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Kinetic modelling of the dispersion of plutonium in the eastern Irish Sea: two approaches

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Abstract

A new model to simulate the dispersion of plutonium in the eastern Irish Sea is presented. The model solves the 3D hydrodynamic equations using normalized σ coordinates in the vertical simultaneously with the suspended matter equation. Pu can be present in three phases: water, suspended matter and bottom sediments. Reduction and oxidation reactions are also included in the model, in terms of reaction rates, since Pu can be present in the marine environment in principally two different oxidation states. Two kinetic models are presented to describe the transfers of radionuclides between the liquid and solid phases: a one-step model consisting of a single reversible reaction and a two-step model consisting of two consecutive reversible reactions. It has been found that both models can properly simulate the contamination of the waters and sediments from the eastern Irish Sea due to the releases from the BNFL Sellafield nuclear fuel processing plant, since the outputs from both models are very similar and in agreement with observations. Also, both models can simulate the speciation of Pu between the reduced and oxidized forms. However, if the dominant source of radionuclides to the water column is redissolution from a contaminated sediment, a process that is actually occurring in the Irish Sea, it has been found that a two-step model must be used. Indeed, a one-step model predicts the redissolution from the sediment to be unrealistically rapid.

Keywords: Plutonium; Irish Sea; Modelling; Hydrodynamics; Kinetic models; Speciation; Redox reactions

1. Introduction

Over the past years, several models to simulate the dispersion of particle reactive, or nonconservative, radionuclides in the marine environment have been developed (Periáñez et al., 1996a; Margvelashvily et al., 1997; Aldridge, 1998; Piasecki, 1998; Cheng et al., 2000; Periáñez, 2000). These models are all based upon kinetic transfer coefficients instead of the less appropriate equilibrium distribution coefficient, k_d. Kinetic transfer coefficients, or rate constants, control forward and backward reactions for the sorption/desorption processes. Thus, it is assumed that a single reversible reaction governs the transfers of radionuclides between the dissolved and solid phases (suspended matter and bottom sediments).

Although the above-mentioned models have been applied to different radionuclides, the case of plutonium is especially complex since it can exist in four different oxidation states in the marine environment. Thus, Pu(III) and Pu(IV) predominate as the reduced

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and Pu(V) and Pu(VI) as the oxidized forms. The reduced Pu is highly particle reactive and has been shown to possess a distribution coefficient that is approximately two orders of magnitude higher than that of the more soluble oxidized Pu (McKay and Pattenden, 1993). Hence, when Pu concentration is measured from a water sample, the result corresponds to the mixture of oxidation states that is found in the particular sample. To overcome this problem, Periáñez (1999) used averaged kinetic transfer coefficients (between oxidized and reduced forms) to simulate Pu dispersion in the eastern Irish Sea, where it is released from the BNFL Sellafield nuclear fuel reprocessing plant, located in the British coast. The same approach was adopted in the case of the English Channel (Periáñez, 2000).

The objectives of this paper consist of developing a more realistic model to simulate plutonium dispersion, which includes redox reactions and the speciation of Pu between the reduced and oxidized forms, and testing and comparing two approaches to describe the transfers of Pu between the liquid and solid phases: a one-step reversible model and a two-step model consisting of two reversible consecutive reactions.

2. Modelling approaches

The model is three-dimensional. It solves the hydrodynamic equations using depth-following σ coordinates in the vertical and a flow-dependent eddy viscosity. Simultaneously, it solves the suspended matter equation (also in σ coordinates), which includes deposition and erosion terms. Finally, the equations for radionuclides are solved. The model includes three phases: water, suspended matter particles and the active fraction of the sediment, that consists of particles with a diameter <62.5 μm (Benes et al., 1994), that is, muddy sediments. Although McCubbin et al. (1999) have reported that the oxidation rate is different for Pu(IV) associated with particle and colloidal forms, the role of colloids has been neglected at this stage of model development since, on the other hand, Boust et al. (1996) have found that a maximum of 10–15% of plutonium is in colloidal form in the Sellafield effluent.

2.1. Hydrodynamics

The three dimensional hydrodynamic equations are written using normalized σ coordinates in the vertical. This way, a constant number of grid boxes is used in the vertical at each horizontal grid point and resolution is not reduced in the shallower areas. The transformation to σ coordinates is (see, for instance, Davies, 1985):

$$\sigma = \frac{z+\zeta}{h+\zeta} \tag{1}$$

where h is the undisturbed depth of water, ζ is the sea surface displacement from the mean level due to tidal oscillations and z coordinate is measured from the mean sea level to the bottom. Thus, the hydrodynamic equations are transformed from the interval $-\zeta \le z \le h$ into the constant interval $0 \le \sigma \le 1$. The form of the equations in normalized coordinates has been given previously (Periáñez, 1998), where a model to simulate the dispersion of conservative radionuclides is presented, and will not be repeated here. The boundary conditions applied at the sea surface are:

$$\rho_w \left(N \frac{\partial u}{\partial \sigma}\right)_{\sigma=0} = -(h+\zeta)F_s \tag{2}$$

$$\rho_w \left(N \frac{\partial v}{\partial \sigma}\right)_{\sigma=0} = -(h+\zeta)G_s \tag{3}$$

where u and v are water velocities along the x and y axis, respectively, F_s and G_s denote the components of the wind stress acting on the sea surface along the x and y directions, N is eddy viscosity and ρ_w is the water density. Similarly, at the sea bed:

$$\rho_w \left(N \frac{\partial u}{\partial \sigma}\right)_{\sigma=1} = -(h+\zeta)F_b \tag{4}$$

$$\rho_w \left(N \frac{\partial v}{\partial \sigma}\right)_{\sigma=1} = -(h+\zeta)G_b \tag{5}$$

where F_b and G_b are the two components of the bed stress. The hydrodynamic model can be calibrated using both a linear and a quadratic law for bottom friction (Periáñez, 1998). There are no appreciable differences in the dispersion patterns of radionuclides obtained when the hydrodynamic model is calibrated using linear or quadratic friction.

A flow-dependent eddy viscosity, N, has been used in the model. This formulation has been used previously and has given good results for tidal flow studies (Jones and Davies, 1996; Davies et al., 1997):

$$N = C_N\sqrt{\bar{u}^2 + \bar{v}^2}h \tag{6}$$

where $C_N = 0.0025$ is a dimensionless experimentally measured coefficient and $\bar{u}$ and $\bar{v}$ are depth mean currents along the x and y axis, respectively.

2.2. Suspended matter

The three dimensional suspended matter equation has been obtained by transforming the equation proposed by Nicholson and O'Connor (1986) into σ coordinates. Details can be seen in Periáñez (1999) and will not be repeated here. The equation includes advection/diffusion of particles and vertical fall. Erosion and deposition are incorporated into the sea-bed boundary condition of the equation. As usual in suspended matter studies, it is considered that only particles with diameter < 62.5 μm can remain in the water column as suspended matter, since larger particles will sink rapidly to the bottom and, thus, their horizontal movement is negligible (Belderson, 1964; Clarke, 1995; Periáñez et al., 1996b). Indeed, Eisma (1981) has pointed out that for all practical purposes, muds can be regarded as synonymous with suspended matter. Although bed load transport of coarser sediments may exist and heavy particles can move by a series of suspension and deposition events, this is not included in the model since, as found by Aston et al. (1985), virtually all the plutonium is associated with the small particles. Also, McKay and Walker (1990) found that Pu specific activity in the muddy sediments is of the order of 20 times greater than that of the sand.

Settling velocity of suspended matter particles increases when particles flocculate during settling (Eisma, 1993). A standard formula to represent this process has been used in the model (Nicholson and O'Connor, 1986; Pejrup, 1988; Mehta, 1989; Clarke and Elliott, 1998; Eisma, 1993). Settling velocities of the order of 10^{-6} m/s are obtained from such formula (Periáñez, 1999) for the typical suspended matter concentrations of the eastern Irish Sea, which is the order of magnitude that can be found in the literature (Prandle, 1997; Prandle et al., 1993) for the fall velocity of mud particles.

Also, a source term is included in the suspended matter equation in those grid cells located along the coastline. This term represents the input of particles from runoff of continental waters. All details can be seen in Periáñez (1999).

