U- and Th-isotopes in an Estuarine System in Southwest Spain: Tidal and Seasonal Variations

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The presence of U- and Th-isotopes in suspended matter from an estuarine system which surrounds a phosphate fertilizer processing complex has been investigated. A clear radioactive impact from the complex has been confirmed since up to 86 and 116 µg/g of U and Th respectively have been detected. The effect of tides and seasonal conditions, temperature and salinity, on the results has also been investigated. Some distribution coefficients are given. Copyright © 1996 Elsevier Science Ltd

Introduction

The Odiel river is located in the southwest of Spain and discharges its waters to the Atlantic Ocean. In the lower reaches, it forms an estuarine tidal system which surrounds a large industrial area where a phosphate fertilizer complex is located. This complex releases part of its wastes directly into the Odiel river.

It is well known that such wastes contain significant amounts of natural radionuclides: Ra, U-, Th-isotopes and their daughters. The presence of Ra-isotopes in water and suspended matter samples collected from the Odiel river has already been studied (Periáñez and García-León, 1993; Periáñez et al., 1994). These studies have revealed that a clear radioactive impact is being produced by the fertilizer complex since, for instance, up to 670 mBq/L of ^{226}Ra have been detected in a water sample collected close to the complex.

Although there are some data on the U- and Th-isotopes content in the Odiel river suspended matter (Martínez-Aguirre et al., 1994), a more detailed study is carried out. The objective of this work is to achieve a complete understanding of the distribution of U and Th in suspended matter in the Odiel river, including the effect of tidal and seasonal conditions on the radionuclide concentrations. This information, together with some K_d distribution coefficients which have also been measured, will be necessary to complete some modelling works on the dispersion of radionuclides in aquatic tidal systems (including the transfers between solid and liquid phases) which are being carried out by our group.

The next section describes the sampling work as well as the isotope determination methods. In following sections the results are presented and discussed.

Experimental

Samples of river water were collected along the Odiel river basin (see Fig. 1) during July 1990 (dry season) and March 1991 (wet season) to study the influence of seasonal conditions on the U and Th concentrations. Water samples were collected in plastic bottles. Two samples were taken from each sampling station: one during high water and the other during low water to study the influence of tidal oscillations. The water was filtered as soon as possible through previously weighed Nuclepore filters, 0.4 µm pore size, so as to separate the suspended matter. The filter was then dried and weighed to calculate the mass of recovered matter. After this, the filter was covered with HCl and placed into an ultrasonic bath for some half an hour during which time the suspended matter is separated from the filter and dissolved. The filter was then washed with HNO_3 which is added to the HCl to form aqua regia. This solution is heated slowly to dissolve all remaining particles. After cooling, ^{232}U and ^{229}Th spikes and some Fe carrier were added to the solution. Precipitation of Fe with oxyhydroxides with concentrated amonium hydroxide follows.

