

Anthropogenic contamination analyzed by TTPIXE in samples from the Odiel salt marsh at the SW Spain

J. E. Martín,* A. Martínez-Aguirre,* M. A. Respaldiza,* M. F. da Silva**

*Departamento, de FAMN, Facultad de Física, Universidad. de Sevilla, Apdo. 1065, 41080 Sevilla, Spain

**Departamento de Física, ITN, E. N. 10, 2685 Sacavém, Portugal

The studied marsh area is located at the southwest of Spain in an estuarine system formed by the confluence of the Odiel river and the Atlantic ocean. 23 samples collected in the marsh have been analysed by Thick Target Proton Induced X-ray Emission using 2 Me V protons from the 3 MV Van de Graaff accelerator of the ITN. Elemental concentrations in the samples are affected by the Atlantic ocean, the materials transported by the Odiel river and the wastes discharged by the factories of a nearby industrial area. The study has shown that certain areas of the estuary present high concentrations of P, Cu, Zn, As and Pb, which were attributed to the operation of a phosphate fertilizer factory and a Cu extraction factory. The mining activity carried out near the source of the river could be also responsible of part of this contamination. Finally, the spatial distribution of the contamination has reflected the dynamic of the Odiel river waters, due to tidal movements, into the marsh area.

Introduction

The materials transported by the Odiel river waters into its estuary are the result of the rock-weathering and the biological activity along its basin. The process of rock-weathering results in the introduction of certain amounts of mineral particles into the water column. These particles will be transported downstream the river suffering a continuous weathering along the river basin. This weathering yields a wide range in particle sizes and particles with different composition than those of the original rocks. The final set of mineral fractions: quartz, alumino-silicate minerals, Al, Fe and Mn hydroxides, calcite, etc., reflects the rock types and weathering conditions along the river basin.¹ On the other hand, the biological activity in the river introduces into the water column some biogenic particles: organic matter, carbonate and opal (amorphous SiO₂), which have been formed by organisms in the water or in the bottom of the river.¹

At the estuarine area of the river a large industrial complex is located, which is discharging part of its wastes into the Odiel river. These wastes belong basically to RTM, a Cu extraction factory and FESA, a factory which produces phosphoric acid for fertilizers.

RTM extracts Cu from minerals rich in Cu by oxidation followed by an electrolytic Cu purification. These minerals are mainly Cu and Fe sulphides (30% Cu, 26% Fe, 29% S) which also contain certain amounts of Zn, As, Pb, Mg, quartz, Ca, Ag and Au. S is eliminated by fixing SO₂ (gaseous) produced in the oxidation process as sulfuric acid. Some ashes containing As are collected from the SO₂ cleaning.² Fe is separated by using sand in the oxidation process producing fayalite [(FeO)₂SiO₂]. Zn is finally contained in a waste called "pucha" which is also formed in the oxidation process. Both, the fayalite and the pucha contain some amounts of other elements and different

compounds of S, Fe and Cu. Ag, Au and other metals are contained in the final mud.

The other factory, FESA, processes phosphate rock, fluoroapatite [Ca₁₀(PO₄)₆F₂] with sulphuric acid to produce phosphoric acid. Hydrofluoric acid is one of the by-products of the reaction and reacts with quartz impurities. Thus, F is finally recovered as fluorosilicic acid H₂SiF₆. Another by-product is phosphogypsum (> 90% dehydrated gypsum, CaSO₄ · 2H₂O), which also contains large amounts of impurities (quartz, fluorides, phosphates, organic matter and Al and Fe minerals).² Residual amounts of phosphoric, sulfuric and fluoride acids can still remain inside the phosphogypsum porosities. These acid residues give the phosphogypsum acid nature which allows to retain trace elements from the original rock in dissolution.² This factory also produces sulphuric acid for its own consume, which is extracted from pyrite minerals (FeS₂) following a similar oxidation and fixing process carried out in RTM.

Part of the wastes remain in the acid residual waters which are released directly into the Odiel river at its estuary. However, most of these wastes are stored in uncovered piles at the Tinto marsh (see Fig. 1). Thus, the Tinto river is affected by the leaching of different elements from these uncovered piles.³ In addition to these wastes, uncontrolled inputs in the Odiel river between the factories⁴ and around Nuevo Puerto harbour (see Fig. 1) may occur during the unload of phosphate rock, pyrite and other raw goods.

