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Monitoring the Impact of the Aznalcóllar Mining Spill on Recent Sediments from the Guadalquivir Estuary, Southwest Spain

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On 25th April 1998 part of the tailings pond dike of the "Los Frailes" pyrite zinc mine, situated in Aznalcóllar, collapsed, releasing an estimated 3million 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 a tributary of the Guadalquivir River. It occurred in the vicinity of the Doñana Park, the major marsh protected area in Europe which harbors seventy percent of all European bird species. Because of its international importance, 132000 ha of Doñana have been protected under national, EU or international law and conventions.

The results presented in this paper are part of the interdisciplinary group of expert monitoring the impact of the spillage in the area of the Natural Park (Grimalt & MacPherson, 1999; DelValls et al., 1999; Gómez-Parra et al., 2000). The aims of this work are to assess both the concentrations of Fe, Mn, Zn, Cd, Pb and Cu in the sediments of the estuary, and the chemical form in which they occur. To establish the impact of the Aznalcóllar mining spill in the estuarine ecosystem these results have been combined to define the recent enrichment of heavy metals in the estuarine surface sediments. Also the potential environmental risk associated with the heavy metals was evaluated using comparisons of total concentrations of heavy metals in sediments to sediment quality values (DelValls et al., 1997, 1998a,b).

MATERIALS AND METHODS

We selected different stations to cover the influences of the contamination from the Aznalcóllar accident: GL2 and GL6 stations during May 1998 and GL2, GL4 and GL6 in the Guadalquivir river and GR2, GR4 and GR6 in the Guadiamar river in September 1998 (Fig.1). Composite sediment samples (3-4 grabs per sample) were collected at each station. Sediment samples were collected with a 0.025 m^2 Van Veen grab, transferred to a cooler and transported to the laboratory. Sediment samples were dried at 60°C and gently homogenized prior to chemical analysis. Total metal concentrations were determined after digesting the sediment samples by method described by Loring and Rantala (1992).

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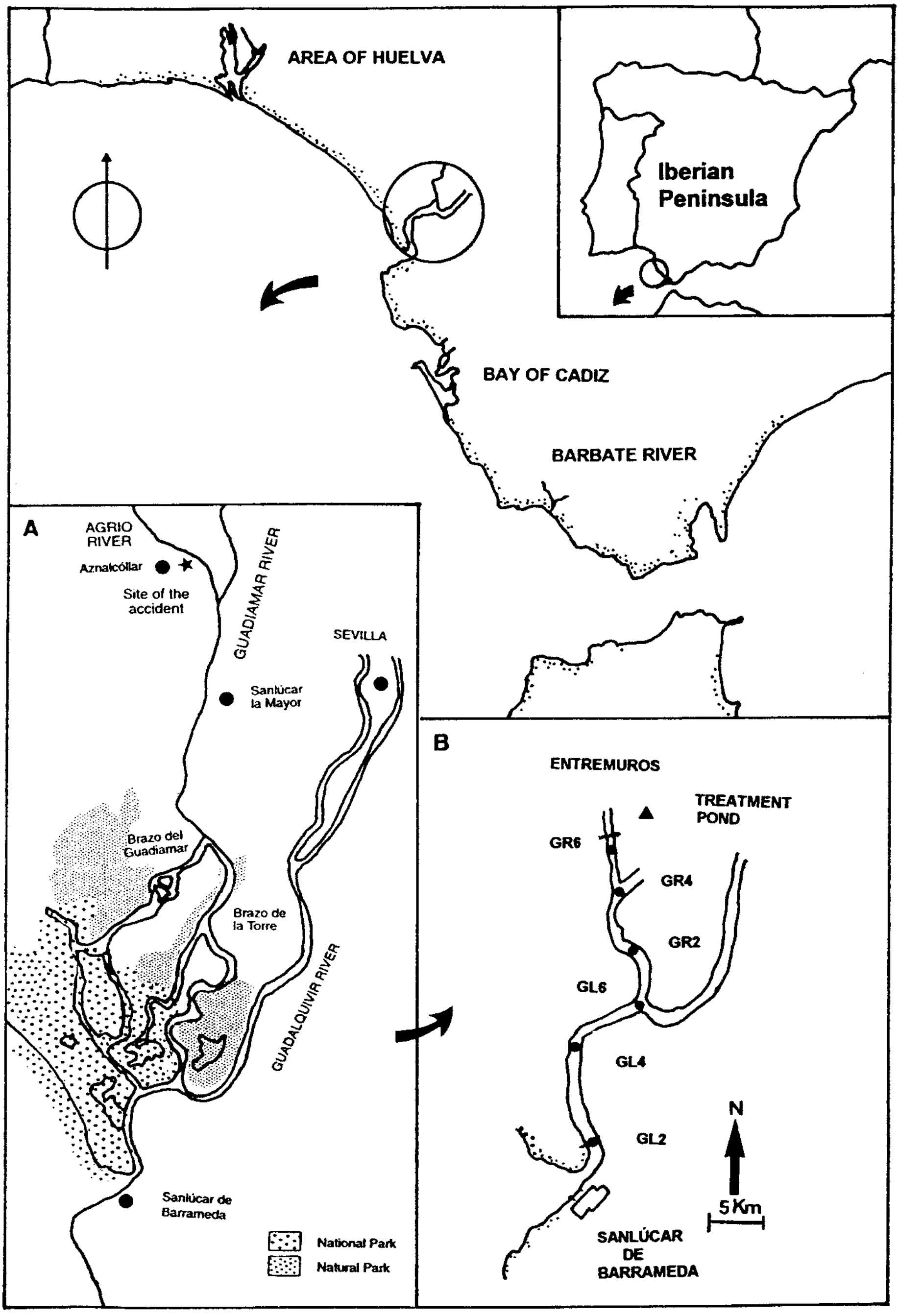

