Modelling the physico-chemical speciation of plutonium in the eastern Irish Sea

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Abstract

A numerical model to simulate the speciation of ^{239,240}Pu in the eastern Irish Sea is presented. The model solves the three dimensional hydrodynamic equations, using normalized σ coordinates in the vertical direction. Simultaneously, the equation for suspended matter, that includes advection, diffusion, settling, deposition and erosion of the sediment, is solved too. Thus, the tidal dispersion of non-conservative radionuclides can be simulated. Reduction and oxidation reactions are included in the model; they are described in terms of reaction velocities. It is considered that Pu can be present in solution, suspended matter and bottom sediments. Also, Pu can be in reduced and oxidized forms in each of these three phases. Thus, six equations are solved, whose solutions give the temporal evolution of Pu concentration in each phase for both reduced and oxidized forms. The model has been applied to the eastern Irish sea, where Pu is released from the Sellafield nuclear fuel reprocessing plant. Observed and computed Pu distributions in water and bottom sediments have been compared. Also, the model gives the percentage of Pu that is reduced and oxidized in each phase. Finally, distribution coefficients for total Pu (reduced plus oxidized), oxidized and reduced Pu have been calculated over the sea. Results are, in general, in agreement with observations.

Keywords: Plutonium; Speciation; Irish Sea; Sellafield; Modelling

1. Introduction

Over recent years, there has been an increasing interest in developing models to simulate the dispersion of non-conservative radionuclides in aquatic environments since these models can be used as predictive instruments that can be applied in the assessment of radioactive contamination following an accidental release of radionuclides.

The first models for non-conservative radionuclides were long-term dispersion models, in which the transfer of radionuclides between the liquid and solid phases was described in terms of equilibrium distribution coefficients (Gurbutt, Kershaw & Durance, 1987; Abril & García-León, 1993a). Periáñez, Abril & García-León (1996a) developed a model to simulate the dispersion of non-conservative radionuclides in tidal waters based upon kinetic transfer coefficients and thus the model could be used under non-equilibrium conditions. This model was applied to simulate the dispersion of ^{226}Ra, ^{238}U and ^{232}Th in a Spanish estuary (Periáñez, Abril & García-León, 1996b; Periáñez & Martínez-Aguirre, 1997a). Recently, Periáñez (in press) developed a three dimensional model to simulate the tidal dispersion of non-conservative radionuclides in the marine environment, also based upon kinetic transfer coefficients. A similar model was also developed by Margvelashvily, Maderich and Zheleznyak (1997).

Abril and García-León (1993b) and Periáñez (in press) applied their respective models to simulate the dispersion in the Irish Sea of plutonium released from the nuclear fuel reprocessing plant at Sellafield. However, the behaviour of Pu in aquatic systems is of considerable complexity due to the fact that it can simultaneously exist in different oxidation states. Thus, Pu (III) and Pu (IV) predominate as the reduced 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 two orders of magnitude higher than that of the more soluble oxidized Pu (McKay & Pattenden, 1993; Mitchell, Vives i Batlle, Downes, Condren, León-Vintró & Sanchez-Cabeza, 1995). Hence the values observed in field measurements represent the properties of the mixture of oxidation states that is present in the particular sample. To overcome this problem, Abril and García-León (1993b) and Periáñez (in press) used a mean distribution coefficient and mean kinetic transfer coefficients, respectively, in their models. Nevertheless, the main difficulty is that the oxidation state of Pu changes with time: Pu is released in a reduced form and after some days an equilibrium in the partition of Pu between the reduced and oxidized species is achieved (Pentreath, Harvey & Lovett, 1986).

The objective of this paper is to present the first results on a Pu dispersion model that includes reduction and oxidation (redox) reactions in a simple way. Thus, mean kinetic transfer coefficients are not used (reduced and oxidized Pu have their corresponding specific coefficients) and the model can also give information on the speciation state of Pu in water, suspended matter and bottom sediments. Moreover, the model calculates total distribution coefficients and distribution coefficients for the reduced and oxidized Pu separately.

The model solves the three dimensional hydrodynamic equations using normalized σ coordinates in the vertical, so that vertical resolution is not reduced in the shallower regions, the equation for suspended matter, which is also written in σ coordinates and includes advection, diffusion, settling, deposition and erosion of the sediment, and the equations whose solutions give the time evolution of reduced and oxidized Pu in water, suspended matter and bottom sediments. In this way, the tidal dispersion of reduced and oxidized Pu is obtained.

The model is presented in the next section. Thereafter, the model results are presented and discussed.

2. The model

2.1. Redox reactions

Redox reactions will be described in terms of reaction velocities. 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 velocity β_1. Similarly, the rate at which Pu is reduced is considered to be proportional to the concentration of oxidized Pu. The proportionality factor will now be the reduction velocity, denoted as β_2.

An estimation of the values of β_1 and β_2 can be obtained from the laboratory experiments carried out by Boust, Mitchell, Garcia, Condren, León-Vintró and Leclerc (1996). Filtered sea water was spiked with Pu(IV) at a well known concentration and the oxidation reaction was followed during some 30 d (details can be seen in Boust et al., 1996). The % of oxidized Pu, as a function of time, is given by the points in Fig. 1. In our model, the equations that give the temporal evolution of the concentration of oxidized and reduced Pu, C^{ox} and C^{red} respectively, are:

$$\frac{\partial C^{red}}{\partial t} = -\beta_1 C^{red} + \beta_2 C^{ox} \tag{1}$$

$$\frac{\partial C^{ox}}{\partial t} = \beta_1 C^{red} - \beta_2 C^{ox} \tag{2}$$

If these equations are solved, knowing that at $t = 0$, $C^{ox} = 0$ and $C^{red} = C^{red}(0)$, it follows that

$$C^{ox} = \frac{\beta_1}{\beta_1 + \beta_2} C^{red}(0)(1 - e^{-(\beta_1 + \beta_2)t}). \tag{3}$$
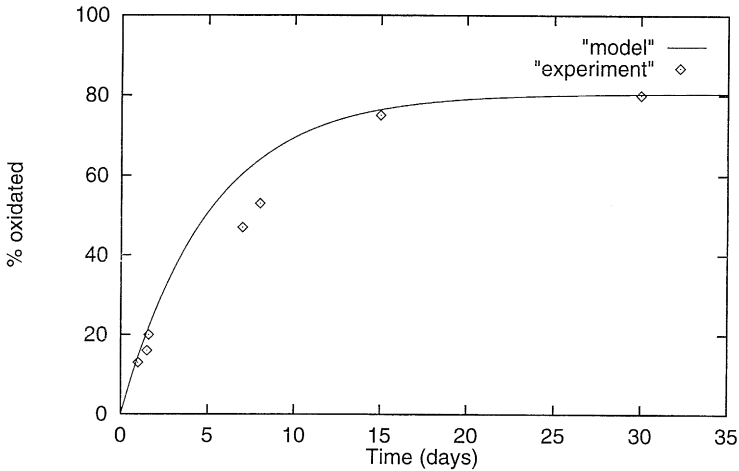

Fig. 1. Percentage of oxidized Pu as a function of time from the experiments of Boust et al. (1996) (points) and the result from numerical fitting to Eq. (3) (line).

