Transfer of Natural Radionuclides from Soils to Plants in a Marsh Enhanced by the Operation of Non-Nuclear Industries

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ABSTRACT

Two sampling campaigns were performed in 1993 at the marsh area (Odiel marsh) located in southwestern Spain, in the city of Huelva. Spartina densiflora *and substrate soil (5 cm deep) samples were collected in several locations across the area in each campaign. Activity concentrations of* ^{210}Po*, U- and Th-isotopes were determined in the plant and the substrate samples. The production of phosphoric acid from phosphate mineral in the vicinity clearly enhances the concentrations of these radionuclides in certain areas of the marsh. Moreover, concentrations in plants are affected by the concentration of the same element in its substrate. Indeed, high concentration levels in plants are coincident with high concentration in soils. However, concentration ratios (CR), defined as the ratio between the concentration of an element in the plant and of that in its substrate, are higher when substrate concentrations are low, whereas low CR values are found in areas where substrate concentrations are high. Moreover, both variables (CR and soil concentration) seem to be non-linearly related, at least, in the case of radionuclides from the* ^{238}U *decay chain.*

INTRODUCTION

Environmental assessments use food-chain models to determine the dose to man from radionuclides released to the biosphere. Traditional food-chain models require a plant/substrate transfer coefficient, referred to as a concentration ratio (CR). The concentration ratio or transfer coefficient concept, is generally accepted and widely used in environmental transport models and describes the amounts of nuclide expected to enter a plant from its substrate.

The CR approach requires us to assume that the plant and substrate concentrations are linearly related and that the line defining the relationship goes through the origin. The variability of CR has previously been addressed, but few have specifically addressed the linearity assumption. This assumption implies that, under comparable conditions, the CR for an element is constant, regardless of substrate concentration (Sheppard & Sheppard, 1985).

However, plant uptake of elements, both essential and non-essential for growth, differs and may follow a non-linear relationship. Cannon (1952) has stated that U may be a micronutrient for higher plants, which means that CR was not linearly related to the substrate concentration.

Mordberg *et al.* (1976) obtained CR values by fitting linear and hyperbolic functions to data obtained using different soil concentrations of isotopes in the U–Ra series. They showed that the CR was constant over their observed soil concentrations. Cannon (1952) also suggested a linear relationship existing for U between plant and soil concentrations. However, Morishima *et al.* (1976) reported a non-linear relationship for U between vegetable and soil concentrations. Lopatkina *et al.* (1970) have suggested that the linearity assumption may hold only for primitive plant forms. Sheppard and Sheppard (1985) studied the linearity assumption for U in plants and substrate at two ore bodies on the Precambrian Shield. They found that the relationship between CR and substrate concentration observed in native plants tends to be hyperbolic, with a tendency for CR values to be larger at lower substrate concentrations. It appears, therefore, that U may behave as an essential element at low substrate concentrations. Many data suggest that plant concentrations are unrelated to soil concentrations, and when a line is fitted to the data, the intercept is usually greater than zero (Simon & Ibrahim, 1987). Log-normal distributions of concentration ratios were reported by Sheppard and Evenden (1988). They proposed that the linearity assumption, although contrary to what is usually expected for nutrients (essential) elements, may be valid for limited ranges of soil concentrations or for elements not physiologically regulated by plants. Many experiments designed to measure CR values have used only a few different soil concentrations and thus, cannot statistically assess the linearity assumption. Simon and Ibrahim (1987) proposed that a curvilinear relationship reflecting a saturation-type mechanism in plants was more appropriate.

A hypothetical relationship for the CR for essential and non-essential elements over a range of substrate concentrations is shown in Fig. 1. This relationship means that plants readily take up elements essential for plant growth when substrate concentrations are low, whereas plant uptake of non-essential elements is generally constant in this substrate concentration range (Timperley *et al.*, 1970; Mengel & Kirkby, 1979). At high substrate concentrations, plant uptake of essential and non-essential elements can either be constant (no toxicity) or can decrease, leading to toxicity or death. Toxicity begins at a toxicity threshold, the substrate concentration at which plant growth, and hence uptake, begin to be impaired. Lethal substrate concentrations of an essential or non-essential element may not exist, and in that case, the CR may be constant for several orders of magnitude.

The CR concept is CR = C_p/C_s = constant, and it is probably useful for non-essential elements at non-toxic substrate levels. The lack of correlation between plant and substrate concentrations for non-essential elements could be explained if the element is mimicking an essential element (Sheppard & Sheppard, 1985). This fact would result in a non-linear relationship between the CR and the substrate concentration at low substrate concentration. This relationship could be modelled as:

$$C_p = a + bC_s, \qquad (1)$$

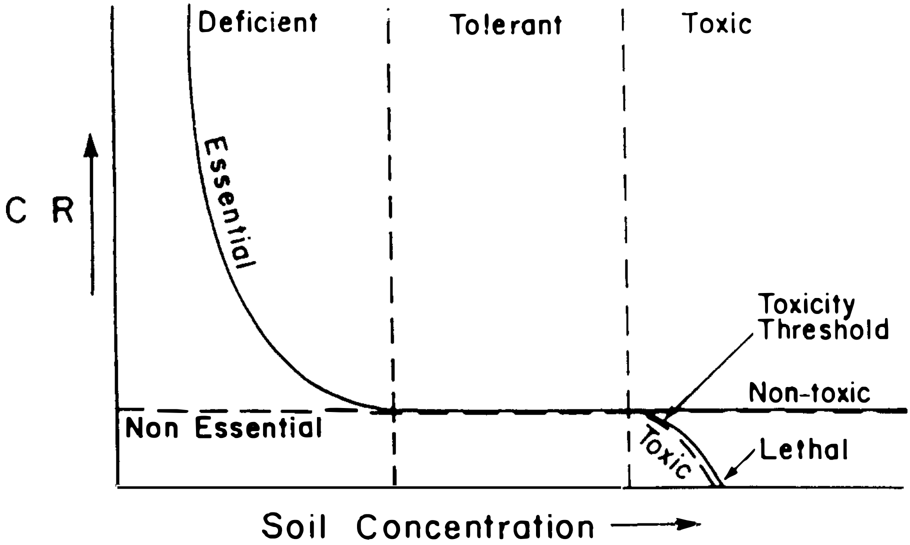

Fig. 1. Hypothetical relationship of CR vs soil concentration for both essential and non-essential elements through the deficient to toxic soil-concentration range (Sheppard & Sheppard, 1985).

where C_p is the concentration in the plant and C_s is the concentration in the substrate. This results in:

$$\mathrm{CR} = \frac{C_p}{C_s} = \frac{a}{C_s} + b. \tag{2}$$

If the first relationship does not have a zero intercept ($a \neq 0$), this would mean that CR (C_p/C_s) is dependent on the substrate concentration.

Tracy *et al.* (1983) studied the uptake of ^{226}Ra, ^{210}Pb and U from soils to garden produce. They observed a clear trend of increasing concentrations in plants with increasing concentration in soil substrate. In order to express this trend quantitatively, a linear regression analysis was carried out for the logarithms of the mean vegetable concentration vs the logarithms of the soil concentrations. This involves fitting a function of the form:

$$C_p = aC_s^b \tag{3}$$

or

$$\mathrm{CR} = aC_s^{b-1}, \tag{4}$$

where a and b are parameters to be determined.

A value of b equal to 1.00 would imply a linear relationship ($\mathrm{CR} = C_p/C_s = \mathrm{cte}$). They found that their results were not inconsistent with the linearity assumption, at least for concentrations up to about 37 Bq g^{-1} in soil.

