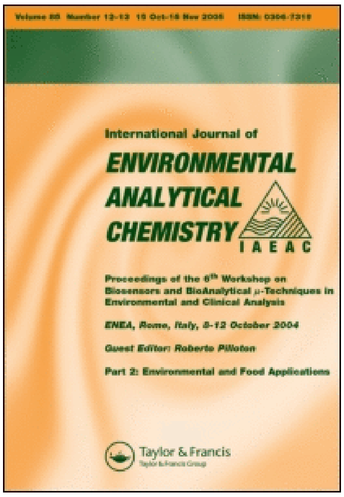

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HEAVY METAL FRACTIONATION IN SEDIMENTS FROM THE TINTO RIVER (SPAIN)

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Seventeen sediment samples from the Tinto and its main tributaries were analyzed for this study. For each of these samples, the association of metals (Cu, Zn, Cd, Pb, Fe, Ni, Cr and Co) was determined in four fractions: acid soluble, reducible, oxidizable and residual. The total metal content was also determined. Results showed high mean concentrations of Fe (109,000 mg/kg), Pb (2330 mg/kg), Zn (901 mg/kg), Cu (805 mg/kg), and Cd (2.7 mg/kg) in the sediments studied. However, the mean values found for Co (21 mg/kg), Cr (56 mg/kg) and Ni (17 mg/kg) are comparable to those in unpolluted areas. Heavy metal fractionation of the Tinto River sediments showed that the metals with the greatest mobility (i.e., metals that could pass easily into the water under changing environmental conditions) are Cd and Zn. These are the metals that showed the highest percentages in the first two fractions (the most labile) and the lowest percentages in the residual fraction. However, the percentage of metal present in the fourth fraction (residual) was high for Cr (78%), Ni (71%), and Co (66%), which implies that these metals are strongly linked to the sediments.

Keywords: Sediment; Heavy metal fractionation; Metal pollution; Sequential extraction

INTRODUCTION

The heavy metal concentration in aquatic ecosystems has increased considerably as a result of human production and consumption activities. In these ecosystems the sediments constitute the main sink for these elements, but when environmental conditions (pH, sediment redox potential) change, sediments can act as a source of metals [1–3].

To assess the environmental impact of polluted sediments, information on total concentrations alone is not sufficient because heavy metals are present in different chemical forms in sediments (easily exchangeable ions, metal carbonates, oxides, sulphides, organometallic compounds, ions in crystal lattices of minerals), which determines their mobilization capacity and their bioavailability [4–6].

Several methods for determining the different forms of metals in sediments are described in scientific literature [7–9]. The most widely-used methods are based on sequential extraction procedures, whereby several reagents are used consecutively to extract operationally-defined phases from the sediment in a sequence.

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For this study, we selected the sequential extraction procedure proposed by the European Union's Standards, Measurements and Testing program (SM&T, formerly BCR) [10,11]. This procedure consists of three successive extractions that allow us to associate the metals with one of the following phases:

Acid soluble phase (*fraction 1*) This phase is comprised of exchangeable metals and others bound to carbonates that can easily enter the water column when, for instance, the pH decreases. This is the fraction with the most labile union to the sediment and, therefore, the most dangerous for the environment.

Reducible phase (*fraction* 2) This fraction is made up of metals associated with iron and manganese oxides that can free themselves if the conditions of the sediment changes from oxic to anoxic. A change to anoxic conditions can be caused, for instance, by the activity of microorganisms present in sediments.

Oxidizable phase (*fraction* 3) This phase shows the amount of metal bound to the organic matter and sulphides that can be freed under oxidizing conditions. These conditions can come about, for example, as a result of sediment resuspension (due to dredging activities, currents, flooding, etc.) and the sediment particles come into contact with oxygen-rich water.

Furthermore, a fourth *residual or inert phase* (*fraction* 4) was determined; this is the difference between the total metal content and the sum of the contents in the three previous phases. The metals that primarily correspond to this fraction are those associated with minerals, which form part of their crystalline structure, and which, as a result, are unlikely to be released from the sediments.

In this study, not only were the total amounts of eight metals (Cd, Co, Cr, Cu, Fe, Ni, Pb, and Zn) determined in superficial sediments of the Tinto River and its estuary, the metal fractionation was also determined. The fractionation allowed us to see the mobility of these metals in the sediments, that is, their ability to enter the water when there are changes in the environmental conditions of the Tinto River (changes in pH, redox potential, etc.)

STUDY AREA

The Tinto River runs through the Province of Huelva in the southwest corner of the Iberian Peninsula. It is 92 km long, has a drainage area of 1680 km^2 and empties into the Gulf of Cádiz [12]. The river is fed by a number of tributaries at different points, the main ones being Santa María, Jarama, Candón and Nicoba (Fig. 1).

