



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

R. Perriñez^{a,*}, A. Absi^b, M. Villa^c, H.P. Moreno^b, G. Manjón^b

^aDepartamento Física Aplicada I, EUITA, Universidad de Sevilla, Ctra Utrera km 1, 41013-Sevilla, Spain

^bDepartamento Física Aplicada II, ETSA, Universidad de Sevilla, Av Reina Mercedes 2, 41012-Sevilla, Spain

^cDepartamento Física Atómica y Nuclear, Universidad de Sevilla, 41080-Sevilla, Spain

Received 22 March 2004; received in revised form 15 July 2004; accepted 30 July 2004

Abstract

A numerical model of the Odiel–Tinto estuary (Spain) has been developed to study the self-cleaning process that was evidenced from ^{226}Ra measurements in water and sediments collected in the period 1999–2002, after direct releases from a fertilizer complex ceased (in 1998). The hydrodynamic model is first calibrated, and standard tidal analysis is carried out to calculate tidal constants required by the dispersion code to determine instantaneous water currents and elevations over the estuary. In this way, long-term simulations may be carried out. The dispersion code includes advective/diffusive transport of radionuclides plus exchanges with bottom sediments described through a kinetic approach. The dispersion model is first tested by comparing computed and measured ^{226}Ra concentrations over the estuary resulting after releases in the Odiel and Tinto rivers. Next, it is applied to simulate the self-cleaning process of the estuary. The time evolution of radium concentrations in bed sediments is in generally good agreement with observations. The computed sediment halving time of the estuary is 510 days, which also is in good agreement with that estimated from measurements.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Radium; Odiel–Tinto estuary; Phosphogypsum; Numerical modelling; Hydrodynamic; Sediment; Kinetic rates

1. Introduction

The Odiel and Tinto rivers (southwest 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 area, including a complex dedicated to the production of phosphoric acid and phosphate fertilizers, is located by the Odiel river. The fertilizer plants have been the main source of natural radionuclides to the estuary: it is well known that the phosphate rock used as raw material by this industry

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

E-mail address: rperianez@us.es (R. Perriñez).

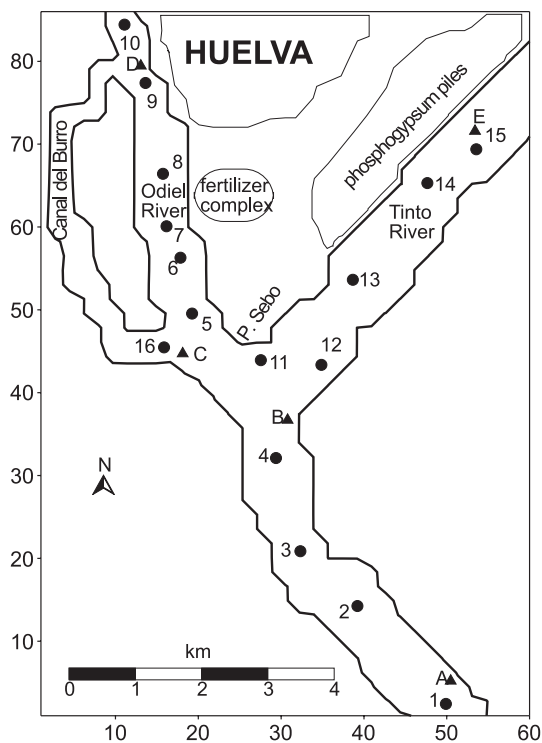


Fig. 1. Map of the area of the estuary covered by the model. Numbered circles indicate the points where samples were collected. Lettered triangles indicate the points where currents measurements were available. Units on the axes give the grid cell number. The sea is approximately 1 km to the south of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

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. This is a form of impure calcium sulfate removed as a precipitate during the process. Phosphogypsum is usually disposed into open air piles or discharged into rivers or estuaries, giving rise to a local radioactive impact. 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 Odriel river (20%) and conveyed with water through a pipeline to phosphogypsum piles (remaining 80%) 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. Because 1998, wastes are not released directly into the Odriel river due to new regulations from the EU, although phosphogypsum is still being disposed in the piles by the Tinto river.

In a first paper (Absi et al., 2004), the time evolution of ²²⁶Ra activities in water and sediments over years 1999–2002 was studied. Results indicated that a self-cleaning process was taking place as a consequence of the new waste policy, because a systematic and continuous decrease in activities was found in the water column and in bed sediments. The objective of this second paper consists of studying such a cleaning process by means of a numerical model of the estuary. This has been done because interpretation of experimental results is not an easy task due to the fact that several processes are affecting the radionuclide dynamics: currents due to tidal oscillations produce advective transport of dissolved radionuclides along the estuary, 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. Thus, a numerical model of the estuary, including all these processes, has been developed. It solves the hydrodynamics of the estuary and the dispersion of ²²⁶Ra, including the interactions between the dissolved and solid (bottom sediments) phases.

The model has been initially tested through its application to simulate two dispersion scenarios. They consist of reproducing the measured ²²⁶Ra concentrations resulting as a consequence of releases carried out by the fertilizer complex in the Odriel River and a discharge into the Tinto River due to an accidental release from the phosphogypsum piles. Once tested, the model is applied to simulate the cleaning process of the estuary.

