# U and Th distribution in solution and suspended matter from rivers affected by the phosphate rock processing in southwestern Spain [1]

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A study is presented on the distribution of U and Th isotopes in the solid and liquid fractions of waters collected along the Odiel and Tinto rivers (southwest Spain). Such rivers are affected by the operation of phosphate fertilizer factories. The analysis of activity concentrations and activity ratios in both fractions provides interesting information on the way in which the factories disturb their close environment.

## 1. Introduction

Recently [1,2] high natural radionuclide activity levels were found in dissolution and bottom sediments collected from the Odiel and Tinto rivers in southwestern Spain (Fig. 1). The anomaly was attributed to an industrial complex surrounded by these rivers in which two phosphate fertilizer factories are located. These factories release their wastes directly to the Odiel river or store them in uncovered piles near the Tinto river channel (Fig. 1).

In this work the distribution of U and Th isotopes in solution and suspended matter of water samples collected from such rivers are reported. The study of the activity concentrations in both fractions confirms that the operation of these factories is responsible for the radioactivity present in the local environment. The additional analysis of some relevant activity ratios provides information on the source term.

## 2. Samples and methods

Six water samples from the Tinto river, seven from the Odiel river and two from the confluence of both rivers (see Fig. 1) were taken during July 1989.

10 liter water samples were collected along the Odiel and Tinto river basins during July 1989 (see Fig. 1). The suspended matter was separated as soon as possible by filtration through Nuclepore filters of 0.45 $\mu$m pore size. The remaining water was immediately acidified to pH $\sim 2$ with concentrated $HNO_3$. Sampling stations were mainly distributed along the lower reaches of the rivers close to the industrial area of Huelva (Odiel river) or to the phosphogypsum piles area (Tinto river). The exceptions were samples O1 and T1, collected far upstream of these areas, close to the sources of the rivers. Samples OT were collected at the confluence of both rivers, station 1 still being close to the industrial area and station 2 on the Atlantic Ocean coast.

U and Th isotopes were extracted using anion exchange resins (Dowex AG1-X8 hydrochloric form) and electroplated onto a stainless steel planchet. $^{236}$U and $^{229}$Th were used for yield determinations. Isotopic activities were measured with Si ion-implanted detector $\alpha$-spectrometry. The radiochemical methods can be found in detail in refs. [2,3].

## 3. Results and discussion

To simplify the discussion we will first present the results obtained for the Odiel river, into which the wastes from the fertilizer factories are directly released, and after that those obtained for the Tinto river, close to the area where the phosphogypsum piles are located (see Fig. 1).

### 3.1. Odiel river

Results on U and Th isotopic activities in the dissolved and particulate fractions are given in Table 1.

