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Contamination and restoration of an estuary affected by phosphogypsum releases

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ABSTRACT

The Huelva Estuary in Huelva, Spain, has been one of the most studied environmental compartments in the past years from the point of view of naturally occurring radioactive material (NORM) releases. It has been historically affected by waste releases, enriched in radionuclides from the U-decay series, from factories located in the area devoted to the production of phosphoric acid and phosphate fertilizers.

Nevertheless, changes in national regulations forced a new waste management practice in 1998, prohibiting releases of phosphogypsum into the rivers. The input of natural radionuclides from phosphate factories to rivers was drastically reduced. Because of this there was a unique opportunity for the study of the response of a contaminated environmental compartment, specifically an estuary affected by tidal influences, after the cessation of the contaminant releases to, in this case, the Huelva Estuary (henceforth referred to as the Estuary).

To investigate the environmental response to this new discharge regime, the specific activities of radionuclides ^{226}Ra and ^{210}Pb in water and sediment samples collected in four campaigns (from 1999 to 2005) were determined and compared with pre-1998 values.

From this study it is possible to infer the most effective mechanisms of decontamination for the Estuary. Decontamination rates of ^{210}Pb and ^{226}Ra in the sediments and water have been calculated using exponential fittings and corresponding half-lives have been deduced from them. The cleaning half-life in the whole area of the Estuary is about 6 and 3.5 years for ^{226}Ra and ^{210}Pb respectively.

The observed trend clearly shows that contamination of the Estuary by natural radionuclides is now decreasing and radioactive levels in waters and sediments are approaching the natural background references. This work attempts to evaluate whether it can be expected that the decontamination of the enhanced levels of natural radioactivity in the Estuary can be performed via natural processes.

1. Introduction

The Huelva Estuary is located in the Southwest of Spain. Two rivers, the Odiel River and the Tinto River, together with a system of channels and several large flat areas affected by tidal flooding are the main elements of this estuary (see Fig. 1).

This is a scenario widely studied due to several factors. The presence of anthropogenic enhancements of metals and uranium isotopes in the waters and sediments of both rivers is historically related to the operation of pyrite mines located on both river heads dating back to the Roman Empire period (Santos-Bermejo et al., 2003). Furthermore, an industrial complex located near the mouth of the Odiel River has been operating since the 1960s. Several industries located along the banks of the Estuary have been releasing large amounts of heavy metals into the rivers, increasing the contamination levels of riverbed sediments (Elbaz-Poulichet et al., 2001).

Finally, since the mid-1960s, two phosphoric acid factories have been producing large amounts of phosphogypsum wastes, the largest quantities being released directly to the Odiel River (until 1998), or discharged as open air stacks. A total surface of 1.2×10^7 m^2 of phosphogypsum stacks is present near the mouth of the Tinto River (Fig. 1). These stacks were also considered as a significant source of contaminants into the Estuary due to the wash up caused by the tidal action (Martínez-Aguirre and García-León, 1991).

The direct and indirect releases of phosphogypsum produced radioactive contamination of different regions of the Estuary due to the fact that those wastes were highly enriched in ^{238}U-daughters, i.e. ^{226}Ra, ^{230}Th, ^{210}Pb and ^{210}Po. A considerable fraction of these radioactive contaminants have been transferred through the years to the estuarine sediments, and spatially distributed by the tidal action (Martínez-Aguirre and García-León, 1994). The radioactive impact in the Huelva estuary has been continuously studied since 1988 (Martínez-Aguirre and García-León, 1991, Martínez-Aguirre and García-León, 1994; Martínez-Aguirre et al., 1996; Bolívar et al., 2002). Also the temporal evolution of this contamination has been analysed

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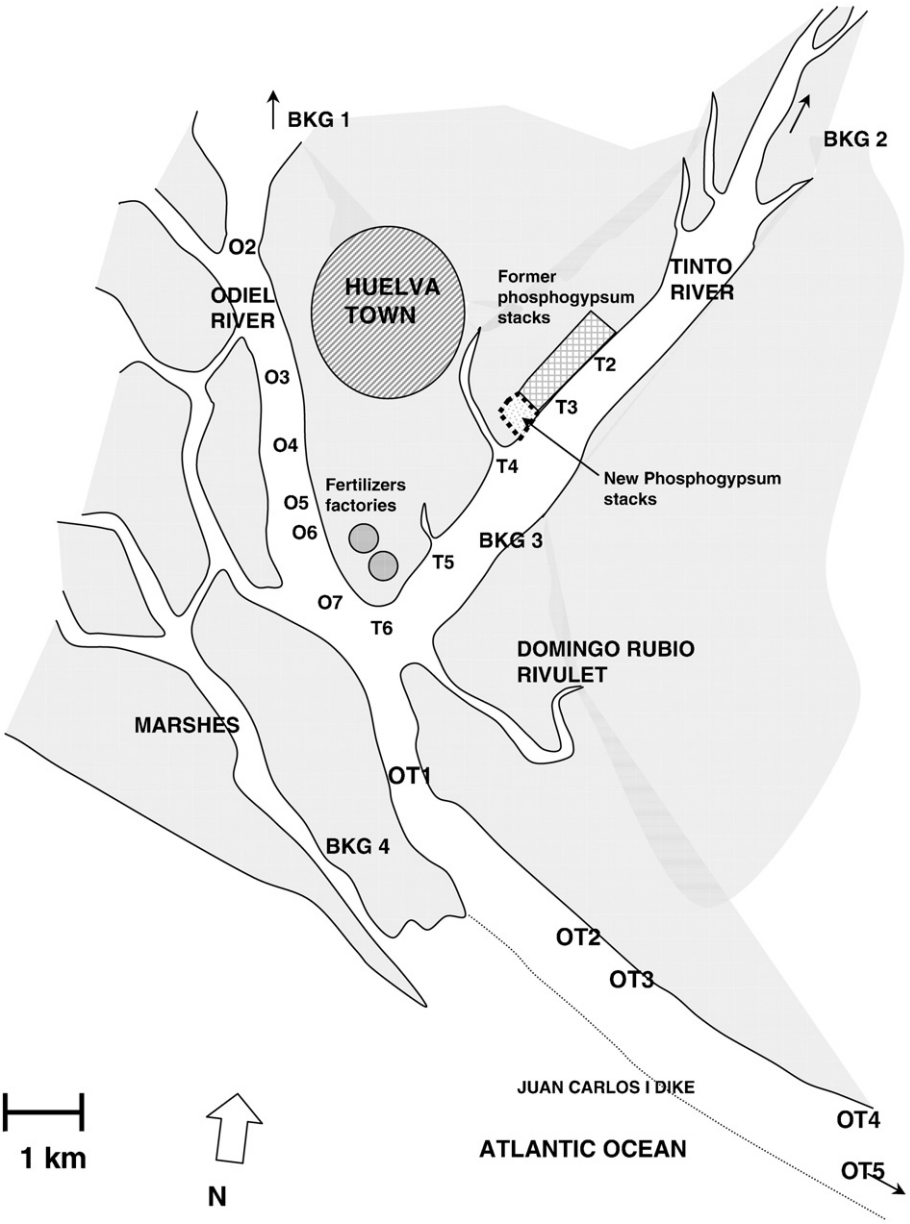

Fig. 1. Map of the estuary of the Odiel and Tinto rivers with waste deposition sites and sampling points. Places where water or sediment samples were collected for the estimation of background reference values are denoted as BKG.

by studying either $^{226}Ra/^{228}Ra$ or $^{230}Th/^{232}Th$ activity ratio depth profiles in sediment cores (San Miguel et al., 2004).

