Sedimentary speciation of U and Th isotopes in a marsh area at the southwest of Spain

A. Martínez-Aguirre, R. Periáñez

Departament Física Aplicada, EUITA, Universidad de Sevilla, Ctra. Utrera km 1, 41013 Sevilla, Spain

A study of the distribution of U and Th-isotopes in different fractions of intertidal sediments collected in a marsh area has been carried out. This marsh area is affected by the releases of natural radionuclides from fertilizer industries carried out into the Odiel river. The study has shown that uranium is mainly located in non-residual fractions of the sediments and particularly coprecipitated with amorphous ferromanganese oxyhydroxides. In the case of Th isotopes, the contribution of residual fractions is higher than that of non-residual fractions, being the main non-residual fraction again the amourphous ferromanganese oxyhydroxides. However, all fractions seems to reflect the same pattern of contamination. Thus, those sediments located along the Odiel river basin have the higher concentration in all sequentially extracted fractions. Some interesting activity and mass ratios have also been investigated.

Introduction

One of the fundamental distinctions in sedimentary geochemistry is that between the lattice-held (i.e., residual) and non-lattice-held (i.e., non-residual) fractions of a sediment. Elements located in lattice sites can be considered to be environmentally immobile, whereas those in non-lattice sites can be considered potentially mobile, i.e., enviromentally reactive, in the chemical and biological processes which occur in the sediment/interstitial water complex.[1] Thus, the knowledge of the distribution of enhanced radionuclides in several sediments from a contaminated area will allow to predict the future movements of these radionuclides and thus, the enhancement of the waters in close contact with them.

During the last years, several studies have been carried out about radionuclide speciation in sediment/soil fractions. Some of them were centered in artificial radionuclides, mostly in the case of those released by Sellafield reprocessing plant[2] and some others about natural radionuclides in river sediments or rocks.[3–5] The aim of these studies was mainly to evaluate the mobility of these radionuclides in the solid matrix and their incorporation from the liquid phase in contact with the solid.

The fertilizer factory complex located at the city of Huelva (southwest of Spain) has been releasing during the last decades solid and liquid wastes into the estuarine area of the Odiel river. These wastes contain large amounts of natural radionuclides, which has been the cause of high activity concentrations found in river waters and bottom sediments.[6] Moreover, the movements of the water due to tidal changes have also produced the contamination of certain areas of the Odiel marshland at the right bank of the Odiel river. The specific location of these radionuclides in the sediments may produce future contamination of the river and salt water species whenever the releases stops.

In a previous paper[7] the chemical speciation of uranium isotopes in sequentially extracted fractions of intertidal sediments collected from the Odiel marsh (southwest Spain) was presented. It was found that coprecipitation with amorphous ferromanganese oxyhydroxides is the main process of incorporation of U isotopes from the water column to the sediment. This means that the U-isotopes have been incorporated to the sediments from the water column (they were previously in solution) and if any pH changes occurs in the waters, they would presumably redissolved from the sediments and move into the solution.

The objective of this work is to present the results obtained in the analysis of Th-isotopes in the same sediment samples in which U has been measured and to compare the U and Th behavior in the several sequentially extracted fractions. The aim of this study is to evaluate the future mobility and incorporation of these radionuclides to the liquid phase in contact with them.

Experimental

Samples and radiochemical procedures

Sampling was carried out in February 1993. Several stations were selected across the Odiel marsh (Fig. 1), which is clearly affected by the inflow of the Odiel river waters. Sediment samples were collected during the low tide at the border of the channel, in areas covered with water during the high tide. At the laboratory, sediment samples were dried and powdered before the analysis. The bulk dry density ($g \cdot cm^{-3}$) and percentage of organic matter were determined in each sediment sample and they are given in Reference 6. The chemical methods used to sequentially extract five sediment fractions are those given by Ivanovich[8] and modified following Crespo.[5]
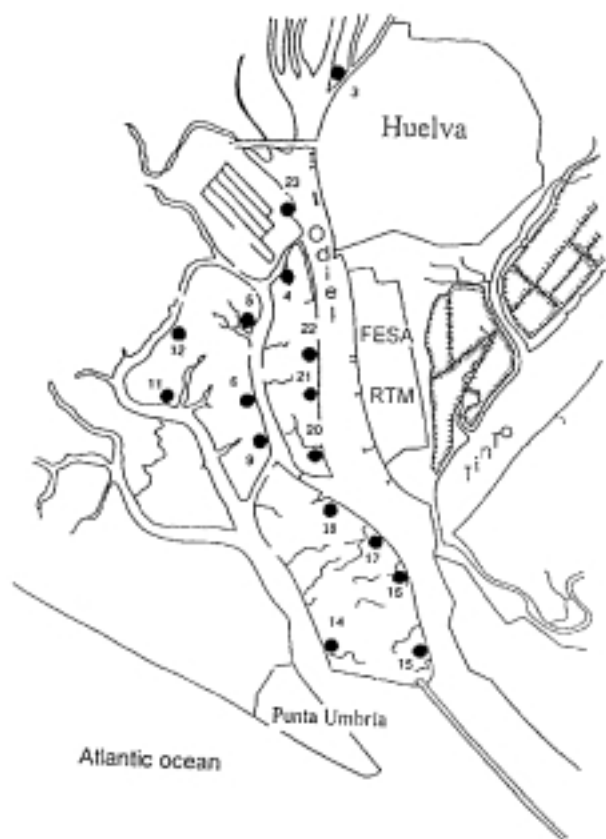
Fig. 1. Location of the sampling stations in the Odiel marsh area
at the Southwest of Spain

