Transfer of Natural Radionuclides from Soils to Plants in a Wet Marshland*

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Soils and two wild plant species (*Spartina densiflora* and *Spartina marítima*) have been collected from the Odiel river marsh and analysed for ^{210}Po and ^{238}U. The radioactivity concentrations in plants and soils reflect the impact of the operation of two phosphoric acid production factories located close to the marsh. Concentration ratios (*CR*) of these radionuclides, between plant and underlying soil, have been studied. First results show that the concentration ratios (*CR*) seem to be dependent on radionuclide soil concentration.

Introduction

It is well known that the use of phosphate rock as raw material for phosphoric acid production provokes the redissemination into the environment of noticeable amounts of natural radioactivity. This is the case for the phosphate-based fertilizer production complex, formed by two factories located at the Odiel river (Southwestern Spain, see Fig. 1). We have previously shown that discharges from such industries clearly spike the Odiel river with easily measurable concentrations of natural radionuclides (Martínez-Aguirre *et al.*, 1994). Furthermore, the Odiel water tidal movements transport the radioactivity into the marsh area located on the right bank of the river, in front of the factories (see Fig. 1), a natural reservation where an important biological activity takes place.

In this paper we present additional data on the radioactivity concentrations of ^{210}Po and ^{238}U in soils from the marsh. We also give first results on the presence of such radionuclides in two marsh plants, *Spartina densiflora* and *Spartina marítima*, which grow in the area. It will be seen that discharges from the fertilizer industries also modify the radioactivity content of such plants. Preliminary results are presented on the behaviour of the concentration ratio (*CR*), defined as the ratio between the radionuclide concentration in the plant and in the underlying soil, for the plants studied.

Samples and Radioanalytical Procedures

The Odiel marsh is mainly composed of four small islands separated by four little channels. The area is affected by the tidal flow of water from the Odiel river, where two phosphoric acid factories are located. They release part of their wastes directly in the river.

The sampling stations are shown in Fig. 1. Both soil and plant samples were collected during low tide in areas covered by water during high tide. Some 1 kg of surface soil (6 cm deep) was taken from each station and stored in plastic bags. Aliquots were dried and powdered in the laboratory. Density and organic matter were determined for each soil sample.

Spartina densiflora and *Spartina maritima* plants were collected from the same areas, although the latter was found only in nine of the stations explored. The roots of the plants were discarded and the leaves and stems were rinsed to remove any trace of solid particles, dried, powdered and analysed as a whole.

Either the soil or plant samples were spiked with known amounts of ^{208}Po and ^{232}U to estimate the recovery yields, digested with concentrated HNO_3 and aqua regia. The residue was then dissolved with 8 M HNO_3. A solvent extraction technique with tributylphosphate (TBP) was used for Po and U extraction. The final Po solution was self-deposited onto silver planchets while that containing U was electroplated onto stainless steel planchets. ^{210}Po and U-isotope activities were measured by ion-implanted Si detector α-spectrometry. Details of the radiochemical and counting methods can be found in Martínez-Aguirre (1991).

Results and Discussion

The ^{210}Po and ^{238}U radioactivity concentrations in mBq g^{-1} dry weight are presented in Table 1 for soils and *Spartina densiflora* and in Table 2 for soils and *Spartina marítima*. Values of concentration rations (*CR*), defined as the ratio between the concentration (dry mass) of a radionuclide in the plant and the