The waste management in the above mentioned factories was forced to change in 1998, due to new regulations in Spain following agreements with the OSPAR convention about non-nuclear industry discharges of radioactive substances into maritime areas (OSPAR commission, 2002, 2007). Since then, all the phosphogypsum wastes must be stored in stacks with no discharges into the marine environment.

According to the new waste management policy, lower radioactive levels were expected to be attained in the Estuary starting from 1998. Thus, the study of the time evolution of the radioactive impact in the Estuary after the change in the waste treatment policy has become relevant. An initial approach to the evaluation of the radioactive cleaning processes in the Estuary was reported by Absi et al. (2004) and Periañez et al. (2005), where the single radionuclide ^{226}Ra was studied. In those investigations, relatively high radioactivity levels were found in the riverbed sediments because, throughout the years, there had been an accumulation of natural radionuclides from phosphogypsum discharges into those sediments. These highly contaminated sediments could be acting as a new source of natural radioactivity into the aquatic phase. Thus, processes like remobilisation of river-bottom sediments or dissolution (desorption) of radionuclides attached to the sediments could be contributing to increase levels of radioactivity found in the river water column.

In this paper, the activity of natural radionuclides in water and sediment samples collected in three campaigns performed in the Estuary after 1998 is presented. The aim of this work is to analyse the temporal evolution of the contamination after the change in the management of the phosphogypsum wastes, determine the role played by contaminated sediments as a source of natural radionuclides in the water and also investigate the different cleaning mechanisms that may exist in the sediments investigated. Finally, it is hoped that it is possible to determine if a natural self-cleaning process of the natural radioactive contamination is taking place in the Estuary.

2. Experimental

2.1. Area of study and sampling

Fig. 1 depicts the present location of the waste storage, where the new isolated phosphogypsum stacks can be seen. Sampling stations are also shown in Fig. 1, and were classified into three different geographical zones. Starting with the Odiel River (denoted with O), the pipeline that directly discharged phosphogypsum wastes was located in front of O4.

Direct releases into the Odiel River were stopped before 1998. Since the 1998 changes in waste management policy the phosphogypsum has been exclusively stored in a self-contained well-isolated pile. The stacks are now surrounded by a perimetral channel that collects all the leachate products, tidal leaching, rain and rivulets lixiviation, among others, and prevents leaching into the Tinto River.

The Tinto River area (denoted with T) is close to the old, non-isolated, phosphogypsum stacks and also to the new isolated ones. The Confluence (denoted with OT) corresponds to the shared Odiel–Tinto mouth, where tidal effects are clearly observed. Finally, the Estuary was also studied as a whole, using the average values of the three areas in which it has been divided: Odiel, Tinto and Confluence.

Four sampling campaigns were carried out at low-tide periods, in 1999 (01 October 1999), 2001 (14 February 2001), 2002 (01 April 2002) and 2005 (01 March 2005). In each campaign 25 L of surface water and 5 kg of bottom sediment, consisting of the upper 10 cm layer, were taken using a surface grab in every sampling station. Water samples were filtered through a Millipore 0.45 μm filter and acidified (1 ml HCl 37% per litre of water) for storage purposes. Sediment samples were dried at 50 ºC on a stove, sieved to remove coarse fractions and homogenised before analyses.

2.2. Measurements

A number of measurement techniques were applied to determine the activity concentration of the different radionuclides. Sediments were partially dissolved using digestion processes through *aqua regia* (HNO_3 and HCl). Thus, the sediment residual fraction was not analysed in the samples.

^{226}Ra and ^{210}Pb were determined by liquid scintillation counting (LSC) using a Quantulus Wallac 1220. A sequential method based on the co-precipitation of Ra and Pb through barium and lead sulphate was used (Villa et al., 2005, 2007). Selective co-precipitation of (Ba–^{226}Ra)SO_4 is found at pH = 4.5, and (Pb–^{210}Pb)SO_4 precipitates at pH = 3. Subsequent dissolution of (Ba–^{226}Ra)SO_4 and (Pb–^{210}Pb)SO_4 was done through EDTA in ammonia media. Measurements for ^{226}Ra took place after 28 days, to attain secular equilibrium between ^{226}Ra and their daughters. Measurement for ^{210}Pb was immediate.

The measurement of ^{210}Pb in water was done via its alpha emitter daughter, ^{210}Po, after waiting 1 year for equilibrium between ^{210}Pb and ^{210}Po. The alpha emitting radionuclide, ^{210}Po, was measured by alpha-spectrometry using PIPS detectors from Canberra. ^{210}Po is spontaneously plated from an acid solution (HCl 1 M) onto a silver disc (Hurtado et al., 2003) using ^{209}Po as an internal yield tracer.

2.3. Background levels

Background reference levels for ^{226}Ra in river water were estimated from measurements made upstream of both rivers, in areas not affected by phosphogypsum releases and sea tides (Absi et al., 2004) (these areas were denoted as BKG1 and BKG2 in Fig. 1). ^{210}Pb background reference levels in river water were also estimated from BKG1 and BKG2. OT5 is located out of the Estuary (Fig. 1) and corresponded to an unaffected seacoast sampling point where typical ^{226}Ra and ^{210}Pb coastal concentrations would be found. Reference values ranged from 3 to 4 mBq l^{-1} for ^{226}Ra and from 1 to 2 mBq l^{-1} for ^{210}Pb.

Background reference values in sediments were obtained from two different methods. In the first case, a sediment core collected in an area of the estuarine system not affected by phosphogypsum releases (BKG4 in Fig. 1) was used (San Miguel et al., 2004). In the second case a sediment core collected within the affected area (BKG3) was used considering the layers corresponding to years previous to waste releases (San Miguel et al. 2004). Both estimations were in agreement and the average background reference values found for ^{226}Ra and ^{210}Pb were 20 Bq kg^{-1} and 40 Bq kg^{-1} respectively.

3. Results

3.1. Natural radionuclides in river water

Table 1 shows ^{226}Ra and ^{210}Pb activity concentration measured in 1990, 1999, 2001, 2002 and 2007 in all sampling points. Figs. 2a and b show ^{226}Ra and ^{210}Pb concentrations in water measured in the three areas of interest (Odiel, Tinto and Confluence) and in the Estuary for all sampling years. The values assigned to the Estuary correspond to the average values of the sampling points from the three different areas. Uncertainties of the mean values were obtained from the standard

Table 1
Activity concentration in water (mBq l^{-1}) in the Huelva Estuary, through the years 1999, 2001, 2002 and 2007 for ^{226}Ra and ^{210}Pb.