F1 = U/Th within carbonates: the original sediment sample is shaken for 6 h in 1M sodium acetate adjusted to pH 5.0 with acetic acid. The supernatant is reserved for the analysis.[9]

F2 = U/Th adsorbed (usually humic material and/or amorphous oxides): the residue from the previous extraction is shaken for 1 hour in 0.1M sodium pyrophosphate solution adjusted to pH 9.8 with 0.1M NaOH. The supernatant is reserved for the analysis.[8]

F3 = U/Th coprecipited with amorphous Fe and Mn oxyhydroxides: the residue from the previous extraction is shaken for 4 hours in the dark in Tamm's acid oxalate (0.2M ammonium oxalate and 0.2 oxalic acid).[10] The supernatant is reserved for the analysis.

F4 = U/Th within crystalline Fe and Mn oxides: the residue from the previous extraction is shaken for 1 hour in Coffin's reagent (0.175M sodium citrate and 0.025M citric acid).[11]

F5 = U/Th within primary minerals and clays = resistant phase

Fractions F1–F3 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/sediment interaction and exchange processes or part of the solid capable of direct interaction with water and thus sharing some geochemical and isotopic characteristics with the liquid phase. Fractions F4 and F5 are defined as residual phases and are not expected to interact on a short time-scale with the liquid phase under normal environmental conditions and thus, taking relatively minor part in direct interactions on medium to short timescales. The resistant fraction (F5) has been obtained by the sustraction between the total concentration[6] in the sediment and the addition of those in each sequentially extracted fraction.

Once the fractions were separated, the supernatant were spiked with well known activities of ^{232}U and ^{229}Th and an anion-exchangeable resin method (Dowex AG1-X8 chloride form) was used for U and Th-isotopes separation and purification.[6] Once separated and purified, electroplating onto stainless steel planchets was carried out. The planchets were finally counted by α-spectrometry with ion implanted detectors.

Results and discussion

In Table 1, the uranium concentrations in ppm and the ^{230}Th and ^{232}Th activity concentrations in mBq/g in each fraction for all studied samples are given. As said above, the concentrations in fraction F5 have been obtained by the difference between the total concentration in the sample[6] and that in all sequentially extracted fractions. The numbers in parentheses are the percentage of the total concentration contained in each fraction. The last six columns of the table give the percentage of the total concentration associated with non-residual (F1+F2+F3) and residual (F4+F5) fractions, respectively.

As can be seen from the table, U is mainly associated with the non-residual fractions of the sediments, particularly with fraction F3. With exception of samples M12 and M14, collected along the Punta Umbria river, 45% or more of the total U is associated with fraction F3. This fact implies that the main process by which U has been incorporated into the sediment is the coprecipitation with amorphous ferromanganese oxyhydroxides. Of the two other non-residual fractions, the carbonate fraction (F1) contribute more (range 12–26%) to the total U in the sediment than the absorbed fraction (F2) (range 1–14%). In samples M12 and M14, the U seems to be equally distributed between fractions F1 and F3, with about 30–40% of the total. For all samples the U concentration in the non-residual fraction (F1+F2+F3) is well above 70% of the total U in the sediment.

Table 1. Uranium concentrations (in ppm) and ^{230}Th and ^{232}Th activities (in mBq/g in each fraction of the sediment samples

