 000 ha of Doñana Area (National and Natural Parks) have been protected under national, regional, EU or international law and conventions. There are also important areas that remain without legal protection such as the southern Guadalquivir estuary which provide the water quality to maintain the ecological health in the Doñana Parks.

Heavy metals tend to be trapped in estuaries and are thus of particular concern in this environment. Metal concentration in the particulate form are 3–5 order of magnitude higher than in the dissolved form as reported by Gómez-Parra et al. (2000) for the Guadalquivir estuary after the mining spill. Because of their large adsorption capabilities, fine-grained sediments represent a major repository for heavy metals and a record of the temporal changes in contamination. Thus, they can be used for historical reconstruction. Vertical profiles of pollutant species in sediment cores have been commonly used as "pollution records" over the last two decades (see review by Valette-Silver, 1993).

Metals accumulated in this way may be subsequently released to the overlaying water column as a result of either physical disturbance, or diagenesis, and the sediments may persist as a source of pollutants long after the cessation of direct discharges. Understanding of the ecological significance of marine sediment contamination by heavy metals has been advanced by numerous studies (i.e., Bryan and Langston, 1992). It is necessary

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to have the more exact information on the physicochemical forms in which heavy metals exist in sediments. In this sense, sequential extraction permits us to precise the origin of metals and to better understand their geochemical cycles and mobility. From the geochemical partitioning studies it can be inferred which amount of heavy metal could be more biologically available (Luoma and Davis, 1983). However, it should be confirmed as potential risk to the environment. Nowadays comparison of total concentration of heavy metals measured in sediments has been performed to benchmark and sediment quality values (DelValls et al., 1997, 1998a,b). Furthermore, the comparison performed using those concentrations of heavy metal associated with different geochemical fractions should inform more precisely of the environmental risk.

The aims of this work therefore are to assess both the vertical profile concentrations of Fe, Mn, Zn, Cd, Pb and Cu in sediment cores of the estuary, and the chemical form in which they occur to determine the impact of the accident. We have used the sediment cores to detect and to assess the impact of the Aznalcóllar tailing–mining spill on the vertical distribution of Fe, Mn, Zn, Cd, Pb and Cu. The results have been combined to define the recent enrichment of heavy metals in the estuarine surface sediments and to establish the background levels in the area. Also the environmental risk associated with the heavy metal total concentrations and with their geochemical fractionation in sediment was evaluated.

2. Material and methods

2.1. Approach

At Aznalcóllar the zinc, lead, copper and manganese-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 river which is a major tributary of the Guadalquivir (Fig. 1(a)). The threat posed to the Doñana parks through inputs of metals by mining activities from the Guadiamar and Guadalquivir rivers has been studied previously to the accidental spill (Cabrera et al., 1987; Albaiges et al., 1987; Arambarri et al., 1996). Also, the early impact of the Aznalcóllar tailing–mining spill has been characterized (DelValls et al., 1999; Gómez-Parra et al., 2000).

We have selected two stations in the Guadalquivir estuary based on the previous studies carried out in the area (Gómez-Parra et al., 2000; Riba et al., 2000) to cover the influence of the contamination from the Aznalcóllar accident in the vertical distribution of the heavy metals (Fig. 1(b)). The GL6 station is located in the confluence of the Guadalquivir river and the Guadiamar river and their surface sediments have been cataloged as impacted by the mining spill (Riba et al., 2000). These same studies cataloged the station GL2 as low impacted by the accident.

