Distribution of natural radionuclides in sequentially extracted fractions of sediments from a marsh area in Southwest Spain: U isotopes

A. Martínez-Aguirre, R. Periañez

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

Abstract

A study of the distribution of U in different fractions of intertidal sediments collected in a marsh area enhanced by the radioactive wastes discharged from a fertilizer complex has been carried out. The study has shown that U isotopes are mainly located in non-residual fractions of the sediments. Coprecipitation with amorphous ferromanganese oxyhydroxides is the main process of incorporation of this element from the water column into the sediment. The residual fractions only contain some 5% of the total U in the sediment. Moreover, all fractions seem to reflect the same pattern of contamination, with in fact a quite good relationship between the U in most extracted fractions. Thus, those sediments located along the Odiel river basin have higher U concentrations in all the sequentially extracted fractions. Concentration ratios for Spartina densiflora have also been studied. In this paper, it has been considered that not all the substrate sediment takes part in the uptake of elements by the plant but only the non-residual fractions. Thus, a study of the dependence of these concentration ratios on the concentration in the non-residual fraction of sediments has been carried out. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

On a historical time scale, sediments may be regarded as a temporary sink for much of the material which passes through the various aquatic chemical and biological cycles operating on the earth's surface. They became an environmental host for many of the waste products discharged by society. Once a substance has been incorporated

into sediments, its ultimate fate depends on a number of very complex factors. An element can be locked permanently into a sediment component or it may subsequently be released and take part in the various bio-geochemical reactions. The ability to predict the subsequent fate is one of the key factors in the assesment of the effect of environmental pollution. 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. environmentally reactive, in the chemical and biological processes which occur in the sediment/interstitial water system (Chester & Aston, 1981).

The distinction of elements between residual and non-residual types is particularly appropriate to the investigation of radionuclide pollution. This is because the processes which are mainly involved in the incorporation of these elements from polluted waters result in their location in the non-residual fractions of the sediments (Chester & Aston, 1981). The residence of the elements in these deposits may be only temporary and their release into the ecosystem represents a potential hazard. The extent to which these releases occur depends largely on the manner in which the element is bound to the sediment and on how the particular kinds of bonds react to various physico-chemical conditions. Thus, it is desirable to know the way(s) in which the elements are bound to the solid components in particular sediment populations. The chemical separation of various components into different fractions offers the most effective approach to the study of element partitioning in sediments because the processes by which most radionuclides are incorporated into the various components are chemical.

During recent years several studies have been carried out on sediment/soil or mineral speciation. Some of these were centered on artificial radionuclides, mostly involving those released by the Sellafield reprocessing plant (Brown et al., 1997) and some others on natural radionuclides in river sediments or rocks (Platter et al., 1992; Crespo et al., 1996). 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 above considerations led to the study of U and Th isotope concentrations in several chemical fractions of bottom sediments collected along the Odiel and Tinto river basins (Martínez-Aguirre et al., 1994b). As has been widely pointed out during recent years (Martínez-Aguirre et al., 1994a, b), both rivers are located in an area clearly enhanced by non-nuclear industries, basically by the fertilizer industries. In the above study, most U and Th isotopes were found to be co-precipitated with amorphous Fe and Mn oxyhydroxides into bottom sediments. However, close to the factories there was also a large content of these isotopes in the residual fraction of the sediments (mainly in the case of Th). This was attributed to the releases of small residual particles from the phosphate rock processing plant to the river basin.

Recently enhancement of U and Th isotopes was also found in intertidal sediment samples collected in the marsh area located opposite to the factories along the Odiel river (Martínez-Aguirre & García-León, 1997). This enhancement was attributed to

water movement into the area. Thus, the main objective of this paper is to identify the location of this contamination (U isotopes) in the various chemical fractions of sediments. This study would allow us to understand more about the capacity of this radionuclide to move across the area if any environmental change occurs in the system. Moreover, the transfer of this radionuclide from different chemical fractions of sediments to the plant *Spartina densiflora* has been also studied. In a previous paper (Martínez-Aguirre et al., 1997), the transfer was studied through the CR (concentration ratios), defined as the ratio between the concentration of an element in the plant and the concentration of the same element in the substrate sediment. In that study, a clear non-linear dependence of the CR on the total concentration in the sediment for the radionuclides of the ^{238}U decay chain was found. In this paper, the uptake of U by the plant is studied by considering only those fractions of the sediments which are mobile (the non-residual fraction) and thus potentially available for plant uptake.