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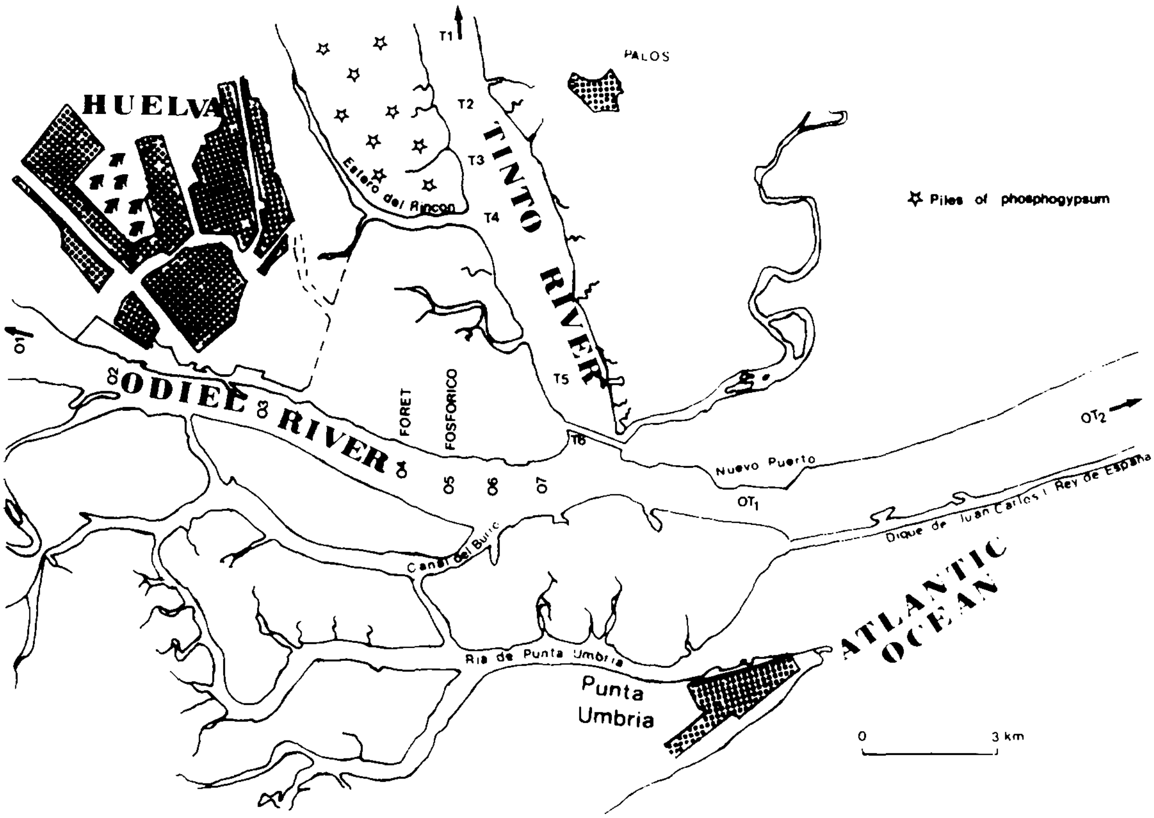


Fig. 1. Map of the Odiel and Tinto rivers. The sampling stations along the river basins, as well as the fertilizer factories (Foret, Fosfórico) and phosphogypsum piles emplacements are shown.

Table 1

U and Th isotopic activities in mBq/l in the dissolved (d) and particulate (s) fractions of water samples taken from the Odiel river. Stations $OT_1$ and $OT_2$ are located at the confluence of the Odiel and Tinto rivers (see Fig. 1). ND = not detected and NM = not measured

| Station | | $^{238}U$ | $^{234}U$ | $^{232}Th$ | $^{230}Th$ | $^{228}Th$ |
|---|---|---|---|---|---|---|
| O1 | d | 198 ± 7 | 316 + 11 | 13.4 ± 0.6 | 49.7 ± 1.7 | 22.9 ± 0.9 |
| | s | 0.115 + 0.013 | 0.215 ± 0.019 | 0.048 + 0.013 | 0.219 + 0.025 | 0.169 ± 0.054 |
| O2 | d | 34.2 ± 1.1 | 36.3 ± 1.2 | 0.58 ± 0.30 | 7.0 ± 1.3 | 2.7 ± 0.8 |
| | s | 1.91 ± 0.07 | 2.02 ± 0.07 | 0.265 ± 0.023 | 1.64 ± 0.06 | 0.228 ± 0.032 |
| O3 | d | 33.0 ± 2.0 | 35.0 ± 2.1 | 1.8 ± 0.1 | 12.0 ± 0.5 | NM |
| | s | 2.24 ± 0.08 | 2.42 ± 0.09 | 0.59 ± 0.04 | 3.7 ± 0.1 | 0.63 ± 0.04 |
| O4 | d | 54.1 ± 3.4 | 58.7 ± 3.7 | 2.2 ± 0.2 | 14.3 ± 0.7 | NM |
| | s | 2.17 ± 0.08 | 2.17 ± 0.08 | 0.52 ± 0.03 | 2.67 ± 0.09 | 0.50 + 0.03 |
| O5 | d | 52.7 ± 3.6 | 54.3 ± 3.7 | 2.5 ± 0.03 | 18.9 ± 1.3 | 7.5 + 1.2 |
| | s | 25.3 + 0.5 | 25.4 ± 0.5 | 2.13 ± 0.08 | 18.3 ± 0.4 | 2.03 ± 0.08 |
| O6 | d | 131 ± 11 | 136 ± 12 | 4.7 ± 0.7 | 34.2 ± 3.3 | 8.8 ± 2.8 |
| | s | 12.1 ± 0.3 | 12.4 + 0.3 | 1.21 ± 0.05 | 9.6 + 0.2 | 1.19 ± 0.05 |
| O7 | d | 35.8 ± 0.9 | 39.2 ± 0.9 | 1.8 ± 0.1 | 11.2 + 0.4 | 2.4 ± 0.2 |
| | s | 11 5 + 0.3 | 12.2 + 0.3 | 2.3 ± 0.1 | 15.9 ± 0.4 | 2.2 ± 0.1 |
| $OT_1$ | d | 49.3 ± 1.3 | 53.7 ± 1.4 | 0.55 ± 0.07 | 3.2 ± 0.2 | 0.50 ± 0.08 |
| | s | 1.19 ± 0.07 | 1.17 ± 0.07 | 0.13 ± 0.02 | 1.13 + 0.06 | ND |
| $OT_2$ | d | 34.5 + 2.0 | 38.2 + 2.2 | 0.08 ± 0.03 | 0.61 ± 0.08 | NM |
| | s | 1.93 ± 0.12 | 2.2 ± 0.1 | 0.48 ± 0.05 | 3.6 ± 0.2 | 0.52 ± 0.05 |