β_1 and β_2 can be obtained from numerical fitting of Eq. (3) to the experimental points presented in Fig. 1. If numerical fitting is carried out, the following reaction velocities are obtained:

$$\beta_1 = 1.85 \times 10^{-6} \, s^{-1},$$

$$\beta_2 = 4.48 \times 10^{-7} \, s^{-1}.$$

The numerical fitting to Eq. (3) is also represented in Fig. 1 as the solid line. It can be seen that the oxidation reaction is almost completed within 15–20 d: 80% of Pu has been converted to the oxidized form.

It must be pointed out that redox reactions occur in the three phases considered in the model: water, suspended matter and bottom sediments. It is assumed that reaction velocities in suspended matter and sediments are the same as in water, which is a simplification since reduction/oxidation conditions may be different in the three phases. Of course, this can lead to discrepancies between model predictions and observations, as will be seen. However, our main objective is to present the model formulation and some preliminary results. The model can be further refined as β_1 and β_2 are better known in the other phases from observations and laboratory experiments. On the other hand, environmental conditions such as light and temperature affect the reaction velocities, which is not considered in the model. Thus, the model sensitivity to changes in β_1 and β_2 has to be studied (see Section 4) due to the uncertainty in their values.

2.2. Hydrodynamics

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

$$\sigma = \frac{(z + \zeta)}{(h + \zeta)} \tag{4}$$

where h is the undisturbed depth of water, ζ is the sea surface displacement from the mean level due to tidal oscillations measured upwards from the undisturbed level and the z coordinate is measured from mean sea level to the bottom. The form of the equations, for a homogeneous sea, in σ coordinates has been given previously (Davies, 1985a) and will not be repeated here. Details of the boundary conditions applied at the sea surface and the sea bottom can be seen in Periáñez (1998a): 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 realistic results are obtained although wind is not included, as will be seen. A linear law for bottom friction has been adopted. Although a quadratic formulation of bottom friction is now more extensively used than the linear law, the latter has been adopted since the tidal regime becomes established faster. Also, there are no appreciable differences in the

dispersion patterns (for dissolved radionuclides) obtained when the hydrodynamic model is calibrated using linear or quadratic friction (Periáñez, 1998a).

A flow-dependent eddy viscosity has been used in the model. This formulation gives good results for tidal flow studies (Jones & Davies, 1996; Davies & Lawrence, 1994; Davies, Kwong & Flather, 1997):

$$N = C_N\sqrt{\bar{u}^2 + \bar{v}^2}h \tag{5}$$

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

2.3. Suspended matter dynamics

The three dimensional equation for suspended matter has been obtained by transforming the equation proposed by Nicholson and O'Connor (1986) into σ coordinates. Details can be seen in Periáñez (in press). Such an equation includes advective-diffusive transport plus vertical fall (settling) of particles. Erosion and sedimentation are incorporated into the sea-bed boundary condition of the equation. Erosion and deposition have been formulated in terms of threshold velocities in such a way that there is erosion only if the sea-bed water velocity is larger that the erosion threshold. Otherwise the erosion term is set to zero. Similarly, there is deposition only if the sea-bed water velocity is smaller than the deposition threshold velocity. Otherwise the deposition term is set to zero.

As usual in suspended matter studies, it is considered that only particles with a diameter $< 62.5\,\mu m$ can remain in the water column as suspended matter, since larger particles will sink rapidly to the bottom and, as a consequence, their horizontal movement is negligible (Belderson, 1964; Clarke, 1995; Periáñez, Abril, & García-León, 1996c). Indeed, Eisma (1981) has pointed out that for all practical purposes muds can be regarded as synonymous with suspended matter.

A standard formula to represent the increase in the settling velocity as the suspended matter concentration increases has been used in the model (Pejrup, 1988; Mehta, 1989; Clarke, 1995; Periáñez, in press). 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 (in press).

2.4. Radionuclide dispersion

The model considers that radionuclides can be present in three phases: solution, suspended matter and active bottom sediments (as denoted by Benes, Cernik & Slavik, 1994), that consist of particles with a diameter $< 62.5\,\mu m$. In each phase, Pu can exist in two oxidation states: reduced and oxidized Pu. Reduction and oxidation processes (that occur in each of the three phases) are governed by the reaction velocities, that were presented above. The transfer of Pu from the solid phase to solution is governed by a kinetic transfer coefficient k_2 and the inverse process by

a kinetic transfer coefficient k_1. However, these coefficients will be different for oxidized and reduced Pu. Thus, the model solves six equations whose solution gives the time evolution of the concentration of reduced and oxidized Pu in water, suspended matter and bottom sediments.

It is known that actinide adsorption tends to be a surface phenomenon (Ramsay & Raw, 1987) and will depend on the surface of particles per water volume unit into each grid cell. This quantity has been denoted as the exchange surface (Periáñez et al., 1996a; Periáñez & Martínez-Aguirre, 1997a). Thus (Periáñez et al., 1996a):

$$k_1 = \chi_1(S_m + S_s) = k_{11} + k_{12} \tag{6}$$

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

$$S_m = 3m/\rho R \tag{7}$$

$$S_s = 3L\phi/R \, \Delta\sigma \, H \tag{8}$$

where m is the suspended matter concentration, ρ is the suspended matter particle density, R is the mean radius of the suspended matter and active sediment particles, $H = h + \zeta$ is the total water depth, L is the average mixing depth (the distance to which the dissolved phase penetrates the sediment), $\Delta\sigma$ is the spacing in the vertical direction and ϕ is a correction factor that takes into account the fact that not all the mass of the sediment is in contact with the water. This description of the transfer of radionuclides between the dissolved and solid phase has been used successfully in previous modelling works (Periáñez et al., 1996b; Periáñez & Martínez-Aguirre, 1997a,b, Martínez-Aguirre & Periáñez, 1998).

The equations that give the three dimensional dispersion of Pu, including advection, diffusion, settling and deposition of suspended matter, erosion of the sediment and transfers between the liquid and solid phase, presented in Periáñez (in press), have been modified to take into account the fact that Pu can exist in reduced and oxidized forms. Thus, instead of three equations six must be solved. The form of the six equations is summarized in the Appendix.

