EVALUATING THE HEAVY METAL CONTAMINATION IN SEDIMENTS FROM THE GUADALQUIVIR ESTUARY AFTER THE AZNALCÓLLAR MINING SPILL (SW SPAIN): A MULTIVARIATE ANALYSIS APPROACH

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Abstract. The Doñana National Park is one of the most important Natural Reserves in west Europe. The park and the Guadalquivir estuary were impacted by the release of 5 million cubic meters of acid waste from the processing of pyrite ore. Here are presented a multivariate analysis approach to evaluate the extension and the magnitude of the accidental spill on the estuarine sediments. Sediments were used to analyze 6 different metals (Fe, Mn, Zn, Cd, Pb, Cu). Also the concentration of the metals in the different geochemical sediment fractions were determined as a means of assessing the potential impact of the acid water from the mine. The analysis of the results obtained permits to establish that the impact of the accident was acute on the ecosystem due to the set up of a treatment plan in June 1998 and to the high hydrodynamic of the estuary that absorb the early impact. Chronic contamination by Cu was also detected during the monitoring of the impact of the accident in the estuary but this did not appear to be related to the accidental spill. Because the likelihood of long term adverse effects from the heavy metal contamination of estuarine sediments, further ecotoxicological evaluations should be carried out for the estuary and the park using an integrated approach.

Keywords: Aznalcóllar acid mine waste, Doñana, Guadalquivier estuary, heavy metals, multivariate analysis approach (MAA)

1. Introduction

On 25 April 1998 part of the tailings pond dike of the ‘Los Frailes’ zinc mine, situated in Aznalcóllar Spain, collapsed, releasing an estimated 5 million cubic meters of acid waste 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 and Natural Parks. One of the areas significantly impacted by the spill was the bottom sediments of the Guadalquivir estuary (Gómez-Parra *et al.*, 2000). The Guadalquivir marshes comprise one of Europe’s largest and ecologically most important wetlands (Albaiges *et al.*, 1987). Because of its international importance, 132 000 ha of Doñana have been protected under national, EU or international law and conventions. Protected areas include the 50 720 ha Coto Doñana National Park (classified as a Special Protection Area for birds by the EU under Directive 79/409) and the 54520 ha

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Natural Park, some of which borders the National Park. Parts of the area have been designated as a Ramsar site (an internationally important wetland under the Ramsar convention), and Biosphere Reserve, and the area was inscribed as a World Heritage Site in 1994. There are also important areas that remain without formal protection such as the southern Guadalquivir estuary.

Understanding the ecological significance of marine sediment contamination by heavy metals has been advanced by numerous studies (Bryan and Langston, 1992). It is necessary to have the more exact information on the physico-chemical forms in which heavy metals exist in sediments. In this sense, sequential extraction permits us to precisely determine 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. However, the predicted bioavailability relative to actual risk should be confirmed as risk to the environment via toxicological assessment. 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 provide a more precise indication of the potential ecological risk.

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 decades (Valette-Silver, 1993).

Multivariate analysis approaches (MAA) have been used in the last years in different marine pollution studies (Zitko, 1994). The use of MAA to link chemical and biological data has permitted to obtain an overview of the potential effect associated with chemicals values (DelValls *et al.*, 1997, 1998a, b) and also to establish site-specific sediment quality values (DelValls and Chapman, 1998). In order to obtain such an overview indicating the heavy metal contamination in the estuary and their influences areas we have combined the results of two different studies: assessment of heavy metal concentrations and their association to geochemical sediment phases in surface sediments and assessment of vertical profiles of metals in the sediments. We have used a multivariate analysis approach (MAA) to combine the result obtained which permits us to identify the sources of the contamination in the estuary and to assess both the extent and the magnitude of the impact of the mining spill on the Guadalquivir estuary ecosystem.

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 which is a major tributary of the Guadalquivir. The threat posed to the Doñana parks through inputs of metals by mining activities from the Guadiamar and Guadalquivir rivers has been studied (Cabrera *et al.*, 1987; Arambarri *et al.*, 1996).

We selected different stations in the Guadalquivir and in the Guadiamar rivers to assess the influences of the contamination from the Aznalcóllar spill. Also these stations permit us to evaluate the field efficiency of the emergency treatment plant to clean up the acid water from the spill (Figure 1).

2.1.1. *Surface Sediment*

We selected the GL2 and GL6 stations during the spring sampling time and GL2, GL4 and GL6 in the Guadalquivir river and GR2, GR4 and GR6 in the Guadiamar river during the autumn sampling time. The criterion for selection was to cover as much of the contaminated field gradient as possible. Composite sediment samples (3–4 grabs per sample) were collected at each of the stations (5 cm in depth). Sediment samples were collected with a 0.025 m^2 Van Veen grab, transferred to a cooler, chilled with ice, and transported to the laboratory. Sediment samples were maintained in the dark at 4 °C until their processing and analysis.

