The Distribution of U, Th and ^{226}Ra Derived from the Phosphate Fertilizer Industries on an Estuarine System in Southwest Spain

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ABSTRACT

This paper reports an extensive study of the presence of natural radioactivity around a phosphate fertilizer factory complex situated in an estuarine area of southwest Spain. The study has concluded that the wastes from such industries are the cause of the enhancement of natural radioactivity in the immediate environment. Thus, significantly high levels of U- and Th-isotopes and ^{226} Ra are detected in water and sediment samples collected in this area. These conclusions based on the enhanced isotopic concentrations are further supported by the measured U, Th and Ra isotopic activity ratios being quite different from any observed elsewhere in undisturbed estuaries. These isotope activity ratios appear to be very sensitive indicators of waste disposal practices in such environments.

INTRODUCTION

Recently, several studies have been carried out in the vicinity of phosphate fertilizer industries in order to establish the significance of the radiological

impact of their operations on the environment as well as on the human population (Strain, 1979; Van der Heidje et al., 1988; Koster et al., 1991; Martínez-Aguirre & García-León, 1991a). While typical rocks contain on average some 2·8 ppm of U (UNSCEAR, 1977), a phosphate rock can contain up to 50–300 ppm of U (Gascoyne, 1982). The European Community imports annually some 15–17 MT of phosphate rock (Baestslé, 1991). The imported material is processed into different products generating wastes such as phosphogypsum. Each year 6–7 MT of phosphogypsum is discharged directly into the sea, and, in addition, some 8–11 MT is deposited as solid wastes in piles (Baestslé, 1991). These piles remain unprotected from rainwater, wind and other elements, and thus they could be connected hydraulically to surface or groundwaters as a potential source of contamination.

The phosphogypsum is mainly composed of $CaSO_4$. This means that it also contains U, Th and Ra in large quantities as a result of co-precipitation with Ca during the process of fertilizer production. It is therefore possible that natural processes could lead to the redistribution of these natural radionuclides into the environment surrounding the waste disposal sites.

Strain (1979) found a significant increase of Ra activities in ground-waters collected around a fertilizer factory at North Carolina, USA. Some other workers (Van der Heidje et al., 1988; Koster et al., 1991) have also studied the presence of natural radioactivity, mainly [226]Ra and [210]Po, in European environments affected by such industries. Also, Paul et al. (1980) investigated significantly high [226]Ra concentrations in phosphogypsum at Kerala, India.

Recently, Martínez-Aguirre and García-León (1991a) found anomalously high U-isotope activities in water and sediment samples collected at the Odiel and Tinto rivers in southwest Spain (Figs 1 and 2). Such enhancements were attributed to an industrial complex surrounded by these rivers in which two phosphate fertilizer factories were located. One factory processes around 1·4 MT per year of phosphate rock from Morocco, while the other uses around 0·2 MT of rock from Morocco, Senegal and Togo. Both factories release their wastes directly to the Odiel river or are stored in uncovered piles (the area marked with stars in Fig. 2). Using the data given by Guimond and Hardin (1989) for phosphate rock from Morocco, the first factory alone may produce around 2·2 TBq of [226]Ra, 2·3 TBq of [238]U and 1·4 TBq of [232]Th each year. Part of this activity can obviously be redistributed over the environment that surrounds the industrial complex.

This paper represents a more complete study of possible redistribution of the radioactivity from the wastes generated by the above phosphate fertilizer factories. To this purpose isotopes of U and Th and [226]Ra have been extracted and determined from different surface water and sediment

Fig. 1. Map of Spain showing the studied area in the Andalousian region.

collected during 1989. The radionuclide concentrations in these samples and the corresponding activity ratios, which reflect the daughters mobility, and probably, also the origin of the radionuclides, will be used to investigate the distribution of radioactivity over this area of southwestern Spain.

SAMPLING AND EXPERIMENTAL METHODS

Samples of river water and sediment were collected along the Odiel and Tinto river basins (Fig. 2) during July 1989. Surface water samples of 7–101 were collected in plastic bottles during low tide, and pH and temperature (°C) were measured at the same time. The suspended matter was separated as soon as possible using $0.45\,\mu$m pore size Nuclepore filters. It has been preserved for future analysis, since it could provide interesting additional information. Then, the filtrate was acidified to pH $\sim$2 by concentrated HNO_3, to avoid the growth of microorganisms and to minimize water/wall interactions. At the same time, bottom sediments were collected. Samples of about 1 kg were collected and stored in plastic bags. Then, in the laboratory, sub-samples were dried and powdered before analysis.