The use of concentration ratios to predict plant concentrations from low substrate concentration for environmental assessment purposes should be investigated further for radionuclides known to mimic essential elements and should be measured under natural conditions (Sheppard & Sheppard, 1985).

This paper reveals a study of the distribution and transfer of ^{210}Po-, U- and Th-isotopes from soils to *Spartina densiflora* (a wild plant species typical of marsh areas in Europe) collected from a saline marsh located in southwest Spain. The presence, in the vicinity, of a fertilizer complex which uses mineral with high U concentration could allow for a wide soil concentration range in the studied area (Martínez-Aguirre & García-León, 1997). Indeed, the main aim of the work is to contribute a bit more in the study about how natural radionuclides are being incorporated in the plant from its substrate concentration. Thus, a study of the CR relationship with the concentration in the soil substrate will follow. Although this species is not directly involved in the human food chain, information on the concentration levels and transfer of radionuclides from contaminated soils will provide important data on the transfer mechanisms in the case of those species more directly involved in the human diet.

SAMPLES AND RADIOANALYTICAL PROCEDURES

Several stations were chosen across the Odiel marsh area of Huelva for sample collection. This area is clearly affected by the wastes released by two fertilizer factories located in the vicinity (see Fig. 2). The area is constituted by four small islands separated by four channels, which are affected, due to tidal movements, by the inflow of the Odiel riverwaters (Martínez-Aguirre & García-León, 1997). Samples (plant and substrate) were collected, during the low tide, at the border of the channels, in areas covered with water during the high tide.

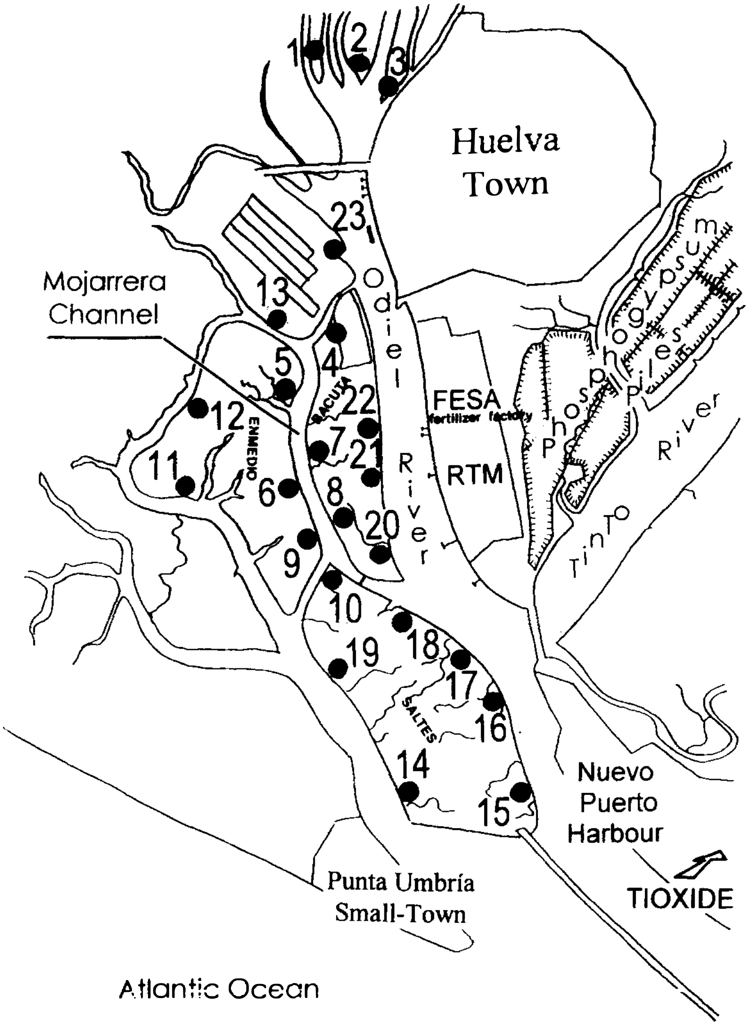

Fig. 2. Location of the sampling stations in the Odiel marsh area. The locations of the fertilizer complex and the phosphogypsum piles are also given.

About 1 kg of soil sample was collected from each station and stored in plastic bags. At the laboratory, they were dried and powdered before the radionuclide analysis. The bulk dry density (g cm^{-3}) and percentage of organic matter were determined in each soil sample. *Spartina densiflora* samples were collected at the same stations and at the same time as soil samples. The roots of the plants were separated in order to study only the overground 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.

Aliquots of each sample (soil and/or plant) were used for Po- and U- and Th-isotopes determinations, separately. They were digested with concentrated HNO_3 and aqua regia and the final residue dissolved in 8M HNO_3. Before the digestion, the samples were spiked with known amounts of ^{208}Po activities for ^{210}Po determination, and of ^{232}U and ^{229}Th activities for U and Th isotopes determinations, separately. Polonium-210 was separated from actinides by a solvent extraction method which used TBP (tributylphosphate) as the extractant phase. Polonium remained in the nitric phase, whereas actinides moved to the organic (TBP) phase (Martínez-Aguirre, 1991). The final Po solution was evaporated and self-deposited on to 2.2 cm diameter silver planchets. Polonium activities were determined by α-spectrometry with ion-implanted detectors.

For U- and Th-isotope determinations, an ion-exchange method was used. After redissolution of the residue with 8M HNO_3, precipitation of iron hydroxides was carried out by adding concentrated ammonium. Uranium- and Th-isotopes were separated and purified in a DOWEX AG1-X8 (chloride form) resin (Martínez-Aguirre, 1991). Final solutions were electroplated on to 2.2-cm diameter stainless steel planchets, separately. Uranium- and Th-isotopes activities were also determined by α-spectrometry with ion-implanted detectors.

RESULTS AND DISCUSSION

In Tables 1 and 2, data on ^{210}Po-, U- and Th-isotopes in soils and *Spartina densiflora* for each sampling station are given, respectively. Table 1 also includes the percentage of organic matter in each soil sample. Moreover, in Table 3, concentration ratios (CR), defined as the concentration of an element in the plant (mBq g^{-1} dry weight) divided by the concentration of the same element in the substrate (mBq g^{-1} dry weight), are also given. The next sections discuss separately, data on soil and plant concentrations and, finally, the CR results.

Soil substrate

In general, by considering the levels of all radionuclides from the ^{238}U decay chain, a reasonably wide range of activity concentration in the soil samples, is found. There are samples with low concentrations of ^{238}U and descendants, which can be considered as clearly non-enhanced by the fertilizer industries. In general, concentration levels in these samples are below 70 mBq g^{-1}, levels similar to those typical in undisturbed soils (ranging from 10 to 50 mBq g^{-1}, UNSCEAR, 1988). These samples were collected in stations further away from the fertilizer industries, in the west part of the Saltés island along the Punta Umbria river. Also, very low concentration levels were found in two stations at the east side of the Bacuta island opposite the fertilizer industries. This fact must be related to the composition of the sample. Indeed, values of density and organic matter (see Table 1) in both samples reflect that high amounts of sandy particles, with low activity concentrations, are contained in such samples.

Some other samples reveal intermediate concentration levels (clearly higher than background, but not very high) for all radionuclides from the ^{238}U decay chain, ranging from about 100 to 300 mBq g^{-1}. These samples are located along the east part of the Enmedio island and the west part of the Bacuta island, washed by the Mojarrera channel. Finally, there are samples with much higher concentration levels than the rest of the samples. The levels are, in general, above 400 mBq g^{-1} for all radionuclides from the ^{238}U decay chain. These samples are located in the east part of the Saltés island and the south of the Northern marsh in the Odiel river, all of them along the Odiel river upstream and downstream from the fertilizer industries. The difference found in the samples collected at the east side of the Saltés island must, again, be related to the composition of the samples. Thus, it can be seen that those samples with low concentrations (15 and 17) have density and organic matter values very different from the other samples (16 and 18) that have quite high concentrations of radionuclides.