U- and Th-isotopes were extracted from the precipitate using anion exchange resins (DOWEX AG 1X8, HCl form) and electroplated onto stainless steel planchets. Activities were measured by Si ion-implanted detector alpha spectrometry. More
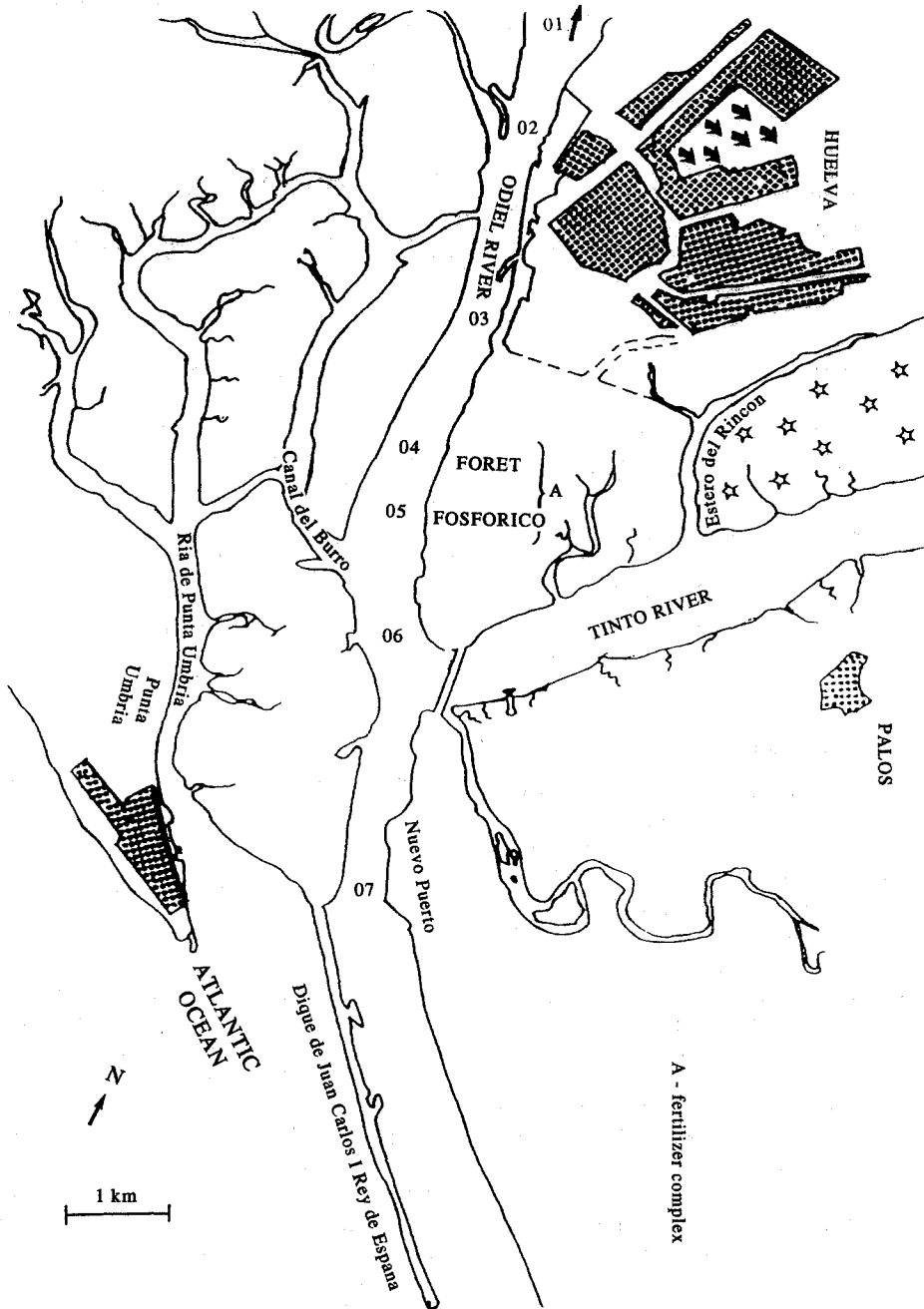
Fig. 1. Map of the Odiel river showing the sampling stations.

details of the radiochemical and measurement methods can be found in Martínez-Aguirre (1991).

Results and Discussion

In what follows, the samples are denoted by 'O' (Odiel). The numbers given to each sample identify the sampling station (see Fig. 1), which are distributed along the lower reaches of the river, close to the fertilizer complex. Station 1 is, however, far upstream of this area near the river source. As it is not supposed to be affected by tidal oscillations, only one sample was collected there.

