Self-cleaning in an estuarine area formerly affected by ^{226}Ra anthropogenic enhancements

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Abstract

The estuary of the Odiel River has been affected by both direct discharges of phosphogypsum (radium enriched industrial waste) and dissolution and weathering of the exposed piles where this radium enriched waste was stored. In 1998 the waste management policy for industries changed. The direct discharges stopped and the new phosphogypsum piles were well protected against dissolution processes, avoiding any transference of radium into the environment. This work presents a study of the evolution with time (1999–2002) of the levels of ^{226}Ra in river water and sediment samples with the new waste management policy. A liquid scintillation technique was used to measure the ^{226}Ra activity concentration in sediment samples. A gas-proportional counter was also used to measure the ^{226}Ra activity concentration in river water samples. The main conclusion is that a systematic and continuous decrease of the activity concentration of ^{226}Ra with time in the Odiel River estuary is occurring. Thus, a possible self-cleaning in the estuary, once the direct waste discharges were avoided, can be inferred.

Keywords: Radium; Estuarine environment; Phosphogypsum

1. Introduction

Phosphoric acid factories have been operating in the town of Huelva (SW of Spain) since the 1960s. A by-product of the phosphoric acid production, so-called phosphogypsum, is the main waste of these industries and is enriched in radionuclides from the uranium series. The Huelva Estuary (SW Spain) has been affected by direct discharges of phosphogypsum into the Odiel River. Until 1998 a fraction of the total waste, approximately 20%, was directly released into river waters through a pipeline. The rest of it was stored in open-air piles not far from the phosphoric acid factories. Since 1998, all the whole waste has been stored in a new pile well protected against uncontrolled waste releases, e.g. releases due to dissolution or weathering processes. In this article, we

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present the new pattern and the evolution with time of ^{226}Ra activity concentrations in the estuary due to the change in the waste management policy.

It is well known that the manufacture of phosphate fertilisers might increase natural radioactivity levels in the areas surrounding the factory. Most of ^{226}Ra from the treated raw material is contained in the phosphogypsum and can be released, associated with the waste, into the environment around the factories.

The Ra-isotopes are considered to be the main contributors to doses from natural radionuclides and usually characterise a possible radioactive impact (Lozano et al., 2000). Nowadays, the interest on radioactivity in the phosphate fertilisers is well documented in the current literature. Azouazi et al. (2001) studied the environmental impact of mining, phosphate manufacture and waste management in Morocco. The use of phosphate fertilisers in agriculture soils was also discussed in other papers (Ioannides et al., 1997). However, the radioactive impact of phosphogypsum discharges is probably the most important objective from an environmental point of view (Koster et al., 1992; Haridasan et al., 2001; Mazzilli et al., 2000).

Since 1988, radioactivity levels in the Huelva Estuary have been extensively studied by researchers from the universities of Sevilla and Huelva, Spain; (Martínez-Aguirre, 1991; Martínez-Aguirre and García-León, 1994; Martínez-Aguirre et al., 1996; Bolívar et al., 1996a). The results of these works (Periáñez and García-León, 1993; Bolívar et al., 2000, 2002) describe the radioactive impact due to direct routine discharges into the Odiel River and to the leaching of radionuclides originally present in the phosphogypsum piles (Bolívar et al., 1995). ^{226}Ra data in these studies were obtained by gas proportional alpha counting, gamma-ray spectrometry or alpha-spectrometry (García-Tenorio and Manjón, 2002). The quality of the ^{226}Ra data was finally assured by liquid scintillation counting (Moreno et al., 2000). These studies continued until 1998, just before the change of the waste management (Bolívar et al., 2002), and provide a better understanding of the evolution with time of the radioactive impact under the new waste management rules.

A detailed description of the Huelva Estuary and the phosphoric acid factories sited in its vicinity can be found in the literature (Bolívar et al., 2000, 2002). For that reason, only a few details are given in the present article. The stuary consists of a tidal estuary formed by the Odiel and Tinto rivers (Fig. 1). Two phosphoric acid factories are located near the sampling stations O4 and O5 (Odiel River), respectively. The phosphogypsum piles are situated in front of the sampling station T3 (Tinto River).

These factories use over 2×10^9 kg per year of phosphate rock, which is mainly imported from Morocco, and release approximately 3×10^9 kg per year of phosphogypsum. Nowadays, a pipe to new open air conveys all the phosphogypsum produced. A water close circuit, that avoids escapes to the close environment, surrounds this new pile. After an initial decantation, the supernatant is transferred into another pool and conveyed back to the factories closing the circuit. In this way, the close environment is well protected and the water consumption is optimised. However, in 1998, just after starting the new waste management, an accident in the phosphogypsum pile took place and high amounts of waste reached the Tinto River waters. The radioactive consequences of this accident are also discussed in this paper.

The aim of this work is to show the evolution with time of the activity concentration of ^{226}Ra in water and sediment samples collected in the Tinto and Odiel rivers after 1998. For that three different sampling campaigns (1999, 2001 and 2002) were carried out. These results are easily compared to previous data because the sampling stations were carefully selected, being the same locations in both periods, before and after 1998.