Finally, the tidal action tends to distribute all material released into the estuary, upward and downward before being definitively deposited at the bottom of the estuary or expelled out into the ocean.¹ Furthermore, the acid nature of the Odiel river, due to the pyrite mining activity and the discharges from the factories, tends to keep some materials in dissolution. The mixing of these acid waters with sea water provokes a large precipitation of elements in the estuary and, the consequent contamination of its bank.¹

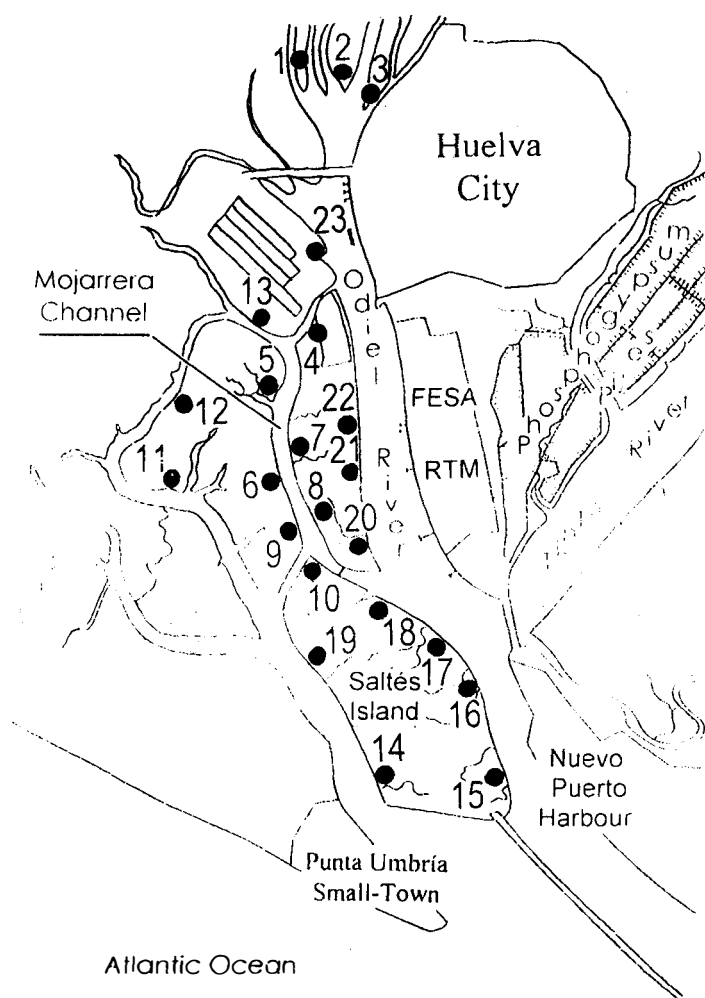


Fig. 1. Map of the estuary formed by the Odiel and Tinto rivers at the Atlantic ocean located near the Huelva city (southwestern Spain). It shows the sampling stations across the Odiel marsh as well as the locations of the phosphate fertilizer factory (FESA) and the Cu extraction factory (RTM)

The contamination that a certain area has suffered may be evaluated by determining its enrichment factor index (EFI), defined as the quotient between the ratio of the average concentration of such element to that of Al and the same ratio in a shale.¹ By evaluating the EFI for an element in a global area or in a sample, it is possible to characterize the global or individual contamination that the area or the sample has been suffering.

The studied area is part of the estuary that the Odiel river forms in its confluence with the Atlantic ocean. It is a natural reservation with high biological activity, mainly composed by four small islands crossed by four small channels. These channels are, due to tidal movement of the waters, highly affected by the income of the Odiel river waters. In a previous work,⁴ a clear contamination in P, S, Ca, Fe, Cu, Zn, As and Pb in bottom sediments collected at the estuary of the Odiel river were found. This paper presents an extension of that work to the Odiel marsh located along the Odiel river opposite to the industrial discharges. The main objective is to determine the extent that such contamination has over all the estuary. In last sense, global and individual EFI have been calculated in the samples collected in the area.

