Enhanced U and Th Concentrations in Soils From a Wet Marshland Washed by Contaminated Riverwaters*

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A study of the presence of U and Th isotopes in soil samples from a saline wet Marshland located close to a phosphoric acid production factory is presented. The samples were collected during low tide in areas washed by water during high tide. The incoming Odiel riverwaters, which directly receive the wastes from this factory, provokes the enhancement of radioactivity in certain zones of the studied area. Comparison of radionuclide concentrations between the fine particle fraction (≤ 63.5 μm) and the total soil fraction has given some hint on the processes by which contamination takes place. Copyright © 1996 Elsevier Science Ltd

Introduction

Large enhancements of natural radionuclides in solution, suspended matter and bottom sediments were previously found at the Odiel and Tinto river basins (Martínez-Aguirre et al., 1994a, 1994b, 1994c). This enhancement was attributed to the wastes released by industries which process phosphate rock for phosphoric acid production. Thus, liquid and solid wastes are directly released into the Odiel river channel. These wastes are later distributed all over the estuary. Close to this factory, at the other side of the Odiel river (see Fig. 1), a large wet marshland (Odiel marsh) is located. It is a natural reservation with an important biological activity. The area is highly affected by the inflow of the Odiel riverwaters during the tides. Thus, presumably, the release of natural radionuclides into the Odiel riverwaters may enhance the concentration levels of natural radionuclides in the marsh. Two main processes could lead to its enhancement. Firstly, radionuclides released in liquid form could be transported by the water toward the marsh. Precipitation and/or ion-exchange processes may follow, affecting the concentration of radionuclides in bottom sediments and soils. Secondly, the factory also releases solid wastes (gypsum particles) directly into the Odiel channel. Of these particles, larger particles would be deposited at the bottom of the river at locations close to the point of release. However, small particles could flow with the water and be deposited at further locations. These particles, with high concentration of natural radionuclides, will enhance the concentration levels at their deposition site. During the transit, precipitation or ion-exchange processes between solution and small suspended particles will also be considered.

Thus, when a location is being contaminated by radionuclides in solution, all sizes of particles would be contaminated. For contamination of a location by transported contaminated fine particles, the concentration of a contaminant in the fine particle fraction would be much higher than in the total soil. In general, both processes may affect the concentration level at a particular location.

In this paper the enhancement produced in soils from the Odiel marshland by the flow of Odiel riverwaters, which receive the wastes released from the fertilizer complex, is presented and discussed. The aims were to determine if any of the zones of the marsh are enhanced by natural radionuclides as well as to identify, if possible, the way by which the contaminants arrive at each zone. For this reason, concentrations of some natural radionuclides have been determined in differents locations across the marsh. In each location, the total soil fraction and the fine particle fraction (≤ 63 μm) were analysed in order to determine the U and Th radionuclides.