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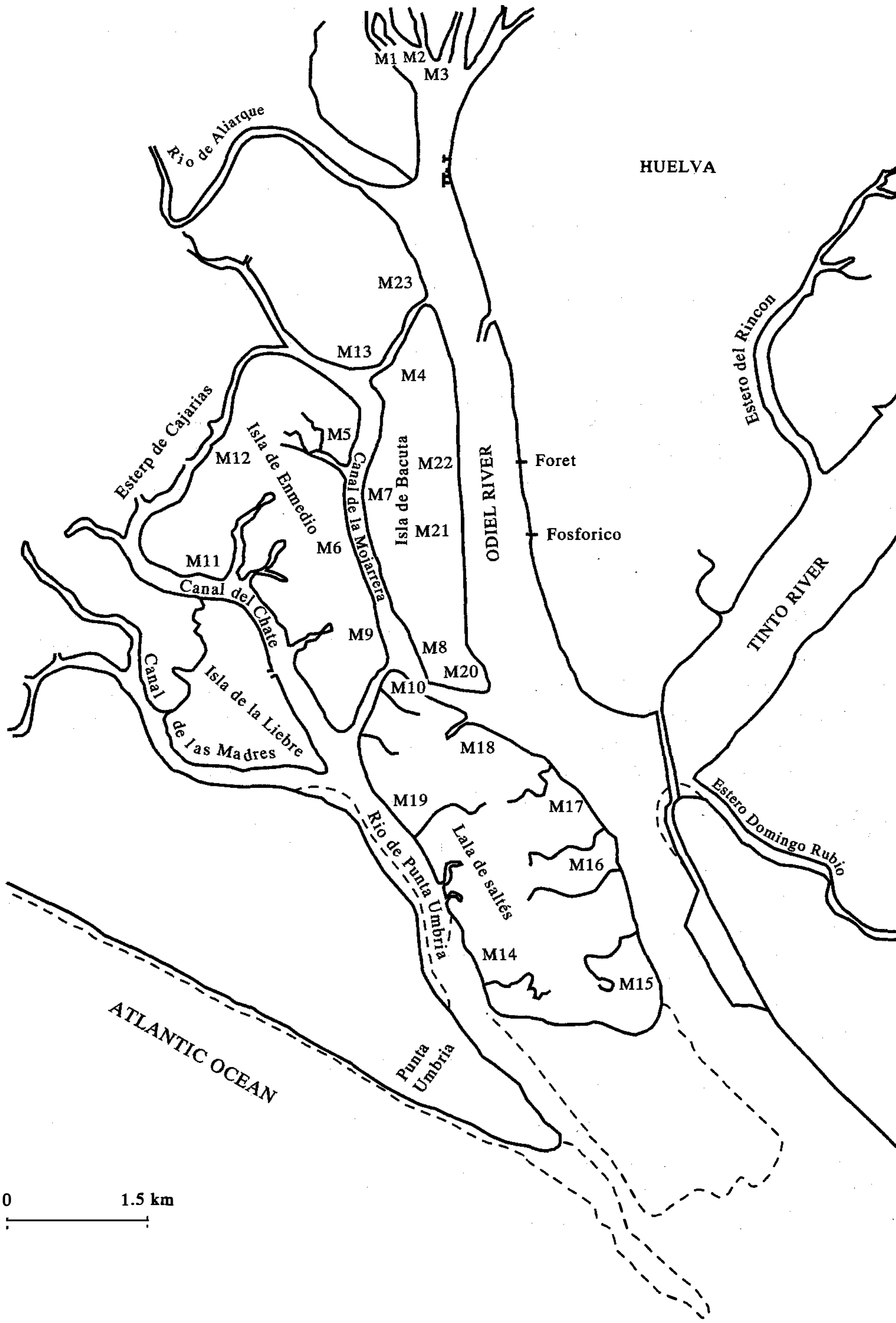

Fig. 1. Location of the sampling stations in the Odiel marsh area. The locations of the fertilizer factories are also given.

concentration (dry mass) of the same radionuclide in the substrate, are given in the same tables.

Soils

Results for ^{210}Po in soils, reported already (Martínez-Aguirre and García-León, 1996) seem to suggest clearly that the intrusion of waters from the Odiel river during high tides disseminates natural radionuclides into the marsh area. The ^{210}Po pattern distribution presented in Table 1 indicates how the waters enter to the marsh. After an input of radioactivity is produced, the contamination plume moves up the river during high tides. Part of this plume enters the marsh through the northern area of Bacuta

Table 1. Data of ^{210}Po and ^{238}U in mBq g^{-1} (dry weight) in soils and *Spartina densiflora* samples from the Odiel marsh. Concentration ratios in each station, defined as the ratio between the concentration of an element in the plant and that in its substrate, are also given