2.3. Plutonium dispersion equations

Redox reactions are described in terms of reaction rates. Thus, the rate at which Pu is oxidized is considered to be proportional to the concentration of reduced Pu at each particular point. The proportionality factor is the oxidation rate β_1. Similarly, the reduction rate β_2 governs the reduction reaction.

The exchanges of radionuclides between the liquid and solid phases are described in terms of kinetic transfer coefficients. Thus, the transfer of Pu from the solid phase to solution is governed by a coefficient k_2 and the inverse process by a coefficient k_1. It is known that actinide sorption by solid particles tends to be a surface phenomenon (Ramsay and Raw, 1987) and will depend on the surface of particles per water volume unit into the grid cell. This quantity has been denoted as the exchange surface (Periáñez et al., 1996a; Periáñez, 1999, 2000). Thus:

$$k_1 = \chi_1(S_\mathrm{m} + S_\mathrm{s}) = k_{11} + k_{12} \tag{7}$$

where S_m and S_s are the exchange surfaces for suspended matter and bottom sediments respectively and χ_1 is a parameter with the dimensions of a velocity. It is denoted as the exchange velocity (Periáñez et al., 1996a). As a first approach, assuming spherical particles and a step function for the grain size distribution of particles, it can be obtained (Periáñez et al., 1996a) that:

$$S_\mathrm{m} = \frac{3m}{\rho R} \tag{8}$$

$$S_\mathrm{s} = \frac{3Lf\phi}{R\Delta\sigma H} \tag{9}$$

where m is the suspended matter concentration, ρ is the suspended matter particle density, R is the mean radius of suspended matter and active sediment particles, $H=h+\zeta$ is total water depth, L is the average mixing depth (the distance to which the dissolved phase penetrates the sediment), $\Delta\sigma$ is spacing in the vertical direction, ϕ is a correction factor that takes into account that not all the sediment particle surface is in contact with water since part of it can be hidden by other particles, and f gives the fraction of active sediments. The kinetic coefficient k_2 is considered constant. This description of the transfer of radionuclides between the dissolved and solid phase has been used successfully in the previous modelling works (Periáñez et al., 1996c; Periáñez, 1999, 2000).

The equations presented in Periáñez (1999), that give the time evolution of Pu concentrations in the three phases considered in the model, include advection/diffusion of radionuclides in water and suspended matter, exchanges of radionuclides between suspended matter and the sediment due to erosion/deposition and transfers between the dissolved and solid phases. These equations have been now modified to include:

- Redox reactions that convert the oxidized Pu in reduced Pu and vice versa.
- The possibility of using a one-step or a two-step model to describe the transfers of radionuclides between the liquid and solid phases.

2.3.1. Model 1: one-step model

In this approach, a single reversible reaction is considered to describe the exchanges of radionuclides between the liquid and solid phases:

$$(R)+(X-S)\underset{k_2}{\overset{k_1}{\rightleftharpoons}}(R-S)+(X) \tag{10}$$

where (R) is the dissolved radionuclide, $(R-S)$ is the radionuclide bound to sites $(-S)$ of the solid particles and (X) is a competitive element that can be replaced by (R) on sites $(-S)$. k_1 and k_2 are the kinetic transfer coefficients, or absorption and desorption rates, respectively, as described above. A scheme showing the processes included in the model is presented in Fig. 1A.

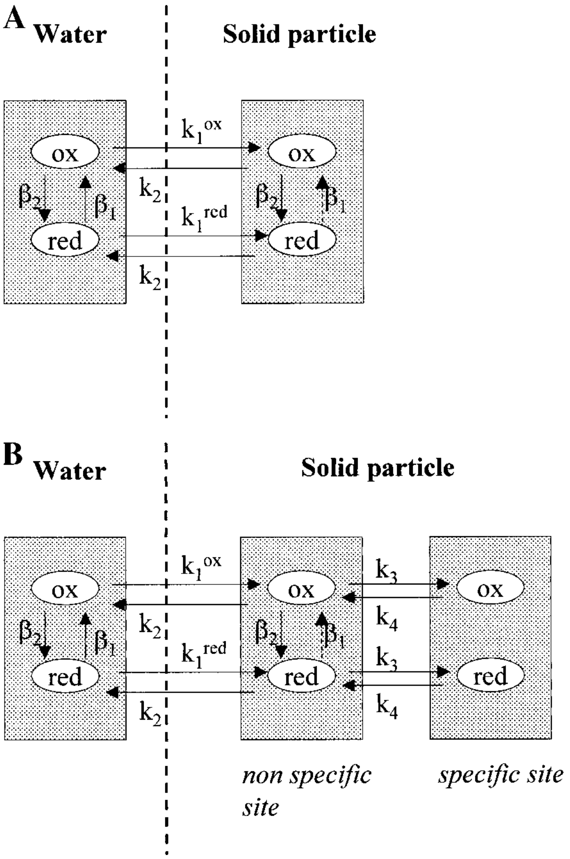

Fig. 1. Scheme showing the interaction between the liquid and solid phases in the one-step (A) and the two-step (B) models. The oxidation reaction is considered in suspended matter, but it is not in the case of bottom sediments (dashed arrow). k_1 will be k_{11} if the solid particle is a suspended matter particle and k_{12} if it is a bottom sediment particle (see text).

The equation that gives the time evolution of oxidized Pu in solution, $C_{\mathrm{d}}^{\mathrm{ox}}$, is:

$$\begin{aligned}\frac{\partial C_{\mathrm{d}}^{\mathrm{ox}}}{\partial t} &= (\mathrm{adv}+\mathrm{dif})_{3\mathrm{D}} - (k_{11}^{\mathrm{ox}}+\pi k_{12}^{\mathrm{ox}})C_{\mathrm{d}}^{\mathrm{ox}} \\ &\quad + k_2\left(mC_{\mathrm{s}}^{\mathrm{ox}}+\pi\frac{A_{\mathrm{s}}^{\mathrm{ox}}L\rho_{\mathrm{m}}f\phi}{\Delta\sigma H}\right) - \lambda C_{\mathrm{d}}^{\mathrm{ox}} \\ &\quad + \beta_1 C_{\mathrm{d}}^{\mathrm{red}} - \beta_2 C_{\mathrm{d}}^{\mathrm{ox}}\end{aligned} \tag{11}$$

where $(\mathrm{adv}+\mathrm{dif})_{3\mathrm{D}}$ represents three dimensional advection plus diffusion of radionuclides. $\pi=0$ unless we are solving the equation for the water layer that is in contact with the sediment; in this case, $\pi=1$ to allow the transfer of radionuclides between water and the bottom sediment. C_s^{ox} and A_s^{ox} are oxidized Pu concentrations in suspended matter and sediments. ρ_m is the sediment bulk density and λ is the radioactive decay constant. The external source should be added to this equation if it exists.

A similar equation is deduced for reduced Pu in solution, C_d^{red}:

$$\frac{\partial C_d^{red}}{\partial t} = (\text{adv} + \text{dif})_{3D} - (k_{11}^{red} + \pi k_{12}^{red}) C_d^{red} + k_2 \left(m C_s^{red} + \pi \frac{A_s^{red} L \rho_m f \phi}{\Delta\sigma H} \right) - \lambda C_d^{red} + \beta_2 C_d^{ox} - \beta_1 C_d^{red} \quad (12)$$

with obvious meaning for the notation.

