Radioactive Impact of Phosphate Ore Processing in a Wet Marshland in Southwestern Spain

A. Martínez-Aguirre & M. García-León

Facultad de Física, Universidad de Sevilla, Apdo. 1065, 41080 Sevilla, Spain

ABSTRACT

In this paper an extensive study of the presence of natural radionuclides in a marshland area located in the vicinity of a phosphoric acid production complex in southwestern Spain is presented. This marsh is a natural reser-vation where significant biological activity takes place. The marsh is highly affected by the inflow of water from the Odiel river which is enhanced with natural radionuclides from industries which use phosphate rocks as raw material for fertilizer production. Sediment samples, collected from the intertidal zone, showed that wastes from the phosphate industries have resulted in enhanced radioactivities in the marsh.

INTRODUCTION

Studies and surveys of natural environmental radiation and radioactivity are of great importance and interest for health physics as well as many other disciplines. The progressive development of the nuclear industry and other contaminating technologies and the widespread and ever-increasing use of radiation and radioactive isotopes requires the evaluation of the background of natural radionuclides and radioactivity in order to detect anthropogenic contamination, assess its impact, and implement appro-priate countermeasures for population and environmental protection.

The radionuclides which contribute most to environmental radiation are the members of the natural radioactive series, ^{238}U and ^{232}Th, and ^{40}K. They are present in rocks and minerals in concentrations that can

vary by several orders of magnitude, depending on the geochemical processes to which the material they came from have been subjected. Any soil would have a concentration of natural radionuclides that is determined by the concentration in the parent material and by the physicochemical phenomena associated with its weathering. Thus, soils on top of sedimentary materials present diverse concentrations of these elements depending on those present in the eroded substrate and on the chemical and physical phenomena associated with the sedimentation.

Phosphate ores contain important amounts of natural radioactive elements, specially ^{238}U and descendants, in concentrations that depend on its geographical and geological origin, but which can reach up to 300 ppm for U. Sedimentary and igneous phosphate ores are used as raw material for the production of phosphoric acid, and, consequently, fertilizers for agricultural purposes. Large-scale production of phosphoric acid results in the redistribution of huge amounts of natural radioactivity. Depending on the technology used to produce fertilizer or phosphoric acid, the distribution of radioactive elements among the various products would be different (Roessler *et al.*, 1979). Sometimes fertilizers and a common by-product, phosphogypsum, contain such high activities of natural radioactive elements that the resulting radiological impact should be considered carefully (Paul *et al.*, 1984; Martínez-Aguirre *et al.*, 1994; Koster *et al.*, 1992; Periañez & García-León, 1993).

The radioactive impact that the industrial complex, which includes two fertilizer plants, located at the south of Spain (Huelva), has over the Odiel and Tinto river basins has been widely studied (Martínez-Aguirre & García-León, 1991; Martínez-Aguirre *et al.*, 1994; Periañez & García-León, 1993). Part of the solid wastes (phosphogypsum) are directly released into the Odiel. Moreover, acid liquid wastes (process waters) resulting from the phosphoric acid production, with high concentration of natural radionuclides in solution, are also released into the Odiel river channel. These releases have affected the concentration level of natural radionuclides in water and bottom sediment of the Odiel river (Martínez-Aguirre *et al.*, 1994). The factories are located in an estuarine system highly affected by the tides. The movement of the water results in a wide distribution of the contamination upstream and downstream the industries.

In this paper we present the results obtained in the study of the presence of natural radionuclides in soils from the Odiel marshland area. The marsh is located at the western margin of the Odiel river, in front of the phosphoric acid production complex. It is highly affected by tidal movements of the Odiel riverwaters and, consequently, its formation regime should be considered as sedimentary. Significant biological activity takes

place at the marsh which is a natural reservation. Four small islands, crossed by four channel form the marsh. We will show that the radioactivity released by the phosphate fertilizer factories wasting activities reaches the marsh and describe how such transport is produced.

SAMPLES AND EXPERIMENTAL METHODS

A total of 13 and 23 surface soil samples were taken from the Odiel marsh located at the western margin of the Odiel river opposite to the fertilizer factories, during February and November 1993, respectively. The samples were collected during the low tide from areas covered with water during the high tide. The density and organic matter content were determined for each soil sample.

