U and Th speciation in river sediments

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Abstract

A study of the distribution of some natural radionuclides in different chemical fractions of river bottom sediments has been carried out. The study has shown that the majority of the total U in sediments is located in the non-residual fractions, while Th is more likely to be present in the residual ones. This difference between U and Th reflects largely a much higher mobility of U relative to Th in surface and near-surface environments. Coprecipitation with amorphous ferromanganese oxyhydroxides is the main process of U and Th incorporation from the water column into the soil particles. Moreover, the distribution of the radionuclides and the analysis of the Th/U mass ratios in different chemical fractions of sediments has made an unequivocal connection between the enhanced U content in river sediments and the wastes discharged into the rivers by the operation of fertilizer industries.

Keywords: Radionuclide pollution; Uranium (U); Thorium (Th); River sediments; Fertilizer industries

1. Introduction

River 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. Thus, sediments 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. 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 later be released and take part in various biogeochemical reactions.

The fundamental distinctions that have been made in sediments geochemistry is that between material brought to the site of deposition in a solid form and that brought in a dissolved form. In that sense the distinction of elements between residual and non-residual types is particularly appropriate to the investigation of radionuclide pol-

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lution [1]. Thus, processes involved in the incorporation of elements from polluted waters results in their location in the non-residual fractions and thus, they can usually be considered to be at least potentially mobile, i.e. environmentally reactive in the chemical and biological processes which occur in the sediments/interstitial water complex. On the other hand, elements located in residual fractions can usually be considered, at least to a first approximation, to be immobile, i.e. environmentally unreactive. Thus, the residence of an element in a deposit may be only temporary, and their release into the ecosystem represents a potential hazard. The extent to which this release occurs depends largely on the manner by which this element is bound to the sediment and on how particular kinds of bonds react to various physico-chemical conditions.

The above considerations have led to the study of the distribution of uranium (U) and thorium (Th) in different fractions of sediments collected at the Odiel and Tinto rivers, which are located in Southwest Spain. Such sediments are clearly affected by the wastes released by two fertilizer factories located in the left margin of the Odiel river as well as by the phosphogypsum piles stored at the right margin of the Tinto river [2].

2. Samples and radiochemical procedures

Sampling was carried out during the summer, 1989. Sediment samples were collected along the Odiel and Tinto river basins and stored in plastic bags; then, at the laboratory they were dried and powdered before the analysis. The location of the sampling stations are shown in Fig. 1. Three sediments from the Odiel river were studied: upstream from the fertilizer industries (SO1), around one of the fertilizer industries (SO2) and downstream from them (SO3). In the Tinto river, sediments from two locations were studied: one around the phosphogypsum pile area (ST1) and another downstream from this zone near the confluence with the Odiel river (ST2). Additionally, another sample (SOT) located downstream of the confluence of both rivers was studied.

One sequential extraction of six sediment fractions (Table 1) has been implemented for each sediment sample [3,4]. The six sequentially leached fractions of the sediment are defined in Table 1. Fractions F1–F4 are referred to as secondary phases expected to represent the non-residual part of the sediment, being either an end product derived from the river water/solid interaction and exchange processes or part of the solid capable of direct interaction with river water and thus sharing 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 a short time-scale with the liquid phase, at least not under normal conditions found in the surface and near-surface environments.

Once the fractions were separated, they were spiked with ^{236}U and ^{229}Th and the extraction of U and Th isotopes was carried out according to the methods given in [3,4]. U and Th activities were measured by α-spectrometry with surface barrier or ion implanted Si detectors.

3. Results and discussion

Percentage distribution of U and Th in the different fractions (taking the content in the unfractionated sediment as 100% [2]) are shown in Figs. 2 and 3. With the exception of samples ST2 for U, the sum of the percentages in the different fractions agrees well with 100%. Analytical problems in chemical separations or heterogeneity in the sediment sample cannot be ignored.

