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Environment International 27 (2002) 639–645

ENVIRONMENT INTERNATIONAL

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Radioactive impact in sediments from an estuarine system affected by industrial wastes releases

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Received 1 October 1999; accepted 16 November 2001

Abstract

A big fertilizer industrial complex and a vast extension of phosphogypsum piles (12 km^2), sited in the estuary formed by the Odiel and Tinto river mouths (southwest of Spain), are producing an unambiguous radioactive impact in their surrounding aquatic environment through radionuclides from the U-series. The levels and distribution of radionuclides in sediments from this estuarine system have been determined. The analyses of radionuclide concentrations and activity ratios have provided us with an interesting information to evaluate the extension, degree and routes of the radioactive impact, as well as for the knowledge of the different pathways followed for the radioactive contamination to disturb this natural system. The obtained results indicate that the main pathway of radioactive contamination of the estuary is through the dissolution in its waters of the radionuclides released by the industrial activities and their later fixation on the particulate materials. Tidal activity also plays an important role in the transport and homogenization along the estuary of the radioactivity released from the fertilizer plants.

Keywords: Estuary; Phosphogypsum; Natural-radioactivity; Sediments; Gamma-spectrometry; Contamination pathways

1. Introduction

In this work, we analyze the different origins and routes of several radionuclides in sediments from an estuarine system formed by the mouths of the Odiel and Tinto rivers. This study belongs to a wider project devoted to study the levels and distribution of natural radioactivity in the south of Spain.

The Odiel and Tinto rivers are located in the southwest of Spain, discharging their waters into the Atlantic Ocean. Their mouths conform an estuarine tidal system that surrounds a large industrial complex with several chemical plants devoted to the production of phosphoric acid and phosphate fertilizers (Fig. 1). In these factories, phosphoric acid is obtained through the chemical treatment of phosphate rock, consisting mainly of phosphorite mineral, which contains high levels of radionuclides from the uranium series (Guimond and Hardin, 1989). In this chemical process, a by-product called phosphogypsum is formed, which is stored in the surroundings of the factories, or released directly into the Odiel river. Due to this by-product accumulating a significant fraction of the radioactivity contained originally in the treated phosphate minerals, it can be concluded that these industries can produce a radioactive impact on their nearby environment (Bolívar, 1995; Bolívar et al., 1995a, 1996a; Rutherford et al., 1994).

These factories process annually over 2×10^6 metric tons of phosphate rock, and they generate about 3×10^6 tons of phosphogypsum. About 80% of this amount is pumped (mixed with seawater) into some pile-stacks sited quite near the factories (on the bank of the Tinto river) to be indefinitely stored, while the remaining amount (20%) is directly released into the waters of the Odiel river estuary, just in front of the factories (Fig. 1).

The phosphogypsum stacks cover about 12 km^2 on the salt marshes of the Tinto river and therefore they generate a high radioactive impact on their surrounding marshland (Bolívar, 1995; Bolívar et al., 1995b). On the contrary, the salt marshes of the Odiel river are not physically perturbed and have been recently declared natural reserve by the Regional Government.

