

# Identification and Effects of Anthropogenic Emissions of U and Th on the Composition of Sediments in a River/ Estuarine System in Southern Spain

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## ABSTRACT

*A study of the distribution of natural radionuclides in different fractions of river bottom sediments has been carried out. The study has shown that the majority of the total U in the sediment is located in the non-residual fraction of the sediment, while Th is more suitable to be present in the residual fraction of the sediments. Also, it has been found that coprecipitation with amorphous ferromanganese oxyhydroxides is the main process of incorporation of U- and Th-isotopes from the water column to suspended matter or bottom sediments. The distribution of the radionuclides and the analysis of some relevant activity ratios in different fractions of sediments has made an unequivocal connection between the enhanced U content in river sediments and the waste discharged into the Odiel and Tinto rivers by the operation in the vicinity of phosphate fertilizer industries.*

## INTRODUCTION

On a historical time-scale, sediments may be regarded as, at least, a temporary sink for much of the material which passes through the various

aquatic chemical and biological cycles operating on the earth's surface. At present, the material which is released and takes part in these cycles can have its composition markedly affected by anthropogenic emissions. Sediments, therefore, become an environmental host for many of the waste products discharged by society. The effects of these man-made emissions, in some situations, can be sufficiently strong to affect highly the composition of the deposited sediments.

In the marine environment, near-shore sediments retain the strongest memory of the impact of the released material on the earth's surface. This is because these sediments accumulate at rates which can be as much as several orders of magnitude higher than those in deep sea and because they are being formed in areas in which many anthropogenic substances initially reach the sea.

Once a substance has been incorporated into a sediment, its ultimate fate depends on a number of very complex factors. An element may be considered to be locked permanently into a sediment component or it may subsequently be released and take part in various bio-geochemical reactions, some of which may be environmentally hazardous. The ability to predict the subsequent fate is therefore one of the key factors in the assessment of the effect of environmental pollution. In order to be able to make even the simplest predictions of this kind, it is necessary to understand something about the mechanism by which these elements are incorporated into the sediments. In that sense, it is not sufficient to carry out chemical analysis of the complete sample of a sediment to deduce the degree of pollution to which the deposits have been subjected.

One of the fundamental distinctions that have long been made in sedimentary geochemistry is that between material brought to the site of deposition in a solid form and that brought in a dissolved (or colloidal) form (Chester & Aston, 1981). For that reason it is advantageous to make a fundamental distinction between the lattice-held (i.e. residual) and non-lattice-held (i.e. non-residual) fractions. This distinction is very important in respect to the subsequent fate of an element incorporated into sediments, whether they have a natural or an anthropogenic origin. The rationale underlying this is that elements located in lattice positions can usually be considered, at least to a first approximation, to be immobile, i.e. environmentally unreactive, whereas those in non-lattice sites can be considered to be at least potentially mobile, i.e. environmentally reactive, in the chemical and biological processes which occur in the sediment; interstitial water complex (Chester & Aston, 1981).

The distinction of elements between residual and non-residual types is particularly appropriate to the investigation of radionuclide pollution. This is because the processes which are mainly involved in the incorpora-

tion of these elements from polluted waters result in their location in the non-residual fractions of the sediments (Chester & Aston, 1981). Because of this, the separation and analysis of the non-residual fraction will often provide more information on the extent to which a sediment has suffered from the effects of pollution than will a total sediment analysis.

The residence of the elements in these deposits may only be temporary, and their release into the ecosystem represents a potential hazard. The extent to which this release occurs depends largely on the manner in which the elements are bound to the sediment and on how particular kinds of bonds react to various physico-chemical conditions. It is therefore desirable to have some knowledge of the way(s) in which the elements are bound to the solid components in particular sediment populations.

This can be studied in three main ways, either by interpretation of the chemical analysis of the total sediment sample, by physical separation and subsequent analysis of the individual fractions or by chemical separation and subsequent analysis of the different fractions.

Potentially, the chemical separation of various components into different fractions offers the most effective approach to the study of elemental partitioning in sediments because the processes by which most of radionuclides are incorporated into the various components are themselves largely chemical in nature (Chester & Aston, 1981).

During the last decades these types of studies have been carried out in the case of trace metals and man made transuranides. However, there are only a few studies on natural radionuclides in river components (e.g. Pennders *et al.*, 1991; Plater *et al.*, 1992).

The above considerations have led to the study of the distribution of U- and Th-isotopes in the different fractions of sediments collected at the Odiel and Tinto river (southwest of Spain). As shown in previous papers (see Martínez-Aguirre & García-León, 1991; Martínez-Aguirre *et al.*, 1993) such sediments contain high amounts of U- and Th-isotopes, the reason for it being the emissions of phosphate fertilizer factories around the area under study. Figure 1 presents a map of both rivers. The industrial complex releases part of its wastes directly to the Odiel river. The remainder of the fertilizer process wastes is placed in piles from which, by different processes, some material appears to reach the Tinto river.

