

# HEAVY METALS IN SEDIMENTS FROM THE TINTO RIVER (SPAIN)

José Usero García, José Morillo Aguado and Ignacio Gracia Manarillo

Universidad de Sevilla. Escuela Superior de Ingenieros  
Dpto. de Ingeniería Química y Ambiental  
Camino de los Descubrimientos, s/n., Isla de la Cartuja  
41092 Seville, Spain  
Phone: + 34 95 4487274, Fax: + 34 95 4463153  
e-mail: usero@esi.us.es

## ABSTRACT

*A complete study was carried out on metal pollution in Tinto River sediments. In the course of the study, samples were taken at 13 sites along the river and its most important tributaries, and at 4 sites in the estuary. The contents of 11 metallic elements (Zn, Cd, Cu, Co, Cr, Fe, Mn, Ni, Pb, As, and Hg) were analysed in each sample. These sediments had previously been subjected to acid digestion ( $\text{HNO}_3\text{-HClO}_4$ ) in a microwave oven. Results show high concentrations of metals typically present in pyrite, especially Cd, Cu, and Zn, in estuary sediments, and As, Fe, and Pb in river sediments. However, the values found for Co, Cr, Ni, and Mn are comparable to those in unpolluted areas.*

## INTRODUCTION

The Tinto River runs through an area known as the Iberian Pyrite Belt in the province of Huelva on the southwest corner of the Iberian Peninsula. The area is the site of some of the world's largest sulphide deposits and has been a rich source of minerals and metals since ancient times. Mining developed rapidly in the nineteenth century because of the large demand for sulphur, one of the basic components for producing  $\text{H}_2\text{SO}_4$  in the chemical industry (Morrall, 1990).

Weathering of spoil and sulphide ores exposed to the atmosphere in abandoned mines releases large quantities of sulphuric acid and heavy metals that are carried downstream by this river. The lower section of the Tinto River widens to form an estuary, and contact with seawater produces a sharp increase in the pH of the water, causing the metals to precipitate toward the sediments (C.M.A., 1998).

The sediments act as a sink for the metals, but these metals can be freed from the sediments through chemical reactions and biological activity. Therefore, sediment composition is often considered a good index for heavy metal pollution in the aquatic environment (Usero et al., 1998).

The main objective of this study is to characterise the sediments of this river and its estuary, paying special attention

to the presence of metals and to the important role that precipitation plays in the chemistry of metals. The samples were classified into different groups by means of cluster analysis.

## MATERIALS AND METHODS

The 17 sampling sites selected appear in Figure 1. Samples were taken with either PVC tubes or impact drags depending on the depth at which the sediment was found. The samples were separated into two portions; pH and redox potential were measured in one portion, and the other portion was put into plastic bottles and stored at 4 °C until its arrival at the laboratory (Kersten and Förstner, 1986).

In the laboratory, samples were homogenised, air-dried (Thomas et al., 1994), and sieved with a 63 µm nylon mesh (Izquierdo et al., 1997). Each sample was subjected to acid ( $\text{HNO}_3\text{-HClO}_4$ ) digestion in a microwave oven to determine total metal contents.

Element content was determined by 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. The Hg and As analyses were

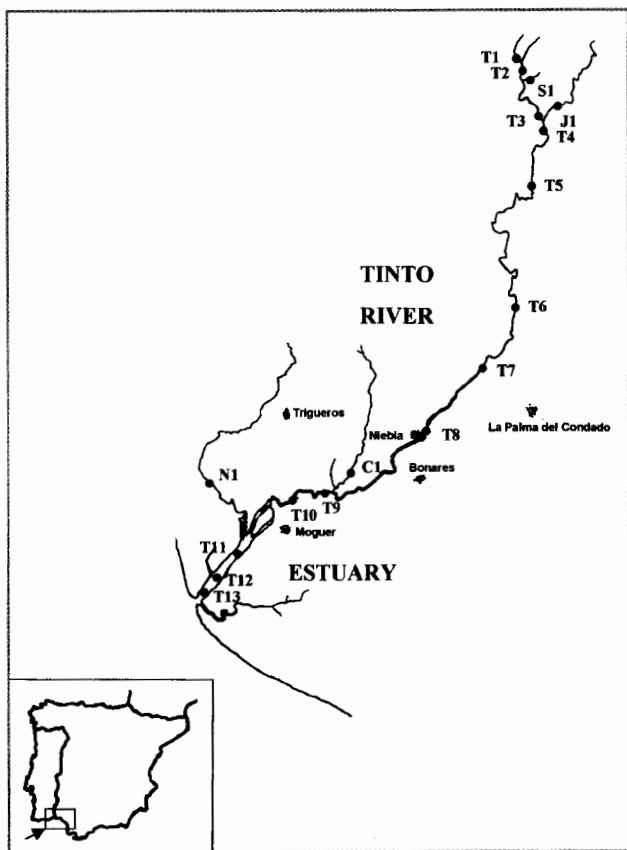


Figure 1. Locations of sampling sites.