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PII: S0160-4120(01)00123-4

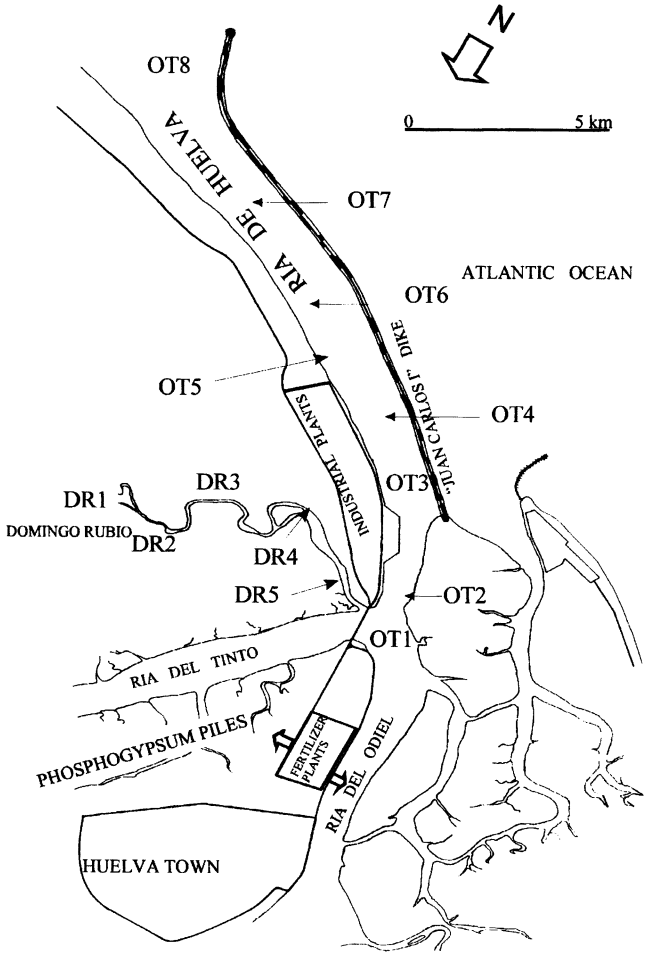

Fig. 1. Map of the Odiel and Tinto river mouths. The location of Huelva Town, fertilizer plants, phosphogypsum piles and the 13 sampling points are marked.

The radioactive impact generated by this industrial complex on the Tinto and the Odiel rivers has been widely studied in previous works through measurements of natural radioactivity in waters and superficial sediments (Periáñez et al., 1996; Martínez-Aguirre and García-León, 1994; Martínez-Aguirre et al., 1994), but these studies were devoted to evaluate this impact in zones of the rivers quite close to the possible sources of radioactive contamination: the fertilizers industries and the phosphogypsum piles. In this work, we extend these studies to more remote zones in the rivers (Fig. 1): the common channel of the Odiel and Tinto river (called Ría de Huelva) and the Estero Domingo Rubio (a rivulet that ends in the Tinto river, opposite the phosphogypsum piles).

An artificial dyke was built in the Ría de Huelva 30 years ago (see Fig. 1) for the construction of a new harbour. As a consequence, the water exchange rate of the rivers with the Atlantic Ocean was altered. The water flow from the rivers is much smaller than the water volume exchanged with the ocean, a fact that can be deduced from the uniform values of pH (in the interval 6.5–7) and salinity determined in the waters of the estuary, which are quite similar to those found in coastal seawaters of this geographical area. On the contrary, the pH values in the waters of both rivers, upstream the estuary, are very low (between 2 and 3) due to the influence of some mining activities developed historically in their margins.

In previous works, we have determined the radioactivity distribution in the phosphoric acid production process, by measurements of alpha and gamma natural radionuclides in representative raw materials, principal steps of the chemical process and in the by-products obtained in the factories sited in the estuary (Bolívar et al., 1993, 1995a, 1996a). In these analyses, activity concentrations for U-series radionuclides between 700 and 1500 Bq/kg, $^{226}Ra/^{238}U$ activity ratios about 1.3 and a good secular equilibrium between ^{226}Ra and ^{210}Po have been determined in the phosphate rocks used in these factories. In general, the concentrations of uranium and daughters in the mineral were 30–50 times higher than in typical unperturbed soils and sediments. On the contrary, the concentrations of radionuclides from the thorium series are in the range found in unperturbed soils, while the ^{40}K and ^{137}Cs concentrations were not detectable by gamma-ray spectrometry in the mineral, with the minimum detectable activity for these radionuclides in our measurements being about 30 and 0.5 Bq/kg, respectively.

It was also concluded in these studies that more than 90% of Po and Ra originally present in the phosphate rock remains in the phosphogypsum, while the percentage of U is much lower (<20%). It is also known that the behaviour of ^{210}Pb in the production process of phosphoric acid used in the factories is quite similar to the ^{226}Ra (Guimond and Hardin, 1989). The rest of radioactivity that flows in the process, which it is associated with the phosphoric acid fraction, remains afterwards in the phosphate fertilizers produced.

In addition, we have shown (Bolívar et al., 1996a) that the waters used for the transport of the phosphogypsum to the piles (20% of suspended matter), and that finally mostly drains into the Tinto river, are especially enriched in U-isotopes (40 Bq/l), the concentrations of ^{226}Ra being lower (0.85Bq/l) but clearly over the levels found in waters from uncontaminated rivers and estuaries (2–3 orders of magnitude).

Consequently, and due to the high levels in U-series radionuclides involved, and to the high radiotoxicity of ^{226}Ra, ^{210}Po and ^{210}Pb, we have investigated the radioecological impact in some zones of the estuary previously detailed, far-off the contamination sources since these contamination sources are mainly placed a few meters from the fertilizer industries where a fraction of the phosphogypsum is released, and in the phosphogypsum piles located in the Tinto river.