Figure 1. Map of the Guadalquivir estuary and the Guadiamar river area showing the general areas sampled and locations of the sampling stations. GR# is selected for the stations located at the Guadiamar river area and GL# for Guadalquivir estuary.

The speciation of the metals in the same samples was determined following the method proposed by Tessier et al. (1979) modified as reported by Riba (1999). Metal recoveries were calculated comparing the sum of the fractions of each metal to the total concentrations of it and was 98 ± 10 %. 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 Metrohm 693 processor. Concentrations of Fe and Mn 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%. Sediment grain size was determined using a laser particle size (Fritsch Analysette 22; DelValls et al., 1998c). Organic carbon concentration was determined using El-Rayis (1985) method.

To evaluate the potential environmental risk two different factors for each metal were calculated: surface enrichment factor (SEF) and the environmental risk

$$SEF = \frac{C_I - C_0}{C_0} \qquad ERF = \frac{C_I - C_{SQV}}{C_{SQV}}$$

factor (ERF): where, C_i is the heavy metal concentration measured in the ecosystem, C_0 is the heavy metal background level established for the ecosystem studied (Riba, 1999), and C_{SQV} is the highest concentration of the studied heavy metals non-associated with biological effects as reported by DelValls & Chapman (1998). The SEF values allow the identification and quantification of the metal enrichment and the ERF establish those stations with heavy metal concentrations associated with an environmental risk.

RESULTS AND DISCUSSION

Sandy sediments were predominant from the Guadalquivir and with similar textures. They were different when compared to those analyzed in the Guadiamar River, in which mud was predominant. Sediments from Guadiamar present lower grain size and higher concentration of organic carbon (1.5 ± 0.2, % dry sediment) than those from Guadalquivir River (0.9 ± 0.2, % dry sediment). These values are similar to those grain sizes and organic carbon concentrations measured in other littoral areas from the Gulf of Cádiz (DelValls et al., 1998c).

Table 1 shows the total concentration of Zn, Cd, Pb, Cu, Fe and Mn in sediments from the Guadalquivir estuary (GL#) in two different periods (May and September, 1998) and those in the Guadiamar stations (GR#). The concentrations of heavy metals in sediments from station GL6 near the Guadiamar River confluence were higher than those from station GL2 and GL4. The concentration of the metals in the Guadiamar river sediments were higher than for the Guadalquivir River for all the metals. The values of the Zn, Pb, and Cd concentrations measured in the GL6 station in May were higher than those concentrations measured in September at stations GR6 and GR4. In general it shows a trend for the accumulation of heavy metals in sediments located at the confluence of both rivers. It could be related to the lower hydrodynamic regimen in the confluence of both rivers.