Approximately 1 g of dried and powdered soil sample were spiked with well known ^{208}Po activities. After digestion of the sample with HNO_3 and aqua regia, the residue is dissolved in 8M HNO_3. A measured volume (5 ml) of TBP (tributilphosphate) was then added to the nitric solution. After shaking for about 5 min, Po is retained in the HNO_3 8M phase whereas the rest of radionuclides move to the TBP phase. Once both phases are separated, the solution which contain the Po is evaporated to dryness and self-deposited (Morón *et al.*, 1988) onto 2·2 cm diameter silver planchets. Po was finally measured by α-spectrometry with surface barrier or ion implanted Si detectors.

Activities of ^{210}Pb, ^{226}Ra, ^{228}Ra and ^{40}K were measured by γ-spectrometry by using a reverse-electrode coaxial Ge detector. Lead-210 was determined by its γ emission of 46·5 keV, ^{226}Ra by its emission of 186·2 keV, after the contribution of the γ emission of ^{235}U to this peak was subtracted. Radium-228 was measured via the 991·07 keV γ emission of ^{228}Ac, once secular equilibrium was achieved and, finally, ^{40}K was measured by its own emission of 1460·8 keV. The efficiency curve was determined by adding well-known activities of ^{152}Eu and ^{133}Ba to two different soil samples which had similar densities than most of the rest of soil samples. They were then air dried and mixed until correctly homogenized. Coincidence decay effects were corrected by comparing the count rate with that from a point source of the same radionuclides (^{152}Eu and ^{133}Ba).

RESULTS AND DISCUSSION

Table 1 gives the radioactive concentrations in mBq/g (dry weight) measured for ^{210}Po, ^{210}Pb, ^{226}Ra, ^{228}Ra and ^{40}K together with the dry

TABLE 1

Activity Concentrations in mBq/g of Natural Radionuclides in Soil Samples Collected at the Odiel Marsh in February* and November 1993†

Code	$D\ (g/cm^3)$	% organ	^{210}Po	^{210}Pb	^{226}Ra	^{228}Ra	^{40}K
M1	0·64	9·05	199 ± 10	236 ± 16	166 ± 25	56·0 ± 5·9	562 ± 27
M2	0·58	9·27	778 ± 41	820 ± 27	711 ± 45	62·5 ± 7·1	439 ± 34
M3	0·60	6·36	643 ± 28	795 ± 23	681 ± 36	84·4 ± 7·3	351 ± 32
M6*	0·38	23·6	264 ± 12	454 ± 27	321 ± 40	24·6 ± 11·1	466 ± 44
M6	0·65	14·2	580 ± 26	673 ± 16	598 ± 25	53·7 ± 4·4	470 ± 24
M5	0·56	14·7	222 ± 11	156 ± 14	161 ± 24	42·8 ± 4·6	511 ± 26
N7*	0·36	20·9	290 ± 31	424 ± 29	280 ± 43	31·3 ± 11·5	504 ± 48
M7	0·73	14·2	213 ± 10	287 ± 12	213 ± 21	48·8 ± 4·0	556 ± 22
M9*	0·43	18·7	341 ± 19	514 ± 36	326 ± 56	24·7 ± 12·2	318 ± 54
M9	0·63	10·5	141 ± 7	161 ± 12	149 ± 20	34·0 ± 3·4	549 ± 20
M8	0·74	15·2	130 ± 7	212 ± 14	130 ± 21	35·8 ± 4·1	520 ± 23
M11*	0·49	18·5	276 ± 14	435 ± 30	304 ± 39	32·2 ± 10·7	448 ± 41
M11	0·96	7·9	64·6 ± 4·0	76·2 ± 12·3	49·0 ± 18·6	28·2 ± 3·6	589 ± 21
M10	0·84	8·6	188 ± 10	161 ± 13	149 ± 22	31·9 ± 4·0	566 ± 24
M12*	0·58	12·9	25·1 ± 1·7	37·4 ± 9·1	26·4 ± 14·8	34·1 ± 2·9	615 ± 18
M12	0·81	12·8	27·9 ± 2·0	24·8 ± 12·3	46·0 ± 22·3	34·3 ± 4·2	538 ± 23
M4	0·71	13·1	210 ± 11	233 ± 13	242 ± 23	52·0 ± 4·3	581 ± 23
M19	0·72	8·6	233 ± 11	268 ± 15	245 ± 26	57·4 ± 5·1	475 ± 25
M13	0·59	15·6	565 ± 23	681 ± 23	673 ± 39	57·4 ± 6·5	370 ± 34
M14*	0·70	9·4	108 ± 6	160 ± 25	143 ± 35	39·5 ± 9·7	490 ± 39
M14	1·33	3 9	41·0 ± 3·2	18·4 ± 10·1	30·4 ± 16·5	27·9 ± 3·1	648 ± 20
M15*	0·54	13·7	367 ± 34	658 ± 30	505 ± 44	41·5 ± 9·9	289 ± 40
M15	0·63	14·1	441 ± 20	589 ± 21	484 ± 32	56·5 ± 6·6	359 ± 32
M16*	0·49	10·7	117 ± 7	137 ± 18	65·4 ± 25·4	34·7 ± 7·9	492 ± 29
M16	1·15	4·5	131 ± 7	162 ± 11	134 ± 16	29·1 ± 3·2	338 ± 17

