Distribution of Trace Metals in Sediments and the Relationship with their Accumulation in Earthworms

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DISTRIBUTION OF TRACE METALS IN SEDIMENTS AND THE RELATIONSHIP WITH THEIR ACCUMULATION IN EARTHWORMS

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Concentrations of Cd, Pb, Cu and Zn and their speciation in river sediments (Guadalquivir River, Spain), were determined. Relationships between trace metal concentrations in sediments and earthworms were studied in order to estimate the rate at which metals accumulated in organisms living in sediments.

The bioavailable fraction of Cd represented more than 50 % of the total Cd found in sediments, and this percentage was much greater than those of the other elements examined. Most of the Cu was present in the organic and residual fractions. Lead and Zn were mainly associated with the crystalline iron oxide fraction.

The application of factorial analysis to the total heavy metal concentrations and some soil properties reduced the number of original variables to only three, namely factors, which explained the total variance of 94 %.

Metals accumulated in earthworms were related by a second grade polynomial equation with fractions where the metals were mainly bound. Cd exhibited the highest accumulation factor, followed by Zn, Pb, and Cu, respectively.

KEY WORDS: Heavy metal speciation, Cd, Cu, Pb, Zn, sediments, earthworms, factorial analysis, regression.

INTRODUCTION

Total metal analysis in sediments may provide information concerning possible pollution levels, but generally and for most elements, there are not sufficient criteria for estimating their biological effects. This is because it is the metal chemical form in the sediment and sediment itself that determine its mobilization capacity and behavior in the environment. An experimental approach commonly used for studying the mobility and bioavailability of metals in sediments is the use of selective sequential extraction procedures.

Several soil and sediment selective sequential extraction schemes have been described and reviewed in the literature.[1-6] Generally, these schemes use a sequence of reagents of increasing reactivity in the dissolution process. Although these reagents are not highly specific in extracting metals from different phases[7-9], they provide a useful means for estimating potentially available metal sediment concentrations.

Depending on physico-chemical characteristics of the sediment, the nature and concentration of the elements, deviations between the results obtained by different sequential extraction schemes may be considerable. The problems found by several authors[1,6,8,10], independently of the speciation scheme used to obtain different fractions, were mainly related to three causes: 1) the limited selectivity of extractants; 2) the trace element redistribution among phases during extraction and, 3) the overload of the chemical system if the content of metal is too high. To partially avoid these problems Rauret *et al.* (1989)[6], have proposed carrying out successive extractions in each one of the steps proposed by Tessier *et al.*, (1979)[5]. This procedure carefully controls the parameters involved in the solubilization of metal extracted by the acetic acid acetate buffer (pH = 5), by hydroxylamine hydrochloride and by hydrogen peroxide.

This paper presents the extent of Cu, Pb, Cd, and Zn, metal pollution in sediments sampled along the Guadalquivir River (Spain), a river moderately affected by urban, commercial, and industrial pollutant inputs. These metals, as well as some sediment chemical properties have been analyzed by multivariate statistical methods, in order to know the behavior of the heavy metals in the zone. This paper also reports the results of a study in which the Rauret *et al.* (1989)[6] sequentiation scheme was applied to determine the solid-phase distribution of trace metals in the sediments. Copper, Pb, Cd and Zn were sequentially extracted from sediments to determine the exchangeable, carbonates, reducible, organic, and residual fractions. Lastly, we have investigated the relationships among the partitioning of trace metals in sediments and their accumulation in earthworms living in these sediments, in order to identify the factors that influence trace metal bioavailability to earthworms, to estimate the rates at which they accumulated metals and their potential use as pollution bioindicators.

MATERIAL AND METHODS

Study area

The study has been carried out along the Guadalquivir river basin (Spain). The Guadalquivir basin is the most economically important area of the south of the Iberian Peninsula; its economic importance stems from its proximity to major metropolitan areas (Cordoba and Seville), which implies the presence of numerous urban, commercial, and industrial pollutants in the vicinity of the sampling stations.

Location of sampling stations are shown in Figure 1. All stations were located in the shore of Guadalquivir River. Twelve sediment samples sites were selected near suspected sources of agricultural or industrial pollution. All samples were collected 29, 30 and 31 May 1990. Station 1 was situated near the source of the river and station 12 in the delta of Guadalquivir River (36° 47′ North latitude and 6° 21′ West longitude).