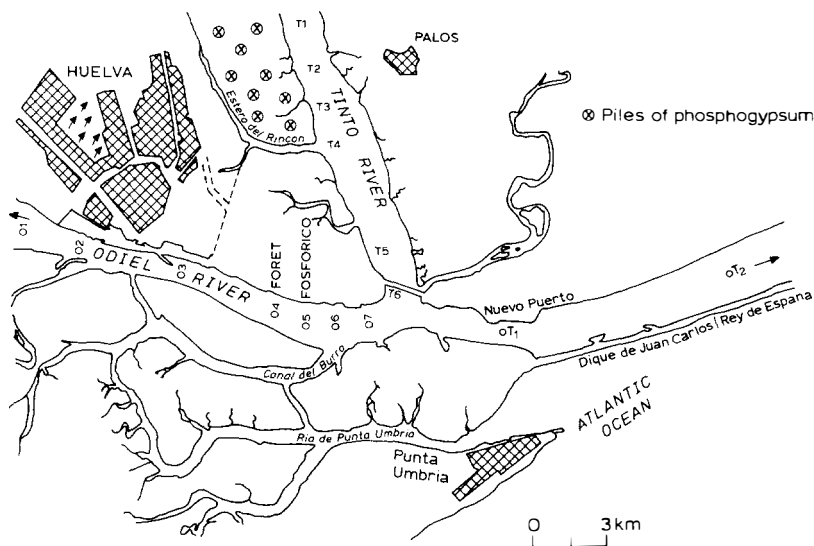The extraction method used for U- and Th-isotope separate is given in

Fig. 2. Map of Odiel and Tinto rivers showing the sampling stations in 1989.

Ivanovich and Murray (1992) and Martínez-Aguirre (1991). Only a brief description is given here. After homogenization, a few grams of dry sediment, spiked with known quantities of ^{236}U and ^{229}Th standard solutions for chemical yield determinations, are digested with HNO_3, aqua regia, $HClO_4$ and HF. The residue left after the above treatment is dissolved in 7M HNO_3. The U and Th are co-precipitated with Fe^{3+} by adding concentrated ammonia to the solution. The U- and Th-isotopes are first separated by using anion exchange resins (Dowex AG 1 X 8 hydrochloric form) conditioned with 8M HCl. Then each fraction is further purified by the removal of Fe whose presence would affect the α-spectral resolution. For this last purification step the resins in the separation columns are conditioned with 7M HNO_3. These purified solutions are dried and U and Th are electroplated on to stainless steel planchets using the procedure of Lally and Eakins (1978). The activities are determined by α-spectrometry using surface barrier Si α-detectors.

In the case of water samples, some 7–10 l of water are spiked with ^{236}U and ^{229}Th standard solutions and then boiled down to approximately 1 l. The U and Th content is then co-precipitated with Fe^{3+} by the addition of $(NH)_4OH$. The precipitate, after separation from supernate by contrifuging, is dissolved by 7M HNO_3. Finally, the same procedure, described above for digested solid samples, is followed.

For the ^{226}Ra analysis in sediment samples, the ^{222}Rn emanation method was used. The samples are first digested with HNO_3, aqua regia, $HClO_4$

and HF and then the residue is dissolved with 8M HCl and the volume made up to 0·5 l. The solution is then transferred into a sealed glass bottle and the original crop of ^{222}Rn expelled by bubbling ultrapure He gas through. After approximately three weeks secular equilibrium between a new crop of ^{222}Rn and ^{226}Ra in solution is reached. The ^{222}Rn is again expelled and collected in a ZnO$_2$-lined quartz counting cell. The ^{222}Rn activity is measured by a gas scintillation counter and from it the ^{226}Ra concentration in the sample is determined (Ivanovich & Murray, 1992).

RESULTS AND DISCUSSION

As already stated, the industrial zone under study is situated on a tongue of land surrounded by the rivers Odiel and Tinto, with their confluence at its tip (Fig. 2). The two rivers are affected differently by the industrial activity. Consequently, the presentation and the discussion of the results will be carried out separately for each river. In the tables and figures the authors have denoted with 'O' and 'SO' the water and sediment samples, respectively, from the Odiel river. Similarly, for the Tinto river samples, prefix letter 'T' and 'ST' have been used. Prefix letters 'OT' and 'SOT' correspond to samples derived from the confluence of the two rivers which forms a common mouth to the Atlantic Ocean. The numbers given to each sample identify the sampling station (Fig. 2).

In addition to the U and Th isotopic activities expressed in mBq/l (for water samples) or mBq/g (for sediment samples), U and Th mass concentrations are also given in μg/l or μg/g. The two are related by the following conversion formulae:

$$[U] = 0·0811 A_{238} \tag{1}$$

$$[Th] = 0·2436 A_{232} \tag{2}$$

where [U] and [Th] are the mass concentrations and A_{238} and A_{232} are the activities of ^{238}U and ^{232}Th, respectively.

Odiel river

The sampling stations are distributed along the lower reaches of the river close to the industrial zone area (Fig. 2). The exception is station 1 which is situated far upstream of this area close to the river source.

Water
The U- and Th-isotope activities are given in Table 1 together with pH values. It is apparent that all radionuclides measured in the collected water

TABLE 1

U- and Th-Isotope Activities (m/Bq/l) and pH of Water Samples Taken Along the Odiel River

Sample	pH	^{238}U	^{234}U	^{232}Th	^{230}Th	^{238}Th
O1	3·01	197·9 ± 6·8	316·3 ± 10·7	13·4 ± 0·6	49·7 ± 1·7	22·9 ± 0·9
O2	7·40	34·2 ± 1·1	36·3 ± 1·2	0·58 ± 0·30	7·02 ± 1·33	2·65 ± 0·78
O3	7·20	33·0 ± 2·0	35·0 ± 2·1	1·81 ± 0·14	12·0 ± 0·5	NM
O4	7·12	54·1 ± 3·4	58·7 ± 3·7	2·21 ± 0·24	14·3 ± 0·7	NM
O5	7·08	52·7 ± 3·6	54·3 ± 3·7	2·51 ± 0·25	18·9 ± 1·3	7·52 ± 1·20
O6	6·80	131·3 ± 11·3	136·2 ± 11·7	4·73 ± 0·67	34·2 ± 3·3	8·83 ± 2·89
O7	6·96	35·8 ± 0·9	39·2 ± 0·9	1·83 ± 0·12	11·2 ± 0·4	2·38 ± 0·15

NM, Not measured.

sample follow the same distribution pattern along the river with two well defined peaks.