2. 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

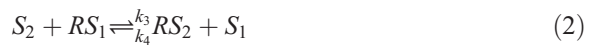
(particles with a diameter $<62.5 \mu\text{m}$). Thus, the active sediments correspond to muddy sediments, following the Wentworth scale of sediment grain size (see, for instance, Pugh, 1987). Larger grain sizes are not considered, because it has been found (Aston et al., 1985) that virtually all the radioactivity is associated with the muddy sediment. This result has also been obtained with a model in which a large grain size sediment fraction is included (Periañez, 1999).

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 because previous calculations have shown that the radionuclide adsorption capacity of suspended matter, given the typical suspended matter concentrations at the estuary, maximum concentrations of the order of 50 ppm (Periañez et al., 1996a), is very small compared with that of the sediment. Moreover, the erosion–deposition rates, obtained from a suspended matter model of the estuary (Periañez et al., 1996a), are small (of the order of $10^{-2} \text{g/cm}^2 \text{year}$). 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).

2.1. Parameterization of sorption/release processes

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 . However, very recent experiments have shown (Ciffroy et al., 2001; El Mrabet et al., 2001) that a two-step kinetic model consisting of two consecutive reactions is more appropriate than a one-step model, consisting of a single reversible reaction, to simulate both the sorption and release kinetics. This two-step model has already been tested in other environments and has been shown to describe the process of redissolution of radionuclides from contaminated marine sediments (Periañez, 2003, 2004). The exchange model that was used by Ciffroy et al. (2001) to describe their experiments considers two successive reversible

reactions. The first describes a reversible isotopic or ion exchange process between dissolved radionuclides and some nonspecific sites, S_1 , present on the particle surfaces. The second slower reaction represents a reversible sorption to more specific sites, S_2 . They can be represented as follows:



where k_3 and k_4 are the kinetic transfer coefficients or sorption and release velocities, respectively, for the second reaction, R is the dissolved radionuclide, X is a competitive element that can be replaced by R on sites S_1 , and RS_i is the radionuclide bound to sites S_i of the solid particle.

The adsorption process is a surface phenomenon that depends on the surface of particles per water volume unit into the grid cell. This quantity has been denoted as the exchange surface (Periañez et al., 1996b). Thus:

$$k_1 = \chi_1 S_E \quad (3)$$

where S_E is the exchange surface, and χ_1 is a parameter with the dimensions of a velocity. It is denoted as the exchange velocity (Periañez et al., 1996b).

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

$$S_E = \frac{3Lf\phi}{\bar{r}H} \quad (4)$$

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 because part of it can be hidden by other particles. Thus, it is also related to sediment porosity. It is implicitly assumed that the radionuclide concentration in pore waters of the sediment, in a sediment layer of thickness L inside which the sediment is homogeneous, corresponds to the concentration in the water column. On the other hand,

diffusion of radionuclides to deeper sediment layers has been neglected due to the low sedimentation rates in the area. The transfer coefficients k_2 , k_3 , and k_4 are considered constants.

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

2.2. Hydrodynamic equations and physical characteristics of the estuary

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

$$\frac{\partial z}{\partial t} + \frac{\partial}{\partial x}[(D+z)u] + \frac{\partial}{\partial y}[(D+z)v] = 0 \quad (5)$$

$$\begin{aligned} \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} + g \frac{\partial z}{\partial x} - \Omega v \\ + K \frac{u\sqrt{u^2+v^2}}{D+z} = 0 \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} + g \frac{\partial z}{\partial y} + \Omega u \\ + K \frac{v\sqrt{u^2+v^2}}{D+z} = 0 \end{aligned} \quad (7)$$

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's 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 because the estuary is very shallow (maximum depth around 19 m) and well mixed in the vertical. Moreover, the stream flows of the rivers are very low, and fast dispersion of fresh water into a much larger volume of salt water occurs (Borrego and Pendón, 1988); 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, they are even smaller: some 3 m³/s in November and no flow during the summer months. The mixing between river and sea water takes place upstream of the studied area, thus horizontal gradients of salinity

are not considered. Indeed, electrical conductivity along the estuary is essentially constant and typical of sea water: average value 38 ± 3 mS/cm (Bolívar et al., 2000). Water temperature is also uniform (Bolívar et al., 2000). Therefore, it can be concluded that water properties over the studied area are uniform and typical of sea water.

The solution of these equations provide 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.

2.3. Radionuclide equations

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

$$\begin{aligned} \frac{\partial(HC_d)}{\partial t} + \frac{\partial(uHC_d)}{\partial x} + \frac{\partial(vHC_d)}{\partial y} \\ = \frac{\partial}{\partial x} \left(HK_D \frac{\partial C_d}{\partial x} \right) + \frac{\partial}{\partial y} \left(HK_D \frac{\partial C_d}{\partial y} \right) \\ - k_1 C_d H + k_2 A_s L \rho_s f \phi \end{aligned} \quad (8)$$

where k_1 is given by Eqs. (3) and (4), total depth is $H=D+z$, K_D is the diffusion coefficient, A_s (Bq/kg) is specific activity in the nonspecific sites of 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 at the points where it exists.