3.1. Uranium

Fig. 2 shows that U is mainly associated with non-residual fractions, particularly with F2 and F3 fractions. More than 40% of U is found associated with the fraction F3 (an exception is sample ST1 with 30% in this fraction). This implies that the main process of U incorporation from the liquid phase (river water) into the sediments is the coprecipitation with amorphous ferromanganese oxyhydroxides. This is a typical process observed in estuarine environments [5].

In sediment SO2 (Fig. 2b), fraction F3 is still one of the main non-residual fractions containing $> 40\%$ of the total U. However, in this sample a

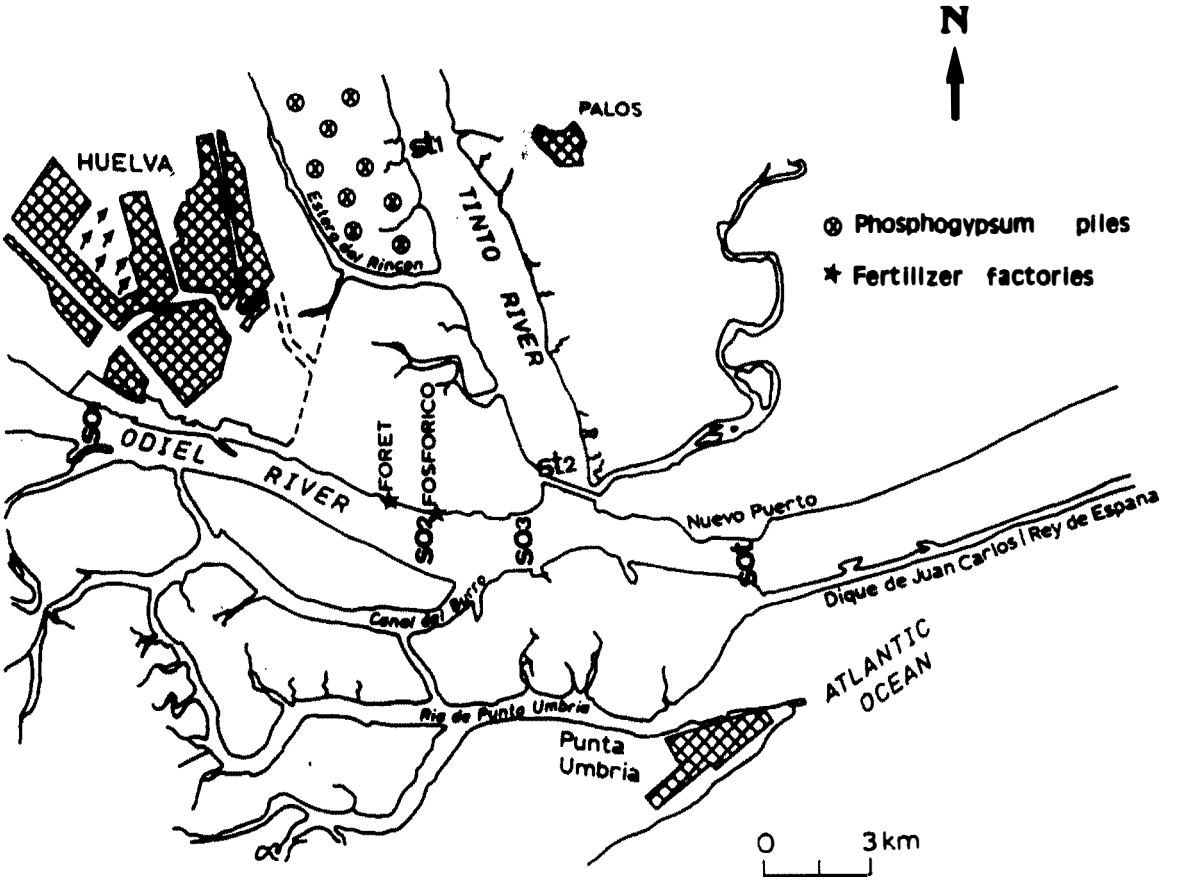

Fig. 1. Map of the studied area showing the location of the sampling points, the fertilizer factories and the phosphogypsum storage area emplacements.

high proportion of U (~50%) is also found in fraction F6 (the primary mineral fraction). This sample (Fig. 1) was taken in the vicinity of a fertilizer factory which releases part of its solid wastes directly into the Odiel river [2,6]. Consequently, this sediment is likely to contain material from the minerals used for the fertilizer production. This material is expected to form a major part of fraction F6 of the sediment at this location.