## SAMPLES AND RADIOCHEMICAL PROCEDURES

Sampling was carried out during the summer of 1989. Sediment samples (about 1 kg wet weight) were collected along the Odiel and Tinto river channels. Sampling stations used are shown in Fig. 1. The samples were

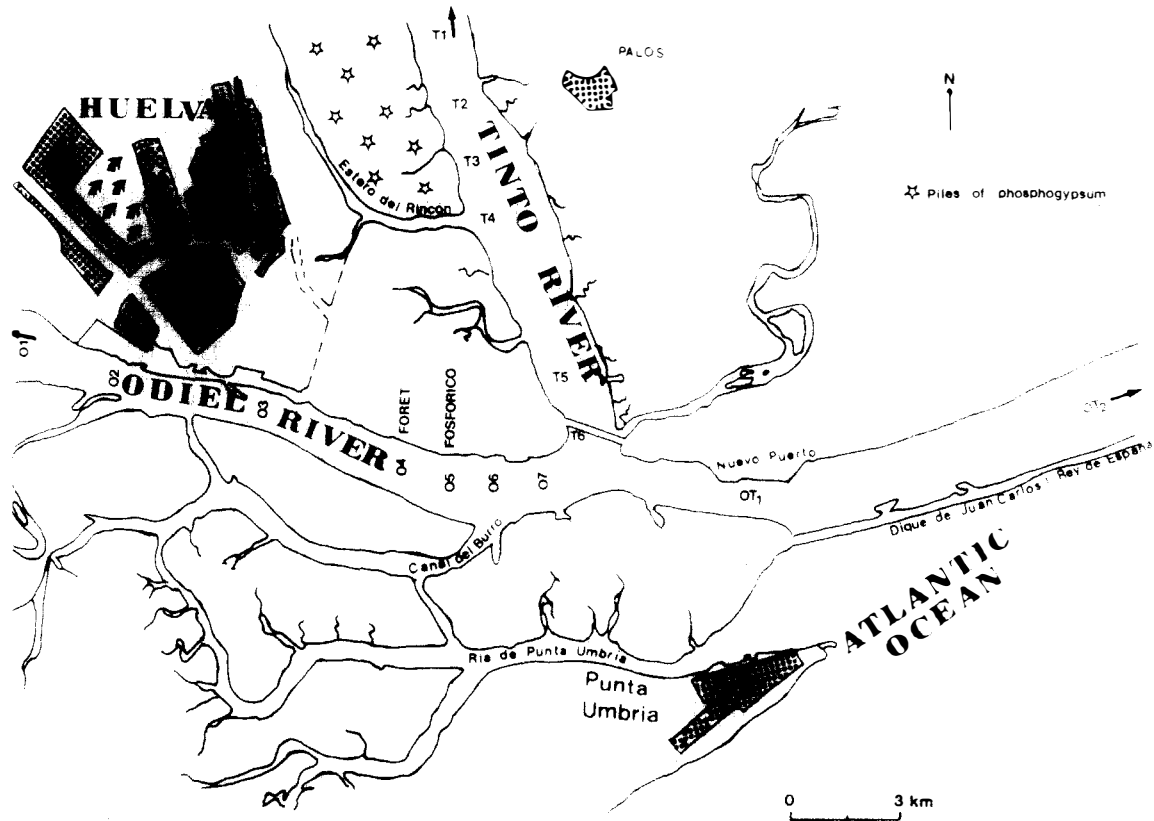


Fig. 1. Map of the Odiel and Tinto river basins. It shows the sampling stations along the river beds together with the phosphogypsum release area and the phosphate fertilizer factory complex location.

stored in plastic bags and adequately identified. Then, at the laboratory, the sediments were dried and powdered before the analysis.

The sediments studied in the Odriel river were those taken near the source of the river (SO1), upstream from the industrial complex (SO2), around one of the phosphate factories (SO5) and downstream from it (SO7). For the Tinto river, sediments were studied from three locations: one near the source of the river (ST1), another around the phosphogypsum piles area (ST2) and, finally, one downstream from such zone (ST6). The sample SOT was taken at the confluence of both rivers. Consequently, with the exception of samples SO1 and ST1, the sediments were all collected in an estuarine area.

One sequential extraction of six sediment fractions has been implemented for each sediment samples. The organic fraction of each sample was also extracted once but from a separate aliquot of each sediment. The six sequentially leached fraction of the sediment are defined in Table 1 together with the additional fraction F7, representing the organic phase.

A detailed account of the analytical techniques used for the separation of each fraction from 2 or 3 g (dry weight) of sediment sample is given in Ivanovich and Harmon (1992) and Martínez-Aguirre (1991).

Once the fractions were separated, they were spiked with well known activities of  $^{236}\text{U}$  and  $^{229}\text{Th}$  and the extraction of U- and Th-isotopes was carried out according to the method given in Ivanovich and Harmon (1992) and Martínez-Aguirre (1991). Finally, U and Th activities are measured by surface barrier or ion implanted Si detector  $\alpha$ -spectrometry.