Tables 1 and 2 present the results obtained for the samples collected in 1990, for low and high water respectively. These give the U and Th concentrations in suspended matter in µg/g and some interesting activity ratios. In the case of the low water samples, there is a high concentration peak in station O4, for both U and Th, revealing the presence of a local source of activity. Up to 86 and 116 µg/g of U and Th respectively have been detected in this sample,

Table 1. Concentrations of U and Th in μg/g for the suspended matter samples collected during low water in 1990. Some activity ratios are also given

Sample	U	Th	^{234}U/^{238}U	^{230}Th/^{232}Th	Th/U
O1	1.10 ± 0.24		1.2 ± 0.3		
O2	1.08 ± 0.13	0.07 ± 0.04	1.27 ± 0.14	7 ± 4	0.06 ± 0.04
O3	2.03 ± 0.24	0.11 ± 0.05	1.39 ± 0.17	9 ± 4	0.05 ± 0.03
O4	86 ± 10	116 ± 6	0.98 ± 0.05	5.28 ± 0.13	1.35 ± 0.17
O5	25.3 ± 1.3	31 ± 3	1.00 ± 0.07	6.1 ± 0.7	1.22 ± 0.13
O6	13.4 ± 1.5	0.052 ± 0.024	1.07 ± 0.17	2.4 ± 1.4	(3.9 ± 1.8) × 10^{-3}
O7	19.1 ± 1.7		1.06 ± 0.06		

values which are much higher than those previously found for suspended matter samples collected from other rivers. Indeed, Moore (1967) has measured U concentrations in Amazon and Mississippi rivers ranging from 1.8 to 2.4 μg/g. On the other hand, Th concentrations in these rivers range from some 8 to 10 μg/g (Moore, 1967). In some japanese rivers Th concentrations range from some 2.2 to 6.7 μg/g (Miyake et al., 1973). Thus, it seems clear that stations O4 and O5, close to the fertilizer complex, are affected by the waste disposal from it.

In the case of the high water samples, the distribution of U and Th is different. The maximum Th concentration is 0.7 μg/g and there is a general homogenization of concentration levels, which may be due to the tidal mixing and to the input of non-contaminated suspended matter from the sea. On the other hand, U concentrations are also lower than during low water, although there is still an important peak in station O5, which is close to the fertilizer complex. This effect was already observed for ^{226}Ra (Periáñez et al., 1994). It is interesting to note that the contamination is very localized around the fertilizer complex. However, some U contamination seems to affect all the studied area downstream the complex during low water.

In general, ^{234}U/^{238}U activity ratios are compatible with the existence of secular equilibrium in those samples in which high U concentrations have been detected. This is not a typical feature for rivers, but it is typical of the minerals used for fertilizer production (Martínez-Aguirre et al., 1994). The secular equilibrium found in the Odiel river suggests an external origin for the suspended matter particles, probably from the fertilizer complex.

The ^{230}Th/^{232}Th activity ratios are > 1 all along the river for both sets of samples. This reveals the high contamination of the river by members of the ^{238}U radioactive chain.

The existence of an external source of activity is confirmed by the Th/U mass ratio. As U is largely more soluble than Th, it is often found in deficient with respect to Th in the solid surface environment. Thus, suspended matter in unperturbed rivers usually have Th/U mass ratios above unity. This is not the case with the Odiel river suspended particles. It can be seen in Tables 1 and 2 that, with the exception of samples O4 and O5 at low water, the Th/U mass ratios are below unity. This reveals the existence of a external source of U contaminated particles to the river. The exceptions are samples O4 and O5 which show Th/U mass ratios above unity, typical of unperturbed rivers suspended particles. However, these samples being the most contaminated, the ratios should be related to the contaminants.

Tables 3 and 4 present the results for the low and high water samples, respectively, collected in 1991. The behaviour of Th is similar to that of the 1990 sampling campaign. There is a concentration peak in station O5, close to the fertilizer complex, during low water and a very homogeneous concentration profile during high water. Nevertheless, there is a significant difference. The concentration levels, including that of the peak in O5, are similar to those found in unperturbed rivers (Moore, 1967; Miyake et al., 1973). Nevertheless, the presence of Th contaminated particles is clear since the Th concentration at station O5, during low water, is some four times larger than in the surroundings.

