

# TRACE METALS IN SEDIMENTS FROM THE "RIA DE HUELVA"

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The Ría de Huelva is an estuarine zone into which flow the Odiel and Tinto rivers, polluted by trace metals. Total contents of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Pb, Cd and Hg were determined in the <630 and <63  $\mu\text{m}$  fractions of bed sediments.

Total trace metal contents in the coarsest fraction are lower than in the finest, although both are highly correlated for most of the metals, allowing an easy grain size effect correction. Total concentrations of Cu, Zn, As, Pb and Hg are very high, having enrichment factor indexes ranging from 35-171. Important proportions of these are in easily soluble and reducible physico-chemical forms, which are readily available for living organisms.

**KEY WORDS:** Estuary, trace metal pollution, sediment, grain size effect, metal speciation.

## INTRODUCTION

The rivers Tinto and Odiel discharge into the Ría de Huelva, after flowing through an area known for its mining activities from times immemorial. The waters of both rivers are acidic (pH occasionally reaches values between 3 and 4), and contain large amounts of heavy metals and other trace metals from erosion and mining activity. In addition, the Ría de Huelva (formed by the union of the mouths of the rivers Tinto and Odiel and the Padre Santo Canal), is one of the most industrialized areas of Southern Spain, and consequently receives the discharge of industrial and urban wastes. The high concentration of heavy metals in waters of the Ría de Huelva has negative effects on other activities of the region, particularly on the shellfish industry, which on occasion has been paralysed.

The Ría de Huelva is an estuarine zone in which processes of flocculation and precipitation of metals take place because of the mixing of river and sea waters.<sup>1,2</sup> Therefore, the fate of most of the dissolved and particulate metals discharged by rivers and waste outlets are sediments.<sup>3,4</sup> Sediments are not only sinks of metals, but the latter can be released from them by chemical reaction and biological activity.<sup>3-6</sup> Therefore, sediment composition is often considered a good index for heavy metal and trace metal pollution of the aquatic environment.<sup>3,4,7</sup>

Total element composition of a particular sediment, as determined by a total chemical analysis, is not indicative of its potential pollution.<sup>6,8</sup> Sediments tend to display marked metal variability, even within short distances, grain size being the most important factor causing this variability, as metals tend to concentrate in the fine fraction.<sup>3,4,7</sup> Grain size effect can be minimized by different methods,<sup>4</sup> the most effective being physical separation of a size range or fraction followed by a chemical analysis of the separate material. Since most of the metals are concentrated in the  $<63\ \mu\text{m}$  fraction and this is relatively easy to separate, numerous studies have already been made on this fraction.<sup>9</sup>

As sediment metals are distributed among a variety of physico-chemical forms which exhibit different chemical reactivities, the measurement of the total concentration of a particular metal provides little indication of potential interaction with abiotic or biotic components present in the environment.<sup>6,10</sup> Partitioning of sediment-bound metals could be determined by thermodynamic calculations or by chemical speciation.<sup>6</sup>

The Ría de Huelva is presently subjected to a Corrective Plan for Control of Industrial Waste Disposal. Data on sediment characterization of the Ría de Huelva are scarce,<sup>11,12</sup> thus this study has two main objectives: (i) to characterize sediments of the Ría de Huelva, specially in respect of metal contents and to establish a simple method to correct grain effects, and (ii) to determine metal distribution in the different chemical forms in which they are in the sediments, to estimate their readiness to dissolve and the degree of bio-availability.

## EXPERIMENTAL

### *Sampling*

Bed sediment samples were taken using an impact drag from a boat, introduced into plastic bottles and frozen.

Samples were collected in January 1989, in two sites of the Ría del Odiel (samples O1 and O2), in two sites of the Ría del Tinto (samples T1 and T2), and in five sites of the Padre Santo Canal (samples C1 to C5). Figure 1 shows the location of the sampling sites.

### *Analysis of Samples*

Samples were homogenized and fractions  $<630\ \mu\text{m}$  and  $<63\ \mu\text{m}$  were separated by sieving, dried at  $60^\circ\text{C}$  and ground to a fine powder.

Fraction  $<630\ \mu\text{m}$  was used for the sediment characterization. Sediment pH values were measured in 1 M KCl at a 1:4 ratio. Total carbon (TC) and total sulphur (TS) were determined by mean of a LECOS SC-132 autoanalyzer with an IR detector. Inorganic carbon (IC) was determined by the Bernard calcimeter method and the loss of weight by ignition at  $500^\circ\text{C}$  for 2 h.