2. Samples and radiochemical procedures

Sampling was carried out in February 1993. Several stations were selected across the Odiel marsh (see Fig. 1), which is clearly affected by the inflow of the Odiel riverwaters. Samples (plant and substrate) were collected during low tide at the border of the channel, in areas covered with water during high tide. In the laboratory, sediment samples were dried and powdered before analysis. The bulk dry density (g cm^{-3}) and percentage of organic matter were determined in each sediment sample and are given in Martínez-Aguirre et al. (1997). *Spartina densiflora* samples were collected at the same stations and at the same time as sediment samples. The roots of the plants were separated in order to study only the above-ground part of the plants. Once separated, the samples were washed with water to remove any trace of solid particles. Finally, they were air-dried and powdered for analysis.

Two to three grams of each homogenized sediment sample were used for sequential extraction. The method used for this sequential extraction was formulated by Short (1986). The original method (Ivanovich et al., 1988) was modified following Crespo et al. (1996). In the studied sediments, the ion-exchangeable fraction has been avoided due to its low U concentration in all cases. After the extraction of each fraction, the residue was washed with distilled water and the solution added to the previous supernate.

(1) $F1 = U$ *within carbonates*: The original sediment sample is shaken for 6 h in 1 M sodium acetate adjusted to pH = 5.0 with acetic acid (ratio = 1/20). The supernate is reserved for analysis (Nissembaum, 1972; Tessier et al., 1979).

(2) $F2 =$ *adsorbed* (*usually humic material and/or amorphous oxides*): The residue from the previous extraction is shaken for 1 h in 0.1 M sodium pyrophosphate solution adjusted to pH = 9.8 with 0.1 M NaOH (ratio = 1/10). The supernate is reserved for analysis (Ivanovich et al., 1988).

(3) $F3 = U$ *coprecipitated with amorphous Fe and Mn oxyhydroxides*: The residue from the previous phase is shaken for 4 h in the dark in Tamm's acid oxalate (0.2 M ammonium oxalate and 0.2 M oxalic acid) (ratio = 1/10). The supernate is reserved for analysis (McKeague & Day, 1966).
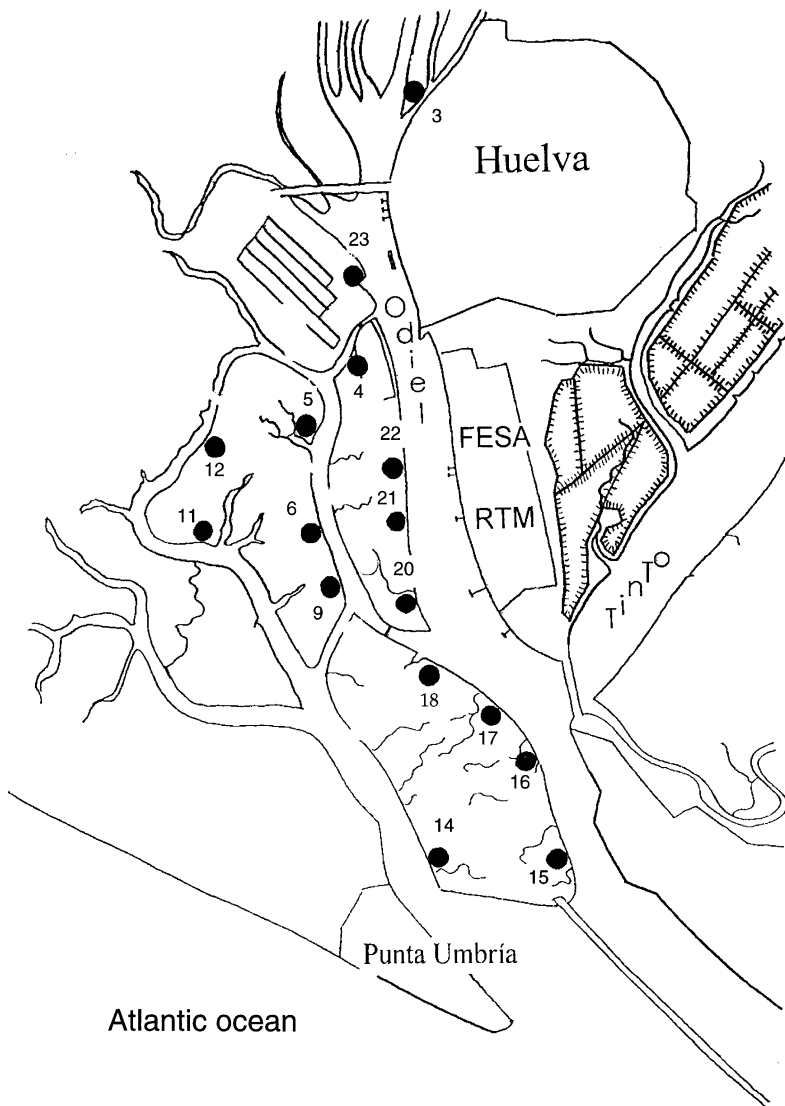
Fig. 1. Location of the sampling stations in the Odiel marsh area in southwest Spain.