Samples and Experimental Methods

Fifteen soil samples were collected in February 1993 across the Odiel marsh located at the right margin of the Odiel river in front of the fertilizer complex. The samples were collected during low tide in areas covered with water during high tide. Density and organic matter content were determined in each soil sample. The fine particle fraction (≤ 63 μm) was separated by using a sieve of 63 μm hole diameter;
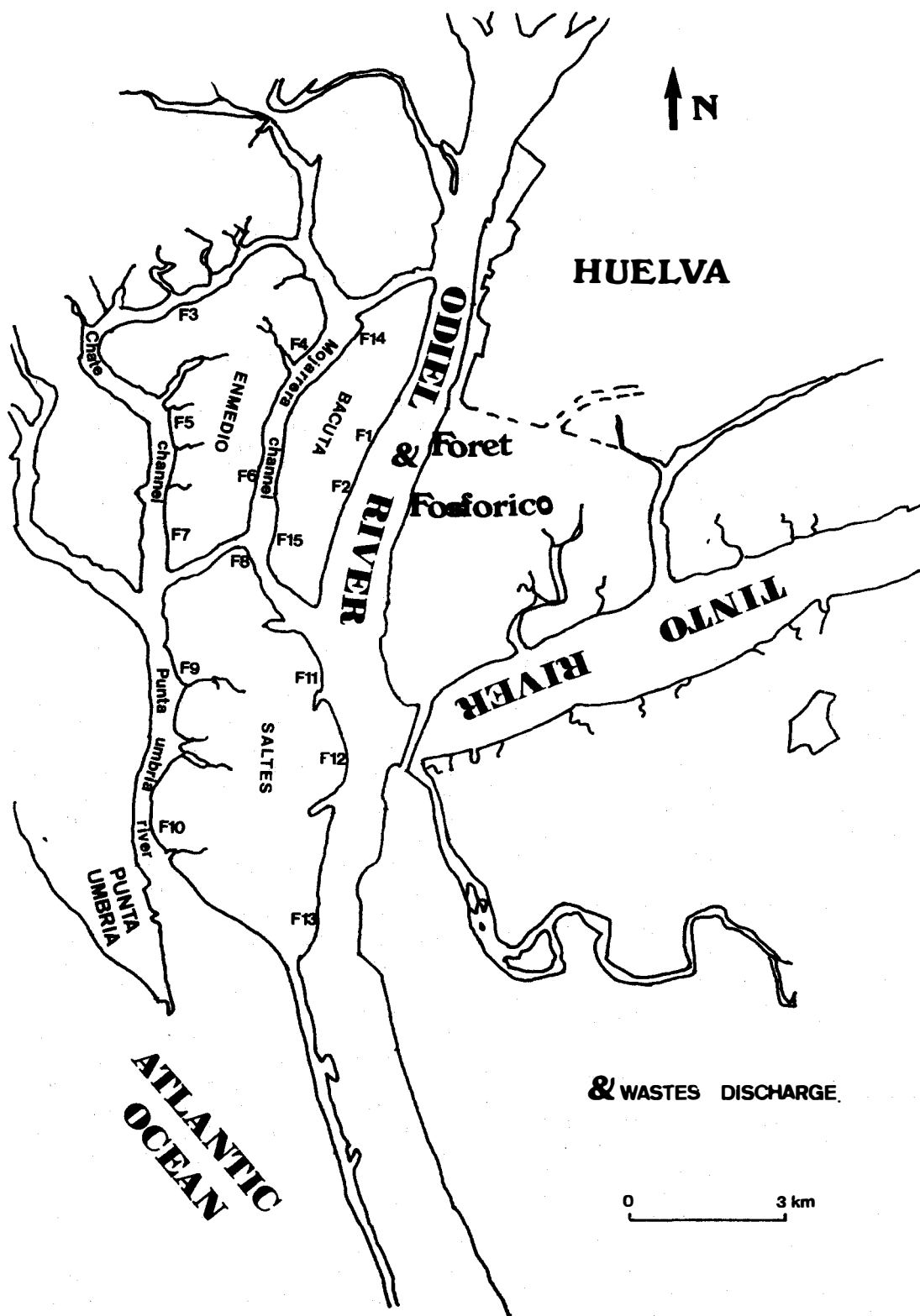
Fig. 1. Map of the estuarine system at the city of Huelva. Sampling stations across the Odiel marsh and location of the fertilizer factories (Foret and Fosforico) are shown.

Table 1. Results obtained in the analysis of U and Th isotopes (μg/g) in the total soil fraction of soils collected across the Odiel wet marshland

Code	U	Th	Th/U	$^{234}U/^{238}U$	$^{230}Th/^{234}U$	$^{230}Th/^{232}Th$
F14	24.9 ± 1.4	5.98 ± 0.55	0.240 ± 0.026	1.119 ± 0.045	0.746 ± 0.056	10.6 ± 0.9
F4	29.2 ± 1.8	6.95 ± 0.50	0.238 ± 0.023	1.010 ± 0.043	0.712 ± 0.053	9.2 ± 0.6
F6	24.5 ± 1.0	5.55 ± 0.45	0.227 ± 0.020	1.115 ± 0.028	0.886 ± 0.051	13.3 ± 1.0
F15	25.6 ± 1.4	5.09 ± 0.40	0.199 ± 0.019	1.093 ± 0.042	0.767 ± 0.053	12.8 ± 0.9
F11	11.5 ± 0.7	5.36 ± 0.33	0.466 ± 0.043	1.147 ± 0.078	0.401 ± 0.034	3.02 ± 0.18
F12	35.1 ± 1.3	8.66 ± 0.81	0.246 ± 0.025	1.134 ± 0.024	0.840 ± 0.050	11.8 ± 1.0
F13	11.5 ± 0.7	7.83 ± 0.40	0.681 ± 0.054	1.187 ± 0.054	0.584 ± 0.040	3.10 ± 0.14
F1	13.3 ± 0.6	5.56 ± 0.61	0.418 ± 0.050	1.148 ± 0.028	0.535 ± 0.048	4.49 ± 0.43
F2	12.6 ± 0.6	5.18 ± 0.40	0.411 ± 0.037	1.209 ± 0.031	0.378 ± 0.028	3.39 ± 0.24
F3	11.9 ± 0.4	6.30 ± 0.65	0.529 ± 0.057	1.073 ± 0.026	0.709 ± 0.055	4.40 ± 0.43
F5	10.1 ± 0.5	6.35 ± 0.47	0.629 ± 0.056	1.113 ± 0.046	0.721 ± 0.053	3.88 ± 0.26
F7	7.51 ± 0.27	5.33 ± 0.56	0.710 ± 0.079	1.074 ± 0.022	0.319 ± 0.032	1.47 ± 0.16
F8	7.70 ± 0.40	5.73 ± 0.38	0.744 ± 0.063	1.223 ± 0.041	0.251 ± 0.020	1.26 ± 0.08
F9	5.97 ± 0.30	4.42 ± 0.34	0.740 ± 0.068	1.173 ± 0.040	0.345 ± 0.029	1.67 ± 0.13
F10	2.99 ± 0.13	4.23 ± 0.34	1.415 ± 0.129	1.177 ± 0.042	0.526 ± 0.045	1.34 ± 0.11