Fractions F1–F4 and F7 are referred to as secondary phases expected to represent the non-residual part of the sediment. These fractions can be derived from the interaction of the solids with the water column as an exchange process or direct interaction. Thus the referred fractions will

**TABLE 1**  
Definition of Sediment Fractions and Reagents Used to Extract Them

<i>Fraction code</i>	<i>Fraction</i>	<i>Reagent</i>
F1	Readily ion-exchangeable	Magnesium chloride
F2	Adsorbed ions in humic material and/or amorphous oxides	Sodium pyrophosphate
F3	Coprecipitated with amorphous ferromanganese oxyhydroxides	Tamm's acid oxalate
F4	Carbonates	Sodium acetate
F5	Crystalline ferromanganese oxyhydroxides	Coffin's reagent
F6	Resistate (clay) minerals	
F7	Organic phase	1% NaOH

share some geochemical and isotopic characteristics with the liquid phase. Fractions F5 and F6 are termed residual phases and are not expected to necessarily interact on short time-scale with the liquid phase, at least not under normal conditions found in the surface and near-surface environment.

## RESULTS AND DISCUSSION

Percentage distributions of U and Th in the different fractions (taking the content in the unfractionated sediment as 100%) are presented in Table 2 for each of the sediments samples. In general, the sum of percentages in the different fractions agrees well with 100%, with the exception of some cases. This is quite frequent when low activities are present. In fact, the errors we give come only from counting statistics and tracer activity determinations and no other source of error has been possible to estimate. Of course, either analytical problems in chemical separations or heterogeneity in the sediment sample cannot be neglected. Nevertheless, the authors' primary goal was reached, i.e. the estimation of the association of natural radionuclides to the different sediment fractions.

### **U-isotopes**

The data show that U is mainly associated with the secondary sediment fractions, particularly with F2 and F3 fractions. With the exception of samples SO1 and ST1, which were sampled upstream from the estuarine area of the rivers, more than 40% of the total U is found associated with the fraction F3 (sample ST2 is also an exception with 30% of U in the fraction F3). This implies that the main process of U incorporation from the liquid phase (river water) into the sediment is the coprecipitation with amorphous ferromanganese oxyhydroxides. This is a typical process observed in estuarine environment (Sjolkovitz, 1976).

In sediment SO5, fraction F3 is still the main secondary solid phase containing more than 40% of the total U. However, in this sample a high proportion of U (near 50%) is also found in phase F6 (the primary mineral fraction). The sample was taken in the vicinity of the fertilizer factories which release part of their solid wastes directly to the Odiel river (Martínez-Aguirre & García-León, 1991; Martínez-Aguirre *et al.*, 1993). Consequently, this sediment is likely to contain material from the minerals used for fertilizer production, probably from solid wastes after processing, with high U content, the material expected to form a major part of fraction F6 of the sediment at this location.

**TABLE 2**

U and Th Mass Distribution in the Different Fractions for Each of the Studied Sediments (100% is attributed to the element mass in the unfractionated sediment)

	% U							% Th						
	F1	F2	F3	F4	F5	F6	F7	F1	F2	F3	F4	F5	F6	F7
SO1	1.5 ± 0.5	7.5 ± 1.0	3.4 ± 0.9	0.8 ± 0.3	4.0 ± 0.5	8.5 ± 6	4.5 ± 0.5	ND	3.6 ± 0.7	7.8 ± 0.7	0.3 ± 0.3	12.4 ± 0.5	9.4 ± 3	0.7 ± 0.3
SO2	ND	28.9 ± 1.8	73.0 ± 9.1	0.9 ± 0.1	0.9 ± 0.1	4.4 ± 0.2	11.0 ± 0.6	0.2 ± 0.1	5.2 ± 0.5	51.0 ± 3.0	0.3 ± 0.1	12.5 ± 1.0	32.0 ± 1.3	0.5 ± 0.1
SO5	0.15 ± 0.02	13.6 ± 0.8	42.7 ± 3.0	2.0 ± 0.1	3.3 ± 0.2	46.1 ± 3.7	7.5 ± 0.4	0.3 ± 0.1	3.7 ± 0.4	20.0 ± 1.4	0.2 ± 0.1	7.1 ± 0.5	65.0 ± 6.0	0.7 ± 0.1
SO7	0.10 ± 0.02	15.8 ± 1.2	40.3 ± 6.1	1.1 ± 0.1	2.2 ± 0.1	6.8 ± 0.3	9.1 ± 0.6	0.11 ± 0.03	2.5 ± 0.1	71.3 ± 7.8	0.3 ± 0.1	11.6 ± 0.8	29.6 ± 2.1	0.5 ± 0.1
SOT	0.17 ± 0.04	28.8 ± 1.8	58.8 ± 4.1	4.4 ± 0.3	3.8 ± 0.3	10.0 ± 0.6	6.3 ± 0.3	ND	5.4 ± 0.6	45.4 ± 4.8	0.5 ± 0.1	7.4 ± 0.8	51.0 ± 6.2	2.1 ± 0.4
ST1	50.0 ± 4.6	6.4 ± 1.6	3.4 ± 0.7	0.9 ± 0.4	7.9 ± 1.6	37.3 ± 3.0	6.4 ± 0.9	3.9 ± 1.4	4.3 ± 1.5	7.5 ± 2.6	0.6 ± 0.3	8.2 ± 2.8	53.6 ± 14.0	0.7 ± 0.4
ST2	0.4 ± 0.1	55.4 ± 3.5	28.7 ± 2.0	0.3 ± 0.1	2.2 ± 0.1	10.7 ± 1.0	0.3 ± 0.1	0.06 ± 0.06	17.7 ± 3.0	32.6 ± 3.2	1.0 ± 0.3	11.0 ± 1.3	70.9 ± 6.0	1.8 ± 0.5
ST6	0.25 ± 0.04	26.7 ± 2.0	78.6 ± 5.0	0.9 ± 0.1	2.1 ± 0.1	6.7 ± 0.3	12.1 ± 0.5	0.13 ± 0.07	4.9 ± 0.6	42.5 ± 4.7	0.12 ± 0.06	11.7 ± 1.3	35.0 ± 3.8	0.5 ± 0.1