(4) $F4 = U$ *within crystalline Fe and Mn oxides*: The residue from the previous phase is shaken for 1 h in Coffin's reagent (0.175 M sodium citrate and 0.025 M citric acid) (ratio $= 1/10$). The residue is reserved for analysis (Anderson & Jenne, 1970).

(5) $F5 = U$ *within primary minerals and clays = Resistant phase*: The final residue is dissolved with HNO_3, aqua regia and $HClO_4$ using a microwave oven. The supernate is reserved for analysis.

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 time scales.

Once the fractions were separated, the supernates were spiked with well-known ^{232}U activities and an anion-exchangeable resin method (Dowex AG1-X8 chloride form) was used for U isotope separation (Martínez-Aguirre, 1994a). Once separated and purified, electroplating onto stainless-steel planchets was carried out. The planchets were finally counted by α-spectrometry with ion-implanted detectors.

The dried plant samples were dissolved in HNO_3 and the same radiochemical method of U extraction (as for sediment fractions) was used. More details on the chemical procedures can be seen in Martínez-Aguirre et al. (1997).

3. Results and discussion

The percentage of the activity concentration of ^{234}U in each sequentially extracted fraction from each sample are presented in Table 1. In the last column of this table, the total ^{234}U concentration (mBq g^{-1}), obtained by the addition of the ^{234}U concentration in each extracted phase, is also given.

Table 1
Percentage of ^{234}U concentration in each sequentially extracted fraction in soils from the Odiel Marsh. In the last column the total ^{234}U concentrations in the soils are also given

Code	F1 (%)	F2 (%)	F3 (%)	F4 (%)	F5 (%)	Total (mBq g^{-1})
M3	13.3	7.6	75.7	1.4	2.0	767 ± 38
M23	21.6	15.2	58.9	4.3		261 ± 10
M4	12.8	9.0	74.7	1.9	1.5	566 ± 16
M22	22.5	11.6	45.9	8.2	11.7	35.5 ± 1.3
M21	27.7	1.4	49.6	7.6	13.7	17.7 ± 0.8
M20	18.9	13.2	62.6	1.7	3.6	248 ± 6
M18	22.4	6.5	68.4	1.2	1.6	541 ± 36
M17	22.4	29.0	31.2	3.3	14.1	28.2 ± 3.0
M16	16.0	10.4	69.6	1.5	2.4	483 ± 17
M15	19.3	7.7	67.8	1.7	3.5	91.3 ± 3.8
M5	14.7	10.7	67.1	5.4	2.2	249 ± 7
M6	22.7	12.5	58.2	2.6	4.0	130 ± 4
M9	20.3	13.2	60.8	3.3	2.6	134 ± 4
M11	27.3	10.1	55.5	4.4	2.8	83.3 ± 2.5
M12	34.6	15.3	34.6	6.0	9.7	43.1 ± 1.3
M14	39.4	13.2	34.1	5.5	7.6	43.1 ± 1.5

The data in Table 1 show that U is mainly associated with the non-residual fractions of the sediments, particularly with the F3 fraction. With the exception of samples M12 and M14, collected along the Punta Umbria river, 50% or more of the total U is associated with fraction F3. This implies that the main process by which U is incorporated into the sediments is by coprecipitation with amorphous ferromanganese oxyhydroxides, which is a typical process in estuarine environments (Sholkovitz, 1976). Of the other two non-residual fractions, the carbonate fraction (F1) seems to contribute more (range 13–40%) to the total U in the sediments than the absorbed fraction (F2) (range 2–15 %) with the exception of samples M17, M12 and M14, in which the U seems to be more equally distributed among all the non-residual fractions.

In Fig. 2, the concentrations of ^{234}U in all samples have been plotted for fractions F1, F2 and F3. As can be seen, all non-residual fractions behave in the same way, with maximum concentrations in samples M16, M18, M3 and M4 and minimal concentrations in samples M15, M17, M21 and M22. As was pointed out in a previous paper (Martínez-Aguirre et al., 1997a), the latter samples contained a large amount of sandy particles. Relative maxima are also observed in samples M20 and M23. The main conclusion is that all samples collected along the Odiel river margin show higher concentrations in the total sediments as well as in all non-residual fractions, whereas those samples with a higher content of sandy particles have the minimal U concentrations in total sediments and in each non-residual fraction.