Sampling point	pH	Chlorinity	^{226}Ra										^{210}Pb					
			1990		1999		2001		2002		2007		1990		1999		2001	
		(g l^{-1})		±σ		±σ		±σ		±σ		±σ		±σ		±σ		±σ
O2	4	NM	86	2	7.3	0.4	7	1	5.4	1.2	7.2	0.8	8	1	2.6	0.2	4.70	0.30
O3	7	6.9	69	1	14	1	7	1	4.7	1.0	NM		10	3	2.4	0.2	2.20	0.20
O4	8	8.3	86	2	12	1	8	1	5.4	1.1	5.1	0.6	29	22	2.3	0.2	1.01	0.07
O5	NM	NM	71	3	17	1	9	2	6.2	1.2	NM		34	22	1.6	0.1	1.76	0.13
O6	NM	NM	NM		13	1	7	1	5.9	0.9	NM		12	1	1.6	0.1	1.40	0.09
O7	NM	NM	37	1	17	1	11	2	4.5	0.5	NM		14	1	2.2	0.1	5.20	0.30
T2	3	16.4	66	2	25	1	9	1	3.8	0.8	NM		NM		16.3	1.0	2.20	0.20
T3	3	16.3	NM		25	1	10	1	4.0	0.7	7.2	0.7	17	1	17.8	0.7	6.20	0.40
T4	3	17.7	78	2	26	1	8	1	3.4	0.7	NM		20	1	27.4	1.4	1.30	0.08
T5	NM	NM	51	1	34	1	11	4	5.0	1.0	NM		27	3	20.3	0.8	1.33	0.09
T6	8	18.4	NM		44	2	8	1	5.1	0.9	5.9	0.6	NM		21.7	1.0	2.03	0.13
OT1	7	18.7	45	2	23	1	NM		4.2	0.8	NM		5	1	2.2	0.2	NM	
OT2	8	19.3	NM		18	1	9	1	4.0	0.8	NM		47	3	1.3	0.1	1.70	0.12
OT3	8	19.5	NM		18	1	9	1	4.0	0.8	5.5	0.7	4	1	2.2	0.1	1.64	0.05
OT4	8	19.3	NM		7	1	9	1	NM		NM		3.6	0.3	0.7	0.2	1.08	0.07
OT5	8	19.3	NM		11	1	5	1	NM		5.4	0.7	2.1	0.2	1.2	0.1	1.00	0.10

The second column corresponds to the uncertainty, calculated as 1σ. Average water chlorinity and pH during low-tide are included. NM stands for "not measured". Data from 1990 are obtained from Absi et al. (2004) and Martínez-Aguirre and García-León (1996b).

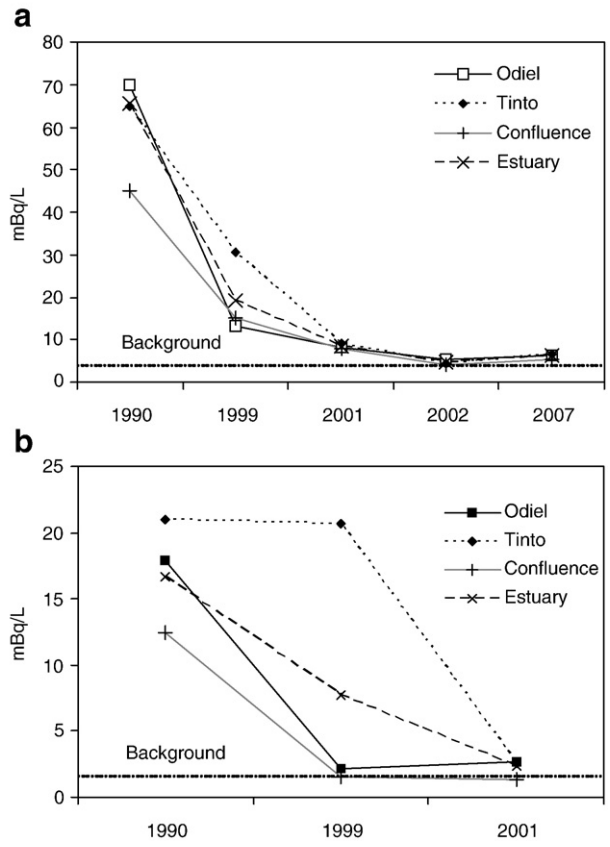

Fig. 2. a) and b) Mean activity concentration (in mBq l^{-1}) in water samples for ^{226}Ra and ^{210}Pb respectively. Average values are obtained from the values in the sampling points corresponding to Odiel River, Tinto River, Confluence and the whole Estuary. The dotted line corresponds to average background.

deviation of activities in the sampling points. Natural background levels of the region are included in the plots and can be used as reference values for evaluating the radioactive impact of phosphoric acid factories in the region.

Concerning the ^{226}Ra activity concentration in river waters, different patterns were expected in Tinto, Odiel and the Confluence. Site O4 was chosen as a representative point of the Odiel area because it is the closest point to the discharge pipeline into the Odiel River; and T4 is a representative point of Tinto since it is close to the phosphogypsum stacks. It is evident from the data that the activity concentration for ^{226}Ra has decreased between 1999 and 2007, coinciding with the cessation of direct releases into the Odiel River. After 1998, the activity concentrations in O4 evolved from 12 ± 0.5 mBq l^{-1} (1999) to 5.4 ± 1.1 mBq l^{-1} (2002) and 5.1 ± 1.1 mBq l^{-1} (2007) for ^{226}Ra. In T4 the activity concentrations decreased from 26 ± 1 mBql^{-1} (1999) to 3.4 ± 0.7 mBq l^{-1} (2001) and 7.2 ± 0.6 mBq l^{-1} (2007) for ^{226}Ra. Considering the Estuary as a whole, the average ^{226}Ra activity concentration fell from 20 ± 10 mBq l^{-1} in 1999 to 6.2 ± 1 mBq l^{-1} in 2007 (Fig. 2a).

Some differences can be seen between the Odiel and Tinto River waters. In 1999 the activity concentration in the Odiel River was 13 ± 3 mBq l^{-1} and dropped to 6.1 ± 1.5 mBq l^{-1} in 2007. However, after the cessation of direct phosphogypsum releases to the Odiel River, there was a clear increase of the ^{226}Ra concentration in the Tinto River in the year 1999, when it rose to 31 ± 9 mBq l^{-1}. This anomalous increase is due to an accident that year when the safety retaining wall was breached due to a period of high rainfall. This breach resulted in a discharge of radioactive material directly into the Tinto River, increasing the activity concentrations in the area (31 ± 9 mBq l^{-1} in the Tinto compared to 13 ± 3 mBq l^{-1} in the Odiel). However in 2007 the mean activity concentration in the Tinto River was 6.5 ± 0.9 mBql^{-1}, comparable to the levels measured in the Odiel River in the same year.

Data for ^{210}Pb activity concentration in the dissolved phase in the Estuary water is presented in Fig. 2b for years 1999 and 2001. It can be seen that the activity concentration in the whole Estuary decreased from 8 mBq l^{-1} in 1999, to 2 ± 2 mBq l^{-1} in 2001.

In the Odiel River and the Confluence, values of the same order were found before the cessation of direct releases. In 1999, ^{210}Pb activity concentration dropped to 2.1 ± 0.4 mBq l^{-1} and 1.5 ± 0.8 mBq l^{-1} respectively.

In the Tinto River, ^{210}Pb concentrations were higher in 1999 (21 ± 4 mBq l^{-1}) than in 1998 (12 mBq l^{-1}), similar to the trend found for ^{226}Ra. Again this increase in activity concentration can be attributed to the breaking of the perimeter channel that isolates the phosphogypsum stack from the river. Typical activity concentrations were restored in 2001, when average ^{210}Pb activity concentrations fell to 2.6 ± 2.0 mBq l^{-1} in the Tinto River.