2.1.2. *Sediment Vertical Profiles*

We selected the GL6 station to study the vertical profiles of heavy metals in its sediments because it was located at the confluence of Guadalquivir and Guadiamar rivers. We selected 8 depths at the GL6 station with the maximum depth of 28 cm. 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. The vertical contaminant profiles in the sediment assess changes from before to after the accident mining spill. The sediment cores were taken by scuba divers, and were transported refrigerated to the laboratory within 3 hr.

Prior to sample collection, all beakers for the collection and storage of sediment samples were thoroughly cleaned with acid (10% HNO_3), 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 (Table I)

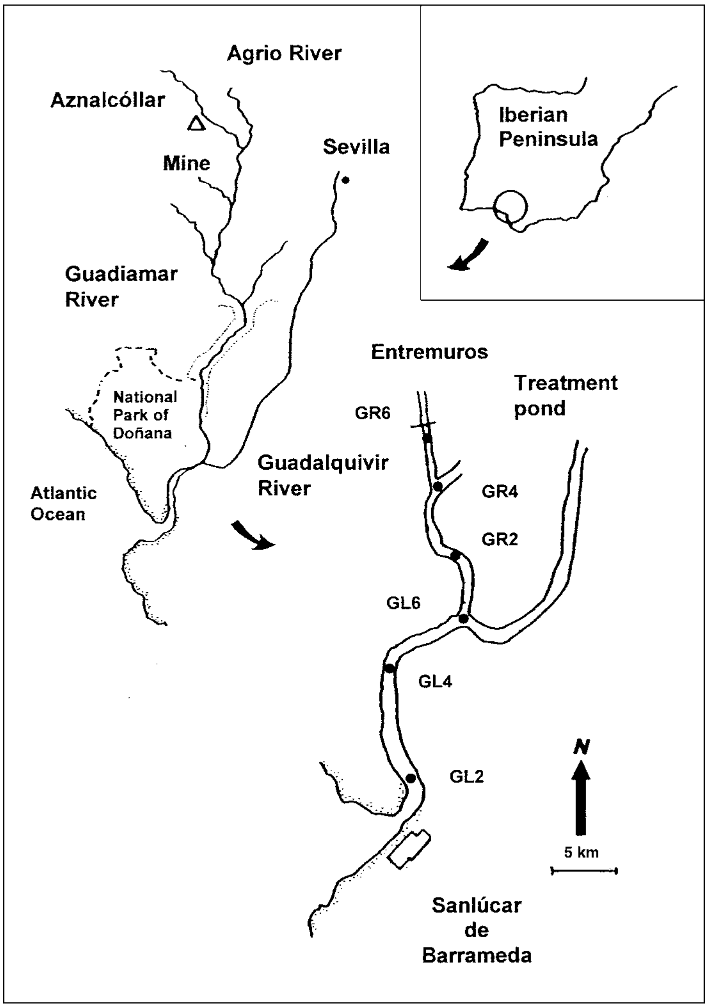

Figure 1. Map of the Guadalquivir estuary and the 'Brazo de la Torre' area showing the general areas sampled and locations of the sampling stations within the sites sampled. GR is selected for the stations located at the 'Brazo de la Torre' area and GL for Guadalquivir estuary.

in the homogenized sediments was 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). Also separate sediment samples for each station were homogenized and totally digested as described by Loring and Rantala (1992). Results are expressed as mg kg^{-1} dry sediment for total analysis and as percent for the speciation study.

The concentration of heavy metals cadmium, lead, copper and zinc was determined by differential pulse anodic stripping voltammetry (DPASV). Measurements

TABLE I

Reagents and conditions employed in the sequential extraction procedure. 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

Fraction	Extraction reagent	Extraction conditions
F1: Exchangeable	1 M $MgCl_2$ at pH 7	Shaken at room temperature for 1 hr
F2: Carbonate	1 M NaOAc ajusted to pH 5 with HOAc	Shaken at room temperature for 5 hr
F3: Fe-Mn Oxides	0.04 M $NH_2OH \cdot HCl$ in 25 (v/v) HOAc	Shaken at 96 °C for 6 hr
F4: Organic matter	0.02 M $HNO_3 + H_2O_2$ (adjusted to pH 2 with HNO_3	Shaken occasionally at 85 °C for 5 hr then shaken
	(On cooling add 3.2 M NH_4Oac in 20% (v/v) HNO_3	on addition of NH_4Oac for a further 0.5 hr
F5: Lithogenic	Aqua regia, HF	As for total metal analysis

were taken with a static drop mercury electrode (SMDE), using the Methrom 693 processor. The concentration of the heavy metals 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 the method of El-Rayis (1985).