Table 1. Summarized heavy metal concentrations (Fe (%), Mn, Zn, Pb, Cd, and Cu <µg g^{-1} -dry sediment->) in sediments from the stations in the Guadalquivir and the Guadiamar river in May and September 1998.

Station	Zn	Pb	Cd	Cu	Fe	Mn
GL2 (05/98)	200.9	27.57	0.81	19.72	2.62	536
GL6 (05/98)	395.6	32.57	1.35	13.13	1.62	413
GL2 (09/98)	133.7	8.43	0.09	5.38	0.91	204
GL4	167.2	7.13	0.37	26.88	2.17	715
GL6 (09/98)	193.3	23.04	0.29	17.19	2.41	458
GR2	743.6	31.07	3.25	41.60	5.76	1562
GR4	289.9	11.90	1.56	78.82	5.85	1163
GR6	162.4	7.22	0.79	20.95	4.06	1452

In order to identify and quantify the metal enrichment a surface enrichment factor (SEF) was calculated for the 6 heavy metals and for each station (Table 2). Positive values of the factor inform us about a contamination associated with the metal. A surface enrichment of the heavy metals Zn and Cd has been shown in the Guadiamar and Guadalquivir rivers with high values in the sediments located in the confluence of both rivers (GR2). The decrease of these SEF from May to September could be associated with the higher hydrodynamic in the area of the Guadalquivir than in the Guadiamar where still high values of SEF. This fact shows an increase of the concentration of the heavy metals Zn and Cd that can be related to the Aznalcóllar mining spill.

Table 2. Surface enrichment (SEF) and environmental risk (ERF) factors expressed as percentages and calculated for May and September 1998 in the stations selected in the Guadalquivir (GL#) and Guadiamar (GR#) rivers.

Station	SEF	SEF_{Cd}	SEF_{Pb}	SEF_{Cu}	SEF_{Fe}	SEF_{M}	ERF_{Z}	ERF_{C}	ERF_{Pb}	ERF_{Cu}
GL2(5/98)	63	406	17	-15	85	24	-11	-67	-84	-74
GL6(5/98)	221	744	38	-43	15	-5	76	-61	-73	-87
GL2(9/98)	-54	138	-35	-69	-72	-80	-40	-90	-98	-95
GL4(9/98)	32	131	-70	17	53	65	-26	-92	-93	-72
GL6(9/98)	44	87	-7	-74	-1	-40	-14	-73	-94	-82
GR2(9/98)	504	1931	32	80	-100	261	231	-63	-36	-58
GR4(9/98)	135	875	-50	241	312	169	29	-86	-70	-19
GR6(9/98)	32	393	-69	-9	186	235	-27	-91	-85	-79

To establish the potential risk effects of the measured enrichment by Zn, Cd, Cu and Pb the ERF values were calculated for each station (Table 2). Positive values of ERF inform us about a potential adverse biological effect associated with the metal. Only the ERF values associated with Zn present positive values in some of the stations located near by the confluence of both rivers. The concentration of Zn on May in the station GL6 was higher than the quality values and could have affected to the ecosystem. Four months later ERF for Zn was negative in the same station and therefore non-associated with adverse biological effect. The ERF values for Zn in the Guadiamar River on September had positive values in the stations GR2 and GR4 near by the confluence of the rivers. These results inform about a potential stress on the ecosystems associated with the heavy metal enrichment from the accidental spill and located in the Guadiamar River and those near by the confluence of both rivers.

Figure 2 summarizes the speciation patterns of Fe, Mn, Zn Cd, Pb and Cu in the Guadalquivir (GL#) and Guadiamar (GR#) rivers. Fe associates mainly to the lithogenic fraction (F5). This fraction is also predominant in the associations of Pb and Cu. Mn is mainly distributed in the Carbonate fraction (F2) although present a higher variability in its associations. Zn and Cd are predominantly associated to those fractions more biologically available (F1 and F4).