TABLE 1—*contd.*

Code	*D (g/cm³)*	*% organ*	^{210}Po	^{210}Pb	^{226}Ra	^{228}Ra	^{40}K
M22*	0·40	15·6	169 ± 9	236 ± 25	136 ± 36	33·6 ± 10·2	443 ± 40
M22	0·93	9·5	44·2 ± 2·5	26·6 ± 11·1	31·7 ± 17·2	33·5 ± 3·2	654 ± 20
M23*	0·39	13·3	124 ± 8	205 ± 23	76·6 ± 35·9	28·6 ± 9·5	545 ± 39
M23	0·67	6·1	194 ± 9	121 ± 13	97·3 ± 20·7	30·8 ± 3·8	445 ± 22
M24*	0·63	11·3	44·9 ± 2·9	34·8 ± 6·8	33·2 ± 11·4	25·2 ± 2·0	604 ± 14
M18*	0·53	11·9	29·0 ± 1·8	34·0 ± 8·4	34·8 ± 13·7	25·7 ± 2·6	703 ± 16
M18	1·12	5·6	54·4 ± 3·7	51·9 ± 11·1	35·3 ± 17·6	21·3 ± 3·1	401 ± 19
M17*	0·52	12·5	40·5 ± 2·3	53·2 ± 6·5	43·3 ± 10·5	28·6 ± 2·1	567 ± 13
M17	0·74	8·8	54·7 ± 3·9	80·6 ± 10·5	29·8 ± 17·8	32·0 ± 3·1	606 ± 18
M20	1·54	1·1	16·2 ± 2·5	15·4 ± 10·1	21·3 ± 16·0	13·2 ± 2·9	287 ± 18
M21	1·54	2·1	37·2 ± 2·5	22·9 ± 10·9	20·3 ± 17·7	16·0 ± 3·3	422 ± 20

[†]Density (dry weight) and organic content (%) in each soil sample are also given.