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).

2.3. MULTIVARIATE ANALYSIS APPROACH

In order to identify the impact of the contamination from the Aznalcóllar mining spill in the ecosystem studied we applied a MAA (Factor Analysis using the Principal Component Analysis (PCA) extraction procedure) to the original set of variables. It is a multivariate statistical technique, to explore variable distributions (surface sediments: n = 40; whereas for the sediment vertical profiles n = 39). The Factor analysis was performed on the correlation matrix; i.e., the variables were auto-scaled (standardized) so as to be treated with equal importance. All analyses were performed using the PCA option of the FACTOR procedure, followed by the basic set-up for factor analysis procedure (P4M) from the BMDP statistical software package (Frane *et al.*, 1985). Information on matrix type, chemical total concentrations, chemical speciation, enrichment factors, and ecological risk factors and sampling stations was used to interpret patterns in the data set.

For surface sediment, the base of data contained information from a total of eight samples (eight cases). Also the database used for the sediment vertical profile study contained information from eight different depths selected in one station (8 cases).

For both surface and vertical analysis, sediment chemical data included: total concentrations of 6 heavy metals (Fe, Mn, Zn, Cd, Pb, and Cu); chemical speciation of the 6 heavy metals expressed as the concentration measured in three different geochemical phases: reactive phase (including the sum of the concentrations measured in F1, F2 and F3), organic phase (F4), and lithogenic phase (F5) (Table I). Geochemical matrix characteristics were covered by the organic carbon concentrations (OC) and by the grain size (σ) distributions. To evaluate the potential ecological risk effect two different factors for each metal were included in the analysis: surface enrichment factor (SEF) and the ecological risk factor (ERF):

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

where, C_i is the total concentration of each heavy metal measured in the sediments, C_0 is the heavy metal background level established for the ecosystem studied (Riba, 1999), and C_{SQV} is the highest concentration of the 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). Different SEF's were used for the Guadalquivir estuary (GL) and the Doñana area (D) (Cabrera *et al.*, 1987).

3. Results and Discussion

Multivariate statistical analysis results are shown in Table II for the surface sediment analysis and Table III for the sediment vertical profiles. The sorted rotated factor loadings (pattern) are coefficients correlating the original variables and the principal factors in these analyses. The variables are reordered so the rotated factor loadings for each factor are clustered together. In the present study, we elected to interpret a variable or group of variables as those associated with a particular factor where loadings were 0.4 or greater, corresponding to an associated explained variance over 65%. This approximates Comrey's (1973) cut-off of 0.55 for a *good* association between an original variable and a factor, and also takes into account discontinuities in the magnitudes of loadings approximately these original variables (Comrey, 1983).

TABLE II

Sorted rotated factor loadings (pattern) of the original 40 variables on the five principal factors. The loading matrix has been rearranged so that the columns appear in decrease order of variance explained by factors. Only loadings greater than 0.4 are shown. Factors are numbered consecutively from left to right in order of decreasing variance explained

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
% Variance	48.9	26.4	7.4	5.3	4.2
Cu (ERF)	0.939	–	–	–	–
Cu	0.934	–	–	–	–
Cu (SEF-GL)	0.929	–	–	–	–
Cu (SEF-D)	0.929	–	–	–	–
Cu (F5)	0.922	–	–	–	–
Fe (SEF–GL)	0.760	–0.477	–	–	–
Cu (F1–F3)	0.714	–	–	–	–
Fe (F5)	0.698	0.546	–	–	–
Fe	0.680	0.505	–	–	–
Mn (F4)	0.650	0.600	–	–	–
Fe (F4)	0.609	–	–	0.535	0.484
Fe (F1–F3)	0.444	–	–	0.478	0.468
Mn (SEF–D)	0.431	0.488	–	0.549	0.452
Mn (SEF–GL)	0.431	0.488	–	0.549	0.452
Cu (F4)	0.400	0.811	–	–	–
Zn (F1–F3)	–	0.948	–	–	–
Zn	–	0.922	–	–	–
Zn (ERF)	–	0.921	–	–	–
Zn (SEF–GL)	–	0.903	–	–	–
Zn (SEF–D)	–	0.903	–	–	–
Cd (F1–F3)	–	0.893	–	–	–
Zn (F5)	–	0.860	–	–	–
Cd (SEF–GL)	–	0.857	–	–	–
Cd (ERF)	–	0.849	–	–	–
Cd	–	0.849	–	–	–
Pb (F1-F3)	–	0.790	0.402	–	–
Pb (F4)	–	0.762	–	–	–
Pb	–	0.530	0.751	–	–
Pb (ERF)	–	0.520	0.761	–	–
Pb (SEF–GL)	–	0.513	0.740	–	–
Pb (SEF–D)	–	0.513	0.740	–	–
Cd (F5)	–	–	0.931	–	–
Pb (F5)	–	–	0.906	–	–
Cd (F4)	–	–	0.858	–	–
Zn (F4)	–	–	0.841	–	–
Mn (F5)	–	–	–	0.931	–
Mn	–	0.488	–	0.571	0.465
Mn (F1–F3)	–	0.508	–	0.481	0.538
OC	–	–	–	–	0.927
σ	–	–	–	–	–0.874