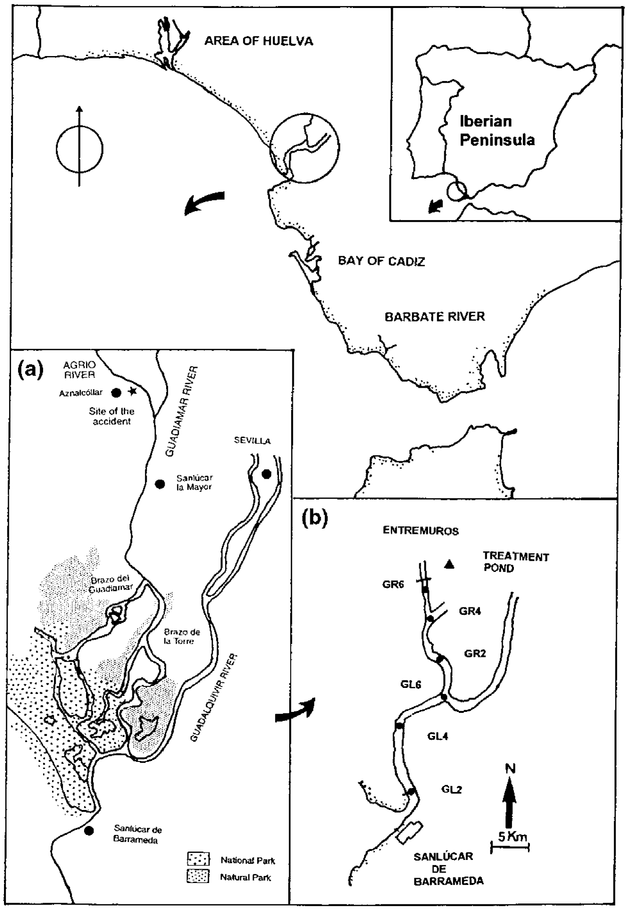

Fig. 1. Map of the Gulf of Cádiz showing the general areas of Barbate river, Bay of Cádiz, Guadalquivir estuary and the area of Huelva. Detailed areas of the Guadalquivir river and the Guadiamar river are showing the locations of the sampling stations GL2 and GL6.

One sediment core was taken in each station during September 1998. The samples were collected by scuba divers, and were transported refrigerated to the laboratory within 3 h. Different depths were selected for the sediment cores sampled at the two stations. In the first 5 cm from the surface, the samples were taken every 1 cm, and then about every 5 cm to reach the maximum depth of 28 cm in the sediment cores sampled at the GL6 station. The maximum depth was of 40 cm in the sediment cores sampled at the GL2 station. The vertical contaminant profiles in the sediment cores assess changes from before to after the accidental spill.

Prior to sample collection, all beakers for the collection and storage of sediment samples were thoroughly cleaned with acid (10% HNO_3), and then rinsed in double-distilled (Milli-Q) water before each use.

2.2. Analytical methods

The sediment was dried at 60°C prior to chemical analysis. Dried sediments were gently homogenized. Solid samples were totally digested following the method described by Loring and Rantala (1992). The speciation of the metals in the homogenized sediments were determined following the method proposed by Tessier et al. (1979) modifying 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). A detailed protocol of the fractionation scheme is described in Table 1. Also and separately for the same station, the homogenized sediments were totally digested such as described by Loring and Rantala (1992) to calculate the percent of recovery for each metal and sample (96 ± 10%). Heavy metals bound to the three first fractions are considered as much more susceptible to remobilization than metals which reside in the lattices of sediment minerals (Luoma and Davis, 1983; Förstner et al., 1989). These fractions would include metals from anthropogenic sources and therefore give some indication of the degree of pollution to which a particular sediment has been exposed. Metals reporting to the lithogenic fraction (residual) could be interpreted as originating from geochemical or natural sources (Coetzee, 1993). The variation of the association of the heavy metals with depth could inform us about a recent enrichment of heavy metals if the concentrations of heavy metal associated with the more mobile fractions ($F1$, $F2$ and $F3$) are higher in the surface than in the bottom of the core. In the case of similar pattern in the association of the heavy metals with the depth it will describe a constant input with the same origin of the heavy metals.

The concentrations of cadmium, lead, copper and zinc were determined by differential pulse anodic stripping voltammetry (DPASV). Measurements were taken with static drop mercury electrode (SMDE), using the Methrom 693 processor. The Fe and Mn concentrations were determined by flame AAS. The analytical procedure was checked using reference material (MESS-1 NRC and CRM 277 BCR) with a percent of recovery higher than 90%.

The organic carbon concentration was determined using El Rayis (1985) method.

Quality assurance/quality control (QA/QC) procedures used in all the processes from the field to the final data were followed from those outlined by Kratochvil and Taylor (1981) and Taylor (1981).