In general, excepting the case of samples with different composition, the differences in activity concentration between samples seem to depend on the location of the sampling sites, which indicates the influence of the inflow of Odiel riverwaters over each area. Thus, the bag of contaminants moves upstream and downstream of the Odiel river. Part of it is clearly moving to the Odiel marsh through the north of the Bacuta island that later flows into the Mojarrera channel.

We can also compare our results with other data obtained in soils from the area of Huelva, but in the Tinto marsh area (see Fig. 2) and around the phosphogypsum piles (Bolivar *et al.*, 1995). Levels below 40 and 60 mBq g^{-1} for ^{210}Po and ^{238}U, respectively, in stations located in the east

TABLE 1

Activity Concentrations (mBq g^{-1}) of some Natural Radionuclides from the U and Th Decay Chains in Soil Samples from the Odiel Marsh Collected in February (F) and November (N) 1993

Code	*O.M. (%)*	^{210}Po	^{238}U	^{234}U	^{232}Th	^{230}Th	^{228}Th
F1			165 ± 7	189 ± 8			
N1	10.8	199 ± 10	181 ± 8	197 ± 8	48.1 ± 2.5	186 ± 9	73.0 ± 7.0
N2	11.5	778 ± 41	698 ± 35	747 ± 37	88.1 ± 6.8	922 ± 52	160 ± 15
N3	14.8	643 ± 28	728 ± 32	751 ± 33	103 ± 5	898 ± 42	149 ± 13
N4	14.6	580 ± 26	540 ± 21	594 ± 23	61.1 ± 4.0	533 ± 26	144 ± 13
N13	15.4	222 ± 11	196 ± 7	217 ± 8	29.8 ± 1.8	112 ± 9	59.3 ± 6.3
F5	20.9	290 ± 31	360 ± 22	364 ± 22			
N5	15.2	213 ± 10	232 ± 9	248 ± 10	41.2 ± 3.0	208 ± 11	48.0 ± 3.3
N6	11.4	141 ± 7	147 ± 6	161 ± 6	31.0 ± 1.8	104 ± 5	14.0 ± 3.7
N7	13.1	130 ± 7	158 ± 6	179 ± 7	30.3 ± 2.2	125 ± 7	36.2 ± 2.5
N8	9.2	64.6 ± 4.0	64.8 ± 3.2	71.9 ± 3.5	26.6 ± 1.9	41.0 ± 2.6	30.9 ± 2.6
N9	9.7	188 ± 10	127 ± 5	142 ± 5	24.4 ± 1.6	101 ± 5	35.0 ± 4.0
F10	12.9	25.1 ± 1.7	95.1 ± 4.9	116 ± 6			
N10	12.7	27.9 ± 2.0	106 ± 4	122 ± 5	23.6 ± 1.6	28.4 ± 1.9	22.5 ± 1.6
N23	14.5	210 ± 11	245 ± 8	281 ± 9	41.4 ± 3.1	216 ± 13	62.1 ± 5.4

N20	9.8	233 ± 11	258 ± 9	283 ± 10	44.1 ± 3.6	256 ± 16	78.5 ± 6.4
N18	17.3	565 ± 23	601 ± 21	630 ± 21	56.4 ± 3.8	443 ± 22	120 ± 12
F17	9.4	108 ± 6	142 ± 10	163 ± 12			
N17	4.8	41.0 ± 3.2	17.6 ± 0.8	18.8 ± 1.0	26.5 ± 2.5	30.0 ± 2.7	32.8 ± 2.9
F16	13.7	367 ± 34	434 ± 16	498 ± 23			
N16	15.5	441 ± 20	511 ± 18	523 ± 19	68.1 ± 4.5	554 ± 23	100 ± 12
N15	4.6	131 ± 7	94.1 ± 3.7	101 ± 4	17.1 ± 1.2	87.4 ± 4.7	46.3 ± 4.5
F12	15.6	163 ± 9	147 ± 6	158 ± 6			
N12	9.3	44.2 ± 2.5	44.8 ± 1.6	48.4 ± 1.8	26.7 ± 1.6	28.1 ± 1.7	25.0 ± 1.7
F11	13.3	124 ± 8	124 ± 6	138 ± 7			
N11	9.2	194 ± 9	75.4 ± 2.6	87.4 ± 3.0	22.0 ± 1.4	71.0 ± 3.7	28.9 ± 4.1
N19	5.7	54.4 ± 3.7	30.1 ± 1.2	34.7 ± 1.4	15.4 ± 1.0	31.7 ± 1.9	16.4 ± 1.3
F14	12.5	40.5 ± 2.3	36.9 ± 1.6	43.4 ± 1.8			
N14	9.4	54.7 ± 3.9	37.8 ± 1.6	43.7 ± 1.8	22.4 ± 1.6	42.8 ± 2.7	22.5 ± 0.4
N21	1.1	16.2 ± 2.5	17.9 ± 0.8	19.3 ± 0.9	4.9 ± 0.3	8.8 ± 0.5	4.3 ± 0.9
N22	2.3	37.2 ± 2.5	32.4 ± 1.3	36.7 ± 1.4	11.8 ± 0.7	16.0 ± 0.9	13.3 ± 1.1

side of the Tinto river, opposite the phosphogypsum piles, and also in the same margin of the phosphogypsum piles upstream the river, and these were considered as non-enhanced, background levels. However, in areas around the gypsum piles, levels higher than 285 ± 4 and 283 ± 18 mBq g^{-1} were found for ^{210}Po and ^{238}U, respectively; these were considered to be increased as a result of the fertilizer industries, particularly the phosphogypsum piles. Thus, it seems that the background levels of such an area are much lower than levels found in soils from the Odiel marsh. Only

TABLE 2

Activity Concentrations (mBq g^{-1}) of some Natural Radionuclides from the U and Th Decay Chains in *Spartina densiflora* Samples Collected at the Odiel Marsh in February (F) and November (N) 1993