TABLE III

Sorted rotated factor loadings (pattern) of the original 39 variables on the seven principal factors. The loading matrix has been rearranged so that the columns appear in decrease order of variance explained by factors. Only loadings greater than 0.4 are shown. Factors are numbered consecutively from left to right in order of decreasing variance explained

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7
Variance	31.2	24.5	16.3	10.1	7.5	3.7	2.8
Cu (ERF)	0.929	–	–	–	–	–	–
Cu	0.929	–	–	–	–	–	–
Cu (SEF–GL)	0.929	–	–	–	–	–	–
Cu (SEF–D)	0.929	–	–	–	–	–	–
Mn (F4)	0.765	–	–	–	–	–	–
Cu (F4)	0.675	–0.528	–	–	–	–	–
Cu (F5)	0.652	–	0.555	–	–	–	–
OC	0.595	–	–	–0.703	–	–	–
Cu (F1–F3)	0.593	–	–	–	–0.559	0.411	–
Mn (F5)	0.461	–	–	–	0.582	–	0.433
Fe (F4)	–0.476	–	–	–	–	0.588	–
Fe	–	0.947	–	–	–	–	–
Fe (SEF–GL)	–	0.947	–	–	–	–	–
Fe (F5)	–	0.858	–	–	0.418	–	–
Mn	–0.421	0.795	–	–	–	–	–
Mn (SEF–GL)	–0.421	0.795	–	–	–	–	–
Mn (SEF-D)	–0.421	0.795	–	–	–	–	–
Pb (ERF)	–	–	0.969	–	–	–	–
Pb (SEF–GL)	–	–	0.969	–	–	–	–
Pb	–	–	0.969	–	–	–	–
Pb (SEF–D)	–	–	0.969	–	–	–	–
Pb (F4)	–	–	–0.652	–	–0.457	–0.491	–
Cd (ERF)	–0.566	–	–	0.616	–	–	–
Cd (SEF–GL)	–0.566	–	–	0.616	–	–	–
Cd	–0.566	–	–	0.616	–	–	–
Cd (F5)	–	0.435	–	0.404	–	–	–
Cd (F1–F3)	–	–0.547	–	0.450	–0.612	–	–
Zn (F1–F3)	–	–0.684	–	0.507	–	–	–
Fe (F1–F3)	–	–	–	0.822	–0.421	–	–
Mn (F1–F3)	–	–	–	0.872	–	–	–
Zn (SEF–GL)	–	–	–	–	–0.902	–	–
Zn (SEF–D)	–	–	–	–	–0.902	–	–
Zn (ERF)	–	–	–	–	–0.902	–	–
Zn	–	–	–	–	–0.902	–	–
Pb (F1–F3)	–	–	–	–	–0.777	0.404	–
Zn (F5)	–	–	–	0.426	–0.682	–	–0.428
Zn (F4)	–	–	–	–0.935	–	–	–
Cd (F4)	–	–	–	–	–	–0.815	–
Pb (F5)	–	–0.662	–	–	–	–	0.619

3.1. SURFACE SEDIMENT ANALYSIS

In order to establish the source and the range of the contamination in the surface sediments from the estuary studied we have applied the MAA to the original 40 variables: the concentration of six heavy metals associated with 3 geochemical sedimentary phases (1–3, 4, 5), the total concentration of the six heavy metals, the average grain size (σ), the concentration of organic carbon (OC), the surface enrichment factors (Guadalquivir river (SEF-GL) and Doñana area (SEF-D)) for the six metals and the ecological risk factor (ERF) for Zn, Pb, Cd and Cu. The application of the MAA indicates that five new variables or principal factors can represent the original variables (Table II). These new factors explain 92.2% of the variance in the original data set. Based on these results, each component is described according to the dominant group of variables, as follows.

The first principal factor is predominant and accounts for 48.8% of the variance; this factor combines the ecological risk factor of Cu, the two enrichment factors (SEF-GL and SEF-D) of Cu, the concentrations of Cu in the geochemical sedimentary phases, the total concentration of Cu, the enrichment factor of Fe (SEF-GL), the concentration of Fe on the lithogenic and the organic phases, the total concentration of Fe, and the concentration of Mn in the organic phase. Also it includes other variables, which present higher loadings associated with other factors (factor 2 and 4). Based on this association, this component describes a contamination source associated with the concentrations of Cu in sediments and their association to the geochemical matrix, specifically to the Fe compounds. These levels of Cu could be associated with a potential ecological risk.

