



Measuring and modelling temporal trends of ^{226}Ra in waters of a Spanish estuary affected by the phosphate industry

R. Perriñez *

Dpto. Física Aplicada 1. EUITA, Universidad de Sevilla, Ctra Utrera km 1, 41013-Sevilla, Spain

Received in revised form 27 July 2004; accepted 16 August 2004

Abstract

The presence and temporal evolution (1990–2001) of ^{226}Ra in a tidal estuary affected by the phosphate industry has been investigated. Water samples collected in the course of four separate sampling campaigns were analysed for ^{226}Ra content using a gas flow proportional counter following Ba coprecipitation. Two ^{226}Ra sources have been identified: direct discharges from the industrial complex and run-off from a phosphogypsum pile. Although activity levels are similar, or even higher, than those found in other environments affected by the phosphate industry, there has been a general decrease in contamination since direct discharges ceased in 1998 due to new regulations from the EU. However, sediments are now acting as a source of Ra to the water column due to redissolution processes. A numerical model of the estuary has been developed to describe quantitatively the experimental results. The model solves the hydrodynamics and the dispersion equation of ^{226}Ra including interactions with sediments. Model results are, in general, in good agreement with observations.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Radium; Odiel-Tinto estuary; Phosphogypsum; Numerical modelling; Hydrodynamic; Sediment

* Tel.: +34 954486474; fax: +34 954486436.

E-mail address: rperianez@us.es.

1. Introduction

The Odiel and Tinto rivers, in the southwest of Spain, form a fully mixed tidal estuary which surrounds the town of Huelva (Fig. 1). Both rivers join at the Punta del Sebo. From this point, they flow together to the Atlantic Ocean.

An industrial complex, containing a plant dedicated to the production of phosphoric acid and phosphate fertilizers, is located by the Odiel river. It is well known that the phosphate rock used as a raw material by this industry contains significant amounts of natural radionuclides, mostly U, Th and Ra. The industrial processing of the phosphate rock leads to a redistribution of radioactivity. For instance, during the wet process for phosphoric acid production, 86% of U and 70% of Th present in the rock are transferred to the phosphoric acid itself, while 80% of the Ra content follows the so-called phosphogypsum path (Guimond & Hardin, 1989). This is a form

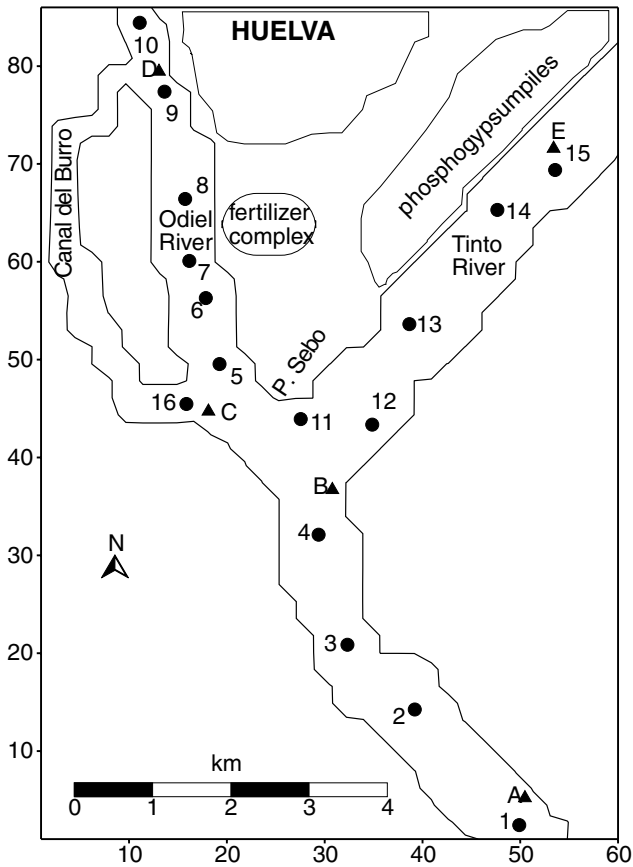


Fig. 1. Map of the area of the estuary covered by the model. Numbered circles indicate the points where water samples were collected. Lettered triangles indicate the points where currents measurements were available. Units on the axes give the grid cell number. The sea is approximately 1 km to the south of point 1.

of impure calcium sulfate removed as a precipitate during the process. Phosphogypsum is usually disposed into piles in the open environment or discharged into rivers or estuaries, giving rise to a local radioactive impact.

The raw material used in the plant is phosphate rock from Senegal, Morocco and Togo, which is treated by the wet process to obtain phosphoric acid. During 1990, for instance, 2×10^6 tons were processed and 3×10^6 tons of phosphogypsum were produced. These wastes were partially released directly into the Odiel river (20%), with the remaining 80% conducted with water through a pipeline to phosphogypsum piles located by the Tinto river (see Fig. 1), where such material is stored in the open air. The gypsum piles cover some 12 km² of the Tinto river margin. Since 1998, wastes are not released directly into the Odiel river due to new regulations from the EU, although phosphogypsum is still being disposed of in the piles by the Tinto river.