ND, Element not detected in such fraction.

Sample ST2 is also of some interest. At this location (see Fig. 1) it was shown by Martínez-Aguirre *et al.* (1993) that some material is discharged directly into the Tinto river from the phosphogypsum piles area. In the case of this sample of the largest fraction of total U resides in fraction F2 (more than 50% of total U) followed by fraction F3 (approximately 30% of total U). From the observed U distribution in ST2 it is inferred that this U is incorporated into the local sediment predominantly by adsorption from the liquid phase. A different chemical association in the wastes must be responsible for the 'anomalous' U distribution observed in sediments from station ST2.

Sediments SO1 and ST1 have a very different composition from the rest. They were collected near the source of both rivers. The main solid fraction is now F6. The reason for this special distribution resides in the low pH of the river waters collected in both locations (3.0 and 2.6, respectively). The low pH at these stations comes probably from the processing effluents from Cuminas located upstream in both rivers. Under such pH conditions a redissolution of U from the solid phase must occur. This would explain the high U concentrations found in the corresponding river waters (Martínez-Aguirre & García-León, 1991; Martínez-Aguirre *et al.*, 1993). This redissolution causes low concentrations in secondary phases and high concentrations in the residual ones in which U is less accessible for leaching. Furthermore, the low pH conditions do not favour the ferromanganese oxyhydroxide precipitation, which explains why the main fractions in secondary phases are F2 for SO1 and F1 for ST1. This latter difference could be explained by the presence of large amounts of metallic ions at station ST1, coming from the copper mines which are located nearby upstream.

The U content of fraction F2 is similar for all the sediments except those sampled at stations SO1 and ST1 where it is much lower. The sediment samples taken near the phosphate processing waste area at the Odiel river (SO2, SO5, SO7 and ST6) have virtually identical U concentrations in fraction F3 and noticeably higher ones than the rest. Moreover, samples SO5 and SO7 have higher U concentration in fraction F6 and a higher total U concentration than the rest of sediments (Martínez-Aguirre *et al.*, 1993). This is taken as evidence that the solid particles from the fertilizer industrial complex characterised by high U content in fraction F6 have reached stations SO5 and SO7 but are not sedimentated further downstream in the estuary.

### **Th-isotopes**

Although, broadly speaking, the same comments can be derived from the data for Th, it can be said that, in general, Th has a higher association



with the fractions of the residual phases, F5 and F6 (more than 30% in the latter), than U. This is consistent with the observed Th tendency in the surface/near-surface environment to hydrolyse easily and to be highly particle reactive in aquatic systems. With the exception of samples SO1 and ST1, the secondary fraction F3 appears to be another favoured solid phase for Th. Thus, in some cases, coprecipitation with amorphous ferromanganese oxyhydroxides is the main process of Th incorporation from the river water to the sediments.

However, as it may be expected, the fraction distribution patterns for different Th-isotopes are not the same for all the samples. For instance, while for samples SO5, SO7 and ST6 (locations nearer the release to the Odiel river (see Fig. 1)) the phase distributions for various Th-isotopes are nearly the same (major fractions being F3 and F6), this is not the case for locations SO2, SOT<sub>1</sub> and ST2 (remote from the release points). In these latter three samples, <sup>230</sup>Th is contained essentially in phase F3 (lower proportion in fraction F6), resembling the U distribution discussed above, while <sup>232</sup>Th and <sup>228</sup>Th are mainly contained in residual fraction F6. This suggests that the material forming sediments at locations SO5, SO7 and ST6 are influenced by the fertilizer production wastes released from the industrial complex.