3.2. Natural radionuclides in river sediments

Table 2 shows ^{226}Ra and ^{210}Pb activity concentrations measured in 1990, 1999, 2001, 2002 and 2005 in the corresponding sampling points,

Table 2
Activity concentration in sediments (Bq kg^{-1}) in the Huelva Estuary, through the years 1990, 1999, 2001, 2002 and 2005 for ^{226}Ra and ^{210}Pb.

Sampling point	^{226}Ra										^{210}Pb							
	1990		1999		2001		2002		2005		1990		1999		2001		2005	
		$\pm\sigma$		$\pm\sigma$		$\pm\sigma$		$\pm\sigma$		$\pm\sigma$		$\pm\sigma$		$\pm\sigma$		$\pm\sigma$		$\pm\sigma$
O2	NM		28	2	56	3	16	3	31	1	634	13	43	2	35	2	NM	
O3	1336	80	82	3	52	2	82	4	48	1	60	1	190	6	136	7	64	4
O4	432	26	318	16	176	10	169	7	NM		624	12	615	19	324	16	NM	
O5	NM		86	2	189	9	35	2	173	4	580	12	233	11	279	14	136	6
O6	NM		158	3	131	16	73	8	78	2	851	17	325	17	449	22	163	7
O7	920	55	184	9	178	9	137	7	71	2	554	11	721	35	314	15	78	4
T2	546	33	93	9	31	1	68	3	31	4	43	1	104	5	191	6	NM	
T3	NM		125	6	15	1	35	3	137	3	442	9	372	24	70	4	168	7
T4	723	43	79	4	21	2	108	5	52	9	NM		143	7	69	4	131	6
T5	670	40	31	2	92	10	205	9	37	1	76	2	62	3	290	8	75	4
T6	NM		NM		NM		NM		NM		NM		295	13	485	14	194	8
OT1	665	40	31	1			76	4	71	2	208	4	111	6	NM		NM	
OT2	NM		NM		46	2	NM		28	4	NM		168	8	146	7	62	4
OT3	NM		NM		NM		NM		43	2	NM		246	12	36	1	NM	
OT4	NM		NM		NM		NM		14	2	NM		5	4	15	1	NM	
OT5	NM		38	2	NM		8	1	18	0	NM		110	6	24	2	17	2

The second column corresponds to the uncertainty, calculated as 1 σ. NM stands for "not measured". Data from 1990 are obtained from Absi et al. (2004) and Martínez-Aguirre and García-León (1996b).

while Figs. 3a and b show the average activity concentrations of ^{226}Ra and ^{210}Pb in sediment samples collected in different parts of the Estuary.

For each radionuclide, the activity concentrations presented a clear trend with time. The sampling point OT4 corresponded to riverbed sediment composed mostly of sand (63 μm to 2 mm in particle diameter) where very low levels of radioactivity were always found, since radionuclides tend to be scavenged by the finer size particles (Livens and Baxter, 1988).

The average values of activity concentration for ^{226}Ra in the Odiel and Tinto rivers' sediments were 140 ± 90 Bq kg^{-1} and 80 ± 40 Bq kg^{-1} respectively in 1999. Activity concentration of ^{226}Ra decreased with time in both rivers, falling to average values of 80 ± 50 Bq kg^{-1} and 60 ± 50 Bq kg^{-1} respectively in 2005.

Regarding ^{210}Pb, the evolution of the activity concentration in sediments from Tinto and Odiel River follows a trend similar to the one observed for ^{226}Ra. In 1999, the activity concentration was 360 ± 250 Bq kg^{-1} and 170 ± 130 Bq kg^{-1} respectively for Odiel and Tinto rivers, and the impact of previous direct releases to Odiel River could be clearly seen. In 2005, activity concentration dropped to 100 ± 50 Bq kg^{-1} and 120 ± 50 Bq kg^{-1} respectively for the Tinto and the Odiel. The average ^{210}Pb levels in the Estuary fell from 260 ± 200 Bq kg^{-1} in 1999 to 110 ± 50 Bq kg^{-1} in 2005.

4. Discussion

4.1. Situation before 1998

Before the changes in waste management policy, two different patterns could be observed for the two rivers that shape the Estuary. In 1990 high values of ^{226}Ra were measured in Odiel River sediments (Martínez-Aguirre and García-León, 1991), with an average of 750 ± 100 Bq kg^{-1}. In O3, which corresponds to a sampling point close to the former pipeline, the measured activity was 1340 ± 80 Bq kg^{-1}. Compared to the 20 ± 2.0 Bq kg^{-1} background reference value, these data indicate an accumulation in the river bottom of part of the radioactivity from the phosphogypsum wastes. Additionally, the high values found in O3, O7 or even OT1 show that due to tidal effects, the riverbed sediments of the Estuary remobilized and there was a subsequent dissemination and homogenization of contamination along the Odiel River and the Confluence (Martínez-Aguirre et al., 1996). The situation around the Tinto area could be expected to be different, because there was no direct source of radioactivity contamination into the river. However, in 1996 the average ^{226}Ra activity concentration in the Tinto riverbed sediments was 650 ± 80 Bq kg^{-1} (Martínez-Aguirre et al., 1996), only slightly lower than in the Odiel area.

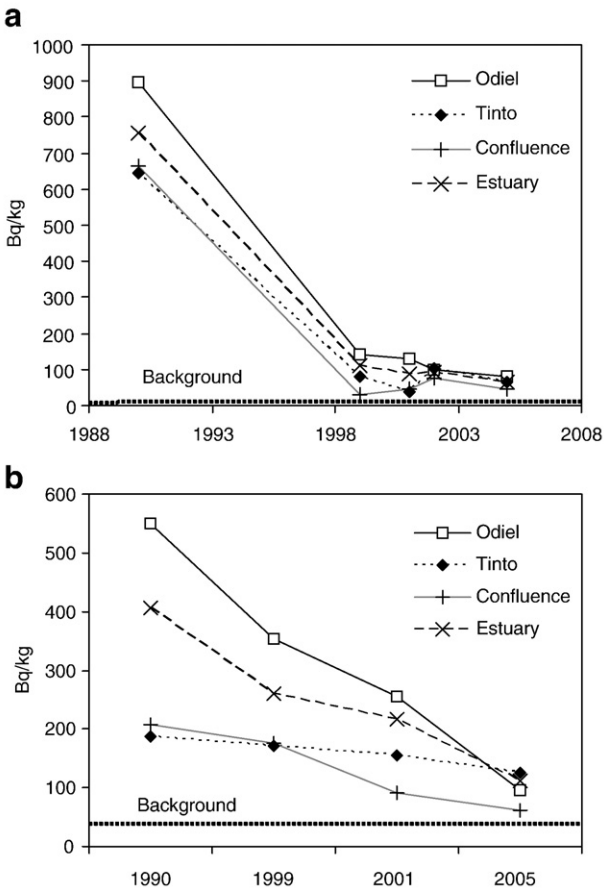

Fig. 3. a) and b) Mean activity concentration (in Bq kg^{-1}) in sediment samples for ^{226}Ra and ^{210}Pb respectively. Average values are obtained from the values in the sampling points corresponding to Odiel River, Tinto River and Confluence. The dotted line corresponds to average background.

The presence of high ^{226}Ra concentrations in an area not affected by direct releases can be explained by two factors.