The equation for the temporal evolution of specific activity in the nonspecific sites of the active sediment fraction is

$$\frac{\partial A_s}{\partial t} = k_1 \frac{C_d H}{L \rho_s f} - k_2 A_s \phi - k_3 A_s + k_4 *A_s \quad (9)$$

where $*A_s$ is specific activity in the specific sites of the active sediment. The equation for the specific sites is

$$\frac{\partial *A_s}{\partial t} = k_3 A_s - k_4 *A_s \quad (10)$$

The total activity of radionuclides in the sediment, A_{tot} , is computed from

$$A_{\text{tot}} = f(A_s + *A_s) \quad (11)$$

2.4. 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 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 applied 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, because 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, because 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.

3. Results and discussion

3.1. Hydrodynamic calculations

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, $K = 0.040$ was set 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 1 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 commented before.

3.2. ^{226}Ra dispersion

3.2.1. Parameters for the model

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 a coefficient was taken as $0.61 \text{ m}^2/\text{s}$.

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

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

Table 1
Observed and computed magnitude and direction of the maximum currents for a tide of coefficient 74.4

Point	Computed		Observed	
	Mag (m/s)	Direc (deg)	Mag (m/s)	Direc (deg)
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.

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 et al., 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 the whole 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, $L=0.01$ m and $\phi=0.1$ were selected.

Barros et al. (2004) have carried out sorption experiments with ^{133}Ba . They have observed that the relation $k_4=k_3/10$ holds between rates governing the second consecutive reaction. Nevertheless, kinetic rates obtained by Barros et al. (2004) cannot be directly used in this model, because they prepared artificial sediment suspensions with given particle sizes. Ciffroy et al. (2001) have found a similar relation for some radionuclides. Thus, we have used in the model that $k_4=k_3/10$.

On the other hand, El Mrabet et al. (2001) have measured a value of 1.4×10^{-7} s $^{-1}$ for k_3 in their experiments carried out with sea water from the southwest coast of Spain. These experiments were carried out with Pu and are probably not adequate for describing Ra behaviour. However, this value has been used due to the lack of data concerning ^{226}Ra . In summary, we have used the following values because acceptable results are obtained with them: $k_3=1.4\times 10^{-7}$ s $^{-1}$ and $k_4=1.4\times 10^{-8}$ s $^{-1}$. Ideally, site-specific kinetic rates should be used. Nevertheless, sensitivity tests have been carried out to study the model response to changes in kinetic rates governing the second reaction. They are described below.

A summary of model parameters, indicating how each value was selected, is given in Table 2.

3.2.2. Model testing

The model has been applied to reproduce the experimental results obtained for different campaigns.

Table 2

Parameters in the model

Parameter	Selection
K_D	Length scale (grid spacing)
χ_1 and k_2	Adsorption experiments with ^{133}Ba
ρ_s	Measured
L and ϕ	Model calibration
R	Standard value
k_3	Adsorption experiments with Pu
k_4	Related to k_3 (from published experiments)

The magnitudes of the external sources are not known. Thus, they had to be selected by trial and error until the model gave appropriate activity levels. 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 (Moreno et al., 2000). Thus, direct discharges are introduced only during such downstream currents. 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. As an example, the time evolution over one tidal cycle of an activity release of arbitrary magnitude carried out at high water in the Odiel River (at the point where discharges from the fertilizer complex occur) is shown in Fig. 2. It can be seen that the patch moves downstream during the ebb. After the flood starts (some 6 h later), radionuclides enter the Tinto River, Canal del Burro, and the Odiel River again. Thus, the discharged radionuclides reach the whole estuary.

The first test of the model was to reproduce measured ^{226}Ra concentrations in the water column for a sampling campaign carried out in 1990, when the source of radionuclides to the estuary was due to direct releases. Some initial conditions for activity concentrations have to be provided. For the simulation corresponding to 1990, a uniform background of 50 Bq/m 3 of ^{226}Ra in solution has been assumed to simulate the effect of previous discharges. The external inputs are added over this background. The sediments of the estuary are also heavily contaminated due to previous discharges from the complex (Mart  nez-Aguirre et al., 1996). Thus, initial specific activities in the sediments of the Odiel and Tinto rivers are fixed, respectively, as 750 and 150 Bq/kg, which are representative of measured activities. Indeed, these