A number of recent studies have investigated the radioactive impact of the phosphate industry in its close environment. Paridaens and Vanmarcke (2001) charted the ²²⁶Ra contamination of the river Laak (Belgium) and some areas that are regularly flooded by the river. Haridasan, Paul, and Desai (2001) found that the surface runoff of water from a phosphogypsum pile placed by the Chitrapuzha river (India) appears to be the major pathway of transport of Ra to the river. McCartney, Davidson, Howe, and Keating (2000) studied the effect of a reduction of the discharges from a phosphate plant in the levels of U and Th isotopes along the Cumbrian coast (UK), while Poole, Allington, and Denoon (1995) conducted a similar study but for ²²⁶Ra.

The effect of the phosphate industry in the Odiel and Tinto estuary has also been investigated. Mart  nez-Aguirre, Garc  a-Le  n, and Ivanovich (1994a) and Bol  var, Garc  a-Tenorio, and Vaca (2000) studied the presence of U and Th isotopes over different areas of the estuary. The presence of ²²⁶Ra in waters of the estuary was investigated by Perri  ez and Garc  a-Le  n (1993), who determined ²²⁶Ra activity concentrations in waters collected from the estuary in two different sampling campaigns in July 1990 and March 1991.

The objective of the present work is to provide a summary of the work carried out at the University of Seville concerning the temporal evolution of the ²²⁶Ra contamination of the estuary, presenting results for sampling campaigns carried out before and after the change in the waste policy of the phosphate plant in 1998. To this effect, two new sampling campaigns were conducted; in October 1999 and February 2001. Results obtained for the four campaigns are presented together. Although the results for the 1990 and 1991 samples have been published previously (Perri  ez & Garc  a-Le  n, 1993), they will also be included here for ease of comparison. It has to be pointed out that sampling campaigns are non-ideal for a temporal trend study, since have been carried out in different months during the four years. Nevertheless, some interesting conclusions may be obtained from them, as will be shown.

Interpretation of experimental results is not an easy task since a number of processes affect concentrations in the dissolved phase. Currents due to tidal oscillations produce advective transport of dissolved radionuclides along the estuary. Furthermore, turbulent diffusion is present and there are also transfers of radionuclides between the dissolved and solid phases (suspended matter particles and bottom

sediments). The solid phase may act as a sink or as a source of radionuclides to the water column, depending on the concentration of radionuclides in each phase and on the rates governing the adsorption and release reactions. To account for these processes, a numerical model of the estuary, including all these factors, has been developed. The model solves the hydrodynamics of the estuary and the dispersion of ^{226}Ra , including the interactions between the dissolved and solid (bottom sediments) phases. The model application allows reproduction of the experimental results for the different campaigns and an estimate to be made of the input of ^{226}Ra from the phosphogypsum piles to the Tinto river.

Details of the sampling and the experimental method for ^{226}Ra extraction and measurement are presented in the next section. This is followed by the presentation and discussion of results. Finally, the model is described and applied.

2. Sampling and analysis

Sampling campaigns were carried out on 19th July 1990, 5th March 1991, 27th October 1999 and 14th February 2001, under low water conditions (1 h after low water in the case of 1991). Samples (see Fig. 1 for positions of the sampling points) were collected in 25 l plastic bottles. The water was filtered soon after sampling, using 0.45 μm pore size Nuclepore filters to remove suspended particles. Filtered samples were 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 aliquots of the water samples. After neutralisation of the filtrate using NH_4OH , ~ 5 mg of BaCl_2 and ~ 20 ml of 1 M H_2SO_4 were added to the sample. Under these conditions Ba–Ra sulfate precipitates after some 20 min of continuous stirring and moderate heating. The precipitate, containing the radium, was collected by filtration through a 0.45 μm Millipore filter. Activity on the filter was measured using a low background gas flow proportional counter previously calibrated for total efficiency vs. precipitate mass thickness.

These procedures have been widely validated and applied. Further details on the method can be found in Morón, García-Tenorio, García-Montaño, García-León, and Madurga (1986), Martínez-Aguirre and García-León (1994) and Periañez and García-León (1993).

3. Experimental results

^{226}Ra concentrations for the four campaigns are presented in Table 1. The levels measured in the first three campaigns are broadly similar (or somewhat higher) to those found in other rivers affected by fertiliser industries. In the Boben River (Slovenia), for example, ^{226}Ra concentrations of ~ 40 mBq/l have been reported in waters from the most affected area (Kobal, Brajnik, Kaluza, & Vengust, 1990), while values in the range 9–68 mBq/l have been reported for affected waters in the Schelde, Netherlands (Koster et al., 1991). More recently, ^{226}Ra concentrations of ~ 30 mBq/l have