Code	F1 U, ppm	F1 ^{230}Th	F1 ^{232}Th	F2 U, ppm	F2 ^{230}Th	F2 ^{232}Th	F3 U, ppm	F3 ^{230}Th	F3 ^{232}Th
M3	7.7±0.5 (3.6)	0.62±0.07 (0.1)	0.18±0.03 (0.1)	4.6±0.4 (7.8)	18.2±1.2 (2.0)	1.8±0.2 (1.7)	44.5±2.8 (77.4)	450±30 (50.1)	47.2±5.2 (45.8)
M23	3.9±0.2 (20.1)	0.37±0.06 (0.2)	0.10±0.03 (0.2)	2.9±0.2 (14.1)	4.9±0.3 (2.2)	1.3±0.1 (3.1)	10.8±0.6 (54.7)	114±9 (52.8)	23.2±2.5 (56.0)
M4	5.6±0.3 (12.2)	0.37±0.05 (0.7)	0.013±0.007 (0.2)	3.8±1.4 (8.6)	8.5±0.6 (1.6)	0.8±0.1 (1.3)	31.9±1.1 (71.2)	354±21 (66.4)	28.2±2.5 (46.2)
M22	0.63±0.05 (21.6)	0.22±0.04 (1.3)	0.072±0.025 (0.7)	0.29±0.04 (11.1)	0.66±0.08 (4.1)	0.21±0.04 (1.8)	0.69±0.04 (45.5)	5.6±0.4 (34.8)	2.6±0.2 (21.9)
M21	0.39±0.04 (25.4)	0.27±0.04 (3.0)	0.025±0.011 (0.5)	0.023±0.006 (1.3)	0.06±0.03 (1.1)	0.012±0.008 (0.2)	0.04±0.04 (45.5)	3.1±0.3 (35.0)	1.1±0.2 (23.3)
M20	3.5±0.2 (16.6)	0.27±0.04 (0.1)	0.051±0.017 (0.1)	2.4±0.1 (11.0)	5.3±0.3 (2.1)	1.4±0.1 (3.1)	12.2±0.4 (54.9)	128±10 (50.0)	15.9±1.3 (36.0)
M18	9.0±0.7 (19.2)	0.40±0.08 (0.1)	0.06±0.013 (0.2)	2.9±0.8 (5.6)	11.1±0.9 (2.5)	1.6±0.2 (2.9)	27.9±2.5 (58.7)	218±23 (49.2)	22.0±2.4 (39.0)
M16	5.7±0.4 (14.8)	0.37±0.06 (0.1)	0.061±0.020 (0.1)	4.2±0.9 (9.6)	6.4±0.7 (1.2)	0.99±0.09 (1.5)	25.4±0.8 (64.3)	182±10 (32.9)	22.9±1.7 (33.6)
M15	1.3±0.1 (17.5)	0.38±0.05 (0.4)	0.035±0.012 (0.2)	0.56±0.17 (7.0)	2.3±0.3 (2.6)	0.50±0.10 (2.9)	4.8±0.2 (61.3)	43±2 (49.0)	6.2±0.4 (36.3)
M5	2.7±0.2 (14.7)	0.30±0.04 (0.1)	0.051±0.016 (0.1)	2.1±0.2 (10.7)	3.8±0.3 (1.8)	0.76±0.10 (1.8)	12.2±0.5 (67.1)	73±20 (35.2)	13.6±0.5 (33.0)
M6	2.2±0.1 (18.3)	0.34±0.05 (0.3)	0.06±0.022 (0.3)	1.2±0.1 (10.1)	4.5±0.4 (4.3)	0.86±0.12 (2.8)	5.8±0.2 (47.0)	71±3 (68.3)	13.3±0.8 (42.9)
M9	2.1±0.1 (19.2)	0.37±0.05 (0.4)	0.068±0.018 (0.2)	1.3±0.1 (12.5)	2.2±0.2 (2.2)	0.55±0.09 (2.3)	5.9±0.2 (57.4)	61±4 (60.4)	11.4±1.0 (46.7)
M11	1.8±0.1 (26.1)	0.35±0.05 (0.5)	0.038±0.013 (0.2)	0.66±0.05 (9.7)	4.5±0.4 (6.4)	0.68±0.03 (3.1)	3.6±0.1 (53.1)	48±3 (67.7)	12.2±1.1 (55.5)
M12	1.1±0.1 (31.1)	0.37±0.06 (1.5)	0.172±0.04 (0.6)	0.49±0.04 (13.7)	2.8±0.2 (9.9)	1.8±0.2 (6.6)	1.15±0.05 (31.1)	13.9±0.6 (49.4)	10.3±0.5 (38.6)
M14	1.2±0.1 (38.6)	1.1±0.1 (2.6)	0.10±0.04 (0.9)	0.42±0.09 (12.9)	4.4±0.3 (10.3)	1.1±0.1 (5.1)	1.21±0.06 (33.4)	22±1 (51.6)	8.0±0.3 (35.7)

