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Environmental control of Tinto and Odiel river basins by PIXE *

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A study of the elemental concentrations of sediments of the rivers Tinto and Odiel, in Huelva, Spain, has been performed using PIXE. Thirteen samples have been collected, seven in the Tinto and six in the Odiel. Concentrations of 19 elements have been determined in each of them. The analysis of the data illustrates the environmental impact of the mining and fertilizer plants in the area.

1. Introduction

Sediments from river basins constitute a natural archive from which many useful data can be obtained. In particular, from the determination of elemental concentrations, specially of heavy elements, the environmental impact of human activity on the fluvial ecosystem can be inferred.

A technique very suited to determine elemental concentrations is TTPIXE [1]. Some of its advantages are the short collection time (a few minutes per sample), the sensitivity (ppm) and the multielemental character, that allows the determination of all elements at the same time.

Our study is about the rivers Tinto and Odiel, in the province of Huelva, in the south-west of Spain. That area was heavily industrialized from 1950 to 1960, and has mining industries and phosphate fertilizer industries placed mostly along the Odiel. As a residue of the fertilizer plants, gypsum piles were formed between the rivers (see fig. 1). We have analyzed 13 samples of sediments, taken in 11 points during the summer of 1989, 5 along the Tinto and 6 along the Odiel. The location of these points is shown on fig. 1.

2. Experimental methods

Each of the samples was homogeneized. The water content was determined by desiccation at 100°C. The organic matter fraction was obtained by calcination at 550°C (table 1). It should be pointed out that sample O5 has a very small content in water and organic matter. We shall see later that this sample is composed mostly of iron and heavy metals coming from the UERT (Unión Explosivos Rio-Tinto SA), a mineral processing plant. On the other hand, samples T1 and O6 have the largest content in organic matter. This may be due to the fact that they are the least affected by industrial pollution.

Later, 333 mg of sediment and 133.5 mg of wax Hoechst-C were mixed, homogeneized and pressed into pellets of 11 mm diameter. The pellets were analyzed by TTPIXE using 1.7 MeV protons from the Van de Graaff accelerator of the LNETI (Sacavém, Portugal) [2]. Characteristic X-rays were measured with a Si(Li) detector, with 0.2 keV resolution at 5.9 keV, connected to a multichannel analyzer through a conventional electronic chain. Two runs were made on each pellet, one with 7 nA intensity, to accumulate 1 μC charge, and the other with 25 nA intensity, to accumulate 20 μC charge, but putting a Cr filter 10 μm wide in front

Table 1
Water and organic matter contents (in %) obtained in Tinto and Odiel river sediments. Numbers within parentheses refer to the error of the last figure.

	Water	Organic matter
T1	4.079 (2)	12.026 (2)
T2A	3.380 (2)	8.505 (2)
T2B	3.308 (2)	8.601 (2)
T3	3.234 (2)	6.724 (2)
T4A	3.188 (2)	7.024 (2)
T4B	3.112 (2)	8.006 (2)
T5	3.032 (2)	6.119 (2)
O1	2.140 (2)	6.985 (2)
O2	2.827 (2)	8.938 (2)
O3	1.962 (2)	8.677 (2)
O4	1.648 (2)	6.047 (2)
O5	0.490 (2)	0.326 (2)
O6	3.810 (2)	13.749 (2)