Experimental

Twenty surface soil samples at the Odiel salt marsh, opposite to the factories and 3 at the northern marsh site at the entrance of the Odiel river in the Huelva estuary (see Fig. 1) were collected. The samples were taken during the low tide in areas covered with water during the high tide. Attending to the geographical situation (see Fig. 1), the samples are classified in four groups: Northern marsh (1–3), Odiel river (15–18, 20–23), Mojarrera channel (4, 13, 5, 7, 6, 8–10) and Punta Umbría river.

Each sample was desiccated, homogenized and calcinated (550 °C) prior to analysis. After calcinating, some 0.1 g of sample was pressed (10 ton) into pellets of 11 mm of diameter on a substrate of 0.4–0.5 g of boric acid. These pellets were analyzed by TPIXE using 2 MeV protons from the 3 MV Van de Graaff accelerator of the ITN. 15° was used as the incoming proton angle and 55° as the outgoing X-ray angle, with respect to the normal of the sample in both cases. An electron gun was used to suppress the charge build-up effects. Characteristic X-rays were measured with a Si(Li) detector, with a resolution of

Table 1. Si, Al, Ti and K concentrations in the samples. Sampling points are divided in 4 groups, from up to down: Northern marsh, Odiel river, Mojarrera channel and Punta Umbria river. Numbers in parentheses refer to the error of the last figures

Sampling point No.	Si, %	Al, %	Si/Al	Ti, %	K, %
1	21.80(6)	9.36(6)	2.329(16)	0.500(6)	2.031(10)
2	15.15(5)	7.62(6)	1.988(18)	0.366(6)	1.459 (9)
3	13.59(5)	7.70(6)	1.765(16)	0.380(6)	1.395 (9)
23	16.93(5)	8.49(6)	1.994(16)	0.430(6)	1.676 (9)
22	35.00(7)	5.96(6)	5.87 (6)	0.330(5)	1.768(10)
21	38.75(6)	3.01(5)	12.87(22)	0.211(4)	1.214 (9)
20	21.06(5)	7.18(6)	2.93(3)	0.505(6)	1.607 (9)
18	12.84(4)	6.73(6)	1.908(17)	0.338(5)	1.307 (8)
17	26.05(6)	9.99(6)	2.608(16)	0.609(6)	2.619(11)
16	13.69(5)	6.89(6)	1.987(18)	0.415(5)	1.391 (8)
15	25.35(6)	5.55(6)	4.57 (5)	0.322(5)	1.588 (9)
13	15.23(5)	7.96(6)	1.913(15)	0.372(5)	1.546 (8)
4	14.95(5)	8.13(6)	1.839(15)	0.386(5)	1.612 (9)
5	17.00(5)	8.16(6)	2.083(17)	0.401(5)	1.824 (9)
7	19.45(5)	8.57(6)	2.270(16)	0.460(5)	1.951 (9)
6	20.50(5)	8.43(6)	2.432(19)	0.476(5)	1.972 (9)
8	17.38(5)	6.76(5)	2.571(21)	0.548(6)	2.028(10)
9	22.29(5)	8.94(6)	2.493(17)	0.479(6)	2.126(10)
10	19.04(5)	8.54(6)	2.230(18)	0.432(5)	1.871(9)
12	27.89(5)	10.52 (6)	2.651(16)	0.577(6)	2.837 (9)
11	21.45(5)	7.94(6)	2.702(22)	0.525(6)	2.063(10)
19	25.81(6)	7.59(6)	3.40 (3)	0.554(6)	1.997(10)
14	22.93(5)	7.83(6)	2.928(23)	0.478(6)	2.031(10)

155 eV at 5.9 keV, connected to a multichannel analyzer through a conventional electronic chain. Two runs were made on each pellet, one with 10 nA intensity, to accumulate 2 μC charge, looking for matrix elements and the other one with 30 nA intensity, to accumulate 3 μC charge, but putting a 1 mm plastic filter in front of the Si(Li), looking for trace elements.

The X-ray spectra were fitted and the elemental concentrations obtained using the GUPIX program.⁵ The results were corrected by the contents of organic matter. The accuracy in the elemental concentrations was checked by analyzing reference sediment samples (IAEA SL-1, NBS SRM 1646 & 2704).