Sample	pH	Redox Potential
T1	4.2	+0.33
T2	2.2	+0.48
S1	1.5	+0.45
T3	2.3	+0.45
J1	6.8	+0.08
T4	2.6	+0.44
T5	2.4	+0.45
T6	2.5	+0.50
T7	2.5	+0.46
T8	2.7	+0.52
C1	6.8	-0.13
T9	2.9	+0.42
T10	6.1	-0.19
N1	6.7	-0.06
T11	6.5	-0.06
T12	6.8	-0.18
T13	6.8	-0.25

Table 1. pH and redox potential (Volt) of the sediments.

al., 1998), we find that the levels of metal pollution are very high for typical pyrite metals: As (1130 mg/kg), Cd (2.75 mg/kg), and Zn (901 mg/kg). However, the values found for Co (21 mg/kg), Cr (56 mg/kg), Ni (17 mg/kg) and Mn (262 mg/kg) are comparable to those in unpolluted areas.

To obtain a global vision of metal levels in the samples under study, we used the Pollution Load Index, PLI (Tomlison et al., 1980), which is defined as follows:

$$PLI = (C_{i1} \cdot C_{i2} \cdot \dots \cdot C_{in})^{1/n}$$

where  $C_{in}$  is the metal concentration in the sediment for element  $i$  divided by the background value for that metal. In this paper, we have considered the average values found in fossil shale (Turekian and Wedepohl, 1961).

carried out by means of cold vapour AAS and hydride generation AAS respectively.

The digestion and analytical procedures were checked by analysis of a sample of river sediment supplied by the Community Bureau of References with a certified concentration of the metals being studied.

## RESULTS AND DISCUSSION

### General characteristics of the sediments

Table 1 shows the pH of the river sediment samples (T1 to T9), which are markedly acid, with values that may be less than 2.5. This low pH is due to the oxidation of pyritic materials, which produces low pH levels in both water and sediments. The samples from some tributaries of the Tinto River (J1, C1, N1) have a pH of around 7 because these rivers and streams do not receive acid drainages. There is a considerable increase in pH in the estuary sediments (T10 to T13, tidal influence area).

Important differences can also be seen in the redox potential of the river samples (positive redox potentials) and the estuary (negative potentials).

### Metal pollution

Table 2 shows the values of metal concentrations in sediment samples. On comparing the results obtained with those found in other zones (Akhter and Salim, 1997; Ciarilli et

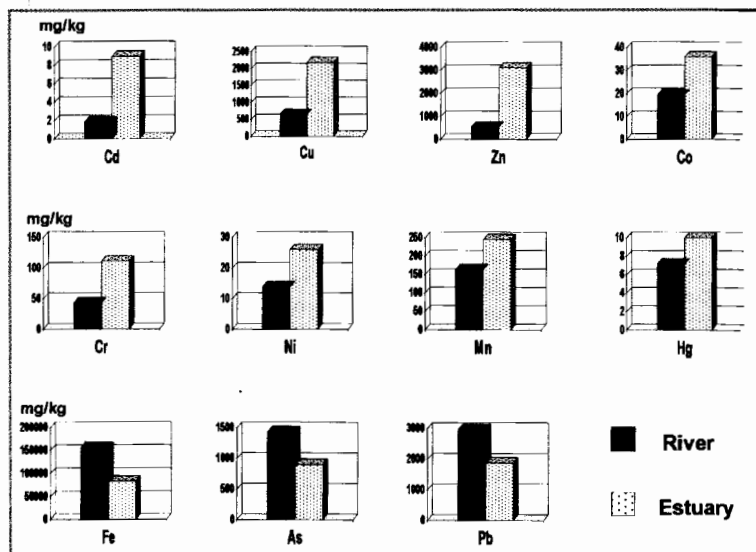


Figure 2. Comparison of the average metal concentrations (mg/kg dry weight) in samples taken from the estuary and the river.