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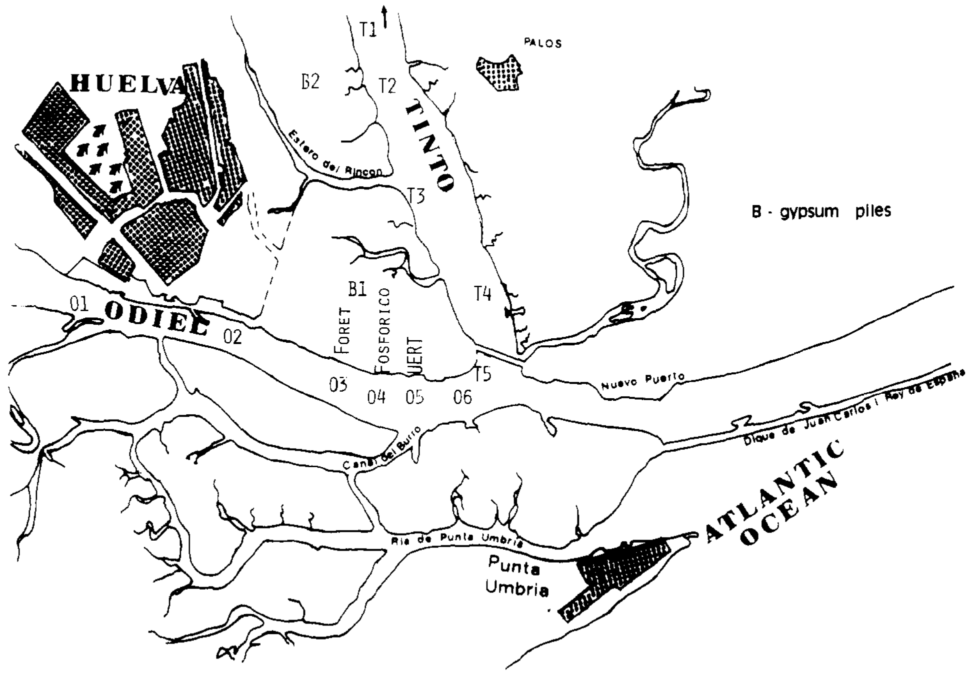

Fig. 1. Map corresponding to the sampling stations of Tinto and Odiel rivers around the town of Huelva (by courtesy of G. Manjón and A. Martínez).

of the Si(Li) detector to suppress the soft X-rays. Charge build-up effects were suppressed by using an electron gun placed inside the scattering chamber.

The X-ray spectra were fitted using the code AXIL [3]. The elemental concentrations were obtained from TTPIXE formalism, using our own code [4]. Light elements ($13 \leq Z \leq 26$) and Sn concentrations were obtained from the data without filter. Heavy elements were obtained from the data with the Cr filter. The content in oxygen was determined assuming a typical stoichiometry for the metallic oxides [4]. The content in C, H, O and N of the wax was given by the manufacturer. The Na an Mg contents were determined by atomic absorption spectrometry.

3. Results and discussions

Concentrations of 19 elements were obtained for each sample. Tables 2 and 3 show the concentration of the major elements (wt.%) in the rivers Tinto and Odiel respectively, and tables 4 and 5 show the concentration of the minor elements (ppm).

Table 2
Mass concentration (in %) of the major elements in Tinto river sediments. Numbers within parentheses refer to the error of the last figure (ND: not detected).

	T1	T2A	T2B	T3	T4A	T4B	T5
Al	1.1 (2)	8.0 (5)	7.6 (4)	9.1 (5)	8.0 (5)	7.6 (4)	7.1 (4)
Si	6.8 (4)	16.5 (8)	18.0 (9)	24 (1)	20 (1)	21 (1)	22 (1)
P	ND	1.0 (1)	0.8 (1)	1.7 (1)	3.6 (3)	3.7 (2)	5.8 (4)
S	12.7 (6)	15.7 (8)	14.5 (7)	4.6 (2)	6.4 (3)	5.8 (3)	5.5 (3)
K	0.55 (3)	2.0 (1)	2.2 (1)	2.1 (1)	1.8 (1)	1.8 (1)	1.6 (1)
Ca	0.34 (2)	11.9 (6)	10.5 (5)	2.9 (2)	1.3 (1)	1.3 (1)	2.7 (1)
Fe	47 (2)	7.7 (4)	8.5 (4)	10.2 (5)	14.1 (7)	14.0 (7)	8.9 (4)

Table 3
Mass concentration (in %) of the major elements in Odiel river sediments. Numbers within parentheses refer to the error of the last figure.