Results and discussion

In Tables 1, 2 and 3 elemental concentrations in each sample are presented. By observing data in Table 1, some differences between samples can be seen. In general, a difference in Si concentration is followed by a difference in Al concentration. Thus, most of samples with high Si concentration have similar or higher Al concentration than those samples with lower Si concentration, giving, in general, Si/Al ratios between 2 and 3. However, samples 15, 21 and 22 are different from the rest of samples. These three samples have also high Si concentration, but the corresponding Al concentrations are the lowest. These two last results imply Si/Al ratios much higher than those of the other samples. The high Si concentration and Si/Al ratio in samples 15, 21 and 22, located along the Odiel river, could

be related with the discharges of fayalite from RTM factory. However, attending to the fayalite stoichiometry ($\text{SiO}_2(\text{FeO})_2$), the Fe concentration in these samples should be four times higher than the Si concentration, if this is the reason of such difference with the rest of samples. Fe concentration in Table 2 reveals that Fe concentration in such samples is even much lower than the Si concentration. This result may indicate a high presence of sandy particles in their composition. This last result can be corroborated attending to the organic content of the samples. Thus, whereas most of samples have an organic content ranging from 10 to 15%, samples 15, 21 and 22 have only 4.6, 1.1 and 2.3% respectively of organic content.

Samples 1, 8, 12 and 17 have also different Si concentration, but similar Si/Al ratio than samples in their surroundings.

The low Si concentration of sample 8, which has also a low Al concentration, could be related with its high Cl concentration of 9.87(2)% whereas the rest of the samples have Cl concentration below 1%, exception being sample 11 with 2.61(1)%. A high amount of NaCl produced by the evaporation of sea water could explain both, the high Cl content and the depletion in Si and Al. If the Cl content is subtracted as NaCl and renormalizing to unity the concentration of the rest of elements, the new Si and Al concentration will be 20.76(5)% and 8.07(6)%, respectively. In this way, the concentration of Si and Al are similar to those in the surroundings (samples 6 and 9).

Samples 1, 12 and 17, have Si, Al, K and Ti concentrations higher than their surrounding samples (see Table 1). However, as can be seen in Tables 2 and 3, the

Table 2. Same as Table 1 but for Fe, S, Ca and P

Sampling point No.	Fe, %	S, %	Ca, %	P, %
1	11.70(3)	1.923(13)	0.869(10)	0.882(16)
2	14.18(4)	3.086(17)	1.939(12)	3.013(22)
3	13.96(4)	3.979(19)	2.141(13)	2.617(21)
23	12.34(3)	0.841(9)	0.927(9)	0.679(13)
22	8.31(3)	0.175(6)	0.981(10)	0.308(15)
21	3.357(20)	0.204(7)	1.196(10)	0.262(18)
20	7.79(3)	1.275(11)	1.414(11)	1.069(16)
18	11.84(3)	1.370(11)	1.784(11)	2.693(19)
17	4.670(22)	0.142(6)	0.445(9)	0.014(12)
16	11.81(3)	1.401(11)	2.476(13)	2.599(20)
15	8.73(3)	1.023(11)	2.222(13)	2.057(21)
13	13.29(3)	0.784(8)	0.897(9)	0.744(13)
4	11.60(3)	2.534(15)	1.882(12)	2.247(19)
5	12.56(3)	1.027(10)	1.210(10)	1.110(15)
7	9.95(3)	0.934(9)	1.315(10)	1.140(15)
6	8.37(3)	1.060(10)	1.186(10)	0.818(14)
8	6.46(2)	1.032(10)	1.671(12)	0.228(11)
9	10.35(3)	1.127(11)	1.424(11)	1.133(16)
10	15.04(4)	0.805(11)	0.671(9)	0.020(10)
12	6.582(20)	1.271(10)	0.798(10)	0.074(14)
11	7.27(3)	1.402(12)	2.501(14)	0.663(15)
19	5.198(23)	1.139(11)	0.726(10)	0.225(14)
14	5.347(23)	1.844(13)	0.728(10)	0.136(12)