2.5. 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 (Davies, 1985b). 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 & 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 of 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 & 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 (1998a,b) has been adopted:

$$C_i = \psi C_{i-1} \tag{9}$$

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 non-dimensional value $\psi = 0.9$ is obtained from a calibration exercise (Periáñez, 1998a,b).

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.

3. Model application and results

The model domain is presented in Fig. 2, where the location of Sellafield nuclear fuel reprocessing plant is also shown. The model's horizontal resolution is $\Delta x = \Delta y = 5000$ m. Ten layers are used in the vertical, thus $\Delta \sigma = 0.1$, and the time step is fixed as $\Delta t = 60$ s. Water depths are introduced from bathymetric maps and range from 55 m in the west to a shallower area along the British coast.

The values given to all the parameters involved in the model are presented in detail in Periáñez (in press). 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, Smith and Camplin (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 with particles in a reduced form.

The values of the kinetic transfer coefficient k_2 and the exchange velocity X_1 for the reduced and oxidized Pu must be given. Nyffeler, Li and Santschi (1984) measured k_2 for a wide set of chemical elements and found a very small variation (an order of magnitude), even for elements with a very different geochemical behaviour. Thus, it has been considered that k_2 has the same value for reduced and oxidized Pu. It has been assumed that $k_2 = 1.16 \times 10^{-5}$ s^{-1}, the value that has been obtained by Nyffeler et al. (1984) for Cs and Cd. This value of k_2 has given good results in previous modelling work when it has been used for Ra, U, Th, Cs and Pu (Periáñez et al., 1996b; Periáñez & Martínez-Aguirre, 1997a; Periáñez, 1998c, in press). The exchange velocity can be estimated from k_2 and the distribution coefficient, k_d, since the following
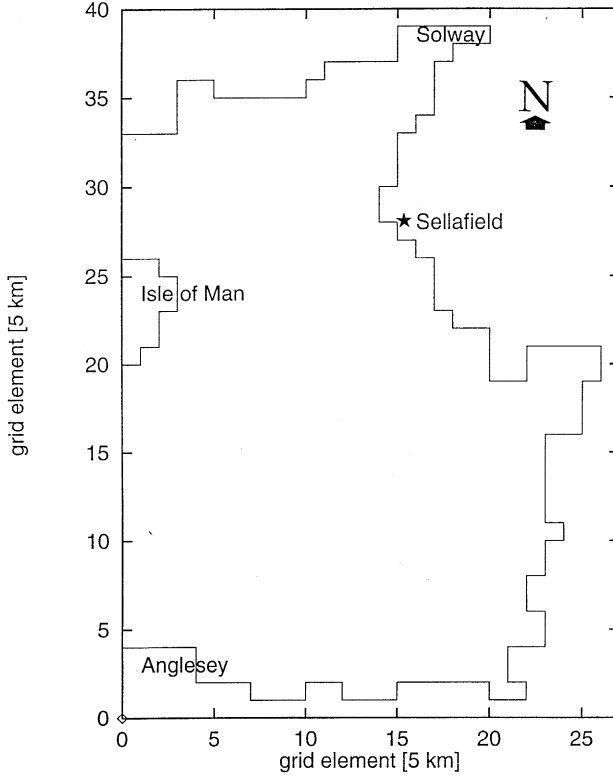
Fig. 2. Model domain. Each unit in the x and y axis is 5000 m (grid element number). The star is the Sellafield nuclear fuel reprocessing plant.

relation holds (Periáñez et al., 1996b):

$$k_d = \frac{\chi_1}{k_2} \frac{3}{\rho R}.$$

(10)

Measured total Pu k_d's in the eastern Irish Sea are of the order of $10^5 \, \mathrm{l \, kg^{-1}}$ (McKay & Walker, 1990; Mitchell et al., 1995), in agreement with the value recommended by IAEA (1985): $1.0 \times 10^5 \, \mathrm{l \, kg^{-1}}$. However, the Pu oxidation state has been shown to have a major influence on the k_d value, being of the order of 10^6 and $10^4 \, \mathrm{l \, kg^{-1}}$ for the reduced and oxidized Pu respectively (Nelson and Lovett, 1978). The same variations have been observed in the Irish Sea (Mitchell et al., 1995). Thus, it has been considered that k_d is 1.0×10^6 and $1.0 \times 10^4 \, \mathrm{l \, kg^{-1}}$ for the reduced and oxidized Pu respectively. From Eq. (10), the exchange velocities for reduced and oxidized Pu are:

$$\chi_1^{\mathrm{red}} = 1.51 \times 10^{-4} \, \mathrm{m \, s^{-1}},$$
$$\chi_1^{\mathrm{ox}} = 1.51 \times 10^{-6} \, \mathrm{m \, s^{-1}}.$$

To obtain these values, it has been taken that $R = 15\ \mu m$ and $\rho = 2600\ kg\ m^{-3}$ (Periáñez et al., 1996b; Periáñez, in press). 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. (6)–(8).

A numerical experiment has been carried out to test the values of the transfer coefficients and the reaction velocities. Let us consider a volume of sea water that contains a certain concentration of suspended matter particles (1 ppm, which is a typical value for the Irish Sea). A known amount of Pu, associated with suspended matter, in a reduced chemical form is added. The four differential equations whose solutions give the temporal evolution of Pu concentrations in water and suspended matter (in both reduced and oxidized forms in each phase) are integrated numerically. These equations include redox reactions in water and suspended matter and transfers of reduced and oxidized Pu between water and suspended matter (they are Eqs. (A1)–(A4) in the Appendix if terms involving advection, diffusion, settling, erosion, deposition and transfers with sediments are removed). The result is presented in Fig. 3, where the time evolution of the % of Pu in reduced and oxidized forms (in both water and suspended matter) is given. It can be seen that equilibrium is reached after some 20 d, as has been reported by other authors (Boust et al., 1996). After 35 d, the amount of Pu associated with solid particles (reduced plus oxidized) is 11.4%. Molero, Sanchez-Cabeza, Merino, Vives i Batlle, Mitchell and Vidal-Cuadras (1995) found that 11% of the total Pu concentration is absorbed onto suspended matter in the Mediterranean Sea. Livingston and Bowen (1977) showed that 30% of Pu was fixed to suspended particles in Atlantic waters. Mitchell, Vives i Batlle, Ryan, Schell,
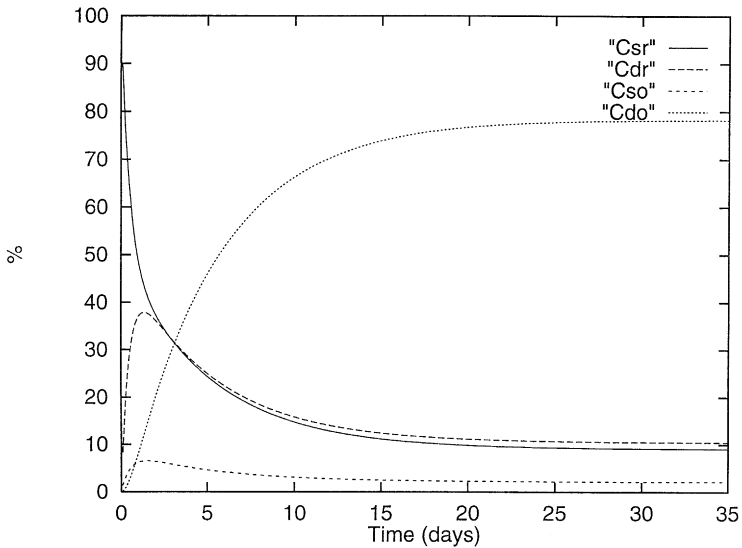