The northern half of the Tinto River basin forms part of the Iberian Pyrite Belt. This area contains many Paleozoic giant and supergiant sulphide deposits, including the largest individual massive bodies on earth [13]. Total ore reserves, distributed in eight supergiant deposits ($>$ 100 million tons) and a number of other smaller deposits, exceed 1500 million tons [14]. The deposits typically contain 50% sulphur, 42% iron, and 2–8% by weight of copper, lead and zinc together [15].

This area has been a rich source of minerals and metals from time immemorial. About 80 mines have been operative during the last hundred years, with a total production of about 300 million tons of polymetallic ores, although, in most cases, sulphur and

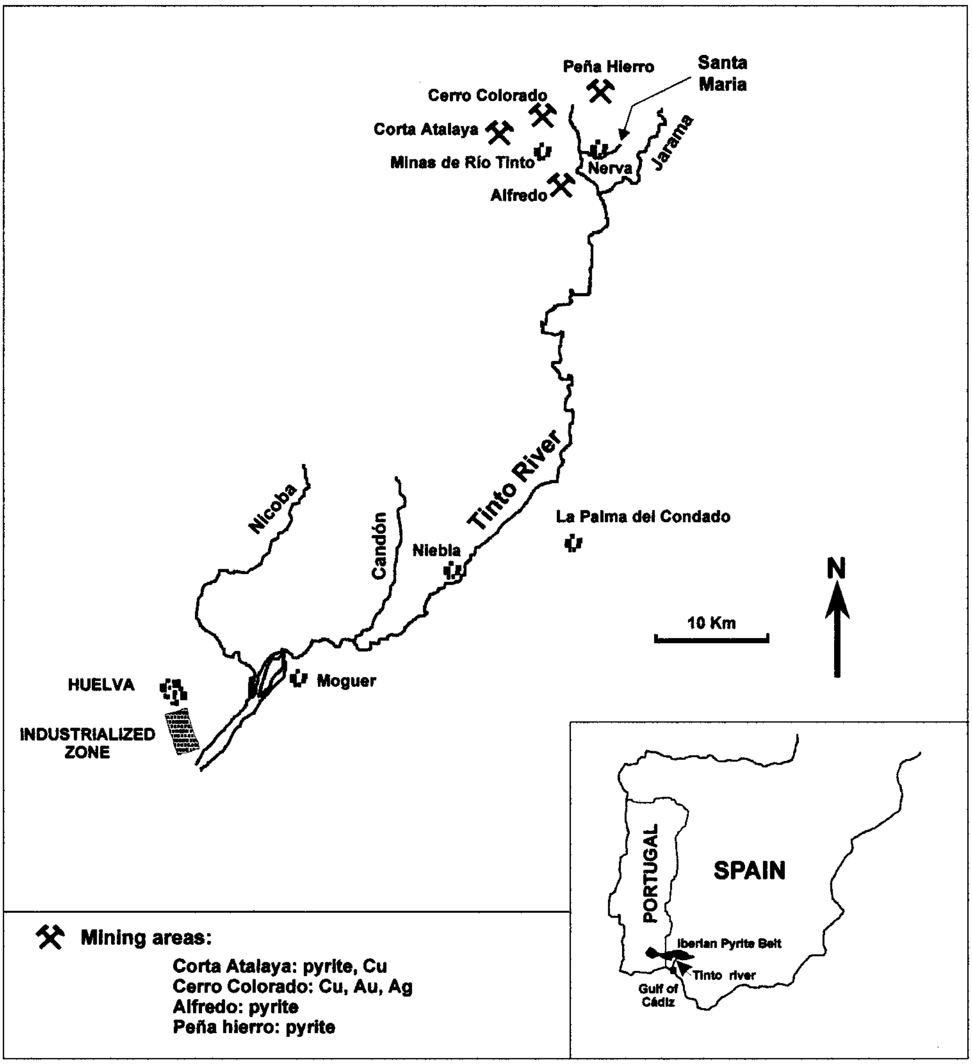

FIGURE 1 Location map of the Tinto River, showing the region of the Iberian pyrite belt and the main mines.

copper have been the main elements processed [14]. Figure 1 shows the main mines along the Tinto River basin.

Spoil and sulfide ores exposed to atmospheric oxygen and moisture, aided by bacteria (e.g. *Thiobacillus thiooxidans*, *Thiobacillus ferroxidans*), can undergo a series of oxidation and hydrolysis reactions producing sulphuric acid and metals [16] that are carried downstream by the river. In addition, the Tinto River estuary is one of the most industrialized areas in southern Spain and, as such, it receives the discharge of industrial waste. As a consequence of all of this, the quality of both the water and sediment of the Tinto River has been seriously affected.

EXPERIMENTAL

Core samples up to 10 cm in length were taken from 17 sampling sites: 10 in the main channel of the river, three in the estuary, and four in tributaries of the Tinto (see Fig. 2). The cores were immediately sealed and stored at 4°C until their arrival at our laboratory.