The same distribution pattern for all sediments in the non-residual fractions can be clearly observed in Fig. 3. In this figure, the ^{234}U concentration in each non-residual phase is plotted versus the total concentration in the non-residual fraction of the

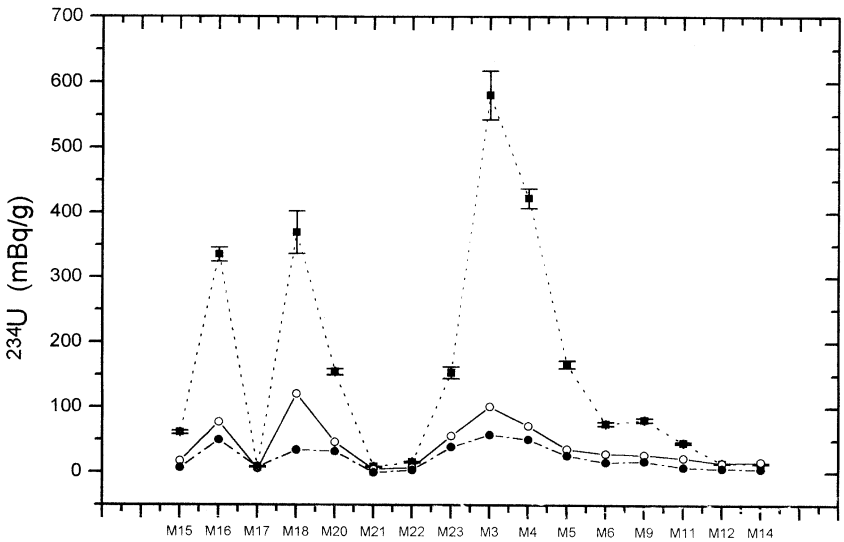Fig. 2. ^{234}U concentrations in mBq g^{-1} in non-residual fractions of soils from the Odiel marsh. F3 (□), F2 (●) and F1 (○). The error bars are 1σ due to counting statistics. Error bars for fractions F1 and F2 are included in the points.
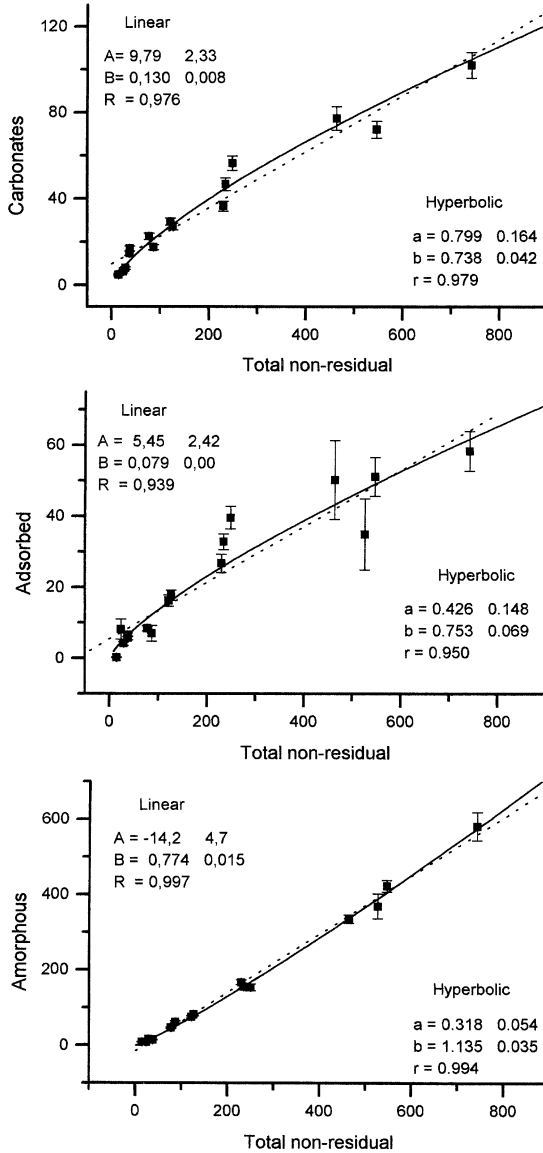
Fig. 3. ^{234}U concentrations in each non-residual fraction versus the ^{234}U concentration in the total non-residual fraction of soils from the Odiel marsh. Fitting functions are also plotted. The continuous line is the hyperbolic fitting and the dashed line the linear fitting.

sediments, considered as the addition of concentration in F1 + F2 + F3. As can be seen, the concentration of ^{234}U in each phase is linearly related to the total ^{234}U concentration in the non-residual fraction of the sediments, with regression coefficients above 0.9 in all cases.