Code	^{210}Po	^{238}U	^{234}U	^{232}Th	^{230}Th	^{228}Th
F1	13.2 ± 1.3	7.10 ± 0.7	8.17 ± 0.80			
N1	23.6 ± 1.6	16.6 ± 1.1	18.5 ± 1.3	2.31 ± 0.29	15.1 ± 1.1	4.14 ± 0.41
N2	21.2 ± 1.1	15.1 ± 1.1	18.3 ± 1.2	1.43 ± 0.18	9.57 ± 0.66	2.66 ± 0.26
N3	25.1 ± 1.3	26.2 ± 1.9	29.7 ± 2.2	2.34 ± 0.25	13.9 ± 0.9	3.22 ± 0.30
N4	45.2 ± 4.5	42.6 ± 2.7	46.4 ± 2.9			
N13	8.60 ± 0.55	6.65 ± 0.47	8.25 ± 0.56	0.41 ± 0.07	2.65 ± 0.24	0.76 ± 0.10
F5		20.4 ± 1.1	21.8 ± 1.9			
N5	5.58 ± 0.41	6.61 ± 0.58	8.00 ± 0.67	0.60 ± 0.06	2.03 ± 0.14	0.55 ± 0.05
N6	6.52 ± 0.43	4.07 ± 0.43	3.96 ± 0.43	0.72 ± 0.07	4.06 ± 0.26	0.95 ± 0.09
N7	8.90 ± 0.77	11.1 ± 0.8	13.6 ± 0.9	1.73 ± 0.18	7.85 ± 0.54	2.13 ± 0.20
N8	9.50 ± 0.76	11.2 ± 0.8	12.7 ± 0.8			
N9	8.97 ± 0.60	6.85 ± 0.56	7.67 ± 0.61	0.84 ± 0.08	5.13 ± 0.32	1.24 ± 0.11
F10	23.8 ± 1.3	13.7 ± 1.1	13.9 ± 1.1			
N10	12.8 ± 0.8	11.5 ± 0.7	12.4 ± 0.8	0.69 ± 0.12	3.89 ± 0.37	1.32 ± 0.18
N23	17.3 ± 1.8	12.7 ± 1.1	14.0 ± 1.2	2.36 ± 0.26	11.6 ± 0.8	2.53 ± 0.27
N20	30.6 ± 1.9	19.1 ± 1.1	19.1 ± 1.1	1.24 ± 0.16	7.89 ± 0.57	2.08 ± 0.22
N18		16.2 ± 1.2	15.3 ± 1.1	1.7 ± 0.1	11.3 ± 0.7	
F17	9.4 ± 0.4	9.0 ± 0.8	9.3 ± 0.8			
N17	8.61 ± 0.58	4.74 ± 0.51	5.11 ± 0.54	0.41 ± 0.07	2.65 ± 0.24	0.76 ± 0.10
F16	26.5 ± 1.1	27.4 ± 2.4	28.2 ± 2.4			
N16	15.0 ± 0.8	17.9 ± 0.9	19.5 ± 0.9	3.02 ± 0.26	19.5 ± 1.1	2.95 ± 0.26
N15	9.92 ± 0.63	8.31 ± 0.66	8.89 ± 0.70			
F12	13.2 ± 0.8	7.28 ± 0.81	7.68 ± 0.85			
N12	13.0 ± 0.7	9.92 ± 0.63	10.7 ± 0.7	1.68 ± 0.22	5.3 ± 0.5	1.85 ± 0.23
F11	13.0 ± 0.8	5.27 ± 0.74	5.52 ± 0.77			
N11	6.82 ± 0.52	3.09 ± 0.26	3.56 ± 0.29	0.69 ± 0.08	2.58 ± 0.20	0.65 ± 0.08
N19	8.36 ± 0.68	2.37 ± 0.20	2.35 ± 0.19			
F14	24.3 ± 1.4	5.63 ± 0.47	6.08 ± 0.54			
N14	15.8 ± 1.2	2.16 ± 0.23	2.36 ± 0.24	1.46 ± 0.15	3.26 ± 0.27	1.80 ± 0.17
N21	5.74 ± 0.48	2.93 ± 0.36	3.11 ± 0.36	0.26 ± 0.05	1.78 ± 0.17	0.36 ± 0.06
N22	9.78 ± 0.69	4.20 ± 0.37	5.30 ± 0.44			

those stations located in the west part of the Saltés island seem to be unaffected by the waste activities of the fertilizer production.

Two radionuclides from the ^{232}Th decay chain were analysed, ^{232}Th and ^{228}Th. Excepting samples from stations at the Northern marsh and the east side of the Saltés island, the concentration levels are quite similar to each other and typical to those in undisturbed soils, around 25 mBq g^{-1} (ranging from 5 to 45 mBq g^{-1}). However, the concentrations at the Northern marsh and at the east of the Saltés island are slightly higher, above 60 mBq g^{-1} for both radionuclides, than those typical for uncontaminated soils. Thus, it seems that part of the marsh is also being contaminated by radionuclides from the ^{232}Th decay chain. Moreover, as in the case of U and daughters, the Northern marsh seems to be the main sink for all radionuclides. However, this contamination is clearly much lower than that produced by radionuclides of the ^{238}U decay chain.

It is of interest here to discuss the relationship between the radionuclides analysed. In Fig. 3(a), concentrations of ^{234}U in mBq g^{-1} versus the ^{238}U concentrations in mBq g^{-1} have been plotted. As expected, concentrations of both isotopes are linearly related, with regression coefficient of 0.99924. With the intercept with the y-axis being nearly zero

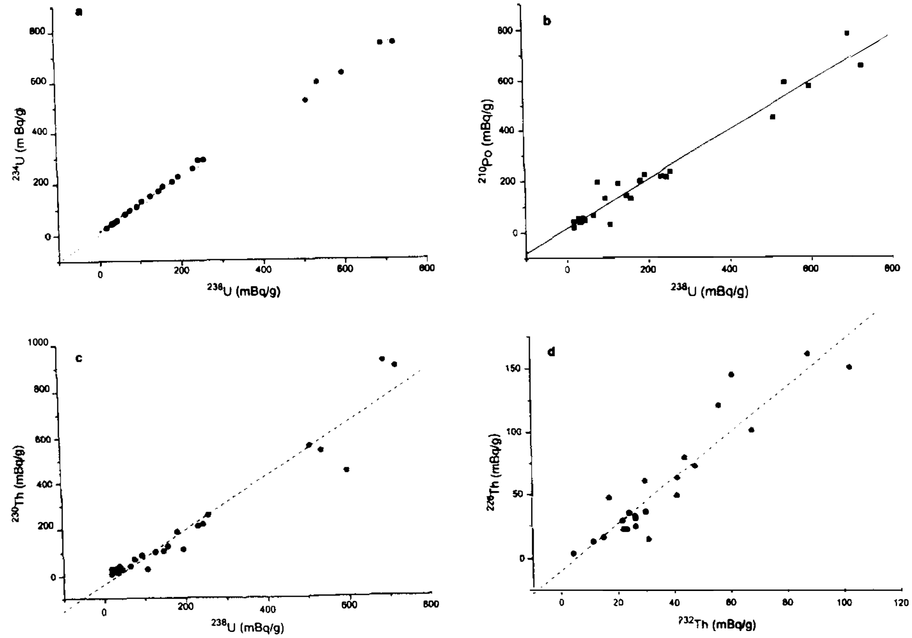

Fig. 3. Relationship between concentrations of radionuclides from the ^{238}U decay chain in soil substrate samples (a) ^{234}U vs ^{238}U, (b) ^{210}Po vs ^{238}U, (c) ^{230}Th vs ^{238}U and (d) ^{228}Th vs ^{232}Th.

TABLE 3
Concentration Ratios (CR), Defined as the Ratio Between the Concentration of an Element in the Plant and that in its Substrate, of Radionuclides Analysed in *Spartina densiflora* Samples Collected at the Odiel Marsh in February (F) and November (N) 1993

Code	^{210}Po	^{238}U	^{234}U	^{232}Th	^{230}Th	^{228}Th
F1		0.043 ± 0.005	0.043 ± 0.005			
N1	0.119 ± 0.010	0.092 ± 0.007	0.094 ± 0.008	0.048 ± 0.006	0.081 ± 0.007	0.057 ± 0.009
N2	0.027 ± 0.002	0.022 ± 0.002	0.024 ± 0.002	0.016 ± 0.001	0.010 ± 0.001	0.017 ± 0.002
N3	0.039 ± 0.003	0.036 ± 0.003	0.040 ± 0.003	0.023 ± 0.003	0.015 ± 0.001	0.022 ± 0.003
N4	0.078 ± 0.008	0.079 ± 0.006	0.078 ± 0.006	0.131 ± 0.013	0.091 ± 0.007	0.057 ± 0.007
N13	0.039 ± 0.003	0.034 ± 0.003	0.038 ± 0.003	0.014 ± 0.004	0.024 ± 0.003	0.013 ± 0.002
F5		0.057 ± 0.005	0.060 ± 0.006			
N5	0.026 ± 0.002	0.028 ± 0.003	0.032 ± 0.003	0.015 ± 0.002	0.010 ± 0.001	0.011 ± 0.001
N6	0.046 ± 0.004	0.028 ± 0.003	0.025 ± 0.003	0.023 ± 0.003	0.039 ± 0.003	0.068 ± 0.019
N7	0.069 ± 0.007	0.070 ± 0.006	0.076 ± 0.006	0.057 ± 0.007	0.063 ± 0.006	0.059 ± 0.007
N8	0.147 ± 0.015	0.173 ± 0.015	0.177 ± 0.014			
N9	0.048 ± 0.004	0.054 ± 0.005	0.054 ± 0.005	0.034 ± 0.004	0.051 ± 0.004	0.035 ± 0.005
F10	0.948 ± 0.082	0.144 ± 0.014	0.120 ± 0.011			
N10	0.460 ± 0.044	0.108 ± 0.008	0.102 ± 0.008	0.029 ± 0.005	0.137 ± 0.016	0.059 ± 0.009