Code	^{210}Po soil	^{238}U	^{210}Po plant	^{238}U	*CR* (^{210}Po)	*CR* (^{238}U)
M1	199 ± 10	268 ± 12	23.6 ± 1.6	16.6 ± 1.1	0.119 ± 0.010	0.062 ± 0.005
M2	778 ± 41	877 ± 19	21.2 ± 1.1	15.1 ± 1.1	0.027 ± 0.002	0.017 ± 0.001
M3	643 ± 28	795 ± 23	25.1 ± 1.3	26.2 ± 1.9	0.039 ± 0.003	0.033 ± 0.003
M23	210 ± 11	320 ± 10	17.3 ± 1.8	12.7 ± 1.1	0.082 ± 0.009	0.040 ± 0.004
M4	580 ± 26	625 ± 11	45.2 ± 4.5	42.6 ± 2.7	0.078 ± 0.008	0.068 ± 0.004
M13	222 ± 11	213 ± 10	8.60 ± 0.55	6.65 ± 0.47	0.039 ± 0.003	0.031 ± 0.003
M5	213 ± 10	267 ± 9	5.58 ± 0.41	6.61 ± 0.58	0.026 ± 0.002	0.025 ± 0.002
M7	130 ± 7	178 ± 9	8.90 ± 0.77	11.1 ± 0.8	0.069 ± 0.007	0.062 ± 0.005
M6	141 ± 7	161 ± 12	6.52 ± 0.43	4.07 ± 0.43	0.046 ± 0.004	0.025 ± 0.003
M9	188 ± 10	150 ± 9	8.97 ± 0.60	6.85 ± 0.56	0.048 ± 0.004	0.046 ± 0.005
M8	64.6 ± 4.0	95.5 ± 8.2	9.50 ± 0.76	11.2 ± 0.8	0.147 ± 0.015	0.117 ± 0.013
M20	233 ± 11	308 ± 14	30.6 ± 1.9	19.1 ± 1.1	0.131 ± 0.010	0.062 ± 0.004
M18	565 ± 23	716 ± 18	50.1 ± 2.4	16.2 ± 1.2	0.089 ± 0.006	0.023 ± 0.002
M17	41.0 ± 3.2	31.3 ± 7.5	8.61 ± 0.58	4.74 ± 0.51	0.210 ± 0.021	0.151 ± 0.040
M16	441 ± 20	494 ± 14	15.0 ± 0.8	17.9 ± 0.9	0.034 ± 0.002	0.036 ± 0.002
M15	131 ± 7	109 ± 7	9.92 ± 0.63	8.31 ± 0.66	0.076 ± 0.006	0.076 ± 0.008
M12	44.2 ± 2.5	61.7 ± 7.6	13.0 ± 0.7	9.92 ± 0.63	0.290 ± 0.023	0.161 ± 0.022
M11	194 ± 9	105 ± 9	6.82 ± 0.52	3.09 ± 0.26	0.035 ± 0.003	0.029 ± 0.003
M10	27.9 ± 2.0	152 ± 9	12.8 ± 0.8	11.5 ± 0.7	0.460 ± 0.044	0.076 ± 0.006
M19	54.4 ± 3.7	46.8 ± 7.4	8.36 ± 0.68	2.37 ± 0.20	0.154 ± 0.016	0.151 ± 0.009
M14	54.7 ± 3.9	75.6 ± 6.9	15.8 ± 1.2	2.16 ± 0.23	0.290 ± 0.030	0.029 ± 0.004
M21	16.2 ± 2.5	30.7 ± 7.3	5.74 ± 0.48	2.93 ± 0.36	0.354 ± 0.062	0.095 ± 0.025
M22	37.2 ± 2.5	58.9 ± 8.1	9.78 ± 0.69	4.20 ± 0.37	0.263 ± 0.026	0.071 ± 0.011

Table 2. Data of ^{210}Po and ^{238}U in mBq g^{-1} (dry weight) in soils and *Spartina maritima* samples from the Odiel marsh. Concentrations ratio in each station are also given