Sample ST1 is also of some interest. At this location (Fig. 1) some material from the phosphogypsum storage area [2] is discharged directly into the Tinto river. Here, the largest fraction of total

Table 1
Definition of sediment fractions and reagents used for their extraction

Fraction code	Fraction	Reagent
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	

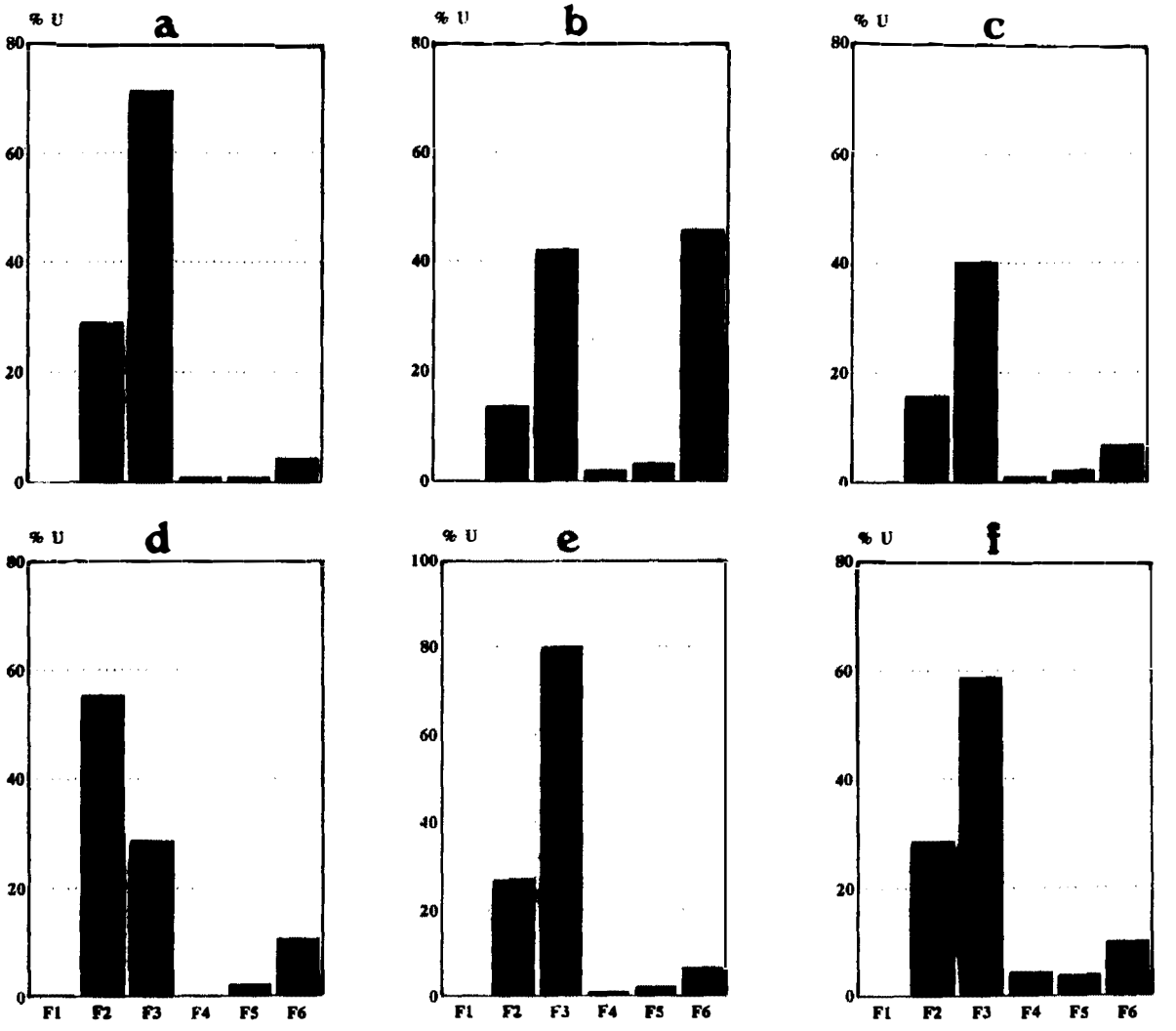

Fig. 2. Percentage distribution of U in each sequentially extracted fractions of samples (a) SO1, (b) SO2, (c) SO3, (d) ST1, (e) ST2 and (f) SOT.