	O1	O2	O3	O4	O5	O6
Al	9.4 (5)	9.4 (5)	1.2 (2)	5.3 (3)	2.3 (2)	8.8 (5)
Si	18.4 (9)	18.1 (9)	5.7 (3)	20 (1)	3.1 (2)	15.1 (8)
P	4.9 (3)	4.6 (3)	3.4 (2)	5.4 (3)	0.6 (1)	7.9 (4)
S	6.9 (4)	6.8 (4)	22 (1)	3.2 (2)	1.6 (1)	5.4 (3)
K	1.8 (1)	2.1 (1)	0.57 (4)	1.0 (1)	0.19 (1)	1.5 (1)
Ca	2.1 (1)	3.0 (2)	32 (2)	15.1 (8)	0.19 (1)	5.2 (3)
Fe	12.3 (6)	11.6 (6)	1.1 (1)	4.5 (2)	56 (3)	11.0 (6)

T2A and T2B are two independent samples corresponding to the same sampling point T2. The same is true for T4A and T4B, corresponding to T4. The fact that results are compatible supports the reproducibility of our analysis.

The sample T1 was taken in Niebla, 40 km up-stream the Tinto River. It was taken originally to provide data free from industrial pollution. However, it has a high content in iron (47%) and other metals, that is characteristic of the zone. In fact, the name "Tinto" refers to the red color of the waters (tinto is the spanish for red wine), coming from iron oxides. It should be noticed that up-stream it the Riotinto mine is placed, from which Fe and Cu are obtained from the pyrite mineral. So the abundance of pyrite in the area can also explain the high content in S (12.7%).

The rest of the samples of river Tinto have much lower values of iron. Sulphur levels also decrease, except in the site T2, where the high levels in sulphur (15.1%) are correlated with high levels in calcium (11.2%). This is due to the proximity of a gypsum pile. In fact, from the sampling point T2 a pipe could be seen draining the pile to the river.

Samples T3 to T5 show an important increase in the concentration of P, as one goes downstream (0.9% for T2, 1.7% for T3, 3.6% for T4 and 5.8% for T5). This contamination comes probably from the factories along the Odiel river and it is introduced in the Tinto river due to the effects of the tides. Similar effects were seen in radiactivity measurements [5].

In the Odiel river, the samples O1 and O2 do not show evidence of anthropogenic contamination, except for the high contents of P and Fe. Samples O3 and O4 were taken close to Foret S.A. and Fosfórico Español S.A. respectively, two plants that produce fertilizers rich in phosphorus. They accumulate solid residues in gypsum piles (B1 and B2 in the map). The contamination in O3 is characterized by the high levels of Zn (1.6%) and Cl (4.7%). This may be related to the presence of salt-works near O3, in the bank opposite to the factory. High levels of S and Ca in O3 and O4 come from gypsum (phosphogypsum) released directly by the factories. It should be noticed that the P-levels lightly increase towards the sea (except for O5, where heavy metals contamination masks this effect), and also affect the Tinto River as we mentioned before.

Sample O5 was taken close to UERT. The content in Fe (56%) is about five times larger than the other samples in the Odiel river and in the Tinto river, with the exception of T1. Similar increases are found in other heavy metals like Zn (2.1%), Pb (4.7×10^3 ppm) and Cu (6.6×10^3 ppm), and consequently there is a reduction in "natural" elements as Al (2.3%) and Si (3.1%). Thus, UERT seems to be the main source of contamination of heavy metals in the river Odiel.

Regarding the minor elements, it should be pointed out that the yttrium, not detected in the Tinto river, can be seen in the Odiel river, with concentrations of about 100–400 ppm. One should expect that the elements coming from the natural composition of the

Table 4
Mass concentration (in 10^3 ppm) of the minor elements in Tinto river sediments. Numbers within parentheses refer to the error of the last figure (ND: not detected).