Table 1
²²⁶Ra activities (mBq/l) in water samples of the Odiel and Tinto rivers

Sample	1990	1991	1999	2001
1			3.6 ± 0.6	9.3 ± 1.2
2			19.1 ± 1.5	8.9 ± 1.4
3			16.4 ± 1.8	9.2 ± 1.2
4	71 ± 2	54.2 ± 1.8	19.6 ± 2.1	
5	82 ± 1	46.6 ± 1.6	16.4 ± 1.6	12.5 ± 1.9
6			13.0 ± 0.6	9.4 ± 1.7
7	106 ± 3	46.5 ± 1.6	17.9 ± 2.2	8.9 ± 2.1
8	670 ± 13	53 ± 2	11.0 ± 0.6	9.4 ± 1.1
9	106 ± 2	25.3 ± 1.2	11.3 ± 1.0	6.6 ± 0.6
10	86 ± 2	21.3 ± 1.4	6.8 ± 0.6	7.2 ± 0.5
11			15.9 ± 1.7	9.7 ± 0.9
12	64 ± 2	33.6 ± 1.5	45 ± 5	10 ± 4
13	69.3 ± 1.9	36.0 ± 1.4	35.3 ± 1.8	8.4 ± 0.6
14			29 ± 4	9.7 ± 1.0
15	67 ± 1	65.6 ± 1.9	25.1 ± 2.3	8.6 ± 0.9
16			14.0 ± 0.9	8.6 ± 1.0

Uncertainties (1σ) are due to counting statistics in sample measurements and in detector calibration. Empty spaces mean that such samples were not collected.

been measured downstream a phosphogypsum pile in the Chitrapuzha River, India (Haridasan et al., 2001).

In the case of the 1990 samples, there is an intense peak of 670 mBq/l at point 8, located close to the pipeline through which direct discharges to the Odiel river were carried out. This shows a clear local radioactive impact in the estuary due to the operation of the fertilizer plant. For the remainder of the estuary, activity concentrations range from 64 to 106 mBq/l, also suggesting a clear contamination if they are compared with values reported above. For samples collected in 1991, the peak in the vicinity of the plant outlet is not apparent. However, activities ranging from 21 to 66 mBq/l are indicative of contamination still being present, although the input from the plant to the Odiel river seems less than during the 1990 sampling. It is interesting to note that there is an activity peak in sample 15, collected in the Tinto river close to the phosphogypsum pile. It seems that some run-off from the phosphogypsum pile to the river is occurring and, as a consequence, ²²⁶Ra is being transported to the river, as has been found in other environments (Haridasan et al., 2001). This is related to the fact that the phosphogypsum storage area is crossed by a number of small streams of natural and artificial origin (Perriñez & García-León, 1993). Some of these may be possible remnants of the wet lands totally integrated in the estuarine system of the rivers only 40 years ago, before industrial activity started in the area (Borrego & Pendón, 1988). Presumably, these streams are capable of transporting activity from the storage area to the main river. This effect was also probably taking place in 1990, although it may have been masked by the high contamination produced by the large discharges that were released into the Odiel. This point will be investigated later with the numerical model of the estuary.

Activity levels detected in the 1999 campaign, ranging from 3.6 to 45 mBq/l, are lower than those obtained in 1990 and 1991. This is likely to be related to the introduction of stricter waste policies in 1998, which resulted in the cessation of direct discharges into the Odiel River. As a consequence, the main source of ^{226}Ra to the estuary that year must have been run-off from the phosphogypsum pile. That this is the case is evidenced by the higher concentrations observed along the Tinto River in comparison to the Odiel River, and by the relative uniformity of measured concentrations in the latter. The pattern is very different from that observed in previous years, when direct discharges were taking place. Nevertheless, concentrations along the Odiel River are still higher than those found in non-perturbed rivers, which are typically in the range 0.09–3.4 mBq/l (Bhat & Krishnaswamy, 1969; Rona & Urry, 1952). The enhanced concentrations can be attributed to the redissolution of ^{226}Ra from a pool of underlying contaminated sediments. Indeed, there is now strong evidence to suggest that contaminated sediments can become a source of remobilised radionuclides when the external input is reduced and desorption reactions dominate over adsorption (Cook, MacKenzie, McDonald, & Jones, 1997; McCartney et al., 2000). This hypothesis will be studied in more detail with the help of the numerical model described below.

Activity levels detected in samples collected in 2001 are rather uniform over all the estuary, ranging from 6.6 to 12.5 mBq/l. Unlike the 1999 data, there is no evidence of run-off of ^{226}Ra from the phosphogypsum pile to the Tinto River. This is not unexpected, given that earth dikes were built around the piles to prevent run-off in the period between the two sampling campaigns. It may, therefore, be assumed that the only important source of ^{226}Ra to the waters of the estuary at the time of this last campaign is remobilisation of this radionuclide from previously contaminated sediments.

4. Model description

The system under study is divided into a number of grid cells or compartments. Two phases are present in each grid cell: dissolved and active bottom sediments (particles with a diameter $<62.5\ \mu\text{m}$). The active sediments correspond to muddy sediments, following the Wentworth scale of sediment grain size (see for instance Pugh, 1987). Larger grain sizes are not considered since it has been shown that virtually all the radioactivity is associated with the muddy sediment (Aston, Assinder, & Kelly, 1985).