Grain size distribution was determined by sieving for particles size  $>63\ \mu\text{m}$  and by mean a Sedigraph 5100 equipment for  $<63\ \mu\text{m}$ .

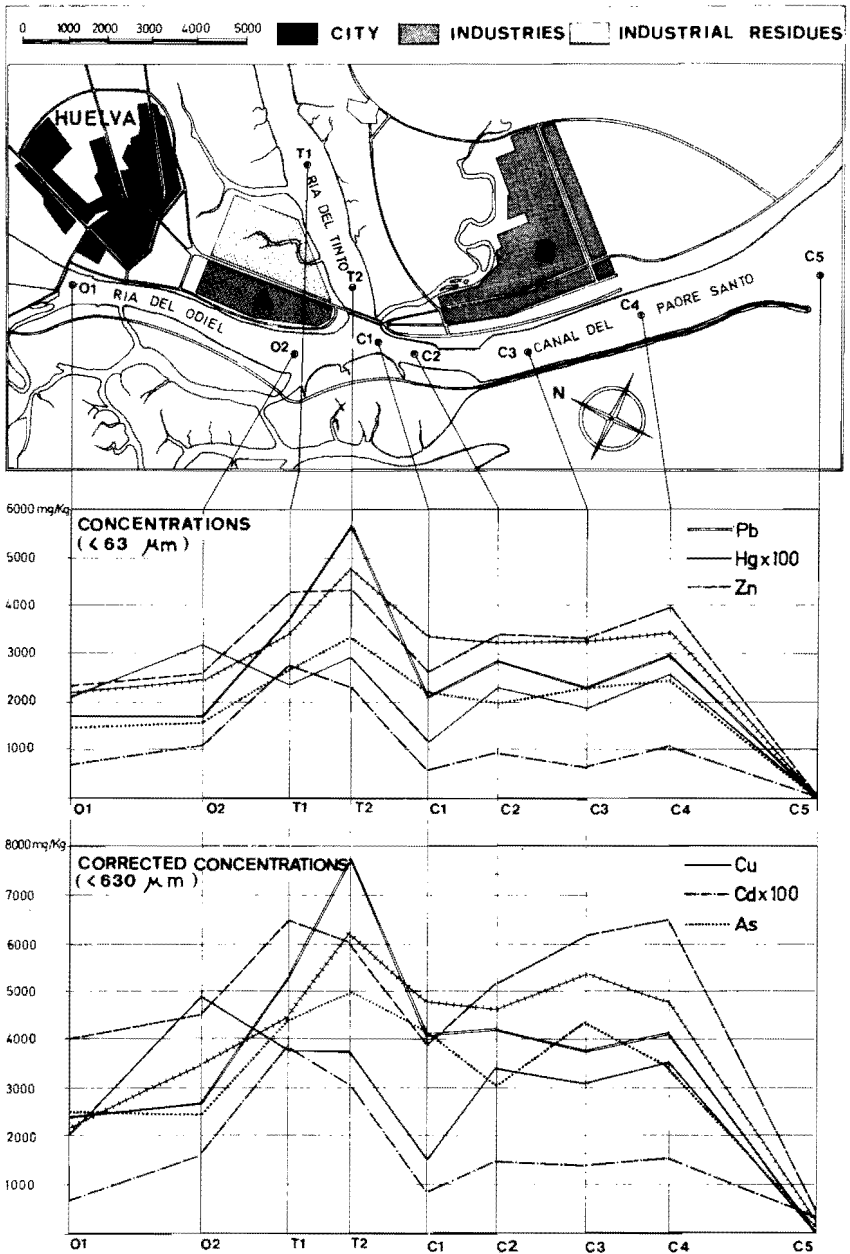


Figure 1 Sampling locations and evolution of the total metal contents throughout the Ría de Huelva.