Sediment samples were collected by manual coring (0–5 cm) from shallow water river sediments and stored in glass jars. It was impossible to obtain earthworms in sampling station 11 and 12.
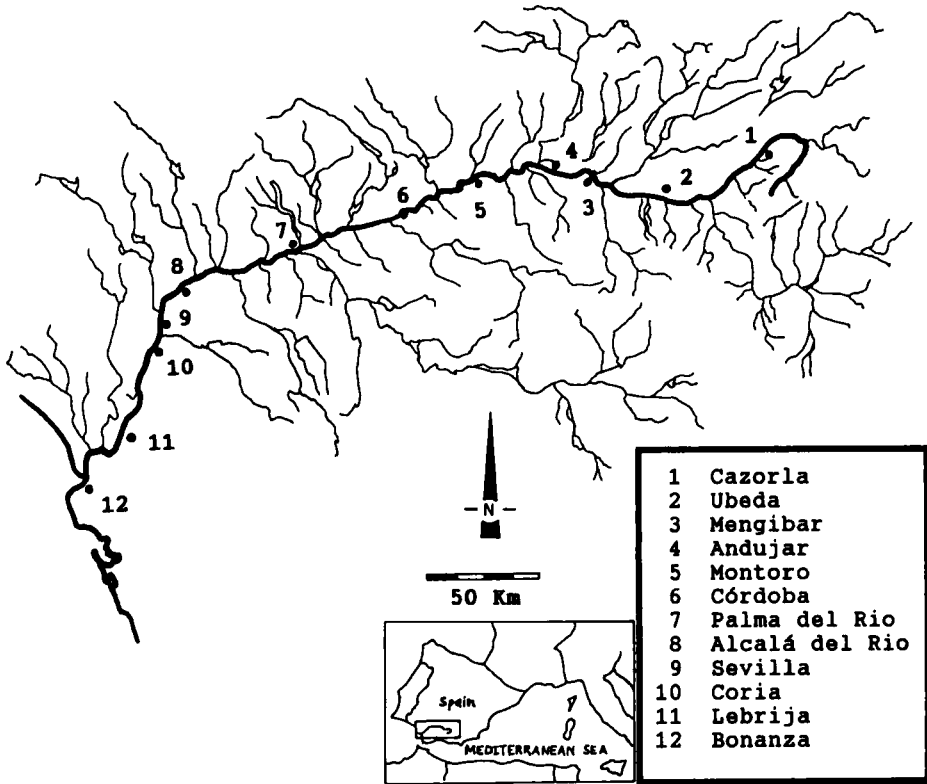
Figure 1   Study area and sampling locations in the Guadalquivir river basin.

Sediment properties

Properties of the surface sediment samples investigated were determined by standard methods. Sediment pH was determined using H_2O according to Folsom *et al.*, (1981)[11]. Sediment solution ratio was 1:2. The percentage of organic material was determined by thermal analysis[11]. Sediment texture was determined according the method of Bouyoucos (1928)[12] and classified by Sediment Survey Manual USA method (1951)[13]. Percentage of carbonate was estimated according to the Clark method (1971)[14] by using 10% HCl.

Total and trace metal concentration

Sediment samples were prepared for metal analysis by drying the sediments in an oven at 60°C for 24 hours. Earthworm (Lumbricus terrestris L.) removed from these sediments, were placed in petri dishes on moist filter paper 3 days to void their gut.

The total content of Cu, Pb, Cd and Zn in the sediment and earthworm samples were digested overnight according to a method previously described.[15]

The sequential scheme procedure was based on the Rauret et al., 1989)[6], which produce five fractions:

Fraction 1 (F1): Exchangeable metals, the sediment sample was extracted for 60 min with 1 M $MgCl_2$ at pH 7.0;

Fraction 2 (F2): metals associate with carbonates or specifically adsorbed. The residue from F1 was leached for 5 h with 1M NaOHAc adjusted a pH 5.0 with HOAc;

Fraction 3 (F3): metals associate with Fe-Mn oxides. The residue from F2 was extracted at 96°C for 6 h with 0.04 $NH_2OH.HCl$ in 25% (v/v) HOAc;

Fraction 4 (F4): metals associate with organic matter and sulfides. The residue from F3 was extracted at 85 °C for 5 h with 30% H_2O_2 adjusted a pH 2.0 with HNO_3 and then at room temperature with 3.2 M NH_4OAc in 20% HNO_3;

Fraction 5 (F5): residual metals. The residue from F4 was digested as for total metals as previously described.[15]

For fractions 2, 3 and 4, successive extractions with the pertinent reagent were performed under control of pH, of extracted iron and manganese and redox potential (Eh), respectively. Preliminary studies, employing four different types of sediments, showed that two successive extractions were sufficient for the studied sediments.

Residues were separate from the supernatant by 30 min centrifugation (HERMLA Z-320 centrifuge) at 4,000 rpm. The content of the five trace out and total metal in the filtered solution was determine by Atomic Absorption Spectrometry (Perkin Elder model 2280). Standard solutions for the metals were prepared for each extraction step in a background solution of the extracting reagents. Sum of extracted trace metals, as a percent of total metal content was calculated. The limits of detection are giving in Table 1.

Statistical analysis

The statistical analysis (correlation matrix, Factorial and Regression Analysis) were conducted on a 386 PC microcomputer using the statistical software program "Statgraphics" (version 5.0, STSC, Inc, Rockville, Maryland, USA)

Table 1 Detection limits for Cu, Pb, Cd, and Zn in the five fractions solutions (μg/g).

Fraction	Cu	Pb	Cd	Zn
Exchangeable	0.29	0.60	0.83	0.71
Carbonates	0.92	2.63	0.43	0.48
Reducible	3.00	3.51	0.10	0.95
Organic matter	0.64	5.46	0.55	1.06
Residual	1.91	1.21	0.71	0.09

Table 2 Some properties of sediments and total concentrations of Cu, Pb, Cd and Zn in µg/g from Guadalquivir.