Suspended matter particles have not been considered in the model, and thus deposition processes and erosion of the sediment have been neglected. This approximation is used since previous calculations have shown that the radionuclide adsorption capacity of suspended matter, given the typical suspended matter concentrations in the estuary (maximum concentrations of the order of 50 ppm) is very small compared with that of the sediment (Periañez, Abril, & García-León, 1996a). Moreover, the erosion-deposition rates, obtained from a suspended matter model of the estuary (Periañez et al., 1996a), are also small ($\sim 10^{-2}\ \text{g/cm}^2/\text{year}$). Thus, as an approximation, it has been considered that the most important phases controlling radionuclide

transport are the dissolved phase and the bottom sediment. This approximation seems realistic given the generally good agreement between model results and observations (see below).

Adsorption and desorption reactions are described in terms of kinetic transfer coefficients. Thus, the adsorption process (transfer of radionuclides from water to the sediment) will be governed by a coefficient k_1 and the inverse process (desorption to the dissolved phase) by a coefficient k_2 .

The adsorption process is a surface phenomenon that depends on the surface of particles per water volume unit into the grid cell. Following the notation of Periañez, Abril, and García-León (1996b), the adsorption coefficient is written as:

$$k_1 = \chi_1 S_E, \quad (1)$$

where S_E is the exchange surface and χ_1 is a parameter with dimensions of velocity, denoted as the exchange velocity.

As a first approach, assuming spherical sediment particles and a step function for the grain size distribution of particles, it can be shown (Periañez et al., 1996b) that

$$S_E = \frac{3Lf\phi}{\bar{r}H}, \quad (2)$$

where \bar{r} is the mean radius of sediment particles, H is the total water depth, L is the average mixing depth (the distance to which the dissolved phase penetrates the sediment), f gives the fraction of active sediment and ϕ is a correction factor that takes into account that not all the exchange surface of the sediment particle is in contact with water since part of it can be hidden by other particles (thus, it is also related to sediment porosity). Consequently, it is implicitly assumed that radionuclide concentrations in sediment pore waters, considering a sediment layer of thickness L inside which the sediment is homogeneous, are equal to those in the water column. On the other hand, diffusion of radionuclides to deeper sediment layers has been neglected given the time scale of the simulations carried out. The transfer coefficient k_2 is considered constant.

Of course, dissolved radionuclides will be transported along the estuary by advective and diffusive processes. Therefore, the hydrodynamic equations must be solved too.

4.1. Hydrodynamic equations and physical characteristics of the estuary

The 2D shallow water hydrodynamic equations are (see for instance Pugh, 1987):

$$\frac{\partial z}{\partial t} + \frac{\partial}{\partial x} [(D+z)u] + \frac{\partial}{\partial y} [(D+z)v] = 0, \quad (3)$$

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} + g \frac{\partial z}{\partial x} - \Omega v + K \frac{u\sqrt{u^2 + v^2}}{D+z} = 0, \quad (4)$$

$$\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} + g \frac{\partial z}{\partial y} + \Omega u + K \frac{v\sqrt{u^2 + v^2}}{D+z} = 0, \quad (5)$$

where u and v are the depth averaged water velocities along the x and y axis, D is the depth of water below the mean sea level, z is the displacement of the water surface above the mean sea level measured upwards, Ω is the Coriolis parameter ($\Omega = 2w\sin\beta$, where w is the earth rotational angular velocity and β is latitude), g is acceleration due to gravity and K is the bed friction coefficient. The use of a 2D model is justified since the estuary is very shallow (maximum depth around 19 m) and well mixed vertically. Moreover, the river flows are very low and a fast dispersion of fresh water into a much larger volume of salt water occurs (Borrego & Pen  n, 1988). The Odiel River flows usually range from less than 1 m³/s during the summer to some 70 m³/s in November. In the case of the Tinto river the corresponding flows are even smaller, with some 3 m³/s in November and no flow during the summer months. This mixing between river and sea water takes place upstream of the studied area, and for this reason horizontal gradients of salinity are not considered here. Indeed, electrical conductivity along the estuary is constant and typical of sea water, with an average value of 37.1 ± 0.5 mS/cm (Bolivar et al., 2000).

The solution of these equations provides the instantaneous values of the two components of the current and the water elevation over the model domain, information required to solve the advection–diffusion dispersion equation of dissolved radionuclides.

4.2. Radionuclide equations

The equation that gives the temporal evolution of activity concentrations in the dissolved phase, C_d (Bq/m³), is:

$$\frac{\partial(HC_d)}{\partial t} + \frac{\partial(uHC_d)}{\partial x} + \frac{\partial(vHC_d)}{\partial y} = \frac{\partial}{\partial x} \left(HK_D \frac{\partial C_d}{\partial x} \right) + \frac{\partial}{\partial y} \left(HK_D \frac{\partial C_d}{\partial y} \right) - k_1 C_d H + k_2 A_s L \rho_s f \phi, \quad (6)$$

where k_1 is given by Eqs. (1) and (2), total depth is $H = D + z$, K_D is the diffusion coefficient, A_s (Bq/kg) is activity concentration in the active sediment and ρ_s is the sediment bulk density expressed in kg/m³. The external source of radionuclides should be added to this equation where necessary.