Code	F4 U, ppm	F4 ^{230}Th	F4 ^{232}Th	F5 U, ppm	F5 ^{230}Th	F5 ^{232}Th	U, % NR	U, % R	^{230}Th, % NR	^{230}Th, % R	^{232}Th, % NR	^{232}Th, % R
M3	0.71±0.06 (1.4)	76.3±4.0 (8.5)	8.5±0.6 (3.2)	1.18±... (2.0)	353±47 (39.3)	45.5±7.2 (44.2)	98.7	3.4	52.4	47.8	47.6	52.4
M23	0.82±0.03 (4.0)	22.0±1.0 (10.2)	3.8±0.3 (9.3)	1.4±0.91 (7.1)	75±16 (34.6)	13±4 (31.4)	88.9	11.1	55.2	44.8	59.3	40.7
M4	0.68±0.09 (1.8)	47.9±2.1 (9.0)	5.1±0.4 (8.3)	2.7±1.2 (6.2)	119±33 (22.3)	26.9±4.7 (44.0)	92.0	8.0	68.7	31.3	47.7	52.3
M22	0.19±0.02 (7.9)	3.1±0.2 (9.4)	1.8±1.1 (14.9)	0.40±0.15 (15.4)	6.5±1.0 (40.4)	7.2±0.8 (60.7)	76.8	23.3	40.2	59.8	24.4	75.6
M21	0.08±0.01 (7.0)	1.3±0.1 (4.7)	0.65±0.09 (13.2)	0.18±0.08 (12.6)	4.1±0.6 (46.2)	3.1±0.4 (62.8)	72.2	19.5	39.1	60.9	24.0	76.0
M20	0.30±0.02 (1.5)	3.8±0.3 (8.6)	3.8±0.3 (8.6)	3.2±0.9 (15.5)	99±19 (38.7)	23.0±3.8 (52.2)	83.0	17.0	52.2	47.8	39.2	60.8
M18	0.46±0.03 (1.0)	23.4±1.0 (9.1)	6.3±0.4 (11.2)	7.5±3.2 (15.5)	160±32 (36.1)	26.3±4.5 (46.7)	83.5	16.5	51.8	48.2	42.1	57.9
M16	0.52±0.04 (1.4)	53.4±2.2 (12.1)	8.8±0.4 (12.9)	4.1±2.0 (10.0)	290±25 (54.0)	35.3±4.8 (51.9)	88.7	11.3	34.2	65.8	35.2	64.8
M15	0.13±0.01 (1.5)	15.8±0.8 (18.1)	2.1±0.2 (12.3)	0.97±0.42 (12.8)	26.1±5.1 (29.9)	8.3±1.2 (48.3)	85.7	14.3	52.0	48.0	39.4	60.6
M5	0.98±0.06 (5.4)	20.2±1.2 (9.7)	4.2±0.4 (10.2)	0.45±0.9 (2.2)	111±23 (51.2)	22.6±5.8 (54.9)	92.5	7.6	37.1	62.9	34.9	65.1
M6	0.23±0.02 (2.1)	12.7±0.5 (12.2)	3.2±0.2 (10.3)	2.7±0.6 (22.5)	15.5±5.9 (14.9)	14±2 (45.7)	75.4	24.6	72.9	27.1	46.0	54.0
M9	0.30±0.02 (3.3)	15.0±0.6 (14.9)	3.2±0.2 (13.0)	0.8±1.5 (9.9)	22.3±6.4 (22.1)	9.2±1.9 (37.8)	89.0	11.0	63.0	37.0	49.2	50.8
M11	0.14±0.01 (4.2)	9.9±0.5 (13.9)	2.4±0.2 (11.0)	0.4±0.3 (6.8)	8.2±4.8 (11.5)	6.6±1.8 (30.2)	89.0	11.1	74.6	25.4	58.8	41.2
M12	0.17±0.01 (5.4)	3.1±0.3 (10.9)	2.0±0.2 (7.3)	0.68±0.16 (18.7)	4.7±1.8 (16.8)	12.5±1.7 (46.9)	75.9	24.1	60.6	39.4	45.8	54.2
M14	0.10±0.01 (5.4)	3.2±0.2 (7.4)	1.5±0.2 (6.7)	0.30±0.19 (9.7)	12.0±2.8 (28.1)	11.0±1.6 (51.6)	84.9	15.1	64.5	35.5	41.7	58.3

Numbers in parenthesis give the percentage of the total concentration contained in each fraction. The last six columns give the percentage of the total concentration contained in the residual (R) and non residual (NR) fractions.