To evaluate the environmental risk two different factors for the heavy metals Zn, Cd, Pb and Cu were included in the analysis. The enrichment factors (EFs) and the environmental risk factor (ERF) defined as,

$$\mathrm{EF} = \frac{C_i - C_0}{C_0}, \qquad \mathrm{ERF} = \frac{C_i - C_{\mathrm{SQV}}}{C_{\mathrm{SQV}}},$$

where C_i is the heavy metal concentration measured in the cores and corresponds to the total concentration for both factors. It also corresponds to the sum of the concentration of each heavy metal in the $F1$, $F2$ and $F3$ fractions for the enrichment factor defined for the reactive fraction. In the case of the calculation of EFs for the lithogenic fraction this C_i concentration corresponds with that measured in the $F5$ fraction. The term C_0 is the heavy metal background level established for cores in this study and for each kind of heavy metal concentration: total concentration, reactive concentration and lithogenic concentration. This concentration is that measured at the samples taken at the highest depth of the sediment cores for each station. The term C_{SQV} is the highest concentration of the studied heavy metals non-associated with biological effects. The C_{SQV} concentrations were calculated from the site-specific quality values reported by DelValls and Chapman (1998). The EF values facilitate the identification and quantification of the metal enrichment and the ERF establish those stations with heavy metal concentrations associated with an environmental risk.

3. Results and discussion

3.1. Organic carbon

Vertical profiles for the organic carbon concentration in sediment cores sampled at stations GL2 and GL6 are shown in Fig. 2. The organic carbon concentrations in

Table 1
Reagents and conditions employed in the sequential extraction procedure[a]

Fraction	Extraction reagent	Extraction conditions
Exchangeable	1 M $MgCl_2$ at pH 7	Shaken at room temperature for 1 h
Carbonate	1 M NaOAc ajusted to pH 5 with HOAc	Shaken at room temperature for 5 h
Fe–Mn oxides	0.04 M $NH_2OH \cdot HCl$ in 25 (v/v) HOAc	Shaken at 96°C for 6 h
Organic matter	0.02 M $HNO_3 + H_2O_2$ (adjusted to pH 2 with HNO_3 On cooling add 3.2 M NH_4O ac in 20% (v/v) HNO_3)	Shaken occasionally at 85°C for 5 h then shaken on addition of NH_4 Oac for a further 0.5 h
Lithogenic	Aqua regia, HF	As for total metal analysis

[a] Method based on Tessier et al. (1979) as modified by Kestern and Förstner (1986) for the $F1$ fraction and according to Loring and Rantala (1992) for the residual or lithogenic fraction.

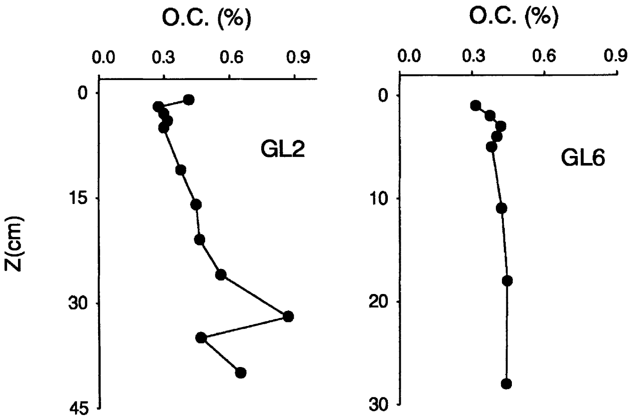

Fig. 2. Vertical distribution of percentage of total organic carbon (dry weight) in sediment cores sampled at the two selected stations in the Guadalquivir estuary.

the sediment cores ranged between <0.3 (1 cm, GL2) and about 0.9 (30 cm, GL2) (% dry weight). The vertical profile for each station shows a different pattern. In the station GL6 the organic carbon concentration increases until it reaches a maximum of about 3–4 cm. Then the variation of the organic carbon concentration is about constant with depth. For the GL2 station the organic carbon decreases from the surface value until it reaches a minimum of about 2 cm and then shows and increases until about 30–35 cm. These vertical profiles have been used to normalize the total concentration of the heavy metal measured in the same sediment core samples. It has been long recognized that the organic carbon concentrations can be used for normalization procedure related to heavy metal pollution studies (i.e., Chapman et al., 1987; DelValls et al., 1998c).

These vertical distribution values are quite lower than those organic carbon concentration profiles measured in other littoral areas (Fig. 1) from the Gulf of Cádiz (Ponce et al., 2000; Blasco et al., 2000). This fact can be related to the high hydrodynamic of the area and the periodic dredging events to permit the navigation through the Guadalquivir river.