The data on the dissolved fraction have been widely discussed in ref. [2]. They reflect the existence of a local source of activity between stations O4 and O6 related to the operation of the phosphate fertilizer complex. In fact, the general levels of activity are clearly higher than those found for unperturbed river systems [4–8]. The case of station O1 was related to the low pH ($\sim 3$) of the waters, which promotes the dissolution of U and Th isotopes from the solid phase to the water. Such an effect causes the lowering of U and Th isotope activities in the particulate fraction at this location, as can be seen in Table 1.

The same conclusions can be derived from a general review of the suspended matter results. It has been found, for instance, that concentrations below 1.36, 1.30 and 1.49 mBq/l of $^{232}$Th, $^{230}$Th and $^{228}$Th, respectively, are present in suspended matter from some Japanese rivers [4]. Comparing with the data in Table 1, the concentrations of $^{232}$Th and $^{228}$Th in the Odiel river suspended matter are very similar to those obtained in the above reference. Only samples taken around the industrial area, stations O5, O6 and O7, present concentrations higher than those in the Japanese rivers. In the case of $^{230}$Th, the trend is different. In fact, the concentrations are, in general, much higher than those given in ref. [4]. Thus, it seems obvious that a local source of activity is present between stations O5 and O7. In fact, the U concentrations at these stations are about ten times higher than in the samples upstream, with the maxima at station O5 where a phosphate factory is located.

The distribution of activity between the dissolved and particulate fractions can also be found from the data in Table 1. Less than 10% of the total U isotope activity is associated with the solid fraction along the Odiel river basin, with a minimum of less than 1% at station O1 (the naturally low pH in these waters could explain the absence of activity in the solids, see ref. [3]). The exceptions are stations O5 and O7 where 25–35% of the total U isotope activities are incorporated into the suspended matter (see Fig. 2a).

Between 20 and 30% of $^{232}$Th and $^{230}$Th total activities appears in the solid fraction, with the exception again of stations O5 and O7. There, the content of $^{232}$Th in suspended matter ranges from 46 to 56% and that of $^{230}$Th from 48 to 49%. Consequently, an important part of the radioactivity released by the fertilizer factories to the Odiel river is associated with solid matter. The distribution of $^{228}$Th between the fractions is different than those of the other Th isotopes. In general, its presence in the dissolved fraction is higher than that for $^{232}$Th or $^{230}$Th. This should be explained in terms of the solubility of $^{228}$Ra, the parent of $^{228}$Th.

