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The presence of ^{226}Ra in an estuary formerly affected by direct discharges of waste from a phosphate fertilizer complex has been investigated. Specific activities ranging from 3.6 to 45.2 mBq/l have been detected. In general, activity levels are lower than those detected when direct discharges were carried out. However, there is still a clear contamination due to the disposal of phosphogypsum in open air piles by the river. Moreover, it seems that ^{226}Ra is being redissolved from the contaminated bed sediments, which also contributes to an enhancement in the activity levels of the estuary waters.

Introduction

Wastes from a phosphate fertilizer processing complex contain important concentrations of some radioactive elements. Thus, during the wet process (one method used to produce phosphoric acid) a waste called phosphogypsum appears. It is mainly composed of Ca sulfate, and also contains important amounts of Ra, U and Th isotopes.¹ Phosphogypsum is discharged directly into surface waters or stored in open air piles. Therefore, the operation of phosphate fertilizer factories may enhance the radioactivity content in their close environment.

The Odiel and Tinto rivers form a tidal estuarine system which is located at the southwest of Spain. A phosphate fertilizer processing complex has been releasing its wastes directly to the Odiel river and disposing phosphogypsum in piles, at the open air, by the Tinto river (Fig. 1). It has been found²⁻⁴ that enhanced levels of ^{226}Ra , U and Th isotopes are present in the estuary. For instance, a peak of 670 mBq/l of ^{226}Ra was detected² in water collected close to the outlet of the fertilizer complex in the Odiel river.

The waste policy of the factory has now changed due to new regulations from the EU. Thus, wastes are not released to the Odiel river, although gypsum is still being disposed in piles by the Tinto river. The objective of this work was to investigate how the new waste policy is affecting the presence of ^{226}Ra in the waters of both rivers.

Experimental

Water samples were collected in October 1999 along the Odiel and Tinto rivers (Fig. 1) during low tide.

In three points of the estuary (O3, O7 and T5), samples were also collected at different times along the tidal cycle to see if there is any influence of the tidal state on the activity levels. The samples were collected in 25 l plastic bottles, and pH was measured at the same time. The water was filtered soon after sampling, using Nuclepore filters of 0.45 μm pore size in order to remove suspended matter, and acidified to pH 2–3 with HNO_3 to avoid the growth of microorganisms and minimize water-wall interactions during storage.

^{226}Ra activities were determined from 0.5 l of each sample. The water was neutralized with NH_4OH . Then some 5 mg of Ba and 20 ml of H_2SO_4 were added to the sample. Ba–Ra sulfate precipitates under these conditions. The precipitate was collected by filtration through 0.45 μm Millipore filters (filter diameter 40.00 mm). After a minimum of 20 days (to allow secular equilibrium of ^{226}Ra with its daughters) the alpha-activity of the precipitate was counted in a LB770 low background gas flow proportional counter, that has ten different counters. All the samples had the same geometry but different thickness. Since ^{226}Ra is an alpha-emitter, self-absorption of the samples must be taken into account. Thus, several calibration samples were prepared with known ^{226}Ra activities and various Ba content of different thickness. The total efficiency was calculated as:

$$R_T = \frac{N}{4TA} \quad (1)$$

where N is the number of alpha-counts, T is the counting time (s), A is the ^{226}Ra activity (Bq) added to the calibration samples. A factor of 4 appears due to the fact that three α -emitters (^{226}Ra daughters) are counted together with ^{226}Ra .