	T1	T2A	T2B	T3	T4A	T4B	T5
Ti	1.7 (1)	3.5 (2)	3.9 (3)	4.1 (2)	4.0 (2)	4.4 (3)	3.8 (2)
Sn	ND	ND	ND	ND	ND	ND	ND
Zn	7.6 (4)	3.3 (2)	1.31 (7)	5.5 (3)	2.2 (1)	2.6 (1)	4.9 (2)
Pb	1.1 (2)	1.9 (1)	1.9 (1)	1.22 (6)	2.8 (1)	3.4 (2)	1.18 (6)
Cl	ND	ND	ND	5.0 (4)	0.8 (2)	0.9 (2)	4.2 (3)
Cu	0.77 (5)	0.61 (3)	0.72 (4)	1.16 (6)	2.2 (1)	2.2 (1)	1.87 (9)
As	2.4 (1)	0.68 (4)	0.86 (4)	1.02 (5)	1.83 (9)	1.73 (9)	1.15 (6)
Mn	0.09 (1)	0.15 (1)	0.20 (2)	0.24 (2)	0.26 (2)	0.26 (2)	0.20 (1)
Cr	ND	0.15 (8)	0.08 (8)	0.12 (6)	0.15 (7)	0.16 (8)	0.25 (8)
Rb	ND	0.027 (3)	0.052 (5)	0.035 (3)	0.033 (5)	ND	ND
Sr	ND	0.16 (1)	0.22 (1)	0.139 (9)	0.27 (2)	0.25 (2)	0.34 (2)
Y	ND	ND	ND	ND	ND	ND	ND

Table 5
Mass concentration (in 10^3 ppm) of the minor elements in Odiel river sediments. Numbers within parentheses refer to the error of the last figure (ND: not detected).

	O1	O2	O3	O4	O5	O6
Ti	4.6 (3)	5.0 (3)	1.6 (2)	2.8 (2)	ND	4.2 (3)
Sn	ND	ND	10(1)	5.7 (7)	ND	ND
Zn	2.7 (1)	2.6 (1)	15.8 (8)	2.4 (1)	21(1)	4.0 (2)
Pb	2.1 (1)	2.1 (1)	0.31 (2)	0.77 (4)	4.7 (3)	1.50 (8)
Cl	0.8 (2)	7.7 (5)	47 (2)	4.8 (3)	0.8 (1)	3.1 (3)
Cu	1.82 (9)	2.2 (1)	0.31 (2)	2.2 (1)	6.6 (3)	2.6 (1)
As	1.83 (9)	1.15 (6)	0.070 (5)	0.32 (2)	2.0 (1)	1.60 (8)
Mn	0.35 (3)	0.34 (2)	0.036 (4)	0.14 (2)	ND	0.25 (2)
Cr	0.13 (8)	ND	0.4 (1)	0.5 (1)	ND	ND
Rb	ND	0.030 (3)	ND	ND	0.04 (1)	ND
Sr	0.39 (2)	0.45 (3)	0.20 (1)	0.40 (2)	ND	0.59 (3)
Y	0.126 (9)	0.26 (2)	0.145 (9)	0.37 (2)	ND	0.31 (2)

sediments should decrease sharply in sites O3, O4 and O5, due to the contribution of anthropogenic material. That is the case for Ti and Mn. Tin and chromium can mostly be seen in O3 and O4, so they are probably produced in the fertilizer plants. Arsenic can be seen in O5 but not in O3 and O4, showing that is probably released by UERT.

To summarize, we have shown that PIXE analysis of sediments provides very useful information to determine the environmental impact of industries in the rivers Tinto and Odiel. This analysis, however, is preliminary and should be confirmed with more data, complemented with chemical and geological information and correlated with measurements of radiactive isotopes.

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