**Table 1** General characteristics of the sediments of the Ría de Huelva

Sampling site	pH	TC %	IC %	TS %	LW %	Grain size distribution			
						630–200 $\mu\text{m}$ %	200–63 $\mu\text{m}$ %	<63 $\mu\text{m}$ %	<2 $\mu\text{m}$ %
O1	6.0	0.57	<0.1	0.55	2.85	71.2	15.6	13.2	2.3
O2	6.2	1.51	<0.1	1.28	6.30	15.2	36.5	48.3	15.8
T1	5.8	1.58	<0.1	2.52	5.50	13.0	38.8	48.2	27.2
T2	6.8	1.92	<0.1	2.84	5.90	6.1	34.7	59.2	24.4
C1	6.2	1.43	<0.1	3.33	4.30	19.0	51.5	29.5	13.6
C2	7.2	1.95	<0.1	1.92	7.25	18.0	27.1	54.9	27.1
C3	6.8	2.21	0.25	1.73	5.60	23.8	27.7	48.5	19.9
C4	6.2	2.17	0.45	2.76	7.55	26.2	6.5	67.3	31.2
C5	8.0	0.84	0.80	<0.1	1.05	95.1	3.9	1.0	<1.0

Total metal contents were determined both in <630 and <63  $\mu\text{m}$  fractions digesting the sample with a mixture of hot conc.  $\text{HNO}_3$ -HCl (1:3). Residues left after acid attack of <630  $\mu\text{m}$  samples were washed with deionized water, dried and weighed. Analysis of Cu, Co, Cd, Zn, Fe, Al, Ni, Cr and Pb in solution was performed by AAS. Cold-vapor and Hydride generation AAS techniques were used for Hg and As respectively.

Metal speciation of <630  $\mu\text{m}$  fraction was performed by the method of Tessier *et al.*<sup>13</sup> with slight modifications. Five fractions were obtained: (a) F1: exchangeable metals. The sediment sample was extracted for 1 h with 1 M  $\text{MgCl}_2$  at pH 7; (b) F2: metals bound to carbonates or specifically adsorbed. The residue from (a) was leached for 54 h with 1 M NaOAc adjusted to pH 5 with HOAc; (c) F3: metals bound to Fe-Mn oxides. The residue from (b) was extracted at 96 °C for 6 h with 0.04 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% (v/v) HOAc; (d) F4: metals bound to organic matter and sulphides. The residue from (c) was extracted at 85 °C for 5 h with 30%  $\text{H}_2\text{O}_2$  adjusted to pH 2 with  $\text{HNO}_3$  and then at room temperature with 3.2 M  $\text{NH}_4\text{OAc}$  in 20% (v/v)  $\text{HNO}_3$ ; (e) F5: residual metals. The residue from (d) was digested with a mixture of conc. HCl- $\text{HNO}_3$  (3:1).

## RESULTS AND DISCUSSION

### General Characteristics of Sediments

Sediments of the Ría de Huelva are moderately acidic or neutral, except one at the end of the Padre Santo Canal (sampling C5), near open sea, which have pH 8 (Table 1).

Inorganic carbon, IC, contents are very low, in many samples being below the detection limit of the method (Table 1).

Sediment organic matter is estimated by the total carbon, TC, and the loss of weight on ignition, LW, (Table 1). Both parameters follow a similar trend throughout the sampling area. Organic matter contents are high, typical for a

sedimentary deposit,<sup>14</sup> except for O1 and C5, located in the border of the estuarine zone.

Total sulphur, TS, values (Table 1), follow a similar trend to TC and LW, with lowest values in sites O1 and C5, although a peak is observed in C1.

Grain size distribution (Table 1) shows that sand content ( $630\text{--}63\ \mu\text{m}$ ) for all the samples is greater than 33%. On the other hand clay content ( $<2\ \mu\text{m}$ ) is greater than 13.6% except for O1 and C5. Therefore these sediments can be classified between sand (sample C5) and clay loam (sample C4).

### *Total Trace Metals in Sediments*

Table 2 shows total trace metal concentrations in both  $<630\ \mu\text{m}$  and  $<63\ \mu\text{m}$  fractions. It can be observed for all the metals that total concentrations in the  $<630\ \mu\text{m}$  fraction are lower than those in the  $<63\ \mu\text{m}$  fraction. This is a result of the grain effect, as trace metals tend to accumulate in the fine fraction.<sup>3,4,7</sup> In fact, it can be noticed that differences between values in those fractions are generally greater in the coarsest sediments (O1 and C5), and lower in the finest (C4).