The second factor accounts for 26.4% of the variance and most of them includes variables associated with Zn and Cd: the ecological risk factor, the two enrichment factors, the concentrations associated with the geochemical sedimentary phases (except in the organic phase and for Cd in the lithogenic), and the total concentrations. Also it includes the concentration of Pb in the reactive and the organic phases. These associations include three different metals from the Aznalcóllar mining spill associated with potential ecological risk related to Zn and Cd. These correlations suggest a contamination source associated with the mining accident that affected the surface sediments in the Guadalquivir estuary.

The third factor accounts for 7.4% of the variance. It is a combination of 8 original variables, 5 associated with Pb (ecological risk factor, 2 enrichment factors, the total concentration and that associated with the lithogenic phase), two with Cd (concentrations associated with the organic and the lithogenic phases) and the concentrations of Zn in the organic phase. These contributions represent a potential ecological risk associated with Pb, which includes the less reactive concentrations of the metals Zn and Cd.

The factors 4 (5.3% of the variance) and 5 (4.2% of the variance) includes different correlations between the concentration of Mn in the less reactive sedimentary phases and the parameters characteristic of the geochemical matrix, the grain size and the concentration of organic carbon. This factor could be related to dredging processes, which occur periodically in the estuary. Due to the lowest variance explained by this factor, the described interpretation may not be highly significant.

In Figure 2 is shown a representation of the estimated factor scores (and their mahalanobis distances –chi squares–) for each case (stations) to the centroid of all cases in the original data. The factor scores quantify the prevalence of every factor for each station and are used to asses the evolution of the sediment contamination from May to September as well as through the estuary. The positive values of factor 1 associated with the stations GL4 and especially in the Guadiamar (GR4) suggests that a potential ecological risk could be associated with these sediments due to the Cu concentrations. The factors 2 and 3 associated with the Aznalcóllar mining spill present positive values in the stations GL6 in both periods May and September and also GL2 in May. However, factor 3 presents marked differences between both periods of time showing higher influence of the accident on May than in September. The decrease in the concentrations of heavy metals from the mine may be associated with two facts: 1) the efficiency of the treatment plant set up in June, and 2) high hydrodynamic activity in this area (Gómez-Parra *et al.*, 2000). The notably high value of the factor 2 in the station GR2 located near the confluence between both rivers confirms that these sediments served as a sink for the metals Zn and Cd from the Aznalcóllar mining spill. This positive value is lower in station GL6 probably due to higher hydrodynamic activity that typically affects this station and, which is absent in the Guadiamar river (at station GR2). In both cases, representing different conditions in the confluence of both rivers, an ecological risk may be associated to the high levels of Zn and Cd so from the Aznalcóllar mining spill. The sediments in the rest of the areas of the estuary were much less affected by the accident.

In summary, the data suggest that the main contamination process that occurred in the surface sediments in the Guadalquivir estuary area is associated with the concentrations of Cu (48% of the variance of the total system). However, high concentrations of the metals Zn and Cd were also detected in the estuary ecosystem (28% of the variance) but appear to remain in specific locations of the estuary. This show an acute contamination impact due to Zn and Cd concentrations and from the accidental spill.

3.2. SEDIMENT VERTICAL PROFILES

In order to establish the extension and the magnitude of the contamination in sediment cores from the estuary studied we have applied the MAA to the original 39 variables: the concentration of six heavy metals associated with 3 geochemical sedimentary phases (1–3, 4, 5), the total concentration of the six heavy metals, the concentration of organic carbon (OC), the surface enrichment factors (Guadalquivir river (SEF-GL) and Doñana area (SEF-D)) for the six metals, and the ecological