particles passing through were considered as the fine particle fraction < 63 μm dia. The amount by weight (%) of small particles in each soil sample was also determined.

The samples were dried, powdered and homogeneized before the analysis. 1 g of sample was spiked with accurately known ^{232}U and ^{229}Th activities. After digestion of the sample with HNO_3 and aqua regia, the residue was redissolved with HNO_3 8 M. Precipitation of actinides with Fe was achieved by adding concentrated ammonium hydroxide to the HNO_3 solution. This precipitate was dissolved in HCl and passed through an anion-exchange resin (Dowex AG1-X8, chloridic form) to separate Th from U. Each solution (Th and U respectively) was then purified by passing through the same resin, separately (Martínez-Aguirre, 1991). Final solutions were electroplated onto stainless steel planchets 2.2 cm dia by the method of Talvitie, 1972. U and Th isotopes were measured by α-spectrometry with surface barrier or ion-implanted Si detectors.

Results and Discussion

Table 1 and Table 2 give the mass concentration in μg/g for U and Th in the total soil fraction and the fine particle fraction, respectively. In the same tables the Th/U mass ratio, $^{234}U/^{238}U$, $^{230}Th/^{234}U$ and $^{230}Th/^{232}Th$ activity ratios are also presented. The location of each sampling station is shown in Fig. 1.

The distribution pattern of U concentrations across the marsh clearly shows that the level of U is governed by the intrusion of water from the Odiel river which transports radioactivity released by the industries. Thus, probably during high tide, contaminated Odiel riverwater invades the marsh through the north of Bacuta island (see Fig. 1). Most of this water flows into the Mojarrera channel which seems to be the main sink for such contamination (levels of U above 20 and 15 μg/g for the total and the fine fractions, respectively). Part of this contaminated water flows into the Estero de Cajarias, to give U concentrations of 12 μg/g at the northwest of the Enmedio island, decreasing downstream the Chate channel and the Punta Umbria channel, to 3 μg/g southwest of Saltés island, for both fractions. Contamination is also clearly observed at the Odiel river margin of the Marsh, with U concentrations ranging from 11.5 to 35 μg/g in the total fraction and from 15 to 52 μg/g in the fine fraction. The highest concentration in both fractions was found at a location on the east side of Saltés island. This station is located very close to the confluence of the rivers Odiel and Tinto. Thus, the mixing of both riverwaters could produce a high deposition of contaminants at this location compared to those stations beside. The contamination is clear if we compare the values with typical U concentrations in uncontaminated soils, normally ranging 2–3 μg/g (UNSCEAR, 1988).