2. Materials and methods

2.1. Sampling

Three sampling campaigns were carried out in the estuary of the Odiel and Tinto rivers after starting the new waste management. After a first sampling campaign, carried out in 1999 in the estuary of the Odiel and Tinto rivers, two additional sampling campaigns were carried out in

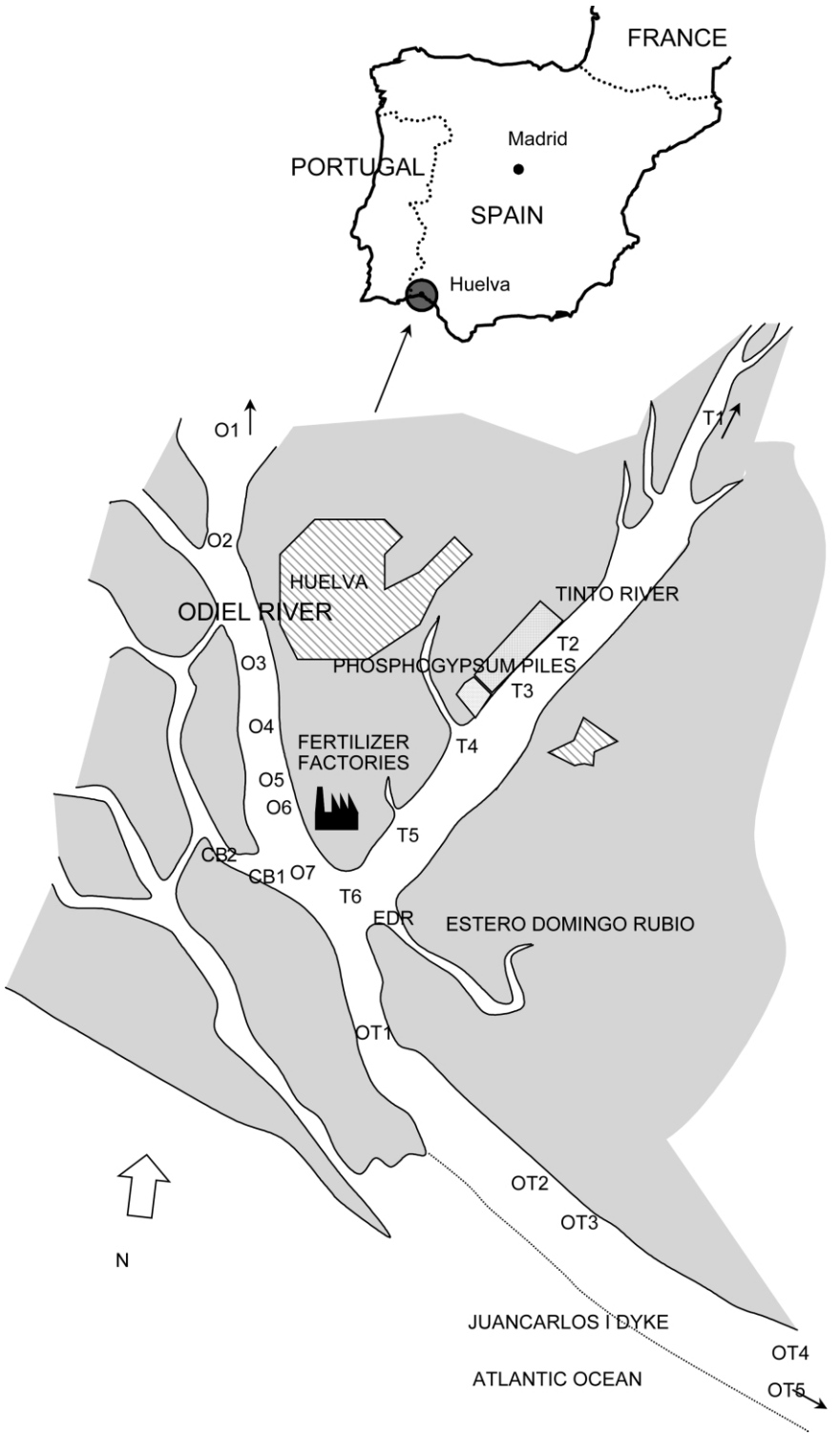

Fig. 1. Sampling stations in the estuary of the Odiel River. The same sampling stations were used in the different sampling campaigns since 1988.

2001 and 2002. River water samples and sediment samples were always collected from the same sampling stations, located near to the phosphogypsum piles and the phosphoric acid factories, in order to obtain a radionuclide distribution in the estuary (Fig. 1). The same sampling points were used in campaigns carried out before 1998, which allows an easy comparison between levels observed before and after 1998. The sampling stations were kept fixed for every sampling campaign, which was carried out in a wet season (October, February and April, respectively).

The two kinds of collected samples were water and sediment. Twenty-five litres of water were collected in every sampling station and the sample was filtered after collection. Afterwards the samples were acidified and stored in darkness. For superficial sediment samples, 5 kg were collected with a dredge, directly from the riverbed, in every sampling station. The samples were then dried and stored.