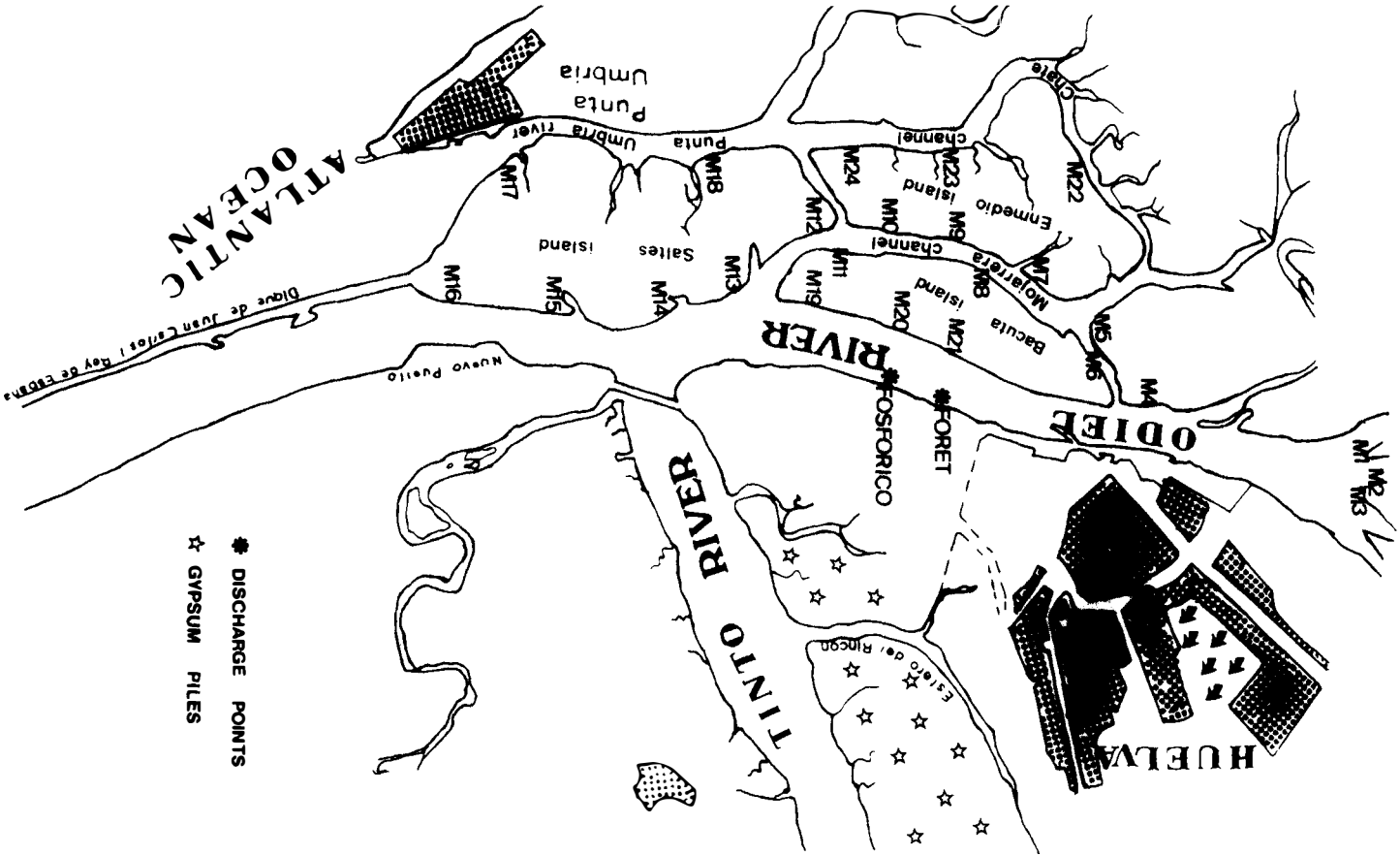

Fig. 1. Map of the Odiel marsh area where the locations of the sampling stations in February and November 1993 are shown.

bulk density and per cent of organic matter in each soil for both sampling campaigns. Location of each sampling station is displayed in Fig. 1 for both sampling campaigns.

Thirteen soil samples were collected at the end of February 1993. It is clear that the range of radioactivity concentrations for all the ^{238}U decay series descendants is wide. Thus, concentrations below 45, 53 and 43 mBq/g for ^{210}Po, ^{210}Pb and ^{226}Ra, respectively, are found in the further part of the marsh, the west side of the Saltes island and the southwest of the Enmedio island. Higher levels, from 100 to 170, 130 to 240 and 60 to 150 mBq/g for the same radionuclides, respectively were measured at the northwest of Enmedio island and east side of the Saltés island. These samples are not clearly enhanced but the levels are higher than those above. Besides that it appears a set of samples where the influence of the industries is clearly seen without further data analysis. Thus, along the Mojarrera channel concentrations higher than 250, 400 and 250 mBq/g are found for ^{210}Po, ^{210}Pb and ^{226}Ra.

The pattern distribution of activity concentrations across the marsh must be logically governed by the tidal intrusion of waters from the Odiel river which transport radioactivity released by the factories. Probably, during high tides, the contaminated Odiel waters invade the marsh through the north of the Bacuta island. Most of this water flows into the Mojarrera channel which is the main sink of such contamination. Besides that, part of this water would flow into the Estero de Cajarias. That is the reason why the northern part of the Enmedio island is clearly enhanced for ^{210}Po, ^{210}Pb and ^{226}Ra. Thus the activity decreases all along the El Chate channel and the Punta Umbría river.

The eastern part of the Saltés island is affected by the radioactivity released from the factories. It is transported inland by the waters at low tide. Differences in activity concentrations between stations at the east of the island must therefore be related to the differences in organic content (see Table 1).