Moreover, each non-residual phase and the total non-residual fraction of the sediments are also linearly related quite well to the total concentration in the sediments, as can be seen in Fig. 4.

Thus, if the slopes of these lines are considered as indicating the contribution of each fraction to the total ^{234}U concentration in the non-residual fraction of the sediments, it seems that the carbonate fraction contributes 13%, the absorbed fraction 7.9% and the amorphous fraction 77.4%. Indeed, the three fractions (by considering the slope of the lines) give 98.2% (practically 100%) of the non-residual fraction of the sediments. Moreover, as could be expected, the three non-residual fractions are also linearly related to each other (see Table 2). However, the above conclusions do not hold for those samples with low ^{234}U concentrations. This can be deduced because in all cases the y intercept differs from zero, even considering its error.

As commented on above, even considering that these lines are reflecting quite well the relationship between phases, in most cases those samples with low concentration are not so well fitted to the lines and in fact, in most cases, the y-intercept above unity
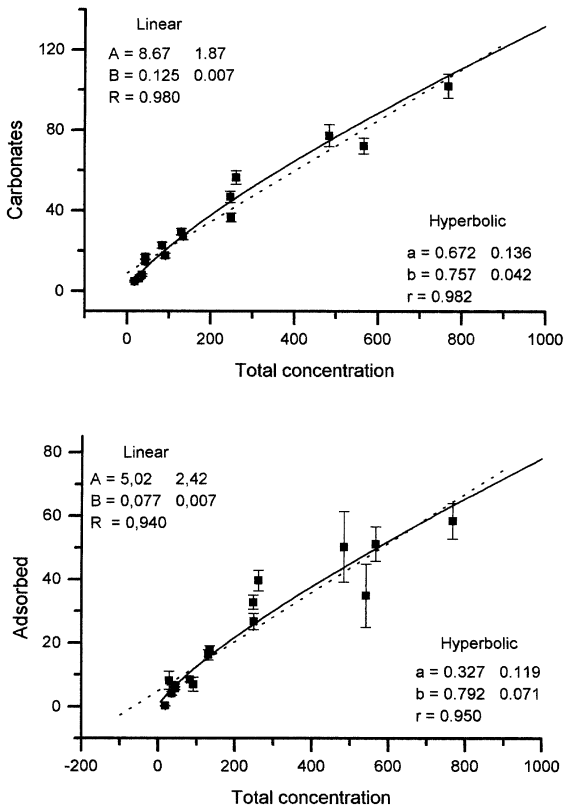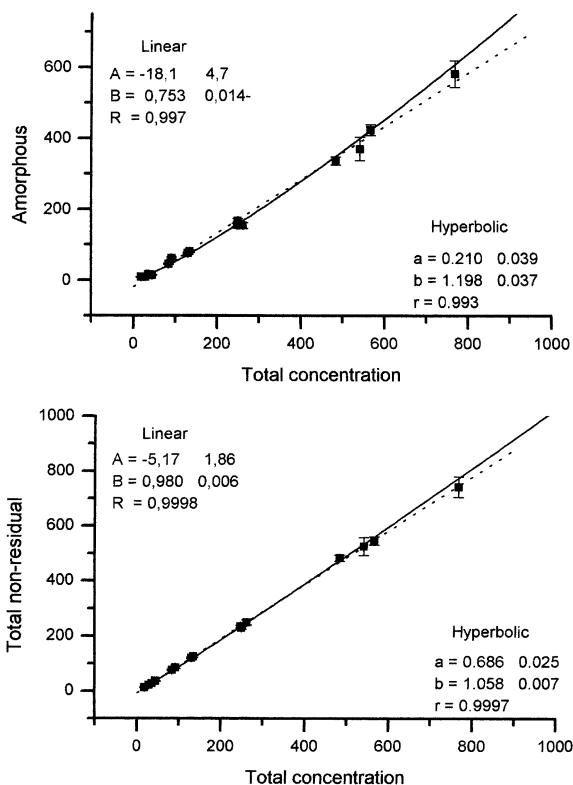

Fig. 4. (continued opposite).

Fig. 4. ^{234}U concentrations in each non-residual fraction versus the total ^{234}U concentrations in the soils from the Odiel marsh. Fitting functions are also plotted. The continuous line is the hyperbolic fitting and the dashed line the linear fitting.