The case of U is different, there are high concentration levels during both high and low water all along the river. Now the contamination is not reduced in the area close to the fertilizer complex, but extends from O2 to O7. This could be a seasonal effect. During the 1990 sampling campaign (summer, dry season) the water salinity was about four times higher than during the 1991 sampling campaign (winter, wet season), see Periáñez (1995). On the other hand, the water temperatures were 27.5 ± 1.2 and 15.0 ± 0.8°C during the sampling campaigns of

Table 2. Concentrations of U and Th in μg/g for the suspended matter samples collected during high water in 1990. Some activity ratios are also given

Sample	U	Th	^{234}U/^{238}U	^{230}Th/^{232}Th	Th/U
O1	1.10 ± 0.24		1.2 ± 0.3		
O2	3.9 ± 0.5	0.12 ± 0.07	1.12 ± 0.16	13 ± 8	0.031 ± 0.018
O3	2.8 ± 0.3	0.19 ± 0.07	1.09 ± 1.10	3.2 ± 1.4	0.07 ± 0.03
O4	9.0 ± 1.0	0.27 ± 0.13	1.24 ± 0.10	17 ± 9	0.030 ± 0.015
O5	69 ± 3		1.04 ± 0.07		
O6	1.6 ± 0.4	0.06 ± 0.04	0.9 ± 0.3	8 ± 5	0.04 ± 0.03
O7	2.4 ± 0.4	0.7 ± 0.2	0.91 ± 0.17	5.1 ± 1.9	0.29 ± 0.10

Table 3. Concentrations of U and Th in μg/g for the suspended matter samples collected during low water in 1991. Some activity ratios are also given

Sample	U	Th	$^{234}U/^{238}U$	$^{230}Th/^{232}Th$	Th/U
O1	1.55 ± 0.19	0.58 ± 0.17	1.67 ± 0.18	2.1 ± 0.7	0.37 ± 0.12
O2	11.2 ± 1.1	0.09 ± 0.06	1.24 ± 0.09	27 ± 19	$(8 ± 5) \times 10^{-3}$
O3	8.7 ± 1.5	0.07 ± 0.04	1.06 ± 0.19	8 ± 5	$(8 ± 5) \times 10^{-3}$
O4	27.9 ± 2.7	0.34 ± 0.15	1.05 ± 0.07	9 ± 4	$(2.8 ± 1.3) \times 10^{-3}$
O5	30 ± 3	11.3 ± 0.9	1.12 ± 0.09	5.8 ± 0.4	0.38 ± 0.05
O6	48 ± 6	2.6 ± 0.5	1.13 ± 0.09	4.6 ± 1.0	0.054 ± 0.012
O7	31 ± 4	2.1 ± 0.6	1.17 ± 0.11	2.3 ± 0.8	0.070 ± 0.021

1990 and 1991 respectively. It is well known that an increase of salinity leads to dissolution of cations from suspended matter. This effect has been found for ^{226}Ra in, for instance, the Pee Dee river (Elsinger and Moore, 1980) and the Odiel river (Periáñez et al., 1994) and for ^{238}U in some laboratory experiments carried out by Bird and Evenden (1994). On the other hand, an increase of water temperature leads to a faster dissolution of ^{238}U from suspended matter (Ames et al., 1983). Thus, during the 1990 sampling campaign the U may have dissolved rapidly while during the 1991 campaign it remained fixed to solid particles for a longer time.

Again, the $^{234}U/^{238}U$ ratios are in general compatible with secular equilibrium in the part of the river close to the complex. The $^{230}Th/^{232}Th$ ratios are again larger than unity, which shows a high contamination by members of the ^{238}U chain. Finally, the Th/U mass ratios are much below unity, which confirms the existence of an external source of activity.