The first factor was the predictable contamination of Tinto by leachate and drainage from the previously non-isolated phosphogypsum stacks. This contamination was caused by rainfall waters, tidal actions and especially by rivulets crossing and contacting the piles. However, the impact of phosphogypsum leaching has been evaluated as relatively low for ^{226}Ra, because although there is a small bound fraction of ^{226}Ra that is immediately dissolved from phosphogypsum, most of the ^{226}Ra in phosphogypsum is very slowly dissolved (Haridasan et al., 2002). According to Haridasan et al. (2002), after the storage in the open stacks, there was an immediate contribution of the more loosely bound fraction of fresh phosphogypsum to the contamination of the Tinto River. The second factor was the homogenization and dispersion of sediments along the Estuary due to tidal effects, which can allow contamination from the Odiel River to enter into the Tinto River. The importance of tidal effects for sediment homogenization in the Estuary was previously studied by Periañez et al., (1994), Periañez et al., (1996a), Periañez et al., (1996b).

For ^{210}Pb, the activity concentration in sediments from Tinto and Odiel Rivers followed a trend similar to the one found for ^{226}Ra. Thus, enhanced levels of ^{210}Pb were found in the Odiel, Tinto and in the Confluence before 1998.

4.2. Self-cleaning processes

We can currently infer a reduction in radioactive contamination of the Estuary. The average ^{226}Ra activity concentration in the waters of the Estuary as a whole fell from 65 ± 18 mBq l^{-1} in 1990, down to 6 ± 1 mBq l^{-1} in 2007. For ^{210}Pb it fell from 17 mBq l^{-1} in 1990 to 2.3 mBq l^{-1} in 2001. Reference values in the area are around 3–4 mBq l^{-1} and 1–3 mBq l^{-1} for ^{226}Ra and ^{210}Pb respectively. Therefore, it is clear that decontamination of the water column in the Estuary is taking place as expected.

The activity concentration of ^{226}Ra also decreased in the sediments from both the Odiel and Tinto rivers, falling from around 700 Bq kg^{-1} in both rivers before 1998 to average values of 80 ± 60 Bq kg^{-1} and 60 ± 50 Bq kg^{-1} respectively in 2005. Furthermore, the average ^{210}Pb specific activity in the whole estuary fell from 370 Bq kg^{-1} in 1990 to around 100 Bq kg^{-1} in 2005.

Two behaviours can be clearly seen. In the first place, the impact of the new policy of waste management can be observed in the current concentration of both radionuclides in the Estuary as a whole, although background values for ^{226}Ra and ^{210}Pb in the area have not been attained yet (20 Bq kg^{-1} and 40 Bq kg^{-1} respectively).

Secondly, it is noticeable from the concentrations found along the sampling points (Table 2) that there was a homogenization of the contamination along the Odiel and Tinto rivers, as the sampling points from O3 to OT3 attained roughly the same concentration levels in 2005.

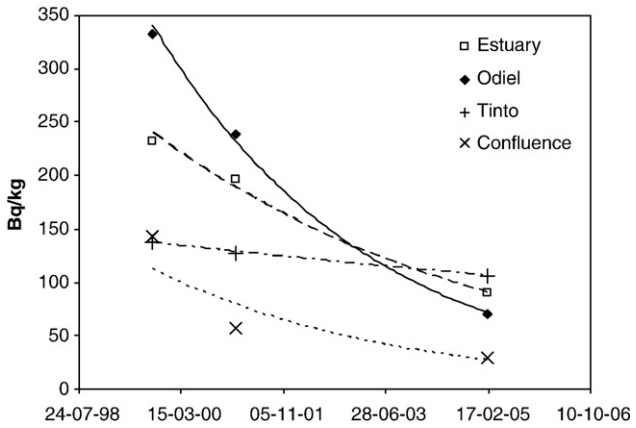

Fig. 4. Average decrease of the activity concentration in sediments in the Estuary for ^{210}Pb fitted to an exponential decay, from 1999 to 2005. Average values of concentrations have been corrected by background reference levels and decay.

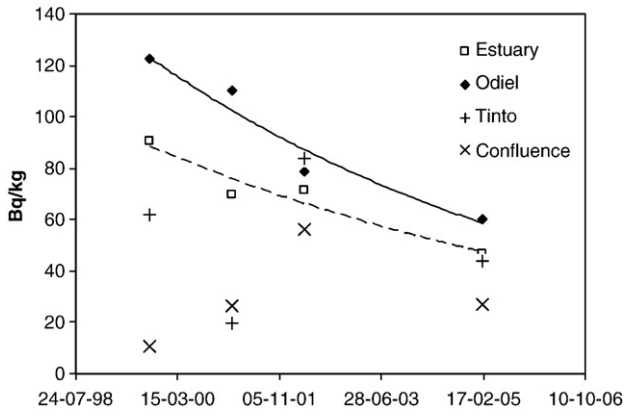

Fig. 5. Average decrease of the activity concentration in sediments in the Estuary for ^{226}Ra fitted to an exponential decay, from 1999 to 2005. Average values of concentrations have been corrected by background reference levels.

The Cumbrian coast was also affected by former releases of phosphogypsum from the Albright and Wilson plant, with a subsequent self-cleaning of the sediments (Camplin et al., 1996; Keating et al., 1996; McCartney et al., 2000; Poole et al., 1995a,b). In the Cumbrian case, the fall in the concentration of natural radionuclides attached to the sediments was found to be related mostly to dissolution and dispersion by tidal flows (Poole et al., 1995b). However, the decreasing temporal evolution of the radioactivity contamination in the Huelva area follows a more complex pattern. While the Cumbrian Coast is located in open sea, the Huelva Estuary is affected by a large variety of parameters such as tides, changes in the pH and salinity, flow currents, floods, acid mine drainage, strong sedimentation processes, etc. We will demonstrate how some of these mechanisms contribute to the evolution of the ^{226}Ra and ^{210}Pb contamination while other mechanisms helped in the removal of ^{226}Ra and ^{210}Pb. The study of the rates of decontamination for ^{226}Ra and ^{210}Pb and the comparison of their half-lives will contribute to the evaluation of the importance of the different mechanisms in the self-cleaning of the Estuary.

The following discussion will describe the areas denoted as Tinto, Odiel and Confluence. However, it is important to note that the separation of the Estuary into three areas is only geographical, because due to the strong tides the three compartments do not behave independently and are not isolated from each other (Periañez et al., 1994, 1996a).

We focus first on the Odiel River and find that the temporal evolution of the average data from ^{210}Pb (Fig. 4, Table 3) and ^{226}Ra (Fig. 5) activity concentrations in sediments can be fitted to an exponential curve with excellent regression coefficients around 0.9–0.99. These numerical fits allow us to calculate the rates of decontamination for the two radionuclides. The differences found between ^{226}Ra and ^{210}Pb decontamination rates will be discussed later. It is possible to compare the rates of decontamination in the different areas of study (Table 3) and observe that, after 1998, the Odiel River has the highest rate of decontamination of the three areas for both ^{226}Ra and ^{210}Pb.

Indeed, in the Tinto River the fall of the contamination in the sediments is much slower than in the Odiel River. As can be seen in Table 2 and Fig. 3b the ^{226}Ra activity concentration in that area does not decrease with time, but remains constant and no fitting can be done for the Tinto area (Fig. 5). For ^{210}Pb, a decrease of activity is found for the Tinto river sediments, but this decrease is slower than in the Odiel River as can be inferred from the rates of decontamination for ^{210}Pb in both areas.