The case of station $OT_2$ is interesting. There, more than 80% of Th isotope activities are contained in the particulate fraction. This is not strange, since this sample must be considered as a seawater sample; and it is known that in such systems Th isotopes are quickly adsorbed onto the surface of solid particles.

In Table 2 some relevant activity ratios for both dissolved and suspended matter are presented. The Th/U mass ratio is also included in the table.

As commented in ref. [2] the activity and mass ratios in dissolved matter help to support the hypothesis of inputs of radioactive material into the Odiel river. Indeed, except for the case of station O1, the values obtained for the $^{234}$U/$^{238}$U activity ratio are compatible with the existence of secular equilibrium. This condition is not, of course, accomplished in the majority of river systems [9]. On the contrary, the value

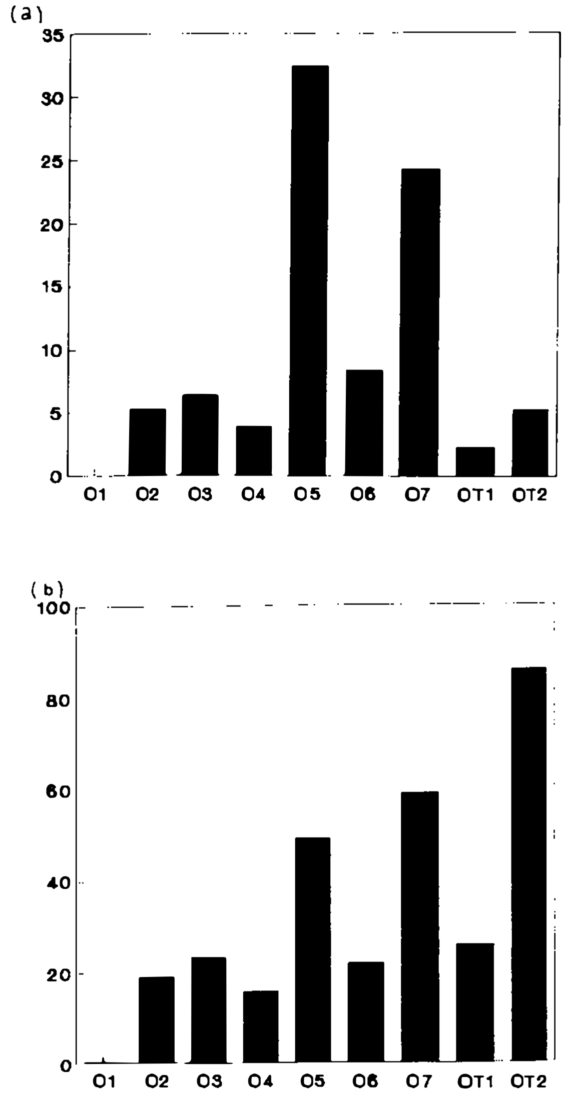


Fig. 2. Content in % of the total activity of $^{238}$U (a) and $^{230}$Th (b) in the suspended fraction along the Odiel river.

Table 2
Activity ratios as well as the Th/U mass ratio in the dissolved (d) and particulate (s) fractions of water samples taken from the Odiel river