Total values in both fractions are linearly correlated for all the elements, except for Co and Ni (Table 2), the significance levels for Cr, Mn, Fe, Cu, Zn, As, Pb, Cd and Hg ( $P < 0.01$ ) being higher than for Al ( $P < 0.05$ ). Correcting the values in the  $<630\ \mu\text{m}$  on the basis of the percentage of dissolved sample, DS, (Table 2), the new values are also linearly correlated with those in the  $<63\ \mu\text{m}$  fraction, except for Ni. The new correlation coefficients are somewhat higher than the previous ones, except for Fe and As, their significance levels remaining equal, except for Fe which decreases to  $P < 0.1$ . Therefore, total trace metal content, except Ni, in the  $<63\ \mu\text{m}$  fraction can be estimated by the content in the  $<630\ \mu\text{m}$  fraction through the corresponding linear equations whose slopes and intercepts are shown in Table 2. For Co this estimation improves correcting the value for the  $<630\ \mu\text{m}$  fraction by the percentage of dissolved sample.

Levels of all the trace metals in the  $<63\ \mu\text{m}$  fraction, except those for Al and Mn, are generally higher than the values in the average fossil shale<sup>15</sup> (Tables 2 and 3). The enrichment factor index, EFI, of trace metals in the sediments of the Ría de Huelva was calculated using the mean values of each trace metal and the average compositions of fossil shales<sup>15</sup> (Table 3). High EFI were found for Fe, Zn, Cu, Pb, As, Hg and Cd, indicating heavy pollution of anthropogenic origin. For Cr, Ni and Co, the EFI were close to one. EFI values less than one were found only for Al and Mn. Low EFI values for Al and Mn can be explained because of the incomplete recovery of the  $\text{HNO}_3\text{-HCl}$  digestion. Treating the remainder of the residues from the  $\text{HNO}_3\text{-HCl}$  attack with a mixture of conc.  $\text{HF-HNO}_3\text{-HClO}_4$ , it was found that the former attack dissolved only a mean of 75 and 72% of Al and Mn respectively, while for Cr the recovery was 90%, and for the rest of the elements was of the order of 99%.

Figure 1 shows the evolution throughout the Ría de Huelva of the contents of those trace metals which showed highest EFI in the sediments. The six metals considered follow a similar trend, with two maxima near to the industrial areas A and B. The first, close to T2, can be attributed both to the river-estuarine

**Table 2** Total contents of trace metals in sediments. Calculated values were determined on the basis of the 630  $\mu\text{m}$  dissolved sample, DS (see text). Slope, intercepts, and correlation coefficients,  $r$ , are for the linear correlation between the values for 63  $\mu\text{m}$  vs. 630  $\mu\text{m}$  or for 63  $\mu\text{m}$  vs. calculated values.