In Fig. 6 we compare the decay patterns found for ^{226}Ra and ^{210}Pb in the Odiel River sediments. In order to better analyse the differences and similarities found in the rates of decontamination for ^{226}Ra and ^{210}Pb, the specific activities found in 1998, when direct releases stopped, have been included in the figure. Regarding ^{226}Ra, a drastic reduction of the activity concentration of ^{226}Ra is found in just 1 year, from 1998 to 1999, that coincides with the change in the waste management policy. This decrease is large and cannot be fitted exponentially. In contrast, in the period 1998–1999, the decrease for ^{210}Pb is slower and can be fitted to the exponential decay that coincides with the exponential decay found from 1999 to 2005, as shown in Figs. 4 and 6.

To explain this difference, we propose that the main cleaning mechanism for ^{226}Ra in that initial period of time is adsorption/desorption effect that resolubilizes it from the sediments to water. This desorption would only take place for the ^{226}Ra attached to the most exchangeable fraction of the sediments, containing most of the radium from the phosphogypsum (Aguado et al., 2004). The remaining ^{226}Ra would be attached to the non-exchangeable fraction, which is not re-dissolved (Haridasan et al. 2002; Aguado et al., 2004). Thus since 1999, the rates of decrease of radium contamination are much slower and can be fitted to an exponential decay.

From 1999 to the present time, we find high half-lives for the decontamination rates of radium in the Estuary. From 1998 to 1999 ^{226}Ra from the exchangeable fraction was directly re-dissolved and

Table 3
Average rates of decontamination for ^{226}Ra and ^{210}Pb in sediments and water.

	Sediments				Water	
	^{226}Ra average $T_{1/2}$ (years)	r^2 exponential fitting	^{210}Pb average $T_{1/2}$ (years)	r^2 exponential fitting	^{226}Ra average $T_{1/2}$ (years)	r^2 exponential fitting
Estuary	5.95	0.94	3.59	0.9997	0.53	0.98
Odiel area	5.03	0.95	2.38	0.9987	0.84	0.98
Tinto area	–	–	14.94	0.9972	0.36	0.95
Confluence	–	–	2.67	0.92	0.16	0.81

Half-lives from the exponential fitting of the decontamination decrease are also shown.

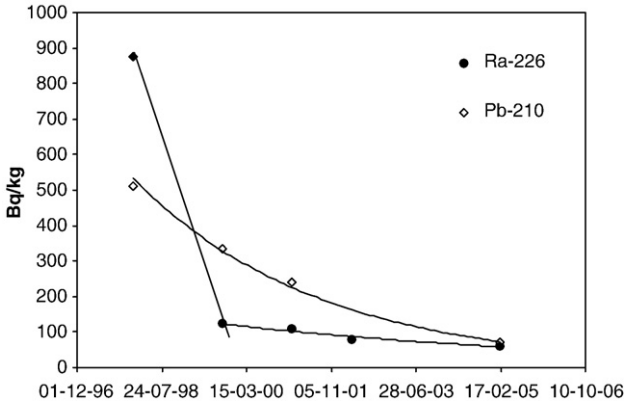

Fig. 6. Average decay in activity concentration in sediments in Odiel River for ^{226}Ra and ^{210}Pb. Data from 1998 to 2005. Average values of concentrations have been corrected by background reference levels, and for decay in the case of ^{210}Pb. Data from 1998 was extrapolated using data available from 1996 and 1990.

washed away, while the decrease in ^{226}Ra concentration observed from 1999 is assumed to be due to other factors such as re-suspension of fine grain particles and removal to the sea, or dilution of the radioactivity with uncontaminated upstream sediments. These factors would contribute more slowly to the decontamination of the area with a half-life in the Odiel River of around 5 years (derived from the exponential fitting), which indicates that a period of 20–25 years would be needed to finally reach background levels, at which point the regeneration of the area could take place.

As ^{210}Pb is highly particle reactive and tends to remain more attached to sediments, it is less affected by desorption mechanisms than ^{226}Ra, which has a lower distribution coefficient than ^{210}Pb (Carvalho, 1997; IAEA, 2002). It is known that alkali earth metals such as radium tend to remain in solution (Clifton et al., 1999), whereas lead is among the least mobile metals (Morillo et al., 2002; Caplat et al., 2005; Nieto et al., 2007). Thus, as our data show, the fraction of ^{210}Pb susceptible of being re-dissolved is eliminated more slowly than in the case of ^{226}Ra. For that reason, the data showing ^{226}Ra decreasing must be fitted to two different curves (Fig. 6), first, a fast initial decreasing step due to redissolution processes and then an exponential decay due to other factors after 1999. In contrast, the decontamination of ^{210}Pb from 1998 to 2005 can be fitted to just a single curve and it is due to several mechanisms acting at the same time: desorption of the most labile fraction together with mechanisms such as removal of former contaminated and sedimentation of clean layers.

It is shown in Table 2 and Figs. 4 and 5 that from 1999 to 2005 the rate of decontamination of ^{210}Pb is faster than for the ^{226}Ra, with a half-life of 3.5 years for the Estuary as a whole. This can be explained by ^{210}Pb removal still being affected by desorption mechanisms, whereas there is no more ^{226}Ra remaining from the exchangeable fraction. In the next few years, we would expect the decay pattern for both ^{226}Ra and ^{210}Pb to converge, since for both radionuclides the non-exchangeable fraction would be the only contribution still remaining in the sediments.

The different behaviour observed for ^{226}Ra and ^{210}Pb in redissolution processes, which affects their binding to sediments or suspended particulate matter (SPM), has been previously documented: according to Nozaki et al. (2001) and Garcia-Solsona et al. (2008), desorption of ^{226}Ra occurs in river-borne sediments when approaching the sea. This desorption is related to the decrease of its adsorption coefficient with increasing ionic strength.

On the contrary, Hatje et al. (2003) found that the increase in pH with increasing salinity favours the sorption of trace metals (lead) onto suspended particulate matter in the Port Jackson Estuary. Furthermore, Nieto et al. (2007) found similar results for trace metals in the Huelva Estuary and concluded that metals and metalloids usually sink in the estuarine sediments due to pH and salinity changes. For this reason, the mobility of ^{210}Pb from sediments would be higher upstream of the Confluence, where lower pH values are observed (Table 1) due to acid mine drainage from upstream pyrite mines (Elbaz-Poulichet et al., 1999), than in the zones more influenced by tides.

To study to what extent these desorption mechanisms are contributing to the decontamination of the Estuary, the decrease in ^{226}Ra concentration in water has been plotted versus time, for the time period 1999 to 2007. The half-lives calculated from numerical fitting to an exponential decay are presented in Table 3.

According to our data, the decrease of ^{226}Ra concentration in the Tinto and Odiel Rivers do not show significant differences, which indicates that no significant leaching of the isolated or non-isolated piles was taking place in the Tinto River. This result is in accordance with the study done in the Chitrapuzha River (India) by Haridasan et al. (2001, 2002), where no significant contribution from old, untied phosphogypsum stacks was expected due to leachate. It was proved that the leaching of old phosphogypsum from the Chitrapuzha area was not really efficient for ^{226}Ra dissolution. It is also in agreement with the results obtained by Aguado et al. (2004). In that work, a selective extraction method was carried out for riverbed sediments from the Huelva Estuary and it was concluded that the ^{226}Ra in these sediments was associated mostly with the most refractory forms.