A more extensive study was carried out during November 1993. During this campaign, 20 soil samples were collected from different (but close to those of the February study) sampling stations in the Odiel marsh. Three additional soil samples were taken from the Northern marsh in order to wider our study (see Fig. 1).

Results are also presented in Table 1, together with the density and per cent of organic matter. Very similar conclusions to those of February can be derived from the analysis of ^{238}U descendant radioactivity data. Thus, it seems clear again that the flow of Odiel waters through the Mojarrera channel is responsible of the natural radioactivity enhancement found at the Odiel marsh. Thus, background levels, below 70, 80 and 50 mBq/g for

^{210}Po, ^{210}Pg and ^{226}Ra were found along El Chate channel and the Punta Umbría river.

Up to 600, 700 and 800 mBq/g activity concentrations for the same radionuclides were found in different stations across the Odiel marsh. It is also true that the general activity levels for ^{210}Po, ^{210}Pb or ^{226}Ra are lower than those found in February. This is not strange if one takes into account the complexity of the dynamics of the system which is being studied. Again, it is important to notice that the sampling stations were not exactly the same. In fact, the majority of samples collected in November were located at places which are covered by water for less time during high tides than those of February.

The cases of samples 20 and 21 deserve some special comments. Being situated close to the source input of radioactivity, but on the other side of the river, the radioactivity levels found are certainly low. Two reasons could explain such effect. Firstly, their density and organic content (see Table 1) reflect the presence of large amount of sand particles: the direct consequence is a lowering of radioactivity concentrations. Secondly, it is known (Periañez *et al.*, 1994) that the transversal velocity across the Odiel river for the dispersion of a given pollutant is, at least, one order of magnitude lower than the longitudinal velocity along the Odiel river. This meaning that once an input of radioactivity has been introduced into the river waters it moves faster in the longitudinal direction, reaching the opposite shoreline highly diluted.

The differences in density and organic matter could also explain the special activity pattern found at the east side of the Saltés island for samples 14 to 16 (see Table 1).

Very high levels of radioactivity were found at the Northern marsh (see Fig. 1), especially for the case of samples N2 and N3. It is apparent that this place is also affected by the phosphoric acid factories. In fact, it has been found that the marsh is an important sink for many other pollutants (Martin *et al.*, 1995). This finding requires further investigation, although it seems clear that the reason for such high radioactivity levels should be related to tidal transport by the Odiel waters. This agrees with the high activity concentrations found in sample N4, located at the Odiel river margin upstream the factories.

The ^{228}Ra radioactivity concentrations are fairly uniform across the studied area in February. An average value of $31{\cdot}3 \pm 2{\cdot}4$ mBq/g could reveal that the area under study is not contaminated by ^{232}Th descendants. This is not surprising since it has been found that the Odiel waters are little contaminated by ^{232}Th and daughters. Concentrations of ^{228}Ra in samples collected in November showed more dispersed values than those of February, ranging from about 13 to 85 mBq/g.

From this viewpoint, the behaviour of the $^{228}Ra/^{226}Ra$ activity ratio for instance, (see column 4 of Table 2), could provide information on the pattern of contamination. However, if we exclude the northern marsh data, the average value of 37 ± 13 mBq/g, agrees with that found in February. In general, higher activity concentrations of ^{228}Ra are found in those samples with high activity concentrations of ^{238}U descendants. Indeed, the ratio *increases* for low ^{226}Ra activities and *decreases* when the ^{226}Ra radioactivity concentration increases, for both samplings, following the geographical trend discussed above (see Fig. 2). A potential fitting of the curve for each sampling, separately, gives similar results

$$R = 8{\cdot}75\,A^{-0{\cdot}71}$$

R being the $^{228}Ra/^{226}Ra$ activity ratio and A the ^{226}Ra activity in mBq/g. The regression coefficient is $-0{\cdot}909$.