Table 3. Same as Table 1 but for Cu, Zn, As and Pb

Sampling point No.	Cu, ppm	Zn, ppm	As, ppm	Pb, ppm
1	1340(30)	2320(40)	1270(50)	1470(170)
2	2000(40)	2900(60)	2070(80)	2300(300)
3	2710(50)	4650(70)	2080(80)	2700(300)
23	2151(21)	3550(30)	1070(30)	1010(110)
22	563(17)	1750(30)	520(30)	350(100)
21	243(10)	810(20)	240(20)	160(70)
20	1504(25)	2090(30)	630(30)	730(110)
18	2392(30)	3600(50)	2500(60)	1910(250)
17	148 (5)	394(8)	56(6)	85(20)
16	2160(30)	3960(50)	2180(50)	1340(210)
15	1136(22)	2940(40)	1120(40)	600(140)
13	1467(25)	4210(50)	1390(40)	530(160)
4	2790(40)	4060(50)	1540(60)	2720(200)
5	1790(30)	4680(60)	1140(50)	1110(170)
7	1727(24)	3610(40)	1030(30)	1210(130)
6	1325(20)	3180(40)	730(30)	630(100)
8	516(13)	1360(22)	277(16)	200(60)
9	1430(30)	4070(50)	870(40)	1050(130)
10	687(24)	5400(60)	770(40)	490(140)
12	523 (9)	1860(20)	143(9)	170(30)
11	1232(19)	3770(40)	534(23)	410(80)
19	654(17)	1920(30)	229(19)	310(60)
14	677(16)	1890(30)	251(17)	200(60)

concentrations of other elements in these samples are the lowest. This fact indicates that the areas where these samples were collected are somehow less affected by the discharges from the factories. Being all samples collected in areas covered by water during the high tide, which produced the contamination, the result indicates that,

probably, these samples are less time flooded by the Odiel waters than the samples collected in their surroundings. This seems to be specially true in the case of sample 17, whose elemental concentrations seem to be the typical ones in soils of an unflooded marsh.

Table 4. Average concentrations and EFI for the analyzed elements in the Odiel marsh (O, EFI_O), the northern marsh (N, EFI_N) and typical composition of a shale. Numbers in parentheses refer to the error of the last figures

Element	O	N	Shale	EFI_O	EFI_N
Si, %	22(7)	17(4)	27.16	0.9(3)	0.62(16)
Al, %	7.7(16)	8.2(10)	8.15	1	1
Ti, %	0.44(10)	0.42(7)	0.39	1.2(4)	1.07(22)
K, %	1.9(4)	1.6(4)	2.69	0.75(22)	0.59(16)
S, %	1.1(6)	3.0(10)	0.26	4(3)	11(4)
Ca, %	1.3(6)	1.6(7)	2.22	0.6(3)	0.7(3)
Fe, %	9(3)	13.3(14)	4.72	2.0(8)	2.8(5)
P, %	0.9(9)	2.2(11)	0.074	13(13)	30(15)
Cu, ppm	1300(800)	2000(700)	45	31(20)	44(16)
Zn, ppm	3000(1400)	3300(1200)	95	33(17)	35(13)
As, ppm	900(600)	1800(500)	13	70(50)	140(40)
Pb, ppm	800(700)	2200(600)	20	40(40)	110(30)

Table 5. Same as Table 4 but EFI related to sample 17 and composition of sample

Element	O	N	Sample 17	EFI_O	EFI_N
Si, %	22(7)	17(4)	26.05(6)	1.1(4)	0.80(21)
Al, %	7.7(16)	8.2(10)	9.99(6)	1	1
Ti, %	0.44(10)	0.42(7)	0.609(6)	0.9(3)	0.84(17)
K, %	1.9(4)	1.6(4)	2.619(11)	0.9(3)	0.74(21)
S, %	1.1(6)	3.0(10)	0.142(6)	10(6)	26(9)
Ca, %	1.3(6)	1.6(7)	0.445(9)	3.8(19)	4.4(20)
Fe, %	9(3)	13.3(14)	4.670(22)	2.5(10)	3.5(6)
P, %	0.9(9)	2.2(11)	0.014(12)	80(110)	190(190)
Cu, ppm	1300(800)	2000(700)	148(5)	11(7)	16(6)
Zn, ppm	3000(1400)	3300(1200)	394(8)	10(5)	10(4)
As, ppm	900(600)	1800(500)	56(6)	21(15)	39(13)
Pb, ppm	800(700)	2200(600)	85(20)	12(11)	32(12)

Tables 2 and 3 show that, excepting the samples above, the marshes (the Odiel and northern marsh) are clearly affected by the discharges from the industries. The northern marsh, the north of the Mojarrera channel and the east side of the Saltés island, are the areas more affected by such discharges. However, from the results, it seems clear that the Punta Umbría river is not affected by the discharges produced into the Odiel river.