3.2. Heavy metal total concentrations

Table 2 shows the total concentration of Zn, Cd, Pb, Cu, Fe and Mn measured at the higher depth and defined

Table 2
Background levels of Zn, Pb, Cd, Cu, Fe and Mn calculated for the two studied stations in the Guadalquivir estuary and compared to previously reported values obtained for other areas located in the Gulf of Cádiz[a]

Metal	Station	Area	Reference
Zn	GL2 (123)	Bay of Cádiz (127)	Ponce et al. (2000)
		Barbate salt-marshes (80)	Cabrera et al. (1987)
	GL6 (156)	Doñana (148)	Cabrera et al. (1987)
		Tinto river (1968)	Cabrera et al. (1992)
		Standard fossil (95)	Turekian and Wedepohl (1961)
Pb	GL2 (23.6)	Bay of Cádiz (38.8)	Ponce et al. (2000)
		Barbate salt-marshes (32.6)	Cabrera et al. (1987)
	GL6 (23.9)	Doñana (30.5)	Cabrera et al. (1987)
		Tinto river (1772)	Cabrera et al. (1992)
		Standard fossil (20)	Turekian and Wedepohl (1961)
Cd	GL2 (0.16)	Bay of Cádiz (0.16)	Ponce et al. (2000)
		Barbate salt-marshes (1.2)	Cabrera et al. (1987)
	GL6 (0.18)	Tinto river (6.7)	Cabrera et al. (1992)
		Standard fossil (0.3)	Turekian and Wedepohl (1961)
Cu	GL2 (23.1)	Bay of Cádiz (61)	Ponce et al. (2000)
		Barbate salt-marshes (34)	Cabrera et al. (1987)
	GL6 (12.3)	Doñana (30)	Cabrera et al. (1987)
		Tinto river (1389)	Cabrera et al. (1992)
		Standard fossil (45)	Turekian and Wedepohl (1961)
Fe	GL2 (1.42)	Bay of Cádiz (2.9)	Establier et al. (1985)
		Barbate salt-marshes (2.7)	Cabrera et al. (1987)
	GL6 (1.43)	Ría del Odiel (11.4)	Blasco et al. (2000)
		Standard fossil (4.7)	Turekian and Wedepohl (1961)
Mn	GL2 (433)	Bay of Cádiz (351)	Establier et al. (1985)
		Barbate salt-marshes (268)	Cabrera et al. (1987)
	GL6 (234)	Doñana (478)	Cabrera et al. (1987)
		Tinto river (214)	Cabrera et al. (1992)
		Standard fossil (850)	Turekian and Wedepohl (1961)

[a] Also the background levels calculated using the standard fossil by Turekian and Wedepohl (1961) is included. Concentrations are expressed as mg Kg^{-1} dry sediment except for Fe expressed as %.

as the background levels in the two stations. These concentrations are compared to previously reported background levels in the area and also in other areas in the Gulf of Cádiz. The values were also compared to those from the standard fossil proposed by Turekian and Wedepohl (1961). The only background levels higher in the GL6 than in the GL2 station were associated with Zn. For Pb, Cd and Fe were about the similar values. For heavy metals Cu and Mn were higher in GL2 station than in GL6. For all metals, except Mn, background levels were lower or similar to those previously reported in the area (Doñana). For all the metals, except Zn in the GL6 station and Zn in GL2 (higher than Barbate area) the values were similar or lower than those proposed for the Bay of Cádiz and the salt-marshes of the Barbate river. The industrial area of Huelva presented for all the metals the highest background levels.

Fig. 3 shows the vertical distribution for the six metals after normalizing their concentration to the concentration of organic carbon. Vertical profiles of Fe, Mn, Zn, Pb and Cd show similar pattern in GL6 station at the confluence of both rivers, with maximum values in surface and about a constant value after the 10 cm in depth, except for Zn that decreases. For Cu a maximum is measured in the first 2–3 cm to reach a minimum about 5 cm, increasing the concentration with depth to reach a maximum in the bottom. For GL2 station the concentrations of Zn, Pb and Fe show fluctuating values versus depth, ($\sim$130, $\sim$280) in Zn; ($\sim$30, $\sim$60) in Pb; and ($\sim$10 000, $\sim$30 000) in Fe. For Cu and Mn the maximum values appear at about 30 cm (45 mg kg^{-1}) for Cu and 35 cm (900 mg kg^{-1}) for Mn. The distributions of Cd show a maximum value at surface decreasing with depth to a constant value of (0.2 mg kg^{-1}) after 10 cm.