The relative distribution of ^{40}K along the marsh also gives interesting information of the enhancement of the studied area. The ^{40}K radioactivity concentration ranges from 290 to 700 mBq/g, which agrees well with the world ^{40}K background range for soils (UNSCEAR, 1988). Nevertheless, it is clear that the ^{40}K activity decreases when the activities from any ^{238}U descendants increase. For instance, in Fig. 3, we show this trend for the case of the pair ^{40}K–^{210}Pb. The only reason for such interesting behaviour could reside in the fact that the phosphate wastes, as the phosphate ores, are very poor in ^{40}K. For instance, Hussein (1994) obtained $19 \pm 2{\cdot}1$ mBq/g for ^{40}K in phosphate ores. Consequently the relative lowering of ^{40}K could mark the intrusion of contaminated material. A similar effect, but on sediment samples, was known in Gallardo *et al.* (1993). The relative distribution of ^{40}K is quite similar for both sampling campaign, as can be seen in Fig. 3, where we have excluded those samples with very different density values. A fitting of this line gives,

$$^{40}K = 600 - 0{\cdot}326\,^{210}Pb$$

with a regression coefficient of $-0{\cdot}8035$.

It is interesting to discuss some isotopic ratios. In Table 2, column 3, we present the $^{210}Pb/^{226}Ra$ radioactivity concentration ratio for both sampling campaigns. This ratio is higher than unity revealing an excess of ^{210}Pb across the marsh related to ^{226}Ra. The $^{210}Pb/^{226}Ra$ activity ratio in the Odiel waters (Martínez-Aguirre & García-León, 1995) shows a different trend. In fact, values from 0·4 to 0·7 can be found close to the source input. The fact that in the marsh, the activity ratio is higher than unity must be related to the higher mobility of ^{226}Ra in nature. Thus, the ^{210}Pb

TABLE 2

Activity Ratios in Soil Samples from the Odiel Marsh Area of Huelva Collected in February (*) and November 1993

Code	$^{210}Po/^{210}Pb$	$^{210}Pb/^{226}Ra$	$^{228}Ra/^{226}Ra$
M1	0·843 ± 0·071	1·422 ± 0·235	0·338 ± 0·062
M2	0·949 ± 0·059	1·153 ± 0·082	0·088 ± 0·011
M3	0·811 ± 0·042	1·167 ± 0·070	0·124 ± 0·012
M6*	0·581 ± 0·043	1·41 ± 0·20	0·077 ± 0·036
M6	0·862 ± 0·044	1·125 ± 0·054	0·090 ± 0·008
M5	1·423 ± 0·146	0·969 ± 0·169	0·266 ± 0·049
M7*	0·684 ± 0·087	1·51 ± 0·25	0·112 ± 0·045
M7	0·742 ± 0·047	1·347 ± 0·144	0·229 ± 0·029
M9*	0·663 ± 0·059	1·58 ± 0·29	0·076 ± 0·040
M9	0·876 ± 0·078	1·081 ± 0·166	0·228 ± 0·023
M8	0·613 ± 0·052	1·631 ± 0·285	0·275 ± 0·054
M11*	0·634 ± 0·054	1·43 ± 0·21	0·106 ± 0·038
M11	0·848 ± 0·147	1·555 ± 0·641	0·576 ± 0·231
M10	1·168 ± 0·113	1·081 ± 0·182	0·215 ± 0·041
M12*	0·671 ± 0·169	1·42 ± 0·87	1·29 ± 0·73
M12	1·125 ± 0·563	0·539 ± 0·374	0·743 ± 0·371
M4	0·901 ± 0·069	0·963 ± 0·106	0·215 ± 0·027
M19	0·869 ± 0·064	1·094 ± 0·131	0·234 ± 0·032
M13	0·830 ± 0·044	1·012 ± 0·068	0·085 ± 0·011
M14*	0·675 ± 0·112	1·12 ± 0·32	0·276 ± 0·096
M14	2·23 ± 1·24	0·605 ± 0·467	0·918 ± 0·508
M15*	0·558 ± 0·058	1·30 ± 0·13	0·082 ± 0·021
M15	0·749 ± 0·043	1·217 ± 0·091	0·117 ± 0·016
M16*	0·854 ± 0·123	2·10 ± 0·86	0·531 ± 0·239
M16	0·809 ± 0·070	1·209 ± 0·166	0·210 ± 0·034
M22*	0·716 ± 0·085	1·73 ± 0·50	0·247 ± 0·099
M22	1·66 ± 0·70	0·839 ± 0·574	1·057 ± 0·582
M23*	0·605 ± 0·078	2·68 ± 1·29	0·313 ± 0·214
M23	1·603 ± 0·187	1·244 ± 0·296	0·317 ± 0·078
M24*	1·29 ± 0·26	1·05 ± 0·41	0·678 ± 0·240
M18*	0·853 ± 0·217	0·98 ± 0·45	0·739 ± 0·300
M18	1·048 ± 0·235	1·470 ± 0·798	0·603 ± 0·313
M17*	0·761 ± 0·102	1·13 ± 0·33	0·660 ± 0·167
M17	0·679 ± 0·101	2·70 ± 1·65	1·117 ± 0·677
M20	1·052 ± 0·710	0·723 ± 0·721	0·620 ± 0·485
M21	1·624 ± 0·780	1·128 ± 1·121	0·788 ± 0·706