Table 2. Activity ratios for fractions F1, F2, F3 and F4

Code	$^{234}U/^{238}U$	F1 $^{230}Th/^{234}U$	$^{230}Th/^{232}Th$	$^{234}U/^{238}U$	F2 $^{230}Th/^{234}U$	$^{230}Th/^{232}Th$	$^{234}U/^{238}U$	F3 $^{230}Th/^{234}U$	$^{230}Th/^{232}Th$	$^{234}U/^{238}U$	F4 $^{230}Th/^{234}U$	$^{230}Th/^{232}Th$
M3	1.073±0.028	0.096±0.001	3.5±0.7	1.035±0.039	0.313±0.036	10.2±0.9	1.059±0.027	0.775±0.071	2.8±0.3	1.198±0.089	7.3±0.7	9.0±0.6
M23	1.189±0.041	0.007±0.001	3.9±1.2	1.105±0.039	0.122±0.013	3.8±0.4	1.150±0.042	0.749±0.071	4.9±0.5	1.121±0.035	1.9±0.1	5.8±0.5
M4	1.043±0.028	0.005±0.001	25±3	1.000±0.049	0.166±0.021	10.3±1.3	1.077±0.011	0.835±0.057	12.5±1.9	1.297±0.170	4.4±0.6	9.4±0.6
M22	1.031±0.062	0.027±0.006	2.8±1.0	1.213±0.167	0.153±0.027	3.1±0.7	1.084±0.065	0.343±0.030	2.2±0.2	1.216±0.148	1.07±0.13	1.8±0.2
M21	1.014±0.117	0.054±0.010	10.4±4.9	0.87±0.12	0.38±0.15	8±6	1.030±0.074	0.351±0.045	2.7±0.5	1.38±0.15	0.96±0.12	2.0±0.3
M20	1.090±0.041	0.006±0.001	5.3±1.9	1.005±0.039	0.164±0.014	3.9±0.4	1.028±0.039	0.824±0.094	8.1±0.9	1.116±0.061	5.7±0.4	8.2±0.4
M18	1.068±0.024	0.004±0.001	5.0±1.8	1.126±0.059	0.228±0.019	6.8±1.1	1.075±0.017	0.589±0.081	9.9±0.4	1.12±0.07	8.3±0.6	8.5±0.4
M16	1.103±0.027	0.005±0.001	7.3±3.0	1.043±0.064	0.068±0.012	6.5±1.4	1.072±0.018	0.542±0.035	7.9±0.5	1.14±0.08	8.8±0.7	7.4±0.3
M15	1.064±0.045	0.021±0.003	11±4	1.026±0.035	0.207±0.025	4.6±1.0	1.042±0.035	0.442±0.12	6.9±0.4	0.95±0.11	16.5±1.8	7.5±0.5
M5	1.097±0.045	0.008±0.001	5.7±1.9	1.036±0.055	0.140±0.018	4.9±0.6	1.110±0.020	0.44±0.12	5.4±1.8	1.179±0.053	1.53±0.13	4.9±0.4
M6	1.088±0.045	0.012±0.002	4.0±1.1	1.062±0.072	0.277±0.035	5.1±0.7	1.049±0.025	0.94±0.05	5.4±0.4	1.17±0.10	3.8±0.3	4.0±0.2
M9	1.073±0.045	0.014±0.002	6.4±2.1	1.111±0.063	0.125±0.015	4.0±0.6	1.121±0.063	0.75±0.06	5.4±0.4	1.212±0.083	3.4±0.3	4.8±0.3
M11	1.010±0.053	0.015±0.002	9.2±3.5	1.157±0.080	0.54±0.06	6.3±1.0	1.05±0.22	1.04±0.08	3.9±0.3	2.04±0.22	2.7±0.3	4.1±0.4
M12	1.080±0.066	0.023±0.004	2.2±0.6	1.097±0.075	0.42±0.05	1.6±0.2	1.051±0.049	0.94±0.06	1.35±0.06	1.22±0.10	1.89±0.3	1.65±0.2
M14	1.111±0.072	0.067±0.008	5.8±1.3	1.101±0.086	0.77±0.09	3.9±0.4	0.981±0.051	1.51±0.09	2.8±0.1	1.92±0.23	1.33±0.15	2.1±0.2

In Fig. 2, the U concentrations (ppm) in all samples have been plotted for the three non-residual fractions. The distribution pattern is the same for all them, with maximum of concentration in samples M3, M4, M16 and M18 and minimal in samples M21, M22, M12 and M14. Relative maxima are also found in samples M23, M20 and M5. The main conclusion is that all samples collected along the Odiel river bank (M3 to M15, Fig. 1) have higher U concentration in all non-residual fraction. The exception of samples M15, M21 and M22 must be related with their much higher content of sandy particles which is reflected in their much lower organic content (1–5%) in compare with the rest of samples (above 10%). Minima concentration in samples M12 and M14 could be related to their location, far away from the industries. Thus, they are presumably non contaminated.

Both residual fractions contribute much less to the total U in the sediments, fraction F4 below 8% and the contribution of fraction F5 is similar to that in fraction F1, up to 20% in same cases. In general, the contribution of the residual fraction (F4+F5) is in all cases under 25%. Furthermore, we should resalt samples M3 and M4, with the higher U concentrations, in which only 3 and 8% of the total U is in the residual fraction. Thus, most of their U concentration may be removed from the sediment into the water column if any environmental change occurs in the system.

For comparison, the percentage distribution of U in samples M3 and M12 is presented in Fig. 3. Sample M3 shows the typical distribution in contaminated samples whereas sample M12 shows the distribution in non contaminated samples.