Characterization of the global contamination

In Table 4, the average concentration and the global EFI for each analyzed element in the samples are shown. The above values have been determined separately for the Odiel marsh (O) and the northern marsh (N). In the same table, the typical concentration of these elements in a shale⁶ are, for comparison, shown.

For the first four elements in Table 4, Si, Al, Ti and K, it is clear that the average concentration of these elements in samples from both marshes are similar to those in a shale, with EFI values close to unity, revealing the natural origin of these elements in the samples. In the case of Fe

and S, both marshes have average concentrations clearly above the concentration in a shale, with EFI values above unity in both cases and for both marshes. The case of Ca is different. The concentration of this element in both marshes is slightly lower than in a shale, giving EFI values below unity in both cases, meaning that the estuary is depleted in Ca respect to a shale. For the five last elements: P, Cu, Zn, As and Pb, it is clear that the results in Table 4, reflect a clear contamination of both marshes by all of them. Both marshes have concentrations in these elements much higher than in a shale and the EFI for each element is well above unity.

As it is well known, the concentration of an element in a sample depends strongly on its own mineral composition, which indeed depends on its geographical location. Thus, it seems more appropriate to evaluate the EFI for each element by comparing with an uncontaminated sample of the same area. As it was commented previously, sample 17 seems to be the less affected sample with elemental concentrations that could be considered as the natural levels in the area. In Table 5, the EFI values for each element in both marshes related to sample 17 are presented. The EFI, close to unity,