With this study we try to evaluate the extension, degree and routes of the radioactive contamination in the sediments

and to obtain information about the behaviour of the different radionuclides injected in this estuarine system.

2. Materials and methods

A total of 13 sampling points were selected in this work, being pointed out in Fig. 1. In every sampling point, a sample of superficial sediment (about 1 kg) was collected. Eight sites (OT1 to OT8) correspond to the Ría de Huelva, while only five sites (DR1 to DR5) were elected from Estero Domingo Rubio, a rivulet that ends opposite to the phosphogypsum piles. It was not possible to take a sediment sample in location DR1. In both cases, the numbering increases in the direction of the water flow.

After collection, the sediment samples were preserved in plastic bags, dried at 105 °C for 48 h and finally, sieved and homogenized. Aliquots of every sample were then used for apparent densities and organic matter determinations, while the remaining material was preserved to make the determinations of mainly natural radionuclides.

^{226}Ra, ^{228}Ra, ^{224}Ra, ^{40}K and ^{137}Cs were determined by gamma-ray spectrometry using a coaxial ultra pure germanium (HPGe) detector. A cylindrical geometry for the gamma-ray measurements has been used, taking into account for the activity determinations the necessary self-absorption corrections on the full energy peak efficiency curve due to the different density of the samples in relation to the elected one for calibration (Bolívar et al., 1994, 1996b; Cutshall et al., 1983). The samples were also sealed and stored in cylindrical vials at least 1 month before counting to assure secular equilibrium between ^{226}Ra and its daughters. The ^{226}Ra determinations were done through the 352 keV gamma-ray emission of its daughter ^{214}Pb.

On the other hand, alpha-emitting radionuclides as ^{210}Po-, U- and Th-isotopes were determined by alpha-particle spectrometry using ion-implanted silicon detectors. For these determinations, the samples (0.5–1 g) were spiked with accurately known activities of ^{232}U, ^{229}Th and ^{208}Po, wet digested in a microwave oven with nitric acid and aqua regia and the dry residue was redissolved in 8 M nitric acid. Afterwards, the isolation of U, Th and Po was carried out through a sequential solvent extraction technique, initially developed by Holm and Fukai (1977) and slightly modified by us. In our case, the Th-isotopes determinations were done independently applying this radiochemical method. The reason was to determine ^{228}Th in the samples without the interference of some ^{228}Th existing in the ^{232}U solution used as a tracer for U-determinations.

The counting source of ^{210}Po is obtained by self-deposition onto silver discs from a 2-M HCl solution (El-Daoushy et al., 1991), while the final solutions of U and Th, after their isolation were electroplated onto stainless-steel discs by the method of Hallstadius (1984). The recoveries obtained for U and Th ranged from 65% to 95%, while slightly lower values for polonium were obtained (albeit >40%).

3. Results and discussion

3.1. Domingo Rubio rivulet

The results obtained for the set of sediment samples collected in the Domingo Rubio rivulet are shown in Table 1. It is observed that the activity concentrations of ^{232}Th, ^{228}Ra and ^{228}Th are relatively uniform along the rivulet, being in addition, similar to the typical values obtained in unperturbed sediments (30–60 Bq/kg) (Somayajulu and Goldberg, 1966; Martin et al., 1978). Similar comments can be made for ^{40}K. On the contrary, the activity concentrations of U-isotopes and daughters are, in most cases, clearly higher than those found in uncontaminated estuarine sediments, with values up to 560 Bq/kg in the case of ^{234}U (typical values of U and daughters in uncontaminated sediments are 20–50 Bq/kg, UNSCEAR, 1988). The contamination from radionuclides of the U-series is clear along all the rivulet, with the exception of the sample more remote from the mouth (DR2) that contains normal levels of all U-series radionuclides studied with the exception of ^{210}Po.