Table 2
Results obtained in fitting the ^{234}U concentrations in different soil fractions by linear and hyperbolic functions. T is the total soil concentration and R the total residual concentration

x	y	Linear fitting $y = A + Bx$			Hyperbolic fitting $y = ax^b$		
		A	B	r	a	b	r
F3	F1	12.7 ± 2.9	0.163 ± 0.013	0.961	1.82 ± 0.41	0.630 ± 0.052	0.959
F3	F2	7.2 ± 2.5	0.101 ± 0.011	0.926	1.10 ± 0.35	0.623 ± 0.069	0.928
F2	F1	4.74 ± 2.72	1.44 ± 0.09	0.980	3.50 ± 0.56	0.774 ± 0.053	0.975
R	F4	-0.082 ± 0.56	0.435 ± 0.045	0.9414	0.321 ± 0.104	1.105 ± 0.143	0.9123
R	F5	0.221 ± 0.544	0.557 ± 0.044	0.9651	0.671 ± 0.136	0.934 ± 0.090	0.9484
T	F4	1.81 ± 43	0.012 ± 0.001	0.9342	0.467 ± 0.123	0.450 ± 0.052	0.9399
T	F5	2.54 ± 0.44	0.017 ± 0.002	0.9575	0.745 ± 0.258	0.415 ± 0.073	0.8732
T	R	4.72 ± 0.61	0.026 ± 0.002	0.9725	1.097 ± 0.204	0.442 ± 0.037	0.9603

would mean that, for zero total or non-residual concentration, the concentration in a specific non-residual phase is above unity. Of course that conclusion would be untrue. In order to clarify the real dependency between phases a hyperbolic relationship has been studied. These results are also presented in Table 2 and in Figs. 3 and 4.

As can be seen, the hyperbolic relationship is as good as the linear one, with regression coefficients well above 0.9 in all cases. However, as can be seen in Figs. 3 and 4, in the hyperbolic fit those samples with low concentration are much better modelled, especially in the case of phases F1 and F2. In fact, hyperbolic modelling gives zero concentration in the phase when the concentration in the total sediments or the non-residual fraction is zero. Moreover, in all cases, the exponent in the hyperbolic fit is clearly different from unity (see Table 2). In the case of the relationships between phase F3 and the non-residual and both with the total concentration in the sediments, both fit approachs give similar results. In fact, the exponent in the hyperbolic fit is nearly unity, being however a bit above unity considering the error in the exponent (see Table 2).

Both residual phases (F4 and F5), with the exception of samples M22, M21 and M17, contribute less than 5% of U to the total U concentration in the sample. The latter three samples contribute a bit higher U concentration (about 10%). This fact could be a consequence of their different compositions relative to the rest of the samples.

Low U concentrations are found in both residual fractions with less than $16 \, mBq \, g^{-1}$ in all cases, and except for those samples collected along the Mojarrera channel (see Fig. 1), the U concentration in the resistant fraction is a little above the concentration in the crystalline one (see Fig. 5). Again the samples collected along the
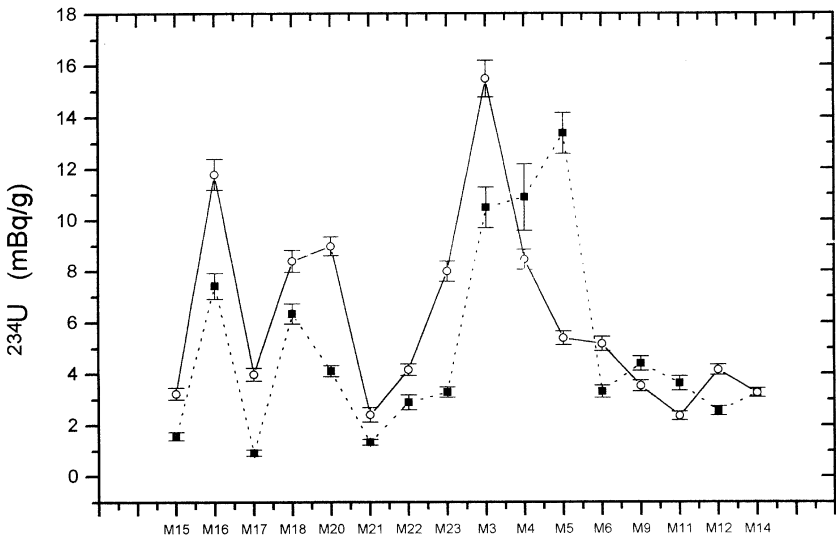

Fig. 5. ^{234}U concentrations in $mBq \, g^{-1}$ in residual fractions of soils from the Odiel marsh. F4 ($\square$) and F5 ($\bigcirc$).