Sampling sites	DS %	Al			Cr			Mn			Fe			Co			Ni		
		630 $\mu\text{m}$	63 $\mu\text{m}$ %	Cal.	630 $\mu\text{m}$	63 $\mu\text{m}$ mg/Kg	Cal.	630 $\mu\text{m}$	63 $\mu\text{m}$ mg/Kg	Cal.	630 $\mu\text{m}$	63 $\mu\text{m}$ %	Cal.	630 $\mu\text{m}$	63 $\mu\text{m}$ mg/Kg	Cal.	630 $\mu\text{m}$	63 $\mu\text{m}$ mg/Kg	Cal.
O1	28.7	2.1	4.8	7.3	45	105	157	280	495	976	7.3	12.1	25.4	15	30	52	30	71	105
O2	43.3	3.7	5.1	8.5	118	195	273	330	415	762	7.9	10.3	18.2	17	24	39	24	76	55
T1	43.4	2.5	4.2	5.8	84	130	194	192	255	442	11.2	15.5	25.8	23	35	81	35	100	81
T2	46.1	3.2	4.3	6.9	125	215	272	195	265	423	10.2	14.8	22.1	23	28	50	28	100	61
C1	38.3	2.0	4.1	5.2	56	105	146	132	240	345	10.0	14.5	26.1	15	30	39	30	88	78
C2	42.4	3.4	5.3	8.0	119	195	281	290	684	684	9.3	13.0	21.9	20	25	47	25	86	59
C3	33.3	2.3	4.1	6.9	63	120	189	280	340	841	7.5	13.2	22.5	19	31	57	31	96	93
C4	51.2	3.8	5.6	7.4	135	195	264	330	410	645	11.9	15.4	23.2	30	32	59	80	96	156
C5	11.8	0.3	—	2.5	19	—	161	100	—	847	0.6	—	5.1	4	—	5	15	—	127
Slope		0.5952	0.4061	0.7344	0.8094	0.6527	0.3700	0.8058	0.4235	0.5143	0.2166	0.5666	0.0456						
Intercept		2.9640	1.8320	-22.54	-22.19	23.13	116.4	-1.5460	3.795	5.1430	17.89	-15.43	85.08						
r		0.7613	0.7676	0.9683	0.9786	0.8396	0.8834	0.8435	0.6175	0.3700	0.8067	0.3387	0.1391						
P		<0.05	<0.05	<0.01	<0.01	<0.01	<0.01	<0.01	<0.1	—	<0.01	—	—						
		Cu			Zn			As			Pb			Cd			Hg		
		630 $\mu\text{m}$	63 $\mu\text{m}$ mg/kg	Cal.	630 $\mu\text{m}$	63 $\mu\text{m}$ mg/Kg	Cal.	630 $\mu\text{m}$	63 $\mu\text{m}$ mg/Kg	Cal.	630 $\mu\text{m}$	63 $\mu\text{m}$ mg/kg	Cal.	630 $\mu\text{m}$	63 $\mu\text{m}$ mg/Kg	Cal.	630 $\mu\text{m}$	63 $\mu\text{m}$ mg/Kg	Cal.
O1		645	2120	2248	1150	2300	4007	730	1410	2544	690	1770	2404	1.8	5.4	6.3	6.0	20.6	20.9
O2		1495	2400	3453	1965	2550	4538	1050	1460	2425	1165	1700	2691	7.0	10.8	16.2	21.1	31.7	48.7
T1		1930	3380	4447	2830	4220	6521	1900	2630	4378	2260	3740	5207	16.9	27.7	38.9	16.6	23.5	38.2
T2		2875	4770	6236	2790	4280	6052	2300	3330	4989	3570	5670	7744	14.2	22.7	30.8	17.3	29.7	37.5
C1		1825	3400	4765	1480	2600	3864	1600	2160	4178	1565	2050	4086	3.5	5.6	9.1	5.7	11.6	14.9
C2		1975	3170	4658	2190	3370	5165	1320	1950	3113	1785	2830	4210	6.2	9.4	14.6	14.4	22.7	33.7
C3		1785	3260	5360	2050	3310	6156	1450	2300	4354	1250	2260	3754	4.6	6.8	13.8	10.3	18.5	30.9
C4		2440	3430	4766	3330	3980	6504	1800	2500	3516	2120	3000	4141	8.1	10.7	15.8	18.1	25.7	35.4
C5		25	—	212	58	—	492	19	—	161	11	—	93	0.4	—	3.4	0.3	—	2.5
Slope		0.7579	0.6095	0.8445	0.8298	0.7658	0.6122	0.6447	0.7700	0.6223	0.7439	0.9824	0.5413						
Intercept		-585.2	503.4	-586.0	-138.7	-179.5	-39.75	-54.60	-435.00	0.0868	-1.1430	9.566	5.293						
r		0.9165	0.9243	0.9107	0.9109	0.9742	0.9056	0.9670	0.9705	0.9871	0.9898	0.8851	0.8949						
P		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01						

**Table 3** Trace elements in the average fossil shale<sup>15</sup> and mean values and Enrichment factor index, EFI, in sediments of the Ria de Huelva

<i>Element</i>	<i>Average shale mg/Kg</i>	<i>Mean values Ria de Huelva mg/Kg</i>	<i>EFI</i>
Al	80 000	46 507	0.6
Fe	47 000	133 769	2.8
Mn	850	353	0.4
Zn	95	3 329	35
Cr	90	158	1.8
Ni	68	89	1.3
Cu	45	3 244	72
Pb	20	2 879	144
Co	019	29	1.5
As	13	2 217	171
Hg	0.4	23	58
Cd	0.3	12	40

boundary effect and to the industrial waste discharges. The same is not observed in O2 probably because Odiel river water is less polluted by trace metals. Minimum values are found in sampling site C5, in the estuary-sea border, where deposition, precipitation, coprecipitation, etc. of trace metals have already finished.

#### *Trace Metals Speciation*

Figure 2 shows mean distribution of the trace metals in the five physico-chemical fractions obtained by the sequential extraction procedure.<sup>13</sup> As had been observed in previous studies,<sup>3,4,16</sup> each elements exhibits a distinctive partitioning pattern among the fractions.