The distribution pattern of U and daughters along Domingo Rubio sediments is very similar for the different radionuclides. In Fig. 2, it is observed that the activity concentrations for the radionuclides of the U-series increase as we approach the mouth of the rivulet in a similar way that increases the electrical conductivity values determined in the waters from the places where the sediments of the Domingo Rubio rivulet were collected. This fact indicates an increase in the proportion of seawaters mixed with the fresh waters, and shows that the levels of U and daughters on the bed of Domingo Rubio are governed by the intrusion of water from the Tinto river, which is very enriched in these radionuclides coming from the phosphogypsum piles and the effluents released into Odiel river waters by the phosphate rock processing. In addition, this pathway of contamination explains the values obtained in the sample DR2: the sample was collected so far from the mouth that the intrusion at this point of water coming from the Tinto river is low, which is

Table 1
Activity concentrations (Bq/kg), apparent densities and organic matter percentages (OM) in the sediment samples from the Domingo Rubio rivulet

Point	^{238}U	^{234}U	^{210}Po	^{232}Th	^{230}Th	^{228}Th
DR2	20.1±3.7	20.6±3.7	181±10	41.6±6.0	33.9±5.6	34.8±4.1
DR3	214±12	236±13	169±17	32.8±2.9	211±14	30.4±2.7
DR4	187±15	226±13	285±16	38.6±2.8	137±8	34.9±2.6
DR5	515±31	560±34	481±28	60.0±3.0	380±16	62.1±3.1

Point	^{226}Ra	^{228}Ra	^{40}K	^{137}Cs	Density (g cm^{-3})	Organic matter (%)
DR2	44.1±2.6	40.1±2.8	382±22	7.8±0.5	1.02	9.2
DR3	140±7	39.8±3.0	340±21	3.7±0.4	0.90	8.3
DR4	116±6	43.0±2.8	363±21	2.1±0.2	0.93	9.9
DR5	226±11	61.0±4.0	330±22	4.4±0.5	0.76	12.7

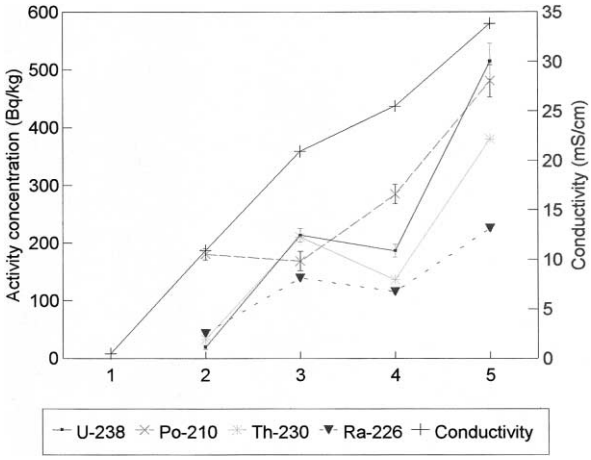

Fig. 2. Activity concentrations (Bq/kg) of ^{238}U, ^{210}Po, ^{230}Th and ^{226}Ra in sediment samples from the Domingo Rubio rivulet. Conductivity values in the water samples collected at the same places are also shown.

confirmed from the conductivity measurement at this point. The high concentration value of ^{210}Po in this last sample can only be then reflecting the accumulation of natural or atmospheric unsupported ^{210}Pb. In the place of collection of this sample, the speed of the waters is very low, supporting the idea of accumulation from atmospheric releases. Reinforcing this explanation, it can be observed that the sample DR2 has the highest content in ^{137}Cs (man-made radionuclide of atmospheric origin) of all samples studied.

The activity concentrations of ^{232}Th and daughters and ^{40}K are typical of uncontaminated sediments over all the rivulet bed, therefore, it is possible to affirm that there is no direct deposition of phosphogypsum as a main pathway of radioactive contamination of its sediments. The activity concentrations of ^{232}Th and ^{40}K are very low in the phosphate rocks used in the factories (Bolívar, 1995; Bolívar et al., 1995a, 1996a), and this deposition would induce a depletion in the concentration of these radionuclides in the sediments. The high values of U and daughters, together with the normal concentrations of Th and K in the sediments, indicate that the main route of contamination will be through the attachment onto the particulate matter of the radioelements originally contained in the phosphogypsum, which have been previously dissolved in the estuarine waters.