| Station | | $^{234}U/^{238}U$ | $^{230}Th/^{234}U$ | $^{230}Th/^{232}Th$ | $^{228}Th/^{232}Th$ | Th/U |
|---|---|---|---|---|---|---|
| O1 | d | 1.60 ± 0.02 | 0.157 ± 0.008 | 3.10 ± 0.14 | 1.70 ± 0.07 | 0.208 ± 0.012 |
| | s | 1.88 ± 0.27 | 1.01 ± 0.14 | 4.6 ± 1.4 | 3.6 ± 1.5 | 1.33 ± 0.37 |
| O2 | d | 1.06 ± 0.03 | 0.71 ± 0.21 | 11.9 ± 6.0 | 4.5 ± 2.5 | 0.053 ± 0.027 |
| | s | 1.05 ± 0.05 | 0.81 ± 0.04 | 6.2 ± 0.6 | 0.86 ± 0.14 | 0.43 ± 0.04 |
| O3 | d | 1.07 ± 0.02 | 0.34 ± 0.03 | 6.6 ± 0.6 | | 0.167 ± 0.017 |
| | s | 1.08 ± 0.05 | 1.52 ± 0.07 | 6.2 ± 0.4 | 1.07 ± 0.09 | 0.806 ± 0.059 |
| O4 | d | 1.08 ± 0.10 | 0.24 ± 0.02 | 6.5 ± 0.7 | | 0.134 ± 0.017 |
| | s | 0.99 ± 0.05 | 1.23 ± 0.06 | 5.1 ± 0.4 | 0.97 ± 0.09 | 0.74 ± 0.06 |
| O5 | d | 1.02 ± 0.09 | 0.37 ± 0.04 | 8.5 ± 0.6 | 3.00 ± 0.25 | 0.151 ± 0.018 |
| | s | 1.00 ± 0.01 | 0.72 ± 0.02 | 8.6 ± 0.3 | 0.95 ± 0.05 | 0.258 ± 0.011 |
| O6 | d | 1.04 ± 0.04 | 0.25 ± 0.03 | 7.2 ± 0.9 | 1.9 ± 0.7 | 0.110 ± 0.018 |
| | s | 1.03 ± 0.02 | 0.77 ± 0.02 | 8.0 ± 0.3 | 0.99 ± 0.06 | 0.307 ± 0.015 |
| O7 | d | 1.10 ± 0.02 | 0.29 ± 0.01 | 6.1 ± 0.4 | 1.3 ± 0.1 | 0.157 ± 0.011 |
| | s | 1.06 ± 0.02 | 1.30 ± 0.04 | 6.8 ± 0.3 | 0.96 ± 0.06 | 0.62 ± 0.03 |
| $OT_1$ | d | 1.09 ± 0.02 | 0.060 ± 0.004 | 5.9 ± 0.7 | 0.91 ± 0.18 | 0.034 ± 0.004 |
| | s | 0.98 ± 0.08 | 0.97 ± 0.08 | 8.8 ± 1.4 | | 0.34 ± 0.06 |
| $OT_2$ | d | 1.11 ± 0.04 | 0.016 ± 0.002 | 7.4 ± 2.8 | | 0.008 ± 0.003 |
| | s | 1.15 ± 0.08 | 1.63 ± 0.12 | 7.4 ± 0.8 | 1.06 ± 0.15 | 0.77 ± 0.09 |

found is typical of the primary minerals used for fertilizer production.

As expected, both the Th/U and $^{230}Th/^{234}U$ mass and activity ratios in the dissolved fraction are much below unity for all the stations, but still higher than in other fluvial systems [10]. Thus, a general contamination with Th isotopes along all the Odiel river channel is confirmed. Finally, values much above unity for the $^{230}Th/^{232}Th$ activity ratio could also reveal the high contamination of the river basin by members of the $^{238}U$ radioactive decay chain.

The study of such ratios for suspended matter gives the same conclusions.

The $^{234}U/^{238}U$ activity along the channel is again close to unity, which is not typical for natural systems [11]. This suggests an external origin of such particles, probably from the fertilizer industries. The case of station O1 is interesting. At this station an excess of the daughter, similar to that found in the solution, is obtained. This should be related to the large interaction between phases due to the low pH of the waters [3].

Values slightly higher or close to unity are found for the $^{230}Th/^{234}U$ activity ratio, except for samples O5 and O6. There, a clear enrichment of $^{234}U$ appears, which confirms the presence around such stations of a local source of activity. However, this can be deduced more clearly from the Th/U mass ratio. In general, values much above unity are found for the Th/U mass ratio is suspended matter in unperturbed rivers [12,13]. In our case the ratio is clearly less than 1.