U resides in fraction F2 (> 50%) followed by fraction F3 (~ 30%). Thus, 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 this station and related to the discharges from the phosphogypsum storage area [2,7].

In Table 2, concentrations of U in $\mu g/g$ contained in the main fractions of the sediments are shown. It is interesting to observe that sediment samples taken near the phosphate waste discharge area of the Odiel river (SO1, SO2, SO3 and ST2) have virtually identical U concentrations in fractions F2 and F3 and these are noticeably higher than the rest of samples (ST1 and SOT). This difference is much clearer in the case of fraction F3. This can be taken as an evidence of the extension of the contamination of the Odiel river basin (even the lowest part of the Tinto river bed). Thus, the liquid wastes discharged from the fertilizer industries affect the river bed upstream and downstream from the industries, probably due to tidal movements of

Table 2
U concentration in $\mu g/g$ in the main fractions of bottom sediments from the Odiel and Tinto rivers

Fraction	SO1	SO2	SO3	ST1	ST2	SOT
F2	12.7 ± 0.8	12.1 ± 0.6	13.7 ± 0.9	8.69 ± 0.54	11.2 ± 0.8	6.86 ± 0.30
F3	31.5 ± 3.6	37.5 ± 2.4	34.9 ± 3.5	4.51 ± 0.26	33.3 ± 2.1	14.1 ± 0.7
F5	0.42 ± 0.04	2.86 ± 0.10	1.92 ± 0.06	0.35 ± 0.02	0.90 ± 0.04	0.92 ± 0.06
F6	1.93 ± 0.07	40.8 ± 2.8	5.89 ± 0.15	1.68 ± 0.13	2.77 ± 0.11	2.44 ± 0.14

the liquid discharges. In the case of the residual phases, it can be observed that samples SO2 and SO3 have higher U concentrations in fractions F5 and F6 than the rest of the samples. This difference is much clearer in the case of fraction F6 of sample SO2. This sample is located in front of the fertilizer factories and presents a U concentration >1 order of magnitude higher than the rest of samples. The U concentration in this fraction decreases downstream on the river bed. This can be taken as evidence that the solid particles from the fertilizer production characterised by a high U content in fraction F6 have reached stations SO2 and SO3 but are not sedimented further downstream in the estuary.

3.2. *Thorium*

Fig. 3 shows the percentage distribution of Th (^{232}Th) in the six sequentially extracted fractions of sediments. It can be observed that Th has a higher association than U to residual fractions F5 and F6, always with $>30\%$ in fraction F6. However, the non-residual fraction F3 appears to be another favoured fraction for Th. Thus, it seems that, as for U, coprecipitation with amorphous ferromanganese oxyhydroxides is the main process of Th incorporation from the river water to the sediment. Basically, we can make the same comments as we did in the case of U. Thus, sample SO2 presents a different percentage distribution than the rest of samples, with $>60\%$ of Th in the mineral fraction F6. Moreover, fraction F2 does not seem to be a favoured fraction for Th. Only sample ST1 has $\sim 15\%$ of Th in this fraction whereas the rest contain $<5\%$ in the same fraction.