Fig. 3. Temporal evolution of the percentages of reduced Pu in solution and suspended matter, Cdr and Csr, and oxidized Pu in water and suspended matter, Cdo and Cso.

Sanchez-Cabeza and Vidal-Cuadras (1991) observed that 2–15% of Pu in the Irish Sea is associated with particles. 88% of Pu in the dissolved phase is in oxidized form a value that is in agreement with measurements: Mitchell et al. (1995) states that the percentage of oxidized Pu in water is 74–94%. k_d distribution coefficients can also be calculated from the results of the numerical experiment. Thus, the k_d for total Pu (oxidized plus reduced) is $1.3 \times 10^5 \, \text{l} \, \text{kg}^{-1}$, in agreement with IAEA (1985) and measurements in the Irish Sea (McKay & Walker, 1990; Mitchell et al., 1995). The k_d of the reduced Pu is $0.87 \times 10^6 \, \text{l} \, \text{kg}^{-1}$ also in agreement with Mitchell et al. (1995) who obtained $(3 \pm 2) \times 10^6 \, \text{l} \, \text{kg}^{-1}$ and with Nelson and Lovett (1978), who found a k_d of $1 \times 10^6 \, \text{l} \, \text{kg}^{-1}$. In the case of oxidized Pu, the computed k_d is $2.8 \times 10^4 \, \text{l} \, \text{kg}^{-1}$. Nelson and Lovett (1978) indicated that the k_d of oxidized Pu is less than $1 \times 10^4 \, \text{l} \, \text{kg}^{-1}$ and Mitchell et al. (1995) obtained $2.5 \times 10^3 \, \text{l} \, \text{kg}^{-1}$. Thus, it seems that a set of realistic parameters has been obtained.

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 (1998a) 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, in press). Computed sedimentation rates are also in agreement with historically deduced net sedimentation rates (Periáñez, in press).

The 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 occurring since the fifties. Thus, instead of starting the model from zero concentrations, we have assumed a uniform background in water, suspended matter and bottom sediments that represent 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. The background magnitude has been selected by a trial and error exercise: $0.01 \, \text{Bq} \, \text{g}^{-1}$ for suspended matter, $0.1 \, \text{Bq} \, \text{g}^{-1}$ for bottom sediments and $0.05 \, \text{Bq/m}^3$ for water. Discharges from Sellafield are carried out over this background and model results are obtained after a simulation time of three months. These results are compared with observations.

Observed (Hetherington, 1976) and computed total Pu (reduced plus oxidized) concentrations in surface water for the year 1974 are presented in Figs. 4a and b, respectively. It seems that activity levels are overestimated in the southern part of the model domain. However, as can be deduced from Fig. 4a, there are no observations over the southern Irish Sea. Nevertheless, activity levels over the sea are, in general, well reproduced by the model. The computed % of Pu in solution is presented in Fig. 4c. As expected, most Pu in solution is present in an oxidized form. Only close to the discharge point is some 70% of the dissolved Pu in a reduced form, which is due to the nature of the discharges. As has been commented on above, all the Pu is released in
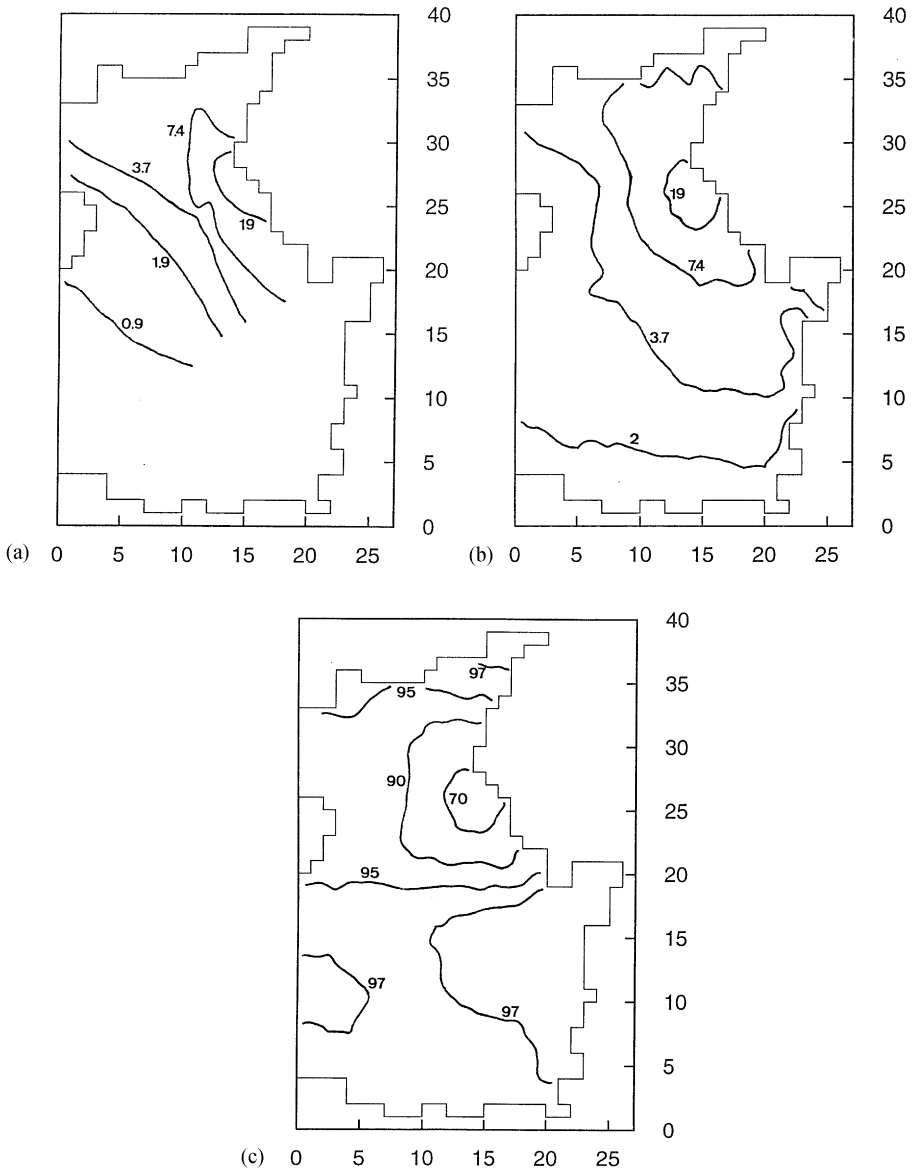
Fig. 4. Distribution of Pu (Bq m^{-3}) in surface water for the year 1974: (a) measured, (b) computed, (c) computed % of oxidized Pu.