The Th contents in fractions F2 and F3 are similar for all the sediment samples (exceptions being locations SO1 and ST1 upstream with much lower Th content). As Th concentrations of the F6 fractions are the same for most of the samples (exceptions being samples SO5 and SO7 located near the fertilizer works) it can be concluded that the river sediments near the industrial complex have incorporated material derived from their wastes.

A final comment can be made concerning the presence of U and Th in the organic phase. There seems to be little association of U with the organic fraction in all the sediment samples studied (5–10% of total U associated with the organic fraction F7), whereas no Th was found in this fraction.

### **Isotope activity ratios**

Some interesting activity or mass ratios are presented in Tables 3–7. In the tables the ratios for the unfractionated sample as well as for water and suspended matter samples collected at the same stations are also given for comparison (Martínez-Aguirre *et al.*, 1993).

Close inspection of the activity ratios in the river water and different sediment solid fractions may assist in deducing useful information about the nature of the radionuclide transfer between various fractions and the source of the incorporated radionuclide in the sediment.

**TABLE 3**

The Th/U Mass Ratio Found in the Fractions Analysed for the Different Sediment Samples. The Ratio is Given for the Unfractionated Sediment Samples as well as for the Solution and Suspended Matter Samples

<i>Fraction</i>	<i>SO1</i>	<i>SO2</i>	<i>SO3</i>	<i>SO7</i>	<i>SOT</i>	<i>ST1</i>	<i>ST2</i>	<i>ST6</i>
Unfractionated	2.5 ± 0.6	0 ± 0.02	0.22 ± 0.01	0.61 ± 0.05	0.55 ± 0.05	2.3 ± 0.6	0.40 ± 0.02	0.28 ± 0.03
F1			0.4 ± 0.1	0.7 ± 0.2		0.18 ± 0.05		0.14 ± 0.04
F2	1.2 ± 0.3	0.062 ± 0.007	0.061 ± 0.006	0.096 ± 0.009	0.102 ± 0.009	1.5 ± 0.5	0.13 ± 0.02	0.053 ± 0.006
F3	5.7 ± 0.9	0.25 ± 0.03	0.106 ± 0.09	1.10 ± 0.16	0.42 ± 0.03	5 ± 1	0.45 ± 0.04	0.15 ± 0.02
F4	1.0 ± 0.9	0.11 ± 0.04	0.026 ± 0.006	0.15 ± 0.03	0.06 ± 0.01	1.3 ± 0.9	1.2 ± 0.5	0.04 ± 0.02
F5	8.1 ± 1	4.5 ± 0.5	0.49 ± 0.03	3.2 ± 0.2	1.0 ± 0.1	2.3 ± 0.5	1.9 ± 0.3	1.6 ± 0.4
F6	3.2 ± 0.3	2.5 ± 0.2	0.31 ± 0.03	2.7 ± 0.3	3.2 ± 0.4	2.6 ± 0.3	1.5 ± 0.1	
F7	0.4 ± 0.2	0.015 ± 0.005	0.021 ± 0.003	0.031 ± 0.006	0.18 ± 0.03	0.25 ± 0.13	2.3 ± 1.0	0.012 ± 0.004
Solution	0.108 ± 0.012	0.053 ± 0.027	0.151 ± 0.018	0.157 ± 0.011	0.034 ± 0.004	0.52 ± 0.03	3.7 ± 1.1	0.042 ± 0.004
Suspended matter	1.33 ± 0.37	0.429 ± 0.042	0.258 ± 0.011	0.62 ± 0.03	0.34 ± 0.06	1.15 ± 0.23	0.21 ± 0.05	0.56 ± 0.13