Table 2. Results obtained in the analysis of U and Th isotopes (μg/g) in the fine fraction of soils collected across the Odiel wet marshland

| Code	U	Th	Th/U	$^{234}U/^{238}U$	$^{230}Th/^{234}U$	$^{230}Th/^{232}Th$
F14	17.8 ± 0.9	6.17 ± 0.59	0.347 ± 0.037	1.072 ± 0.039	0.947 ± 0.069	8.9 ± 0.8
F4	21.6 ± 1.0	6.21 ± 0.31	0.288 ± 0.020	1.091 ± 0.040	0.713 ± 0.039	8.24 ± 0.35
F6	15.7 ± 0.6	5.62 ± 0.57	0.358 ± 0.038	1.030 ± 0.028	1.139 ± 0.074	10.0 ± 0.9
F15	17.1 ± 0.9	8.06 ± 0.93	0.471 ± 0.060	1.091 ± 0.039	1.143 ± 0.092	8.1 ± 0.9
F11	16.2 ± 0.7	8.12 ± 0.38	0.501 ± 0.032	1.073 ± 0.026	0.499 ± 0.029	3.26 ± 0.11
F12	51.6 ± 2.2	12.7 ± 1.3	0.246 ± 0.027	1.031 ± 0.028	0.797 ± 0.063	10.2 ± 0.9
F13	15.2 ± 0.6	12.0 ± 0.7	0.789 ± 0.056	1.132 ± 0.027	0.820 ± 0.051	3.58 ± 0.17
F3	6.91 ± 0.38	5.49 ± 0.52	0.794 ± 0.087	1.219 ± 0.054	0.938 ± 0.076	4.39 ± 0.40
F5	6.42 ± 0.31	6.04 ± 0.46	0.939 ± 0.085	1.145 ± 0.045	0.955 ± 0.70	3.55 ± 0.25
F7	7.74 ± 0.39	6.82 ± 0.32	0.881 ± 0.061	1.138 ± 0.040	0.329 ± 0.022	1.30 ± 0.05
F8	9.33 ± 0.44	5.39 ± 0.37	0.578 ± 0.048	1.134 ± 0.032	0.265 ± 0.021	1.59 ± 0.10
F9	7.81 ± 0.35	7.62 ± 0.57	0.976 ± 0.085	1.151 ± 0.035	0.395 ± 0.032	1.42 ± 0.11
F10	3.02 ± 0.15	7.72 ± 0.56	2.56 ± 0.23	1.203 ± 0.052	0.751 ± 0.065	1.08 ± 0.07
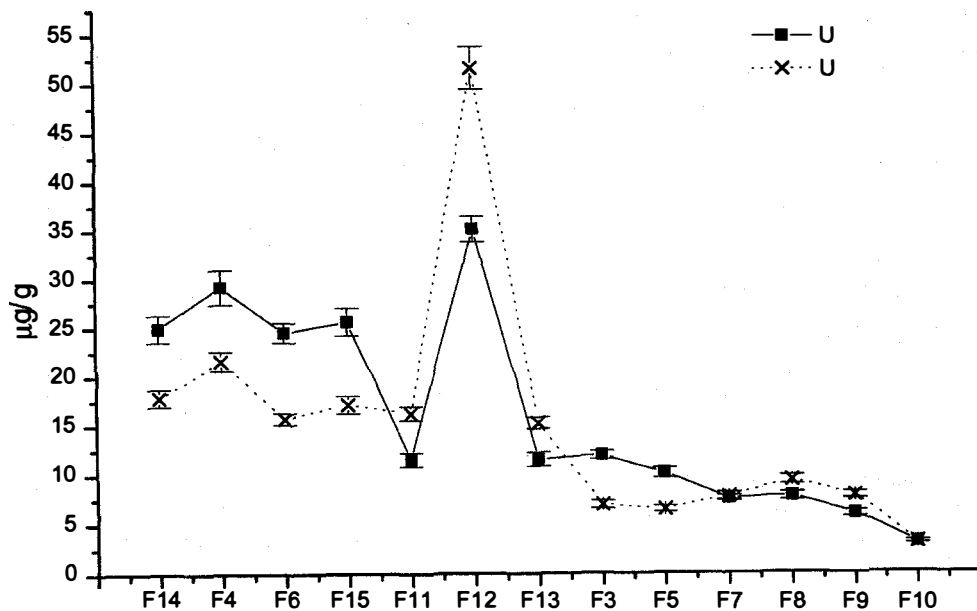
Fig. 2. Distribution of U (μg/g) in the total soil fraction (solid rule) and the fine particle fraction (dashed rule).

Is it interesting to compare the results obtained in the total soil fraction with those in the fine particle fraction, these data are shown in Fig. 2. The pattern of contamination is quite similar for both fractions.