The isotopic data obtained for sample O1 are anomalous relative to the rest of the data set. The very low pH value of 3, due to local geology conditions, accounts for the observed enhanced concentration listed. The head waters of river Odiel are chemically aggressive, resulting in effective leaching and transfer of U and Th from the solid to the aqueous phase of the system. The Th isotopes, mainly insoluble in natural waters, have concentrations at least one order of magnitude higher than in average surface waters (Martínez-Aguirre & García-León, 1992; Osmond & Ivanovich, 1992), reflecting the higher mobility of Th at very low pH values.

Higher concentrations of U- and Th-isotopes also persist downstream between sampling stations O4 and O6, with a clear peak of activity at sampling station O6. A similar pattern was observed for U-isotopes in samples collected in 1988 (Martínez-Aguirre & García-León, 1991a). The observed pattern is indicative of the existence of a local source between stations O4 and O6. The obvious candidate for this local source of radioactivity has to be related to the phosphate manufacturing complex located between stations O4 and O5. The observed shift in the location of the peak of activity from stations O5 and O6 in the two sampling campaigns is a result of a lower tidal input and a higher activity input (higher waste output from the phosphate factories) to the river at the time of sampling. This situation was encountered during the 1988 sampling campaign when the activity peak was observed higher upstream at station O5 (Martínez-Aguirre & García-León, 1991a).

Table 2 presents the U and Th contents of the waters collected in the Odiel river, and the corresponding Th/U mass ratio together with the $^{234}U/^{238}U$, $^{230}Th/^{234}U$ and $^{228}Th/^{232}Th$ activity ratios. In Fig. 3, U and Th concentrations along the river channel are shown. The Th/U ratios found are consistent with the well known fact of higher trend of Th to be associated with the solid phase in rivers. On the other hand, such results are higher than normally encountered in most river waters (Osmond & Ivanovich, 1992) sampled upstream from the estuary. These results, however, are quite similar to the mass ratios obtained for the estuarine waters of the Guadalquivir river (Martínez-Aguirre, 1991; Martínez-Aguirre & García-León, 1992).

The $^{234}U/^{238}U$ activity ratios reported in Table 2 are unusually low for a rriver system. A weighted average for the data for stations O2 to O7 is 1.07 ± 0.02. This value is more typical of a primary mineral activity ratio from a fertilizer manufacturing process than the average disequilibrium observed in rivers (Scott, 1982).

Sample O1 is clearly a different case. Its low pH promotes the dissolution

TABLE 2
U and Th Concentrations (μg/l), Th/U Mass Ratio and Isotopic Activity Ratios in Water Samples Taken Along the Odiel River

Sample	[U]	[Th]	Th/U	$^{234}U/^{238}U$	$^{230}Th/^{234}U$	$^{238}Th/^{232}Th$
O1	15·9 ± 0·6	3·31 ± 0·15	0·208 ± 0·012	1·60 ± 0·02	0·157 ± 0·008	1·70 ± 0·07
O2	2·75 ± 0·09	0·145 ± 0·075	0·053 ± 0·027	1·06 ± 0·03	0·71 ± 0·21	4·51 ± 2·49
O3	2·68 ± 0·16	0·447 ± 0·035	0·167 ± 0·017	1·07 ± 0·02	0·34 ± 0·03	
O4	4·39 ± 0·30	0·546 ± 0·059	0·134 ± 0·017	1·08 ± 0·10	0·24 ± 0·02	
O5	4·28 ± 0·29	0·620 ± 0·061	0·151 ± 0·018	1·02 ± 0·09	0·37 ± 0·04	3·00 ± 0·25
O6	10·7 ± 0·9	1·17 ± 0·16	0·110 ± 0·018	1·04 ± 0·04	0·25 ± 0·03	1·87 ± 0·67
O7	2·88 ± 0·07	0·450 ± 0·029	0·157 ± 0·011	1·10 ± 0·02	0·29 ± 0·01	1·31 ± 0·11
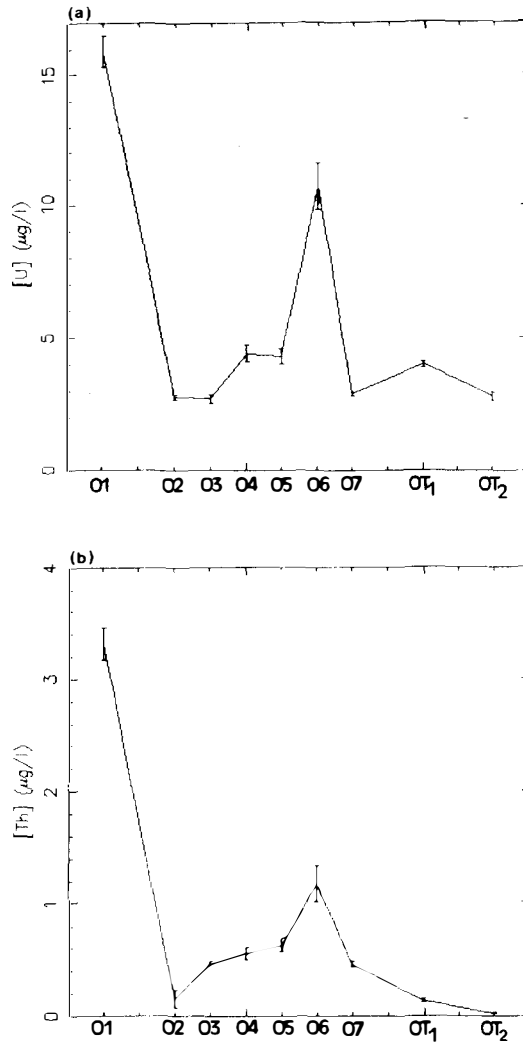
Fig. 3. U concentration (a) and Th concentration (b) in μg/l in water samples along the Odiel river.