residence time in the marsh is higher than that of ^{226}Ra and so the activity ratio becomes higher than 1 as time passes.

It is difficult to discuss the $^{210}Po/^{210}Pb$ activity ratio in a system of such complicated dynamics. There seems to be a small variance in activity of

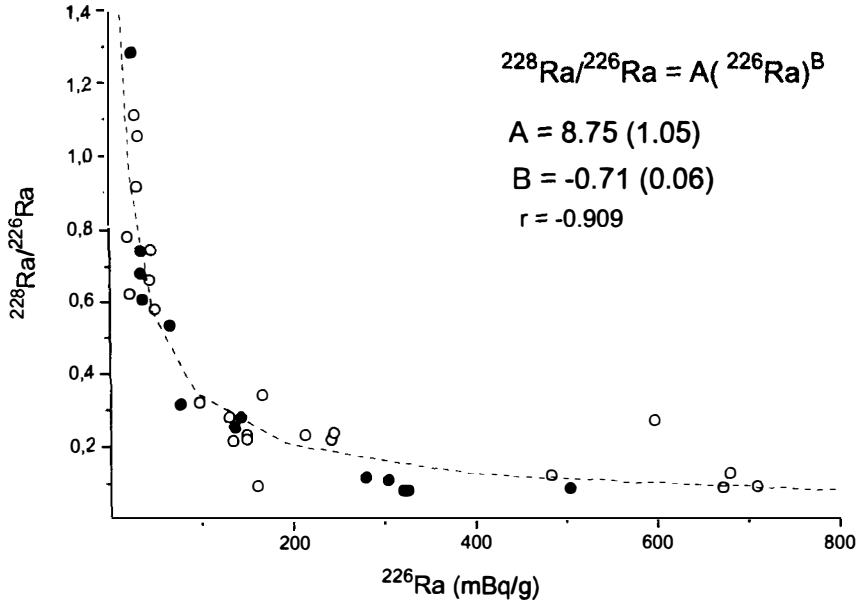

Fig. 2. $^{228}Ra/^{226}Ra$ activity ratio versus the ^{226}Ra concentrations in mBq/g in samples collected in February (●) and in November (○) 1993.

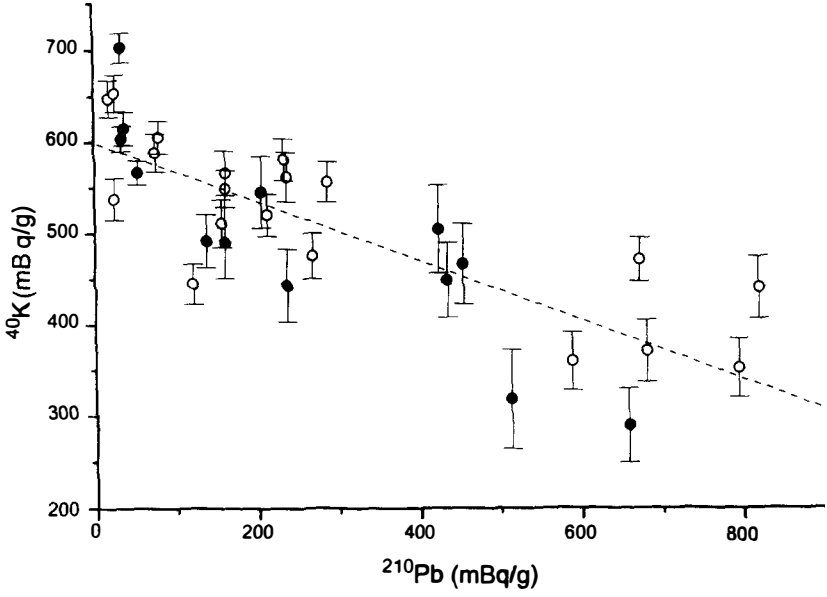

Fig. 3. ^{40}K concentrations in mBq/g versus the concentration of ^{210}Pb in mBq/g in soil samples collected in February (●) and in November (○) 1993.