Fe, Mn and specially Zn concentrations measured in sediment core samples at GL6 stations showed higher values than in the sediment core at GL2 for all the depths. It is noted how the concentration of Zn reach a value of 675 mg kg^{-1} in the surface decreasing to values of about 450 mg kg^{-1} at 30 cm. From this description it can be inferred that vertical profiles at station GL6 were affected for recent inputs of heavy metals from the Aznalcóllar mining spill, specially in the case of the Zn vertical distributions. It also may be detected as an effect of the accidental spill on the vertical profiles of Fe, Mn, Pb and Cd. Because Fe and Mn are heavy metals related to the geochemical matrix their variation between station could be associated with different facts: the dredging that periodically occur in the area to maintain navigation in the river, the location of the GL6 station that can be more affected by overflow events of the Guadiamar river during rainy years, differences in hydrodynamic, etc. The concentrations of Pb, Cd and Cu are similar in the GL6 and in the GL2 stations for most of the measured depths of the core. The distributions of Cu show higher values at deeper. These patterns could be associated with different sources of these heavy metals than the accidental spill. Gómez-Parra et al. (2000) report a potential source of Cu in the Guadalquivir transported by the coastal dynamic and the littoral currents from the chronic affected area of Huelva. For Cd this affirmation should be taken with care because the high variability of the results in the first 5 cm from the GL2 station.

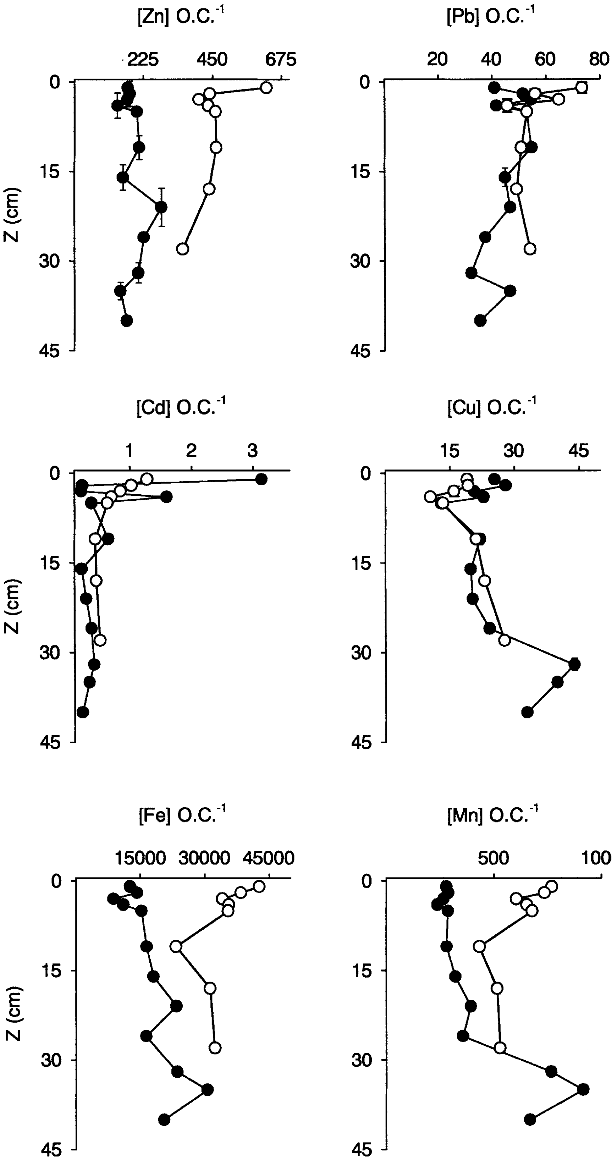

Fig. 3. Vertical profiles of the heavy metal (Zn, Pb, Cd, Cu, Fe and Mn) concentrations (mg kg^{-1}-dry weight) normalized to organic carbon concentrations (% dry weight) in the sediment cores sampled at the two studied stations in the Guadalquivir estuary (filled circles GL2 and empty circles GL6).