Site N°	Soil type	% Organ matter	% Carbonat.	Soil pH	Cu	Pb	Cd	Zn
1	F^1-Ar^2	39.22	5.0–10.0	8.43	6.21	16.5	3.09	22.94
2	F-Ac^3	23.84	≥10.0	8.22	19.70	13.4	2.44	48.34
3	F-Ac	23.72	≥10.0	8.16	22.50	19.8	2.70	71.38
4	F-Ac	24.33	≥10.0	8.19	23.55	33.4	2.17	69.18
5	F-Ac	17.31	≥10.0	8.49	17.05	15.6	1.78	46.68
6	F-Ac	17.94	≥10.0	8.43	15.36	20.3	1.90	52.15
7	F-Ac-Ar	13.71	5.0–10.0	7.98	15.25	28.0	1.78	59.25
8	F-Ar	12.73	≥10.0	7.80	23.76	21.7	1.62	85.50
9	F-Ac-Ar	20.82	≥10.0	7.89	37.17	63.0	2.18	122.25
10	Ar-F	13.73	5.0–10.0	8.59	7.64	17.1	1.85	47.37
11	Ac	23.05	≥10.0	8.38	25.28	25.1	2.32	102.44
12	Ac	25.15	≥10.0	8.21	26.74	33.3	2.57	113.77

1 = Silt; 2 = Sand; 3 = Clay

RESULTS AND DISCUSSIONS

Total metals

Results shown in Table 2 revealed that Cd and Pb levels were higher than the literature values cited for unpolluted fluvial systems, and the normal background concentrations in the Guadalquivir river basin. Their values corresponded quantitatively to medium level polluted regions. In contrast, the values of Cu and Zn found in the studied sediments were in the range of metal levels found in low metal polluted regions.[16-18].

The agricultural (points 2, 3 and specifically point 4) and industrial activities (point 9) jointly with human wastes, were connected with metal concentration levels in Guadalquivir river basin sediments. The variation of pH, the texture and the content of organic matter (see Montoro, point 5), may also be important factors governing the distribution of metals.

Sediments located near the river mouth (points 11 and 12) were affected by the Atlantic Ocean's tide influence. This effect would explain the increase of the metals at these points, because there is not any pollutant activity in the zone. This increase was particularly significant for Cd and Zn.

Factorial analysis

The normalized data set of Table 2 has been statistically analyzed using factor analysis. Principal factor scores (theta values) and factor loadings (beta values) were calculated from the eigenvectors of the scaled data matrix.

Table 3 shows the eigenvalues calculated for the four first factors and the percentage of variance explained by each one. There are only three significant eigenvalues (i.e. greater than unity) that explain the 94 % of the total variability of the data set. The two first principal factors retained 53.6 and 26.2 % of the original variance of the data set, respectively. The third factor accounted for an additional 14.2 % of the original variance.

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SAMPLE SCORES
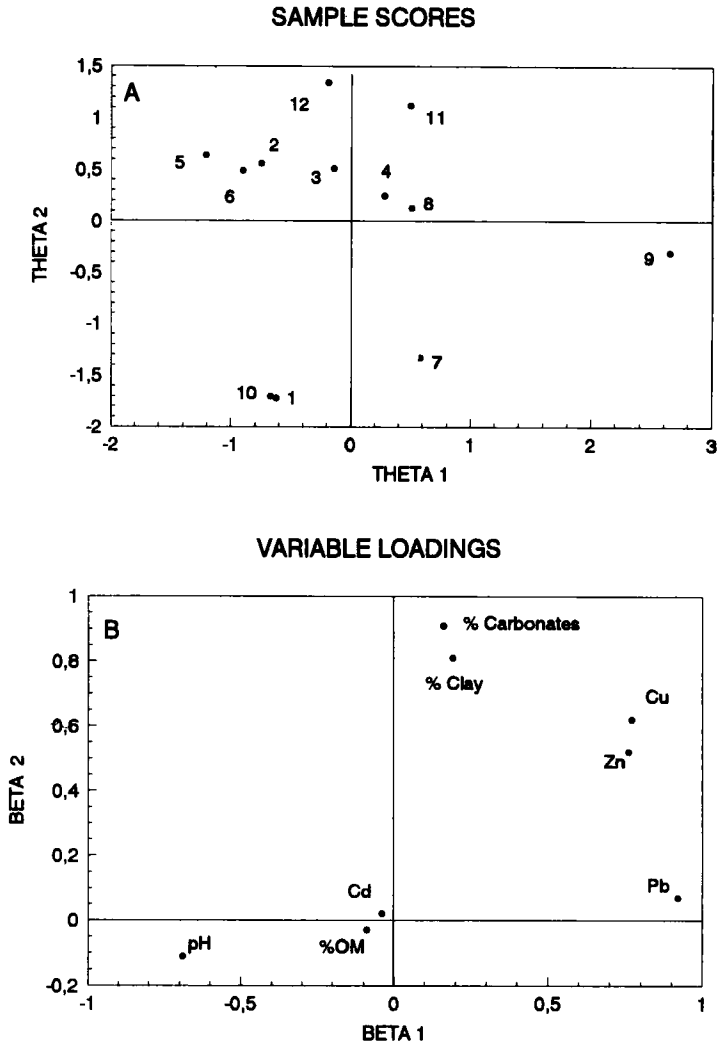
VARIABLE LOADINGS

Figure 2 Plot of the two first factors. A) score samples B) loading variables.