of U-isotope activities from the solid phase to the river system. In such conditions, the ^{234}U-isotope is preferentially mobilized, resulting in ^{234}U-enrichment in the aqueous phase relative to ^{238}U (Gascoyne, 1982) and hence the higher^{234}U/^{238}U activity ratio observed in sample O1.

The ^{230}Th/^{234}U activity ratios reported in Table 2 are anomalously high when compared with other river systems. Thus, typical activity ratios for river waters are around 0·1 or less (Plater *et al.*, 1992; Martínez-Aguirre & García-León, 1992). In the present case the weighted average ^{230}Th/^{234}U

activity ratio from Table 2 is 0.29 ± 0.01. Thus, an abnormal ^{230}Th excess seems to be present in the investigated waters. The source of this anomalously high concentration of ^{230}Th relative to ^{234}U in the aqueous phase is ascribed to the waste input between stations O2 and O7 in the Odiel river.

Finally, the ^{228}Th/^{232}Th activity ratios shown in Table 2 are consistent with the reported values for uncontaminated river water environments (Miyake et al., 1972; Martínez-Aguirre & García-León, 1992).

Sediment

Table 3 presents isotopic activities measured in bottom sediments in the Odiel river. The apparent trend is that U-, Th- and ^{226}Ra-isotopes are enriched between sampling stations SO2 and SO7. The measured activities are well above the typical levels reported in literature for uncontaminated river environments, usually below $5\,\mu g/g$ for U and below $14\,\mu g/g$ for Th (Scott, 1982; Martínez-Aguirre, 1991; Martínez-Aguirre & García-León, 1992; Plater et al., 1992). The high activities here can only be ascribed to the consequences of the phosphate rock processing in the industrial zone along the Odiel river.

The distributions of various radionuclides do not follow the same pattern in detail. Thus, U-isotopes reach their maximum concentrations at sampling stations 5 and 7 while ^{232}Th, ^{228}Th and ^{226}Ra maximum concentrations in bottom sediments are reached at stations 4 and 7. The pattern of ^{230}Th concentrations is yet somewhat different, possibly reflecting its radiogenic origins. Uranium is more soluble than Th and the two elements follow diverse pathways during the processing. Since ^{230}Th is a granddaughter of ^{238}U, it is very likely that it would follow the U-isotope pathway, at least part of the way (e.g. initially, it would be present predominantly in the same minerals as U-isotopes), but, being as insoluble as ^{232}Th, would eventually behave as other Th-isotopes. Hence the observed apparent mixed behaviour.

It is also worthwhile commenting on the results obtained for samples SO6 and SO7. In the first case, a general depletion of activity is observed. This depletion is the result of some radiologically inert substances being locally released from factories located near station 6. This fact explains the evident decrease of activity concentrations. After this sampling station the general high levels observed previously are recovered.

Table 4 presents U and Th concentrations, their mass ratio and ^{234}U/^{238}U, ^{230}Th/^{234}U, ^{226}Ra/^{230}Th, ^{228}Th/^{232}Th and ^{230}Th/^{232}Th activity ratios in bottom sediments for the Odiel river. The Th/U mass ratio of the downstream set of samples ranges between 0.22 and 1.21 which is very low relative to the reported range for clastic sedimentary material of 3–5

TABLE 3

U- and Th- Isotope and ^{226}Ra Activities (mBq/g) in Sediment Samples Taken Along the Odiel River

Sample	^{238}U	^{234}U	^{226}Ra	^{232}Th	^{230}Th	^{228}Th
SO1	24·7 ± 1·3	31·6 ± 1·5	17·6 ± 1·2	20·5 ± 5·1	20·5 ± 5·1	55·4 ± 11·3
SO2	547·9 ± 14·0	590·7 ± 15·0	149·4 ± 1·7	61·2 ± 3·0	506·6 ± 15·3	67·6 ± 3·3
SO3	840·2 ± 24·6	905·3 ± 26·5	224·6 ± 2·1	118·5 ± 11·6	813·5 ± 60·6	97·0 ± 11·5
SO4	631·5 ± 21·2	691·3 ± 22·9	1377 ± 7	249·9 ± 9·6	2042 ± 66	232·2 ± 9·2
SO5	1106 ± 35	1174 ± 37	746·1 ± 20·4	80·0 ± 4·0	2982 ± 90	62·2 ± 3·5
SO6	78·8 ± 3·9	84·3 ± 4·1	40·3 ± 1·0	9·38 ± 0·55	106·1 ± 3·7	8·78 ± 0·52
SO7	1079 ± 41	1133 ± 43	399·3 ± 4·7	216·3 ± 9·8	1645 ± 60	199·4 ± 9·2