2.2. Analytical procedures

An aliquot of 500 ml was taken from every river water sample. After neutralisation, radium was extracted as Ra–$BaSO_4$ by adding H_2SO_4 and $BaCl_2$ solution. The precipitate was recovered in a 0.45 μm pore diameter Millipore filter and dissolved with EDTA 0.2 M in ammonia medium. The solution was mixed with Optiphase Hisafe 3 scintillation cocktail in a 20 ml glass vial to completely fill the volume of the vial. Radiochemical yields were obtained in two different ways for water and sediment samples. In the case of water samples, the variations in the chemical yield for every sample are very small, for that reason it is obtained as an average of the chemical yields of river water samples previously spiked with known amounts of ^{226}Ra. More details about the radiochemical procedure for water samples can be found in Manjón et al. (1997) and Moreno et al. (1999).

An aliquot of 5 g (dry weight) was taken from each sediment sample and spiked with a known activity of ^{133}Ba. The sediment was ashed at 550 °C for 24 h. The ashes were digested with aquaregia and filtered afterwards; H_2O_2 was added during the digestion. Next, the actinides were co-precipitated as hydroxides with Fe^{3+}. The supernatant was finally treated using the same technique as in water samples. The chemical yield for sediment samples was obtained for every single sample by determining the fraction of ^{133}Ba recovered into the vial. ^{133}Ba activity is calculated from the low-energy window of the spectrum obtained from the measurement of the sample by liquid scintillation counting. More details about the quality of ^{133}Ba as a yield tracer and the accuracy of the ^{226}Ra results obtained using this radiochemical procedure can be found in Moreno et al. (2000) and Blackburn and Al-Masri (1992).

Samples were measured in a Quantulus 1220 low-background scintillation spectrometer, 28 days after the preparation of the sample, to allow secular equilibrium to be reached between ^{226}Ra and its daughters. This spectrometer is equipped with a pulse shape analyser (PSA) to achieve separation and simultaneous counting of α- and β-events. A parameter (PSA threshold level) can be adjusted from values 1 to 256 to obtain the best separation between alpha and beta events. The PSA threshold level that minimise the total interference (obtained by adding α and β interference) was 105 as per our sample conditions (glass vial and Wallac Optiphase Hisafe 3 as scintillator).

Using the total alpha spectrum window of a delayed measurement, ^{226}Ra activity can be calculated as:

$$A(^{226}\mathrm{Ra}) = \frac{N_\alpha}{\varepsilon \cdot Y \cdot \delta_{226}(t)}$$

where N_α is the net count rate in total alpha spectrum window, ε is the counting efficiency corrected by $\alpha\beta$ interference, Y is the radiochemical yield and $\delta_{226}(t)$ is the correction to N_α due to the contribution from α-emitters descendants of ^{226}Ra, which depends on the time passed between the sample preparation and the measurement. It can be calculated using Bateman's equations. As the samples were measured 28 days after the

Table 1
Activity concentrations of ^{226}Ra (mBq/l) in filtered river water sampled in the Odiel River near the town of Huelva (South of Spain)

Code	Sampling site	1999	2001	2002
O2	Astillero	7.3±0.4	7.0±0.6	5.4±1.2
O3	Muelle Río Tinto	13.7±0.6	6.8±0.8	4.7±1.0
O4	Foret	12.0±0.5	8.4±1.1	5.4±1.0
O5	Fertiberia	16.6±0.6	9.4±2.3	6.2±1.2
CB1	Canal del Burro	17.7±0.9	8.6±1.0	–
CB2	Canal del Burro	15.9±0.9	7.9±0.8	–
O6	Explosivos Río Tinto	12.7±0.6	7.4±1.4	5.9±1.9
O7	Club Náutico	16.7±0.8	11.0±1.7	4.5±1.4
Mean value		14±3	8±1	5±2

Sampling campaigns were done in 1999, 2001 and 2002 in a low tide period.

radium separation, when secular equilibrium is reached, $\delta_{226}(t) \approx 4$.

3. Results

3.1. Ra activity concentration in river water samples

We present the results obtained in filtered water samples collected after 1998, since when, the phosphoric acid factories only stored their waste into open-air piles by the Tinto River. The results corresponding to 1999 were evaluated as the mean value of the activities determined by liquid scintillation counting and by beta-counting with a gas proportional counter (Periáñez, 2001). Three different zones are distinguished: the Odiel River area where the factories are located, the Tinto River area where the phosphogypsum piles are located and the Odiel River area from the confluence of Tinto and Odiel rivers to the river mouth. The results are presented following this same order.

3.1.1. The Odiel River

Activity concentrations of ^{226}Ra in filtered water samples are listed in Table 1. The activity concentration levels ranged 7–18 mBq/l in 1999, 7–11 mBq/l in 2001 and 4–6 mBq/l in the samples collected in 2002. A systematic decrease with time of activity concentration in river water might be deduced from this table. Indeed, the mean value was 14 mBq/l in 1999, 8 mBq/l in 2001 and 5 mBq/l in 2002. In addition, the activity concentration remains constant along the river, even in front of Fertiberia factory (sampling points: O4, O5), where direct discharges into the river were released before 1998. The decrease can also be observed in sampling stations located downstream, far from the factories.