The enrichment of the particles in $^{238}U$ and descen-

Table 3
Same as Table 1 but for the Tinto river

| Station | | $^{238}U$ | $^{234}U$ | $^{232}Th$ | $^{230}Th$ | $^{228}Th$ |
|---|---|---|---|---|---|---|
| T1 | d | 115 ± 4 | 211 ± 7 | 19.6 ± 0.9 | 52.2 ± 2.2 | 71 ± 3 |
| | s | 0.252 ± 0.027 | 0.317 ± 0.029 | 0.092 ± 0.015 | 0.215 ± 0.021 | 0.125 ± 0.038 |
| T2 | d | 40 ± 2 | 42.6 ± 2.0 | 48 ± 14 | 91 ± 27 | 13 ± 4 |
| | s | 1.08 ± 0.08 | 0.98 ± 0.07 | 0.073 ± 0.015 | 0.89 ± 0.06 | 0.058 ± 0.019 |
| T3 | d | 47.6 ± 2.2 | 51.7 ± 2.4 | 0.78 ± 0.10 | 5.65 ± 0.35 | 1.00 ± 0.13 |
| | s | 1.96 ± 0.09 | 2.04 ± 0.09 | 0.170 ± 0.020 | 1.40 ± 0.06 | 0.153 ± 0.022 |
| T4 | d | 48.1 ± 2.4 | 53.4 ± 2.6 | 21.6 ± 4.9 | 41.1 ± 9.0 | 2.25 ± 0.78 |
| | s | 2.08 ± 0.09 | 2.30 ± 0.10 | 0.133 ± 0.018 | 1.33 ± 0.06 | 0.223 ± 0.025 |
| T5 | d | 42.6 ± 1.0 | 46.1 ± 1.1 | 0.55 ± 0.10 | 3.92 ± 0.28 | ND |
| | s | 1.05 ± 0.08 | 1.27 ± 0.10 | 0.134 ± 0.032 | 1.32 ± 0.08 | 0.116 ± 0.032 |
| T6 | d | 45.8 ± 1.5 | 49.3 ± 1.6 | 0.63 ± 0.07 | 3.80 ± 0.17 | 0.68 ± 0.08 |
| | s | 0.218 ± 0.019 | 0.261 ± 0.032 | 0.041 ± 0.009 | 0.258 ± 0.019 | 0.061 ± 0.029 |

dants can also be deduced from the $^{230}Th/^{232}Th$ activity ratios. Although being below unity, they are still higher than expected for unperturbed rivers [4,12].

Finally, as found in the current literature [4,12] the $^{228}Th/^{232}Th$ activity ratio is close to unity, except for station O1. There, there exists an excess of $^{228}Th$ as occurs for dissolved matter. The effect is similar to that obtained for the $^{234}U/^{238}U$ activity ratio and should be explained in the same way.

### 3.2. *Tinto river*

Results for U and Th isotopic activities are given in Table 3. As in the case of the Odiel river the dissolved fraction data have already been discussed in ref. [2]. We only mention here the more relevant conclusions.

From stations T2 to $OT_2$ the activities of U isotopes are only slightly higher than those found for other rivers [7,9,10], presenting a quite flat pattern. Thus, it is difficult to deduce from them any influence of the phosphogypsum piles area in the Tinto river. For the case of Th isotopes, the situation is clearly different. Two well defined peaks of Th isotope activities appear at stations T2 and T4, with values higher than those found in the Odiel river. Excluding the two maxima, Th isotope activities are lower than those found in the Odiel river and similar to those reported for other world rivers [4,5,8,10]. The maxima were explained as the result of radioactivity transported from the phosphogypsum piles to the Tinto river, by natural or artificial rivulets which cross it. The high activities obtained for station T1 is, as in the case of station O1 of the Odiel river, a consequence of the low natural pH ( ~ 2) of the waters.

On the contrary, from analysis of the activities in suspended matter one cannot deduce any contamination of the Tinto river coming from the phosphogypsum piles area. In fact, only the $^{230}Th$ activities around the area are slightly higher than those found in the current literature [4]. As will be seen later the study of the activity ratios will clarify this point.

As for the distribution of the activity between solid and liquid fractions, some comments can be made in the case of the Tinto river.