a reduced form. Oxidation takes place after the release and over 90% of the Pu is then in an oxidized form in agreement with observations, as discussed above (Mitchell et al., 1995). Also, no significant changes in the speciation of Pu throughout the sea have been obtained.

The computed total Pu specific activity in surface suspended matter is presented in Fig. 5a. Unfortunately, there are no measurements to compare with. The computed % 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 for water (Fig. 4b), although it seems 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 form 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 less soluble than oxidized Pu. Only in a region in the southeastern sea is some 40% of Pu present in suspended matter in an oxidized form (see Fig. 5b). With the exception of this region and the vicinity of the discharge point, where most Pu is reduced (due to the nature of the discharges), the speciation of Pu in suspended matter remains rather uniform, 25–35% of Pu being in oxidized form. Thus, the model is overestimating the fraction of oxidized Pu since Mitchell et al. (1995) found that almost all the plutonium in suspended matter (some 97%) is in a reduced form. This may be due to the simple model that has been adopted for the redox reaction, as has been discussed above (see Section 2.1).

Observed (Pentreath, 1985) and computed total Pu distributions in surface water for year 1979 are presented in Figs. 6a and b, respectively. Again, it seems that the model overestimates the Pu concentrations in the southern part of the sea. However, realistic activity levels and shapes of isolines are, in general, given by the model.

Total Pu concentrations in sediments for year 1977 are shown in Fig. 7a (observed; Pentreath, 1985) and Fig. 7b (computed). Good agreement between measured and computed activity levels has been obtained. Percentage of reduced Pu in the sediment is presented in Fig. 7c. The maximum percentage of reduced Pu is 33%. Thus, most Pu in the sediment is in an oxidized form, while in suspended matter Pu is mainly in a reduced form. It is possible that Pu is incorporated into the sediment mainly from water, where most Pu is present in an oxidized form, but this result again may be due to the simple formulation of the redox reactions (different values of β_1 and β_2 should be used in the sediment due to the fact that reduction/oxidation conditions are different than in the water column).

Boust et al. (1996) measured ^{239,240}Pu concentrations in surface water, surface suspended matter and bottom sediments at different distances southwest and north-west from Sellafield in the course of research expeditions carried out in the period 1989–94. Experimental and model results are compared in Fig. 8a (water), Fig. 8b (suspended matter) and Fig. 8c (bottom sediments). Lines represent specific activity profiles following the directions of the sampling of Boust et al. (1996). It can be seen that, in general, activity levels are reproduced by the model in the three phases.

Computed distribution coefficients for total, reduced and oxidized Pu are given in Figs. 9a, b and c, respectively. In the case of total Pu, computed k_d's are, in most of the sea, of the order of $10^5 \, l \, kg^{-1}$, in agreement with the measurements of McKay and Walker (1990), Mitchell et al. (1995) and the recommended value of IAEA (1985). It can also be observed that k_ds diminish with increasing distance from Sellafield. This effect was also obtained from observations (Mitchell et al., 1985) and was attributed to
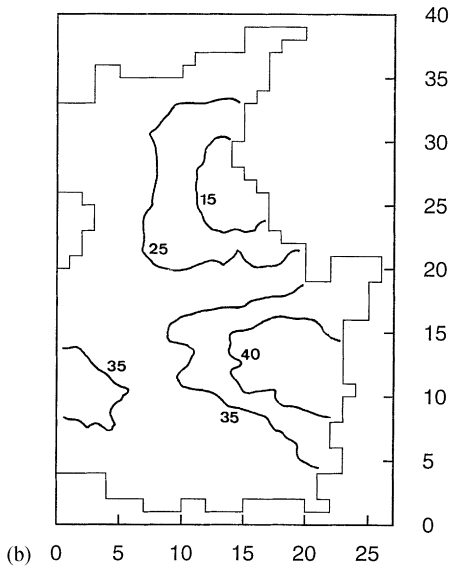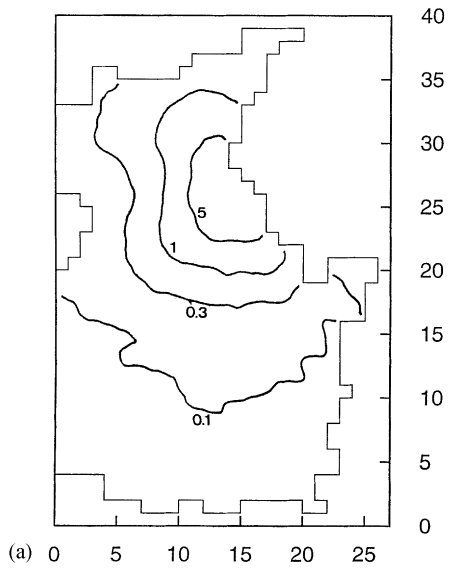
Fig. 5. Distribution of Pu in surface suspended matter (Bq g^{-1}) for the year 1974: (a) computed concentration, (b) computed % of oxidized Pu.
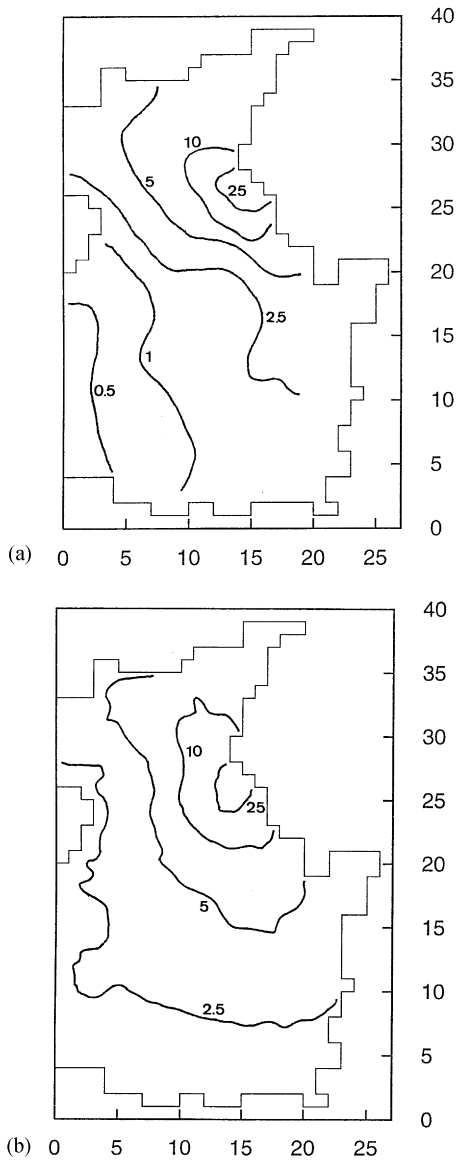
Fig. 6. Distribution of Pu (Bq m^{-3}) in surface water for year 1979: (a) measured, (b) computed.