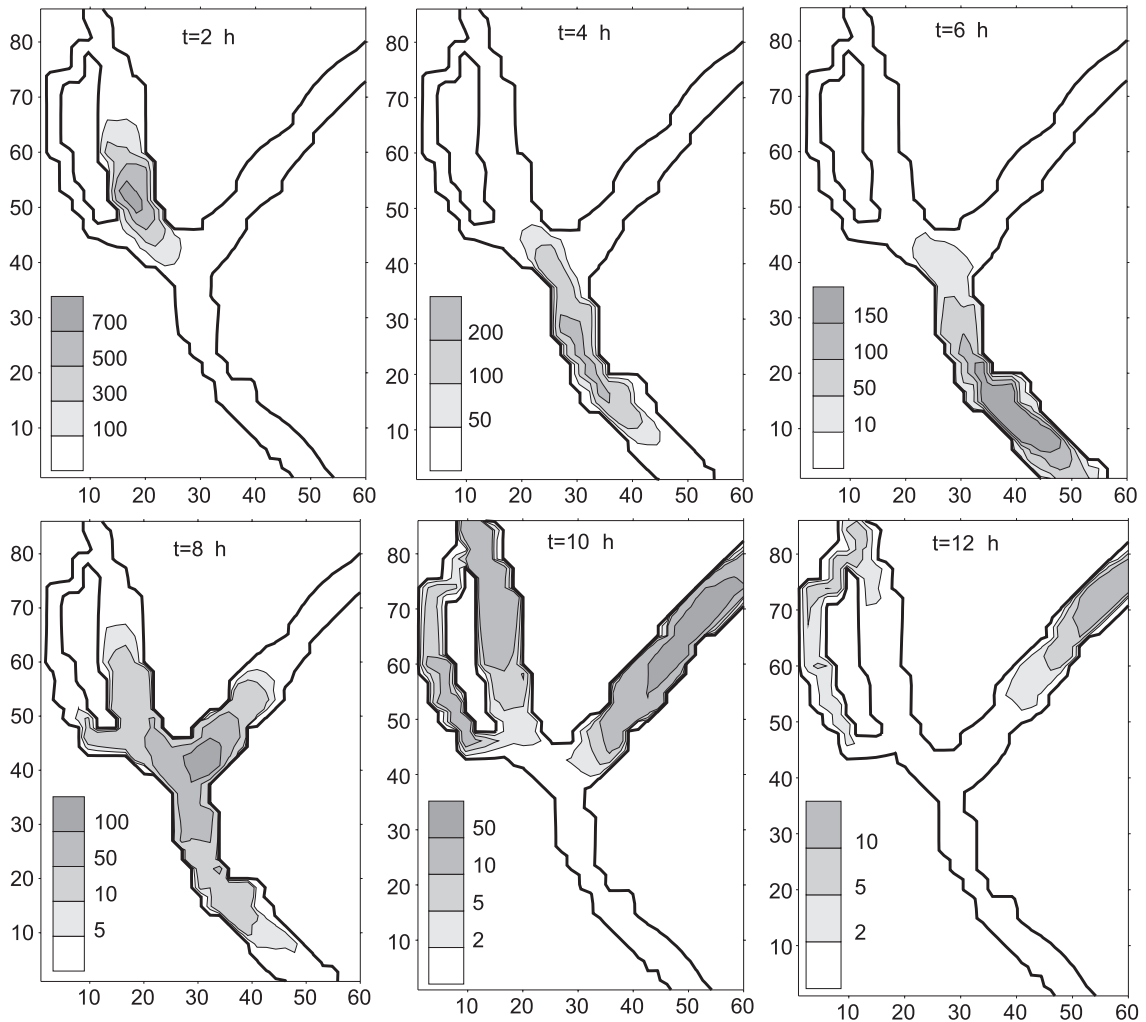


Fig. 2. Time evolution of dissolved concentrations resulting after an activity input of arbitrary magnitude carried out in the Odiel River during high water.

range from 360 to 1300 Bq/kg in the Odiel River and from 90 to 720 Bq/kg in the Tinto River (Martínez-Aguirre et al., 1996). The input to the Odiel river from the fertilizer plant has been fixed at 7.0×10^5 Bq/s. Given the temporal sequence of the source described above, this implies an input of approximately 1.1×10^{13} Bq of ^{226}Ra per year. This number is similar, to an order of magnitude, to the estimation of Van der Heijden et al. (1988) for the annual ^{226}Ra input to the Nieuwe Waterweg (Netherlands) from fertilizer processing. It must be noted however that there is no 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 estimation must be interpreted with care, and indeed they are simply indicating reasonable values. Model results for the simulation corresponding to 1990 are presented in Fig. 3a, where measurements have been obtained from Perriñez and García-León (1993). The model gives a realistic distribution of ^{226}Ra over the estuary, producing activity levels in good agreement, in general, with measurements.

The model has also been applied to reproduce observations obtained for the sampling campaign carried out in 1999, obtained from Absi et al.

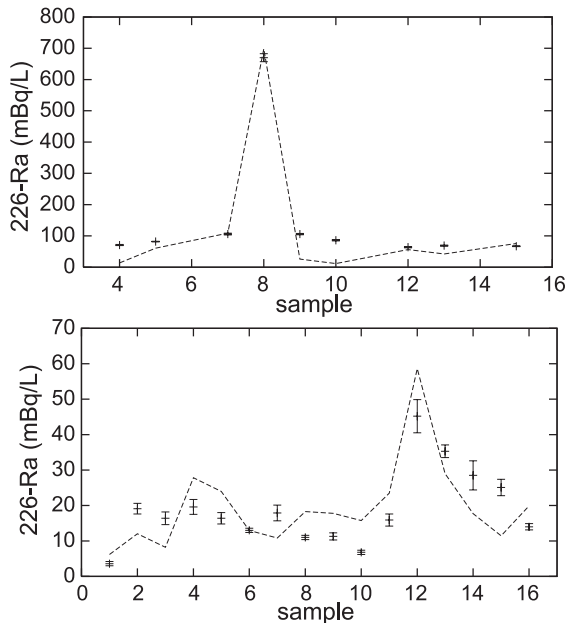


Fig. 3. Comparisons between measurements (points) and model results (lines) for two sampling campaigns: top, 1990 and bottom, 1999.