The varimax loadings matrix of the three first factors (Table 4) shows that the first factor was mainly formed by Cu, Pb, Zn and sediment pH. Factor 2 was defined by carbonates and clay content. Cadmium behaves in a different way, appearing in factor 3 associated to organic matter content. More detailed information about similarities and differences between samples and variables emerges from both Figures 2 and 3. The variable loading plots (Figures 2b and 3b) show three groups of variables, the first formed by Cu, Pb and Zn, the second one formed by Cd and the percentage of organic matter and the third one formed by the percentage of clay and carbonates. The pH variable is not related to any of them.

SAMPLE SCORES
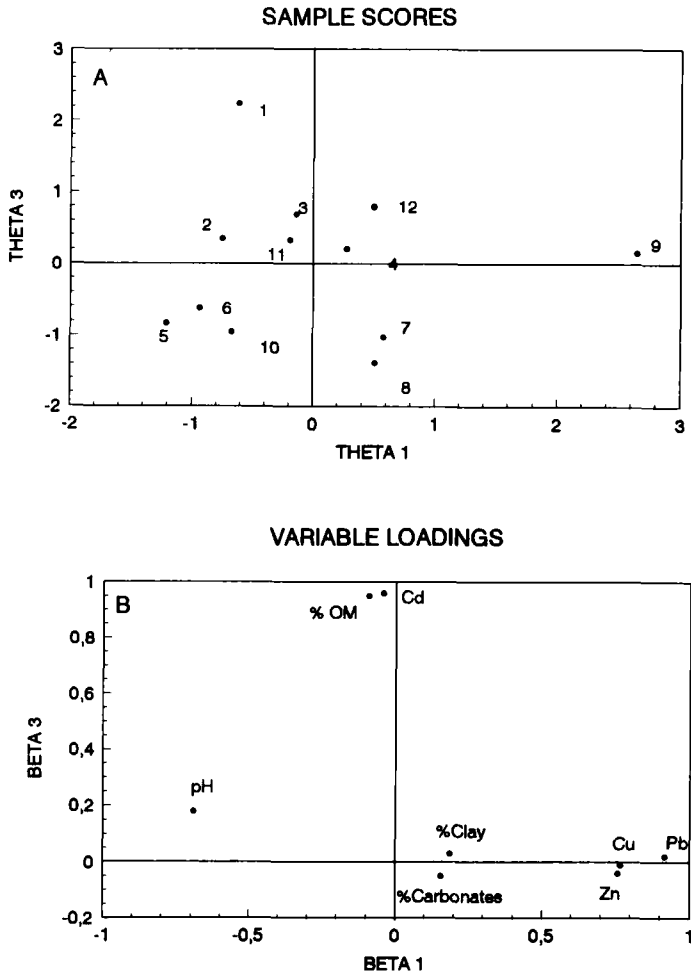
VARIABLE LOADINGS

Figure 3 Plot of the first and third factors. A) scores samples B) loading variables.

The sample score plot of the two first factors (Figure 2a) illustrates the sample similarity on the basis of Cu, Pb, and Zn content versus the percentage of clay and carbonates. The sediments seem to be grouped in three categories. Points 1 and 10, with low contents of Cu, Pb, Zn heavy metals, percentages of clay, and carbonates, formed one class (I), which was far from the other sediments. Points 2, 3, 5, 6 y 12 formed another group (class II), which was very closed to group III formed by points 4, 8 and 11. Points 9 and 7 were outlier of the three mentioned groups. The sample score plot of the first and third principal factors (Figure 3 a) shows a different distribution of sampling points depending on the four metal levels content and the percentage of organic matter. Point 9 with higher levels of Cu, Pb and Zn and point 1 with higher levels of Cd and organic matter are clearly separated from other sediments.

Table 3 Eigenvalues and accumulated variance explained by the four first rotated factors.

	Eigenvalues	% Variance	% Accumulated Variance
FACTOR I	3,802	53,6	53,6
FACTOR II	1,857	26,2	79,7
FACTOR III	1,007	14,2	93,9
FACTOR IV	0,259	3,6	97,6

The F.A. shows clearly that in sediments taken at points 7, 8 and principally in station 9, there is an important emission of Cu, Pb and Zn. These sediments have also the lowest pH values of the studied samples. On the other hand, Cd sources are totally different, being the points located near the river source (station 1, 2, 3 and 4) and those sites at the mouth (station 11 and 12) which have significant levels of Cd. This high level of Cd is related to the high content of organic matter.

Partitioning of Cu, Pb, Cd, and Zn

Table 5 shows the experimental results obtained in the five fractions when controlled successive extraction steps were used. The application of the Rauret *et al.* methodology[6] makes possible the avoidance of the problems associated with trace element redistribution and overloaded chemical systems. The second subfraction of each step was especially important in the most relevant fractions of each metal of the most polluted sediments, such as the sediments from points 9, 11 and 12, above all in the case of Zn.