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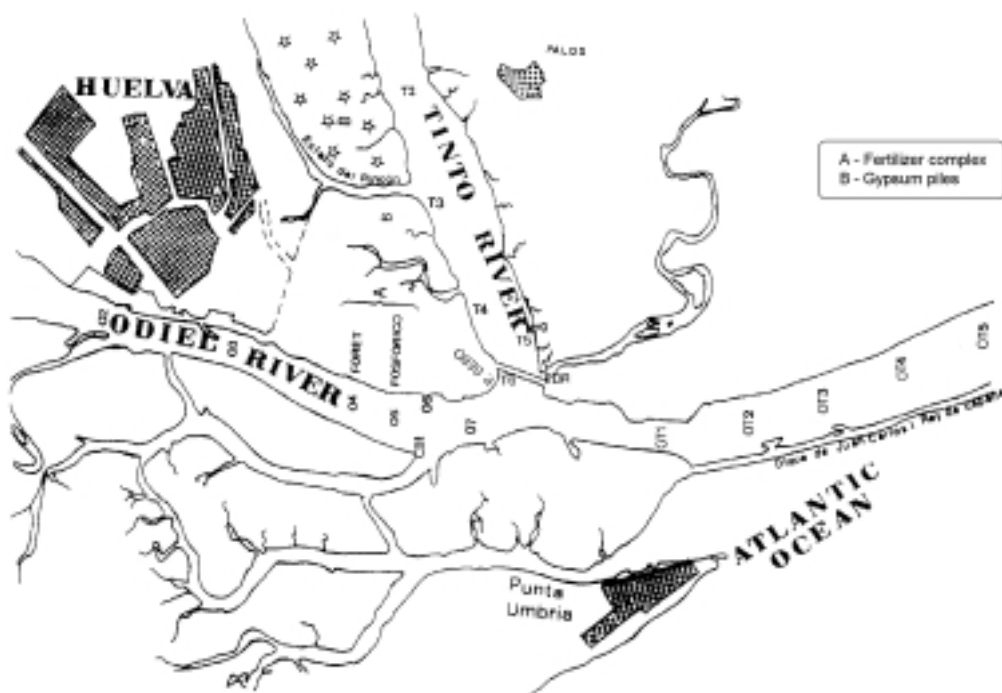


Fig. 1. Map of the Odiel and Tinto rivers showing the sampling points, the fertilizer complex and the phosphogypsum piles

A calibration line was obtained for each detector, that allows to interpolate the total efficiency for a sample of a given thickness e in mg/cm^2 . The line was similar for all detectors. As an example, we show one of them:

$$R_T (\%) = (23.6 \pm 1.9) - (2.2 \pm 1.7)e \quad (2)$$

^{226}Ra activity of the sample in Bq/l is obtained from:

$$A_{226} = \frac{N}{4TR_T V} \quad (3)$$

where V is the sample volume in liters (0.5 l). The method for ^{226}Ra separation and measurement was described earlier.^{2,5-7}

Results

^{226}Ra activities and pH of the samples are presented in Table 1. In general, activities are higher than those found in non-contaminated rivers: these range from 0.085 mBq/l (St. Lawrence river),⁸ to 3.4 mBq/l (Ganges river).⁹ Moreover, they are similar to activities detected in some rivers affected by the discharge of wastes from fertilizer factories, as is the case of Boben river (Slovenia)¹⁰ and the Schelde (Netherlands).¹¹ In the first case 43 mBq/l of ^{226}Ra were measured; in the second, activities were detected from 9 to 68 mBq/l . However, activities in the estuary are, in general, lower (7 to 670 mBq/l) than those detected when direct discharges to the Odiel river were carried out.²

Table 1. ^{226}Ra activities (A_{226}) in water samples of the Odiel and Tinto rivers. Errors (1σ) are due to counting statistics in measurements of sample and in calibration lines

Sample	Time	A_{226} , mBq/l	pH
O2	l.w.	6.8 ± 0.6	5
O3	l.w.	11.3 ± 1.0	5
O3	13:15	9.9 ± 0.9	NM
O3	14:45	12.4 ± 1.2	NM
O3	h.w.	10.7 ± 0.6	NM
O4	l.w.	11.0 ± 0.6	5
O5	l.w.	17.9 ± 2.2	6
O6	l.w.	13.0 ± 0.6	6
O7	l.w.	16.4 ± 1.6	5
O7	13:00	23.4 ± 1.3	NM
O7	h.w.	14.2 ± 0.7	NM
CB1	l.w.	14.0 ± 0.9	6
OT1	l.w.	19.6 ± 2.1	5
OT2	l.w.	16.4 ± 1.8	6
OT3	l.w.	19.1 ± 1.5	5
OT4	l.w.	3.6 ± 0.6	7
OT5	l.w.	7.7 ± 0.9	7
T2	l.w.	25.1 ± 2.3	4
T3	l.w.	28.5 ± 4.1	5
T4	l.w.	35.3 ± 1.8	4
T5	l.w.	45.2 ± 4.7	5
T5	12:55	46 ± 7	NM
T5	15:05	23.2 ± 1.0	NM
T5	h.w.	19.1 ± 1.3	NM
EDR	l.w.	27.8 ± 2.1	5
T6	l.w.	15.9 ± 1.7	5

NM – not measured.

l.w. – low water (11:00 h) and h.w. high water (17:20 h).