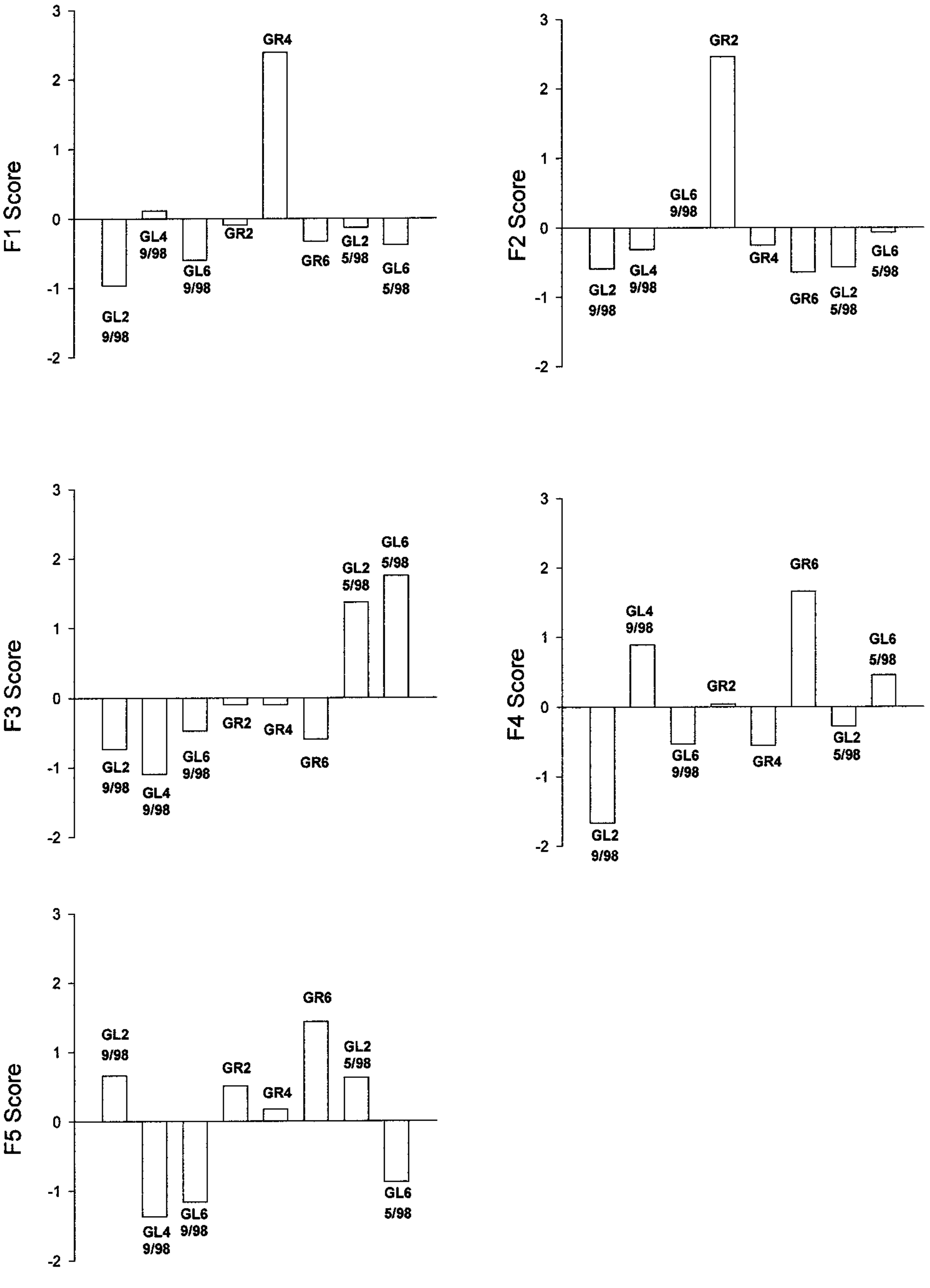

Figure 2. Factor scores estimated for each of the eight cases evaluated in the Guadalquivir estuary (GL2 and GL6 at two different periods) to the centroid of all cases for the original data. The factor scores quantify the prevalence of every factor for each station and are used to asses the evolution of the sediment contamination from May to September as well as through the estuary.

risk factor (ERF) for Zn, Pb, Cd and Cu. The application of the MAA indicates that seven principal factors can represent the original variables (Table III). These new factors explain 96.1% of the variance in the original data set. Based on these results, each component is described according to the dominant group of variables, as follows.

The predominant factor 1 accounts for 31.2% of the total variance. It has high positive loadings on all the variables related to Cu: the ecological risk factor, the two enrichment factor, the concentrations in the geochemical sedimentary phases and the total concentration. Factor 1 also includes the concentration of Mn in the organic and the lithogenic phases and the organic carbon content. This factor represents a contamination of Cu associated with a potential ecological risk, which is associated with Mn and organic components of the geochemical matrix.

Factor 2 accounts for 24.5% of the variance and combines six variables associated with non-reactive concentrations of Fe and Mn metals. Also, this factor includes some negative associations with reactive concentrations of Zn, Cd and Pb although these variables were present at higher loadings associated with other factors. This factor combines variables that represent the characteristic of the geochemical sedimentary matrix.

Factor 3 accounts for 16.3% of the variance and identifies a contamination phenomena associated with Pb. The factor combines the variables of Pb: the ecological risk factor, the two enrichment factors and the total concentrations of Pb. Note that the concentrations of Pb associated with the organic phases appear as negative loadings in the factor.

The factor 4 accounts for 10.1% of the variance and includes combination of the variables associated with Cd: the ecological risk factor, the enrichment factor, the concentrations of Cd in the geochemical sedimentary phases and the total concentration. Also, it includes the concentrations of the more reactive heavy metals Zn, Fe, and Mn. These relationships suggest a source of contamination by Cd associated with the mining accident.