TABLE 4

U and Th Concentrations (μg/g), Th/U Mass Ratio and Isotopic Activity Ratios in Sediment Samples Along the Odiel River

Sample	[U]	[Th]	Th/U	$^{234}U/^{238}U$	$^{230}Th/^{234}U$	$^{226}Ra/^{230}Th$	$^{228}Th/^{232}Th$	$^{230}Th/^{232}Th$
SO1	1.99 ± 0.10	5.05 ± 1.22	2.54 ± 0.63	1.28 ± 0.08	0.65 ± 0.16	0.86 ± 0.22	2.70 ± 0.78	1.00 ± 0.32
SO2	44.0 ± 1.1	15.1 ± 0.7	0.343 ± 0.019	1.08 ± 0.02	0.86 ± 0.03	0.30 ± 0.01	1.11 ± 0.06	8.3 ± 0.4
SO3	67.6 ± 2.0	29.2 ± 2.8	0.431 ± 0.044	1.08 ± 0.01	0.90 ± 0.07	0.28 ± 0.02	1.11 ± 0.06	8.3 ± 0.4
SO4	50.8 ± 1.7	61.7 ± 2.4	1.21 ± 0.06	1.10 ± 0.03	2.95 ± 0.14	0.67 ± 0.02	0.96 ± 0.03	8.2 ± 0.2
SO5	89.0 ± 2.8	19.7 ± 1.0	0.222 ± 0.013	1.06 ± 0.02	2.54 ± 0.11	0.25 ± 0.01	0.78 ± 0.05	37.3 ± 1.6
SO6	6.34 ± 0.31	2.43 ± 0.14	0.383 ± 0.028	1.07 ± 0.04	1.26 ± 0.08	0.38 ± 0.02	0.89 ± 0.06	10.8 ± 0.5
SO7	86.8 ± 3.3	53.3 ± 2.4	0.614 ± 0.036	1.05 ± 0.02	1.45 ± 0.08	0.24 ± 0.01	0.92 ± 0.04	7.6 ± 0.2

(Gascoyne, 1992). Similarly, Th/U mass ratios of 5 or greater have been found in sediments of the Guadalquivir river, representing typical values for river sediments from unperturbed environments Martínez-Aguirre & García-León, 1992). Thus, it is clear that bottom sediments collected from sampling stations 2–7 in the Odiel river are all considerably U-enriched. However, on the other hand, it seems that such U-enrichment is less important for sampling station 4, where the mass ratio is 1·22. This result is compatible with that commented before (Table 3), and could support, although not definitively, the hypothesis by which a different process of fertilizer manufacturing, or primary mineral, is being used at the factories located near stations 4 and 5.

The weighted average of the ^{234}U/^{238}U activity ratio for samples SO2 to SO7 is 1·07 ± 0·02, a value close to secular equilibrium value of unity and not typical of undisturbed river system (Osmond & Ivanovich, 1992; Plater *et al.*, 1992). These anomalous U-isotopes activity ratios coupled with observed U-enrichment indicate that the origin of the activities found in the Odiel river channel is related to the phosphate fertilizer operations.

Other daughter/parent activity ratios quoted in Table 4 support the above observations. They also focus on the location(s) of waste inputs to the river. Thus, ^{230}Th/^{232}Th activity ratio reaches a maximum at station 5 while ^{230}Th/^{234}U and ^{226}Ra/^{230}Th activity ratios reach their respective maxima at station 4. This suggests that the wastes from outlets located near these two stations differ in relative contents of U and Th. This conclusion is supported by considering the Th/U mass ratio data.

The isotopic data for sample SO1 are different from the rest of the set. The low pH measured in the upstream environment is believed to be the cause of the anomalous activity ratios observed for this sediment sample. Further explanation would require a speciation study which is currently in progress.

Tinto river

As mentioned earlier, the phosphate industries situated alongside the Odiel river near stations O4 and O5 store part of their wastes in the form of phosphogypsum in the zone marked with stars in Fig. 2. These wastes have been piling up continuously over the last 30 years. Some measurements carried out on the phosphogypsum samples themselves have yielded specific activities of up to 2700, 2000 and 900 mBq/g of ^{210}Po, ^{226}Ra and ^{238}U respectively (Martínez-Aguirre, 1991). In view of this observation, it was deemed of interest to investigate the possible dissemination of radioactivity from such piled material on the Tinto river waters and sediments. Consequently, samples of river water and bottom sediments

were taken at the sampling stations designated T1–T6 in the Tinto river, and further downstream of the confluence with the Odiel river in the station designated OT_1 and OT_2. Station 1 is located near the source of the river, stations 2–4 are in contact with the phosphogypsum piles, and stations 5 and 6 are in the vicinity of the confluence with the Odiel river selected to monitor any possible impact of contamination in the latter river.

Water
Isotopic activities in water samples from the Tinto river are given in Table 5. The low pH of sample T1, which has the same explanation as in the case of sample O1, explains its rather high U- and Th-isotope content and the rest of the interpretations about the origin of T1 isotopic signatures is the same as already stated for sample O1 above.