Hours are local times.

Discussion

The general behavior of ^{226}Ra activities for all the samples collected during low water is presented in Fig. 2. It seems clear that the Tinto river (samples T2 to EDR) is more contaminated than the Odiel river (samples O2 to CB1). This can be attributed to the gypsum piles that are located by the Tinto river. They are crossed by a number of streams of natural and artificial origin that carry water to the river or receive water from it, depending on the tidal state. Presumably, these streams are transporting Ra from the piles to the main river. The lower pH of samples T2 and T4 reveals that some external input exists. Before the change of the waste policy of the factory, the Odiel river was clearly more contaminated.²

In samples OT4 and OT5, collected close to the sea, activities decrease to 3.6 and 7.7 mBq/l, approaching to the average ^{226}Ra activity in Atlantic open waters (1.07 mBq/l).¹² In sample O2, the activity is lower than in the rest of the Odiel river samples due to the fact that this point is some kilometers upstream from the fertilizer complex, thus it remains relatively unaffected. Activity levels detected along the Odiel river (samples O3 to OT3) are rather uniform. This contrasts with the situation when direct discharges were carried out: in this case a clear activity peak could be detected close to the factory outlet.² However, activity levels are still higher than those found in non perturbed rivers and in sample O2 (whose activity should be close to the background level of the Odiel river, as commented above). This activity enhancement in the Odiel river can be due to a redissolution of ^{226}Ra from the heavily contaminated bottom sediments.⁴ A modelling study was carried out¹³ for the Odiel river in which it was found that the river would remain contaminated, even if direct discharges stop, due to the redissolution of Ra from the sediment. It seems that this is occurring.

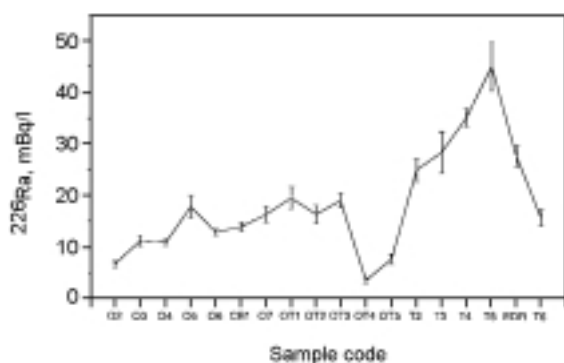


Fig. 2. ^{226}Ra specific activities (mBq/l) obtained along the Odiel and Tinto rivers during low tide. See Fig. 1 for the location of the sampling points

Clear differences in the ^{226}Ra activities along the tidal cycle cannot be seen in points O3 and O7. This is not the case of point T5, where activity during low tide is a factor 2 higher than activity during high tide. A possible explanation is that during high tide the river water invades the gypsum piles through the small streams (see above). When the waters go down, they transport Ra washed from the piles, giving place to a ^{226}Ra signal that is detected downstream from the gypsum piles during low tide.

The average ^{226}Ra activity in the estuary is 18.5 mBq/l. Taking a mean water volume of $6.2 \cdot 10^7 \text{ m}^3$, the total ^{226}Ra content in waters of the estuary is of the order of $1.2 \cdot 10^9 \text{ Bq}$. In year 1990, when direct discharges were still carried out, the content was² some $6.0 \cdot 10^9 \text{ Bq}$. Thus, at least $4.8 \cdot 10^9 \text{ Bq}$ of ^{226}Ra have been introduced into the Atlantic Ocean from the estuary.

Conclusions

The presence of ^{226}Ra in waters of an estuary formerly affected by direct releases from wastes of a phosphate fertilizer factory has been investigated. A general decrease has been found in the activity levels, although one of the rivers (Tinto) is enhanced due to the presence of phosphogypsum piles that are partially flooded during high tide. Although activity levels in the Odiel river are lower than those detected when direct discharges were carried out, the river is still contaminated. Presumably this is due to the redissolution of Ra from the contaminated bed sediments.

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