Less than 5% of the U isotopes total activities is associated with the solid fraction along the Tinto river, with a minimum in sample T1, which should be explained as in the case of sample O1 of the Odiel river (see Fig. 3a). The case of Th isotopes is different. Again, a minimum of activity incorporated into the solid fraction is found in sample T1. The reason is as given before. However, minima (less than 5%) are also found for samples T2 and T4 where maxima in solution appeared (see Fig. 3b). In the other samples the content of Th isotope activities in suspended matter ranges from 20 to 30%. This clearly shows that the Tinto river

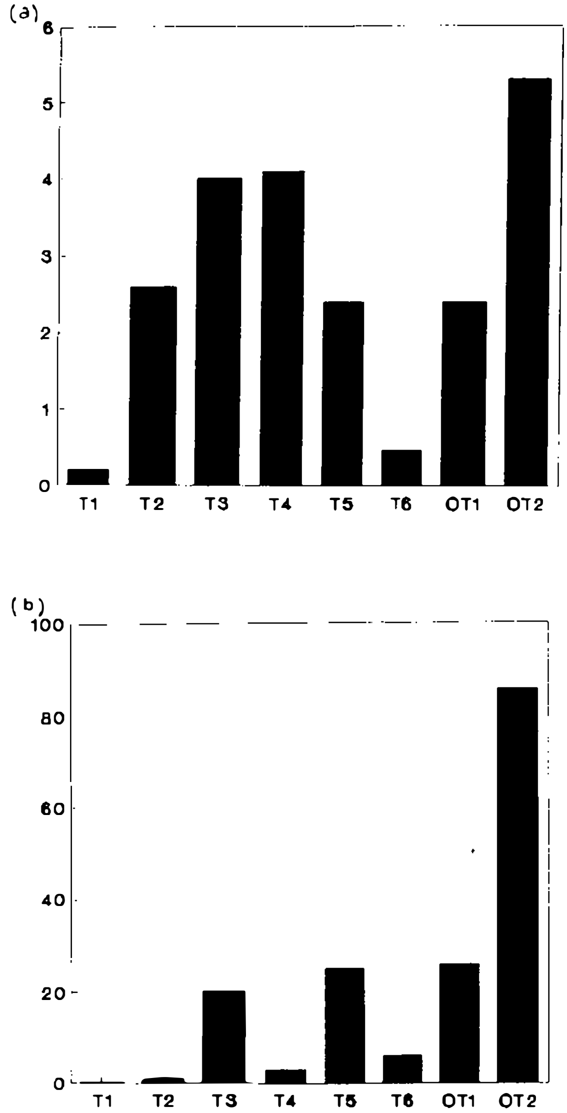


Fig. 3. Same as Fig. 2 but for the Tinto river.

is receiving radioactive materials from the phosphogypsum piles area through the points T2 and T4. The case of $^{228}Th$ is different. In all cases, 90% or more is incorporated into the dissolved fraction. The reason is as explained before, when commenting on the same effect in the Odiel river.

As already stated, the study of activity ratios and the Th/U mass ratio clarifies the problem a little (Table 4).

In the dissolved fraction [2] the $^{234}U/^{238}U$ activity ratio approaches unity, except for station T1, reflecting the typical equilibrium of primary minerals. The Th/U mass ratio and the $^{230}Th/^{234}U$ activity ratio are always below unity, as in unperturbed systems [4,6], except in the case of stations T2 and T4, where they are higher