N23	0.082 ± 0.009	0.052 ± 0.005	0.050 ± 0.004	0.057 ± 0.008	0.054 ± 0.005	0.041 ± 0.006
N20	0.131 ± 0.010	0.074 ± 0.005	0.067 ± 0.005	0.028 ± 0.004	0.031 ± 0.003	0.026 ± 0.003
N18		0.027 ± 0.002	0.024 ± 0.002	0.030 ± 0.003	0.026 ± 0.002	
F17	0.087 ± 0.006	0.063 ± 0.007	0.057 ± 0.006			
N17	0.210 ± 0.021	0.269 ± 0.031	0.272 ± 0.032	0.015 ± 0.003	0.088 ± 0.011	0.023 ± 0.004
F16	0.072 ± 0.007	0.063 ± 0.006	0.057 ± 0.005			
N16	0.034 ± 0.002	0.035 ± 0.002	0.037 ± 0.002	0.044 ± 0.005	0.035 ± 0.002	0.030 ± 0.004
N15	0.076 ± 0.006	0.088 ± 0.008	0.088 ± 0.008			
F12	0.078 ± 0.006	0.050 ± 0.006	0.049 ± 0.006			
N12	0.290 ± 0.023	0.221 ± 0.016	0.221 ± 0.017	0.063 ± 0.009	0.189 ± 0.021	0.074 ± 0.010
F11	0.105 ± 0.009	0.043 ± 0.006	0.040 ± 0.006			
N11	0.035 ± 0.003	0.041 ± 0.004	0.041 ± 0.004	0.031 ± 0.004	0.036 ± 0.003	0.022 ± 0.004
N19	0.154 ± 0.016	0.079 ± 0.007	0.068 ± 0.006			
F14	0.600 ± 0.049	0.153 ± 0.014	0.140 ± 0.014			
N14	0.290 ± 0.030	0.057 ± 0.007	0.054 ± 0.006	0.065 ± 0.008	0.076 ± 0.008	0.080 ± 0.011
N21	0.354 ± 0.062	0.164 ± 0.021	0.161 ± 0.020	0.053 ± 0.011	0.202 ± 0.022	0.084 ± 0.022
N22	0.263 ± 0.026	0.130 ± 0.013	0.144 ± 0.013			

(6.6 ± 2.8), the slope of the line would yield the value of the $^{234}U/^{238}U$ activity ratio in the area. In this case, the slope of the line, 1.047 ± 0.009, reflects a slight excess of the daughter isotope. However, with the *y*-intercept being above zero, the excess of ^{234}U increases for those samples with low concentration. In Fig. 3(b) and 3(c), concentrations of ^{210}Po and ^{230}Th, respectively, vs. the ^{238}U concentration are given. These figures clearly show that both radionuclides are also linearly related with the U concentration in the soil ($r = 0.9768$ and 0.9684, respectively). Thus, the contamination from all radionuclides of the ^{238}U decay chain is again confirmed. The slope of these lines, 0.948 ± 0.045 and 1.151 ± 0.065, respectively, would give the $^{210}Po/^{238}U$ and $^{230}Th/^{238}U$ activity ratio for a *y*-intercept zero. In the case of the first figure, with a *y*-intercept of -14.5 ± 14.3, secular equilibrium seems to be real for all samples. However, in the second figure, with a *y*-intercept of -38.0 ± 20.4, a slight excess of ^{230}Th for soil with high concentrations (those soils clearly enhanced) exists, decreasing to secular equilibrium for soil with background concentrations. However, solving these small variations, all radionuclides from the ^{238}U decay chain seem to be present close to secular equilibrium in most soils.

The case of both radionuclides from the ^{232}Th decay chain (^{232}Th and ^{228}Th) is slightly different. Both radionuclides are also quite well linearly related ($r = 0.9296$). However, with a *y*-intercept of nearly zero (-9.97 ± 6.90), now the slope of the line is 1.795 ± 0.155, which represents the $^{228}Th/^{232}Th$ activity ratio in the soils. Thus, an excess of the daughter isotope appears in the soil samples. Again, the excess decreases for soils with low concentrations. This slight excess of ^{228}Th should be related to the higher mobility of ^{228}Ra, intermediary radionuclide in the decay chain.

Comparing radionuclides from different decay chains (^{232}Th with ^{238}U and ^{230}Th), it can be observed that they are also linearly related, ^{232}Th concentration increases when ^{238}U and ^{230}Th concentration increases but, in these cases, the *y*-intercept is clearly different from zero (15.0 ± 2.4 and 18.6 ± 1.8, respectively). This fact reflects the fact that the $^{232}Th/^{238}U$ and $^{232}Th/^{230}Th$ activity ratios are not constant across the marsh. In Fig. 4(a) and 4(b), these activity ratios versus the ^{238}U and ^{230}Th concentrations, respectively, are plotted. These curves reflect the variation of these activity ratios and can be expressed mathematically as hyperbolic functions:

$$R = aC^b, \tag{5}$$

where R is the activity ratio, C is the concentration of the radionuclide (^{238}U or ^{230}Th) in the soil, and a and b are parameters to be determined.

Using eqn (5), in the case of Fig. 4(a) and 4(b), the following functions are obtained:

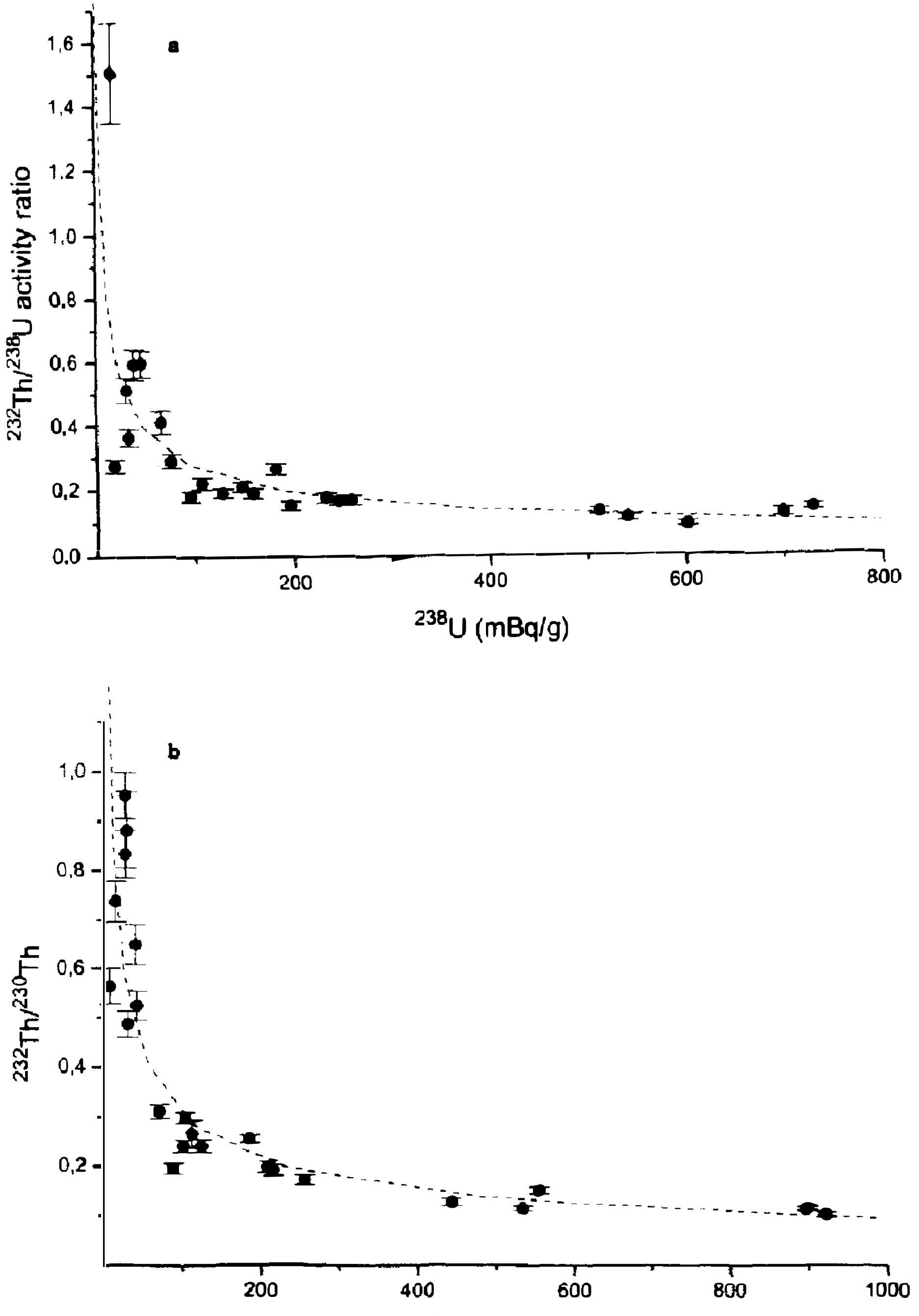

Fig. 4. ^{232}Th/^{238}U activity ratio vs. the concentration of ^{238}U (mBq g^{-1}) (a) and ^{232}Th/^{230}Th activity ratio vs. the concentration of ^{230}Th (b) in the soil substrate samples.

$$^{232}\mathrm{Th}/^{238}\mathrm{U} = 2.57(^{238}\mathrm{U})^{-0.488} \tag{6}$$

and

$$^{232}\mathrm{Th}/^{230}\mathrm{Th} = 3.14(^{230}\mathrm{Th})^{-0.508}, \tag{7}$$

with regression coefficients of −0.8623 and −0.9267, respectively.

These relationships may reflect that these activity ratios remain constant only for concentrations of ^{238}U and ^{230}Th above some 200 mBq g^{-1}. For concentrations below this value, contamination of radionuclides from the ^{232}Th decay chain seems to be undistinguished.

Spartina densiflora

The same radionuclides were analysed in samples of *Spartina densiflora*, whose results are presented in Table 2. The activities range, in general, from 2 to 50 mBq g^{-1} for ^{210}Po and U isotopes, with the activity concentrations of ^{210}Po being higher than those of U-isotopes in most samples. There is a difference of one order of magnitude between the highest and the lowest concentrations. As in the case of soil substrates, the highest concentrations in *Spartina densiflora* were found at the Northern marsh and at the east side of the Saltés island. Thus, in general, the highest radioactive concentrations in plants are found in those collected in areas with the highest radioactive concentration in the soil substrate, and the lowest in those with the lowest concentrations in the substrate. Concentrations of ^{230}Th are generally lower than those of ^{210}Po and U-isotopes. However, the same pattern of distribution is observed. Concentrations of radionuclides from the ^{232}Th decay chain are clearly much lower than those of radionuclides from the ^{238}U decay chain (ranging from 0.26 to 4.14 for both Th isotopes). In general, the concentration of ^{228}Th is higher than that of ^{232}Th. This fact should be related with the higher mobility of ^{228}Ra. However, it is also true that the radioactive concentration of both isotopes in plants collected in the Northern marsh and in the east side of the Saltés island are higher than in those samples collected in other stations.

It seems interesting to study the relationship between these radionuclides. In Fig. 5(a), radioactive concentrations of both U isotopes are plotted. It can be clearly observed that both isotopes are quite well linearly related ($r = 0.996$), as was found in the case of the soil substrate samples. Moreover, again the slope of the line (1.073 ± 0.018), for a y-axis intercept zero (0.174 ± 0.262), would give the ^{234}U/^{238}U activity ratio of the plant. Thus, there is again a slight excess of the daughter isotope. The relation-