(2004). The only source now considered is runoff from the phosphogypsum piles that occurred as the result of an accident since direct discharges ceased in 1998. It has been fixed as 3.0×10^5 Bq/s for all grid cells in the Tinto River in contact with the phosphogypsum piles. A comparison between measured and computed ^{226}Ra activity levels in water is presented in Fig. 3b. It can be seen that the model gives a realistic representation of activity levels along the estuary.

A long-term simulation has been finally carried out to compare computed and measured specific activities in bottom sediments. A constant input from the fertilizer complex is introduced starting the model from clean water and sediments. After 2 years of release, specific activities over the estuary bed are extracted from the model. Because the input of radionuclides has taken place since the sixties, when industrial activity started in the area, the magnitude of the source has been amplified to allow actual activity levels in the sediments to be reached in only 2 years of simulation. This technique has been previously used in the calculations described in Perri  ez and Mart  nez-Aguirre (1997). Computed specific activities, together with measured concentrations (Mart  nez-

Aguirre et al., 1996), are presented in Fig. 4. In general, the distribution of ^{226}Ra over the sediments is reproduced by the model. Maximum concentrations are obtained in the Odiel River, in the area where discharges from the fertilizer complex occur, with decreasing activities going north and south from this area. An activity peak is also measured in the Tinto River that is not reproduced by the model. It must be taken into account that sampling was carried out during a wet season and rains may produce runoff events from the phosphogypsum piles. These runoff episodes, not included in the simulation, are probably responsible for the activity peak detected in the Tinto River. It is also interesting to note that activity gradients in the transverse direction are apparent in the Odiel River. On the other hand, the Tinto River is relatively mixed in the transverse direction.

It can be concluded that, in general, activity levels and distribution of ^{226}Ra in the water column and sediment are reproduced by the model.

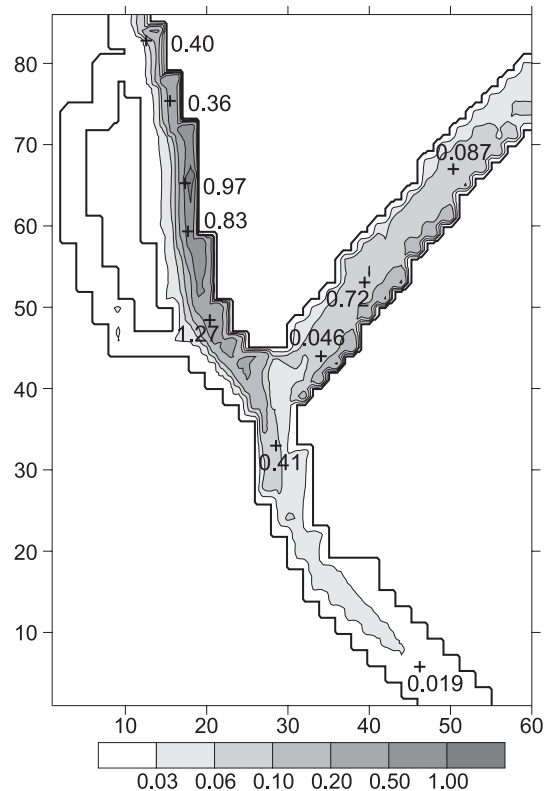


Fig. 4. Computed distribution of ^{226}Ra in sediments (Bq/g) and measured concentrations (from Mart  nez-Aguirre et al., 1996).

3.2.3. Modelling self-cleaning of the estuary

Once the model has been tested through the comparison of measured and computed specific activities in the water column and bottom sediments, it has been applied to study the self-cleaning processes of the estuary after the end of discharges from the fertilizer complex. The model has been started from the ^{226}Ra distribution in water and sediments obtained after the 2-year simulation described above. The distribution of radium between the two sediment phases is also provided by the simulation; some 40% of radium in the sediment is in the nonspecific sites. These conditions are assumed to be representative of the moment at which releases ceased. A 4-year simulation is then carried out starting from these initial conditions and without external releases. This simulation provides the ^{226}Ra distribution in sediments for years 1999, 2000, and 2001 to be compared with measured distributions (Absi et al., 2004).

The computed time evolution of ^{226}Ra inventories in bed sediments and in the water column for the whole estuary are presented in Fig. 5. It can be seen that the total radium content in the estuary bed decreases due to redissolution. The sediment halving time (time in which activity in the sediment decreases by a factor of 2) is 510 days. This number agrees relatively well with the 630 days halving time estimated from measurements (Absi et al., 2004). The inventory in the water column oscillates at a frequency of 15 days, which corresponds to the spring/neap tide cycles (only 1 year is shown in Fig. 5 to show these oscillations clearly), but the halving time for the dissolved phase is of the order of 300 days. This number, although of the same magnitude, is higher than the estimate obtained from measurements (some 130 days).