In the case of oxidized Pu in suspended matter, C_s^{ox}, the equation is:

$$\frac{\partial (m C_s^{ox})}{\partial t} = (\text{adv} + \text{dif})_{3D} - \text{sett}^{ox} + \pi(\text{res}^{ox} - \text{dep}^{ox}) + k_{11}^{ox} C_d^{ox} - k_2 m C_s^{ox} - \lambda m C_s^{ox} + m(\beta_1 C_s^{red} - \beta_2 C_s^{ox}) \quad (13)$$

where m is the suspended matter concentration and sett, res and dep mean settling, resuspension and deposition (see Periáñez, 1999, for details). The equation for reduced Pu is:

$$\frac{\partial (m C_s^{red})}{\partial t} = (\text{adv} + \text{dif})_{3D} - \text{sett}^{red} + \pi(\text{res}^{red} - \text{dep}^{red}) + k_{11}^{red} C_d^{red} - k_2 m C_s^{red} - \lambda m C_s^{red} + m(\beta_2 C_s^{ox} - \beta_1 C_s^{red}) \quad (14)$$

The equation for oxidized Pu in the active fraction of the sediment is:

$$\frac{\partial A_s^{ox}}{\partial t} = k_{12}^{ox} \frac{C_d^{ox}(b) H \Delta\sigma}{L \rho_m f} - k_2 A_s^{ox} \phi + (\text{dep}^{ox} - \text{res}^{ox}) - \lambda A_s^{ox} - \beta_2 A_s^{ox} \quad (15)$$

where (b) means that such magnitude must be evaluated at the deepest water layer (in contact with the sediment). dep and res mean deposition and resuspension (see Periáñez, 1999, for details).

For reduced Pu:

$$\frac{\partial A_s^{red}}{\partial t} = k_{12}^{red} \frac{C_d^{red}(b) H \Delta\sigma}{L \rho_m f} - k_2 A_s^{red} \phi + (\text{dep}^{red} - \text{res}^{red}) - \lambda A_s^{red} + \beta_2 A_s^{ox} \quad (16)$$

It can be seen that the same reaction rates β_1 and β_2 have been considered for the three phases. This is due to the fact that they have been obtained from the laboratory experiments of Boust et al. (1996), and only the values corresponding to water can be determined from such experiments. Also, as can be deduced from the equations and seen in Fig. 1A, the oxidation reaction is not considered in the bottom sediments due to the fact that sediment conditions are generally anoxic (Kershaw et al., 1986).

2.3.2. Model 2: two-step model

Models using a single reversible reaction have been widely used to simulate the behaviour of nonconservative radionuclides in the marine environment (Periáñez et al., 1996c; Margvelashvily et al., 1997; Aldridge, 1998; Piasecki, 1998; Cheng et al., 2000; Periáñez, 2000). However, very recent experiments (Ciffroy et al., 2001; El Mrabet et al., 2001) have shown that a model involving the existence of two successive reversible reactions properly simulates both the sorption and release kinetics. This is now particularly important since there is evidence of redissolution of radionuclides from the contaminated sediments of the Irish Sea, which are acting as a source of long-lived Sellafield waste radionuclides due to the reduction of the discharges from the reprocessing plant (Cook et al., 1997; MacKenzie et al., 1998; Mitchell et al., 1999).

The exchange model, that is the 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 and slower reaction represents a reversible sorption to more specific sites, $(-S_2)$. They can be represented as follows:

$$(R) + (X - S_1) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (R - S_1) + (X) \quad (17)$$

$$(-S_2) + (R - S_1) \underset{k_4}{\overset{k_3}{\rightleftharpoons}} (R - S_2) + (-S_1) \quad (18)$$

where k_3 and k_4 are the kinetic transfer coefficients, or sorption and release rates, respectively, for the second reaction. The interaction between the dissolved and solid phases is described in the scheme of Fig. 1B. As in the case of model 1, the sorption of radionuclides is governed by kinetic coefficients k_1^{ox} and k_1^{red} for oxidized and reduced Pu, respectively. The release is governed by the same transfer coefficient k_2 for both oxidized and reduced forms. The slower reaction that exchanges radionuclides between the nonspecific and the specific sites is governed by the kinetic coefficients k_3 and k_4. As a first approximation, it is considered that these coefficients are the same for both the reduced and oxidized forms. As in El Mrabet et al. (2001), it is considered that the oxidation state does not change once that Pu has reached the specific sites in solid particles.

The equations that give the time evolution of oxidized and reduced Pu in solution are the same as in model 1. In the case of suspended matter, they are:

$$\begin{aligned}\frac{\partial(mC_s^{\mathrm{ox}})}{\partial t} = {} & (\mathrm{adv}+\mathrm{dif})_{3\mathrm{D}} - \mathrm{sett}^{\mathrm{ox}} + \pi(\mathrm{res}-\mathrm{dep})^{\mathrm{ox}} \\ & + k_{11}^{\mathrm{ox}}C_d^{\mathrm{ox}} - k_2 mC_s^{\mathrm{ox}} - \lambda mC_s^{\mathrm{ox}} \\ & + m(\beta_1 C_s^{\mathrm{red}} - \beta_2 C_s^{\mathrm{ox}} - k_3 C_s^{\mathrm{ox}} + k_4{*}C_s^{\mathrm{ox}})\end{aligned} \tag{19}$$

Note that the last terms in this equation represent the second reaction, that is, the exchanges of radionuclides with the specific sites. Radionuclide concentrations and processes associated to the specific sites are denoted by an asterisk at the left. The equation for the reduced Pu is:

$$\begin{aligned}\frac{\partial(mC_s^{\mathrm{red}})}{\partial t} = {} & (\mathrm{adv}+\mathrm{dif})_{3\mathrm{D}} - \mathrm{sett}^{\mathrm{red}} + \pi(\mathrm{res}-\mathrm{dep})^{\mathrm{red}} \\ & + k_{11}^{\mathrm{red}}C_d^{\mathrm{red}} - k_2 mC_s^{\mathrm{red}} - \lambda mC_s^{\mathrm{red}} \\ & + m(-\beta_1 C_s^{\mathrm{red}} + \beta_2 C_s^{\mathrm{ox}} \\ & - k_3 C_s^{\mathrm{red}} + k_4{*}C_s^{\mathrm{red}})\end{aligned} \tag{20}$$

The equations that give the time evolution of concentrations in the specific sites are:

$$\begin{aligned}\frac{\partial(m{*}C_s^{\mathrm{ox}})}{\partial t} = {} & {*}(\mathrm{adv}+\mathrm{dif})_{3\mathrm{D}} - {*}\mathrm{sett}^{\mathrm{ox}} \\ & + \pi{*}(\mathrm{res}-\mathrm{dep})^{\mathrm{ox}} - \lambda m{*}C_s^{\mathrm{ox}} \\ & + m(k_3 C_s^{\mathrm{ox}} - k_4{*}C_s^{\mathrm{ox}})\end{aligned} \tag{21}$$

$$\begin{aligned}\frac{\partial(m{*}C_s^{\mathrm{red}})}{\partial t} = {} & {*}(\mathrm{adv}+\mathrm{dif})_{3\mathrm{D}} - {*}\mathrm{sett}^{\mathrm{red}} \\ & + \pi{*}(\mathrm{res}-\mathrm{dep})^{\mathrm{red}} - \lambda m{*}C_s^{\mathrm{red}} \\ & + m(k_3 C_s^{\mathrm{red}} - k_4{*}C_s^{\mathrm{red}})\end{aligned} \tag{22}$$

The equations for the active sediment fraction are:

$$\begin{aligned}\frac{\partial A_s^{\mathrm{ox}}}{\partial t} = {} & k_{12}^{\mathrm{ox}}\frac{C_d^{\mathrm{ox}}(b)H\Delta\sigma}{L\rho_s f} - k_2\phi A_s^{\mathrm{ox}} + (\mathrm{dep}-\mathrm{res})^{\mathrm{ox}} \\ & - \lambda A_s^{\mathrm{ox}} - \beta_2 A_s^{\mathrm{ox}} - k_3 A_s^{\mathrm{ox}} + k_4{*}A_s^{\mathrm{ox}}\end{aligned} \tag{23}$$

where (b) means that this parameter must be evaluated at the deepest water layer (in contact with the sediment). Also, for reduced Pu,

$$\begin{aligned}\frac{\partial A_s^{\mathrm{red}}}{\partial t} = {} & k_{12}^{\mathrm{red}}\frac{C_d^{\mathrm{red}}(b)H\Delta\sigma}{L\rho_s f} - k_2\phi A_s^{\mathrm{red}} + (\mathrm{dep}-\mathrm{res})^{\mathrm{red}} \\ & - \lambda A_s^{\mathrm{red}} + \beta_2 A_s^{\mathrm{ox}} - k_3 A_s^{\mathrm{red}} + k_4{*}A_s^{\mathrm{red}}\end{aligned} \tag{24}$$