Some distribution coefficients for ^{238}U, ^{232}Th and ^{230}Th are presented in Table 5. The activities of U and Th isotopes in the liquid phase have been obtained from Periáñez (1995). In the case of ^{238}U, our results are in agreement with the values found in literature. Indeed, IAEA (1985) showed that K_d for U in coastal waters can range from 0.2×10^3 to 5×10^3 kg/kg. The K_ds are very similar for both Th-isotopes, suggesting that they are distributed between water and suspended matter in the same way. However,

values below the range of variation which can be seen in the literature have been obtained. IAEA (1985) indicate that K_d for Th can range from 500×10^3 to $10,000 \times 10^3$ kg/kg. Nevertheless, a clear conclusion from these results is the large K_d variation between different sampling points (up to two orders of magnitude). This variation comes from the K_d definition itself: it assumes an equilibrium situation for the exchanges between solid and liquid phases. This situation is not always achieved when an in situ measurement of K_d is made, especially in sites where the input into the system is changing with time (man made pollution). Thus, when a K_d measurement is carried out, an extensive determination of the sampling conditions (salinity, temperature, pH...) should be made in order to be able to interpret the result. It is probable that the equilibrium conditions can not easily be reached in nature. Thus, laboratory experiments and mathematical simulations are important tools which can help to understand the mechanisms of distribution of radioactivity in aquatic environments. This work has been successfully carried out in our group in the case of ^{226}Ra (Periáñez et al., 1996a,b).

Conclusions

The presence of significant concentrations of U and Th in suspended matter samples collected from the Odiel river can be attributed to waste disposal

Table 4. Concentrations of U and Th in μg/g for the suspended matter samples collected during high water in 1991. Some activity ratios are also given

Sample	U	Th	$^{234}U/^{238}U$	$^{230}Th/^{232}Th$	Th/U
O1	1.55 ± 0.19	0.58 ± 0.17	1.67 ± 0.18	2.1 ± 0.7	0.37 ± 0.12
O2	63 ± 5	0.8 ± 0.3	1.196 ± 0.024	4.0 ± 1.6	0.013 ± 0.005
O3	31 ± 3	0.41 ± 0.19	1.32 ± 0.09	4.7 ± 2.3	0.13 ± 0.006
O4	119 ± 10	0.46 ± 0.17	1.071 ± 0.013	2.2 ± 0.9	$(3.9 ± 1.5) \times 10^{-3}$
O5	94 ± 8	0.30 ± 0.11	1.115 ± 0.022	5.7 ± 2.2	$(3.2 ± 1.2) \times 10^{-3}$
O6		0.13 ± 0.05		1.5 ± 0.7	
O7	33 ± 3	0.33 ± 0.17	1.27 ± 0.06	3.6 ± 2.0	0.010 ± 0.005

Table 5. Distribution coefficients (kg/kg) for the 1990 low water samples

Sample	^{238}U	^{232}Th	^{230}Th
O1	$(0.15 ± 0.3) \times 10^3$		
O2	$(0.38 ± 0.05) \times 10^3$	$(0.7 ± 0.4) \times 10^3$	$(0.59 ± 0.17) \times 10^3$
O3	$(0.91 ± 0.12) \times 10^3$	$(0.7 ± 0.3) \times 10^3$	$(0.91 ± 0.17) \times 10^3$
O4	$(12.5 ± 1.6) \times 10^3$	$(13.8 ± 1.8) \times 10^3$	$(13.3 ± 1.6) \times 10^3$
O5	$(4.8 ± 0.4) \times 10^3$	$(53 ± 18) \times 10^3$	$(30 ± 4) \times 10^3$
O6	$(3.0 ± 0.4) \times 10^3$	$(0.2 ± 0.1) \times 10^3$	$(0.07 ± 0.02) \times 10^3$
O7	$(3.8 ± 0.4) \times 10^3$		

from a phosphate fertilizer complex located close to the river. Tides and seasons (through salinity and temperature) affect the distribution of U and Th along the estuary. Some activity ratios have also been investigated, which have confirmed the external origin of the contaminated suspended matter particles. The K_d for U- and Th-isotopes has been calculated. The results show important variations from one sampling station to another, which are due to the fact that equilibrium conditions which are necessary for a correct K_d calculation are not easily achieved in Nature.

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