Code	^{210}Po soil	^{238}U	^{210}Po plant	^{238}U	*CR* (^{210}Po)	*CR* (^{238}U)
M1	199 ± 10	268 ± 12	36.2 ± 1.9	36.5 ± 2.8	0.182 ± 0.013	0.136 ± 0.012
M2	778 ± 41	877 ± 19	40.6 ± 1.1	49.6 ± 3.1	0.052 ± 0.003	0.057 ± 0.004
M3	643 ± 28	838 ± 18	43.4 ± 2.1	48.8 ± 3.0	0.068 ± 0.004	0.058 ± 0.004
M6	141 ± 7	189 ± 8	13.8 ± 1.0	12.4 ± 0.8	0.098 ± 0.009	0.066 ± 0.005
M18	565 ± 23	716 ± 18	22.6 ± 1.1	17.5 ± 1.1	0.040 ± 0.003	0.024 ± 0.002
M16	441 ± 20	494 ± 14	9.92 ± 0.45	6.20 ± 0.37	0.023 ± 0.001	0.013 ± 0.001
M11	194 ± 9	105 ± 9	14.7 ± 0.9	8.42 ± 0.58	0.076 ± 0.006	0.080 ± 0.009
M19	54.4 ± 3.7	46.8 ± 7.4	5.05 ± 0.41	3.51 ± 0.26	0.093 ± 0.010	0.075 ± 0.013
M14	54.7 ± 3.9	75.6 ± 6.9	5.86 ± 0.45	3.01 ± 0.42	0.107 ± 0.011	0.040 ± 0.007

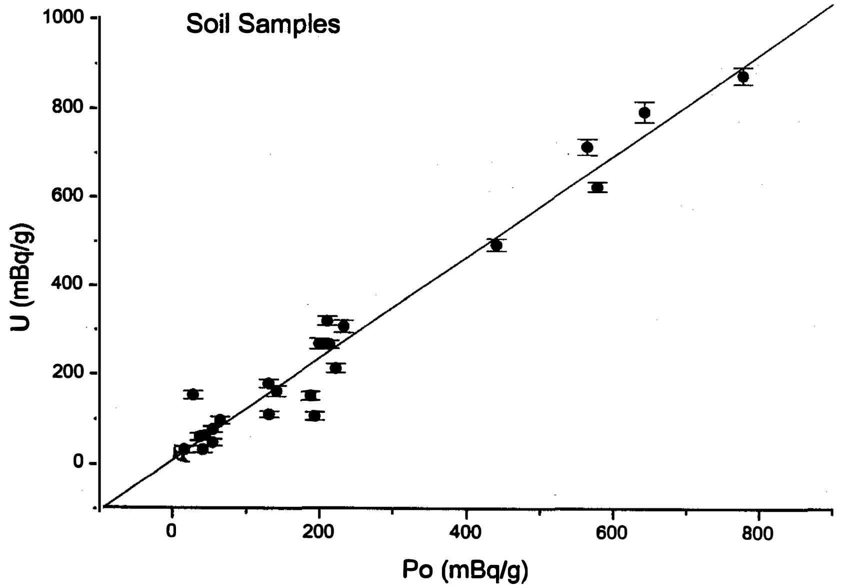

Fig. 2. ^{238}U activity concentrations vs ^{210}Po activity concentrations in soil samples. $U = (8.12 \pm 15.8) + (1.143 \pm 0.051)\ Po$ with $r = 0.980$.

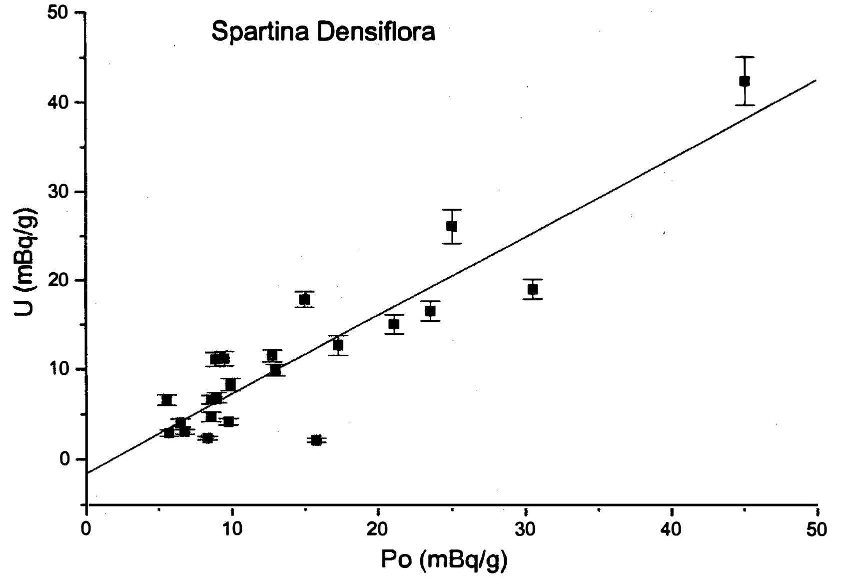

Fig. 3. ^{238}U activity concentrations vs ^{210}Po activity concentrations in *Spartina densiflora* samples. $U = (-1.57 \pm 1.57) + (0.885 \pm 0.091)$ Po with $r = 0.908$.