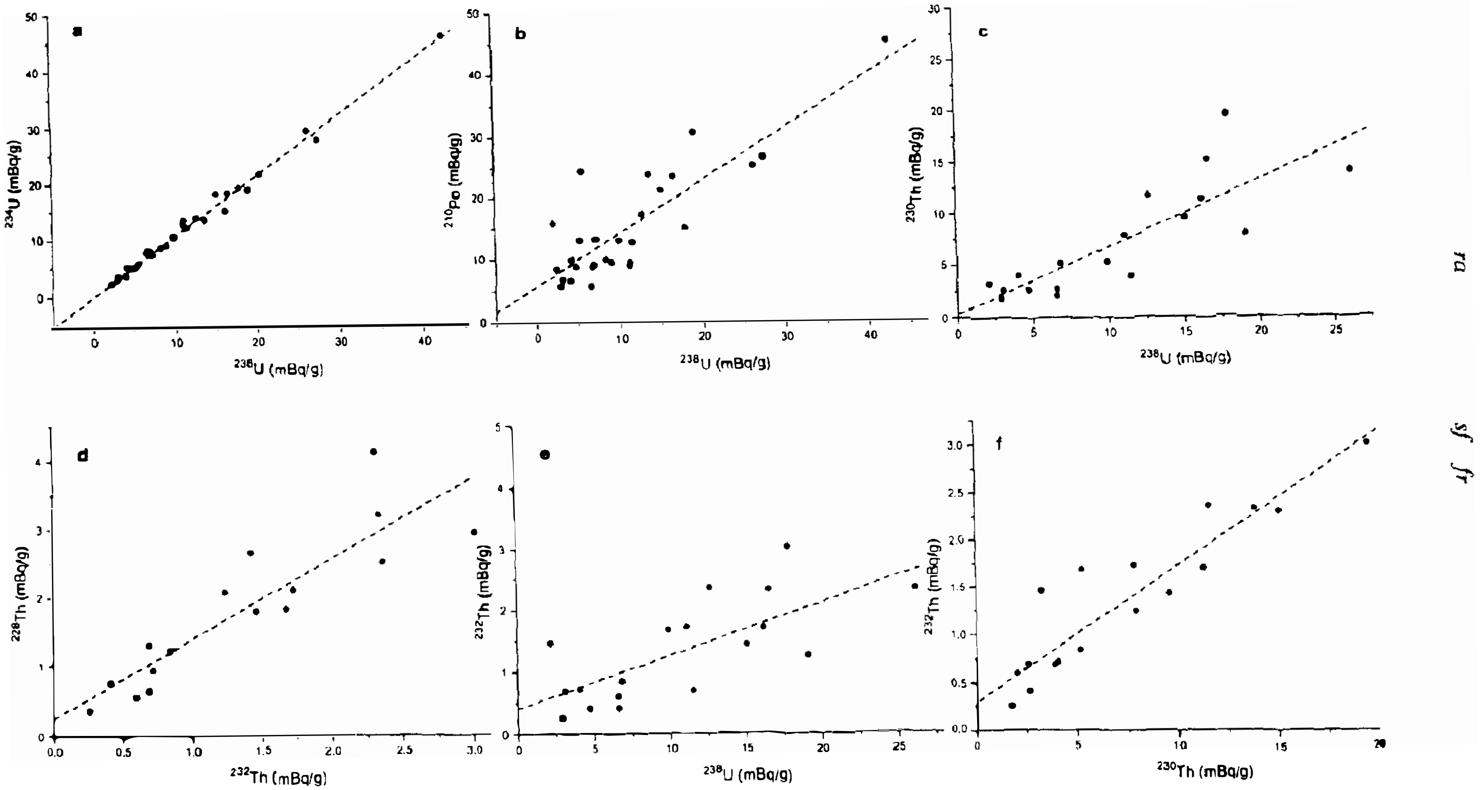

Fig. 5. Relationship between concentrations of radionuclides from the ^{238}U decay chain in *Spartina densiflora* samples (a) ^{234}U vs. ^{238}U, (b) ^{210}Po vs. ^{238}U, (c) ^{230}Th vs. ^{238}U, (d) ^{228}Th vs. ^{232}Th, (e) ^{232}Th vs. ^{238}U and (f) ^{232}Th vs. ^{230}Th.

ship between the concentrations of ^{210}Po and that of ^{238}U [see Fig. 5(b)], is not clear. However, there is still a clear trend of increasing ^{210}Po concentrations when concentrations of ^{238}U increase ($r = 0.8515$). Comparing the U concentration in the plant with the *y*-intercept of this line (5.59 ± 1.45), the latter must be considered clearly different to zero. This *y*-intercept reflects the variation in the ^{210}Po/^{238}U activity ratio with the ^{238}U concentration in the plant. Thus, for a low U concentration (background levels), there is an excess of ^{210}Po compared to ^{238}U. This excess decreases to secular equilibrium for high ^{238}U concentrations. In fact, for plants with enhanced concentrations, both radionuclides are practically in secular equilibrium.

Again, a linear relationship ($r = 0.8223$) can be found between the ^{230}Th and ^{238}U concentration in the plants [see Fig. 5(c)]. In this case, the value close to zero of the *y*-intercept (0.368 ± 1.39) gives a ^{230}Th/^{238}U activity ratio quite constant across all the area (0.638 ± 0.110). This value of the activity ratio reflects a clear deficity of ^{230}Th in the plants, opposite to that found in soils. This difference between activity ratios in soils and plants can be explained by the lower mobility of Th compared to U.

Both Th isotopes from the same decay chain (^{232}Th and ^{228}Th) are also linearly related ($r = 0.8950$), as can be observed in Fig. 5(d). The value of the *y*-intercept, gives practically secular equilibrium between isotopes in all samples.

More interesting seems to be the relationship of the ^{232}Th concentrations with the ^{238}U and ^{230}Th concentrations [see Fig. 5(e) and 5(f)]. The concentration of ^{232}Th in the plant clearly increases as the concentration of U and/or ^{230}Th increases, following linear relationships (regression coefficients of 0.7220 and 0.9248, respectively). As they are isotopes of the same element, the relationship between both Th isotopes is much better. In both cases, the *y*-axis intercept is nearly zero, given ^{232}Th/^{238}U and ^{232}Th/^{230}Th activity ratios of 0.087 ± 0.021 and 0.143 ± 0.015, respectively.

Concentration ratios

We were also interested in the study of the biological uptake and transfer of these radionuclides from the soil substrate to the plant. Thus, we have calculated the experimental values of the concentration ratios for each radionuclide in each station. The results are presented in Table 3. For ^{210}Po, concentration ratios ranging from 0.026 ± 0.002 to 0.948 ± 0.082, with a mean value of 0.172 ± 0.204, were found. The standard deviation of this mean value reflects the high dispersion of the data. In fact, differences above one order of magnitude are found. Moreover, it is interesting to notice that different values of this factor depend on the activity concentration of the soil substrate. Thus, high concentration ratios appear in stations with low activity concentrations in the substrate, and low in more contaminated stations. The same occurs in the case of all radionuclides from the ^{238}U decay chain. For both U isotopes (^{238}U and ^{234}U), the experimental concentration ratios range from 0.022 ± 0.002 to 0.269 ± 0.031 for ^{238}U and from 0.024 ± 0.002 to 0.272 ± 0.032 for ^{234}U, with mean values of 0.083 ± 0.061 and 0.082 ± 0.060, respectively. Again, in both cases, the concentration ratio (CR) depends on the activity concentration of the elements in the soil substrate. The same is found in the case of the concentration ratio for ^{230}Th. It ranges from 0.010 ± 0.001 to 0.202 ± 0.022, with a mean value of 0.065 ± 0.057. Thus, it seems that the behaviour of the concentration ratio, which means the uptake by plants of radionuclides from its substrate, depends on the activity concentration of the element in the soil substrate.

In the case of both Th isotopes from the ^{232}Th decay chain, the concentration ratio ranges from 0.014 ± 0.004 to 0.065 ± 0.008 for ^{232}Th and from 0.011 ± 0.001 to 0.084 ± 0.022 for ^{228}Th, with mean values 0.036 ± 0.018 and 0.042 ± 0.025, respectively. The dispersion of the data seems to be not as high as that for radionuclides from the ^{238}U decay chain. However, we must consider that, in this case, the range of Th concentration in the soil substrate is not as wide as in the case of U and daughters.

In order to study the behaviour of the concentration ratios for these radionuclides, concentration ratios versus the activity concentration at the radionuclide in the soil substrate have been plotted in Fig. 6 for ^{238}U and daughters and in Fig. 7 for ^{232}Th and ^{228}Th. The CR values clearly decrease when the activity concentration in the substrate soil increases. In fact, the data can be modelled by fitting functions of the form:

$$\mathrm{CR} = aC_s^b \tag{8}$$

Thus, if $b = 0$, this would mean that the concentration ratio is constant, regardless of the activity concentration in the soil substrate. Functions of this type have been fitted for ^{210}Po, ^{238}U, ^{234}U and ^{230}Th, and these results are presented in Table 4. Thus, for all radionuclides from the ^{238}U, the b value of the hyperbolic function is clearly different from zero, -0.750 ± 0.097, -0.445 ± 0.081, -0.438 ± 0.082 and -0.573 ± 0.098 for ^{210}Po, ^{234}U, ^{234}U and ^{230}Th, respectively. However, the linearity assumption may fit better in the case of U isotopes. Thus, it seems that all these radionuclides follow the behaviour of an essential element for the plant

TABLE 4

Concentration Ratio (CR) Fitted Functions for Radionuclides from the ^{238}U Decay Chain

Radionuclide	CR = aC_s^b	σ_a	σ_b	r
^{210}Po	CR = 4.06 $C_s^{-0.750}$	1.96	0.097	−0.8296
^{238}U	CR = 0.59 $C_s^{-0.445}$	0.239	0.081	−0.7137
^{234}U	CR = 0.588 $C_s^{-0.438}$	0.247	0.082	−0.7030
^{230}Th	CR = 0.717 $C_s^{-0.573}$	0.349	0.098	−0.8256

C_s means the concentration of the radionuclide in the soil substrate.