Sample	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
T1	2160	2.98	14	24	1220	227000	12	163	13	575	340
T2	1650	1.39	7.6	44	708	111000	8.9	59	4.4	2260	264
S1	2120	0.96	16	13	483	29400	29	45	1.6	4020	328
T3	2350	3.25	31	26	831	85800	30	61	4.9	13400	1260
J1	102	0.32	17	66	119	48500	1.5	851	27	425	119
T4	989	2.22	35	53	629	71000	7.2	216	18	6300	594
T5	984	1.97	34	58	803	52500	5.9	262	27	2210	852
T6	2370	1.58	15	11	222	420000	0.40	130	16	132	412
T7	946	2.16	29	45	955	66600	3.2	216	18	2340	576
T8	1540	0.68	6.8	33	264	197000	1.1	158	6.7	387	228
C1	11	0.14	8.0	52	30	29400	0.44	722	25	24	101
T9	441	0.88	8.7	43	226	256000	1.4	249	7.2	927	244
T10	846	2.37	14	94	637	87300	2.3	113	21	1020	568
N1	10	0.13	7.9	58	22	28200	0.21	479	21	17	68
T11	720	3.36	41	61	1760	59600	3.8	171	12	2160	1050
T12	840	10.4	42	120	2070	119000	11	313	36	1110	5280
T13	1140	12.0	26	151	2700	71400	14	250	30	2380	3040
Mean value	1130	2.75	21	56	805	115000	7.8	262	17	2330	901

Table 2. Total contents of trace metals (mg/kg dry weight) in sediments from the Tinto River.

Table 3 shows the PLI at each sampling point, with the maximum PLIs in the estuary samples. 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.

To establish which metals contribute the most to the differences observed in the PLI, Figure 2 first shows the average values that are obtained for samples from the main river channel (T1 - T19) and later, those of the estuary (area with tidal influence).

The metal concentrations in the samples taken from the estuary are higher than in the river, especially for Cd, Cu, and Zn, probably because of the precipitation of these metals in that area. However, the greatest levels of As, Fe, and Pb can be found in the sediments of this river in spite of the high acidity of its waters and sediments. Many authors (Chapman et al., 1983; Fuge et al., 1994; Van Geen et al., 1997) have proven that these metals (As, Fe, and Pb) are insoluble at low pH values in rivers with similar characteristics. The waters of the Tinto River have high contents of dissolved iron and may cause this

element to become saturated and to precipitate (hydrated iron oxides), even under acid conditions. On the other hand, it is well documented that amorphous and crystalline iron oxides remove As from solution under acid conditions (Parfitt and Russell, 1977; Pierce and Moore, 1983). Their affinity for forming anions is particularly high, and it is believed that this species is specifically adsorbed (Chapman et al., 1983). Finally, the river water has a high sulphate content that can lead to the precipitation of Pb as lead sulphate or as lead jarosite.

### Cluster analysis

The cluster analysis used in this work was performed using the BMP2M Biomedical Computer Program.

Cluster analysis initially considers each case as a separate cluster. Then the clusters are joined one at a time according to an agglomerative algorithm, until all cases are combined into one cluster. The algorithm uses the Euclidean distance between centroid clusters as a criterion for joining clusters.

The results of the cluster analysis were output in the form of a dendrogram (Figure 3) showing the degree of similarity between individual samples (the vertical distance is proportional to the degree of dissimilarity between clusters). It may be observed that the samples can be classified into the following groups:

- The group made up of samples J1, C1 and N1 from the Tinto River tributaries.
- The group composed of samples T4, T5, T7, T10, and T11, which stand out because of their high lead contents.
- The group made up of samples T1, T2, T6, T8, and T9, which have the highest iron concentrations.

Sample	PLI	Sample	PLI	Sample	PLI
T1	4.0	T5	4.6	T10	3.4
T2	2.9	T6	2.1	N1	0.6
S1	2.5	T7	4.0	T11	4.6
T3	5.4	T8	2.0	T12	8.3
J1	1.8	C1	0.7	T13	8.3
T4	4.8	T9	2.3		

Table 3. Pollution Load Index (PLI) in sediments.

- The group made up of samples S1 and T3, with high arsenic and lead contents.
- The group composed of samples T12 and T13, which have the greatest PLI.