3.3. Environmental risk factor

In order to establish the potential risk effects of the measured enrichment by Zn, Cd, Cu and Pb in the

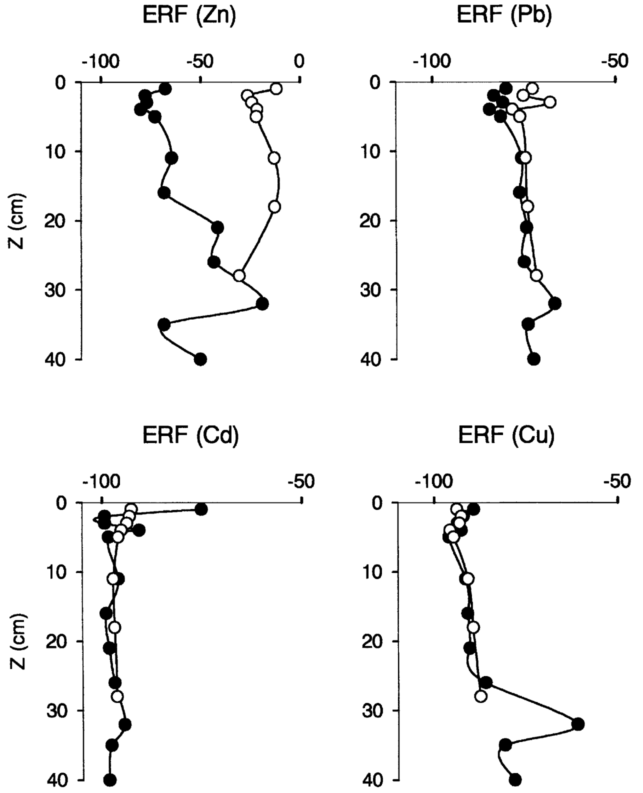

Fig. 4. Vertical profiles of the heavy metal (Zn, Cd, Pb and Cu) environmental risk factors for the sediment cores sampled at the two stations selected in the Guadalquivir estuary (filled circles GL2 and empty circles GL6).

studied area the ERFs were calculated by comparison of the measured concentration of heavy metals in surface sediment versus sediment quality values (DelValls and Chapman, 1998). The concentration of Fe and Mn were not taken into account in the calculation because they have not been associated with toxic effects at their environmental concentration.

The results of these calculations (ERF factors) expressed as percentage are presented in Fig. 4 for both cases at the GL2 and GL6 stations and for the Zn, Pb, Cd and Cu. The positive values of the factor inform us about a potential adverse biological effect associated with the metal. Only the ERF values associated with Zn present values close to 0 in the station GL6 being higher than those measured in GL2 station. For the Pb, Cd and Cu the ERF were lower than −50 so not of concern for both stations. Based on the obtained results the concentration of Zn analyzed in sediments sampled in the sediment core from the station GL6 were close to those quality values and could have affected to the ecosystem. These results inform about a potential stress on the ecosystems from the sediments located in the Guadiamar river and those nearby the confluence of both rivers.