Specific sites:

$$\begin{aligned}\frac{\partial{*}A_s^{\mathrm{ox}}}{\partial t} = {} & {*}(\mathrm{dep}-\mathrm{res})^{\mathrm{ox}} - \lambda{*}A_s^{\mathrm{ox}} \\ & + k_3 A_s^{\mathrm{ox}} - k_4{*}A_s^{\mathrm{ox}}\end{aligned} \tag{25}$$

$$\begin{aligned}\frac{\partial{*}A_s^{\mathrm{red}}}{\partial t} = {} & {*}(\mathrm{dep}-\mathrm{res})^{\mathrm{red}} - \lambda{*}A_s^{\mathrm{red}} \\ & + k_3 A_s^{\mathrm{red}} - k_4{*}A_s^{\mathrm{red}}\end{aligned} \tag{26}$$

2.4. Numerical solution

The hydrodynamic equations are solved using an explicit finite difference scheme, although the vertical diffusion term is solved using the Saul'ev implicit scheme to retain stability. At land boundaries, the normal component of the current is set to zero. Along open boundaries, amplitude and phase of the surface elevation at the M_2 frequency are specified from observations (Howarth, 1990) and the surface current component that is normal to the boundary is obtained from a radiation condition (Kowalick and Murty, 1993). Only the main tidal component, M_2, has been used since we are mainly interested in testing the formulation of the three-dimensional dispersion model for Pu, including chemical reactions. Thus, only the M_2 tide has been used since realistic results are obtained, as will be shown. However, a result improvement should be expected if weaker components (at least S_2 and N_2) are included.

The advection and horizontal diffusion terms are solved using second order accuracy schemes (Kowalick and Murty, 1993) and vertical diffusion is again treated using the Saul'ev method. Along land boundaries, no fluxes of suspended particles and Pu are considered. The open boundary condition described in Periáñez (1998) and Periáñez (1999) has been adopted:

$$C_i = \psi C_{i-1} \tag{27}$$

where C_i represents the concentration of suspended matter and Pu along the boundary and C_{i-1} represents the concentration just inside the computational domain. The nondimensional value $\psi = 0.9$ is obtained from a calibration exercise (Periáñez, 1998, 1999).

A FORTRAN code has been developed to solve the equations involved in the model. It was implemented on a HP SPP-2000 X-Class computer. One month of computation with the single state model (Periáñez, 1999) takes about 2.5 h. With the one-step and two-step models, 3.8 and 4.5 h, respectively, are required.

3. Results and discussion

The horizontal resolution of the model is $\Delta x = \Delta y =$ 5000 m. Ten layers are used in the vertical, thus $\Delta\sigma = 0.1$, and time step is fixed as $\Delta t = 60$ s. Water depths are introduced from bathymetric maps. The model domain is presented in Fig. 2. No wind effects are considered since we are mainly interested in testing and tuning the formulation of the three-dimensional dispersion model including redox reactions and two kinetic models, and realistic results are obtained although wind is not included, as will be seen.

The values given to all the parameters involved in the model are presented in detail in Periáñez (1999). The source of virtually all Pu to the Irish Sea is the discharge from Sellafield through a pipeline that extends 2.5 km beyond high water. The magnitudes of the discharges have been compiled from McKay and Pattenden (1993) and Hunt et al. (1997), and have been used as the Pu input to the model. It has also been reported (Pentreath, 1985) that about 99% of the discharged Pu is associated to particles in a reduced form.

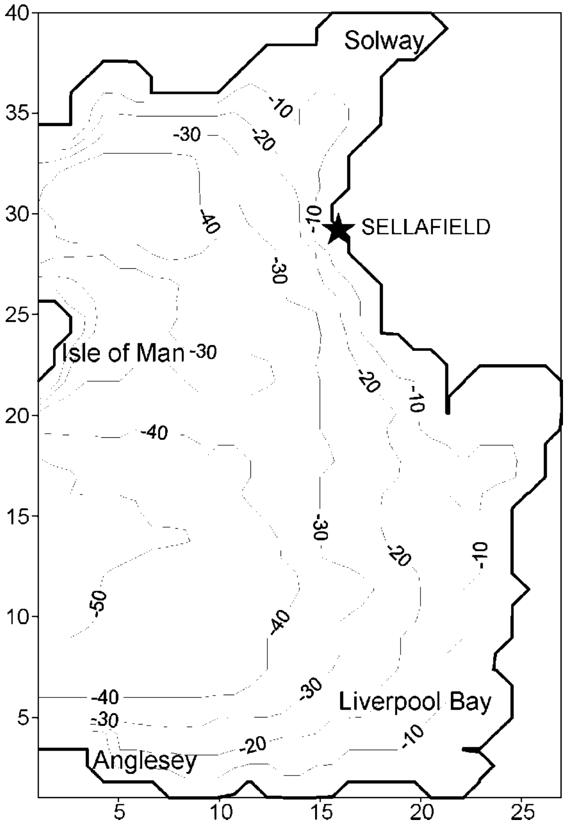

Fig. 2. Model domain. Depths are given in m. Each unit in the x and y axis is 5000 m (grid cell number). The location of Sellafield reprocessing plant is also shown.

Values for all the kinetic coefficients must also be given. Nyffeler et al. (1984) measured k_2 for a wide set of elements and found a very small variation (less than an order of magnitude) even for elements with a very different geochemical behaviour. Thus, it has been considered that k_2 is the same for oxidized and reduced Pu and equal to the average value for the mixture of oxidation states used in Periáñez (1999): $k_2 = 1.16 \times 10^{-5}$ s^{-1}. The exchange velocities rates can be deduced from the coefficient k_2 and the corresponding distribution coefficients, k_d, for reduced and oxidized Pu (which have been measured by Mitchell et al., 1995), following the method indicated in Periáñez

(1999). Indeed, the following relation between these magnitudes holds (Periáñez et al., 1996c):

$$k_{\mathrm{d}} = \frac{\chi_1}{k_2}\frac{3}{\rho R} \tag{28}$$

Thus, the following values are obtained: $\chi_1^{\mathrm{red}} = 1.51 \times 10^{-4}$ ms^{-1} and $\chi_1^{\mathrm{ox}} = 1.51 \times 10^{-6}$ ms^{-1}. Once the exchange velocities are known, kinetic transfer coefficients k_{11} and k_{12} for both oxidized and reduced Pu can be obtained from Eqs. (7)–(9).

The reaction rates have been obtained from the experiments of Boust et al. (1996): $\beta_1 = 1.85 \times 10^{-6}$ s^{-1} and $\beta_2 = 4.48 \times 10^{-7}$ s^{-1}.

Finally, kinetic coefficients for the second reaction in the two-step model, k_3 and k_4, must also be given. From the experiments of Ciffroy et al. (2001), it is obtained that k_3 is about one order of magnitude larger than k_4. 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 marine water from the southwest of Spain. Thus, the following values have finally been used in the model, since acceptable results are obtained with them:

$$k_3 = 1.2 \times 10^{-7}\ \mathrm{s}^{-1}$$

$$k_4 = 1.2 \times 10^{-8}\ \mathrm{s}^{-1}$$

Of course, model results could be refined if specific values for the Irish Sea are used when available.