The equation for the temporal evolution of activity concentration in the active sediment fraction is:

$$\frac{\partial A_s}{\partial t} = k_1 \frac{C_d H}{L \rho_s f} - k_2 A_s \phi. \quad (7)$$

4.3. Computational scheme

The hydrodynamic equations are solved using an explicit finite difference scheme. The grid cell size is $\Delta x = \Delta y = 125$ m and the time step is fixed as $\Delta t = 6$ s. The CFL criterion is satisfied with these selections. Water elevations are specified for each time step along the southern boundary from observations. A radiation condition is ap-

plied along the northern and eastern open boundaries. Along the coast, the current component that is normal to the boundary is set to zero. Water depths were introduced for each grid cell from bathymetric maps.

Instead of solving the hydrodynamic equations simultaneously with the dispersion equations, the hydrodynamic model is calibrated and validated in advance to speed up simulations. Once the hydrodynamics have been validated, standard tidal analysis is used to determine the tidal constants (amplitude and phase) for each grid cell. These constants are evaluated for both components of the flow (u and v) and for the water elevation (z), and for all the tidal constituents included in the model. Once the tidal constants are known, computation of flow and water elevation just involves the calculation and addition of a few cosine terms since the constants are stored in files that are read by the dispersion model. The net residual flow over the estuary must also be calculated by the hydrodynamic model and added to the instantaneous flow obtained from the tidal constants, since a residual transport cannot be generated with the pure harmonic currents that are given by the tidal analysis.

The Monotonic Second Order Upstream (MSOU) explicit scheme is used to solve the advective transport in the dispersion equation of dissolved radionuclides. A second order accuracy scheme has also been used to solve the diffusion terms. It is considered that there is no flux of radionuclides through land boundaries. Along open boundaries, the boundary condition described in Periañez (1998) is applied.

5. Model results

Only the two main tidal constituents, M_2 and S_2 , have been included. As will be shown below, this is enough to have a realistic representation of the dispersion patterns of ^{226}Ra .

The calibration of the hydrodynamic model consisted of selecting the optimum value for the bed friction coefficient K . After some model runs, it was selected as $K = 0.040$ for the Tinto river and $K = 0.005$ for the rest of the estuary. With these selections, a reasonable agreement between observed and computed currents has been achieved. A comparison between observed and computed magnitude and direction of the maximum currents for several locations in the estuary (see Fig. 1) is presented in Table 2 for a situation of medium tides (coefficient 74.4). Once that water circulation is reproduced by the hydrodynamic model, results are treated with standard tidal analysis to calculate the tidal constants to be used by the dispersion model to compute current and water elevation at any position and instant of time, as discussed previously.

A value that depends on a horizontal length scale (set as the grid spacing) is chosen for the diffusion coefficient. Indeed, following Breton and Salomon (1995) such coefficient was taken as $0.61 \text{ m}^2/\text{s}$.

Since the dispersion model is not restricted by the CFL stability criterion, the time step in the dispersion model has been increased to 30 s. However, stability conditions imposed by the dispersion equation are satisfied with this value.

Table 2

Observed and computed magnitude and direction of the maximum currents for a tide of coefficient 74.4

Point	Computed		Observed	
	Magnitude (m/s)	Direction (�)	Magnitude (m/s)	Direction (�)
A	0.62	129.4	0.66	126.6
B	0.53	95.6	0.56	127.1
C	0.56	132.5	0.67	141.8
D	0.47	127.2	0.49	162.1
E	0.54	45.8	0.48	52.2

The orientation is measured anticlockwise from east. Points are shown in Fig. 1.

Some parameters must be defined to simulate the dispersion of ^{226}Ra including the interactions with sediments. The coefficients χ_1 and k_2 were obtained from adsorption laboratory experiments carried out with ^{133}Ba , a γ emitter whose chemical behaviour is very similar to that of Ra. They were carried out with unfiltered water of the Odiel estuary in such a way that laboratory conditions (temperature, pH, salinity, movement of water) were as close as possible to the natural conditions. The time increase of ^{133}Ba activity in suspended sediments enables the coefficients to be calculated (Laissaoui, Abril, Perri  ez, Garc  a-Le  n, & Garc  a-Monta  o, 1998). The values obtained were $\chi_1 = 0.55 \times 10^{-7}$ m/s and $k_2 = 8.17 \times 10^{-6}$ s $^{-1}$. The mean radius of active sediment particles is taken as $R = 15$ μm and the average bulk density of sediments has been measured: 900 kg/m 3 . The fraction of active sediments has been taken as $f = 0.5$ for all the estuary. Although this parameter will probably change from one position to another, the selection of a constant (but realistic) value seems enough to describe the general dispersion patterns of ^{226}Ra . After a calibration exercise, values of $L = 0.01$ m and $\phi = 0.1$ were selected. Although not presented, sensitivity tests were carried out to study the model response to changes in the parameters. These showed that the selection of the parameter values is adequate.