The Zn association in May slightly differs when compared to the situation in September, being in May the biologically available fractions higher than in September. The pattern found in the Guadiamar River is similar to that in the Guadalquivir during May and is almost the same for the three stations although with different total concentrations. In summary these results confirm the appreciation about the effect of the Aznalcóllar mining spill on the sediments from the studied stations, which informs about an enrichment of more biologically available concentrations of the heavy metals Zn and Cd that can stress the ecosystem mostly due to the Zn concentrations.

To compare these associations with different estuarine and littoral ecosystems in the Gulf of Cádiz affected by different origin and grades of heavy metal contamination we have selected some previously reported results (Sáenz, 1998) in three different areas (Fig. 3 and 4). The ría of Huelva (two stations H1 and H2) is chronically affected by mining activities over the last centuries (mines were set up 5000 years ago). The Bay of Cádiz (one station BC) and the salt marshes of the Barbate river (one station, BR), are areas considered non-contaminated (DelValls et al., 1998c).

Bioavailability is a function of particular geochemical fractions where metals are associated and may be influenced by physiological factors of organisms such as age, sexual condition, and diet (Phillips and Rainbow, 1993). Theoretically fractions F1, F2 and F4 are recognized as the major reservoirs for biologically available metals under favorable conditions and the amount of associated metal constitute a greater danger than the total amount (Kersten and Förstner, 1991).