In Table 2, the activity concentration of ^{230}Th for all samples in each extrated fraction is also presented. As can be seen from all non-residual fractions, ^{230}Th is mainly associated with fraction F3, ranging from 33 to 68%.
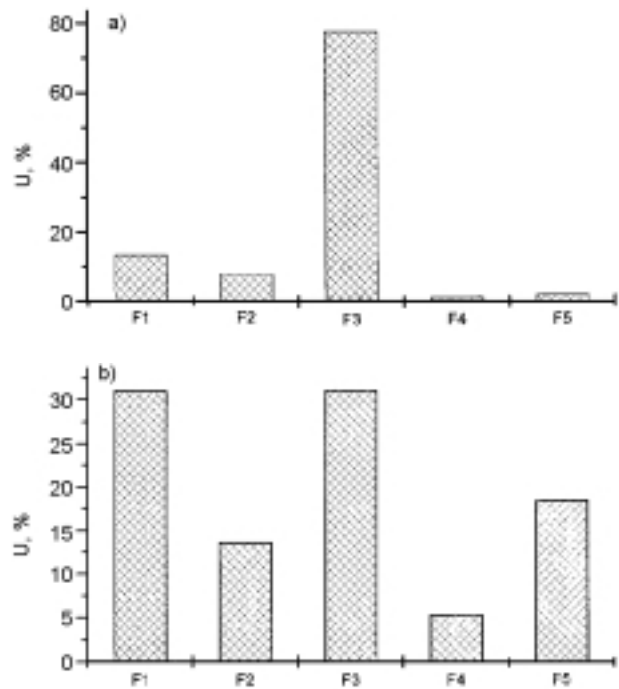

Fig. 3. Percentage of U distribution in sequentially extracted fractions of sediment samples M3 (a) and M12 (b)

This implies that as in the case of U-isotopes, the main process by which ^{230}Th is incorporated to the sediments is coprecipitation with amorphous ferromanganese oxyhydroxides, which is a typical process in estuarine environments.[12] For the other two non-residual fractions, the carbonate fraction (F1) does not contribute significantly (below 3%) to the ^{230}Th in the sediment and the absorbed fraction (F2) contributes in most cases much less than 10%. The clearest difference between U and ^{230}Th is the much higher contribution of the latter to the residual fractions (F4+F5) of the sediments. Whereas less than 25% of U was found between these two phases, most sediments contain more than 25% of ^{230}Th in residual fractions (Table 2). In fact, in several samples the contribution of the residual fraction to the total concentration is higher than the contribution of the non-residual fractions, opposite to what was found in the case of U. From both fractions, the crystalline Fe and Mn oxide fractions (range 7–19%) contribute much less than the resistate one (above 15%).

In Fig. 4, percentages of ^{230}Th distribution in samples M3 and M21 are presented. For ^{230}Th the pattern distribution between fractions is similar for contaminated and non contaminated samples (as in sample M3). However, the distributions seems to be slightly different for samples M21 and M22, which seems to have higher content of sandy particles.
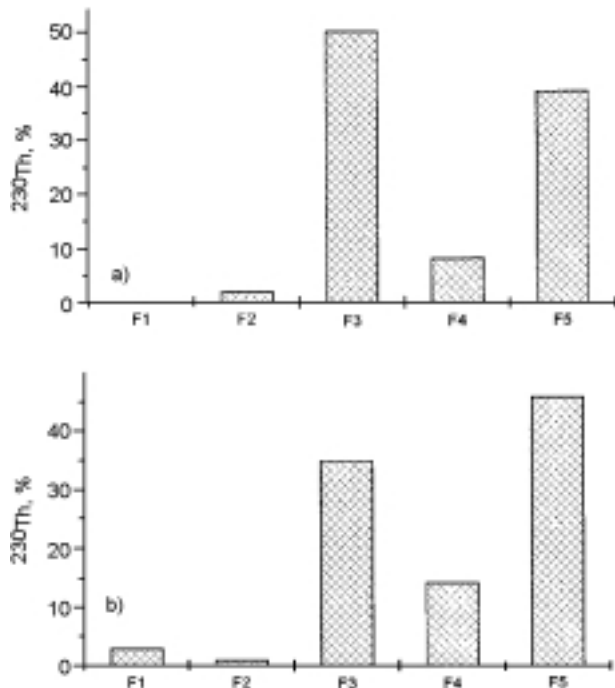

Fig. 2. U concentration in ppm in fractions F1 (black square), F2 (open circle) and F3 (open square) of intertidal sediments collected at the Odiel marsh. The error bars are 1σ due to counting statistics

Fig. 4. Percentage of ^{230}Th distribution in sequentially extracted fractions of sediment samples M3 (a) and M21 (b)
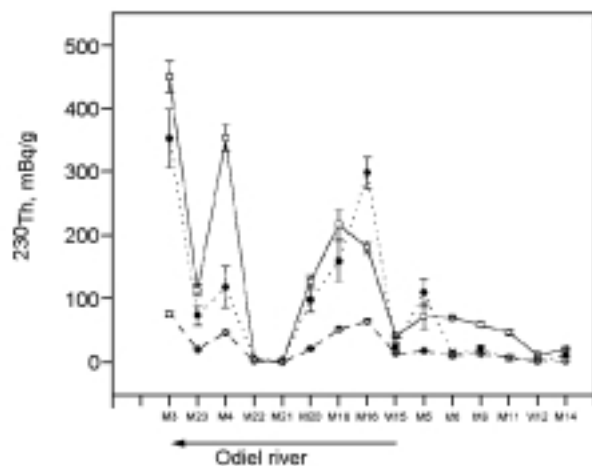

Fig. 5. ^{230}Th concentrations in mBq/g in fractions F3 (open square), F4 (open circle) and F5 (black circle) of intertidal sediments from the Odiel marsh

In Fig. 5, ^{230}Th activity concentration has been plotted for fractions F3, F4 and F5. As can be seen, the pattern distribution of activity concentration is the same for all fractions. Thus, as in the case of U, there are maxima of concentration in samples M3, M4, M18 and M16 and minima in samples M21, M22, M15 and in samples along the Punta Umbria river (M12 and M14).