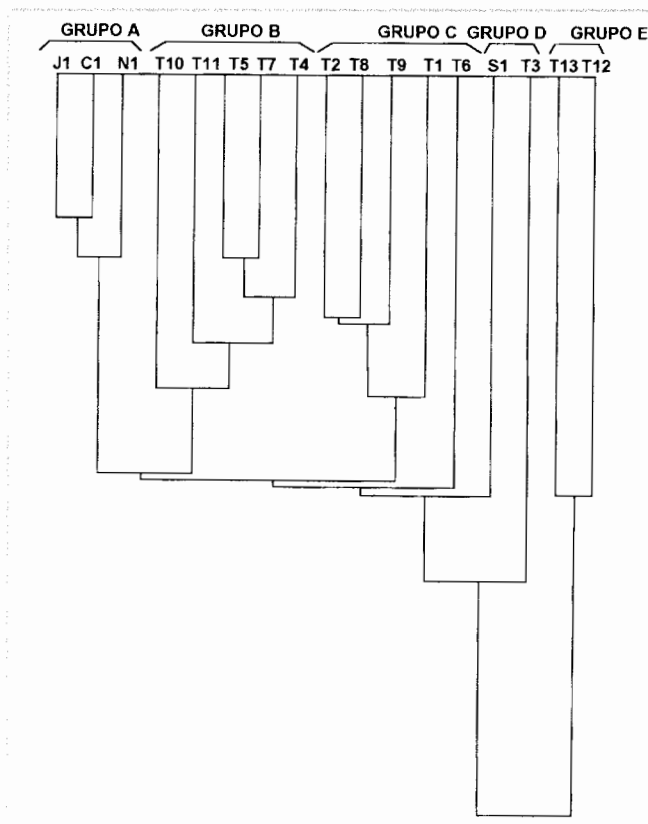


Figure 3. Dendrogram showing clustering of sampling sites.

## CONCLUSIONS

The sediments from the Tinto River and estuary are highly polluted with metals, especially by typical pyrite constituents (Fe, Cu, Pb, As, and Zn).

The greatest PLIs (Pollution Load Indexes) are found in the estuary (tidal influence area) because of the precipitation of these metals resulting from the pH of the waters.

The highest concentrations of Cd, Cu, and Zn are found in the estuary. However, the greatest levels of As, Fe, and Pb can be found in the sediments of this river.

The samples were classified by cluster analysis.

## REFERENCES

Akhter, M. and A. Salim, 1997. Heavy metal concentrations in sediments from the coast of Bahrain. *International Environmental Health Research*, 7 (1): 85-93.  
 C.M.A. (Consejería de Medio Ambiente de Andalucía), 1997.

Plan de policía de aguas del litoral andaluz. C.M.A. Seville, Spain.

Chapman, B.M., D.R. Jones and R.F. Jung, 1983. Processes controlling metal ion attenuation in acid mine drainage streams. *Geochimica Cosmochimica Acta*, 47: 1957-1973.

Ciarilli, L., R. Giordano, G. Lombardi, E. Beccaloni, A. Sepe and S. Costantine, 1998. Antarctic marine sediments distribution of elements and textural characters. *Microchemica Journal*, 59 (1): 77-88.

Fuge, R., N.J.C. Pearce and W.T. Perkins, 1994. In: C.N. Alpers and D.W. Blowes (Eds.). *Environmental geochemistry of sulphide oxidation*. American Chemical Society, Symposium Series. Acid mine drainage in Wales and influence of ochre precipitation on water chemistry, 550: 261-274.

Izquierdo, C., J. Usero and I. Gracia, 1997. Speciation of heavy metals in sediments from salt marshes on the Southern Atlantic Coast of Spain. *Marine Pollution Bulletin*, 2: 123-128.

Kersten, M. and U. Förstner, 1986. Chemical fractionation of heavy metals in anoxic estuarine and coastal sediments. *Water Science and Technology*, 18: 121-130.

Morral, F.M., 1990. A mini-history of Río Tinto. *Canadian Mining and Metallurgical Bulletin*, 83: 150-154.

Parfitt, R.L. and J.D. Russell, 1977. Adsorption on hydrous oxides, IV. Mechanisms of adsorption of various ions on goethite. *Soil Science Journal*, 28: 297-305.

Pierce, M.L. and C.B. Moore, 1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Water Research*, 16: 1247-1253.

Thomas, R.P., A.M. Ure, C.M. Davidson, D. Littlejohn, G. Raurer, R. Rubio and J.F. López-Sánchez, 1994. Three-stage sequential extraction procedure for the determination of metals in river sediments. *Analitica Chimica Acta*, 286: 423-429.

Tomlison, D.L., J.G. Wilson, J.G., C.R. Harris and D.W. Jeffrey, 1980. Problems in the assessment of heavy metal level in estuarine sediments and the formation of a pollution index. *Helgol Meeresunters*, 33: 566-575.

Turekian, K.K. and K.H. Wedepohl, 1961. Distribution of the elements in some major units of the earth crust. *Bulletin Geology Society American*, 72: 1961.

Usero, J., M. Gamero, J. Morillo and I. Gracia, 1998. Comparative study of three sequential extraction procedures for metals in marine sediments. *Environmental International*, 24 (4): 487-496.

Van Geen, A., J.F. Adkins, E.A. Boyle, C.H. Nelson and A. Palanques, 1997. A 120 yr record of widespread contamination from mining of the Iberian Pyrite Belt. *Geology*, 25 (4): 291-294.