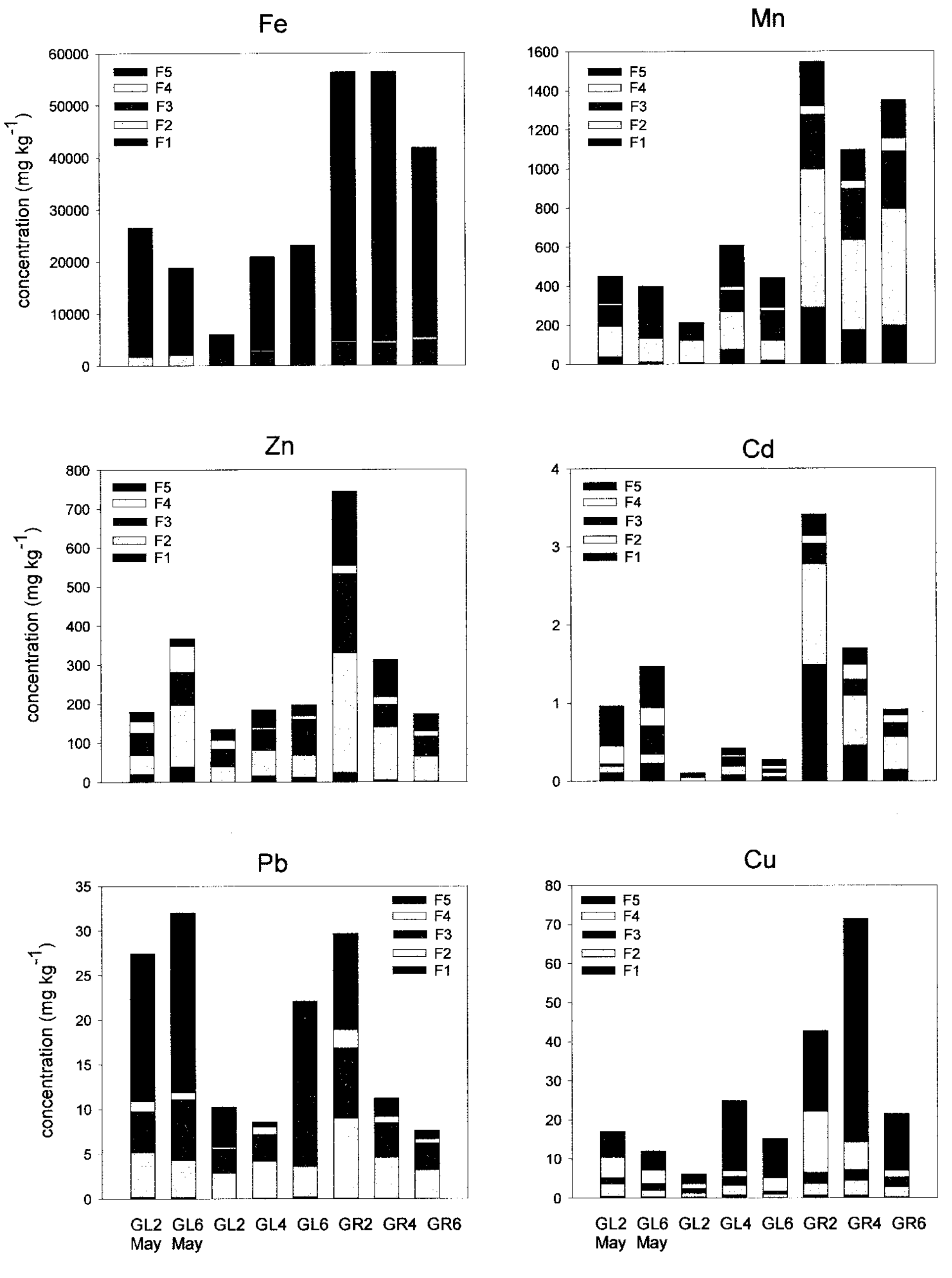

Figure 2. Heavy metal distribution (Fe, Mn Zn, Cd, Pb and Cu) in the five geochemical fractions: F1 (exchangeable), F2 (carbonates), F3 (Fe and Mn hydroxides), F4 (organic matter) and F5 (lithogenic or non-reactive fraction) for the sediments samples in the Guadalquivir (GL#) and the Guadiamar (GR#) estuaries during both sampling periods.

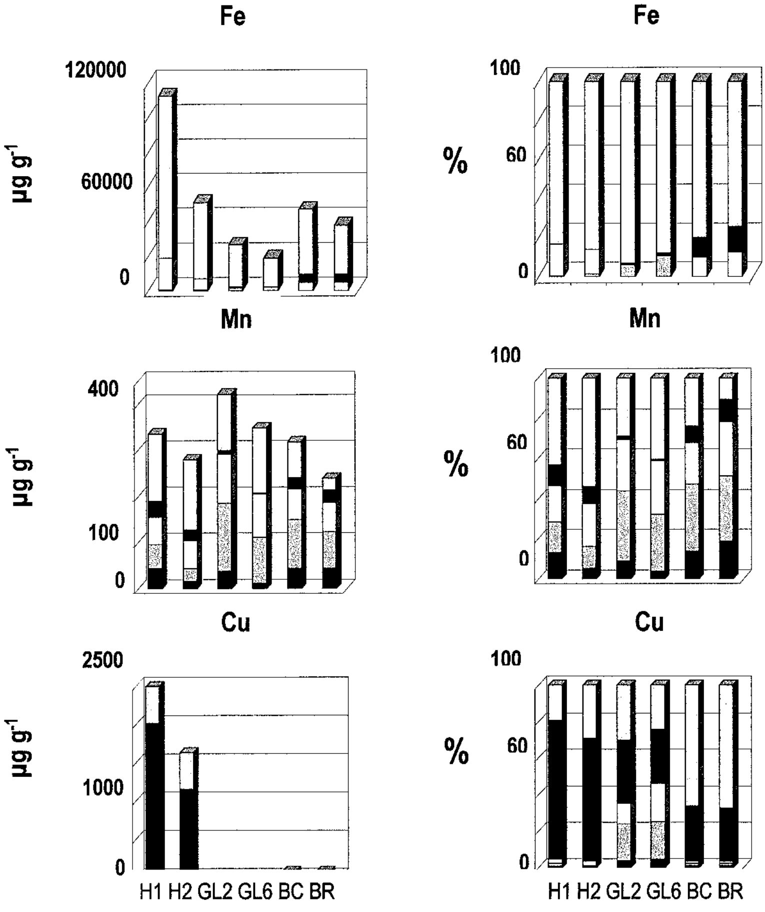

Figure 3 Example of the heavy metal (Fe, Mn, and Cu) partitioning (total concentration expressed as µg g^{-1} of dry sediment and percentage) in the five different geochemical fractions of the sediments from the GL2 and GL6 stations in the Guadalquivir River. They are compared to the chemical speciation reported by other authors (Sáenz, 1998) in different estuarine and littoral areas of the Gulf of Cádiz: ría of Huelva (H1 and H2), Bay of Cádiz (BC) and in the salt-marshes of the Barbate river (BR).