Odiel river margin have the higher U concentrations in the resistant fraction, with the maximum in sample M3 collected north of the Odiel river. The maximum found in sample M5 for fraction F4, similar to those found in samples M3 and M4, cannot be explained at the moment.

As has been previously pointed out, intertidal sediments from the Odiel marsh are clearly affected by the releases from the fertilizer complex in the area. Moreover, such enhancement seems to be mainly produced by precipitation of Fe and Mn oxyhydroxides from the contamination moving along the Odiel river. Moreover, the maximum U concentration found in the same samples may be related to particles released by the factories which arrive in the area latter. However, the amount of particles arriving must be very small due to the low U concentration in the resistant fractions of all samples.

As in the case of the non-residual fractions, there is also a relationship between the ^{234}U concentration in each residual phase and the total ^{234}U concentration in the residual fraction (F4 + F5). The results obtained in the fitting are given in Table 2. As can be seen in that table, both functions (linear and hyperbolic) fit the experimental data quite well, with regression coefficients above 0.9 in all cases. However, as can be seen from the y-intercept (close to zero) and the exponent (close to unity) in the linear and hyperbolic fitting respectively, both relationships are clearly linear.

All results commented on above for ^{234}U are the same for ^{238}U.

As can be seen in Table 3, where the ^{234}U/^{238}U activity ratios for all fractions in all samples are shown, both U isotopes are practically in secular equilibrium in all phases, with no clear differences between phases and samples. The non-residual fractions represent that part of the sediments which is in contact with the river water. Thus these ratios (~1) imply that all the rivers are affected by fertilizer production

Table 3
^{234}U/^{238}U activity ratios in each sequentially extracted fraction in soils from the Odiel Marsh

Code	F1	F2	F3	F4	F5
M3	1.073 ± 0.028	1.035 ± 0.039	1.059 ± 0.027	1.198 ± 0.089	1.230 ± 0.040
M23	1.189 ± 0.041	1.105 ± 0.039	1.150 ± 0.042	1.121 ± 0.035	
M4	1.043 ± 0.028	1.090 ± 0.049	1.077 ± 0.011	1.297 ± 0.170	1.134 ± 0.049
M22	1.031 ± 0.082	1.213 ± 0.167	1.084 ± 0.065	1.216 ± 0.148	1.099 ± 0.057
M21	1.014 ± 0.117	0.87 ± 0.32	1.030 ± 0.074	1.39 ± 0.15	1.00 ± 0.14
M20	1.090 ± 0.041	1.095 ± 0.039	1.028 ± 0.019	1.116 ± 0.061	1.067 ± 0.037
M18	1.088 ± 0.024	1.126 ± 0.059	1.075 ± 0.017	1.12 ± 0.07	1.029 ± 0.055
M17	1.091 ± 0.093	1.119 ± 0.045	1.210 ± 0.099	1.29 ± 0.23	1.036 ± 0.072
M16	1.103 ± 0.027	1.043 ± 0.054	1.072 ± 0.018	1.14 ± 0.08	0.99 ± 0.05
M15	1.064 ± 0.045	1.026 ± 0.35	1.042 ± 0.035	0.95 ± 0.11	1.22 ± 0.10
M5	1.097 ± 0.045	1.036 ± 0.055	1.110 ± 0.020	1.139 ± 0.053	1.096 ± 0.056
M6	1.088 ± 0.045	1.082 ± 0.072	1.049 ± 0.025	1.17 ± 0.10	1.482 ± 0.095
M9	1.073 ± 0.045	1.111 ± 0.053	1.121 ± 0.028	1.212 ± 0.083	1.125 ± 0.074
M11	1.010 ± 0.053	1.137 ± 0.080	1.05 ± 0.22	2.04 ± 0.22	1.070 ± 0.096
M12	1.080 ± 0.066	1.097 ± 0.075	1.051 ± 0.049	1.22 ± 0.10	1.119 ± 0.057
M14	1.111 ± 0.072	1.101 ± 0.086	0.981 ± 0.051	1.92 ± 0.23	1.124 ± 0.066

since in typical river water this ratio ranges at 1.2–1.3. The ratios found in the residual fractions (also ~1) do not show the typical deficit in ^{234}U for soils and sediments. Moreover, to clarify the constancy of this activity ratio in specific phases and in the total sediments, the ^{234}U concentrations have been plotted versus the ^{238}U concentrations. A linear relationship has been found in the case of each specific fraction, the non-residual fraction, the residual fraction and the total sediment. The y-intercept and the slope of these lines with their error bars are given in Table 4. As can be seen, considering the error bars, the y-intercepts of the lines are practically zero. This fact must be reflecting the constancy of the ^{234}U/^{238}U activity ratio in each of the fractions, considered as the slopes of the lines. Moreover, in all cases the slope of the line is close to unity, reflecting again that both U isotopes are in secular equilibrium in the area.