Again, those samples along the Odiel river channel are clearly enhanced compared to other areas. The minimal concentrations in samples M21, M22 and M15, located along the Odiel channel, must again be related with their higher content of sandy particles.

The case of ^{232}Th is similar to that of ^{230}Th. From all non-residual fractions, coprecipitation with amorphous ferromanganese oxyhydroxides (range 33–56%) is the main process of ^{232}Th incorporation from the water column into the sediment. Exceptions are again samples M21 and M22 with about 20% of ^{232}Th in this fraction. Fractions F1 and F2 do not contribute significantly to the concentration in the total sediment, under 1% in fraction F1 and 7% in fraction F2. The main difference with ^{230}Th is that in those samples along the Odiel river channel the contribution of the residual ^{232}Th to the total concentration is generally similar or higher than the non-residual contribution. Only those samples with low organic content (higher content in sandy particles) the contribution of residual fractions to the total concentration is clearly higher than the non-residual contribution as can be seen in Fig. 6 where the distribution pattern for ^{232}Th in samples M3 and M21 is presented.
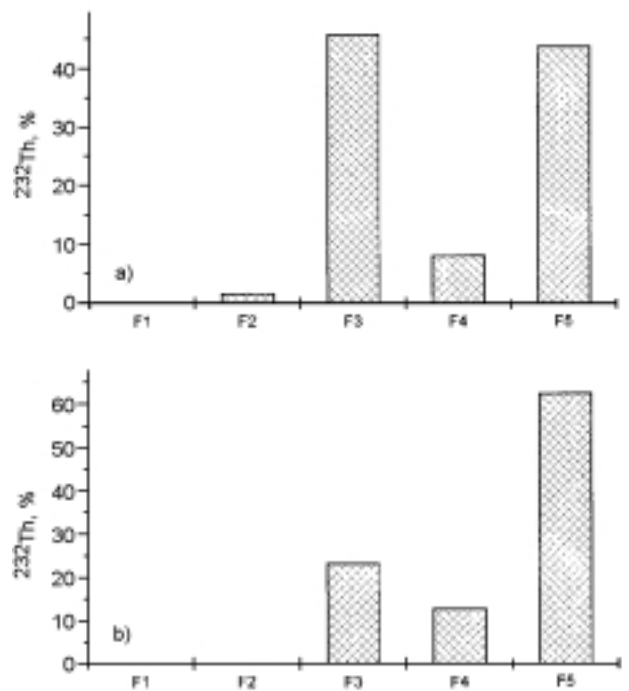

Fig. 6. Percentage of ^{232}Th distribution in sequentially extracted fractions of sediment samples M3 (a) and M21 (b)
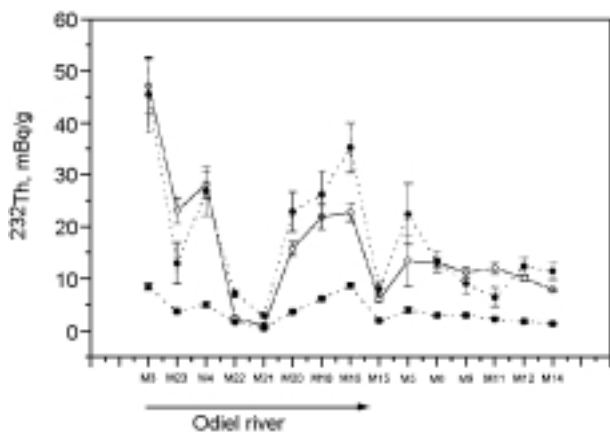
Fig. 7. ^{232}Th concentrations in mBq/g in fractions F3 (open circle), F4 (black square) and F5 (black circle) of intertidal sediments from the Odiel marsh

In Fig. 7, the ^{232}Th activity concentration has been plotted for fractions F3, F4 and F5. The distribution patterns are again the same as those obtained for U and ^{230}Th: maxima in samples M3, M4, M18 and M16 minima in samples M21 and M22. The explanation must be considered the same as that given above for U and ^{230}Th.