Some of the previously commented conclusions can be also confirmed studying activity ratios, where the most representatives are given in Table 2. The ^{230}Th/^{232}Th activity ratios are higher than 1 (between 4 and 6), except for the DR2 sample, showing a clear contamination by U-series radionuclides, since this activity ratio has a value around the unity in unperturbed estuarine sediments (Somayajulu and Goldberg, 1966; Martin et al., 1978). On the contrary, a secular equilibrium between ^{232}Th and daughters is observed, which is also normal in estuarine sediments not contaminated by detectable amounts of Th-series radionuclides (Martin et al., 1978). In addition, the enhancements of U and its daughters in samples DR3 to DR5 are also ratified through several activity ratios like ^{232}Th/^{234}U (around 0.1) and ^{226}Ra/^{228}Ra (about 3–4), which present values in both cases around unity in uncontaminated sediments. Finally, the particular values of the activity ratios found between radinuclides of the U-series (^{226}Ra/^{234}U, ^{210}Po/^{234}U, …) will give us information about the pathway of contamination of these sediments as will be explained with more detail analyzing the Ría de Huelva samples. We must emphasize that these last activity ratios have similar values in the samples DR3 to DR5 to those found in the estuary.

Table 2
More significant activity ratios in the sediment samples taken from the Domingo Rubio rivulet

Point	^{230}Th/^{232}Th	^{228}Th/^{232}Th	^{234}U/^{238}U	^{230}Th/^{234}U	^{232}Th/^{234}U
DR2	0.81 ± 0.12	0.88 ± 0.13	1.03 ± 0.03	1.64 ± 0.04	2.0 ± 0.05
DR3	6.4 ± 0.4	0.93 ± 0.08	1.10 ± 0.02	0.89 ± 0.08	0.140 ± 0.014
DR4	3.6 ± 0.2	0.95 ± 0.06	1.21 ± 0.03	0.61 ± 0.05	0.171 ± 0.016
DR5	6.3 ± 0.2	1.09 ± 0.03	1.09 ± 0.03	0.68 ± 0.05	0.107 ± 0.008

Point	^{210}Po/^{234}U	^{210}Po/^{230}Th	^{210}Po/^{226}Ra	^{226}Ra/^{234}U	^{226}Ra/^{228}Ra
DR2	8.8 ± 1.6	5.3 ± 0.9	4.1 ± 0.3	2.1 ± 0.4	1.10 ± 0.10
DR3	0.72 ± 0.08	0.8 ± 0.09	1.21 ± 0.13	0.59 ± 0.04	3.5 ± 0.3
DR4	1.26 ± 0.10	2.08 ± 0.17	2.5 ± 0.2	0.51 ± 0.04	2.7 ± 0.3
DR5	0.86 ± 0.07	1.27 ± 0.04	2.13 ± 0.16	0.40 ± 0.03	3.7 ± 0.3

3.2. Ría de Huelva

Table 3 presents the apparent densities, organic matter and the activities concentrations for the different natural

Table 3
Activity concentrations (Bq/kg), apparent densities and organic matter percentages (OM) in the sediment samples from the Ría de Huelva

Point	^{226}Ra	^{228}Ra	^{40}K	^{137}Cs	Density (g cm^{-3})	Organic matter (%)
OT1	163 ± 8	43.2 ± 3.2	361 ± 22	4.0 ± 0.4	1.00	8.1
OT2	203 ± 10	50.6 ± 3.8	374 ± 23	5.1 ± 0.6	0.89	8.6
OT3	225 ± 11	58.1 ± 4.0	365 ± 22	1.8 ± 0.4	0.94	8.3
OT4	115 ± 6	40.2 ± 3.2	402 ± 24	2.1 ± 0.5	0.96	9.0
OT5	164 ± 8	46.7 ± 3.6	319 ± 21	2.3 ± 0.4	1.09	8.1
OT6	66.0 ± 3.5	20.7 ± 1.7	236 ± 14	0.4 ± 0.2	1.69	3.7
OT7	204 ± 11	57.1 ± 3.8	341 ± 20	2.4 ± 0.3	0.98	9.5
OT8	49.3 ± 2.8	19.9 ± 1.7	235 ± 14	1.65 ± 0.23	1.57	4.6
Average	179 ± 16	49.3 ± 3.0	360 ± 12	2.5 ± 0.5	1.14 ± 0.11	7.5 ± 0.8