**TABLE 4**  
Same as Table 3 but for  $^{234}\text{U}/^{238}\text{U}$  Activity Ratio

<i>Fraction</i>	<i>SO1</i>	<i>SO2</i>	<i>SO5</i>	<i>SO7</i>	<i>SOT</i>	<i>ST1</i>	<i>ST2</i>	<i>ST6</i>
Unfractionated	1.28 ± 0.08	1.08 ± 0.02	1.06 ± 0.02	1.05 ± 0.02	1.02 ± 0.03	1.07 ± 0.07	1.02 ± 0.02	1.03 ± 0.02
F1	1.87 ± 0.76		1.11 ± 0.13	0.95 ± 0.17	0.68 ± 0.35	1.33 ± 0.11	0.81 ± 0.21	0.95 ± 0.10
F2	1.40 ± 0.28	1.05 ± 0.02	1.05 ± 0.02	1.09 ± 0.03	1.04 ± 0.03	0.94 ± 0.24	1.02 ± 0.03	1.09 ± 0.03
F3	1.09 ± 0.18	1.09 ± 0.02	1.04 ± 0.01	0.96 ± 0.04	1.09 ± 0.02	1.19 ± 0.24	1.08 ± 0.04	1.04 ± 0.01
F4	1.5 ± 0.7	1.19 ± 0.13	1.08 ± 0.04	1.10 ± 0.08	1.06 ± 0.05	1.20 ± 0.66	1.71 ± 0.50	1.05 ± 0.12
F5	1.60 ± 0.28	1.9 ± 0.2	1.03 ± 0.03	1.05 ± 0.03	1.29 ± 0.09	1.3 ± 0.3	1.06 ± 0.09	1.06 ± 0.04
F6	0.88 ± 0.05	0.94 ± 0.04	1.07 ± 0.01	1.02 ± 0.02	0.98 ± 0.05	1.00 ± 0.08	0.93 ± 0.08	1.13 ± 0.04
F7	1.44 ± 0.22	1.08 ± 0.04	1.01 ± 0.02	1.10 ± 0.03	1.05 ± 0.04	0.92 ± 0.17	2.07 ± 0.75	1.12 ± 0.03
Solution	1.60 ± 0.02	1.06 ± 0.03	1.02 ± 0.09	1.10 ± 0.02	1.09 ± 0.02	1.83 ± 0.03	1.07 ± 0.04	1.08 ± 0.03
Suspended matter	1.88 ± 0.27	1.05 ± 0.05	1.00 ± 0.01	1.06 ± 0.02	0.98 ± 0.08	1.26 ± 0.17	0.91 ± 0.09	1.20 ± 0.15

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**TABLE 5**  
Same as Table 3 but for  $^{230}\text{Th}/^{234}\text{U}$  Activity Ratio

<i>Fraction</i>	<i>SO1</i>	<i>SO2</i>	<i>SO5</i>	<i>SO7</i>	<i>SOT</i>	<i>ST1</i>	<i>ST2</i>	<i>ST6</i>
Unfractionated	0.65 ± 0.16	0.86 ± 0.03	2.5 ± 0.1	1.45 ± 0.08	0.92 ± 0.06	1.21 ± 0.25	1.72 ± 0.07	0.92 ± 0.05
F1	0.47 ± 0.18		1.62 ± 0.17	1.21 ± 0.23	1.26 ± 0.60	0.35 ± 0.04	1.37 ± 0.35	0.31 ± 0.08
F2	0.77 ± 0.18	0.22 ± 0.02	0.33 ± 0.02	0.20 ± 0.01	0.22 ± 0.01	5 ± 1	0.92 ± 0.07	0.14 ± 0.01
F3	2.4 ± 0.4	0.89 ± 0.11	0.87 ± 0.07	2.6 ± 0.4	1.04 ± 0.07	9 ± 1	2.6 ± 0.2	0.67 ± 0.06
F4	0.97 ± 0.49	0.39 ± 0.05	0.38 ± 0.02	0.25 ± 0.03	0.13 ± 0.01	2.6 ± 1	2.0 ± 0.4	0.24 ± 0.04
F5	2.2 ± 0.3	6.9 ± 0.7	3.8 ± 0.2	6.6 ± 0.4	1.92 ± 0.14	2.5 ± 0.5	10.4 ± 0.9	5.2 ± 0.3
F6	0.99 ± 0.09	1.28 ± 0.07	3.7 ± 0.4	4.9 ± 0.2	1.07 ± 0.12	1.21 ± 0.13	1.56 ± 0.16	3.1 ± 0.2
F7	0.18 ± 0.05	0.061 ± 0.006	0.124 ± 0.007	0.069 ± 0.006	0.49 ± 0.04	0.29 ± 0.11	0.71 ± 0.21	0.044 ± 0.004
Solution	0.157 ± 0.008	0.71 ± 0.21	0.37 ± 0.04	0.29 ± 0.01	0.060 ± 0.004	0.25 ± 0.01	2.1 ± 0.6	0.077 ± 0.004
Suspended matter	1.04 ± 0.14	0.81 ± 0.04	0.71 ± 0.02	1.30 ± 0.04	0.97 ± 0.08	0.68 ± 0.09	0.91 ± 0.09	0.98 ± 0.11