^{210}Po in the samples from the global values, which could be related to the difference in mobilities of both radionuclides in nature.

CONCLUSIONS

Natural radioactivity has been studied in soils collected during two sampling campaigns from the Odiel marsh in the southwest of Spain. The results have shown that the inflow of water from the Odiel river, which receives the wastes from a phosphoric acid production complex, clearly enhanced the concentration of ^{238}U decay series descendants in certain zones of the marsh. The analysis of some isotopic activity ratios provides some information on the mobility and dynamics of natural radionuclides in the environment. The study of the ^{228}Ra/^{226}Ra activity ratio as well as the relative distribution of ^{40}K across the marsh has provided us with valuable information to help identify the extent and source of the contamination.

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REFERENCES

Gallardo, M. C., García-León, M., Mundi, M. & Respaldiza, M. A. (1993). Gamma-Spectrometric Analysis of River Sediments collected around Phosphate Fertilizer Industries. *Nucl. Geophys.*, **7,** 461–8.

Hussein, E. M. (1994). Radioactivity of phosphate ore, superphosphate and phosphogypsum in Abu-Zaabal phosphate plant, Egypt. *Health Phys.*, **67,** 280–2.

Koster, H. W., Marwitz, P. A., Berger, G. W., van Weers, A. W., Hegel, P. & Niewenhvize, J. (1991). ^{210}Po, ^{210}Pb and ^{226}Ra in aquatic ecosystems and polders; anthropogenic sources, distribution and enhanced radiation in The Netherlands. In: *V International Symposium on the Natural Radiation Environment*, Salzburg, Austria, September 1991.

Martin, J. M., Martínez-Aguirre, A. & Respaldiza, M. A. (1995). Heavy Metals Enhancements in a Wet Marshland by the operation of Phosphoric Acid Factories. In preparation.

Martínez-Aguirre, A. & García-León, M. (1991). Natural Radioactivity Enhancements by human activities in rivers of Southwest Spain. *J. Radioanal. Nucl. Chem., Letters*, **155,** 97–105.

Martínez-Aguirre, A. & García-León, M. (1995). ^{210}Pb distribution in riverwaters and sediments near phosphate fertilizer factories. Submitted to *Applied Radiation and Isotopes.*

Martínez-Aguirre, A., García-León, M. & Ivanovich, M. (1994). The distribution of U, Th and ^{226}Ra derived from the phosphate fertilizer industries on an Estuarine System in Southwest Spain. *J. Environ. Radioactivity*, **22,** 155–77.

Morón, M. C., Martínez-Aguirre, A. & García-León, M. (1988). Determination and levels of U, Th and Po in different environmental samples. In *International Conference on Environmental Radioactivity in the Mediterranean Area*, Eds: SNE-ENS, Barcelona, 1988, 111 pp.

Paul, A., Londhe, V. & Pillai, K. (1980). ^{228}Ra and ^{226}Ra levels in a river environment and its modification by human activities. In *Natural Radiation Environment III*, Vol. 2. US Department of Energy, pp. 1633–54.

Periañez, R. & García-León, M. (1993). Ra-isotopes around a phosphate fertilizer complex in an estuarine system at the southwest of Spain. *J. Radioanal. Nucl. Chem., Articles*, **172,** 71–9.

Periañez, R., García-León, M. & Abril, J. M. (1964). A modelling study of ^{226}Ra dispersion in an Estuarine System in South-West Spain. *J. Environ. Radioactivity*, **24,** 159–79.

Roessler, C. E., Smith, Z. A., Bolch, W. E. & Prince, R. J. (1978). Uranium and Radium-226 in Florida phosphate materials. *Health Phys.*, **37,** 269–77.

UNSCEAR (1988). *Sources, Effects and Risks of Ionizing Radiation.* Annex A. Exposure from Natural Sources of Radiation. United Nations Scientific Committee on the Effects of Atomic Radiation, United Nations, New York.