In a previous paper (Martínez-Aguirre et al., 1997), the uptake of natural radionuclides by *S. densiflora* was studied through the concentration ratios (CR), defined as the ratio between the concentration of an element in the plant and that in its substrate. The concentration factors (CR) for *S. densiflora*, calculated from the total concentration in the substrate, was shown clearly to decrease when the activity concentration in the sediment increases. Indeed, the data could be modelled by fitting hyperbolic functions ($CR = aC^b$), where C is the total concentration in the sediments. This fact was also found by other authors (e.g. Sheppard & Sheppard, 1985; Sheppard & Evenden, 1988).

However, not all the sediment is involved in the uptake of radionuclides by the plant. Radionuclides contained in both residual fractions (F4 and F5) can be considered as immobile and thus not available for plant uptake. Thus radionuclides must be taken up by the plant from any or all of the non-residual fractions. Concentration factors (CR) of ^{234}U have been calculated by assuming that the plant takes up this radionuclide from only the non-residual fraction of the sediments (F1 + F2 + F3). In Fig. 6 concentration factors have been plotted versus the concentrations in the non-residual fractions of the sediments. As could be expected, due to U being mostly contained in the non-residual fractions of the sediments, the results obtained from the total sediment concentrations (taken from Martínez-Aguirre et al., 1997b), and the total non-residual concentrations are quite similar (see Table 5). Thus the hyperbolic character of the uptake of U isotopes by the plant is again confirmed.

Table 4
Data for the lines (^{234}U $= A + B^{238}$U) for specific fractions of the soils

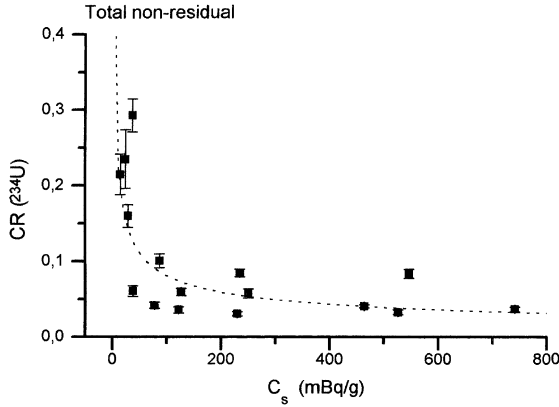| Fraction	A	B	r
F1	0.032 ± 0.667	1.085 ± 0.014	0.9989
F2	0.690 ± 0.641	1.019 ± 0.023	0.9966
F3	1.009 ± 1.432	1.067 ± 0.007	0.9997
F4	0.457 ± 0.290	1.123 ± 0.055	0.9847
F5	0.107 ± 0.359	1.093 ± 0.056	0.9832
NR	1.841 ± 1.977	1.064 ± 0.007	0.9997
T	2.067 ± 1.995	1.067 ± 0.007	0.9997

Fig. 6. Concentration ratios (CR) for ^{234}U versus the total non-residual concentration.

Table 5
Concentrations ratios (CR) calculated from the total non-residual fraction and the total soil concentration

Phase		$CR = aC_s^b$	σ_b	r
NR	^{234}U	$CR = 0.643\ C_S^{-0.449}$	0.106	-0.748
	^{238}U	$CR = 0.585\ C_S^{-0.438}$	0.107	-0.738
T	^{234}U	$CR = 0.588\ C_S^{-0.438}$	0.082	-0.703
	^{238}U	$CR = 0.590\ C_S^{-0.445}$	0.081	-0.714

4. Conclusions

U isotope concentrations in several sequentially extracted fractions of intertidal sediments collected in a marsh area which is clearly enhanced by phosphoric acid production have been studied. The residence of this element 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 U contamination in all the area can be clearly observed in all fractions of the sediments, with a clear relationship on the U concentration between fractions. Moreover, uranium concentration ratios for *S. densiflora* have been studied considering that only the non-residual part of the substrate sediment takes part in the uptake of elements by the plant. This study has again shown the hyperbolic character of U uptake by this plant.

Acknowledgements

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