Point	^{238}U	^{234}U	^{210}Po	^{232}Th	^{230}Th	^{228}Th
OT1	337 ± 21	371 ± 23	343 ± 19	43.1 ± 2.3	260 ± 12	43.0 ± 2.3
OT2	370 ± 40	394 ± 42	418 ± 23	55.7 ± 2.9	331 ± 15	61.9 ± 3.1
OT3	413 ± 24	434 ± 25	491 ± 43	66.7 ± 3.8	443 ± 21	65.8 ± 3.7
OT4	209 ± 14	228 ± 15	293 ± 20	37.4 ± 2.1	202 ± 9	52.0 ± 2.8
OT5	266 ± 18	280 ± 19	421 ± 30	42.4 ± 2.4	290 ± 13	40.9 ± 2.4
OT6	103 ± 7	107 ± 7	153 ± 12	17.6 ± 1.2	99 ± 5	19.3 ± 1.3
OT7	367 ± 25	389 ± 26	716 ± 90	67.5 ± 3.2	299 ± 13	64.6 ± 3.1
OT8	108 ± 6	106 ± 7	187 ± 28	20.2 ± 1.1	134 ± 6	19.0 ± 1.1
Average	327 ± 31	349 ± 32	447 ± 61	52.2 ± 5.3	304 ± 33	54.7 ± 4.5

radionuclides measured in the sediment samples collected in the Ría de Huelva, common channel of the Odiel and Tinto rivers.

The apparent density values are around 1 g cm^{-3} in the majority of the sampling points, except for OT6 and OT8, which presents higher values due to their very high SiO_2 contents (around 1.6–1.7 g cm^{-3}). These two special samples are also characterized by their very low content in organic matter (4%).

The concentrations of U-isotopes, ^{230}Th, ^{226}Ra and ^{210}Po in all samples are very much higher than in unperturbed sediments (even one order of magnitude higher, see Table 4). A relatively uniform radioactive contamination by U-series radionuclides is observed across the Ría de Huelva bed sediments (with a small negative gradient in the concentration in the direction opposite to the contamination sources). The contamination reaches zones at least 15 km from the contamination sources (fertilizer plants and phosphogypsum stacks), as can be deduced from the results for OT8, which is near the open Atlantic Ocean.

The concentrations of most significant radionuclides from the U-series along the Ría de Huelva are also shown in Fig. 3. It is found for the several radionuclides studied that they have similar patterns of concentrations, with OT6 and OT8 being the samples with a very much lower content of radioactivity. The results in these two samples are in total concordance with their high percentage of sand, since it is well known that sandy material does not have a tendency to accumulate anthropogenic material.

Normal levels of Th-series radionuclides and ^{40}K have been measured in the samples, indicating that the sediments show undetectable contamination sources of these isotopes in the estuary. We observe also that the content in ^{232}Th, ^{40}K and ^{137}Cs in OT6 and OT8 samples are clearly lower than the levels found in the remaining sampling stations, in concordance with its high sand content.

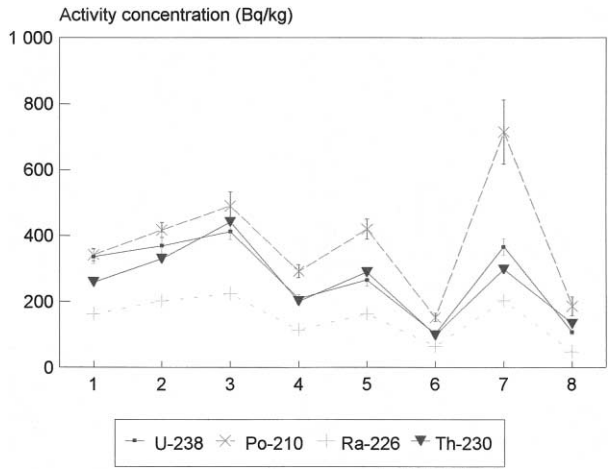

Fig. 3. Activity concentrations (Bq/kg) of ^{238}U, ^{210}Po, ^{226}Ra and ^{230}Th in sediment samples from the Ría de Huelva.

The contamination of radionuclides from the U-series in the sediments of the Ría de Huelva is also ratified, for example, by the values of some activity ratios like ^{230}Th/^{232}Th and ^{226}Ra/^{228}Ra that are shown in Table 4, which are much higher than 1, while their values are about unity in uncontaminated estuarine sediments.

The surface sediment samples from Ría de Huelva could have been contaminated either by direct transport and accumulation of particulate phosphogypsum released by the fertilizer factories, or by the deposition on the sediments of radionuclides previously dissolved in the waters, after their release in the Odiel river or after being leached/dissolved from the phosphogypsum piles. We can distinguish the relative importance of these possible ways of radioactive contamination through two methods: either by analyzing the activity concentrations or the activity ratios found in the sediments.