island. There the radioactivity is distributed, with the major amount passing into the Mojarrera channel. When the waters move downriver, during low tides the plume would move to the east of Saltés island. Thus concentrations of ^{210}Po up to 780 mBq g^{-1} were found, which are clearly above typical levels in uncontaminated soils. However, the farther part of the marsh (Punta Umbria river) seems to be unaffected by the fertilizer production, with activity concentrations similar to uncontamined soils (UNSCEAR, 1988).

The same conclusions can be derived by examining the ^{238}U results, with concentrations up to 880 mBq g^{-1} in the same areas as those with high ^{210}Po concentrations. If we compare ^{210}Po with ^{238}U concentrations, as in Fig. 2, both radionuclides are linearly related with a regression coefficient of 0.980. This relationship reveals the same origin for both radionuclides in the soils. In general, the ^{238}U activity concentrations are slightly above the ^{210}Po activity concentrations, with a ratio (U/Po) of 1.143 ± 0.051, given by the slope of the line.

It is interesting to note that both for ^{210}Po and ^{238}U the levels in the northern marsh (samples M1, M2 and M3) are higher than in the rest of the samples. This suggests these locations are the sink for, at least, those radionuclides most likely related to tidal interactions.

Plants

The levels of ^{210}Po and ^{238}U in both Spartina species are very similar, ranging from 6 to 50 mBq g^{-1} for ^{210}Po and from 2 to 50 mBq g^{-1} for ^{238}U. The case of samples located at the northern marsh is interesting since again the highest levels are found there. Furthermore, the radioactivity concentrations found for *Spartina maritima* are higher than those for *Spartina densiflora*. It can be related to the fact that *Spartina maritima* samples in such stations are covered by water for a longer period than those of *Spartina densiflora*.

The distribution pattern of ^{210}Po and ^{238}U concentrations found in soils is reflected also in the plants, thus showing that releases from the factories enter into the biosphere. Furthermore, as was found in soils, a linear relationship (Fig. 3) is found for both radionuclides, with a regression coefficient of 0.980. Moreover, the slope of the line (0.885 ± 0.091) indicates that, contrary to what was found in soils, the ^{210}Po concentrations in plants are slightly greater than the ^{238}U concentrations.

Concentrations ratios (CR)

The transfer of ^{210}Po and ^{238}U from soil to plants was also studied by using the concept of concentration ratio (*CR*). Theoretically it should give information on the amount of radionuclide which enters the plant from its substrate. It is certainly important for understanding the dissemination of radioactivity in nature as a whole.

Tables 1 and 2 give the *CR* values obtained for *Spartina densiflora* and *Spartina maritima*, for ^{210}Po and ^{238}U. The *CR* values range from 0.026 to 0.460 and from 0.017 to 0.161 for ^{210}Po and ^{238}U, respectively. In general, the *CR* is higher for ^{210}Po than for ^{238}U, reflecting a greater transfer of ^{210}Po to the plant than that of ^{238}U. In the case of *Spartina maritima*, the *CR* values range from 0.023 to 0.182 for ^{210}Po and from 0.013 to 0.136 for ^{238}U. Again, the *CR* for ^{210}Po is higher than for ^{238}U, but the differences are much less significant than in the case of *Spartina densiflora*. Comparing the *CR* values for both plant