The average ^{226}Ra concentration in the water column after 4 years of redissolution is 2.8 Bq/m^3 . It has been obtained from the total inventory of dissolved radium at the end of the simulation and the average water volume in the estuary, $6.2 \times 10^7 \text{ m}^3$. This estimate is in agreement with the average concentration obtained for year 2002 from observations (Absi et al., 2004): 5 ± 2 , 4 ± 2 , and $4.1 \pm 0.1 \text{ Bq/m}^3$ for the Odiel River, Tinto River, and the Odiel River from the Odiel–Tinto confluence to the sea, respectively.

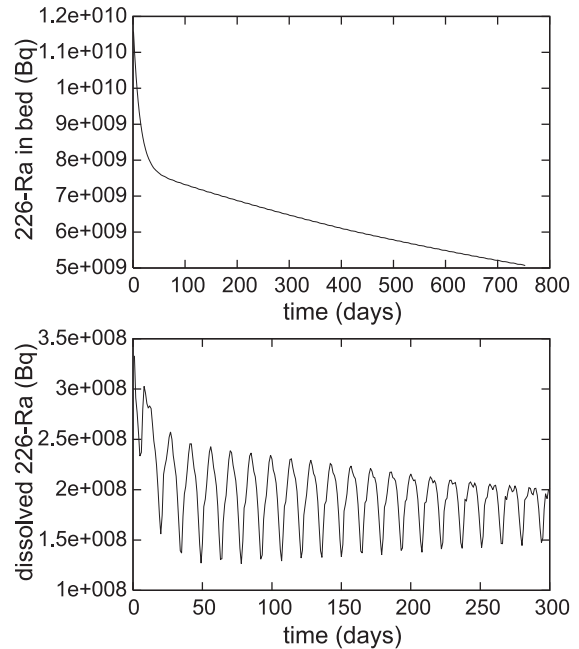


Fig. 5. Time evolution of the ^{226}Ra inventories for the whole estuary in bed sediments and in the water column during the self-cleaning process.

The computed distributions of ^{226}Ra in sediments corresponding to years 1999, 2001, and 2002 are presented in Fig. 6, together with the measured concentrations. These three figures provide a general view of the sediment cleaning process over the estuary. There are some local activity maxima in the Tinto River not reproduced by the model, which are probably due to episodic release events from the phosphogypsum piles, but, in general, the decrease in ^{226}Ra concentrations is well reproduced by the model, especially in the area of the Odiel River where direct discharges took place. If these maps are compared with that presented in Fig. 4, it also seems that the cleaning process is more efficient in this region, which is the most contaminated. In the rest of the estuary, the specific activity in the sediment decreases more slowly.

As an example, the time evolution of radium concentration in the sediment at grid cell (17,60), that is close to the area where direct releases were carried out, is presented in Fig. 7. Radium concentrations in the nonspecific sites decrease quickly due to the redissolution process. The

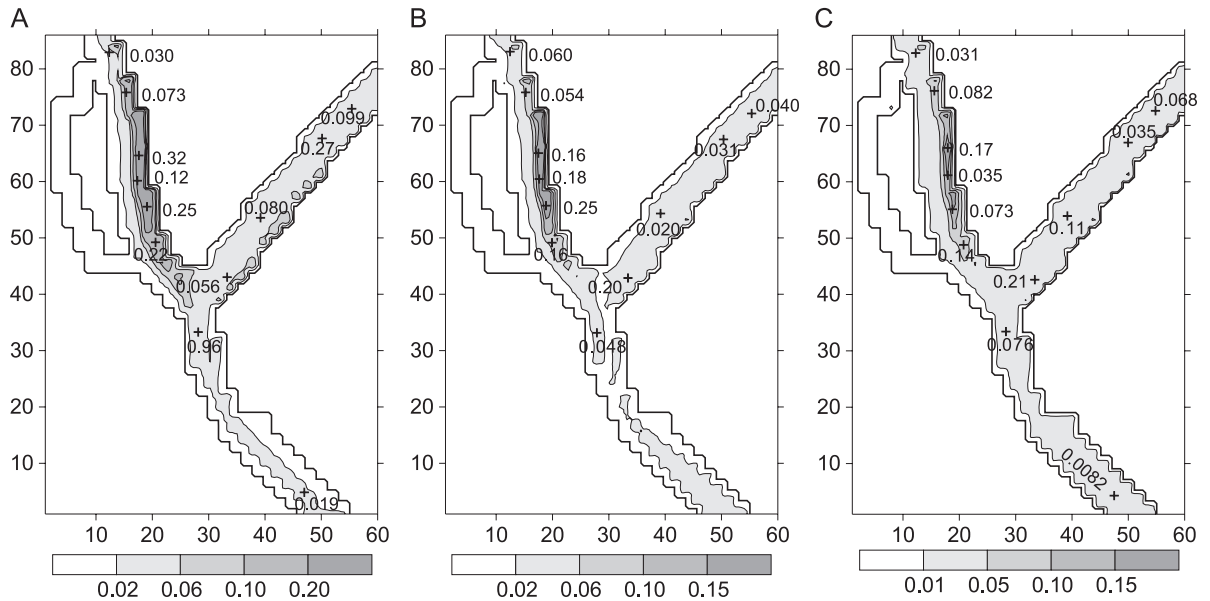


Fig. 6. Computed distribution of ^{226}Ra in sediments (Bq/g) and measured concentrations for years 1999 (A), 2001 (B), and 2002 (C).