Unlike the Odiel river data, the U-isotope concentrations for the rest of the samples from the Tinto river present a rather flat distribution extented to the sampling station OT_2 (see Figs 3 and 4 for comparison of U and Th patterns in both rivers). The U concentration from stations T2 to OT_2 remain similar to the lowest values in the Odiel river (see Table 1) and are only slightly higher than the value for the Guadalquivir river (Martínez-Aguirre, 1991; Martínez-Aguirre & García-León, 1991*b*, 1992) and the average for world rivers (Scott, 1982).

The situation is different for Th-isotopes which display two well defined peaks (stations T2 and T4). The U and Th content distributions are given for the Tinto river water samples in Fig. 4 to contrast their respective stages. Excluding the two maxima, Th-isotope concentrations are lower than those found in the Odiel river and very similar to those reported for other world rivers (Miyake *et al.*, 1964, 1972; Moore, 1967; Santschi *et al.*, 1979; Martínez-Aguirre, 1991; Plater *et al.*, 1992). The measured activities at stations 2 and 4 are significatively higher than those encountered in the Odiel river (this is less obvious for [228]Th but the pattern is clearly similar). This suggests that some activity inputs must occur near these stations.

Sample T4 was collected at the mouth of Estero del Rincón, a small tributary to the Tinto river, which crosses the phosphogypsum storage area (Fig. 2). Presumably such a stream is capable of transporting radioactive material from such an area to the main river. The case of sample T2 is more difficult to interpret. Nevertheless, the phosphogypsum storage area is crossed by a number of small streams of natural or artificial origin. Some of these may be possible remnants of the wetlands totally integrated in the estuarine system of the Odiel and Tinto rivers only 30 years ago, before industrial activity started in this area (Borrego-Flores & Pendón-Martín, 1988). Any one of these streams could have the same effect at station 2 as Estero del Rincón at station 4.

TABLE 5

U- and Th-Isotope Activities (mBq/l) and pH of the Water Samples Taken Along the Tinto River

Sample	pH	^{238}U	^{234}U	^{232}Th	^{230}Th	^{228}Th
T1	2·58	115·2 ± 4·0	210·7 ± 7·1	19·6 ± 0·9	52·2 ± 2·2	70·5 ± 2·9
T2	6·50	39·8 ± 2·2	42·6 ± 2·0	47·9 ± 14·5	91·2 ± 27·0	12·9 ± 4·3
T3	6·75	47·6 ± 2·2	51·7 ± 2·4	0·78 ± 0·10	5·65 ± 0·35	1·00 ± 0·13
T4	7·00	48·1 ± 2·4	53·4 ± 2·6	21·6 ± 4·9	41·4 ± 9·0	2·25 ± 0·78
T5	7·35	42·6 ± 1·0	46·1 ± 1·1	0·55 ± 0·10	3·92 ± 0·28	ND
T6	7·77	45·8 ± 1·5	49·3 ± 1·6	0·63 ± 0·07	3·80 ± 0·17	0·68 ± 0·08
OT$_1$	7·90	49·3 ± 1·3	53·7 ± 1·4	0·55 ± 0·07	3·22 ± 0·17	0·50 ± 0·08
OT$_2$	7·85	34·5 ± 2·0	38·2 ± 2·2	0·083 ± 0·030	0·610 ± 0·082	ND

ND, Not detected.
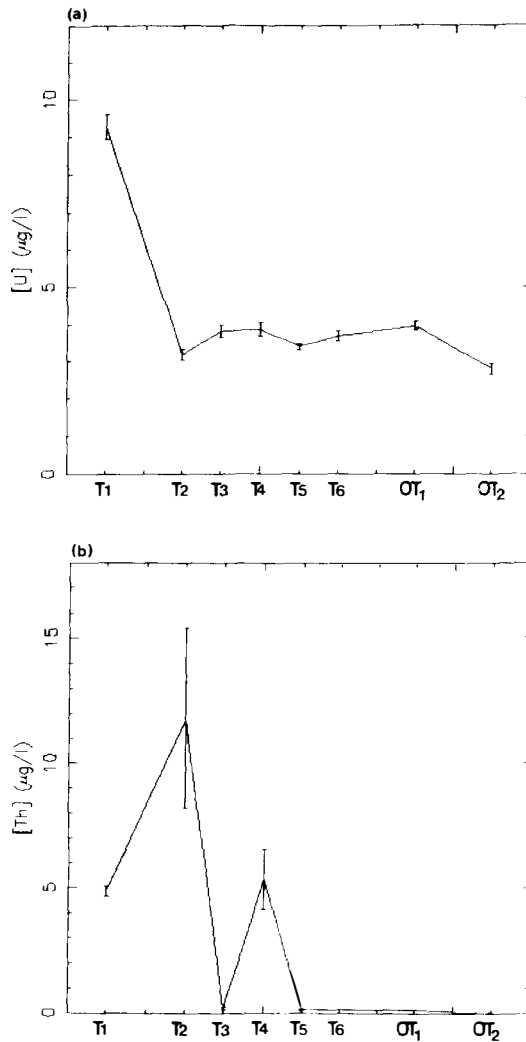
Fig. 4. U concentration (a) and Th concentration (b) in $\mu g/l$ in water samples along the Tinto river.