Values for residual fraction should be considered as the background levels in sediments from the Guadalquivir river basin (Table 5). In fact those values were not statistically different ($p < 0.05$) from the normal values found in the Guadalquivir valley[17]. This "inert phase" corresponds with the part of the metal which cannot be mobilized.

Figures 4 and 5 show the percentages of total Cu, Pb, Cd and Zn associated with each of the five sequential fractions for all sampling points.

Copper   Although there was a considerable variation in the proportion of total copper present in the various fractions, most of it was present in the residual fraction (F5) or associated with the organic matter fraction (F4) (Figure 4). These results agree with previous

Table 4 Varimax rotated factor loadings matrix

Variable	Factor I	Factor II	Factor III
Soil pH	–0,691	–0,116	0,182
% Org. matter	–0,099	–0,037	0,958
% Clay	0,194	0,813	0,037
% Carbonates	0,164	0,192	–0,051
Cu	0,776	0,626	–0,019
Pb	0,925	0,079	0,025
Cd	–0,047	0,021	0,960
Zn	0,762	0,524	–0,049

Table 5 Cu, Pb, Cd and Zn concentrations in sediments from Guadalquivir river in μg/g.

		S.1	S.2	S.3	S.4	S.5	S.6	S.7	S.8	S.9	S.10	S.11	S.12
	COPPER												
Exchangeable		N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Subfraction 1	N.D	1.35	1.35	D	1.72	1.54	1.46	1.68	1.46	1.54	1.18	1.15
	Subfraction 2	N.D	1.24	0.99	1.07	1.50	1.41	0.97	D	1.09	D	1.00	1.11
Carbonates (sum)		N.D	2.59	2.34	1.07	3.22	2.95	2.43	1.68	2.55	1.54	2.18	2.26
	Subfraction 1	N.D	N.D	N.D	D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Subfraction 2	N.D	D	N.D	D	D	N.D	N.D	N.D	N.D	N.D	D	D
Reducible (sum)		N.D	D	N.D	D	D	N.D	N.D	N.D	N.D	N.D	D	D
	Subfraction 1	D	2.21	2.55	1.65	1.58	1.51	1.74	5.25	10.92	D	3.39	4.50
	Subfraction 2	N.D	1.98	2.19	2.60	1.22	1.41	D	2.76	5.12	D	2.28	2.89
Organic (sum)		D	4.19	4.74	4.25	2.80	2.92	1.74	8.01	16.04	D	5.67	7.39
Residual		3.05	10.40	10.80	10.58	7.06	8.06	5.99	8.55	11.32	3.82	11.54	10.99
	LEAD												
Exchangeable		N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Subfraction 1	N.D	N.D	N.D	N.D	D	3.13	4.35	2.93	8.01	3.35	3.40	3.46
	Subfraction 2	N.D	N.D	N.D	2.97	3.18	3.71	3.78	D	6.94	2.91	4.32	4.58
Carbonates (sum)		N.D	N.D	N.D	2.97	3.18	6.84	8.13	2.93	14.95	6.26	7.72	8.04
	Subfraction 1	15.10	11.70	16.75	26.25	8.22	12.43	14.16	7.60	16.84	8.30	11.26	14.09
	Subfraction 2	N.D	N.D	N.D	5.32	N.D	N.D	D	3.60	9.11	N.D	D	4.70
Reducible (sum)		15.10	11.70	16.75	31.57	8.22	12.43	14.16	11.20	25.95	8.30	11.26	18.79
	Subfraction 1	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	D	N.D	N.D	N.D
	Subfraction 2	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Organic (sum)		N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	D	N.D	N.D	N.D
Residual		1.40	2.47	2.03	3.23	2.82	3.28	2.80	3.17	10.23	2.00	3.60	3.53
	CADMIUM												
Exchangeable		N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Subfraction 1	0.63	0.55	0.51	0.57	0.59	0.81	0.77	0.60	0.52	0.62	0.47	0.56
	Subfraction 2	0.53	0.52	0.51	0.48	0.41	D	N.D	N.D	D	N.D	D	D
Carbonates (sum)		1.16	1.07	1.02	1.05	1.00	0.81	0.77	0.60	0.52	0.62	0.47	0.56
	Subfraction 1	1.30	0.68	0.63	0.53	0.44	0.53	0.29	0.28	0.43	0.72	0.43	0.27
	Subfraction 2	N.D	N.D	N.D	N.D	N.D	N.D	D	D	N.D	0.18	0.20	0.23
Reducible (sum)		1.30	0.68	0.63	0.53	0.44	0.53	0.29	0.28	0.43	0.90	0.64	0.50
	Subfraction 1	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	Subfraction 2	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D ·	N.D	N.D	N.D
Organic (sum)		N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Residual		0.28	0.46	0.35	0.34	0.46	0.46	0.48	0.50	0.50	0.29	0.80	0.56
	ZINC												
Exchangeable		N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.43	D	N.D	N.D	N.D
	Subfraction 1	2.55	3.42	6.86	4.41	2.28	9.34	7.28	12.21	11.05	5.72	14.71	13.75
	Subfraction 2	1.37	1.25	3.27	1.97	1.22	3.46	3.66	6.48	8.83	2.14	3.49	10.09
Carbonates (sum)		3.92	4.67	10.13	6.38	3.50	12.80	10.94	18.69	19.88	7.86	18.20	23.84
	Subfraction 1	8.20	10.79	20.01	16.96	6.92	10.53	16.35	14.33	45.28	8.49	34.21	31.09
	Subfraction 2	2.47	4.71	7.74	8.57	8.80	9.17	9.02	11.41	19.15	7.93	14.83	15.20
Reducible (sum)		10.67	15.50	27.75	25.53	15.72	19.70	25.37	25.74	64.43	16.42	49.04	46.29
	Subfraction 1	D	1.95	1.83	1.51	1.13	1.47	3.43	4.07	6.42	2.17	3.95	3.92
	Subfraction 2	1.21	3.07	3.76	2.72	1.03	D	1.32	1.92	2.94	D	2.05	1.91
Organic (sum)		1.21	5.02	5.59	4.23	2.16	1.47	4.75	5.99	9.36	2.17	6.00	5.83
Residual		6.19	21.86	17.46	21.30	20.14	23.01	17.44	23.31	23.07	15.31	30.77	29.37