the nature of the discharges, since almost all the Pu in the releases is associated with suspended particles (Mitchell et al., 1985; Periáñez, in press) and no significant changes in the speciation of Pu between oxidized and reduced forms over the sea have been found, as commented on above. The computed k_d's for oxidized Pu are of the order of $10^4 \, \mathrm{l \, kg^{-1}}$, a value that, as shown above, is slightly higher than that found in
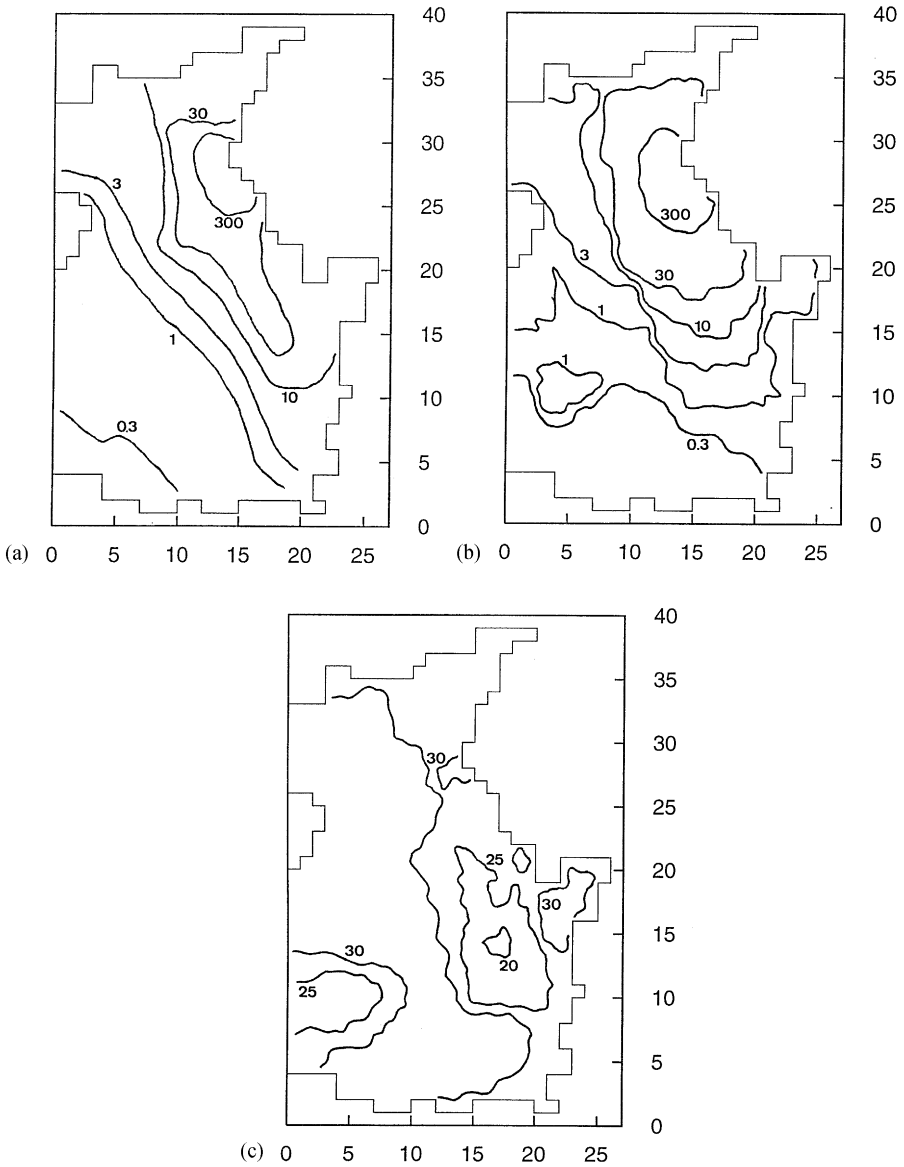
Fig. 7. Distribution of Pu (kBq m^{-2}) in bottom sediments for the year 1977: (a) measured, (b) computed, (c) computed % of reduced Pu.

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^{-1}, in agreement with the findings of Mitchell et al. (1995) and Nelson and Lovett (1978) (see above).
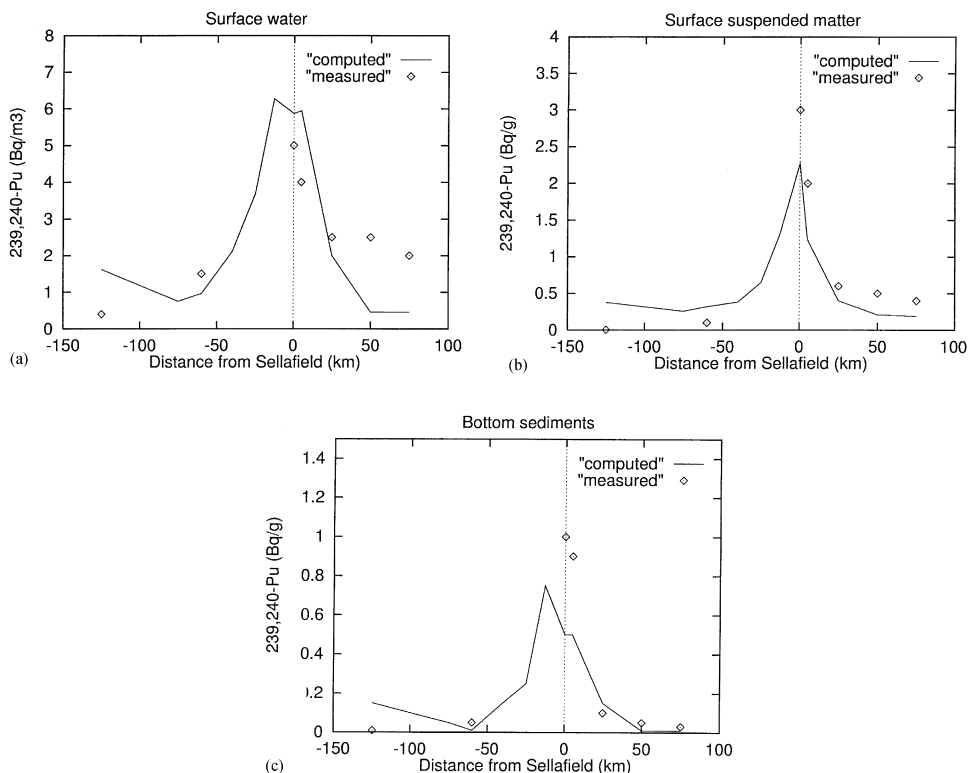
Fig. 8. Measured and computed ^{239,240}Pu specific activities in water (a) suspended matter (b) and bottom sediments (c) northwest (positive distances) and southwest (negative distances) from Sellafield.