**TABLE 6**  
Same as Table 3 but for  $^{228}\text{Th}/^{232}\text{Th}$  Activity Ratio

<i>Fraction</i>	<i>SO1</i>	<i>SO2</i>	<i>SO5</i>	<i>SO7</i>	<i>SOT</i>	<i>ST1</i>	<i>ST2</i>	<i>ST6</i>
Unfractionated	2.7 ± 0.8	1.11 ± 0.06	0.78 ± 0.05	0.92 ± 0.04	1.04 ± 0.09		1.11 ± 0.05	0.86 ± 0.10
F1			1.84 ± 0.68	0.65 ± 0.48		2.7 ± 0.8		
F2	3.2 ± 0.7	1.43 ± 0.17	1.31 ± 0.14	1.08 ± 0.09	1.36 ± 0.13	3.6 ± 0.8	1.38 ± 0.18	1.51 ± 0.17
F3	2.0 ± 0.2	0.95 ± 0.06	0.76 ± 0.05	0.78 ± 0.04	0.98 ± 0.38	2.7 ± 0.4	1.30 ± 0.10	1.15 ± 0.08
F4	10 ± 9		1.37 ± 0.49	2.1 ± 0.5	0.79 ± 0.34	3.3 ± 2.0		5.5 ± 3.7
F5	2.2 ± 0.2	1.05 ± 0.08	0.86 ± 0.06	0.82 ± 0.04	1.20 ± 0.11	3.2 ± 0.5	1.50 ± 0.21	1.14 ± 0.11
F6	0.81 ± 0.05	0.91 ± 0.05	0.73 ± 0.05	0.82 ± 0.04	0.51 ± 0.07	0.87 ± 0.11	0.88 ± 0.08	1.06 ± 0.09
F7		3.6 ± 1.3	1.74 ± 0.38	1.33 ± 0.35	1.43 ± 0.36		1.63 ± 0.84	3.1 ± 1.2
Solution	1.70 ± 0.07	4.5 ± 2.5	3.0 ± 0.3	1.31 ± 0.11	0.91 ± 0.18	3.6 ± 0.1	0.27 ± 0.05	1.09 ± 0.17
Suspended matter	3.6 ± 1.5	0.86 ± 0.14	0.95 ± 0.05	0.96 ± 0.06		1.4 ± 0.5	0.79 ± 0.30	1.5 ± 0.8

**TABLE 7**  
Same as Table 3 but for  $^{230}\text{Th}/^{232}\text{Th}$  Activity Ratio

<i>Fraction</i>	<i>SO1</i>	<i>SO2</i>	<i>SO5</i>	<i>SO7</i>	<i>SOT</i>	<i>ST1</i>	<i>ST2</i>	<i>ST6</i>
Unfractionated	1.00 ± 0.31	8.3 ± 0.4	37.3 ± 1.6	7.6 ± 0.2	5.2 ± 0.3	1.77 ± 0.56	2.30 ± 0.09	10.3 ± 0.8
F1		5.2 ± 2.4	12.7 ± 3.6	5.5 ± 2.0		8.5 ± 2.1		6.0 ± 3.5
F2	2.8 ± 0.6	11.5 ± 1.1	17.6 ± 1.5	6.9 ± 0.4	6.8 ± 0.5	9.7 ± 2.1	23 ± 2	8.9 ± 0.8
F3	1.41 ± 0.17	21.1 ± 0.5	26 ± 1	7.4 ± 0.3	8.4 ± 0.4	6.6 ± 0.9	19.4 ± 1.2	14.0 ± 0.8
F4	4.4 ± 3.7	13.0 ± 3.9	48 ± 10	5.5 ± 1.1	7.5 ± 2.0	7.1 ± 3.9	8.4 ± 2.9	22 ± 10
F5	1.42 ± 0.15	8.9 ± 0.5	24 ± 1	6.6 ± 0.2	7.3 ± 0.5	4.3 ± 0.6	17.0 ± 1.8	10.5 ± 0.8
F6	0.85 ± 0.05	1.48 ± 0.07	39 ± 2	5.7 ± 0.2	1.18 ± 0.09	1.18 ± 0.13	0.72 ± 0.13	7.0 ± 0.4
F7	2.0 ± 0.9	13.2 ± 4.3	18.1 ± 2.7	7.4 ± 1.5	8.8 ± 1.6	3.2 ± 2.1	2.0 ± 0.8	12.5 ± 4.1
Solution	3.70 ± 0.14	12 ± 6	8.5 ± 0.6	6.1 ± 0.4	5.8 ± 0.7	2.67 ± 0.09	1.90 ± 0.21	6.0 ± 0.6
Suspended matter	4.6 ± 1.4	6.2 ± 0.6	8.6 ± 0.3	6.8 ± 0.3	8.8 ± 1.4	2.4 ± 0.4	12.1 ± 2.7	6.4 ± 1.4

First of all, the Th/U mass ratio (Table 3) in fraction F6 for all the solid samples analysed except for sample SO5 is close to the typical value for near-surface rocks of 3-5 (Roger & Adams, 1969). The exception is sample SO5 which has a much lower Th/U mass ratio confirming U enrichment relative to Th typical of the phosphate mineral utilised in the fertilizer production. (Martínez-Aguirre *et al.*, 1993).