In Table 3, Th concentrations in $\mu g/g$ in the main fractions of the sediments are shown. It can be observed that, excepting sample SO3, the Th content in the non-residual fractions F2 and F3 is quite similar in all stations. Station SO3 has a higher concentration of Th in both non-residual fractions. This is more evident in the case of fractions F3, with ~ 1 order of magnitude higher concentrations in sample SO3 than in the case of the rest of samples. It seems that the dissolved Th is quickly coprecipitated on the river bed. Thus, Th contained in the liquid discharges seems to affect only the sediments closest to the fertilizer industries. In the case of the residual fractions, samples SO2 and SO3 present higher concentrations in both fractions than the rest of samples, whereas the rest have similar Th concentrations. Thus, it can be concluded that the river sediments near the fertilizer industries have incorporated Th derived from the liquid and solid wastes but it does not reach stations further upstream or downstream along the river.

3.3. *Th / U mass ratios*

Interaction of non-residual fractions with solution is essentially reflected in the Th/U mass ratio. It is well known that Th is a particularly insoluble element in natural waters and it is usually found associated with solid matter. Thus, this ratio is typically much below unity in waters and above unity in solid particles. These facts can be clearly obtained by studying the values of such ratio in the main fractions of sediments from the Odiel and Tinto rivers which are presented in Table 4.

In the case of non-residual fractions F2 and F3, and excepting fraction F3 of sample SO3, the Th/U mass ratio is much below unity and typical of liquid phases. In fact, these values are similar to those found in water samples from the same rivers [2]. The exception of phase F3 of sample SO3 seems to be related to the fact that Th is