If we consider that the main pathway of contamination is through direct deposition of particulate phosphogypsum, and attending to the high U and daughters concentrations levels found in the sediments, a high fraction of the sediments must be formed by this by-product. This fact should be reflected in a big decrease of the ^{40}K and ^{137}Cs activity concentrations in the contaminated sediment samples in relation to the normal values in unperturbed sediments, since, as it was previously indicated, the phosphogypsum contains very low levels of these radionuclides (less than 30 and 0.5 Bq/kg, respectively).

This is not our case, since the samples of Ría de Huelva with a clear contamination by U-series radionuclides contain concentrations of ^{40}K and ^{137}Cs similar to those measured in uncontaminated soils and sediments (Bolívar, 1995; Periáñez et al., 1996; Martínez-Aguirre and García-León, 1994).

Table 4
More significant activity ratios in the sediment samples taken from the Ría de Huelva

Point	^{230}Th/^{232}Th	^{228}Th/^{232}Th	^{234}U/^{238}U	^{230}Th/^{234}U	^{232}Th/^{234}U
OT1	6.0 ± 0.2	1.05 ± 0.04	1.10 ± 0.04	0.70 ± 0.05	0.116 ± 0.009
OT2	5.9 ± 0.2	1.17 ± 0.04	1.06 ± 0.11	0.84 ± 0.09	0.141 ± 0.017
OT3	6.6 ± 0.2	0.91 ± 0.04	1.05 ± 0.02	1.02 ± 0.08	0.154 ± 0.012
OT4	5.4 ± 0.2	1.07 ± 0.05	1.09 ± 0.05	0.89 ± 0.07	0.164 ± 0.014
OT5	6.8 ± 0.3	0.91 ± 0.05	1.05 ± 0.05	1.04 ± 0.08	0.151 ± 0.012
OT6	5.6 ± 0.3	1.06 ± 0.08	1.03 ± 0.05	0.92 ± 0.08	0.164 ± 0.014
OT7	4.4 ± 0.1	0.95 ± 0.03	1.06 ± 0.05	0.77 ± 0.06	0.170 ± 0.010
OT8	6.6 ± 0.2	0.95 ± 0.05	1.02 ± 0.06	1.26 ± 0.10	0.190 ± 0.010
Average	5.9 ± 0.3	1.01 ± 0.03	1.06 ± 0.02	0.93 ± 0.06	0.156 ± 0.008

Point	^{210}Po/^{234}U	^{210}Po/^{230}Th	^{210}Po/^{226}Ra	^{226}Ra/^{234}U	^{226}Ra/^{228}Ra
OT1	0.92 ± 0.08	1.32 ± 0.09	2.10 ± 0.15	0.44 ± 0.03	3.8 ± 0.3
OT2	1.06 ± 0.13	1.26 ± 009	2.06 ± 0.15	0.51 ± 0.06	4.0 ± 0.4
OT3	1.13 ± 0.12	1.11 ± 0.11	2.2 ± 0.2	0.52 ± 0.04	3.9 ± 0.3
OT4	1.28 ± 0.12	1.45 ± 0.12	2.5 ± 0.2	0.50 ± 0.04	2.9 ± 0.3
OT5	1.50 ± 0.15	1.45 ± 0.12	2.6 ± 0.2	0.59 ± 0.05	3.5 ± 0.3
OT6	1.43 ± 0.14	1.54 ± 0.14	2.3 ± 0.2	0.62 ± 0.05	3.2 ± 0.3
OT7	1.84 ± 0.26	2.4 ± 0.3	3.5 ± 0.5	0.52 ± 0.04	3.6 ± 0.3
OT8	1.76 ± 0.29	1.40 ± 0.22	3.8 ± 0.6	0.46 ± 0.04	2.5 ± 0.2
Average	1.36 ± 0.12	1.49 ± 0.14	2.6 ± 0.2	0.52 ± 0.02	3.42 ± 0.18

In addition, all the superficial sediments analyzed have values in organic content and apparent densities very different from those found in the phosphogypsum (1.25 g cm^{-3}). All these data indicate that the main route of contamination of the estuarine bed is by radionuclides previously dissolved in the waters.

The values of activity ratios (Table 4) found in the sediment samples ratify this last hypothesis. The average values of $^{226}Ra/^{234}U$ and $^{210}Po/^{226}Ra$ activity ratios in the sediments are 0.52 ± 0.02 and 2.6 ± 0.2, respectively, about six times lower and three times higher, respectively, than the values measured in the phosphogypsum samples (Bolívar et al., 1995a, 1996a) (Fig. 4). If a direct deposition of phosphogypsum on the sediments is the main way of contamination, we should find in the sediments similar or relatively near $^{226}Ra/^{234}U$ and $^{210}Po/^{226}Ra$ activity ratios than in the phosphogypsum, which is not the case.