In the laboratory, the cores were extruded and sectioned. The first 3 cm section of each core was used in this study [2]. For grain size correction the $< 63\,\mu m$ fraction was chosen for analysis [17–19]. All the sieving and sequential extraction procedures were performed in a glove box purged with nitrogen [4].

The total metal contents were determined by digesting the samples with a mixture of HNO_3–$HClO_4$ in a microwave oven [20]. High-pressure CEM 3010 digestion bombs (consisting of a body, made of a specific microwave-transparent polymer, with a

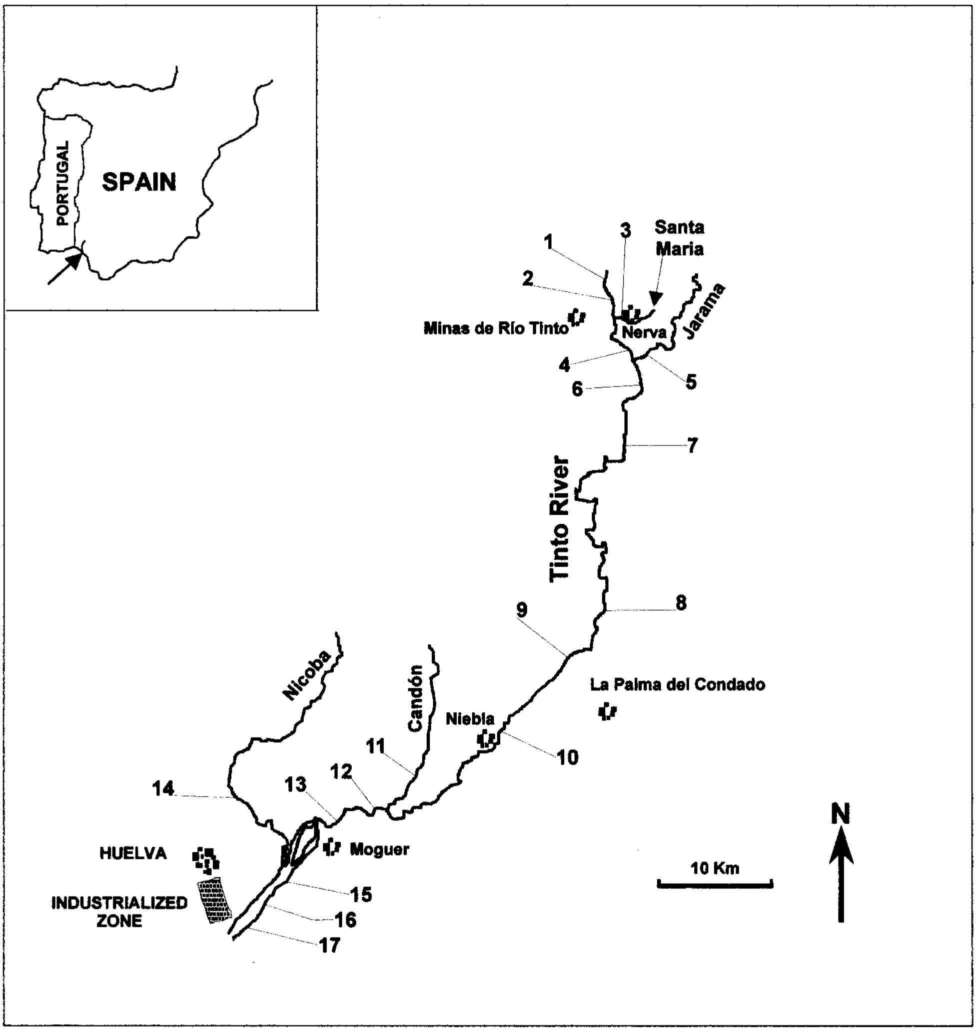

FIGURE 2 Locations of sampling sites.

teflon cup and cover) were used for sample digestion. These bombs are designed specifically for microwave heating, are chemically inert, and combine the advantages of closed high pressure (13.8 bar) and high-temperature digestion.

The metal fractionation was determined by means of the sequential extraction scheme proposed by the European Union's Standards, Measurements and Testing program (SM&T, formerly BCR). This scheme consists of three successive extractions (Table I) that allow us to determine the metal contents at three phases: acid soluble, reducible and oxidizable.

The analysis of the metals in the solutions obtained from both the digestion of the samples and sequential extraction was carried out by means of atomic absorption spectrophotometry (AAS) using a double-beam Perkin–Elmer 2380 AAS with deuterium background correction and, in some cases (low concentrations), by graphite furnace atomic absorption spectrometry (GFAAS) using a Perkin–Elmer 4110 ZL with Zeeman background correction.

All reagents were Merck analytical grade or suprapur quality. Standard working solutions of the elements analysed were prepared from the corresponding 1000 mg/l Merck titrisol solutions using the extractants employed in each step of the sequential extraction procedure as matrices [21]. All standard reagent solutions were stored in polyethylene bottles.