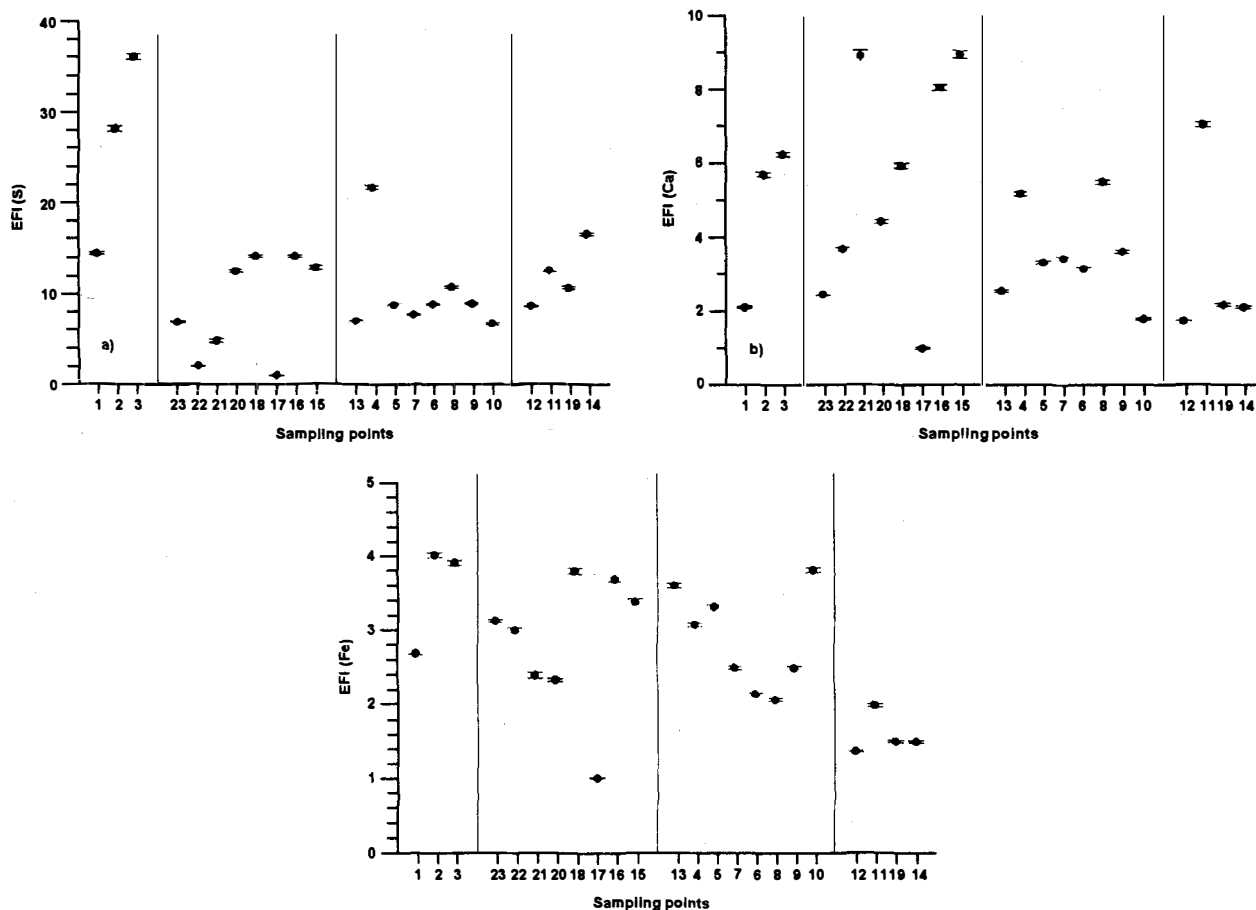


Fig. 2. EFI values evaluated in each sampling station for S (a), Ca (b) and Fe (c)

for Si, Ti and K, in Table 5 reflect that both marshes have concentrations of these elements typical of the area. Thus, it seems clearer now that there are not anthropogenic discharges of these elements in the estuary. As it can be observed, the EFI for the rest of elements is well above unity, but there are some differences versus the EFI determined with the concentration of a shale. Now, the EFI for S, Ca and P are higher than previously, and those for the rest of elements, excepting Fe, are lower but still being well above unity. From the results, it can be extracted the high contamination of both marshes by P, which is coherent with the presence of the fertilizer industries. Moreover, the depletion in Ca previously found, has disappeared and the results show a little contamination of both marshes by this element. The decrease of the EFI for Cu, Zn, As and Pb, may be related with the mineral composition of the marshes, which are still highly affected by anthropogenic emission of these elements in the area.

Spatial distribution of the contamination

As it was mentioned previously, by determining the individual EFI for each sample it is possible to study the

spatial distribution of the contamination in the estuary, which must be related to the Odiel water movements into the marsh.

In Figs 2a, 2b and 2c, the spatial distribution of EFI for S, Ca and Fe, respectively, related to sample 17, are plotted. The highest EFI for these three elements are found in samples collected at the entrance of the Odiel river into the estuary (the northern marsh), at the east side of the Saltés island and at the north of the Mojarrera channel.

The spatial distribution of EFI values for the rest of elements, P, Cu, Zn, As and Pb are presented in Figs 3a, 3b, 3c, 3d and 3e, respectively. The EFI for these elements are higher than those for Ca and Fe, specially in the case of P, which have values above 200 at the northern marsh and at the east side of the Saltés island. The Punta Umbría river shows generally the lowest EFI values, excepting sample 11. For all elements, sample 4 has the highest EFI from all samples collected at the Mojarrera channel, values that decrease downstream the channel. This fact shows that the north of the Mojarrera channel (see Fig. 1) is the main entrance of contaminated Odiel waters into the Odiel marsh. However, some contamination coming from the south of this island cannot be considered as negligible. The