In general,  $^{234}\text{U}/^{238}\text{U}$  and  $^{228}\text{Th}/^{232}\text{Th}$  activity ratios (Tables 4 and 6) are above unity in secondary fractions (F1–F4) and below unity in the residual fractions F5 and F6. These signatures are the consequence of a combination of two main processes (Kigoshi, 1971; Osmond & Cowart, 1992; Osmond & Ivanovich, 1992). The displacements by alpha-recoil processes could produce a transfer of daughter radionuclides to the secondary fractions given the consequent defect of them in the residual ones. Furthermore, by considering the fact that Ra is more mobile than Th, U more mobile than  $^{230}\text{Th}$  and  $^{234}\text{U}$  more mobile (by oxidation to the more soluble +6 state of valency) than  $^{238}\text{U}$ , a migration of these radionuclides (U and Ra) to more external fractions could be produced. This migration would be reflected by an excess of daughter radionuclides in the secondary phases along with a defect of them in the residual ones. We also have to consider the fact that the secondary phase is in interaction with the liquid phase. Thus, at least some of them should reflect the excesses and defects typical of this phase.

The interaction of secondary fractions with solution is essentially reflected in the  $^{230}\text{Th}/^{234}\text{U}$  activity ratio (Table 5). It is well known that Th is a particularly insoluble element in natural waters and it is usually found associated with solid matter. Thus, such an activity ratio is typically much below unity in waters. Consequently, the authors have found a  $^{230}\text{Th}$  defect in most of the secondary fractions whereas in the residual fractions the activity ratio is  $\geq 1$ . Besides that, among all the secondary fractions, it is the fraction F2 which, in most of the cases, presents activity ratio similar to that in solution, while in fraction F3 it is similar to that in suspended particles. This occurs also for the  $^{228}\text{Th}/^{232}\text{Th}$  activity ratio. Since the F2 fraction is formed by direct ion sorption from solution, the result is logical; whereas the authors' findings for the F3 fraction could be revealing that either U or Th is incorporated to suspended matter by coprecipitation with amorphous ferromanganese oxyhydroxides on to the surface of the particles.

The majority of sediment components have  $^{230}\text{Th}/^{232}\text{Th}$  activity ratios (Table 7) above unity. This is the result of the general U enrichment in the sediments of both rivers as well as in the river water and suspended particles near the fertilizer industrial complex (Martínez-Aguirre *et al.*, 1993). In fraction F6 of samples SO5, SO7 and ST6, the  $^{230}\text{Th}/^{232}\text{Th}$  activity

ratio is much higher than unity whereas in other sediment samples more distant from the fertilizer complex discharge points, this activity ratio in fraction F6 is near unity and similar to that found in other unperturbed systems such as the Guadalquivir river (Martínez-Aguirre & García-León, 1993). This is in agreement with the high proportion of material coming directly from the point of waste discharge into the Odiel river.

A different radionuclide distribution is observed in the secondary fractions of sediment samples SO1 and ST1. In the former sample, fraction F2 has yielded activity ratios very similar to those found in solution and suspended matter (Martínez-Aguirre *et al.*, 1993), indicating that the process of interaction between the solid and aqueous phases at that location in the Odiel river is governed by ion sorption. In contrast, for sample ST1 the activity ratios in fraction F1 resemble most those found in river water and suspended sediments at that location (Martínez-Aguirre *et al.*, 1993), indicating that ion-exchange is the main process by which radionuclides are incorporated out of river water into sediment via suspended matter. This would explain the unusually high  $^{234}\text{U}/^{238}\text{U}$  and  $^{228}\text{Th}/^{232}\text{Th}$  activity ratios found in suspended particles at that location in the Tinto river.

Finally, the activity ratios in the organic fraction (F7) resemble strongly those found in river water. The only exception to this observation is sample ST1 in which the  $^{234}\text{U}$  excess observed in solution was not found in the organic fraction.

## CONCLUSIONS

The U- and Th-isotopes distribution in different fractions of bottom sediments from the Odiel and Tinto rivers has provided much information on their environmental behaviour. Under estuarine conditions U- and Th-isotopes occur mainly in the secondary fractions although Th-isotopes tend to reside more in residual fractions than U-isotopes. These differences between U and Th reflect largely much higher solubility (and hence mobility) of U relative to Th in surface and near-surface environments. Furthermore, in the case of U at least, the observed distribution over the different fractions of the sediments is affected by the pH of the surrounding waters. Analysis of different sediment fractions as discussed in this paper can also be useful in revealing radionuclide sources. Thus, for instance,  $^{230}\text{Th}$  follows the distribution of its U-isotope precursors in the U decay chain more than that of  $^{232}\text{Th}$  when their sources in a riverine system are different. The sediment fractionation and analysis presented here has made an unequivocal connection between the enhanced U



content and respective activity ratios in the river sediment in the vicinity of phosphate fertilizer industries and the waste discharge point in Odiel and Tinto rivers.

Finally, the comparison of several activity ratios, as  $^{234}\text{U}/^{238}\text{U}$ ,  $^{230}\text{Th}/^{234}\text{U}$  and  $^{228}\text{Th}/^{232}\text{Th}$ , for instance, in the secondary fractions with those found in river waters or suspended matter gives interesting information on the nature of exchange processes between aqueous and solid phases in river systems.

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