The model has been applied to reproduce the experimental results obtained for the different campaigns. Two ^{226}Ra sources were considered: the direct discharge from the fertilizer complex to the Odiel river and run-off from the phosphogypsum pile to the Tinto river, as discussed before. Since the magnitudes of the sources were not known, they had to be selected from trial and error exercises until the model gave the correct activity levels. Run-off was considered as a continuous source. On the other hand, it is known that the fertilizer plant does not release its wastes continuously, but during downstream currents that occur during the ebb tide. Thus, direct discharges were introduced (for 1990 and 1991) only during such downstream currents.

The source due to run-off from phosphogypsum piles was estimated as 667 Bq/s of ^{226}Ra for all coastal cells along the Tinto river that are in contact with the piles. Taking into account that there are 17 grid cells in these conditions, this represents a total input of 1.1×10^4 Bq/s. This source magnitude was used for all simulations.

The model computes the dispersion of ^{226}Ra until stable oscillations in concentrations are obtained (because of tidal oscillations, a stationary situation is not

reached). Results are extracted from the model at the same tidal state in which sampling was performed.

Some initial conditions for activity concentrations had to be provided. For the simulation corresponding to 1990, an uniform background of 50 Bq/m^3 of ^{226}Ra in solution was assumed to simulate the effect of previous discharges. The external inputs were carried out over this background. The sediments of the estuary are also heavily contaminated due to previous discharges from the complex (Martínez-Aguirre, García-León, & Ivanovich, 1994b). Thus, initial activity in the active sediments of the Odiel and Tinto rivers were fixed, respectively, at 1500 and 300 Bq/kg. The input to the Odiel river from the fertilizer plant was estimated as $7.0 \times 10^5 \text{ Bq/s}$. Given the temporal sequence of the source described above, this implies an input of approximately $1.1 \times 10^{13} \text{ Bq}$ of ^{226}Ra per year. It must be noted, however, that there is not any reason to suppose that the input is constant through the year. Activity levels detected around the fertilizer complex mainly represent the effect of releases carried out immediately before sampling. Thus, our annual input estimations must be interpreted with care. Model results for the simulation corresponding to 1990 are presented in Fig. 2(a). The model gives a realistic distribution of ^{226}Ra over the estuary, producing activity levels in good agreement, in general, with measurements. The dashed line corresponds to a simulation in which the source due to run-off from the phosphogypsum pile is not included. If it is not, activity levels in the region of sampling point 15 are slightly lower than the measured level.

For the simulation corresponding to 1991, the same initial conditions were used in the sediments, although background in water was fixed as 40 Bq/m^3 . The release from the fertilizer plant to the Odiel River was in this case estimated as $7.0 \times 10^4 \text{ Bq/s}$, one order of magnitude smaller than the 1990 value (this does not directly mean that the annual input is also one order of magnitude smaller, due to the reasons commented above). Model results are compared with observations in Fig. 2(b). In general, model results are in good agreement with observations. Again, the dashed line corresponds to the simulation without the run-off source. Due to the lower input from the plant, the effect of run-off is clearly more relevant than in 1990 (effectively, it seems that run-off from the phosphogypsum pile is masked by the high direct releases from the complex in the 1990 campaign).

In the case of the 1999 simulation, background in water was fixed as 10 Bq/m^3 and initial concentrations in active sediments were taken to be 1000 and 150 Bq/kg for the Odiel and Tinto rivers respectively. The only source considered in this case was run-off, since direct discharges ceased in 1998. A comparison between measured and computed ^{226}Ra activity levels is presented in Fig. 2(c). It can be seen that the model gives a realistic representation of activity levels along the estuary. The simulation has been repeated exactly in the same way but without considering interactions with the sediments. The result of this simulation is also presented in Fig. 2(c) (dashed line). It seems clear that sediments are now acting as a source of ^{226}Ra to the water column since computed activity levels are significantly lower than the measured ones if the sediment is not included