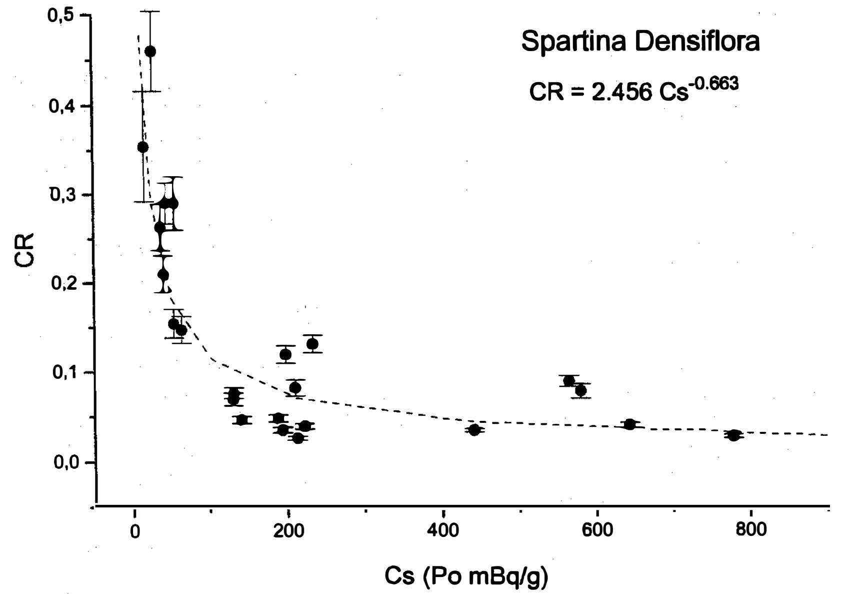

Fig. 4. ^{210}Po concentration ratio (CR) in *Spartina densiflora* vs ^{210}Po concentration in the underlying soil in mBq g^{-1}. $CR = 2.456C_s^{-0.663}$.

species, there seems to be a tendency for a lower CR in the case of *Spartina densiflora* than in *Spartina maritima*; this is clearer in the case of ^{238}U.

It can be observed that CR depends on soil concentrations. At this stage of the study it is not possible to identify clearly any trend for the case of *Spartina maritima* samples. However, it seems that for *Spartina densiflora* the CR decreases when the concentration in the soil increases; this is clear for ^{210}Po, but not so clear for ^{238}U. This behaviour can be seen in Figs 4 and 5, where the CR values for ^{210}Po and ^{238}U for *Spartina densiflora* vs the concentration of the same radionuclides in the underlying soil are plotted, respectively. The continuous lines represent the best fit of the curve

$$CR = aC_s^b \tag{1}$$

to the experimental data where C_s is the radioactivity concentration in the soil and $b \leq 1$. The parameters of these fits are given in Table 3 for both plant species.

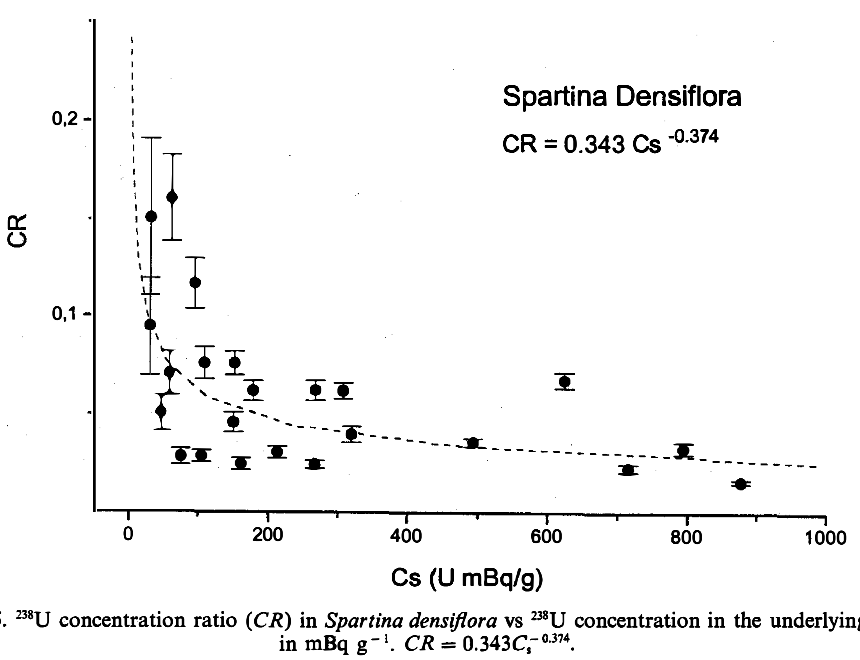

Fig. 5. ^{238}U concentration ratio (CR) in *Spartina densiflora* vs ^{238}U concentration in the underlying soil in mBq g^{-1}. $CR = 0.343C_s^{-0.374}$.