It should also be commented that, since the model formulation is three dimensional, it can be applied to study vertical variations of parameters like radionuclide concentrations in water and suspended matter and distribution coefficients. Discussion of this point can be found in Periáñez (in press) and will not be repeated here.

4. Model sensitivity to β_1 and β_2

The model sensitivity to the choice of boundary conditions for the dispersion equations, diffusion coefficients, parameters involved in the suspended matter sub-model, kinetic transfer coefficient k_2 and exchange velocity χ_1 has already been studied (Periáñez, in press). Results will not be repeated here.

The model sensitivity to changes in reaction velocities has been investigated due to the uncertainties associated with these parameters. The numerical experiment described in Section 3 has been repeated for different values of β_1 and β_2. The results are summarized in Table 1, where the percentage of Pu fixed to the solid matter, the
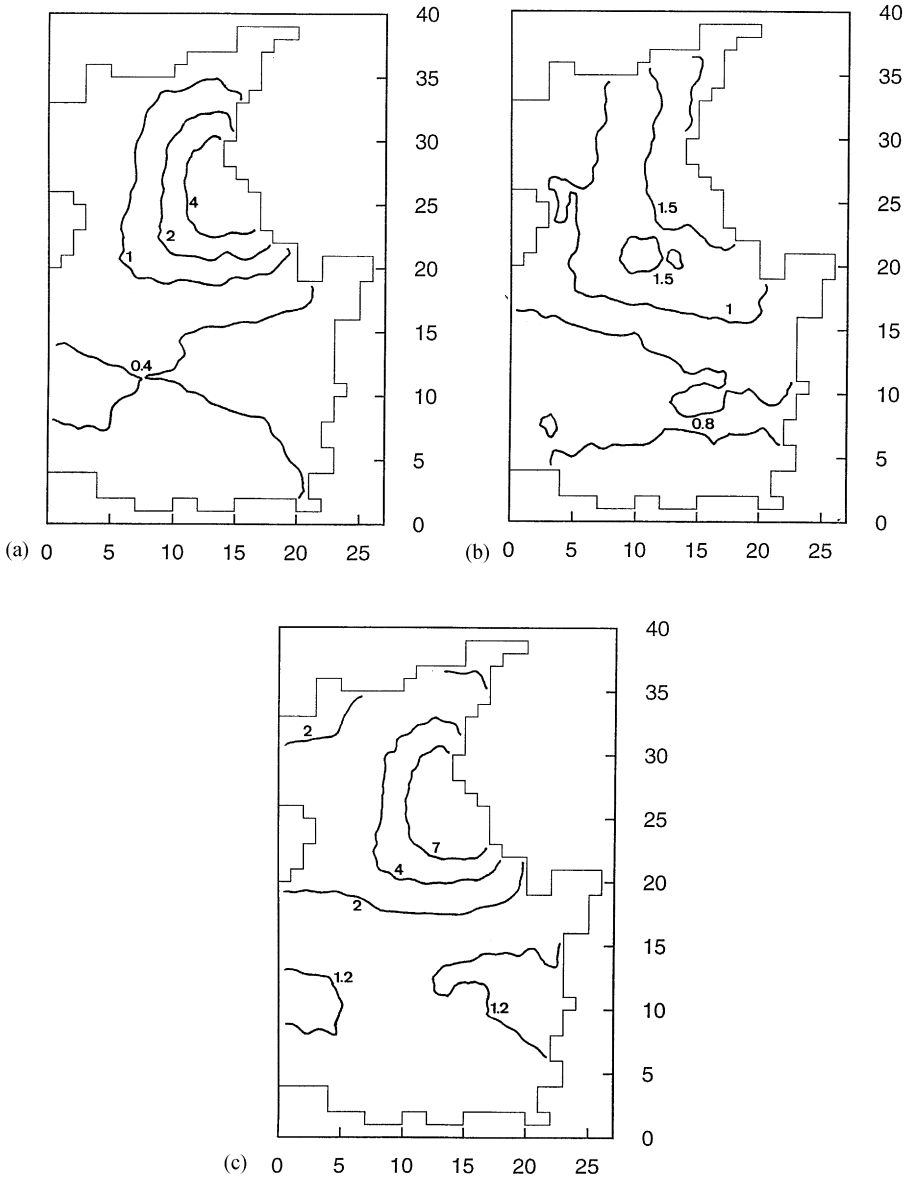
Fig. 9. Computed distribution coefficients $(L\,kg^{-1})$: (a) total Pu $(\times 10^5)$, (b) reduced Pu $(\times 10^6)$, (c) oxidized Pu$(\times 10^4)$.

percentage of oxidized Pu in the water and the percentage of reduced Pu in the suspended matter are given together with the values of β_1 and β_2 in each experiment. Experiment 1 is carried out with the parameters used in the model (experiment presented in Section 3). It can be seen that %ox is in agreement with measurements

Table 1
Model sensitivity to the reaction velocities.

Experiment	β_1 (s^{-1})	β_2 (s^{-1})	% solid	% ox	% red
1	1.85×10^{-6}	4.48×10^{-7}	11.4	88.0	81.0
2	3.70×10^{-6}	4.48×10^{-7}	7.0	93.4	67.2
3	3.70×10^{-6}	2.24×10^{-7}	4.17	96.6	59.5
4	1.85×10^{-6}	8.96×10^{-7}	18.1	78.7	84.2
5	1.85×10^{-6}	1.34×10^{-6}	23.0	70.9	85.6
6	9.25×10^{-7}	8.96×10^{-7}	26.1	65.4	91.5
7	9.25×10^{-7}	1.34×10^{-6}	31.1	55.6	92.2
8	6.17×10^{-7}	1.34×10^{-6}	35.5	45.4	94.8

% solid is the percentage of Pu associated with suspended matter after 35 d, %ox is the percentage of oxidized Pu in solution and %red is the percentage of reduced Pu in suspended matter.