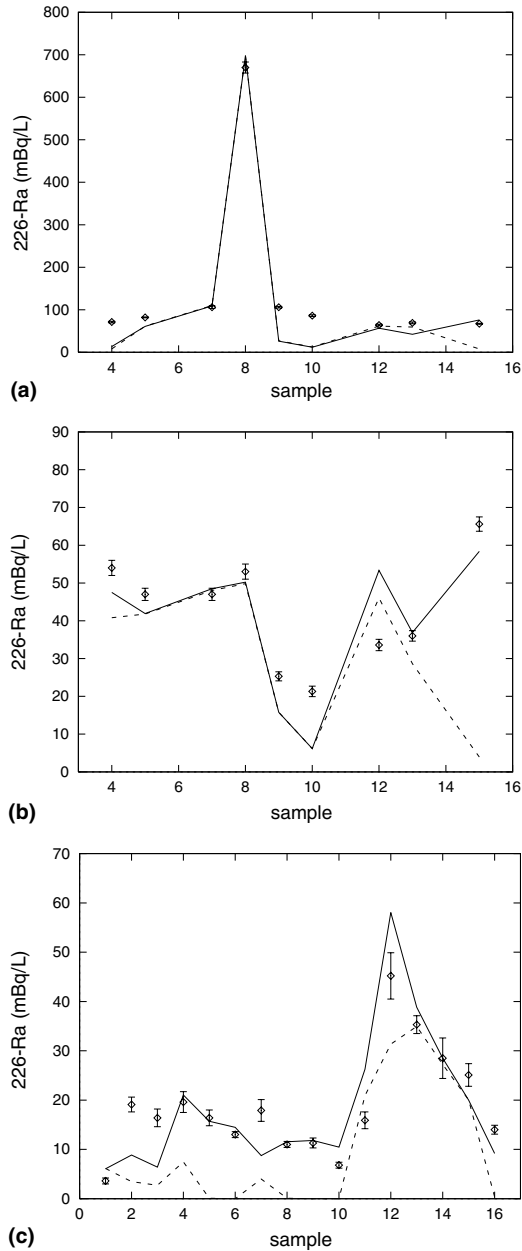


Fig. 2. Comparisons between measurements and model results for three sampling campaigns: (a) 1990. The dashed line corresponds to a simulation in which the run-off source is not considered; (b) 1991. The dashed line has the same meaning as above; (c) 1999. The dashed line corresponds to a simulation in which the sediments are not included in the model.

in the calculations. The difference between the simulations is smaller along the Tinto river, where the input from the phosphogypsum piles is the dominant source. It seems, on the other hand, that the most important source of ^{226}Ra to the Odiel river is redissolution from the contaminated sediment, as indicated by the difference in activity levels between the simulations. Indeed, the net input of ^{226}Ra , for the whole estuary, from redissolution has been calculated as the difference between the redissolved and adsorbed Ra. In this way, it has been estimated that some 5×10^9 Bq have been transferred to the water column from the estuary sediments. Although model results seem rather conclusive with respect to the role played by sediments, these results would have to be confirmed by measuring the sediment itself. This work is currently being carried out.

The model has not been applied to the 2001 samples since essentially a flat distribution has been measured, not being evidence of run-off from the phosphogypsum pile nor any other external source of ^{226}Ra .

6. Conclusions

The presence and temporal evolution of ^{226}Ra levels in a tidal estuary of south-west Spain affected by the phosphate industry has been investigated in the period 1990–2001. Two ^{226}Ra sources can be identified: direct discharges from the phosphate industry and run-off from a phosphogypsum pile. Direct discharges were the dominant source for 1990 and 1991, when detected activity levels are higher than those found in other rivers affected by similar industries. Discharges ceased in 1998 due to new regulations from the EU. From samples collected in 1991 and, specially, in 1999, the radioactive impact due to run-off from the phosphogypsum pile became evident. Moreover, it seems that the heavily contaminated sediments were acting as a source of ^{226}Ra to the water column due to redissolution processes in 1999. Finally, essentially constant activities were measured in 2001, suggesting that run-off from the phosphogypsum pile is not presently occurring. These results have been studied in more detail with the help of a numerical model.

The model solves the 2D shallow water hydrodynamic equations for the estuary. Once calibrated, model results are treated using standard tidal analysis to calculate the tidal constants that will be read by the dispersion model to compute the instantaneous currents over the estuary. This way, faster computations can be carried out than if the hydrodynamic equations are solved simultaneously with dispersion. The dispersion model includes advection–diffusion of dissolved radionuclides plus interactions with sediments. These absorption–desorption reactions are described in terms of kinetic transfer coefficients. In general, model results are in agreement with measurements. Indeed, model results have supported the hypothesis outlined above.

As a general conclusion, although a reduction in activity levels through the years has been obtained, the process of cleaning of a given estuarine environment will probably be slower than might be expected after a reduction (or cessation) of waste disposal due to the redissolution of pollutants from the previously contaminated sediments.

Acknowledgements

Work supported by ENRESA, FEDER project 1FD97-0900-CO2-01 and EU 5th Framework Programme (1998-2002) Nuclear Fission and Radiation Protection Contract FIGE-CT-2000-00085.