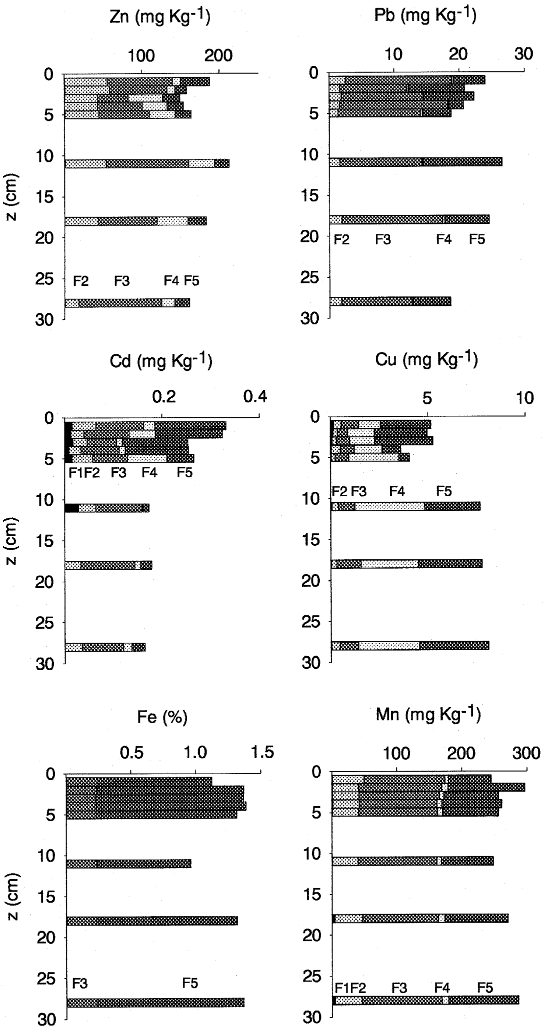

Fig. 5. Vertical profiles of the heavy metal partitioning (Zn, Pb, Cd, Cu, Fe and Mn) in the five geochemical fractions: *F*1 (exchangeable), *F*2 (carbonates), *F*3 (Fe and Mn hydroxides), *F*4 (organic matter) and *F*5 (lithogenic or non-reactive fraction) for the sediments core sampled at the GL6 station. Units are expressed as mg kg^{-1}, except Fe as % dry weight.

3.4. Heavy metal speciation

Fig. 5 summarizes the speciation patterns of the heavy metals Fe, Mn, Zn, Cd, Pb and Cu at different depths of the sediment core sampled at station GL6. In general, Fe is more associated with the lithogenic fraction (*F*5), and most of the Mn is appearing in the Fe–Mn oxides fraction (*F*3). This association of Mn also includes some traces associated with the *F*1 fraction. This predominant association to the residual fraction and the Fe–Mn oxides is also apparent to the Pb. The three heavy metals show a similar distribution with depth about their association. The heavy metal Cu associates predominantly to the organic matter and to the lithogenic fractions. The total concentration is lower in surface than in the bottom of the sediment core but its association with the different phases presents a similar behavior with depth.

On the other hand, Zn and Cd are more related to the biologically available fractions $F1$–$F3$ and their associations present a different distribution with the geochemical fractions versus depth. The Cd presents association with the first ($F1$) and more mobile fraction in the surface (first 10 cm) of the sediment core. The heavy metal Zn presents a typical distribution of a recent enrichment of the metal, which could be biologically available. It mainly associates with the fractions $F2$ and $F3$ especially in the surface although this association is also present in the deeper sediment core.

To confirm this pattern versus depth and to evaluate the recent enrichment of the different heavy metals two different EFs were calculated. The value of the reactive enrichment factor ($F1 + F2 + F3$) calculated for the higher depth was used as background level for this reactive enrichment factor. Also, this enrichment factor was calculated for each depth. A similar factor was calculated, but defined by the concentration of heavy metal associated with the lithogenic fraction ($F5$). The vertical distribution of these two factors versus depth is showed in the Fig. 6. In general, Zn, Cd and Mn present higher values for the factors calculated for the reactive than for the lithogenic fractions, except for Zn at 10 cm, for Cd at 10 and 20 cm and for Mn at 10 cm. In the case of Cd and Mn the reactive EFs were higher in the surface of the core (first 5 cm). For Zn the reactive factors were higher in all the depth except at that of about 10 cm. This pattern confirms the enrichment of the heavy metals Zn, Cd and Mn in the superficial sediments at the confluence of both rivers. These results confirm the appreciation about the effect of the Aznalcóllar mining spill on the sediments from the GL6 station, which informs about an enrichment of more biologically available concentrations of the heavy metals Zn and Cd. This enrichment can stress the ecosystem mostly due to the Zn concentrations. From the results obtained it has confirmed the existence of an impact possibly from the Aznalcóllar mining spill on sediments located nearby the confluence of the rivers Guadiamar and Guadalquivir. The association of Zn and in low extension Cd to the more mobile fractions of the sediments constitutes an important source of potentially available trace metals that could be remobilized and incorporated to the estuarine ecosystem.

In summary it could be proposed that the effect of the accidental spill related to the concentration of the metals Zn and Cd has been detected as an acute effect on the estuary ecosystem but remain in specific points of the estuary.

4. Conclusions

The spillage from the Los Frailes mine is a social and ecological disaster and the magnitude of the ecological damage to one of the Europe's last great wildernesses will only become apparent over time.