The experiments of Ciffroy et al. (2001), however, have been carried out over a relatively short time scale (of the order of one week). Thus, one can question the relevance of the second reaction for a longer (several months) simulation. A very simple box model to study the behaviour of both approaches has been developed so as to address this point. Consider a water container of volume V with a given amount of bottom sediment in it. Let F be the flow of water leaving the container (that simulates advective transport). The equations that give the time evolution of activities in water, nonspecific and specific sediment sites are:

$$\begin{aligned} \frac{\partial C_{\mathrm{d}}}{\partial t} &= -k_1 C_{\mathrm{d}} + k_2 A_{\mathrm{s}} - \frac{F}{V} C_{\mathrm{d}} \\ \frac{\partial A_{\mathrm{s}}}{\partial t} &= k_1 C_{\mathrm{d}} - (k_2 + k_3) A_{\mathrm{s}} + k_4 {}^{*}A_{\mathrm{s}} \\ \frac{\partial {}^{*}A_{\mathrm{s}}}{\partial t} &= k_3 A_{\mathrm{s}} - k_4 {}^{*}A_{\mathrm{s}} \end{aligned} \tag{29}$$

It is assumed that the contaminated water leaving the container is replaced by clean water. It has been taken $F = 0.01\,V/\Delta t$, so that only 1% of the water in the box leaves each time step. Kinetic coefficients are the same used in the Irish Sea: $k_1 = 5.0 \times 10^{-5}$, $k_2 = 1.16 \times 10^{-5}$, $k_3 = 1.2 \times 10^{-7}$ and $k_4 = 1.2 \times 10^{-8}$ s^{-1}. Although k_1 depends on the exchange surface (Eqs. (7) and (9)), it has been taken here as a constant (but realistic) value. Also, redox reactions are not considered at this point. These equations have been numerically solved for 100 days starting from a contaminated sediment and clean water (as will be shown below, the main differences between models 1 and 2 arise when simulating redissolution from contaminated sediments). It must be noticed that model 1 is obtained from the equations simply making $k_3 = k_4 = 0$. Results are presented in Fig. 3A (fraction of radionuclides in the dissolved phase) and B (fraction in the sediment) for both models. It can be seen

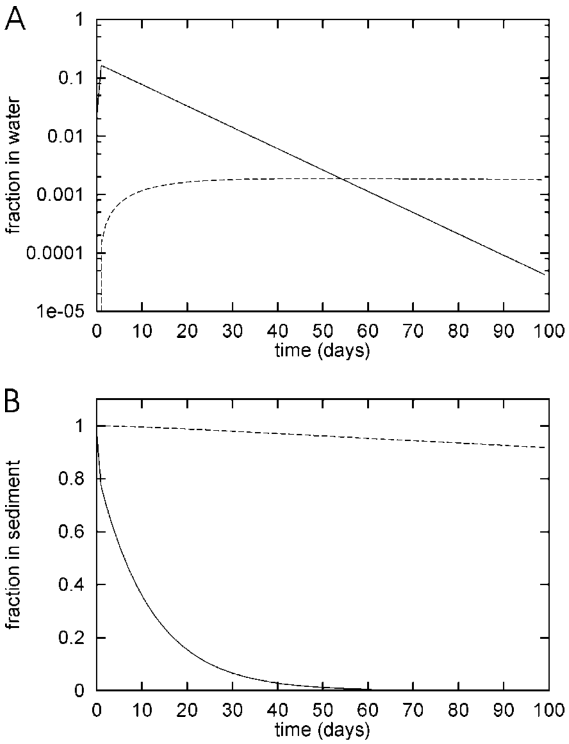

Fig. 3. Fraction of radionuclides in the dissolved phase (A) and sediments (B) for a one-step (solid line) and a two-step (dashed line) model. In the two-step model, the sediment fraction includes the content in both specific and nonspecific sites.

that model 1 produces a very fast redissolution in the first days, and after some 60 days, the sediment is completely clean. The fraction of radionuclides in the water phase also decreases exponentially due to the advection process: the global result is a fast cleaning of the container. On the other hand, if a two-step model is used (assuming that at $t=0$, all the activity is in the specific sediment sites), a slow redissolution is obtained. Indeed, less than 10% of the radionuclides is redissolved after 100 days. The fraction of radionuclides in the water phase remains low (of the order of 0.1%), due to the slow redissolution rate and advective removal. However, a stationary state is reached for the dissolved phase since the input rate of radionuclides from the sediment becomes equal to the advection removal rate. It can be concluded that the behaviour of a one-step and a two-step model is rather different. Although such behaviour has been tested in a very simple and idealized situation, it seems evident that it is worth carrying out a more realistic comparison of both approaches in a real marine dispersion model.

The hydrodynamic part of the model was tested by comparing observed and computed values of tidal elevation amplitudes and phases, current profiles at several locations and semi-major axis magnitude and orientation of the M_2 tidal current ellipse at several depths and locations. Details can be seen in Periáñez (1998) and will not be repeated here. Similarly, observed and computed suspended matter concentrations in surface and bottom waters have been compared for several locations. Model results are in agreement with observations (Periáñez, 1999). Computed sedimentation rates are also in agreement with historically deduced net sedimentation rates (Periáñez, 1999).

Exactly the same simulations presented in Periáñez (1999) have been repeated with models 1 and 2, taking now into account that Pu is released in a reduced form.

Observed and computed distributions of ^{239,240}Pu have been compared for several years. The input from Sellafield was introduced in the model for each year. However, the input has been taking place since the fifties. Thus, instead of starting the model from zero concentrations, we have assumed for each simulation an uniform background in water, suspended matter and bottom sediments that represents the effect of previous discharges. It has been shown (Periáñez et al., 1994) that model results do not depend upon the way the background is created. Thus, the same results would be obtained if a large discharge is performed and some time is allowed to elapse so that the discharge is distributed over the sea. To save CPU time, the uniform background option was chosen. Discharges from Sellafield are carried out over this background and model results are obtained after a simulation time of 3 months. These results are compared with observations. The background magnitude is selected from a trial and error exercise, so that model results are in agreement with observations, and it is assumed to be uniform over all the model domain. The shapes of the computed sediment concentration isolines are not affected by the initial conditions since these consider an uniform contamination. Also, relative variations of Pu concentrations from one point to another are not affected by the initial conditions. These facts indicate that, although initial inventories are defined at the start of each simulation, the model is working correctly.

The computed total Pu (reduced plus oxidized) distribution in surface waters for year 1974 is presented in Fig. 4a and b for models 1 and 2, respectively. The computed percentage of oxidized Pu in solution (with model 2, although there are virtually no differences between both models) is shown in Fig. 4c, and the observed total Pu distribution (Hetherington, 1976) in Fig. 4d. It can be seen that there is little difference between the outputs from both models and that activity levels over the sea are, in general, well reproduced by the models. As can be seen in Fig. 4c, most Pu in solution is in an oxidized form. Only close to the discharge point some 30% of Pu is in a reduced form, which is due to the nature of the discharges: all Pu is released in a reduced form. Oxidation takes place after the release and over 90% of Pu is then in an oxidized form (Mitchell et al., 1995). Simulations are in agreement with these observations. Also, there are no significant changes in the speciation of Pu throughout the sea, as was also found by Mitchell et al. (1995).

The total Pu specific activity in surface suspended matter computed with model 2 is presented in Fig. 5a. Unfortunately, there are no measurements to compare with. The computed percentage of oxidized Pu in suspended matter is shown in Fig. 5b. It can be seen that concentrations over 5 Bq g^{-1} are obtained close to Sellafield outlet. Also, isolines for suspended matter are similar to those of water (Fig. 4), although it seems