specific sites go on absorbing radionuclides over a few days, and then concentration also decreases in this phase, although at a slower rate than in the

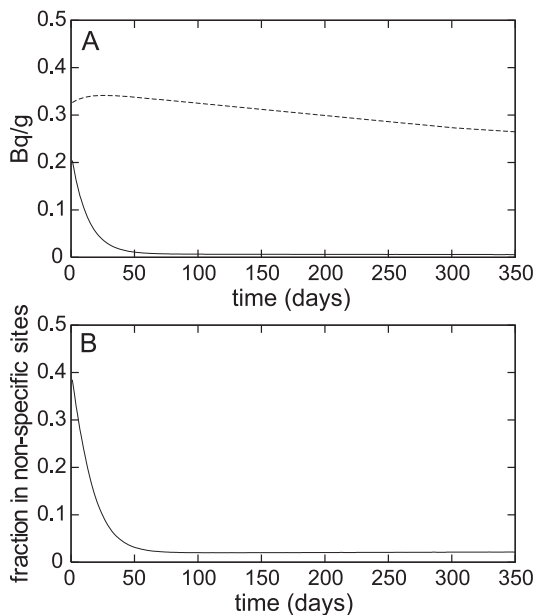


Fig. 7. Time evolution of the ^{226}Ra concentration in bed sediment at grid cell (17,20) during the self-cleaning process. (A) Specific activity in the nonspecific (solid line) and specific (dashed line) sites. (B) Fraction of ^{226}Ra in the nonspecific sites.

case of the nonspecific sites. Thus, Ra goes from the specific to the nonspecific sites, and from this phase is dissolved. The time evolution of the ^{226}Ra fraction that is present in the sediment in the nonspecific sites is shown in Fig. 7B. It decreases from 40% to less than 5%.

3.2.4. Model sensitivity to variations in kinetic rates

The coefficients governing the first reaction, χ_1 and k_2 , have been obtained from laboratory experiments carried out with water and natural sediments of the Odiel River. ^{133}Ba was used, which is a good indicator of ^{226}Ra behaviour (Barros et al., 2004). Moreover, the sensitivity of the water–sediment interaction formulation used in this work to changes in χ_1 and k_2 has already been studied (Perri  ez et al., 1996c). Thus, only the sensitivity of the sediment halving time to changes in kinetic rates governing the second reaction will be described here.

Results of the sensitivity analysis are summarized in Table 3, where computed sediment halving times for different k_3 and k_3/k_4 values are given.

Experiments carried out with the nominal k_3 value indicate that the halving time is reduced well below the experimental value if k_4 is increased (in particular, a fast cleaning of the sediment is obtained if $k_4=k_3$). On the other hand, a decrease in k_4 with respect to the

Table 3
Sensitivity of sediment halving time ($T_{1/2}$) to changes in k_3 and k_3/k_4 ratio

k_3 (s^{-1})	k_4	$T_{1/2}$ (d)
Nominal	Nominal ($=k_3/10$)	510
Nominal	$=k_3$	50
Nominal	$=k_3/5$	212
Nominal	$=k_3/15$	938
7.0×10^{-7}	$=k_3/10$	236
7.0×10^{-7}	$=k_3/5$	107
7.0×10^{-7}	$=k_3/15$	406
2.8×10^{-8}	$=k_3/10$	1400
2.8×10^{-8}	$=k_3/5$	716
2.8×10^{-8}	$=k_3/15$	6058

nominal value ($k_4=k_3/15$) increases the halving time in almost a factor of 2 (938 d).

An increase in k_3 by a factor of 5 reduces the halving time for all k_4 values. On the other hand, a reduction in k_3 by a factor of 5 produces larger halving times in all simulations. These results appear to be contradictory. However, it must be taken into account that some 60% of radium is initially in the specific sites of the sediment (Section 3.2.3). This means that some of this radium must be dissolved (together with most of radium in the nonspecific sites) if concentration in the sediment must be reduced in a factor 2 (to obtain the halving time). An increase in k_3 also implies an increase in k_4 . Thus, there is a higher transfer of radionuclides from the specific to the nonspecific sites. From this phase, radionuclides are easily dissolved because k_2 is one order of magnitude larger than k_3 , and, in consequence, dissolution dominates over migration from the nonspecific to the specific sites. Similarly, a decrease in k_3 produces larger halving times because k_4 is further reduced.

4. Conclusions

A model to simulate the dispersion of ^{226}Ra in a tidal estuary has been described. The model solves the hydrodynamic equations offline, and standard tidal analysis is carried out to determine the tidal constants required by the dispersion code to calculate instantaneous currents over the estuary. The dispersion model includes advective/diffusive transport and exchanges of radionuclides between the dissolved phase and bed sediments. These exchanges are described by means of

kinetic transfer coefficients. The model has been initially tested through the comparison of computed and measured activity levels resulting after external releases occurring into the Odiel and Tinto rivers from the fertilizer complex and phosphogypsum piles, respectively. Once tested, the model has been used to simulate the self-cleaning process of the estuary observed after the fertilizer complex ceased its direct releases into the Odiel River. In general, temporal trends of specific activities in bed sediments are reproduced by the model. The computed sediment halftime is 510 days, that is in relative good agreement with the 630 days value deduced from observations.