Table 4
Same as Table 2 but for the Tinto river

| Station | | $^{234}U/^{238}U$ | $^{230}Th/^{234}U$ | $^{230}Th/^{232}Th$ | $^{228}Th/^{232}Th$ | Th/U |
|---|---|---|---|---|---|---|
| T1 | d | $1.83 \pm 0.03$ | $0.25 \pm 0.01$ | $2.67 \pm 0.09$ | $3.60 \pm 0.12$ | $0.52 \pm 0.03$ |
| | s | $1.26 \pm 0.17$ | $0.68 \pm 0.09$ | $2.4 \pm 0.4$ | $1.4 \pm 0.5$ | $1.15 \pm 0.23$ |
| T2 | d | $1.07 \pm 0.04$ | $2.14 \pm 0.64$ | $1.90 \pm 0.21$ | $0.27 \pm 0.05$ | $3.7 \pm 1.1$ |
| | s | $0.91 \pm 0.09$ | $0.91 \pm 0.09$ | $12.1 \pm 2.7$ | $0.79 \pm 0.30$ | $0.209 \pm 0.049$ |
| T3 | d | $1.09 \pm 0.04$ | $0.11 \pm 0.01$ | $7.2 \pm 0.8$ | $1.27 \pm 0.22$ | $0.050 \pm 0.006$ |
| | s | $1.04 \pm 0.06$ | $0.69 \pm 0.04$ | $8.3 \pm 1.0$ | $0.91 \pm 0.16$ | $0.266 \pm 0.034$ |
| T4 | d | $1.11 \pm 0.04$ | $0.77 \pm 0.17$ | $1.90 \pm 0.21$ | $0.10 \pm 0.03$ | $1.38 \pm 0.32$ |
| | s | $1.11 \pm 0.06$ | $0.58 \pm 0.04$ | $10.0 \pm 1.4$ | $1.67 \pm 0.30$ | $0.198 \pm 0.031$ |
| T5 | d | $1.08 \pm 0.02$ | $0.085 \pm 0.007$ | $7.1 \pm 1.3$ | | $0.040 \pm 0.007$ |
| | s | $1.22 \pm 0.13$ | $1.04 \pm 0.10$ | $9.4 \pm 2.0$ | $0.81 \pm 0.28$ | $0.405 \pm 0.090$ |
| T6 | d | $1.08 \pm 0.03$ | $0.077 \pm 0.004$ | $6.03 \pm 0.61$ | $1.09 \pm 0.17$ | $0.042 \pm 0.004$ |
| | s | $1.20 \pm 0.15$ | $0.98 \pm 0.11$ | $6.4 \pm 1.4$ | $1.50 \pm 0.76$ | $0.56 \pm 0.13$ |

than 1. This confirms the role of contamination of sampling points T2 and T4 in the Tinto river. Both ratios decrease quickly along the Tinto channel, which reflects fast Th association with the solid matter. The $^{230}Th/^{232}Th$ activity ratio is always higher than those found in normal aqueous systems. This is due to the presence of $^{234}U$ in solution. However, the value of this activity ratio at stations T2 and T4 reveals that some material, rich in $^{232}Th$, is being incorporated into the river. The origin of such material is clearly the phosphogypsum piles. Indeed, the $^{228}Th/^{232}Th$ activity ratio is very close to 1, except for stations T2 and T4, where an important defect of $^{228}Th$ appears. The reason for such a defect is the absence of $^{228}Ra$ in solution. This is due to the fact that Ra in phosphogypsum is very insoluble. Therefore, the material transported into the river by rivulets at stations T2 and T4 must be very poor in Ra isotopes.

Again the ratios obtained for the suspended fraction confirm the already commented conclusions. As in the Odiel river, the $^{234}U/^{238}U$ is close to unity along the Tinto river channel. The Th/U mass ratio for suspended particles reveals U enrichment of the particles all along the channel, since it is on average below unity, very different to the data in the current literature [12,13]. The excess of $^{230}Th$ observed from the $^{230}Th/^{232}Th$ activity ratio, not usual in other fluvial systems [4,15], supports such a conclusion. Finally, values much below unity for the $^{230}Th/^{234}U$ activity ratio near stations T3 and T4, as found at stations O5 and O6 of the Odiel river, also suggest that U-enriched material is being incorporated into the river. The rest of the stations have values of this activity ratio similar to those found in the current literature [14]. The $^{228}Th/^{232}Th$ activity ratio is, in general, compatible with the existence of secular equilibrium between both isotopes. They, in fact, agree well with the values in the current literature [4,15].

We do not mention here the case of station T1, since the comments are the same as those made for station O1 of the Odiel river.


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