3.1.2. The Tinto River

Table 2 shows the activity concentration of ^{226}Ra in filtered water samples collected in the Tinto River after 1998. The activity concentration is different depending on the sampling station, but a systematic decrease with time can be observed. Thus, the ^{226}Ra activity concentration ranged 24–44 mBq/l in 1999, 8–11 mBq/l in 2001 and 3–5 mBq/l in 2002. Furthermore, the mean value of the activity concentration was 31 mBq/l in 1999, 9 mBq/l in 2001 and 4 mBq/l in 2002.

Table 2
Activity concentrations of ^{226}Ra (mBq/l) in filtered river water sampled in the Tinto River near the town of Huelva (South of Spain)

Code	Sampling site	Before 1998	1999	2001	2002
T1	Niebla (40 km upstream)	15±1			
T2	Tubería	66±1	24.6±1.1	8.6±0.9	3.8±0.8
T3	Palos de la Frontera	69±2	25.5±1.0	9.9±1.0	4.0±0.7
T4	Frente al Estero del Rincón	64±2	34.0±1.3	8.4±0.6	3.4±0.7
T5	Muelle La Rábida		44.4±1.7	11±4	5.0±1.0
EDR	Estero Domingo Rubio		30.1±1.9	8.2±0.5	–
T6	Monumento a Colón		24.9±1.3	8.4±0.8	5.1±0.9
Mean value		66±3	31±8	9±1	4±2

Sampling campaigns were done in 1999, 2001 and 2002 in a low tide period.

Table 3
Activity concentrations of ^{226}Ra (mBq/l) in filtered river water sampled in the Odiel River after the Tinto River–Odiel River confluence near the town of Huelva (South of Spain)

Code	Sampling site	1999	2001	2002
OT1	Muelle Juan Gonzalo	22.5±1.1	–	4.2±0.8
OT2	Emisario de TIOXIDE	18.3±0.9	9.2±1.2	4.0±0.8
OT3	Muelle TIOXIDE	18.1±0.9	8.9±1.4	4.0±0.8
OT4	Muelle de Vigía	6.5±0.6	9.3±1.2	–
Mean value		16±7	9.1±0.2	4.1±0.1
OT5	Mazagón	10.8±0.8	4.7±0.5	–

Sampling campaigns were done in 1999, 2001 and 2002.

3.1.3. The Tinto River–Odiel River confluence

The activity concentrations of ^{226}Ra in filtered water samples collected after 1998 in the Odiel River, between the Tinto River–Odiel River confluence and the Atlantic Ocean, are presented in Table 3.

If only mean values are considered, the results obtained in the confluence can be considered similar to the mean levels observed in the Odiel River area. Indeed, the activity concentration levels present 14 mBq/l, 8 mBq/l and 5 mBq/l in the Odiel River in 1999, 2001 and 2002; whereas in the confluence the results were 16 mBq/l, 9 mBq/l and 4 mBq/l, respectively. Moreover, the mean activity concentration was 9 mBq/l in 2001 and 4 mBq/l in 2002, in the Tinto River, which is similar to the levels observed in the rest of the estuary for the same years.

A typical activity concentration level, 7 mBq/l, calculated as the mean value of the measurements, can be considered for the whole estuary in 2001 and 2002.

Table 4
Activity concentrations of ^{226}Ra (Bq/kg) in sediments sampled in the Odiel River near the town of Huelva (South of Spain)

Code	Sampling site	1999	2001	2002
O2	Astillero	30±1	60±2	31±3
O3	Muelle Río Tinto	73±4	54±1	82±4
O4	Foret	322±12	160±6	169±7
O5	Fertiberia	124±2	177±5	35±2
O6	Explosivos Río Tinto	253±5	246±12	73±8
O7	Club Náutico	222±7	158±5	137±7

Sampling campaigns were done in 1999, 2001 and 2002 in a low tide period.

3.2. Ra activity concentration in sediments

3.2.1. The Odiel River

Activity concentrations in sediment samples collected in the Odiel River area, where the phosphoric acid factories are located, are listed in Table 4. These results correspond to samples collected in 1999, 2001 and 2002. Two different zones can be distinguished. In the samples O2 and O3, the activity concentrations were lower with no time dependence. Therefore, the mean values were 51 Bq/kg in 1999, 57 Bq/kg in 2001 and 60 Bq/kg in 2002 in that zone. However, the results were higher and time dependent, decreasing with the years, in the samples collected in front of the factories (O4, O5) and near the confluence (O6, O7). Thus, the mean value was 230 Bq/kg in 1999, 185 Bq/kg in 2001 and 103 Bq/kg in 2002. An important fact is that the factories discharges were done (before 1998) just after the high tide, so that the waste was all swept along the river. For that reason, the activity concentration levels remained high downstream.

Table 5
Activity concentrations of ^{226}Ra (Bq/kg) in sediments sampled in the Tinto River near the town of Huelva (South of Spain)

Code	Sampling site	Before 1998	1999	2001	2002
T2	Tubería	94±22	99±2	40±1	68±3
T3	Palos de la Frontera	87±20	271±8	31±1	35±3
T4	Frente al Estero del Rincón	718±62	80±2	20±1	108±5
T5	Muelle La Rábida	46±1	56±1	196±8	205±9

Sampling campaigns were done in 1999, 2001 and 2002 in a low tide period.