growth. Moreover, if activity concentrations in the soil substrate above 200 mBq g^{-1} are only considered, the CR value would be apparently constant. Thus, considering only those stations with high activity concentrations in the soil substrate, CR values of 0.050 ± 0.023, 0.046 ± 0.020 and 0.023 ± 0.011 are obtained for ^{210}Po, U-isotopes and ^{230}Th, respectively. In this case, if the CR value is used to predict plant concentrations from substrate concentration, it will underpredict plant concentration when the substrate concentration is less than ~200 mBq g^{-1}. Sheppard and Sheppard (1985) found that the CR for natural U in native plants at the

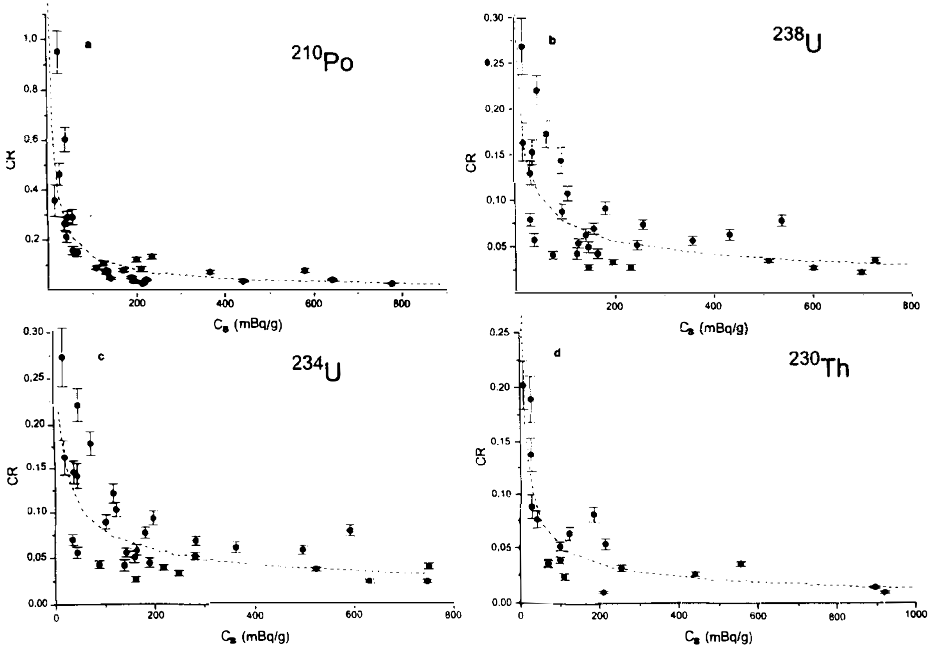

Fig. 6. Concentration ratios vs. the activity concentration of the element in the soil substrate for (a) ^{210}Po, (b) ^{238}U, (c) ^{234}U and (d) ^{230}Th.

Precambrian Shield appeared to be dependent upon substrate concentration below ~20 μg g^{-1}. They assumed the use of the CR concept to predict U concentration in plants to be valid when substrate concentrations are higher than about 20 μg g^{-1}. In our case, this fact seems to be true for all radionuclides from the ^{238}U decay chain. The case of both Th isotopes from the ^{232}Th decay chain is not very clear. The CR values (see Fig. 7) seem to be more or less constant compared with those of radionuclides from the ^{238}U decay chain, with mean values of 0.036 ± 0.017 and

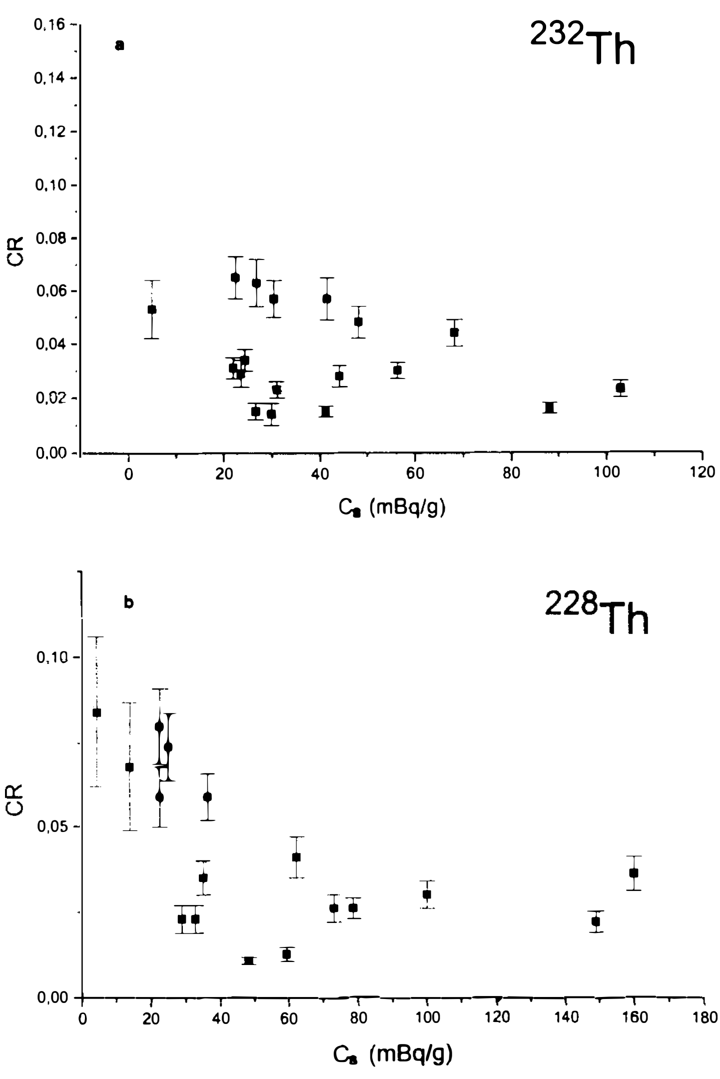

Fig. 7. Concentration ratios vs. the activity concentration of the element in the soil substrate for (a) ^{232}Th and (b) ^{228}Th.

0.042 ± 0.025 for ^{232}Th and ^{228}Th, respectively. However, the range of activity concentration of these radionuclides in the soil substrate, should be considered carefully.

Thus, it seems that, when studying the uptake of radionuclides by plants from its substrate concentration, it is necessary to consider a reasonably wide range of activity concentration in the soil substrate. Otherwise, nothing can be clearly predicted. It seems that at least those radionuclides from the ^{238}U decay chain behave as essential elements for the growth of the plant. However, whether these elements are essential or are mimicking essential elements cannot be determined within this study.

CONCLUSIONS

Concentrations of ^{210}Po, U- and Th-isotopes in *Spartina densiflora* and soil substrate samples collected from a saline wet marsh have been studied. The activity concentrations show clearly the influence that the radioactivity contained in the phosphate rock used for the phosphoric acid production has over the concentration of natural radionuclides in certain zones of the marsh, affecting the plants and the soils. Indeed, the stations more influenced by the Odiel waters present the highest concentrations in soils and plants.

Concentration ratios for all radionuclides in the plant were determined. The concentration ratio of an element seems to be dependent on the activity concentration of the same element in its soil substrate. Thus, high CRs appear in plants growing in soils with a low concentration of radionuclides, whereas low CRs appear in plants growing in soils with high concentrations. Moreover, the relationship between the CR and the activity concentration of the soil substrate seems to be hyperbolic, at least in the case of radionuclides from the ^{238}U decay chain. As a consequence, if the CR value is used to predict plant concentrations from substrate concentration, it will underpredict plant concentration when the substrate concentration is less than $\sim 200\,\mathrm{mBq\,g^{-1}}$. However, in the case of ^{232}Th and ^{228}Th, the narrow range of activity concentration of these radionuclides in the soil substrate, could be the reason for the apparent constancy of the CR with substrate concentration.

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