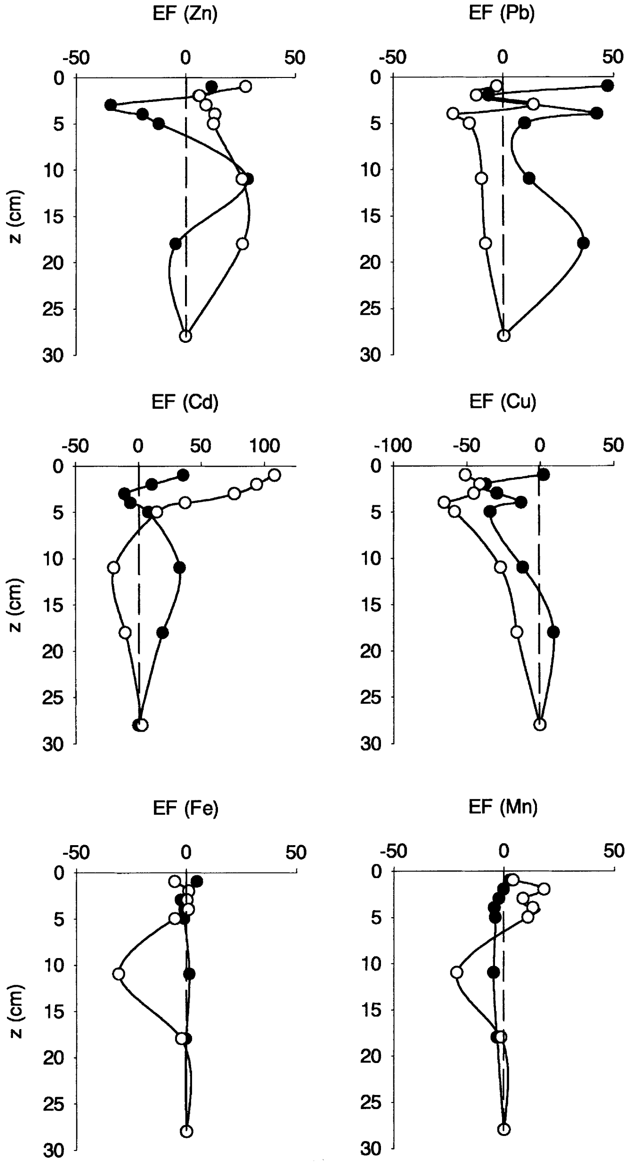

Fig. 6. Vertical profiles of the enrichment factors (EF) for the heavy metal partitioning (Zn, Pb, Cd, Cu, Fe and Mn) in the three more mobile geochemical fractions, $F1 + F2 + F3$ (empty circles) and in the lithogenic fraction, $F5$ (filled circles) for the sediment core sampled at the GL6 station.

Within the context of this study, we can derive a number of conclusions regarding the extension and the magnitude of the contamination measured in the area, including aspects related to the environmental risk associated with the mining spill. These conclusion are summarized below:

(a) The vertical distribution of the heavy metal Zn measured in sediments cores sampled nearby the confluence of the Guadiamar and Guadalquivir rivers (station GL6) presents the higher values in the concentration associated with samples from the surface of the sediments. The decrease of the concentration with depth and the similar background level calculated for this metal, inform about a recent enrichment of this heavy metal in the surface. Although the Zn presents high values on surface sediment studied they are on the limits of the sediment quality guidelines proposed by different authors so of concern but without biological effect confirmed. Further studies should be carried out to establish the real biological adverse effect associated with these concentrations of heavy metals.

(b) The geochemical fractionation of the heavy metals Zn and Cd confirms the enrichment of both metals in the station GL6. Also, their associations with the more mobile fractions inform about a potential remobilization of the heavy metals bounded to the sediment and a potential bioavailability of these concentrations. These associations to the reactive fraction are predominant in the surface and detect an impact of the accidental spill in this station.

(c) The Aznalcóllar mining spill has affected some of the areas of the estuary. The effect can be cataloged such as acute affecting only specific stations in the surface sediments (station GL6). The fact of the set up of the treatment plant on June 1998 (Gómez-Parra et al., 2000; Riba et al., 2000) helped to avoid a more strong effect of the accident on the estuarine ecosystem of the Guadiamar and Guadalquivir rivers. Because the long term activation in adverse effect typical from the heavy metal contamination further ecotoxicological evaluations should be carried out for the estuary and the parks.

During the first days of the Aznalcóllar mining spill high concentrations of heavy metals were introduced in the estuarine ecosystem. Nevertheless, the set up of the treatment plant and the inner capacity of the estuarine ecosystem to eliminate these concentrations, based on the high hydrodynamic regimen, has permitted a low impact of the accident on sediments of the area. However, the high concentrations of some of the metals (Zn and Cd) in some of the areas close to the sediment quality values need to be evaluated on the biological effect associated to them under an integrated point of view.

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