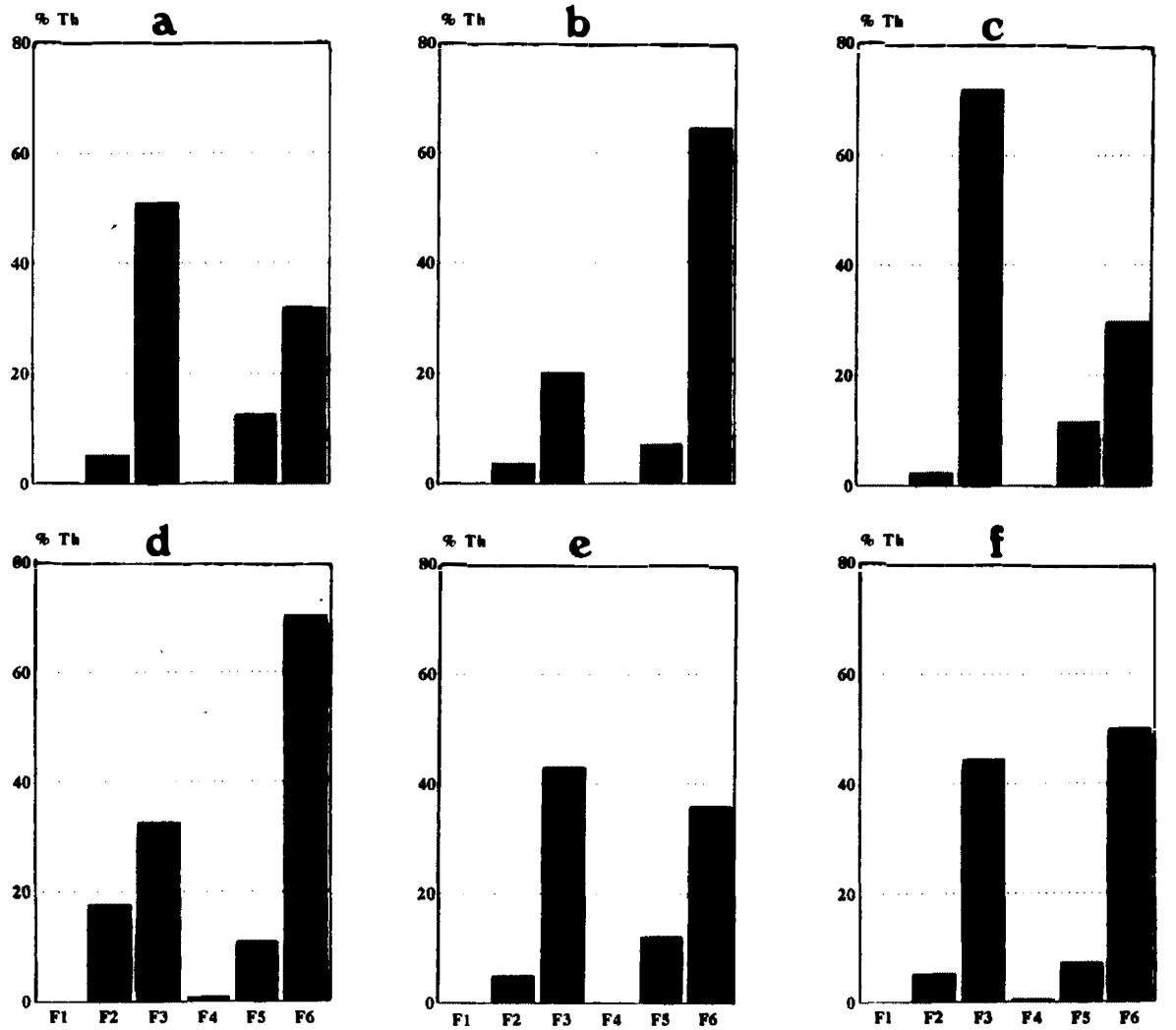

Fig. 3. Percentage distribution of Th in each sequentially extracted fractions of samples (a) SO1, (b) SO2, (c) SO3, (d) ST1, (e) ST2 and (f) SOT.

Table 3
Th concentration in $\mu g/g$ in main fractions of bottom sediments from the Odiel and Tinto rivers

Fraction	SO1	SO2	S03	ST1	ST2	SOT
F2	0.79 ± 0.08	0.74 ± 0.06	1.31 ± 0.08	1.10 ± 0.12	0.59 ± 0.05	0.70 ± 0.05
F3	7.71 ± 0.51	3.97 ± 0.22	38.4 ± 4.0	2.02 ± 0.14	5.05 ± 0.39	5.88 ± 0.36
F5	1.89 ± 0.13	1.41 ± 0.07	6.22 ± 0.33	0.68 ± 0.08	1.44 ± 0.11	0.96 ± 0.07
F6	4.83 ± 0.22	12.7 ± 1.1	15.8 ± 0.80	4.36 ± 0.31	4.21 ± 0.33	6.61 ± 0.63

Table 4
Th/U mass ratio in main fractions of bottom sediments from the Odiel and Tinto rivers

Fraction	SO1	SO2	SO3	ST1	ST2	SOT
F2	0.062 ± 0.007	0.061 ± 0.006	0.096 ± 0.009	0.127 ± 0.016	0.053 ± 0.006	0.102 ± 0.009
F3	0.245 ± 0.032	0.10 ± 0.009	1.10 ± 0.16	0.448 ± 0.040	0.152 ± 0.015	0.417 ± 0.032
F5	4.5 ± 0.5	0.493 ± 0.030	3.24 ± 0.20	1.94 ± 0.25	1.60 ± 0.14	1.04 ± 0.10
F6	2.50 ± 0.15	0.311 ± 0.034	2.68 ± 0.15	2.60 ± 0.27	1.52 ± 0.13	2.71 ± 0.30

quickly coprecipitated on the surface of suspended matter which are deposited downstream at such a point and not further downstream. It is also interesting to observe that this ratio is much lower in fraction F2 than in F3. This could be interpreted by the fact that Th is not easily adsorbed onto solid particles compared with U. In fact all stations present similar values of this ratio in fraction F2, independently of the concentration of U and/or Th in the fraction. In the residual fractions F5 and F6 the Th/U mass ratio for all samples, except sample SO2, has values above unity and close to the typical value for near-surface rocks of 3.5 [8]. The exception of both residual fractions of sample SO2 confirms the U enrichment relative to Th typical of the phosphate mineral utilised in the fertilizer production [7].

4. Conclusions

The U and Th 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 occur mainly in the non-residual fractions although Th tends to reside more in residual fractions than U. These differences between U and Th reflect largely the much higher solubility (and hence mobility) of U related to Th in surface and near-surface environments. The sediment fractionation and analysis presented here has made an unequivocal connection between the enhanced U content and respective Th/U mass ratios in river sediments close to the fertilizer factories and the wastes discharge point in the Odiel and Tinto rivers.

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