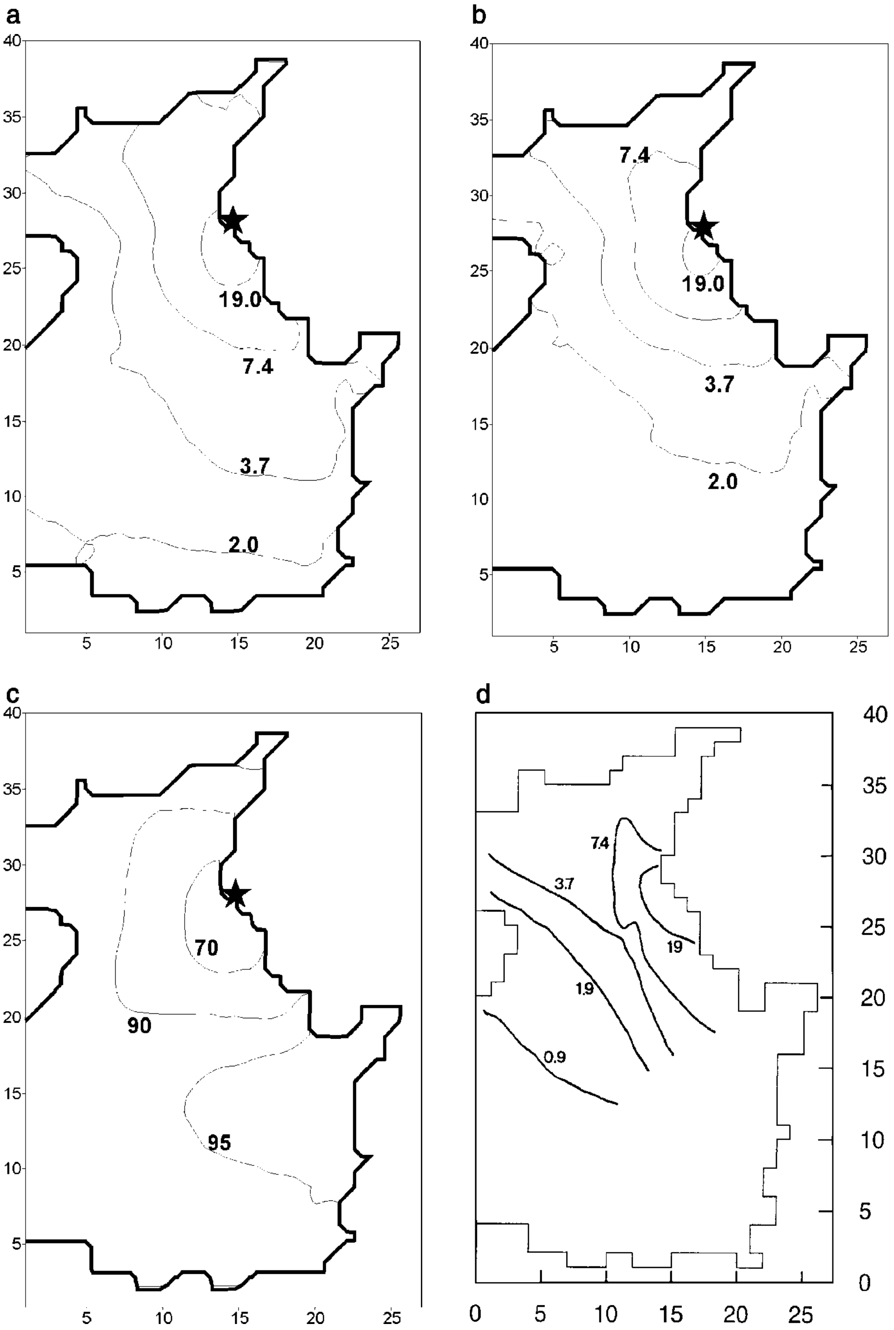

Fig. 4. (a) Computed distribution of total Pu in surface waters (Bq m^{-3}) for year 1974 with model 1. (b) Same as (a) but with model 2. (c) Computed percentage of oxidized Pu in water. (d) Observed Pu distribution. Sellafield location is shown as a star.

that concentrations in suspended matter decrease faster than in water as we move away from Sellafield. This is due to the fact that particles are removed from the water column by deposition processes. Most Pu in suspended matter is in a reduced form, which is in agreement with the well-known fact that reduced Pu is

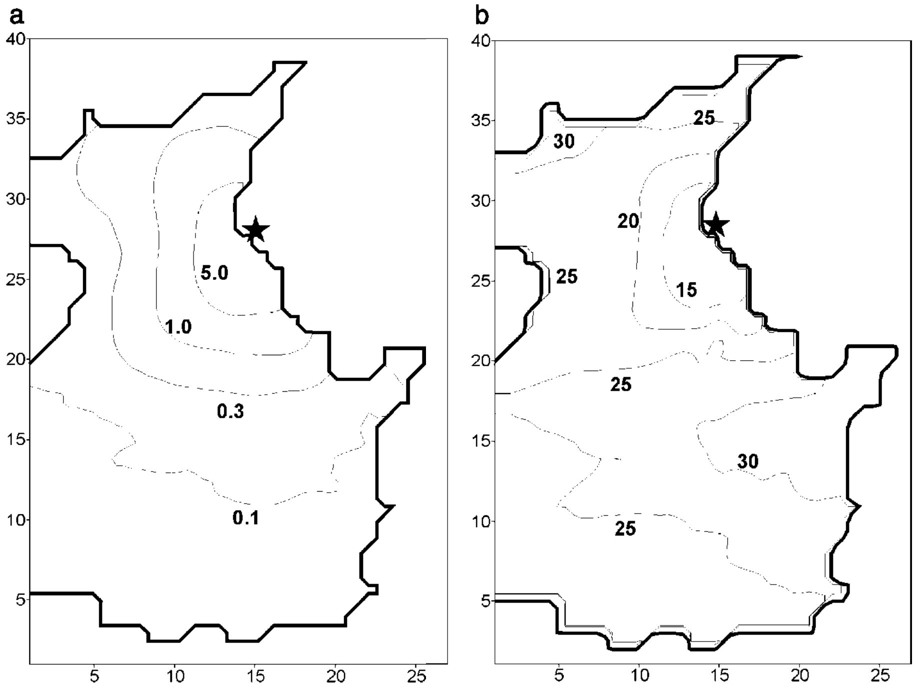

Fig. 5. Distribution of Pu in surface suspended matter (Bq g^{-1}) for year 1974 and model 2. (a) Computed concentration, (b) computed percentage of oxidized Pu. Sellafield location is shown as a star.

less soluble than oxidized Pu. Essentially, the same results are obtained with model 1.

The computed total Pu in surface waters for year 1979 is presented in Fig. 6a and b (models 1 and 2, respectively). The observed distribution is presented in Fig. 6c (Pentreath, 1985). As can be seen, there is little difference between the outputs of both models. Also, activity levels are, in general, reproduced by computations.

The computed distribution of total Pu in sediments for year 1977 is presented in Fig. 7a and b (models 1 and 2, respectively). The computed percentage of reduced Pu in the sediment is shown in Fig. 7c and the observed distribution of total Pu is presented in Fig. 7d (Pentreath, 1985). Again, both models are giving a realistic representation of the activity levels detected in the sediments. As should be expected, most Pu in the sediment is in a reduced form.

Results obtained with model 1 are in closer agreement with observed distributions of plutonium than results obtained with the model that considers a single (average) oxidation state of Pu (the model presented in Periáñez, 1999). Results are more clearly improved in the case of the dissolved phase in the area of the release from Sellafield. Since Pu is released in a reduced form and reduced Pu is more particle reactive, an effect of considering redox speciation in the model is to reduce Pu concentrations in water in the area of Sellafield: plutonium is lost from solution and fixed to suspended particles and bottom sediments. On the other hand, the single oxidation state model produces higher Pu concentrations in water in the area of the release point since such “average plutonium” is less reactive than reduced plutonium. Also, model 1 gives a considerably larger amount of information than the single state model, like proportions of reduced and oxidized Pu in water, suspended matter and bottom sediments. Some experimental evidences can be reproduced, for instance, the fact that there are no changes in the oxidation state of plutonium throughout the sea (unless close to the discharge point where an oxidation of the released Pu occurs). Moreover, distribution coefficients (k_d’s), that would be obtained from a field measurement as the ratio of specific activity in suspended matter and water, can be calculated with model 1 for reduced, oxidized and total Pu. In the case of total