Table 6
Activity concentrations of ^{226}Ra (Bq/kg) in sediments sampled in the Odiel River after the Tinto River–Odiel River confluence near the town of Huelva (South of Spain)

Code	Sampling site	1999	2001	2002
OT1	Muelle Juan Gonzalo	961 ± 29	48 ± 1	76 ± 4
OT5	Mazagón	19 ± 1	–	8.2 ± 0.8

Sampling campaigns were done in 1999, 2001 and 2002.

3.2.2. The Tinto River

The results corresponding to the sediment samples collected in the Tinto River are listed in Table 5. The mean value was 127 Bq/kg in 1999, 72 Bq/kg in 2001 and 104 Bq/kg in 2002. Concerning to the sampling points situated in front of the open-air pile (T2, T3 and T4), the activity concentration levels systematically decreased in 2001. Those levels can be compared to the same sample location in 1999, when a clear maximum peak was observed in front of the open-air pile (T3). In contrast, the activity concentrations were similar for T2, T3 and T4, in both the years 2001 and 2002.

3.2.3. The Tinto River–Odiel River confluence

The activity concentration levels obtained in the Odiel River after the Tinto–Odiel confluence are listed in Table 6. Only two sampling stations were considered. OT1 is located downstream just after the confluence and OT5 is located close to the Odiel River mouth. The levels were higher in OT1 sampling point than in OT5, far from the confluence zone, in the three campaigns. The high activity was found in OT1 in 1999, 961 Bq/kg; results suggest that OT1 is a catchment area for sediments containing ^{226}Ra from Tinto and Odiel River. Nevertheless, in 2001 and 2002, the activity concentration lowed to safer levels. Finally, activity concentration in OT5 ranges 8–19 Bq/kg, this indicates that the area, far from the confluence zone (OT1), is free of waste discharges.

4. Discussion

4.1. The Odiel River

The results obtained in this work, corresponding to samples collected after 1998, can be compared to the reported levels observed before 1998 in the same area (Periáñez and García-León, 1993; Moreno et al., 2000), when the phosphogypsum waste was directly discharged into the Odiel River. The activity concentrations of ^{226}Ra in the Odiel River water, corresponding to the different campaigns, before and after 1998, are presented in Fig. 2.

As reference background levels we consider the values obtained in OT5, which corresponds to a seawater unaffected sample point, given that it is situated almost in the open sea, its activity concentration ranges 5–11 mBq/l, Carvalho (1997) gives a value of 3.5 mBq/l for a sampling point situated in the open sea of the Tagus Estuary (Portugal). O1 is a river water sampling point that belongs to a non-contaminated area, upstream Odiel River (20 km), the mean value for ^{226}Ra in river water in O1 is 6 mBq/l. Finally, the ^{226}Ra in the Guadalquivir River in 1990 (Martínez-Aguirre, 1991) can be also used as reference to evaluate the radioactive impact of phosphoric acid factories in the Huelva Estuary nowadays. The ^{226}Ra levels ranged 6–27 mBq/l in the Guadalquivir River in Sevilla City, 100 km far from Huelva.

In Fig. 2, two different patterns can be easily observed for water samples. In the first one, before 1998, high activity concentration levels near the factories (O3, O4 and O5) show the radioactive impact of former direct discharges. In the second pattern, after 1998, lower activity concentration levels, an order of magnitude lower, are observed

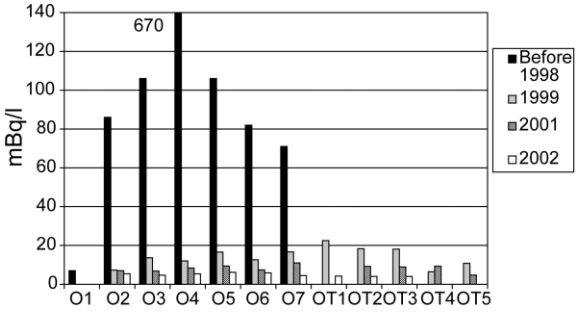

Fig. 2. Activity concentrations of ^{226}Ra in filtered water samples collected in the Odiel River near the town of Huelva. Typical results obtained in the sampling campaigns developed before 1998 are presented for a comparison.

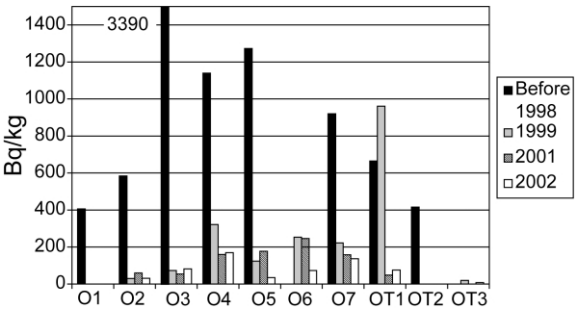

Fig. 3. Activity concentrations of ^{226}Ra in sediment samples collected in the Odiel River near the town of Huelva. Results obtained in the sampling campaigns developed before 1998 are presented for a comparison.

for the rest of the sampling points. The interruption of direct discharges into the river, that decreased the activity concentration levels in river waters, and the arrival of upstream clean waters due to abundant rainfalls, might explain the lower activity concentrations observed in samples collected after 1998. These three sampling campaigns were done in wet periods, when rainfalls were relatively abundant.