All the trace metals, except Zn, Cd and Cu, present the highest proportion in the residual fraction F5. Fraction F5 contains mainly primary and secondary minerals, which may hold trace metals within their crystal structure, therefore these metals are not expected to be released into solution over a reasonable time span under the conditions normally encountered in nature.<sup>13</sup> Copper shows a tendency to accumulate in fraction F4, as had been found by other authors,<sup>4</sup> while Zn and Cd accumulate in F3 and F1 respectively. In these sediments another important proportion of trace metals is associated to Fe-Mn oxides, F3, as expected for estuarine sediments, from which they can be easily released by lowering pH and changes in the redox conditions.

It is interesting that, although the proportion of trace metals in F1 is not high, except for Cd and Zn, F1, the "exchangeable phase" is rather important as it represents very loosely bound trace metals and may regulate and/or reflect the composition of surface water.<sup>3</sup> For those sediments in which the content of calcium carbonate is negligible (Table 1), F2 represents specifically adsorbed trace metals which can be dissolved at pH 5. Neither is the proportion of trace metals in F2 high except for Zn. However, the sums of F1 plus F2 (which appears on the

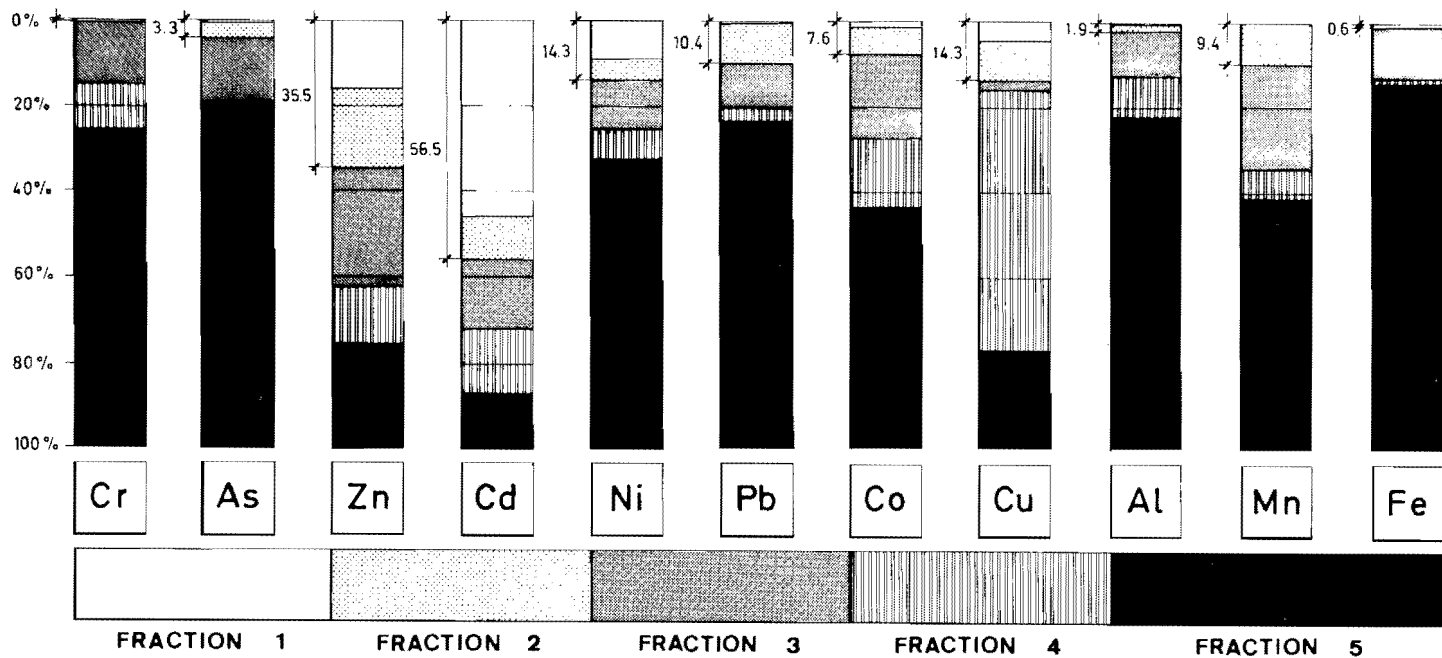


Figure 2 Mean values of the speciation of trace metals in the sediments of the Ria de Huelva.



left of the upper part of each bar in Figure 2), reach considerable values (35.5–10.4%) for some metals, e.g.: Zn, Cd, Pb and Cu, which is extremely important because this represents the proportion of trace metals readily available for living organisms.

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