The association of the Fe and Mn in all the systems presents a similar pattern being predominant the association to the lithogenic fraction for Fe and to the Carbonates and Fe-Mn oxides for Mn. In the Guadalquivir estuary Cu presents a relative affinity to bound to the biologically available fractions F1 and F4 compared to the other areas, being higher this affinity in the ría of Huelva than in the other two areas. Pb associates to the reactive fractions only in the areas of Cádiz and Barbate being non-significant its association to mobile fractions in Guadalquivir and Huelva. In the Guadalquivir estuary Cd associates to the biologically available fractions lower than in all of the other three ecosystems although the association presented in the station GL6 is similar to those reported for the other areas.

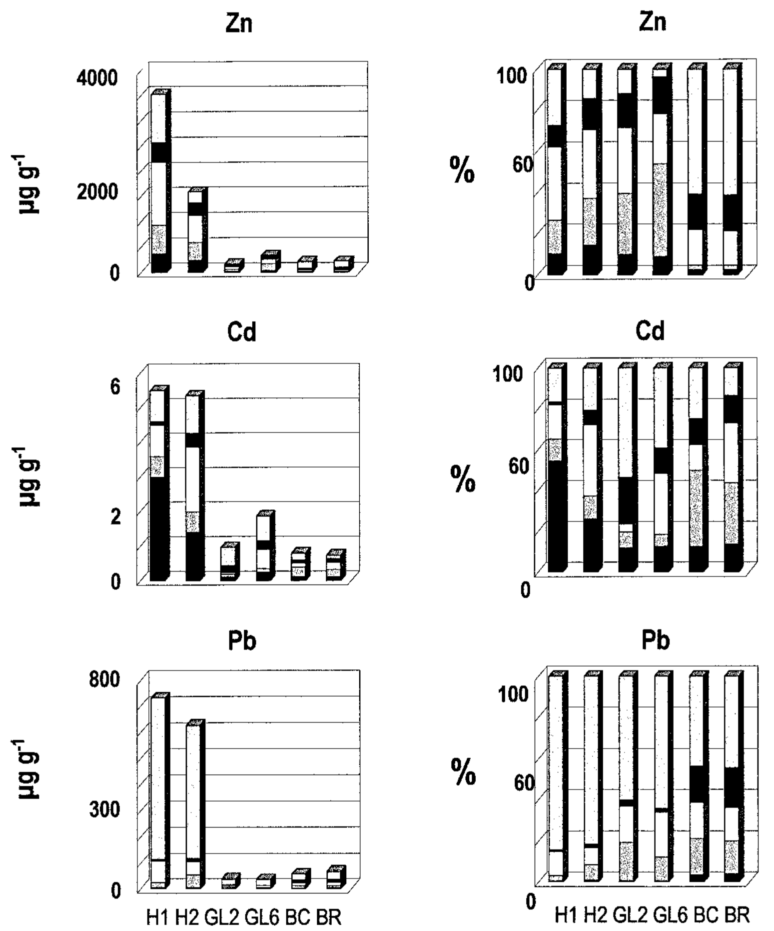

Figure 4 Example of the heavy metal (Zn, Cd and Pb) partitioning (total concentration expressed as μg g^{-1} of dry sediment and percentage) in the five different geochemical fractions of the sediments from the GL2 and GL6 stations in the Guadalquivir River. They are compared to the chemical speciation reported by other authors (Sáenz, 1998) in different estuarine and littoral areas of the Gulf of Cádiz: ría of Huelva (H1 and H2), Bay of Cádiz (BC) and in the salt-marshes of the Barbate river (BR).

Finally, the heavy metal Zn presents the higher association with the reactive fractions in the Guadalquivir estuary when compared to the other ecosystems. The sums of the association within the first three fractions account for more than 70% of the total Zn being of more than 95% when the organic matter associations are considered.