The accuracy of the analytical procedures for total metal determinations was checked using CRM 320 (sediment reference material). Replicate analysis of this CRM showed good accuracy, with recovery rates for metals around 89–105%.

In order to determine the precision of the analytical processes, three samples, taken in the upper area (sample 4), middle area (sample 10) and lower area (sample 15) of the river, were analysed in triplicate. The average values of the variation coefficients obtained (Table II) can be considered satisfactory for environmental analysis.

TABLE I Extractants used at each extraction step and the extraction phases of sediments in the sequential extraction procedure

Extraction step	*Reagent–concentration* (mol l^{-1})–*time* (h)	*Sediment phase*
1	Acetic acid (CH_3COOH)-0.11–16	Acid soluble (exchangeable ions, carbonates)
2	Hydroxylamine hydrochloride (NH_2OHHCl)–0.5 (pH 2 with HNO_3)–16	Reducible (iron/manganese oxides)
3	Hydrogen peroxide H_2O_2–8.8–1 at room temperature + 2 h at 85°C + ammonium acetate ($CH_3COO\ NH_4$)–1.0 (pH 2 with HNO_3)–16	Oxidizable (organic substances and sulfides)

TABLE II Average values of the variation coefficients (%) obtained in the triplicate analysis of the three samples (4, 10 and 15)

Sediment phase	*Cd*	*Co*	*Cr*	*Cu*	*Fe*	*Ni*	*Pb*	*Zn*
Acid soluble	6.3	15	16	4.6	5.6	11	7.8	6.4
Reducible	15	18	19	5.0	6.7	20	9.6	6.3
Oxidizable	14	13	8.0	6.3	10	16	11	7.6
Total content	5.3	6.7	4.3	3.7	5.2	8.3	6.1	6.0

RESULTS AND DISCUSSION

Metal Pollution

The concentrations of Fe, Pb, Zn, Cu and Cd (Table III) in the Tinto River sediments were very high in comparison to those obtained from sediments from other rivers that also empty into the Gulf of Cádiz (Table IV). Only in the case of the Odiel River, which is also greatly affected by mining activity, are similar values obtained for these metals. However, the mean levels of Co, Cr and Ni are similar to or even, in some cases, lower than those found in other rivers in the area.

The pyritic nature of the land and the mining activity in the Tinto water basin have greatly affected the composition of sediments. Table V shows a comparison of the metal concentrations in the Tinto River sediments and in a pyritic mineral from the area [26] with the average shale values [27]. Such comparisons assume that average shale values can be used to represent typical metal concentrations in fine-grained sediments (background values); though they are not always valid, they are commonly made to quantify the extent of metal enrichment [4,28–31]. Pb, Cu, Zn, Cd and Fe show high enrichment

TABLE III Heavy metals (mg/kg, dry mass) in sediments from the Tinto River

Sample	*Cd*	*Co*	*Cr*	*Cu*	*Fe*	*Ni*	*Pb*	*Zn*
1	3.0	14	24	1220	227,000	13	575	340
2	1.4	7.6	44	708	111,000	4.4	2260	264
3	0.96	16	13	483	29,400	1.6	4020	328
4	3.2	31	26	831	320,000	4.9	13,400	1260
5	0.32	17	66	119	48,500	27	425	119
6	2.2	35	53	629	71,000	18	6300	594
7	2.0	34	58	803	52,500	27	2210	852
8	1.6	15	11	222	85,800	16	132	412
9	2.2	29	45	955	66,600	18	2340	576
10	0.68	6.8	33	264	197,000	6.7	387	228
11	0.14	8.0	52	30	29,400	25	24	101
12	0.88	8.7	43	226	256,000	7.2	927	244
13	2.4	14	94	637	87,300	21	1020	568
14	0.13	7.9	58	22	28,200	21	17	68
15	3.4	41	61	1760	59,600	12	2160	1050
16	10	42	120	2070	119,000	36	1110	5280
17	12	26	151	2700	71,400	30	2380	3040
Mean value	2.7	21	56	805	109,000	17	2330	901

TABLE IV Heavy metal concentrations (mg/kg) in sediments from the Tinto River compared to those in sediments from other nearby rivers

River	*Cd*	*Co*	*Cr*	*Cu*	*Fe*	*Ni*	*Pb*	*Zn*	*Data source*
Tinto	2.7	21	56	805	109,000	17	2330	901	This repot
Odiel	6.2	NA	101	714	93,000	27	565	1136	C.M.A. (1992) [22]
Guadiana	ND	2–15	5–100	10–150	NA	NA	15–50	30–1500	Nelson and Lamothe (1993) [23]
Guadalquivir	0.24	30	44	35	34,700	28	31	154	Cruces (2000) [24]
Guadalete	ND	NA	60	44	NA	34	21	145	C.M.A. (1999) [22]
Carreras	NA	NA	12–125	4–73	NA	NA	4–86	41–208	Ruiz (2001) [25]
Piedras	NA	NA	65–120	32–103	NA	NA	3–298	57–311	Ruiz (2001) [25]

ND: not detected.
NA: not analysed.