Table 3. Relationship between concentration ratio (CR) of ^{210}Po and ^{238}U in soils and *Spartina* species of the type C_s^b. r is the correlation coefficient of the lines log CR vs log C_s. s_a is the error in the y-axis intercept and s_b the error in the slope

Radionuclide	r	Relationship	s_a	s_b
Spartina densiflora				
^{210}Po	−0.817	$CR = 2.456C_s^{-0.663}$	0.549	0.105
^{238}U	0.612	$CR = 0.343C_s^{-0.334}$	0.082	0.106
Spartina maritima				
^{210}Po	−0.603	$CR = 0.504C_s^{-0.360}$	0.218	0.182
^{238}U	−0.354	$CR = 0.177C_s^{-0.225}$	0.097	0.227

A first approach should consider the CR to be independent of C_s, being constant over several orders of magnitude. However, according to experimental evidence such a situation seems to be only valid for non-essential elements at non-toxic substrate levels (Mengel and Kirkby, 1979; Timperley *et al.*, 1970). In fact, Sheppard and Sheppard (1985) suggest a non-linear relationship between CR and C_s for essential elements or when an element mimics an essential element. Moreover, Tracy *et al.* (1983) studied the uptake of ^{226}Ra, ^{210}Pb and U from soils to garden plants. They observed a clear trend towards increasing concentration in plants with increasing concentration in soils. Such trends were modelled by functions of the type

$$C_p = aC_s^{b'} \quad (2)$$

C_p being the element concentration in soil and $b' \geq 1$. Equation (2) is identical with equation (1) since $CR = C_p/C_s$ and $b = b' - 1$, so that our results seem to follow the same trend as that found by Tracy *et al.* (1983) for other plant species.

A final comment can be made regarding the results obtained. Figure 6 presents a hypothetical relationship of CR vs C_s for essential and non-essential elements, taken from Sheppard and Sheppard (1985). According to this, plants readily take up elements essential for growth when C_s is low, whereas CR is generally constant for non-essential elements at this C_s range (Mengel and Kirkby, 1979; Timperley *et al.*, 1970). When C_s increases, CR can either remain

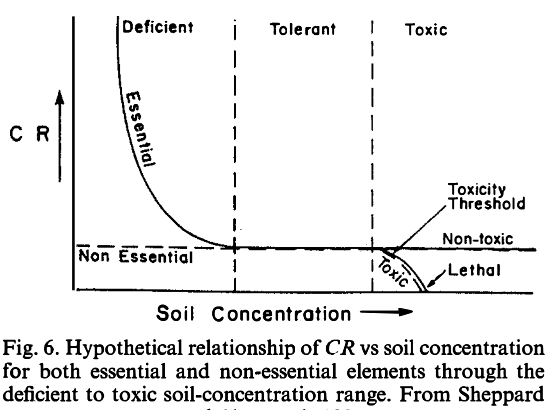

Fig. 6. Hypothetical relationship of CR vs soil concentration for both essential and non-essential elements through the deficient to toxic soil-concentration range. From Sheppard and Sheppard, 1985.

constant (no toxicity) or can decrease, leading to toxicity or death. Toxicity begins at a toxicity threshold of C_s, and from then CR tends to decrease. Lethal C_s values of essential or non-essential elements may not exist. In that case CR may be constant over several orders of magnitude of C_s.

The preliminary nature of our results makes it difficult to provide definitive conclusions. Nevertheless, it is relatively clear that ^{210}Po follows the above mentioned pattern, with a behaviour typical of essential elements. This is not so evident in the case of ^{238}U. However, as stated by Sheppard and Sheppard (1985), U behaves as an essential element at low C_s. Such behaviour is even clearer for ^{210}Po for the plant species studied, although for *Spartina maritima* this is not very clear, but at least ^{210}Po seems to follow the same pattern.

Conclusions

^{210}Po and ^{238}U radioactivity concentrations have been studied in samples of soils and two wild plants, *Spartina densiflora* and *Spartina maritima*, collected from the Odiel river marsh area. Results have shown that the operation of the two phosphoric acid production factories, located close to the marsh, have an impact on it by enhancing the radioactivity levels in both soils and plants. The distribution pattern of radioactivity along the marsh indicates that the Odiel river waters intrude into such area by tidal movements. Concentration ratios (CR) have been studied for both *Spartina* species. It has been found that the CR is not constant, but depends on soil radioactivity concentrations, C_s. In fact it is higher for low C_s than for high C_s. This finding has been obtained previously for other plant species and radionuclides, and opens an interesting line of research.

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