From these comparisons it is confirmed the existence of an impact from the Aznalcóllar mining spill on sediments located near by 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 biologically available trace metals. These metals present associations higher (in the Zn case) than those previously reported for a high mining contaminated area such as the ría of Huelva. However, the total concentrations measured for both metals in the Guadalquivir estuary were very much lower than those monitored in the mining area of Huelva (Tinto and Odiel Rivers). It gives an interesting indication of the fundamental difference between the long-term effects of continuous heavy metal discharge over centuries (located in the Tinto and Odiel rivers) and the effect of an isolated, albeit very large, single discharge (described in this study).

In summary it could be proposed that the effect of the Aznalcóllar mining 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. 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 a treatment plant (Gómez-Parra et al., 2000) and the inner capacity of the estuarine ecosystem to accept this 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 stations 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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REFERENCES

DelValls TA, Chapman PM (1998) Site-specific sediment quality values for the Gulf of Cádiz (Spain) and San Francisco Bay (USA), using the sediment quality triad and multivariate analysis. Cienc Mar 24:313-336

DelValls TA, Lubián LM, Forja JM, Gómez-Parra A (1997) Comparative ecotoxicity of interstitial waters using Microtox® and the rotifer Brachionus plicatilis. Environ Toxicol Chem 16: 2323-2332

DelValls TA, Forja JM, Gómez-Parra A (1998a) The use of multivariate analysis to link sediment contamination and toxicity data for establish sediment quality guidelines in the Gulf of Cádiz (Spain). Cienc Mar 24:127-154.

DelValls TA, Blasco J, Sarasquete MC, Forja JM, Gómez-Parra A (1998b) Evaluation of heavy metal sediment toxicity in littoral ecosystems using juveniles of the fish Sparus aurata. Ecotoxicol Environ Saf 41:157-167

DelValls TA, Forja JM, González-Mazo E, Blasco J, Gómez-Parra A (1998c) Determining contamination sources in marine sediments using multivariate analysis. Trend Anal Chem 17:181-192

DelValls TA, Saez V, Arias A, Blasco J. (1999) Thallium in the marine environment: first ecotoxicological assessments in the Guadalquivir estuary and its potential adverse effect in the “Doñana european natural reserve" after the Aznalcóllar mining spill (S.W. Spain). Cienc Mar 25:161-175

El Rayis OA (1985) Re-assessment of the titration method for determination of organic carbon in recent sediments. Rapp Comm int Mer Mediterranean 29: 45-47

Gómez-Parra A, Forja JM, DelValls TA, Sáenz I, Riba I (2000) Early contamination by heavy metals of the Guadalquivir estuary after tha Aznalcóllar mining spill (SW Spain). Mar Pollut Bull 40:1115-1123

Grimalt JO, Macpherson E. Eds (1999) Special issue: The environmental impact of the mine tailing accident in Aznalcóllar (S.W. Spain). Sci Tot Environ 242: 1-337

Kestern M, Förstner U (1991). Speciation of trace elements in sediments. In Trace Element Speciation: Analytical Methods and Problems, ed. G.E. Batley, pp. 245-317. CRC Press, Boca Raton

Loring DH, Rantala RTT (1992) Manual for the geochemical analyses of marine sediments and suspended particulate matter. Earth Sci Rev 32: 235-283.

Phillips DJH, Rainbow (1993) Biomonitoring of trace aquatic contaminants. Elsevier Applied Science, London, 371 pp.

Riba I (1999) Evaluación del impacto del vertido de Aznalcóllar en los sedimentos del estuario del río Guadalquivir tras el accidente minero de 1998. Tesis de Licenciatura. Facultad de Ciencias del Mar. Universidad de Cádiz. pp. 172.

Sáenz V (1998) Distribución espacial y especiación de metales pesados en sedimentos de tres sistemas litorales del Golfo de Cádiz. Tesis de Doctorado. Facultad de Ciencias del Mar. Universidad de Cádiz. pp. 382

Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedures for the speciation of particulate trace metals. Anal Chem 51: 844-851.