TABLE V Comparison between background values [27], Zarza ore values [26] and Tinto sediment values for metals. All the results are expressed in mg/kg

Element	*Background value* [27]	*Sulphide ore* (*La Zarza*) [26]	*Tinto river*	*Enrichment factor for sulphide ore*[a]	*Enrichment factor for Tinto river*[b]
Cd	0.3	6.9	2.7	23	9
Co	19	100	21	5.2	1.1
Cr	90	7	56	0.1	0.6
Cu	45	6900	805	153	18
Fe	47,000	420,000	109,000	8.9	2.3
Ni	68	13	17	0.2	0.2
Pb	20	7600	2330	380	116
Zn	95	13,000	901	137	9.5

[a] Sulphide ore/background value.
[b] Tinto river/background value.

factors both in the pyritic mineral and in the sediments, and in both cases the maximum values are obtained for Pb and Cu; however, the enrichment factors for Cr and Ni, both in the mineral and in the sediments, are less than one.

The metal content in Tinto River sediments has a twofold origin: natural and anthropogenic. Erosion of the naturally-occurring sulphide lode deposits of the Iberian Pyrite Belt has provided a significant source of heavy metals for millions of years. Among the human sources are mining activity (in the sulphide deposits) and industrial activity (there is a large chemical pole in the estuary of the river).

Spatial Variation of Metal Concentrations

All of the mining in the Tinto River basin has taken place at the headwaters, where there is a large sulphur deposit that has been exploited for as long as man can remember. Although, the mining activity has been concentrated at the headwaters of the Tinto, the composition of the water and the sediments have been affected from its source to its mouth. The results from this study show that all the samples from the main river bed are very rich in the metals that characterize the minerals of the area (Fe, Pb, Zn, Cu and Cd).

Only two of the Tinto's tributaries, the Candón and the Nicoba, do not present any metallic contamination as they are not affected by mining activity. The level of metals in the sediments of these tributaries are low in comparison to those obtained from the rest of the samples, and they present values similar to average shale values.

On reaching the estuary (sites 15–17) there is an increase in the metal levels, as shown in Fig. 3. In this area, the acid, metal-rich waters of the Tinto River mix with seawater and undergo a notable increase in pH, which causes a large portion of the metals to precipitate toward the sediments. This tendency is especially pronounced for Cu, Cd and Zn. The maximum values of these metals are reached in sample 16 for Zn (5280 mg/kg), and in 17 for Cd (12 mg/kg) and Cu (2700 mg/kg). However, the levels of Fe and Pb found in the sediments of non-estuarial parts of the river are higher than in the estuary. Specifically, the highest levels of Fe and Pb (320,000 and 13,400 mg/kg, respectively), are found in sample 4, from the upper part of the Tinto River (which is greatly affected by mining activities). In this area, the sediments contain great quantities of very iron- and lead-rich detrital pyrite grain [13,32].