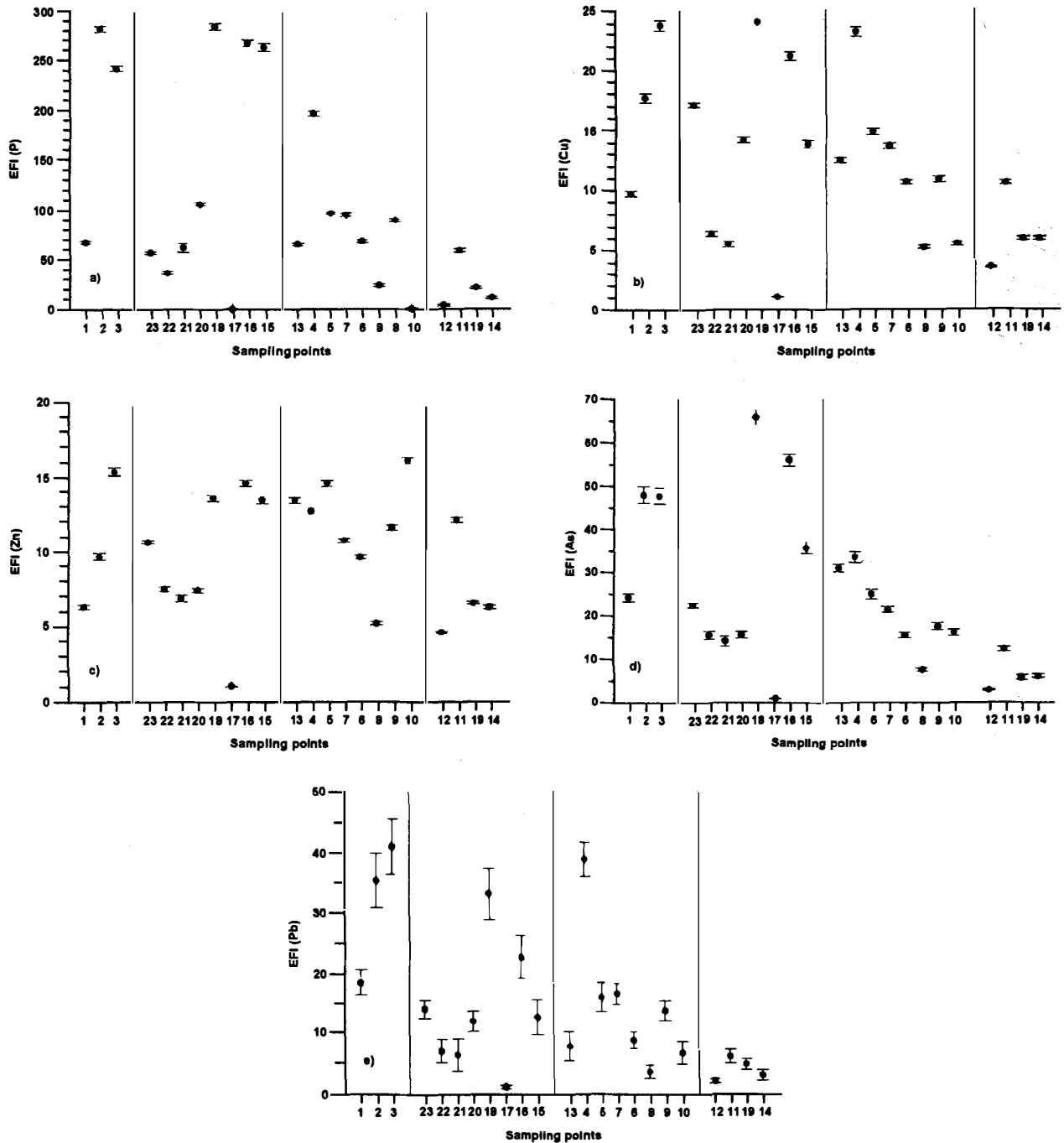


Fig. 3. Same as Fig. 2. but for P (a), Cu (b), Zn (c), As (d) and Pb (e)

case of sample 8, with low EFI for all elements, must be related, as was commented previously, with its high content in NaCl produced by the evaporation of sea water on the area.

There is a high and general contamination by P in all the estuary, with the highest EFI at the northern marsh and at the confluence of the Odiel and Tinto rivers (east side of the Saltés island). FESA factory is, by tidal movements of the Odiel waters, responsible of this contamination since both

rivers do not transport P in their waters. Moreover, since both RTM and FESA factories contain in their wastes part of the other elements with similar spatial distribution of EFI to that of P, it can be concluded that these factories are also responsible of the general contamination in S, Ca, Fe, Cu, Zn, As and Pb. However, some inputs of pollutants, owed to the mining activity at the source of the Odiel river, cannot be discarded as an additional source of contamination of the estuary in these elements, excepting Ca.

Conclusions

The present study reveals the high and general contamination that the operation of a Cu extraction factory and a phosphoric acid factory, produce in the Odiel and in the northern marshes located at the Huelva estuary, at the southwest of Spain. This contamination is produced by the tidal movements of the Odiel river waters in the estuary which receives directly part of the wastes discharged from the factories. From all analyzed elements, P has the highest EFI values in all the estuary. Indeed, EFI values above 200 have been found in certain areas of the marsh. Furthermore, the northern marsh, the north of the Mojarrera channel and the east side of Saltés island, seem to be the areas more affected by the pollutants released by the industries.

The conclusions are in accordance with a previous study of the radioactive contamination in the same marshes.⁷

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