A complete cleaning of ^{226}Ra in water from phosphogypsum contamination should be attained between 2 and 4 years in both Tinto and Odiel River. Our data show that bottom river sediments are not acting as the main source of ^{226}Ra in river waters via desorption mechanisms. Otherwise, either a concentration increase or a slower decrease in river water would be expected. However, according to ^{226}Ra decontamination rates, only 2 to 4 years are needed for the Estuary as a whole to reach natural levels. This conclusion is in agreement with data from 2007, where background reference levels were already attained in the Estuary waters.

It is then deduced that there must be other mechanisms contributing to a large extent to the long-term reduction of the concentration of natural radionuclides in the sediments.

The drag of fine grained particles to the sea also contributes to the decrease of the inventory of radioactivity in the Estuary. In suspended matter dynamics studies, only particles with a diameter <0.63 μm (muddy fractions) are considered (Carvalho, 1995; Periañez, 1999), since larger particles will sink rapidly to the bottom and consequently their horizontal movement is negligible. The radionuclides attached to the muddy fraction are, on the other hand, able to be swept to the sea. Furthermore, radioactivity is predominantly fixed to sediments with decreasing particle size (Livens and Baxter, 1988; Keating et al., 1996) and particles below 0.63 μm constitute the largest fraction of Tinto and Odiel river sediments (Table 4). Thus, the transport and re-suspension of fine particles are a probable cause for the dispersion of radioactivity along the Estuary. This was demonstrated by Periañez et al. (1994), who also showed that this transport is enhanced by strong tidal currents within the Estuary.

The transport of particles re-suspended from the bottom sediments is also enhanced by "flood effects" after heavy rains or sudden changes in the flow of the rivers due to rains upstream. It has been shown that the flows of both the Tinto and Odiel rivers respond very quickly to

Table 4
Particle size classes in the Huelva Estuary.

Sampling point	Content (%) weight		
	Grand	Sand	Mud (<0. 63 μm)
O3	0.1	9.7	90.3
T4	1.1	66.9	32.0
T5	0.1	7.1	92.8
OT2	1.8	5.8	92.4

Data from López-González et al. (2006).

rainfall periods and heavy rains, as both courses flow through impermeable materials (Olías et al, 2004). From 1980 to 2005, the average water discharge was close to 100 and 500 hm^3/year in the Tinto and Odiel rivers, respectively (Cánovas et al., 2007). Moreover, their flows show strong seasonal variations, with flood episodes of discharges of more than 10 m^3/s occurring 17% of the time (Sainz et al., 2004; Cánovas et al., 2008) that might increase the transport of contaminated particles mostly in the final course of both rivers.

Finally, another mechanism influencing the self-cleaning found in the Estuary is the sedimentation of new fresh particles from both upstream (thick grained sands) and predominantly marine origin (muds) (Periañez et al., 1996b), that dilute activity concentration in the bottom sediments. The dilution of contamination due to fresh sediments has also been reported by Carvalho (1995) in sand sediments in the Tagus Estuary. According to the models by Periañez et al. (1996b), concentration of suspended particle matter is 28 ppm, and sedimentation is slowly taking place. Furthermore, San Miguel et al. (2004) found high sedimentation rates, ranging from 1.10–1.16 cm/year, in the Odiel River near the confluence point, and 1.19–1.23 cm/year and even higher than 1.23 cm/year in the Tinto River, in two cores located in front of the phosphogypsum stacks. The sedimentation rate found in other channels from the area ranges from 0.31–0.48 cm/year. The origin of this increase in sedimentation rates are anthropogenic activities carried out in the Estuary in recent years (San Miguel et al., 2004). Taking the current high sedimentation rates into account, the final fate of the contaminated sediments would be to be buried under clean sediments.

5. Summary and Conclusions

The Odiel and Tinto rivers, forming the Huelva Estuary, were affected in the past by phosphogypsum waste contamination and enhanced concentration of natural radionuclides from the U-series were found in their water and sediments. In 1998 direct discharges of phosphogypsum to the Odiel River were stopped and new isolated phosphogypsum stacks were constructed. Since then, no phosphogypsum has been directly released to the Huelva Estuary. After 1998, observations in the Estuary river waters show significant decrease in activity concentrations for ^{226}Ra and ^{210}Pb, which are now approaching background levels. A continuous decrease in specific activity of ^{226}Ra and ^{210}Pb in the Estuary riverbed sediments has also been observed through the years, although background levels have not yet been reached.

This study concludes that a natural cleaning of the Huelva Estuary is taking place for ^{226}Ra and ^{210}Pb. The rate of decontamination of ^{226}Ra and ^{210}Pb in sediments in the whole Estuary has half-lives of 6 and 3.5 years respectively. Major sources that contribute to the cleaning of the Estuary are: a) Tidal currents into the Estuary, homogenizing the sediments and the contamination along the rivers, but also disturbing the sediments and inducing the transport of fine grain particles and suspended particulate matter to the sea. b) Dilution of the activities due to deposition of fresh, uncontaminated layers of sediments not affected by phosphogypsum releases and, to a lesser extent, c) adsorption/desorption of the radionuclides from the sediments to the river water. These mechanisms affect ^{226}Ra and ^{210}Pb differently in the Estuary: most of the exchangeable fraction of ^{226}Ra was desorbed from the sediment and transported to the sea between 1998 and 1999, whereas desorption effects of ^{210}Pb from the exchangeable fraction are slower and are still taking place in the sediments.

References

Absi A, Villa M, Manjón G, Moreno HP, Periañez R. Self-cleaning in an estuarine area formerly affected by ^{226}Ra anthropogenic enhancements. Sci Total Environ 2004;329:183–95.

Aguado JL, Bolívar JP, García-Tenorio R. Sequential extraction of ^{226}Ra in sediments from an estuary affected historically by anthropogenic inputs of natural radionuclides. J Environ Radioactiv 2004;74:117–26.

Bolívar JP, García-Tenorio R, Mas JL, Vaca F. Radioactive impact in sediments from an estuarine system affected by industrial wastes releases. Environ Int 2002;27:639–45.

Camplin WC, Baxter AJ, Round GD. The radiological impact of discharges of natural radionuclides from a phosphate plant in the United Kingdom. Environ Int 1996;22 (Suppl. 1):259–70.

Cánovas CR, Olías M, Nieto JM, Sarmiento AM, Cerón JC. Hydrogeochemical characteristics of the Tinto and Odiel Rivers (SW Spain). Factors controlling metal contents. Sci Total Environ 2007;373:363–82.

Cánovas CR, Hubbard CG, Olías M, Nieto JM, Black S, Coleman ML. Hydrochemical variations and contaminant load in the Río Tinto (Spain) during flood events. J Hydrol 2008;350:25–40.

Caplat B, Texier H, Barillier D, Lelievre C. Heavy metals mobility in harbour contaminated sediments: the case of Port-en-Bessin. Mar Pollut Bull 2005;50:504–11.

Carvalho FP. ^{210}Pb and ^{210}Po in sediments and suspended matter in the Tagus estuary, Portugal. Local enhancement of natural levels by wastes from phosphate ore processing industry. Sci Total Environ 1995;159:201–14.

Carvalho FP. Distribution, cycling and mean resident times of ^{226}Ra, ^{210}Pb and ^{210}Po in the Tagus estuary. Sci Total Environ 1997;196:151–61.