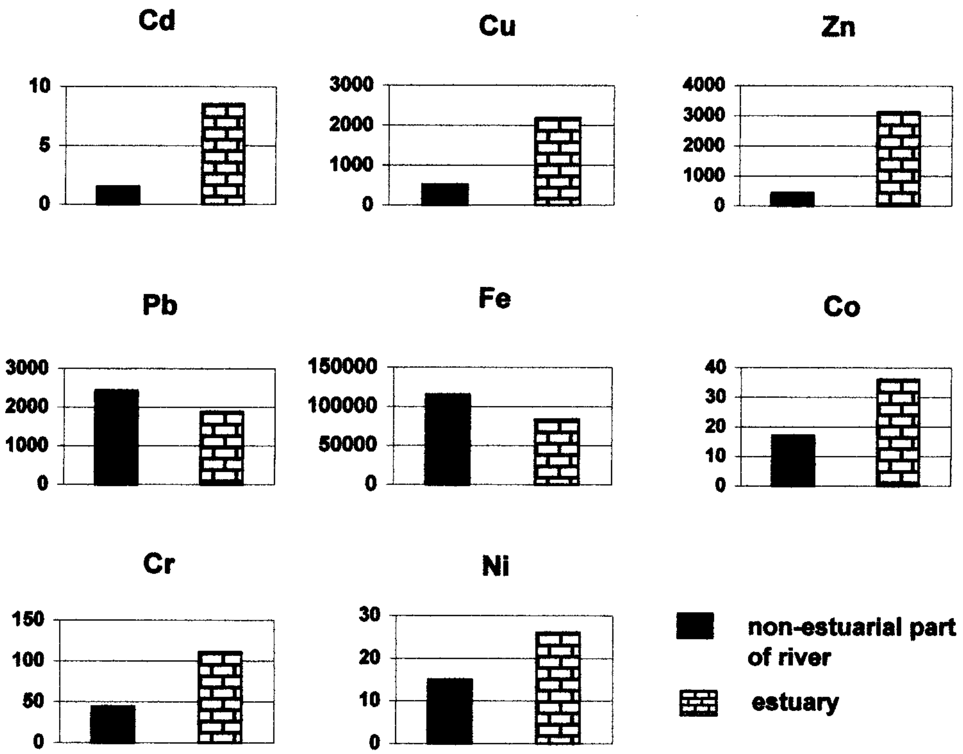

FIGURE 3 Comparison of the average metal concentrations (mg/kg, dry mass) in samples taken from the non-estuarial part of river (sites 1–14) and those from the estuary (sites 15–17).

Heavy Metal Fractionation

Tables VI and VII show the results obtained from the sequential extraction and Fig. 4 shows a bar diagram of the distribution among fractions obtained from the samples taken from the non-estuarial part of the river (sites 1–14) and from the estuary (sites 15–17). Below, in order to simplify things, we will call these two areas "the river" (the non-estuarial part of the river) and "the estuary" (the tidal influence area).

When we compare the results from the river with those from the estuary we find important differences. The metals studied present greater mobility in the estuary since in this area the percentage of the residual fraction is lower and the percentages of the other fractions, in particular the reducible fraction, are greater. It is logical that the residual fraction should diminish since the sediments in the estuary contain a smaller amount of pyrite mineral remains. These minerals have large amounts of metals with very little mobility. Moreover, the remarkable increase in the reducible fraction is due to the fact that in the estuary the waters of the Tinto River, which are very acidic (they can reach pH values of up to 1.5) and which contain large amounts of Fe and other dissolved metals, mix with the sea water (pH 8.2), thus causing an abrupt rise in the pH values to nearly 8. This increase in the pH causes the precipitation of the Fe (whose precipitation interval is between pH 3 and 5 when it is in Fe^{2+} form and between pH 3.5 and 7.5 when it is in Fe^{3+} form) and other metals that co-precipitate with it and become part of the reducible fraction. The heavy metals are bound to

TABLE VI Metal fractionation of Zn, Cd, Cu, and Pb in the sediment samples. All the results are expressed in mg/kg of dry sediment

Element	*Sample*	*F*1	*F*2	*F*3	*F*4	*Sample*	*F*1	*F*2	*F*3	*F*4
Zn	1	115	5.2	20	200	10	102	7.5	29	90
	2	58	4.3	19	183	11	3.8	9.3	1.6	86
	3	19	1.1	38	270	12	100	11	45	89
	4	183	6.7	67	1000	13	202	152	83	131
	5	7.4	10	10	92	14	2.1	6.2	0.70	59
	6	96	7.7	77	413	15	199	156	194	501
	7	74	12	148	618	16	1840	1620	256	1560
	8	127	25	8.4	252	17	1130	991	347	572
	9	44	11	161	360	Mean value	253	179	88	381
Cd	1	0.96	0.16	0.14	1.72	10	0.23	0.03	0.21	0.21
	2	0.46	0.10	0.20	0.63	11	0.07	0.03	0.03	0.01
	3	0.05	0.01	0.27	0.63	12	0.36	0.05	0.19	0.28
	4	0.66	0.06	0.36	2.17	13	1.01	0.91	0.30	0.15
	5	0.15	0.07	0.09	0.01	14	0.05	0.02	0.01	0.05
	6	0.36	0.06	0.43	1.37	15	0.91	0.91	0.73	0.81
	7	0.32	0.08	0.60	0.97	16	3.26	5.73	0.79	0.62
	8	0.25	0.07	0.38	0.88	17	2.86	5.62	1.28	2.24
	9	0.20	0.04	0.48	1.44	Mean value	0.72	0.82	0.38	0.83
Cu	1	398	40	268	514	10	102	12	63	87
	2	135	29	130	414	11	2.1	3.5	3.8	21
	3	81	3.7	162	236	12	52	12	60	102
	4	96	19	240	476	13	35	264	233	105
	5	20	15	35	49	14	1.2	3.1	1.9	16
	6	58	14	203	354	15	49	366	522	823
	7	34	8.7	290	470	16	7.8	1330	385	347
	8	74	16	25	107	17	8.8	1620	592	479
	9	29	15	370	541	Mean value	70	222	210	302
Pb	1	0.8	2.9	3.9	567	10	2.5	2.1	2.6	380
	2	3.0	30	9.5	2220	11	0.6	8.3	4.4	11
	3	157	1030	38	2800	12	0.2	0.7	2.7	923
	4	279	3720	788	8600	13	1.0	375	1.3	642
	5	37	163	42	183	14	0.4	5.5	3.3	7.8
	6	227	2370	125	3580	15	4.0	878	29	1250
	7	152	207	69	1780	16	1.0	849	0.8	260
	8	3.2	23	2.5	103	17	2.2	1760	0.9	618
	9	53	205	19	2060	Mean value	54	684	67	1530

the reducible phase associated with hydrous Fe oxides either by co-precipitation or by absorption into pre-existing coatins [33]. These results are in agreement with the known ability of hydrous Fe oxides to scavenge metals from solution and are in accordance with those reported by numerous authors [33–37].