In fact, the conclusions found above are the same in both cases. It is also possible to make some other remarks. If we consider, first, only those stations with clear enhancement, which means locations in the
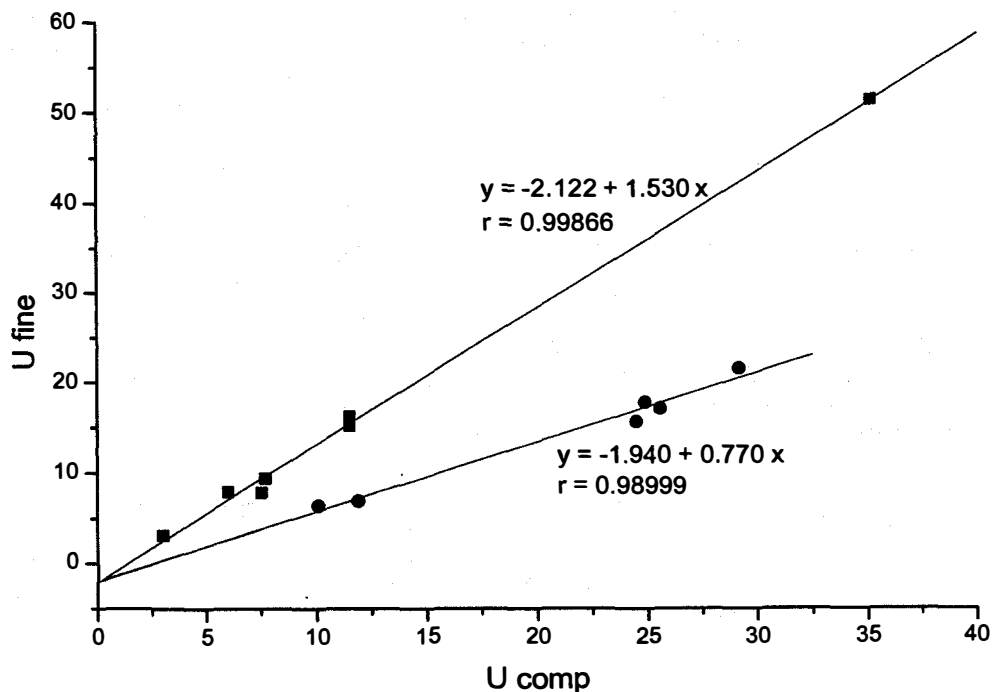

Fig. 3. U concentrations in μg/g in the fine particle fraction vs the U concentrations in μg/g in the total soil fraction. The lower line contains concentrations in samples collected along the Mojarrera and Chate channel (with U concentration higher in the fine fraction than in the total soil) and the upper line those samples collected along the Odiel and Punta Umbria rivers (with U concentrations higher in the total soil sample than in the fine fraction).

Mojarrera channel, west of Enmedio island and east of Saltés island, we observe two different pattern distributions. There are stations which have higher U concentrations in the total fraction than in the fine fraction and stations with the opposite situation. Those stations with lower concentrations in the fine fraction are located along the Mojarrera channel and east of Enmedio island. Presumably, these locations farther away from the industries would be less affected by the arrival of contaminated suspended particles. Thus, precipitation and/or ion-exchange between solution and soil would be favoured at the locations with enhanced concentrations which could lead to lower or similar concentrations in the fine fraction than in the total soil fraction. However, in those stations at the east of Saltés island, which are also clearly contaminated, the concentration in the fine particle fraction is higher than that of the total soil. It follows that a certain amount of the contaminated particles released from the factory has probably been deposited in this zone. The difference between both situations can be observed in Fig. 3. In this figure the U concentrations in the fine fraction have been plotted vs the U concentration in the total soil. As can be seen, the data in this figure can be grouped along two lines, with regression coefficients of 0.9987 and 0.9911, respectively. The upper line contains samples located at the Odiel river margin together with those presumably uncontaminated and the lower line those located along the Mojarrera and Chate channels. At the zero intercepts with the y axis, the slope of these lines would represent the constant value of the ratio between the U concentration in the fine fraction and that in the total soil for each zone

respectively. In both cases the y intercept is slightly below zero (-2.122 ± 0.544 and -1.940 ± 1.22, respectively) and slopes are 1.53 ± 0.04 for samples at the Odiel margin and 0.77 ± 0.06 for samples in the Mojarrera and Chate channels.