Clifton J, McDonald P, Plater A, Oldfield F. Derivation of a grain-size proxy to aid the modelling and prediction of radionuclide activity in salt marshes and mud flats of the eastern Irish Sea. Estuar Coast Shelf S 1999;48:511–8.

Elbaz-Poulichet F, Braungardt C, Achterberg E, Morley N, Cossa D, Eckers JM, Nomérange P, Cruzado A, Leblanc M. Metal biogeochemistry in the Tinto–Odiel rivers (Southern Spain) and in the Gulf of Cadiz: a synthesis of the results of TOROS project. Cont Shelf Res 2001;21:1961–73.

Elbaz-Poulichet F, Morley NH, Cruzado A, Velasquez Z, Achterberg EP, Braungardt CP. Trace metal and nutrient distribution in an extremely low pH (2.5) river–estuarine system, the Ria of Huelva (South-West Spain). Sci Total Environ 1999;227:73–83.

Garcia-Solsona E, Masqué P, Garcia-Orellana J, Rapaglia J, Beck AJ, Cochran JK, Bokuniewicz HJ, Zaggia L, Collavini F. Estimating submarine groundwater discharge around Isola La Cura, northern Venice Lagoon (Italy), by using the radium quartet. Mar Chem 2008;109:292–306.

Haridasan PP, Paul AC, Desai MVM. Natural radionuclides in the aquatic environment of a phosphogypsum disposal area. J Environ Radioactiv 2001;53:155–65.

Haridasan PP, Maniyan CG, Pillai PMB, Khan AH. Dissolution characteristics of ^{226}Ra from phosphogypsum. J Environ Radioactiv 2002;62:287–94.

Hatje V, Payne TE, Hill DM, McOrist G, Birch GF, Szymczak R. Kinetics of trace element uptake and release by particles in estuarine waters: effects of pH, salinity, and particle loading. Environ Int 2003;29:619–29.

Hurtado S, García-Tenorio R, García-León M. ^{210}Pb determination in lead shields for low-level γ-spectrometry applying two independent radiometric techniques. Nucl Instrum Meth A 2003;497:381–8.

IAEA. Sediment distribution coefficients and concentration factors for biota in the marine environment. Technical Reports Series; 2002. No. 422.

Keating GE, McCartney M, Davidson M. Investigation of technological enhancement of natural decay series radionuclides by manufacture of phosphates on the Cumbrian coast. J Environ Radioactiv 1996;32:53–66.

Livens FR, Baxter MS. Particle size and radionuclide levels in some west Cumbrian soils. Sci Total Environ 1988;70:1–17.

López-González N, Borrego J, Morales JA, Carro B, Lozano-Soria O. Metal fractionation in oxic sediments of an estuary affected by acid mine drainage (south-western Spain). Estuar Coast Shelf S 2006;68:297–304.

McCartney M, Davidson CM, Howe SE, Keating GE. Temporal changes in the distribution of natural radionuclides along the Cumbrian coast following the reduction of discharges from a phosphoric acid production plant. J Environ Radioactiv 2000;49:279–91.

Martínez-Aguirre A, García-León M. Natural radioactivity enhancement by human activities in rivers of southwest of Spain. J Radioanal Nucl Ch 1991;155(2):97–106.

Martínez-Aguirre A, García-León M. The distribution of U, Th and ^{226}Ra derived from the phosphate fertilizer industries on an estuarine system in southwest Spain. J Environ Radioactiv 1994;22:155–77.

Martínez-Aguirre A, García-León M, Gascó C, Travesí A. Anthropogenic emissions of ^{210}Po, ^{210}Pb and ^{226}Ra in an estuarine environment. J Radioanal Nucl Ch 1996;207(2): 357–67.

Martínez-Aguirre, García-León M. ^{210}Pb distribution in riverwaters and sediments near phosphate fertilizer factories. Appl Radiat Isotopes 1996;54:599–602.

Morillo J, Usero J, Gracia I. Partitioning of metals in sediments from the Odiel River (Spain). Environ Int 2002;28:263–71.

Nieto JM, Sarmiento AM, Olías M, Canovas CR, Riba I, Kalman J, Delvalls TA. Acid mine drainage pollution in the Tinto and Odiel rivers (Iberian Pyrite Belt, SW Spain) and bioavailability of the transported metals to the Huelva Estuary. Environ Int 2007;33: 445–55.

Nozaki Y, Yamamoto Y, Manaka T, Amakawa H, Snidvongs A. Dissolved barium and radium isotopes in the Chao Phraya River estuarine mixing zone in Thailand. Cont Shelf Res 2001;21:1435–48.

Olías M, Nieto JM, Sarmiento AM, Cerón JC, Cánovas CR. Seasonal water quality variations in a river affected by acid mine drainage: the Odiel River (South West Spain). Sci Total Environ 2004;333:267–81.

OSPAR Commission. Discharges of radioactive substances into the maritime area by non-nuclear industry; 2002.

OSPAR Commission. PARCOM Recommendation 91/4 on Radioactive Discharges, Spanish Implementation Report; 2007.

Periañez R, García-León M, Abril JM. Radium isotopes in suspended matter in an estuarine system in the southwest of Spain. J Radioanal Nucl Ch 1994;183(2):395–407.

Periañez R, Martínez-Aguirre A, García-León M. U- and Th-isotopes in an estuarine system in southwest Spain: tidal and seasonal variations. Appl Radiat Isotopes 1996a;47:1121–5.

Periañez R, Abril JM, García-León M. Modelling the suspended matter distribution in an estuarine system: application to the Odiel river in southwest Spain. Ecol Model 1996b;87:169–79.
Periañez R. Three dimensional modelling of the tidal dispersion of non conservative radionuclides in the marine environment: application to 239, 240Pu dispersion in the eastern Irish Sea. J Mar Syst 1999;22:37–51.
Periañez R, Absi A, Villa M, Moreno HP, Manjón G. Self-cleaning in an estuarine area formerly affected by ^{226}Ra anthropogenic enhancements: numerical simulations. Sci Total Environ 2005;339:207–18.
Poole AJ, Allington DJ, Baxter AJ, Young AK. The natural radioactivity of phosphate ore and associated waste products discharged into the eastern Irish Sea from a phosphoric acid production plant. Sci Total Environ 1995a;173–174:137–49.
Poole AJ, Allington DJ, Denoon DC. Temporal and spatial survey of dissolved 226Ra in coastal waters of the eastern Irish Sea. Sci Total Environ 1995b;30:233–47.
Sainz A, Grande JA, de la Torre ML. Characterisation of heavy metal discharge into the Ria of Huelva. Environ Int 2004;30:557–66.
San Miguel EG, J.P. y Bolívar, García-Tenorio R. Vertical distribution of Th-isotope ratios, ^{210}Pb, ^{226}Ra and ^{137}Cs in sediment cores from an estuary affected by anthropogenic releases. Sci Total Environ 2004(318):143–57.
Santos-Bermejo JC, Beltrán R, Gómez-Ariza JL. Spatial variations of heavy metals contamination in sediments from Odiel river (Southwest Spain). Environ Int 2003;29: 69–77.
Villa M, Moreno HP, Manjón G. Determination of ^{226}Ra and ^{224}Ra in sediments samples by liquid scintillation counting. Radiat Meas 2005;39:543–50.
Villa M, Hurtado S, Manjón G, García-Tenorio R. Calibration and measurement of ^{210}Pb using two independent techniques. Radiat Meas 2007;42:1552–60.