Zn and Cd, which show comparable environmental behavior [38,39], are the most mobile heavy metals given that they present the greatest percentages in the first two fractions. The Cd and Zn partitioning patterns found are not unusual: high percentages of total Cd and Zn have been found associated with more labile fractions by numerous researchers [40,41]. This tendency is especially pronounced in the estuary samples in which more than 60% of these two elements extracted were distributed between the first two fractions. The high mobility of these metals facilitates their being taken up by benthic invertebrates living in sediments. Benthic invertebrates represent an important link in the transfer of metals to higher trophic levels because of their close association with sediment and their ability to accumulate metals [42]. Furthermore, they are often a major component in the diet of many fish [43]. The incorporation of

TABLE VII Metal fractionation of Fe, Ni, Cr, and Co in the sediment samples. All the results are expressed in mg/kg of dry sediment

Element	*Sample*	*F*1	*F*2	*F*3	*F*4	*Sample*	*F*1	*F*2	*F*3	*F*4
Fe	1	3360	38,500	31,500	154,000	10	2720	41,500	46,900	106,000
	2	1020	5070	1720	103,000	11	69	1980	322	27,000
	3	4760	1020	14,500	9120	12	1590	21,200	9190	224,000
	4	7430	54,800	121,000	137,000	13	649	20,800	6340	59,500
	5	237	5290	1630	41,300	14	60	1290	224	26,600
	6	1590	2290	39,200	27,900	15	769	28,600	25,400	4830
	7	2210	4550	25,700	20,000	16	1220	30,100	3650	84,000
	8	2400	2520	38,000	42,900	17	888	36,000	14,500	20,000
	9	2630	14,100	38,400	11,500	Mean value	1980	18,200	24,600	64,600
Ni	1	6.9	0.22	0.50	5.4	10	1.3	0.21	1.2	4.0
	2	2.0	0.09	0.54	1.8	11	1.6	1.3	1.7	20
	3	0.74	0.34	0.40	0.1	12	0.88	0.13	0.7	5.5
	4	1.1	0.07	2.6	1.1	13	1.0	1.4	1.1	18
	5	1.5	0.85	1.3	23	14	1.3	1.6	1.7	16
	6	1.5	0.32	3.6	13	15	0.4	0.23	0.8	11
	7	1.9	0.56	5.7	19	16	5.5	6.1	4.6	20
	8	1.2	0.33	0.20	14	17	5.5	3.5	2.8	18
	9	0.41	0.35	2.4	15	Mean value	2.0	1.0	1.9	12
Cr	1	0.61	0.25	2.6	21	10	0.54	0.09	4.6	28
	2	1.1	1.2	1.4	40	11	0.13	0.20	2.9	49
	3	0.58	0.23	0.63	12	12	0.31	1.4	1.2	40
	4	0.64	0.28	2.2	23	13	1.0	27	5.1	61
	5	0.10	0.42	4.2	61	14	0.12	0.20	3.2	54
	6	0.70	1.1	4.8	46	15	0.63	15	3.4	42
	7	0.48	1.4	5.6	51	16	0.21	31	7.4	81
	8	0.12	0.04	1.0	10	17	0.45	60	6.2	84
	9	0.49	1.0	4.5	39	Mean value	0.50	8.3	3.6	44
Co	1	2.5	0.20	0.76	10	10	20	0.30	2.0	2.5
	2	2.0	0.35	1.5	3.8	11	1.5	2.5	0.81	3.2
	3	2.2	0.30	2.4	11	12	2.2	0.16	2.1	4.2
	4	2.3	0.15	3.3	26	13	2.0	1.3	2.4	8.3
	5	3.5	1.5	1.9	10	14	1.3	1.6	0.33	4.7
	6	2.0	0.49	1.2	21	15	0.10	1.2	9.6	30
	7	2.0	1.4	1.1	20	16	10	9.4	5.6	17
	8	2.5	0.79	0.05	12	17	4.2	4.2	7.0	11
	9	0.86	0.30	3.2	25	Mean value	2.5	1.5	2.7	13