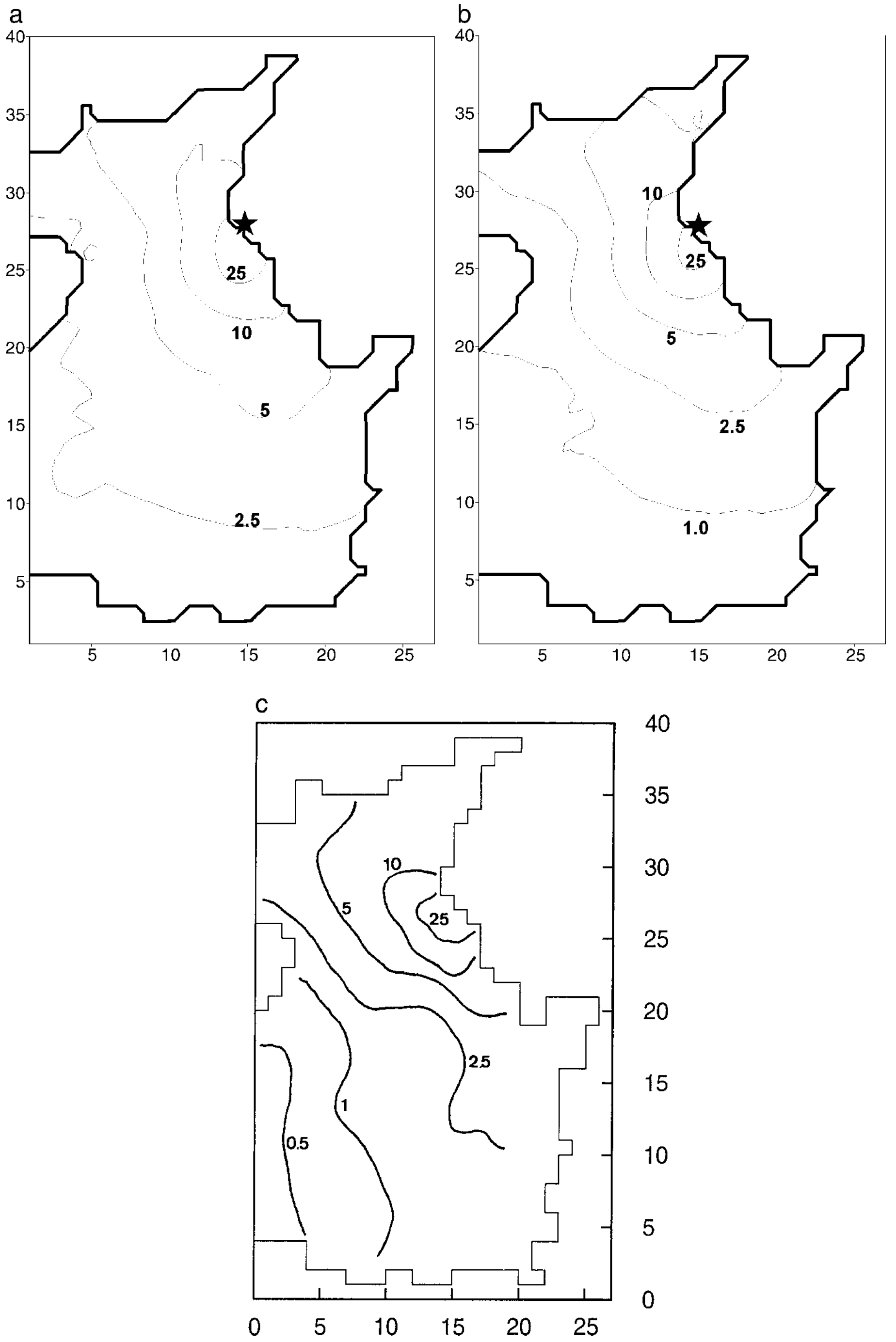

Fig. 6. (a) Computed distribution of total Pu in surface waters (Bq m^{-3}) for year 1979 with model 1. (b) Same as (a) but with model 2. (c) Observed Pu distribution. Sellafield location is shown as a star.

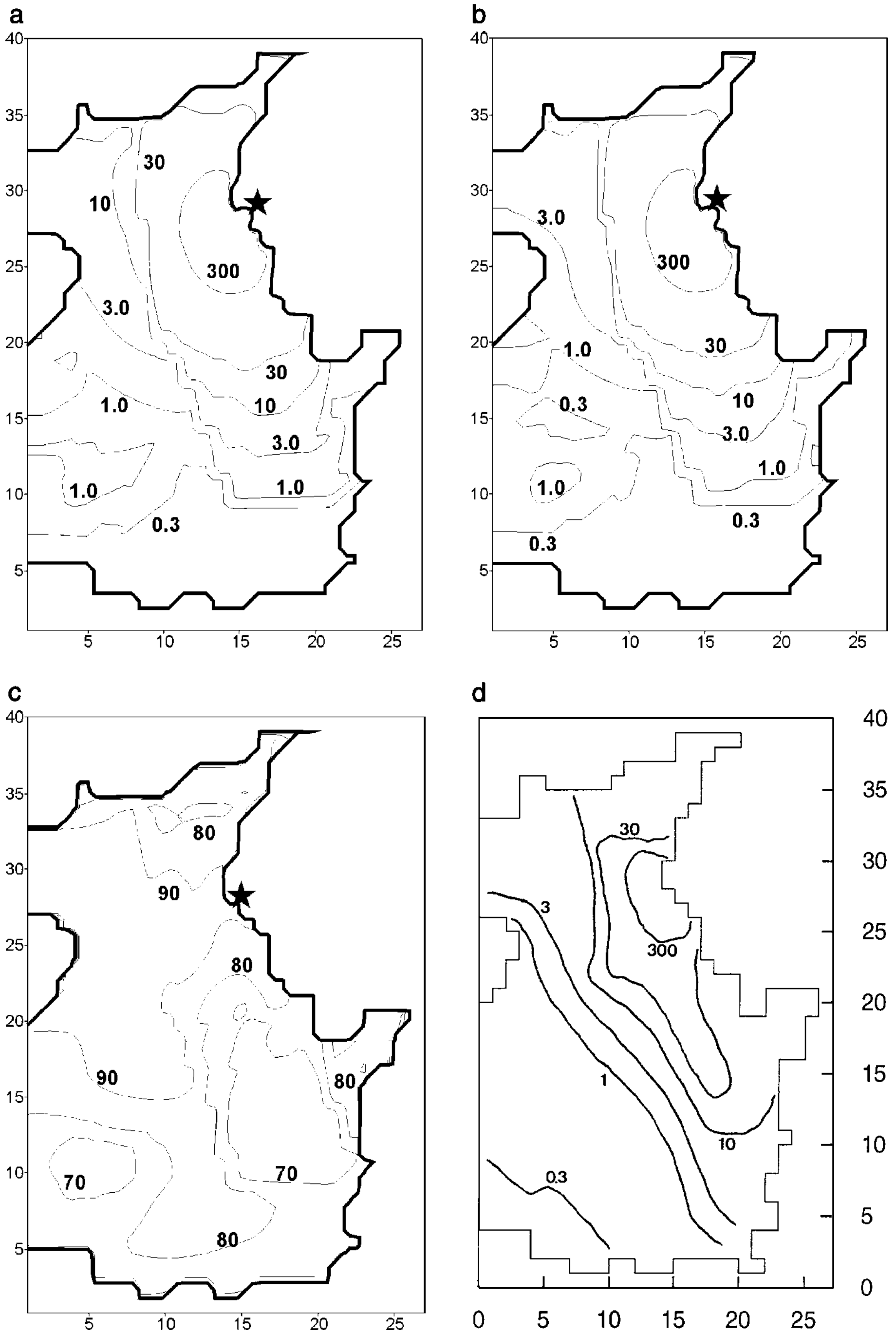

Fig. 7. (a) Computed distribution of total Pu in bottom sediments (kBq m^{-2}) for year 1977 obtained with model 1. (b) Same as (a) but with model 2. (c) Computed percentage of reduced Pu in the sediment. (d) Observed Pu distribution. Sellafield location is shown as a star.