N.D = Not Detectable D = Detectable

works[5,22-25], which also found important percentages of Cu associated with detrital and organic matter. Among the rest of the movilizable fractions (F1, F2 and F3), only the carbonates fraction had certain relevance in accordance with previous results[15]. The preference of Cu for organic matter is supported by the high stability constant of Cu complexes

% of Cu bonded to each fraction

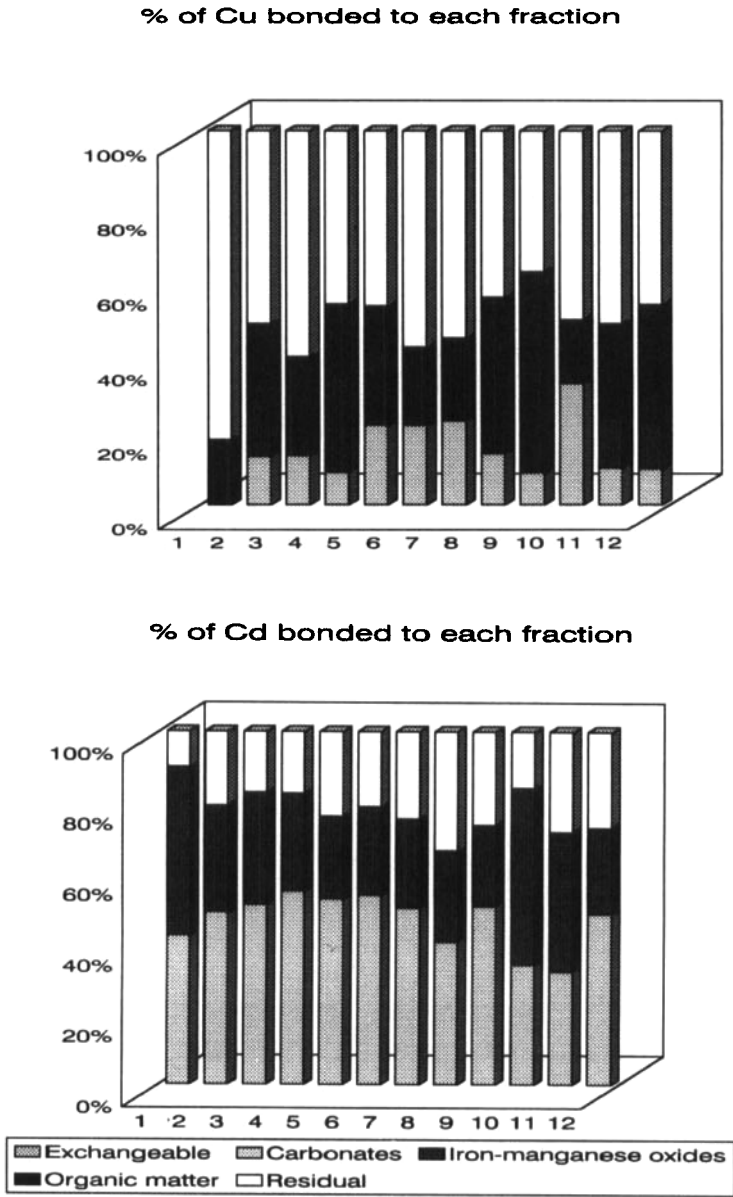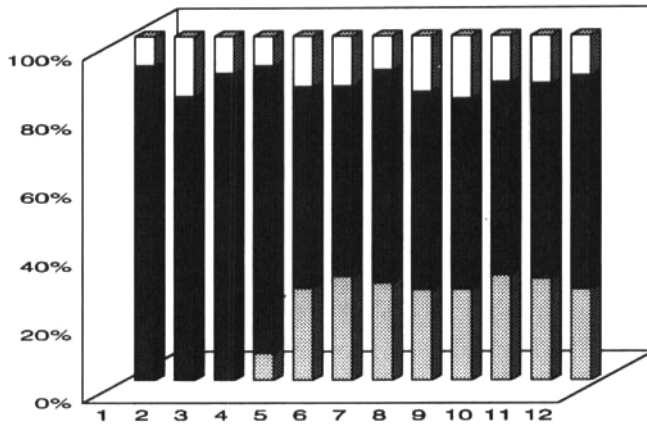

% of Cd bonded to each fraction

Figure 4   Percentage of total Cu and Cd associated with each of five sequential fractions for all sampling points in sediments from the Guadalquivir river.