The factor 5 accounting for 7.5% of the variance, has positive loadings on variables associated with Zn: the ecological risk factor, the enrichment factors, the concentrations of the metal in the geochemical fractions of the sediment and the total concentration. Also, this factor includes other concentrations of metals (Cu, Pb and Cd) associated with the more reactive fractions of the sediment. Based on this association, this component also describes a contamination associated with the mining spill but related to the concentration of Zn.

The factors 6 (5.3% of the variance) and 7 (4.2% of the variance) includes different correlations between the concentration of heavy metals in different geochemical fractions. The loadings are lower than those associated with other factors except for the concentrations of Cd and Fe associated with the organic phase. Due to the low explained variance provided by this factor the interpretation may not be highly significant.

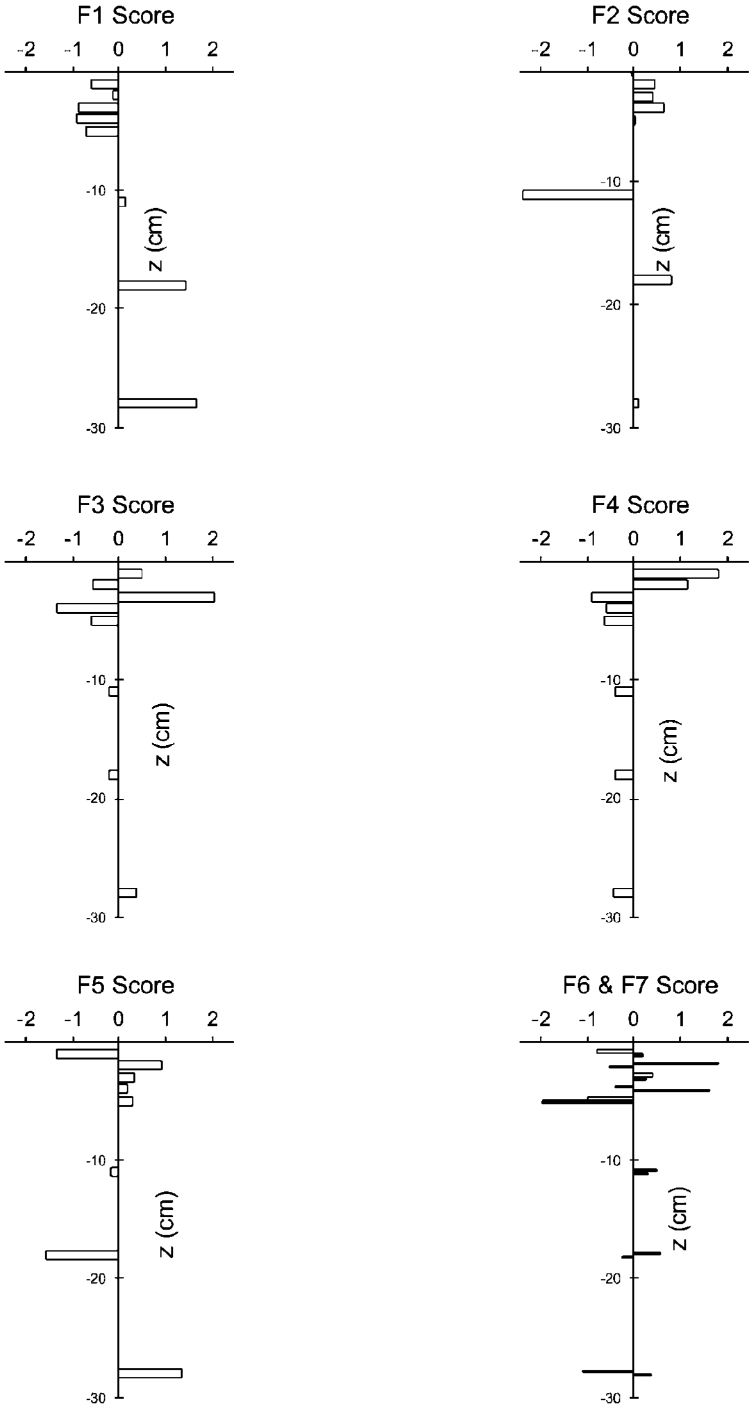

Figure 3. Factor scores estimated for each of the nine cases evaluated (equal to the 8 depths selected) in the station GL6 to the centroid of all cases for the original data. The factor scores quantify the prevalence of every factor for each depth and are used to assess the evolution of the sediment contamination from May to September.