In the years 1999 and 2001, values are higher than 8 mBq/l, this might point to a source of contamination of ^{226}Ra in water. However, those values can be also considered natural concentration levels if we compare them to the levels achieved in non-contaminated sample points, OT5, O1 and in Guadalquivir river. Specifically, the high levels found in 1999 are attributed to the accident occurred in the phosphogypsum piles before the sampling campaign (described later) that introduced phosphate waste from Tinto River into Odiel River.

Finally, the possible cleaning effect of uncontaminated upstream river waters is confirmed with the results obtained in 2002, when activity concentrations decreased an order of magnitude in relation to 1999. The mean value for ^{226}Ra in 2002 is 5 mBq/l, which is close to the mean value of river water in O1 (6 mBq/l) and seawater in OT5 (7.75 mBq/l).

Fig. 3 shows the results obtained for sediment samples before and after 1998 in the Odiel River. The activity concentration of ^{226}Ra in sediments was above 3000 Bq/kg in February 1993 (Martínez-Aguirre et al., 1996). In samples collected after 1998, the activity concentration is lower than 500 Bq/kg. A systematic decrease can be seen from those data, pointing the cleaning of the contaminated riverbed of the Odiel River, until reaching in the year 2002 an average value of 85 Bq/kg in the whole affected zone.

Finally, the maximum peak, located in front of the factories (O4), where direct releases were done, was not observed after 1998; instead, a clear homogenisation of the Odiel riverbed sediments is taking place. Thus, O4, O5, O6 and O7 sampling points have similar values of ^{226}Ra activity.

The homogenisation process is probably due to transportation and mixing of the sediments due to the current and the tides, but processes of adsorption and desorption along the river of the ^{226}Ra particles attached to the sediment should also be discussed.

We can compare our results to the ones from an aquatic environment of a phosphogypsum disposal area in the Chitrapuza River, India (Haridasan et al., 2001). The fertilizer plant arrangement is similar to the fertilizer plant in Huelva Estuary. The average value for ^{226}Ra in the affected zone of Chitrapuza is 6–30 mBq/l in water and 200–1300 Bq/kg in sediments. Contamination in Chitrapuza is lower than it was in Odiel River before 1998, where activities ranged 200–3400 Bq/kg. This is because ^{226}Ra in Odiel River used to come from direct discharges into the river, whereas in Chitrapuza the contamination comes from the piles of stored phosphogypsum. However, if we compare those values to the averages in Odiel River in the year 2002, which are 5 mBq/l in water and 88 Bq/kg in sediments, the improvement that is taking place in the Huelva Estuary is clear.

Activity concentrations in non-affected areas nearby the Chitrapuza River are 1 mBq/l and 12.6 Bq/kg in water and sediments, respectively, which are lower values than the ones of Odiel River. Furthermore, activity concentration in water from Tagus Estuary, which is not affected by phosphogypsum discharges, ranges from 0.9 to 8.2 mBq/l (Carvalho, 1997), also lower concentration levels than that in Odiel. Nevertheless, closer water natural reference values in river water can be

found in Guadalquivir River, where activity ranges 6–27 mBq/l, in O1, where activity is over 6 mBq/l, or even in the seawater reference value, OT5, with 8 mBq/l.

According to Al-Masri et al. (2002), there is another factor that must be taken into account. The impact of loading cargoes of phosphate ore into ships on the near environment at the Syrian Coast was evaluated and an increasing of activity concentrations of radium, ^{210}Pb and ^{210}Po was found in zones close to the port where the phosphate ore loading is carried out. The unloading of phosphate ore in Huelva Estuary takes place in front of the factories (O3) and therefore this area might be affected. However, more time is needed to establish the possible impact of the phosphate ore unloading.

4.2. The Tinto River

The results obtained in the water samples collected after 1998 can be also compared to the results obtained in the previous sampling campaigns (Periáñez and García-León, 1993; Moreno et al., 2000). Those results are shown in Table 2. In the case of the samples collected in the Tinto River, the activity concentrations of ^{226}Ra were usually higher in samples collected before 1998, above 60 mBq/l in the sampling station T2 (Tubería), and lower in samples collected after 1998, below 30 mBq/l in T2. We consider two different geographical patterns. Firstly, the sampling station T1 (Niebla), which is located 40 km far from the estuary area and can be considered as not affected. Secondly, the sampling stations close to the phosphogypsum piles, T2, T3, T4 and T5. Some open-air piles of phosphogypsum, with an activity of 500 Bq/kg of ^{226}Ra (Bolívar et al., 1996b), are located in a neighbouring area of Tinto River, between the sampling stations T2 (Tubería) and T4 (Estero del Rincón). Thus, before 1998, high concentrations were found near T2, T3 and T4 sampling stations.