(Mitchell et al., 1995), but %red is slightly low when compared with observations (Mitchell et al., 1995). In experiments 2 and 3 oxidation is enhanced by increasing β_1 (experiment 2) or increasing β_1 and simultaneously decreasing β_2 (experiment 3). In these cases, %ox is still in agreement with observations but too low values for %red occur. In experiments 4–8 reduction is enhanced by increasing β_2 or by simultaneously increasing β_2 and decreasing β_1. As reduction increases %red shifts to values closer to observations, but too low values for %ox are obtained (see experiment 8). Thus, changes in β_1 and β_2 due to changes in environmental conditions may affect the distribution of Pu between oxidized and reduced forms. If these variations in reaction velocities and also different values for them in water, suspended matter and bottom sediments are included in the model, results would probably be improved (in particular the Pu distribution between reduced and oxidized forms in suspended matter and bottom sediments).

5. Conclusions

A numerical model that simulates the physico-chemical speciation of Pu in the eastern Irish Sea has been developed. The model simultaneously solves the hydrodynamic equations, the suspended matter equation and six equations whose solution gives the temporal evolution of reduced and oxidized Pu concentrations in water, suspended matter and bottom sediments. Reduction and oxidation reactions are described in terms of the reaction velocities, which have been deduced from laboratory experiments. The transfer of radionuclides between water and the solid phase is described in terms of kinetic transfer coefficients, which have different values for reduced and oxidized Pu.

In general, the observed and computed Pu distributions in water and bottom sediments are in agreement. It has been obtained that most Pu in solution is in oxidized form. Also, the Pu distribution between reduced and oxidized forms, in

solution, remains rather uniform over the sea, which is in agreement with previous measurements. On the other hand, Pu in suspended matter is mainly in a reduced form, although in a percentage that is lower than observations. Also, it has been found that most Pu in the sediment is in an oxidized form. These two results may be a consequence of the simple model that has been used to describe redox reactions, since probably reaction velocities in the sediment should be different to these in the water column.

Computed distribution coefficients for reduced, oxidized and total Pu are, in general, in agreement with observations. A decrease in the total k_d with increasing distance from the Sellafield discharge point has been obtained, which is in agreement with previous observations.

Acknowledgements

Appendix A

A.1. Dissolved phase

The equation that gives the temporal evolution of oxidized Pu in solution, C_d^{ox} (Bq m^{-3}), is

$$\frac{\partial C_d^{ox}}{\partial t} = (\text{adv} + \text{dif})_{3D} - (k_{11}^{ox} + \pi k_{12}^{ox})C_d^{ox} + k_2\left(mC_s^{ox} + \pi\frac{A_s^{ox}L\rho_m f\phi}{\Delta\sigma H} \times 10^3\right)$$
$$- \lambda C_d^{ox} + \beta_1 C_d^{red} - \beta_2 C_d^{ox} \tag{A.1}$$

where $(\text{adv} + \text{dif})_{3D}$ 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, both in Bq g^{-1}. The sediment bulk density, ρ_m, is expressed in kg m^{-3} and λ is the radioactive decay constant. f gives the fraction of active sediments. 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} (Bq m^{-3}):

$$\frac{\partial C_d^{red}}{\partial t} = (\text{adv} + \text{dif})_{3D} - (k_{11}^{red} + \pi k_{12}^{red})C_d^{red} + k_2\left(mC_s^{red} + \pi\frac{A_s^{red}L\rho_m f\phi}{\Delta\sigma H} \times 10^3\right)$$
$$- \lambda C_d^{red} + \beta_2 C_d^{ox} - \beta_1 C_d^{red} \tag{A.2}$$

with obvious meanings for the notation.

A.2. Suspended matter

In the case of oxidized Pu, C_s^{ox} (Bq g^{-1}):

$$\frac{\partial(mC_s^{ox})}{\partial t} = (\text{adv} + \text{dif})_{3D} - \text{sett}^{ox} + \pi(\text{res}^{ox} - \text{dep}^{ox}) + k_{11}^{ox}C_d^{ox} - k_2mC_s^{ox}$$

$$- \lambda mC_s^{ox} + m(\beta_1 C_s^{red} - \beta_2 C_s^{ox}) \tag{A.3}$$

where m is the suspended matter concentration in g m^{-3} and sett, res and dep means settling, resuspension and erosion (see Periáñez (in press) for details). The equation for reduced Pu is

$$\frac{\partial(mC_s^{red})}{\partial t} = (\text{adv} + \text{dif})_{3D} - \text{sett}^{red} + \pi(\text{res}^{red} - \text{dep}^{red}) + k_{11}^{red}C_d^{red} - k_2mC_s^{red}$$

$$- \lambda mC_s^{red} + m(\beta_2 C_s^{ox} - \beta_1 C_s^{red}) \tag{A.4}$$

A.3. Active bottom sediments

Oxidized Pu:

$$\frac{\partial A_s^{ox}}{\partial t} = k_{12}^{ox}\frac{C_d^{ox}(b)H\,\Delta\sigma}{L\rho_m f} \times 10^{-3} - k_2 A_s^{ox}\phi$$

$$+ (\text{dep}^{ox} - \text{res}^{ox}) - \lambda A_s^{ox} + \beta_1 A_s^{red} - \beta_2 A_s^{ox} \tag{A.5}$$

where (d) means that this parameter must be evaluated at the deepest water layer (in contact with the sediment). dep and res means deposition and resuspension (see Periáñez (in press) for details).

Reduced Pu:

$$\frac{\partial A_s^{red}}{\partial t} = k_{12}^{red}\frac{C_d^{red}(b)H\,\Delta\sigma}{L\rho_m f} \times 10^{-3} - k_2 A_s^{red}\phi$$

$$+ (\text{dep}^{red} - \text{res}^{red}) - \lambda A_s^{red} + \beta_2 A_s^{ox} - \beta_1 A_s^{red}. \tag{A.6}$$

The total activity (reduced plus oxidized) in the sediment (active plus non active) can be obtained as

$$A = f(A_s^{ox} + A_s^{red}). \tag{A.7}$$

A.4. Distribution coefficients

Oxidized Pu:

$$k_d^{ox} = \frac{C_s^{ox}}{C_d^{ox}} \tag{A.8}$$

Reduced Pu:

$$k_d^{\text{red}} = \frac{C_s^{\text{red}}}{C_d^{\text{red}}} \qquad\qquad (A.9)$$

Total k_{d}:

$$k_{\text{d}} = \frac{(C_s^{\text{ox}} + C_s^{\text{red}})}{(C_d^{\text{ox}} + C_d^{\text{red}})}. \qquad\qquad (A.10)$$

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