Some interesting activity or mass ratios have also been investigated and are presented in Table 2. They are not given for fraction F5 because of the large uncertainties which do not allow to see the differences between samples. From data of the ^{234}U/^{238}U activity ratios it can be seen that both isotopes are practically in secular equilibrium in all fractions, with no clear differences between fractions and samples. The non-residual fractions represent that part of the sediment which is in contact with the water. Thus, the ratios (~1) imply that both radionuclides are in secular equilibrium in the water column and, thus it can be concluded, since the typical ratio in river water ranges 1.2–1.3, that all the area is affected by the fertilizer production. Moreover, the ratios found in the residual fractions (also ~1) do not show the typical deficit in ^{234}U in soils and sediments.

The interaction of non-residual fractions with the liquid phase should be essentially reflected in the ^{230}Th/^{234}U activity ratios of these fractions. As it is well known, Th is a particularly insoluble element in natural waters and it is usually found associated to solid matter. Thus, the general deficit of this radionuclide in the water column should be reflected in fractions F1, F2 and F3. In fact, a clear ^{230}Th deficit has been found in all non-residual fractions. However, this ratio increases from fraction F1 to F3 in all samples and being generally higher in those samples collected further away from the industries, along the Punta Umbria river. As should be expected, this ratio is generally larger than unity in both residual fractions, showing a general excess of ^{230}Th in compare with ^{234}U.

All fractions of the sediments have the ^{230}Th/^{232}Th activity ratios well above unity, with not much differences between fractions and samples. This fact could be considered as a consequence of the release of U and daughters from the fertilizer factories. However, the activity ratio seems to be lower in samples M12 and M14 (far away from the industries) than in the rest of samples.

Conclusions

U and Th-isotope concentrations in several sequentially extracted fractions of intertidal sediments collected in a marsh area, clearly enhanced by the phosphoric acid production in the surroundings, have been studied. The residence of these radionuclides in the non-residual fractions of the sediments has been pointed out, with a preferential incorporation from the water column by coprecipitation with amorphous ferromanganese oxyhydroxides. However, the same pattern of contamination has been found for all radionuclides and in all fractions. This pattern shows, as expected, that all the Odiel river bank is enhanced by the fertilizer production. The main difference between U and Th isotopes is that the U is mainly associated to non-residual fractions (above 70%) whereas the contribution of residual Th is similar or even higher than the non-residual Th. Moreover, the residual contribution of ^{232}Th is generally higher than the residual ^{230}Th.

The main conclusion of this work is that the contamination from the fertilizer productions affects most areas of the Odiel Marsh as it can be observed in all fractions of the sediments, particularly in the case of the fractions precipitated with amorphous ferromanganese oxyhydroxides. The contamination is higher in the case of radionuclides from the ^{238}U decay chain, however a small contamination in ^{232}Th can be also observed. Furthermore, due to the localization of these radionuclides, a change in the environmental conditions of the waters may produce a future redissolution of the radionuclides from the sediments into the liquid phase.

References

1. R. CHESTER, S. R. ASTON, The partitioning of trace metals and transuranics in sediments, in: Techniques for Identifying Transuranics Speciation in Aquatic Enviroments, IAEA, Vienna, 1981, p. 173.
2. J. E. BROWN, P. MCDONALD, A. PARKER, J. E. RAE, Discharge Patterns of Radionuclides and the Influence of Early Diagenesis in a Saltmarsh of the Ribble Estuary, NW England. Radioprotection-Colloques 32, C2, 1997, p. 245.
3. A. J. PLATER, M. IVANOVICH, R. E. DUGDALE, Appl. Geochem., 7 (1992) 101.
4. A. MARTÌNEZ-AGUIRRE, M. GARCÍA-LEÓN, M. IVANOVICH, J. Environ. Radioact., 23 (1994) 231.
5. M. T. CRESPO, L. PÉREZ DEL VILLAR, A. JIMENEZ, M. PELAYO, A. QUEJIDO, M. SÁNCHEZ, Appl. Radiation Isotopes, 47 (1996) 927.
6. A. MARTÍNEZ-AGUIRRE, M. GARCÍA-LEÓN, J. Environ. Radioact., 34 (1977) 45.
7. A. MARTÍNEZ-AGUIRRE, R. PERIÁÑEZ, J. Environ. Radioact., 45 (1999) 67.
8. M. IVANOVICH, G. LONGWORTH, M. M. WILKINS, S. E. HASLER, M. J. LLOYS, Measurements of effective K_D factors for the long-lived uranium and thorium isotopes in samples of London Clay (Bradwell) and Mudrock (Fulbeck), Harwell Laboratory Report NSS-R117, 1988. Nuclear Physics Division, Oxfordshire OX11 ORA.
9. A. TESSIER, P. G. C. CAMPBELL, M. BISSON, Anal. Chem., 51 (1979) 844.
10. J. MCKEAGUE, J. H. DAY, Can. J. Soil Sci., 46 (1966) 13.
11. B. J. ANDERSON, E. A. JENNE, Soil Sci., 109 (1970) 163.
12. E. R. SHOLKOVITZ, Geochim. Cosmochim. Acta, 40 (1976) 831.