The material discharged at stations 2 and 4 must also contain U. The fact that enhanced levels of U have not been observed is probably related to the differential mobilities of Th and U in aqueous systems. The U being much more mobile than Th, it will tend to redistribute more rapidly in the mass of water along the river channel, resulting in a smoother distribution pattern, compared to Th which will be incorporated to the solid particles very fast. The isotope activity ratios presented in Table 6 for stations 2 and 4 may help to support this proposition.

TABLE 6
U and Th Concentrations (μg/l), Th/U Mass Ratios and Isotopic Activity Ratios in Water Samples Along the Tinto River

Sample	[U]	[Th]	Th/U	$^{234}U/^{238}U$	$^{230}Th/^{234}U$	$^{228}Th/^{232}Th$	$^{230}Th/^{232}Th$
T1	9·26 ± 0·32	4·82 ± 0·23	0·521 ± 0·031	1·83 ± 0·03	0·25 ± 0·01	3·60 ± 0·12	2·67 ± 0·09
T2	3·20 ± 0·15	11·8 ± 3·6	3·69 ± 1·13	1·07 ± 0·04	2·14 ± 0·64	0·27 ± 0·05	1·90 ± 0·21
T3	3·82 ± 0·18	0·193 ± 0·028	0·050 ± 0·006	1·09 ± 0·04	0·11 ± 0·01	1·27 ± 0·22	7·2 ± 0·8
T4	3·87 ± 0·19	5·33 ± 1·21	1·38 ± 0·32	1·11 ± 0·04	0·77 ± 0·17	0·10 ± 0·03	1·90 ± 0·21
T5	3·42 ± 0·08	0·136 ± 0·024	0·040 ± 0·007	1·08 ± 0·02	0·085 ± 0·007		7·1 ± 0·3
T6	3·68 ± 0·12	0·155 ± 0·015	0·042 ± 0·004	1·08 ± 0·03	0·077 ± 0·004	1·09 ± 0·17	6·0 ± 0·6
OT$_1$	3·97 ± 0·11	0·135 ± 0·016	0·034 ± 0·004	1·09 ± 0·02	0·060 ± 0·004	0·91 ± 0·18	5·9 ± 0·7
OT$_2$	2·80 ± 0·16	0·021 ± 0·008	0·008 ± 0·003	1·11 ± 0·05	0·016 ± 0·002		7·4 ± 2·8

The weight average of the $^{234}U/^{238}U$ activity ratio of 1.09 ± 0.02 (excluding sample T1) is statistically identical to the weighted average obtained for the Odiel river water samples. Therefore, similar conclusions can be drawn on the origin of U-isotope signatures. However, the impact of the presence of the phosphogypsum piles on the Tinto river waters with respect to U-isotopes is not as high as that of the direct input of phosphate fertilizer process wastes on the Odiel river. In fact, it is very difficult to identify the sources of U activities from the data presented in Table 6. If anything, the only firm conclusion is that any Th-enrichment at stations 2 and 4 is rapidly removed from the aqueous column and presumably adsorbed onto the solid particles surface. In fact, all other Th/U mass ratios are $\sim 10^{-2}$, in good agreement with published data for other river systems (Scott, 1982; Martínez-Aguirre, 1991).

The $^{230}Th/^{234}U$ activity ratios are consistent with the above arguments, adding weight to the conclusion that discharge to the Tinto river from the phosphogypsum piles contains a great deal more Th than U. The decrease in the $^{228}Th/^{232}Th$ activity ratio at stations 2 and 4 in the Tinto river reflects the relative immobility of ^{228}Ra, a precursor of ^{228}Th in the decay series, in the phosphogypsum piles.

Sediment

The isotope radioactivity in bottom sediments in the Tinto river are given in Table 7. If compared to published U data for bottom sediments in other river systems (Scott, 1982; Descamps & Foulquier, 1988; Morón et al., 1988; Plater et al., 1992) it becomes clear that the river bottom sediments are accumulating U and its daughters. The concentrations of ^{238}U, ^{234}U, ^{226}Ra and ^{230}Th are lower than those reported in Table 3 for the Odiel river but significantly higher than the published levels for undisturbed river systems, always below 60 mBq/g for all of them (Scott, 1982; Martínez-Aguirre , 1991; Martínez-Aguirre & García-León, 1992; Plater et al., 1992). This is not the case of ^{232}Th and its daughter ^{228}Th, where the concentrations are similar to those found in the literature for unperturbed systems, usually below 57 mBq/g for ^{232}Th (Scott, 1982; Martínez-Aguirre , 1991; Martínez-Aguirre & García-León, 1992).

However, the fact that all U-derived activities increase towards the confluence with the Odiel river may reflect a possible transfer of radioactive material from the Odiel river to the Tinto river. The ways through which this occurs should be investigated, but must be related mainly to the tidal cycle and suspended matter dynamics.