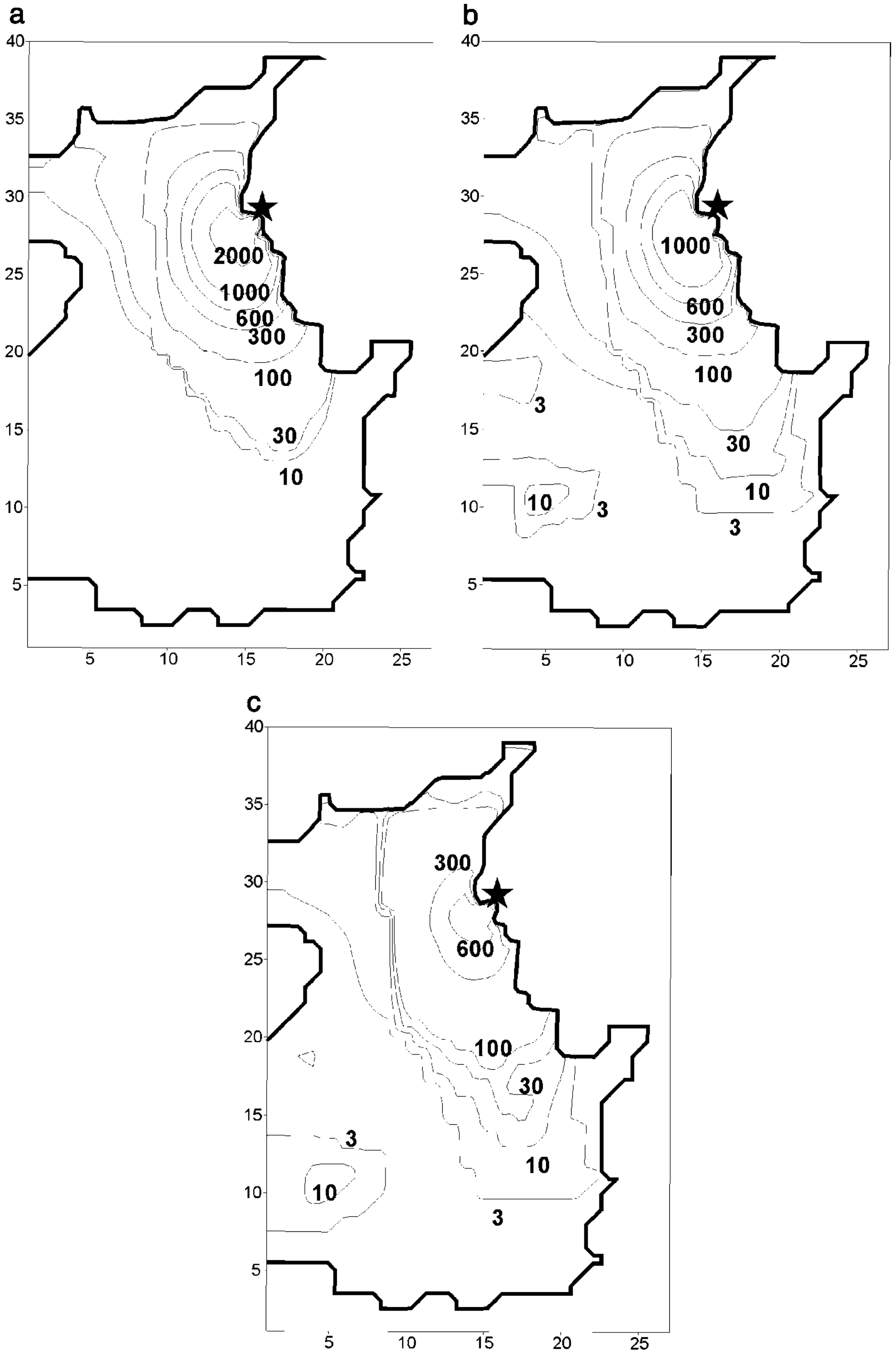

Fig. 8. Computed concentrations of total ^{239,240}Pu in bottom sediments (Bq kg^{-1} dry) for years 1983 (a), 1988 (b) and 1995 (c). Sellafield location is shown as a star.

Pu, computed k_d's are, in most of the sea, of the order of 10^5 l/kg, in agreement with measurements of McKay and Walker (1990), Mitchell et al. (1995) and the recommended value of IAEA (1985). It is also found that k_d's diminish with increasing distance from Sellafield. This effect was also obtained from observations (Mitchell et al., 1995) and was attributed to the nature of discharges, since almost all the plutonium in the releases is associated with suspended particles (Mitchell et al., 1995) and no significant changes in the speciation of Pu between oxidized and reduced forms over the sea have been found, as commented above. The computed k_d's for oxidized Pu are of the order of 10^4 l/kg, value that is slightly higher than that found in the literature (Mitchell et al., 1995; Nelson and Lovett, 1978). However, k_d's for reduced Pu are of the order of 10^6 l/kg, in agreement with the findings of Mitchell et al. (1995) and Nelson and Lovett (1978). Similar results are obtained with model 2.

At this point, it seems that the two-step model presents no advantages over the one-step model, since both can give good estimations of the activity levels detected in the sea and the speciation of Pu between the reduced and oxidized forms. Furthermore, the two-step model is, obviously, computationally more expensive. Differences between both models arise when simulating the redissolution process from a contaminated sediment. As commented above, it seems that sediments from the Irish Sea are behaving as a source of Sellafield waste radionuclides, now that releases from the plant have been reduced and the desorption reaction dominates sorption (Cook et al., 1997; MacKenzie et al., 1998; Mitchell et al., 1999).

The models have been started with actual Pu concentrations in the sediments and no input from Sellafield is introduced. Zero concentrations for water and suspended matter have also been assumed. From the time evolution of the computed Pu concentrations in the sediments, it is possible to calculate the sediment halving time. This is defined as the time in which concentration in the sediment is reduced by a factor 2. The sediment halving time calculated with model 1 is 1.8 years. This is clearly in contrast with the 112 years obtained with model 2. Cook et al. (1997) estimated, from observations, a halving time of the order of 350 years. Leonard et al. (1999) gave an estimation of 58 years. Our result is between these two estimations. However, the model result should be compared with the value of Leonard et al. (1999) since conditions of our simulation are equivalent to the assumptions made by these authors to estimate the halving time. The result obtained from model 2 is similar to Leonard's estimation. Of course, results could be probably improved if k_3 and k_4 specific values for the Irish Sea are used. On the other hand, model 1 produces an unrealistically rapid redissolution rate from the sediment. Although kinetic coefficients in model 1 could be changed in such a way that redissolution is slowed down and sediment halving time is increased to the value obtained with model 2, this would give a wrong partition of plutonium between the dissolved and solid phases. Hence, the necessity of using a two-step model to simulate redissolution from contaminated sediments.

It has also been found that the oxidation state of Pu in the sediment affects the halving times. If only 50% of Pu in the sediment is considered to be in a reduced form, then the halving time reduces to 60 years. A reduction to 39 years is obtained if only 25% of Pu is considered to be initially reduced in the sediment. This is due to the fact that oxidized Pu is more soluble than reduced Pu.

Thus, it can be concluded that a two-step model should be used if the dominant source of radionuclides to the water column is redissolution from a contaminated sediment. If the dominant source is an external input, both one-step and two-step models give realistic results. Model 2 has also been tested under more recent Irish Sea conditions, when redissolution from contaminated sediments is an important source of Pu to the water column. The computed Pu distribution in surface sediments for years 1983, 1988 and 1995 can be seen in Fig. 8. Activity levels given by the model are, in general, in agreement with those observed in the Irish Sea (Kershaw et al., 1999). It seems that model 2 can reproduce the behaviour of Pu in the sea under recent conditions, when the dominant source of Pu is redissolution from the contaminated sediments.

4. Conclusions

A numerical 3D model to simulate the dispersion of plutonium in the eastern Irish Sea has been developed. The model solves the hydrodynamic equations and the suspended matter equations simultaneously with the equations that give the time evolution of Pu concentrations in the three phases considered in the model: water, suspended matter and bottom sediments. Redox reactions are also included in the model in terms of reaction rates. Two kinetic models have been used to describe the transfers of Pu between the liquid and solid phases, a one-step model consisting of a single reversible reaction and a two-step model consisting of two consecutive reversible reactions.

The inclusion of redox reactions implies an improvement of results with respect to those obtained with the single state model described in Periáñez (1999). Also, an important amount of valuable information concerning chemical speciation is given by the model (models 1 and 2).

From our calculations, it is concluded that a one-step kinetic model is enough to properly simulate the contamination of the sea due to an external input of radionuclides, since results obtained with the one-step and the two-step models are essentially the same. Such one-step models have been widely used before (Piasecki, 1998; Margvelashvily et al., 1997; Aldridge, 1998; Periáñez et al., 1996a; Periáñez, 1999, 2000). However, if the interest consists of studying the redissolution of radionuclides from a contaminated sediment and subsequent transport, it seems clear that a two-step model must be applied. Sediment halving time computed with the one-step model is much lower than the value estimated from observations, while halving time computed with the two-step model is in closer agreement with that. On the other hand, it has been pointed out that the oxidation state of Pu in the sediment affects the redissolution process, in such a way that halving times can be significantly reduced if most Pu in the sediment is in an oxidized form.

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