References

- Aston, S. R., Assinder, D. J., & Kelly, M. (1985). Plutonium in intertidal and estuarine sediments in the northern Irish Sea. *Estuarine Coastal and Shelf Science*, 20, 761–771.
- Bhat, S. G., & Krishnaswamy, S. (1969). Isotopes of U and Ra in Indian rivers. *Proceedings of the Indian Academy of Sciences*, 70, 1–17.
- Bolívar, J. P., García-Tenorio, R., & Vaca, F. (2000). Radioecological study of an estuarine system located in the south of Spain. *Water Research*, 34, 2941–2950.
- Borrego, J., & Pendón, J. G. (1988). Algunos ejemplos de influencia de los procesos antrópicos en el medio sedimentario: la ría de Huelva. *Henares Revista de Geología*, 2, 299–305 (in Spanish).
- Breton, M., & Salomon, J. C. (1995). A 2D long term advection dispersion model for the Channel and southern North Sea. *Journal of Marine Systems*, 6, 495–513.
- Cook, G. T., MacKenzie, A. B., McDonald, P., & Jones, S. R. (1997). Remobilization of Sellafield derived radionuclides and transport from the north east Irish Sea. *Journal of Environmental Radioactivity*, 35, 227–241.
- Guimond, R. J., & Hardin, J. M. (1989). Radioactivity released from phosphate containing fertilizers and from gypsum. *Radiation Physics and Chemistry*, 34, 309–315.
- Haridasan, P. P., Paul, A. C., & Desai, M. V. M. (2001). Natural radionuclides in the aquatic environment of a phosphogypsum disposal area. *Journal of Environmental Radioactivity*, 53, 155–165.
- Kobal, I., Brajnik, D., Kaluza, F., & Vengust, M. (1990). Radionuclides in effluent from coal mines, a coal fired power plant, and a phosphate processing plant in Zasavje, Slovenia (Yugoslavia). *Health Physics*, 58, 81–85.
- Koster, H. W., Harwitz, P. A., Borger, G. W., van Weers, A. W., Hagel, P., & Nieuwenhuize, J. (1991). Po-210, Pb-210, Ra-226 in aquatic ecosystems and polders, anthropogenic sources, distribution and enhanced radiation doses in the Netherlands. In *Fifth International Symposium on the Natural Radiation Environment*, Salzburg.
- Laissaoui, A., Abril, J. M., Perriñez, R., García-León, M., & García-Montaño, E. (1998). Determining kinetic transfer coefficients for radionuclides in estuarine waters: reference values for ^{133}Ba and effects of salinity and suspended load concentrations. *Journal of Radioanalytical Nuclear Chemistry*, 237, 55–61.
- Martínez-Aguirre, A., & García-León, M. (1994). Natural radionuclides in the Guadalquivir River at the south of Spain. *Journal of Radioanalytical Nuclear Chemistry*, 178, 337–350.
- Martínez-Aguirre, A., García-León, M., & Ivanovich, M. (1994a). U and Th distribution in solution and suspended matter from rivers affected by phosphate rock processing in southwestern Spain. *Nuclear Instruments and Methods A*, 339, 287–293.
- Martínez-Aguirre, A., García-León, M., & Ivanovich, M. (1994b). The distribution of U, Th and ^{226}Ra derived from the phosphate fertilizer industries on an estuarine system in southwest Spain. *Journal of Environmental Radioactivity*, 22, 155–177.
- McCartney, M., Davidson, C. M., Howe, S. E., & Keating, G. E. (2000). Temporal changes in the distribution of natural radionuclides along the Cumbrian coast following the reduction of discharges from a phosphoric acid production plant. *Journal of Environmental Radioactivity*, 49, 279–291.
- Morón, M. C., García-Tenorio, R., García-Montaño, E., García-León, M., & Madurga, G. (1986). An easy method for the determination of Ra isotopes and actinide alpha emitters from the same water sample. *Applied Radiation Isotopes*, 37, 383–389.

- Paridaens, J., & Vanmarcke, H. (2001). Radium contamination of the banks of the river Laak as a consequence of the phosphate industry in Belgium. *Journal of Environmental Radioactivity*, 54, 53–60.
- Periañez, R. (1998). A three dimensional σ coordinate model to simulate the dispersion of radionuclides in the marine environment: application to the Irish Sea. *Ecological Modelling*, 114, 59–70.
- Periañez, R., & García-León, M. (1993). Ra-isotopes around a phosphate fertilizer complex in an estuarine system at the southwest of Spain. *Journal of Radioanalytical Nuclear Chemistry*, 172, 71–79.
- Periañez, R., Abril, J. M., & García-León, M. (1996a). Modelling the suspended matter distribution in an estuarine system. Application to the Odiel river in southwest Spain. *Ecological Modelling*, 87, 169–179.
- Periañez, R., Abril, J. M., & García-León, M. (1996b). Modelling the dispersion of non-conservative radionuclides in tidal waters. Part 1: conceptual and mathematical model. *Journal of Environmental Radioactivity*, 31, 127–141.
- Poole, A. J., Allington, D. J., & Denoon, D. C. (1995). Temporal and spatial survey of dissolved ^{226}Ra in coastal waters of the eastern Irish Sea. *Science of the Total Environment*, 168, 233–247.
- Pugh, D. T. (1987). *Tides, surges and mean sea level*. Chichester: Wiley.
- Rona, E., & Urry, E. D. (1952). Radioactivity of ocean sediments VIII: Ra and U content of ocean and river waters. *American Journal of Sciences*, 250, 242–262.