The corresponding activity ratios for the Tinto river bottom sediments are presented in Table 8. Again, as in the case of the Odiel river, the weighted average $^{234}U/^{238}U$ activity ratio of 1.04 ± 0.03 suggests an

TABLE 7
U- and Th-Isotope and ^{226}Ra Activities (mBq/g) in Sediment Samples Taken Along the Tinto River

Sample	^{238}U	^{234}U	^{226}Ra	^{232}Th	^{230}Th	^{228}Th
ST1	15·7 ± 1·3	16·8 ± 0·8	25·2 ± 0·9	11·5 ± 3·0	20·3 ± 4·0	ND
ST2	195·2 ± 4·4	198·5 ± 4·5	146·0 ± 2·7	30·8 ± 1·0	341·7 ± 11·6	34·3 ± 1·5
ST3	74·5 ± 2·8	80·9 ± 3·0	33·2 ± 0·5	45·0 ± 4·0	66·4 ± 5·2	48·9 ± 4·8
ST4	133·1 ± 3·8	137·8 ± 3·9	49·6 ± 1·1	36·1 ± 3·6	88·6 ± 6·6	36·3 ± 4·1
ST5	342·0 ± 7·5	363·8 ± 7·9	46·1 ± 1·0	25·3 ± 2·0	231·0 ± 12·3	30·8 ± 2·3
ST6	516·9 ± 15·9	531·2 ± 16·3	149·9 ± 0·8	47·5 ± 4·0	490·8 ± 23·3	41·0 ± 4·0
SOT$_1$	299·0 ± 12·6	304·5 ± 12·8	50·3 ± 1·7	53·7 ± 4·1	279·5 ± 15·1	55·4 ± 4·0

ND, Not detected.

TABLE 8
U and Th Concentrations (μg/g), Th/U Mass Ratio and Isotopic Activity Ratios in Sediment Samples Along the Tinto River

Sample	[U]	[Th]	Th/U	$^{234}U/^{238}U$	$^{230}Th/^{234}U$	$^{226}Ra/^{230}Th$	$^{228}Th/^{232}Th$	$^{230}Th/^{232}Th$
ST1	$1\cdot26 \pm 0\cdot06$	$2\cdot84 \pm 0\cdot74$	$2\cdot24 \pm 0\cdot59$	$1\cdot07 \pm 0\cdot07$	$1\cdot21 \pm 0\cdot25$	$1\cdot24 \pm 0\cdot25$		$1\cdot77 \pm 0\cdot56$
ST2	$15\cdot7 \pm 0\cdot5$	$7\cdot6 \pm 0\cdot3$	$0\cdot485 \pm 0\cdot023$	$1\cdot02 \pm 0\cdot02$	$1\cdot72 \pm 0\cdot07$	$0\cdot43 \pm 0\cdot02$	$1\cdot11 \pm 0\cdot05$	$11\cdot1 \pm 0\cdot5$
ST3	$6\cdot0 \pm 0\cdot2$	$11\cdot1 \pm 1\cdot0$	$1\cdot85 \pm 0\cdot18$	$1\cdot09 \pm 0\cdot05$	$0\cdot82 \pm 0\cdot07$	$0\cdot50 \pm 0\cdot04$	$1\cdot09 \pm 0\cdot13$	$1\cdot48 \pm 0\cdot15$
ST4	$10\cdot7 \pm 0\cdot3$	$8\cdot9 \pm 0\cdot9$	$0\cdot831 \pm 0\cdot087$	$1\cdot04 \pm 0\cdot03$	$0\cdot64 \pm 0\cdot05$	$0\cdot56 \pm 0\cdot04$	$1\cdot01 \pm 0\cdot14$	$2\cdot46 \pm 0\cdot26$
ST5	$27\cdot5 \pm 0\cdot6$	$6\cdot2 \pm 0\cdot5$	$0\cdot226 \pm 0\cdot019$	$1\cdot06 \pm 0\cdot02$	$0\cdot64 \pm 0\cdot04$	$0\cdot20 \pm 0\cdot01$	$1\cdot22 \pm 0\cdot10$	$9\cdot2 \pm 0\cdot6$
ST6	$41\cdot6 \pm 1\cdot3$	$11\cdot7 \pm 1\cdot0$	$0\cdot282 \pm 0\cdot025$	$1\cdot03 \pm 0\cdot02$	$0\cdot92 \pm 0\cdot05$	$0\cdot31 \pm 0\cdot02$	$0\cdot86 \pm 0\cdot10$	$10\cdot3 \pm 0\cdot8$
SOT$_1$	$24\cdot0 \pm 1\cdot0$	$13\cdot2 \pm 1\cdot0$	$0\cdot550 \pm 0\cdot048$	$1\cdot02 \pm 0\cdot03$	$0\cdot92 \pm 0\cdot06$	$0\cdot18 \pm 0\cdot01$	$1\cdot04 \pm 0\cdot09$	$5\cdot2 \pm 0\cdot3$

artificial origin of U-isotope signatures such as phosphogypsum piles situated along its right bank.

The general trend in the isotopic ratios suggest a U-enrichment in the Tinto river bottom sediments. Observations made from the sediments in the Odiel river are also valid for the Tinto river case.

CONCLUSIONS

A careful sampling campaign carried out in 1989 for river water and bottom sediment samples along the Odiel and Tinto rivers (southwest Spain) has yielded comprehensive U, Th and [226]Ra isotopic data. These data have been interpreted to establish the connection between the observed anomalously high concentrations of U-, Th- and [226]Ra-isotopes in waters and sediments, and the operations of phosphate fertilizer factories located in a zone virtually surrounded by both rivers. The conclusion based on the isotopic data is that both liquid and solid wastes arising from the fertilizer production, and discharged from this industrial zone, are responsible for the observed radioactivity enhancement in the immediate environment of the fertilizer plants.

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