It has to be commented that processes of migration of radionuclides inside the sediment core have not been considered in the model. Although their effects in the relatively short-term simulations that are carried out may be of secondary relevance (because model results are in relative good agreement with observations), a more detailed model should include a layered bed sediment. This further development of the model should be undertaken in the next future.

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.

References

- Absi A, Villa M, Moreno HP, Manjón G, Periañez R. Self-cleaning in an estuarine area formerly affected by ^{226}Ra anthropogenic discharges. *Sci Total Environ* 2004;329:183–95.
- Aston SR, Assinder DJ, Kelly M. Plutonium in intertidal and estuarine sediments in the northern Irish Sea. *Estuar Coast Shelf Sci* 1985;20:761–71.
- Barros H, Laissaoui A, Abril JM. Trends of radionuclide sorption by estuarine sediments Experimental studies using ^{133}Ba as a tracer. *Sci Total Environ* 2004;319:253–67.
- Bolívar JP, García-Tenorio R, Vaca F. Radioecological study of an estuarine system located in the south of Spain. *Water Res* 2000;34:2941–50.
- Borrego J, Pendón JG. Algunos ejemplos de influencia de los procesos antrópicos en el medio sedimentario: la ría de Huelva. *Henares Rev Geol* 1988;2:299–305 (in Spanish).
- Breton M, Salomon JC. A 2D long term advection dispersion model for the Channel and southern North Sea. *J Mar Syst* 1995;6: 495–513.

- Ciffroy P, Garnier JM, Pham MK. Kinetics of the adsorption and desorption of radionuclides of Co, Mn, Cs, Fe, Ag and Cd in freshwater systems: experimental and modelling approaches. *J Environ Radioact* 2001;55:71–91.
- El Mrabet R, Abril JM, Manjón G, García-Tenorio R. Experimental and modelling study of plutonium uptake by suspended matter in aquatic environments from southern Spain. *Water Res* 2001;35:4184–90.
- Laïssaoui A, Abril JM, Perriñez R, García-León M, García-Montaño E. Determining kinetic transfer coefficients for radionuclides in estuarine waters: reference values for ^{135}Ba and effects of salinity and suspended load concentrations. *J Radioanal Nucl Chem* 1998;237:55–61.
- Martínez-Aguirre A, García-León M, Gascó C, Travesi A. Anthropogenic emissions of ^{210}Po , ^{210}Pb , and ^{226}Ra in an estuarine environment. *J Radioanal Nucl Chem* 1996;207:357–67.
- Moreno H, Absi A, Vioque I, Manjón G, García-Tenorio R. Application of a liquid scintillation technique to the measurement of ^{226}Ra and ^{224}Ra in samples affected by non-nuclear industry wastes. *J Radioanal Nucl Chem* 2000;245:309–15.
- Perriñez R. A three dimensional σ coordinate model to simulate the dispersion of radionuclides in the marine environment: application to the Irish Sea. *Ecol Model* 1998;114:59–70.
- Perriñez R. Three dimensional modelling of the tidal dispersion of non conservative radionuclides in the marine environment: application to $^{239,240}\text{Pu}$ dispersion in the eastern Irish Sea. *J Mar Syst* 1999;22:37–51.
- Perriñez R. Kinetic modelling of the dispersion of plutonium in the eastern Irish Sea: two approaches. *J Mar Syst* 2003;38:259–75.
- Perriñez R. Testing the behaviour of different kinetic models for uptake-release of radionuclides between water and sediments when implemented on a marine dispersion model. *J Environ Radioact* 2004;71:243–59.
- Perriñez R, García-León M. Ra-isotopes around a phosphate fertilizer complex in an estuarine system at the southwest of Spain. *J Radioanal Nucl Chem* 1993;172:71–9.
- Perriñez R, Martínez-Aguirre A. A six-phase model to simulate the contamination by non-conservative radionuclides of sediments, soils and plants in a marsh area Application to the Odiel marsh in southwest Spain. *J Environ Radioact* 1997;37:29–54.
- Perriñez 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* 1996;87:169–79.
- Perriñez R, Abril JM, García-León M. Modelling the dispersion of non conservative radionuclides in tidal waters: Part 1 Conceptual and mathematical model. *J Environ Radioact* 1996;31:127–41.
- Perriñez R, Abril JM, García-León M. Modelling the dispersion of non conservative radionuclides in tidal waters: Part 2 Application to ^{226}Ra dispersion in an estuarine system. *J Environ Radioact* 1996;31:253–72.
- Pugh DT. Tides, surges and mean sea level. Chichester: Wiley; 1987.
- Van der Heijde HB, Klijn PJ, Passchier WF. Radiological impact of the disposal of phosphogypsum. *Radiat Prot Dosim* 1988;24:419–23.