% of Pb bonded to each fraction
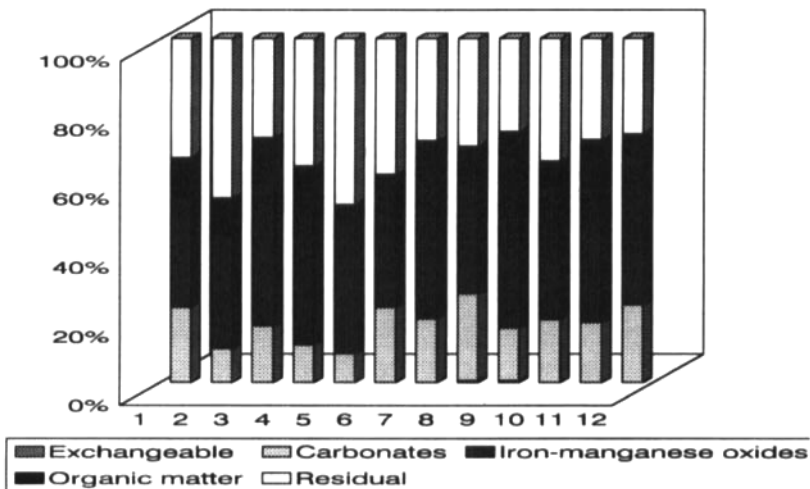
% of Zn bonded to each fraction

Figure 5 Percentage of total Pb and Zn associated with each of five sequential fractions for all sampling points in sediments from the Guadalquivir river.

with organic matter[24]. Other studies have pointed to Cu as being associated with the organic matter fraction[25,26].

The importance of the Cu residual fraction in the sediments from the Guadalquivir River was due to the low total levels of Cu found in the fluvial system; the greater the percentage of metal in the residual fraction, the smaller the total metal concentration in the zone.

Lead In the case of Pb, Fe-Mn oxides fraction (F3) dominated the distribution with an average over 50 %, and at some points more than 75 %. The contribution of the carbonates fraction (F2) was rather important, accounting for an average of 25 %, except for the sediments near the mouth of the river. Several authors reported similar distribution models for this metal.[6,23,28–31]

The evolution of the concentration and the percentage of this metal along the river were very interesting. Thus, in the three points nearest to the source (sediments 1, 2 and 3), which have the lowest total concentration metal levels, Pb was found between the non soluble forms (F5) and bonded to crystalline oxides (F3). At point 4 (Andujar), when the total level of Pb increased from 19.80 to 33.40 μg/g, 9 % of Pb was found to be associated with carbonates. At the next stations (points 5 to 12) the percentage of Pb associated with carbonates increased to 45 %. The greater the total Pb level concentration in sediments the bigger percentage of easily mobilize Pb chemical forms. Only in the most polluted sediment (point 9, close to Sevilla), a low percentage of Pb (~10%) was associated with organic matter.

Zinc The chemical forms of Zn associated with different sediment fractions have a high variability[27,32]. The carbonates and Fe-Mn oxides fractions were always the largest, but the percentage represented for each of both fractions depends on the sediment pollution. In the studied samples, where the amount of Zn is not very high, the Fe-Mn oxides fraction was always the largest (50 %), the residual fraction was the second largest, with percentages over 25 %, followed by the carbonates fraction (F2) with a percentage over 20 %. Pb and Zn were mainly associated with the crystalline oxides fraction (F3). Zn and Pb oxides have a stability constant high enough to be concentrated at this site. Pb was more highly associated with this fraction than Zn, indicating that Pb formed complexes with Fe and Mn oxides that are more stable than those formed with Zn. Several other workers have found Zn and Pb to be highly associated with Fe and Mn oxides.[23,29]

The high content of carbonates (> 10%) in these sediments may explain the relative high levels of Zn and Pb in the carbonates fraction, which might provide a suitable pH for metal precipitation at that site. Calcium carbonate may act as a strong absorbent for heavy metals. Double salts like $CaCO_3.ZnCO_3$ and $CaCO_3.PbCO_3$, probably present in the sample, would justify our results.

Cadmium The carbonate fraction dominates the distribution with a percentage over 50 %. Significant amounts of Cd was present in the Fe-Mn oxides fraction (over 25 %) and the rest of Cd was associated with the residual fraction.

The high contents of Cd in F2, which agrees with the findings of Elsorkkary and Long (1978)[33], could be explained by the low solubility of cadmium associated with carbonates and the low stability constant of the complex formed with the organic matter, that could be

considered labile[34]. This behavior makes Cd become concentrated in the carbonates fraction. The sums of F1 and F2 represents Cd bioavailability, that are more than 50 % of the total. Andersson (1977)[35] suggested that Cd may be rather easily taken up by organisms living in sediments, Cd-organic complex, if present, are not tightly bound to sediment particles. These characteristics, plus the hazards of its presence to human health, suggest that more frequent examination of the levels of this element in sediment samples may be necessary to determine potential health hazards to residents living near contaminated areas.