Figure 3 shows a representation of the estimated factor scores (and their mahalanobis distances –chi squares–) for each case (depth of the sediment core) to the centroid of all cases in the original data. The factor scores quantify the prevalence of every factor for each depth of the sediment core and are used to assess the temporal evolution of the contamination in the sediments located at the confluence of both rivers (GL6). The positive values of the factor 1 associated with the higher depths of the core and the negative values related to the surface suggests that contamination by Cu may be a chronic event in the area of station GL6 and supports the finding obtained in the application of the MAA to the surface sediments regarding Cu contamination. Factor 2 presents a negative value at 12 cm being positive for the rest of depths. It may be explained to the differences in grain size occurring at this depth (Riba, 1999).

Factors 4 and 5 are associated with concentrations of Cd and Zn from the Aznalcóllar mining spill. From the profile of 4 it is clear that this factor decreases with depth, maintaining a negative and approximately constant score after the first 3 cm. This pattern indicates early contamination from accident in the surface sediments located at the confluence of the rivers due mainly to Cd and those concentrations of Zn and Pb associated with the reactive fraction of the sediments. The factor 5 presents positive values in the first depths (except for the first centimeter) being negative at depth higher than 10 cm. It confirms the acute contamination impact of the accident on the sediments sampled at the confluence of the rivers that can provoke an ecological risk to the sediment of the Guadalquivir estuary.

In summary, from the vertical profiles of the factor scores it could be inferred that the predominant contamination in the area is due to a potential chronic contamination phenomena by Cu. The heterogeneity of factors 2 and 3 can not permit us to establish a variation of the geochemical matrix and the contamination by Pb with depth. However, the similar information provide by factor 4 and 5 and the approximately equal pattern of their distribution with depth permit us to assess the effect of the Aznalcóllar mining spill on sediments located in station GL6. Both factors justify a low value of variance (17.6) which suggests an acute contamination of the concentration of Cd and Zn in the area. Furthermore, the negative values of both factors at depth higher than 12 cm informs that this contamination was not there before.

We have used together total concentrations of heavy metals and the enrichment and ecological factors to link the information from the concentration and the chemical speciation with the potential risk assessment. It produces that eigenvalues are likely to be bilateral but the main objective of this study was to find the relationship between the enrichment of heavy metals from the Aznalcóllar mining spill (SEF) and also de ecological risk effect associated with the enrichment (ERF) with the chemical speciation of the heavy metals measured in the sediments

4. Conclusions

The spillage from the Los Frailes mine is a social and ecological disaster, resulting in a huge financial loss for the economies of the region, including farming, fishing, tourism and the mining industry itself. The magnitude of the ecological damage to one of the Europe's last great wildernesses will only become apparent over time.

The MAA used in this assessment represented an useful tool to assess the contamination of the area. The use of the MAA to link the results obtained in the monitoring of the Aznalcóllar mining spill on sediments from the Guadalquivir estuary has permitted us to establish the early impact on the estuarine ecosystem. Within the context of this study, we can derive a number of conclusions regarding the source, the extension and the magnitude of the contamination measured in the area. These conclusion are summarized below:

(a) Although the high heterogeneity of the surface sediments do not offer a clear trend in the source and distribution of the contamination it can be demonstrated when compared to the vertical profile results that a contamination due to Cu is the predominant effect on the ecosystems of the estuary. The chronic character of this contamination should be confirmed and also the ecological risk evaluated by a specific study to establish the adverse effect. The source or sources of these Cu concentrations should be established in next studies because they were not related to the Aznalcóllar mining spill.

(b) The other potential and second in predominance in the ecosystem studied is the contamination by Pb. This contamination can not be associated with the Aznalcóllar mining spill and due to the high spread of the results in both MAA performed none trends can be deduced in their behavior. However, the low concentrations measured make this contamination as not concerned in the area.

(c) The Aznalcóllar mining spill has affected some of the areas of the estuary. The contamination effect can be cataloged such as acute affecting only specific stations in the surface sediments, which presents low hydrodynamic regimen. The sediment core study present the effect of the accident located in the first centimeters of the sediment so confirms the acute characteristic of the impact. The fact of the set up of the treatment plant on June 1998 helped to avoid a more strong effect of the accident on the estuarine ecosystem of the Guadiamar and Guadalquivir rivers.

(d) Although both metals Cd and Zn present high values on 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 effects associated with these concentrations of heavy metals.

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 accept 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 stations close to the sediment quality values need to be evaluated on the biological effect associated to them. Furthermore, the chronic contamination due to Cu and potentially Pb detected in this study should be also checked in relation to their potential biological effects under an integrated point of view.

It is also important to take into account that all the heavy metal concentrations except for Mn are very much lower than those monitored in the well-known mining area of Huelva (defined by the 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 and the effect of an isolated, albeit very large, single discharge such as the Aznalcóllar mining spill. 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 park under an integrated point of view.

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