The second column of Tables 1 and 2, shows the concentrations of Th in $\mu g/g$ for the total soil and the fine fraction, respectively. The range of Th concentrations is not as wide as that for U, being wider in the case of the fine fraction. Thus, Th concentrations ranging from 4.2 to 8.7 $\mu g/g$ in the total soil and from 5.4 to 12.7 $\mu g/g$ in the fine samples are found. In both cases, as was found for U, the higher Th concentrations are found on the east side of Saltés island and the lowest along the Punta Umbria river. It seems clear than only stations in the eastern part of Saltés island are slightly enhanced by Th. However, all Th concentrations are similar to those typical for uncontaminated soils. If the Th contents in both analysis are compared (see Fig. 4), the concentration of Th in the fine particles samples is higher than that in the complete samples at locations on the east side of Saltés island, whereas in the rest, both seem to have the same Th content. This again could reflect that a certain amount of small particles, enhanced with natural radionuclides, are reaching the east of Saltés island, confirming the conclusions previously given for U.

It is also interesting to analyse the results of the Th/U mass ratios. As is well known, Th is highly reactive towards solid particles given Th/U mass about unity in the solid surface environment (Ivanovich and Harmon, 1982). If we consider the data on Th/U ratios in Tables 1 and 2, with the
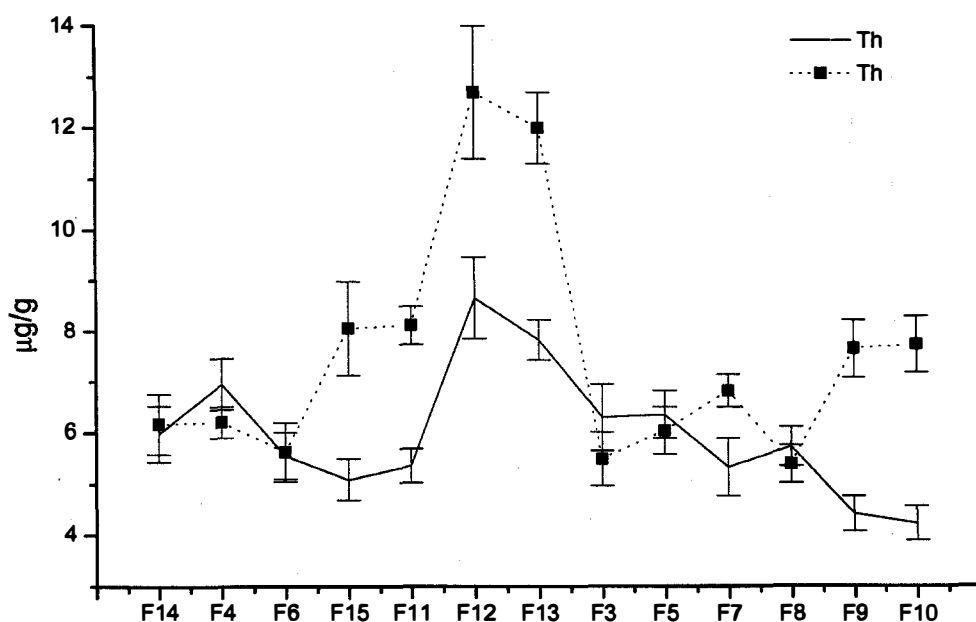

Fig. 4. Distribution of Th ($\mu g/g$) in the total soil fraction (solid rule) and the fine particle fraction (dashed rule).

exception of F10, all data reflect an excess of U compared to Th. However, the ratio is much lower in stations clearly contaminated, and is increased in samples along the Punta Umbria river. This fact reflects the contamination by U compared to Th, typical of the phosphate rock used for phosphoric acid production. The variation of this mass ratio with the U concentrations showed the same pattern for both fractions. Thus, in both fractions, total and fine, the Th/U mass ratio of a sample depends in the same way on the U concentration. The dependance of the Th/U mass ratio with the degree of contamination can be clearly observed in Fig. 5, where the Th/U mass ratio vs the U concentrations for the total soil and fine fractions has been plotted. Fitting them separately for both fractions, yields the same relationship:

$$Th/U = 4.22[U]^{-0.835}$$

with

$$r = -0.9258.$$

The $^{230}Th/^{234}U$ activity ratio, contrary to what could be expected, is much below unity in presumably uncontaminated stations and much closer to unity in stations clearly contaminated. Due to the higher Th association with the solid phases, a $^{230}Th/^{234}U$ activity ratio above unity would be expected at uncontaminated stations. However, we must keep in mind that this area is washed with marine waters from the Atlantic Ocean. As is well known, marine waters contain much more U in solution than ^{230}Th, giving $^{230}Th/^{234}U$ activity ratios much below unity. Because this area is of sedimentary origin with large amounts of organic compounds, radionuclides in solution would affect the soils by different exchange processes. This process would give the soils similar characteristics to the dissolved phase. As a consequence the $^{230}Th/^{234}U$ activity ratio is also much below unity. However, in clearly contaminated soils, because the processes are the same, the areas are highly affected by the industrial discharges, so the amount of ^{230}Th in solution is relatively much higher and will produce a much higher activity ratio in the washed soil. The difference in activity ratios in soils must be related to the possibility of capture of the ^{230}Th present in solution. In general, this activity ratio is higher in the fine particle fraction than in the complete sample, which reflects the effect of the waters in the soils. The influence that isotopic activities in water have over the soil can also be observed in the $^{234}U/^{238}U$ activity ratios of the soil. Most samples present both isotopes in equilibrium or in a slight excess of the daughter typical of waters.

Contamination from the phosphoric acid industry is also observed in the $^{230}Th/^{232}Th$ activity ratios (see column 6 of Table 1 and Table 2). These ratios show similar values in the complete sample and the fine fraction being, however, much higher in those stations with clearly enhanced radioactivity than in those uncontaminated, due again to a higher presence of ^{230}Th in the wastes from the industries.
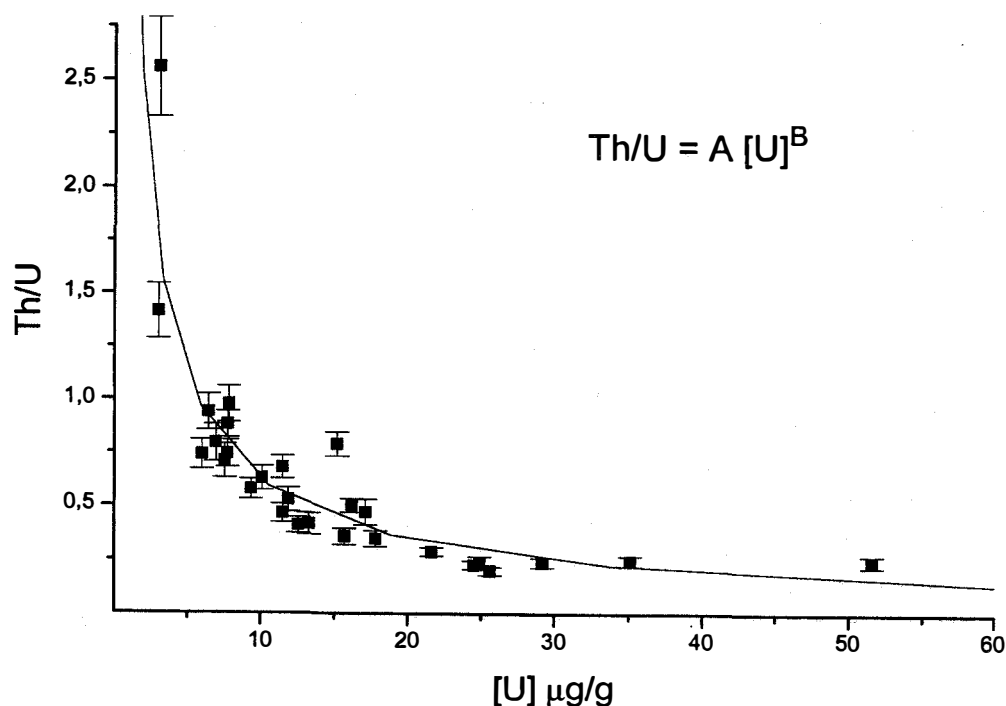

Fig. 5. Th/U mass ratio vs the U concentration in both fractions of soils. A = 4.22 ± 0.32 and B = − 0.835 ± 0.067 with a regression coefficient of the log/log linear relationship of − 0.9258.

Conclusions

The study has shown that certain areas of the Odiel marsh are clearly affected by the waste releases from the phosphoric acid production factory into the Odiel river. The enhancement is produced by the inflow of contaminated Odiel riverwaters into the marsh. Comparison of the U and Th concentrations between the fine particle fraction (≤ 63 μm) and the total soil fraction has given some hints on the ways in which this contamination takes place.

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