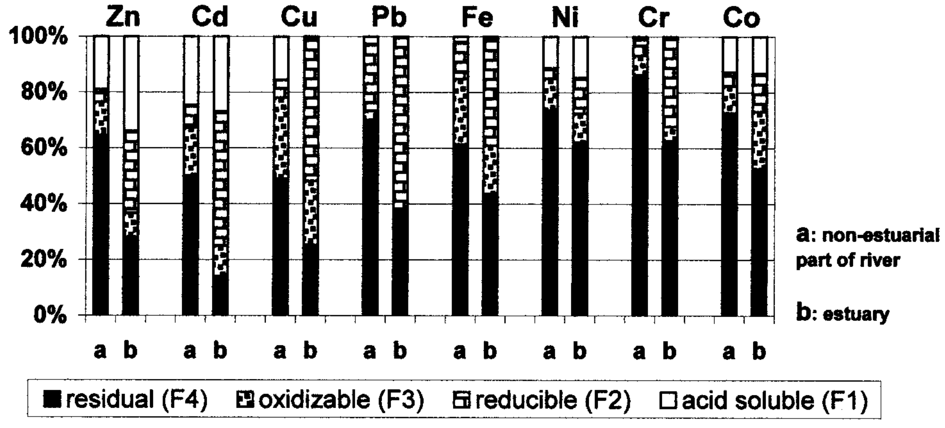

FIGURE 4 Mean values (%) of metal fractionation in sediments.

these elements into the food chain represents a considerable danger because of their toxicity.

The chemical partitioning of Cu in the river sediments is clearly different from that in the estuary sediments. In the river, a high percentage (49%) is associated with the residual fraction, and the rest is divided, for the most part, between the oxidable fraction (29%) and the acid-soluble fraction (16%). However, in the estuary, it is mainly extracted from the reducible fraction (51%) and, to a lesser degree, the residual (25%) and oxidable (23%) fractions; the percentage of Cu found in the acid-soluble fraction found in the estuary is negligible.

In the case of Pb, it is worth noting that the percentage obtained in the reducible fraction (62%) in the estuary is remarkably higher than that obtained in the river (24%). This result is similar to those reported by Jones and Turki [29] and Xiangdong *et al.* [44] who found that most of the Pb was present in Fe–Mn oxide fraction (reducible) in estuary sediments. However, in the river a higher percentage of Pb was found in the residual fraction (70%). The behavior of Fe is similar to that of Pb (i.e. it presents a higher percentage in the reducible fraction in the estuary and in the residual fraction in the river.)

It is also worth noting that the mobility of these last three metals studied (Cu, Pb and Fe) in the estuary (an area of great importance, ecologically speaking) depends primarily on the possible dissolution of the reducible fraction since undoubtedly it is the mobile fraction that contains the highest percentages of these elements. With such high total concentrations of these elements in the estuary sediments, the dissolution of this fraction would free great amounts of Fe, Pb and Cu into the water column. This phenomenon would put the aquatic ecosystem in great danger since Cu and Pb are very toxic to aquatic organisms and fish [45,46].

Among the metals studied, Ni, Co and Cr are those that present the smallest differences in distribution between phases in the river and the estuary, although there is an increase in the percentage of the reducible fraction in the estuary. Furthermore, these are the metals that reach the greatest percentages in the residual fractions: more than 60% in the river and 50% in the estuary. These results are in agreement with other studies on contaminated sediments [4,29,47] in which large amounts of these elements were found in the residual fraction. Thus, given that these elements have low mobility and are found in small concentrations in the sediments studied, it is unlikely that the sediments of this river are an important source of Ni, Co and Cr for its waters.

CONCLUSIONS

The sediments from the Tinto River and estuary are highly polluted with Fe, Pb, Zn, Cu, and Cd. Except for Fe and Pb, the greatest metal contents are found in the estuary because of the precipitation of metals that results from the rise in pH and the salinity of the waters (when the river and sea waters mix).

This study provides valuable information on the potential mobility of heavy metals in river sediments polluted by acid mine drainage. From the data obtained in the sequential extraction, we can conclude that there are significant differences in the distribution of the metals studied. Cd and Zn are the metals that present the greatest mobility. Large amounts of these elements are present in the first two fractions. The elements with the least mobility are Ni, Co and Cr since they reach the greatest percentages in the residual fraction. What is more, these metals are present in the sediments in low concentrations and thus it is unlikely that large amounts of them should be freed into the water column. Whether Cu, Pb and Fe are freed into the estuary depends largely on the possible dissolution of the reducible fraction as it contains a large proportion of these elements.

All of the metals studied have greater mobility in the estuary than in the river because they are richest in the most labile fractions. In the estuary, the reducible fraction increases and the residual fraction decreases, mainly as a result of the precipitation of metals associated with hydrous Fe oxides that occurs in the estuary when the river and sea waters mix.

The metals studied can be ordered according to the percentage extracted in the first fraction (the most labile and bioavailable):

Cd > Zn > Cu > Co > Ni > Pb > Fe > Cr (non-estuarial part of the river)
Zn > Cd > Ni > Co > Fe > Cu > Cr > Pb (estuary)

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