Although nowadays the new phosphogypsum piles are well protected against uncontrolled discharges by an artificial current of water that surrounds them, an accidental release happened in 1998, just before the sampling campaign of 1999, and some phosphogypsum could have reached the Tinto River, causing a local contamination of the neighbouring marshes and Tinto River, most severely at T3 and T5 sampling stations. Furthermore, the mean value, 31 mBq/l, calculated in 1999 is similar to the levels reported in typical ^{226}Ra activity concentrations in water collected near another unprotected phosphogypsum disposal area (Haridasan et al., 2001) and higher than the mean value observed in Odiel River (14 mBq/l). These facts suggest that the high levels observed in 1999 in the whole Tinto River, in spite of being lower than before 1998, must be considered anomalous due to this accident and are a direct consequence of the accident in the piles.

However, the decrease observed in the Tinto River in 1999–2001 could be related to a natural self-cleaning of the ^{226}Ra released by the accident. Nevertheless, a systematic maximum of activity is observed in T5 every year, which could be related to dissolution processes in the old phosphogypsum piles and transport of low amounts of radium throughout rivulets into the Tinto River.

The results obtained in samples collected in 2001 and 2002 are clearly lower than the results from samples collected in 1999 and before 1998. It can also be seen that activity concentrations in all samples from both 2001 and 2002 are between 3 and 10 mBq/l, typical activities of ^{226}Ra in the non-contaminated areas O1 and T1. Thus, ^{226}Ra concentration in the Tinto River ranges from 3 to 5 mBq/l in 2002, in the range of the natural activity concentration levels mentioned before and pointing to a cleaning process of radionuclides also in the Tinto River, after the new waste management procedures were introduced.

The similar mean value of activity concentration calculated in both Tinto and Odiel rivers in 2001 and in 2002 points to an homogenisation process, suggesting that the self-cleaning is extended to the whole estuary.

The results obtained in sediments in the 1999, 2001 and 2002 campaigns can be compared to the levels found in sediment samples collected before 1998 (Martínez-Aguirre and García-León, 1994; Martínez-Aguirre et al., 1996; Bolívar et al., 2002). Table 5 shows the typical activity concentration levels observed before 1998, comparing them to

the values obtained from 1999 to 2002. The levels before 1998 were above 500 Bq/kg in sample T4. The presence of these enhanced levels of ^{226}Ra was related to the influence of the stored phosphogypsum. The phosphogypsum was conveyed through some pipes from the factory to the piles. Once there, the contaminated drainage water got mixed with clean waters from the marsh and flowed into Tinto River through the rivulets that surround the area. In the new pile, the current of water is arranged in a closed circuit that avoids contact with waters from the marsh. Hence, the activity concentration levels decreased below 200 Bq/kg after 1998, in spite of the pile accident.

In both 2001 and 2002, there is a relative maximum at the T5 sampling point. As it was mentioned above for water samples, these high activity concentration levels could be related to low-level input of radium from the old unprotected phosphogypsum piles located close to the Tinto River. Furthermore, activity concentrations in 2002 in all sampling points do not diminish but increase slightly. This confirms the hypothesis that there is dissolution and weathering processes taking place in the unprotected old phosphogypsum piles and ^{226}Ra is swept to Tinto River trough the rivulets that cover the drainage water near the piles.

4.3. The Tinto River– Odiel River confluence

As it was already seen, the concentrations in water are very homogeneous after and before the Odiel–Tinto confluence in 1999, 2001 and also in 2002 (Fig. 2).

In the water samples from 1999, it is possible to see the influence of contamination from Tinto River; it can be seen a slight maximum of ^{226}Ra concentration in OT1, whereas activity concentrations decrease as we get further from the confluence zone, when during high tides, contaminated waters are mixed with clean waters from the sea.

However, in 2002, the activity concentrations in water along the confluence reached the values of non-affected areas, O1 (20 km far from the industrial area) and OT5 (at the very end of the confluence, in the open sea). The cleaning and homogenisation process can be then confirmed in 2002. Indeed, the relative maximum, observed in 1999 near the confluence, is not found in 2001 and 2002. Furthermore, the activity concentration range decreased in the confluence from 4–9 mBq/l in 2001 to 3–5 mBq/l in 2002.

It is not possible to compare the results for water samples after and before 1998 because the zone limited by the Tinto River–Odiel River confluence point and the Atlantic Ocean was not sampled in previous sampling campaigns.

However, the results in sediment samples before 1998 are available and can be seen in Fig. 3. As usual, activity concentrations were lower after 1998 in this zone. In this sense, the result corresponding to OT1 in 1999 can be considered anomalous. We can explain this result as a consequence of the pile accident occurred in 1999 if we compare the activity concentrations in sediments in OT1 and OT5 to those in the zone located before the confluence. Thus, the level observed in OT1 in 1999 is the highest of Odiel River, and higher than the levels observed in the Tinto River in 1999. Moreover, activity concentration in OT1 was lower before 1998. Consequently, the origin of this increase could be the accident that occurred in the new pile by the Tinto River, which flows into Odiel River, sweeping a big part of the contaminated sediments not only into the confluence, but also into the upstream part of the Odiel River, during the high tide.