Earthworm–sediments relationships

The aim of this section was to identify factors influencing trace metal bioavailability to earthworms and to estimate the rates at which metals accumulate in them. To this end, we have investigated the relationships between the partitioning of trace metals in sediments and their accumulation in earthworms.

Trace metal levels in the earthworms (Table 6) were related with the trace metal concentrations in each fraction (F1 to F5). Correlation coefficients were not calculated with F1, as the latter values were lower than or close to the analytical detection limits.

Highly significant statistical correlation coefficients ($p < 0.01$) were found between Zn found in earthworms and Zn found in F3 and F4. Copper, Cd and Pb earthworm levels were significantly correlated ($p < 0.05$) with Cu associated to (F2 and F4), Cd (F3) and Pb (F2) respectively.

Several regression approaches were attempted with the trace metal concentrations in earthworm as the dependent variable and the trace metal concentrations in various sediment fractions as the independent variables. Due to the high colinearity existing among the amount of metals associated to the different fractions, only the first coefficient had a significant level ($p<0.05$), that usually corresponded to the fraction where the metal was mainly associated. Thus F2 for Pb, F3 for Cd, F4 for Cu and F3 for Zn.

When the sediment metal concentration is low the accumulation in earthworms is not very high, and the relationship to sediment metal pollution seems to be lineal; therefore, in this case the elimination mechanism appears to be effective. However, when the sediment metal levels increase the accumulation increases exponentially, depending on the sediment

Table 6 Metal concentrations in earthworm tissues from various sampling sites of Guadalquivir river basin.

Sample site	Cu	Pb	Cd	Zn
1	11,00	7,6	6,66	50,66
2	5,85	7,3	1,28	74,28
3	5,00	5,9	1,18	88,57
4	4,95	4,4	1,06	84,72
5	3,58	3,1	2,00	75,71
6	3,52	7,5	1,12	70,42
7	8,57	12,1	2,07	107,14
8	1,57	1,7	1,28	78,57
9	10,28	15,0	1,59	252,17
10	4,01	6,4	1,25	93,05

metal concentration. For that reason the regression is non linear and the model must be a polynomial equation, which first derivative will be zero when the sediment metal concentration is zero (the accumulation in earthworm must be zero when there is no metal in sediment).

$$dCe/cCs = 0, \text{ when } Cs = 0$$
$$\text{it means that} \qquad dCe/dCs = K_1Cs \qquad [1]$$

where

K_1 = rate constant for uptake of metals, (accumulation coefficient).
Ce = metal concentration in earthworm.
Cs = metal concentration in the sediment fraction.
    The polynomial equation that best fitted the model was:

$$Ce = a + K_{1/2}*Cs^2. \qquad [2]$$

The regression equations obtained for the 4 metals were:

$$Cd_e = 0,70 + 3,22\ Cd(F3)^2 \qquad R^2 = 0,89 \qquad [3]$$
$$Cu_e = 2,77 + 0,020\ Cu(F4)^2 \qquad R^2 = 0,77 \qquad [4]$$
$$Pb_e = 5,15 + 0,04\ Pb(F2)^2 \qquad R^2 = 0,86 \qquad [5]$$
$$Zn_e = 59,94 + 0,046\ Zn(F3)^2 \qquad R^2 = 0,95 \qquad [6]$$

    The independent term show the amount of the metal in earthworm not explained by the corresponding fraction and the coefficient shows the accumulation factor. Cd has the highest accumulation factor, with a value of 6.44, followed by Zn, Pb and Cu with accumulation factors of 0.092, 0.08 and 0.04, respectively. The high value found for the Zn equation independent term should be related to the variable behavior of Zn in sediments, that probably needs a more complicated mathematical model to better explain its behavior.

CONCLUSIONS

Total metal analysis of the Guadalquivir River basin sediments revealed relatively low (specifically Cu and Zn) to moderate (Pb and Cd) pollution levels.
    The application of factorial analysis to the heavy metal sediment levels and some chemical sediment parameters reduced the number of variables to only three new variables, called principal factors, that are linear combinations of the original ones, which let us obtain a graphical picture of the overall situation.
    The variable loading and sample score plots of the three factors gave information about similarities and differences among samples and variables. Thus, Cd metal was related to organic matter content, Zn was related to Cu and Pb, and the percentage of clay was related to the percentage of carbonates.

The speciation of heavy metals with selective extracting agents gave additional information about the fundamental reactions governing the behavior of elements in sediments. Of the metal distribution found in the four studied metals, cadmium appeared to be the most readily solubilized, due to the fact that this metal was mainly associated with the carbonates fraction, that makes this element potentially bioavailable. Zinc and Pb were primarily found to be associated with the Fe-Mn oxides fraction and Cu was found mainly in the residual fraction or associated with the organic matter fraction.

The Cu, Pb, Cd and Zn levels in earthworms were related to Cu (F4), Pb(F2), Cd(F3), and Zn(F3), respectively, by a second grade polynomial equation. This model allowed us to estimate the rates at which metals accumulated in earthworms from sediments, which was called the accumulation factor. The accumulation factor of Cd was the highest, followed by Zn, Pb, and Cu, respectively.

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