Thus, $^{226}Ra/^{234}U$ and $^{210}Po/^{226}Ra$ activity ratios obtained for these sediments indicate that the contamination of the sediments is not directly related to the content of these radionuclides in particulate phosphogypsum. Instead, their incorporation onto the sediments plays an important role in the behaviour of every radionuclide in this aquatic system. However, another previously commented way of U-series contamination produced by the fertilizer plants activities cannot be underestimated, because the activity ratios of the commented radionuclides can be different from the activity ratios in the fresh particulate phosphogypsum.

Also, it is interesting to remark that, as was indicated before, the comments done about the pathways of contamination of the sediments from Ría de Huelva can be extrapolated to the Domingo Rubio rivulet, because ^{137}Cs and ^{40}K concentrations were similar in both zones, as well as the activity ratios between radionuclides of the U- and Th-series.

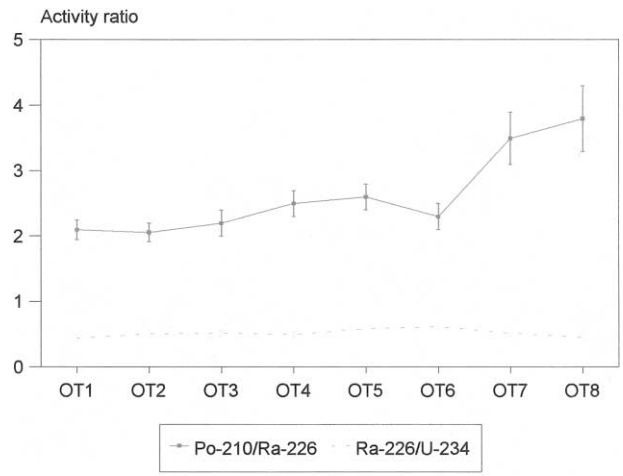

Fig. 4. $^{210}Po/^{226}Ra$ and $^{226}Ra/^{234}U$ activity ratios measured in sediments from the Ría de Huelva channel.

The very uniform values of some isotopic ratios like $^{230}Th/^{232}Th$ (5.9 ± 0.3) and $^{226}Ra/^{228}Ra$ (3.4 ± 0.2) along the bed indicate that the contamination has been produced through the same route in all sampling points, and also that there are no other ^{230}Th and ^{226}Ra sources along the estuary different from the phosphate rock processing plants. This last conclusion is specially remarked, because along the Ría de Huelva channel are placed several chemical industries, which release some wastes into its waters. Together with the small gradients observed in the U-series concentrations along the estuary, it can be deduced that the tidal effects play an important role in the distribution of the radioactive contamination along this estuarine system.

In relation to the isotopic activity ratios $^{230}Th/^{232}Th$ and $^{226}Ra/^{228}Ra$, it is interesting to note that there are no differences between the sandy (OT6 and OT8) and the remaining samples, showing the fact that even when they have a smaller contamination level, the pathway for their contamination is similar.

4. Conclusions

High activity concentrations of U-series radionuclides in sediments along the beds of the Ría de Huelva channel and the Domingo Rubio rivulet have been found, while the levels of Th-series radionuclides and ^{40}K were typical of unperturbed estuarine sediments. Activity concentrations of U and daughters were even one order of magnitude higher than uncontaminated typical sediments from this geographical area. This radioactive contamination can be attributed to the wastes from a phosphate fertilizer complex located in the Odiel river mouth, which increases distribution along the estuary.

Some activity ratios have also been investigated, which have confirmed the external origin of this radioactive contamination (direct or indirect releases of some fertilizer plants), indicating together with the absolute activity values, that the main pathway of contamination of the sediments is through the dissolution in the estuarine waters of the radionuclides released by the industrial activities with their later deposition onto the sediment material.

The relative uniformity found in the concentrations of U and daughters in the sediments of the Ría de Huelva, even in remote locations from the contamination sources, and the uniformity of some isotopic activity ratios, indicate that the tidal activity plays an important role in the transport and distribution along the estuary of the radioactivity released by the fertilizer plants.

Acknowledgments

This work has been partially supported by ENRESA, the regional goverment of Andalucia (Junta de Andalucia) and the CICYT project 1FD97-0900-C02-02 (AMB).

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