In 2001, the activity concentrations in the sediments of the Odiel River are relatively higher than in OT1. However, the activity concentration tends to a homogenisation all along the river in 2002. Furthermore, a systematic decrease is also observed. The lower value obtained in 2002 in OT1, confirm the self-cleaning and homogenisation processes that is occurring in Tinto–Odiel Estuary.

4.4. Rate of de-contamination in the estuary

An attempt to estimate the recovery times of the estuary was done, despite that there are only available the data of three sampling campaigns. We have represented the decay of the ^{226}Ra activity concentration in both water and sediment samples in the three campaigns. First of all, we have used the mentioned reference background values to

correct the activity levels. We find that ^{226}Ra decays exponentially in both sediment and water samples. The halving times are very similar in Odiel River, Tinto River and in the confluence, that is the reason why we have decided to obtain a halving time for the cleaning of the whole estuary.

^{226}Ra concentration in the water of the estuary is decreasing, yielding an effective half-time of 130 days. The effective half-time for the cleaning of the sediment is approximately 2 years, although further campaigns must be done to establish this value accurately. The residence time of the radionuclide in the sediments depends on transportation and mixing of the sediments and the sedimentation rate of new uncontaminated layers of sediment.

In a general way, the transference of radium from the aqueous solution to the sediment in presence of high concentrations of SO_4^{2-} and CO_3^{2-} is done by co-precipitation with Ba, Ca, Mg, Fe or Mn (Molinari and Snodgrass, 1990), due to the insolubility of salts such as sulfates and carbonates. In addition, the transference of radium from water into sediment can also be driven by adsorption of suspended matter.

The behaviour of ^{226}Ra from phosphogypsum samples has been studied by Moreno et al. (1999) and Aguado (2003). Phosphogypsum is composed by a soluble phase and an insoluble phase in water. When fresh phosphogysum waste is released to a river or it is stored in the piles, the soluble fraction, containing a portion of the ^{226}Ra, is dissolved by river or rain water. The refractory insoluble fraction, also containing ^{226}Ra, is transferred directly to sediment with the waste. Given that the ^{226}Ra contained in Odiel estuary sediments comes from the phosphogypsum insoluble phase, the diminishing and homogenisation of ^{226}Ra in sediments is mainly related to the current of fresh water that scavenges the sediment, sweeping the contaminated sediments away. In addition, a factor, which could be taken into account in the decrease of ^{226}Ra in the sediments, would be the mixture of the phosphogypsum waste enriched in ^{226}Ra, previously incorporated to the sediment, and new sedimentary material with low ^{226}Ra activity concentrations.

Further studies, using radionuclides with different geochemical behaviour, are needed to obtain more information about the most influential factors of sediment cleaning in Huelva estuary.

We compare the obtained residence times with the ones obtained in an ecosystem influenced by similar circumstances. The Cumbrian Coast (Irish Sea, UK) was affected by the waste from the Albright and Wilson phosphogypsum plant that was released to the Saltom Bay. Since 1992, the discharges to the Irish Sea have decreased drastically due to a new treatment system in the plant. The cleaning of ^{226}Ra in the zone of the affected Cumbrian Coast, had a half-time of 70 days for water samples (Poole et al., 1995). The differences in the residence times in both ecosystems could be due to the very different characteristics of the areas involved. Thus, Huelva Estuary is a less energetic system in relation to the marine dynamic and this leads to longer residence times of the contaminants in water.

5. Conclusions

The new waste policy has produced a change in the radioactive characteristics of the whole Huelva estuary, and a regeneration of the zone is taking place. Specifically we can conclude that, in the Odiel River, the stoppage of the direct discharges into the river has drastically diminished the activity concentrations for both water and sediments. Nevertheless, a total restoration cannot be deduced today as the sediments located in front of the factories have still high activity concentration levels. In the case of the Tinto River, the waste from the new pile of phosphogypsum cannot usually reach the river and the river itself is cleaning the former contaminated area. Excluding the year 1999, when an accident in the phosphogypsum piles happened and it increased ^{226}Ra levels. In spite of that, the activity concentration levels, in both water and sediments, corresponding to 2002, present values of ^{226}Ra close to non-contaminated areas. Finally, this cleaning process was confirmed studying the Tinto River–Odiel River confluence and hence the whole Odiel River. In water samples, the activity concentrations are low enough to consider that the cleaning is completed. However,

total cleaning has not been reached completely in sediment samples.

Two facts are pointing the cleaning of the estuary. First, the activity concentrations in riverbeds sediments were similar in both Tinto and Odiel rivers, even in the most contaminated areas during the former waste releases. Secondly, the activity concentrations in the sediments are diminishing drastically in the whole area. The decontamination half-time for ^{226}Ra in river waters and sediments in the estuary has been estimated in 130 days and 2 years, respectively.

Acknowledgments

This work has been partially financed by ENRESA (Spanish Radioactive Waste Management Company). Sampling campaigns were supported by Junta de Andalucía (Regional Government of Andalusia, Spain). Comments and proposals by Dr R. García-Tenorio are deeply acknowledged.

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