

Testing the behaviour of different kinetic models for uptake/release of radionuclides between water and sediments when implemented in a marine dispersion model

R. Perriáñez *

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

Abstract

Three kinetic models for adsorption/release of ^{137}Cs between water and sediments have been tested when they are included in a previously validated dispersion model of the English Channel. Radionuclides are released to the Channel from La Hague nuclear fuel reprocessing plant (France). The kinetic models are a 1-step model consisting of a single reversible reaction, a 2-step model consisting of two consecutive reversible reactions and an irreversible model consisting of three parallel reactions: two reversible and one irreversible. The models have been tested under three typical situations that correspond to the source terms that can generally be found: instantaneous release, continuous release and redissolution of radionuclides from contaminated sediments. Differences between the models become more evident when contact times between water and sediments are larger (continuous release) and in the case of redissolution from sediments. Time scales for the redissolution process are rather different between the three models. The 1-step model produces a redissolution that is too fast when compared with experimental evidence. The irreversible model requires that saturation effects of the irreversible phase are included. Probably, the 2-step model represents the best compromise between ease and level of detail of the description of sorption/release processes.

Keywords: Kinetic model; Dispersion model; Adsorption; Sediment phase; Caesium; English Channel

* Tel.: +34-954-486-474; fax: +34-954-486-436.

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

1. Introduction

Over the past years there has been an increasing interest in developing numerical models to simulate the dispersion of non-conservative radionuclides in the aquatic environment. The first models (see for instance [Abril and García-León, 1993](#)) were based upon the equilibrium distribution coefficient, which is defined as the ratio of specific activity in the solid phase and specific activity in solution; or the partition coefficient, which gives the fraction of the total activity in a parcel of water that remains dissolved ([Nielsen, 1995](#); [Harms, 1997](#))

$$PC_w = \frac{1}{1 + k_d m} \quad (1)$$

where k_d is the distribution coefficient of the corresponding radionuclide and m is the suspended load concentration. However, if distribution coefficients are used, it is supposed that uptake/release reactions quickly reach an equilibrium ([Duursma and Carroll, 1996](#)). In coastal environments, geochemical, physical and sedimentological processes often occur on time scales that are of the order of one tidal cycle. These rapid coastal processes are likely to influence the outcome of interactions between sediments and contaminated waters. For instance, if contact time between water and sediments in a bay is shorter than the time required by uptake/release reactions to reach equilibrium, the dispersion of dissolved radionuclides will be greater than predicted by these equilibrium models ([Carroll et al., 1997](#)). At the same time, these models will be overestimating the activity fixed to the solid phase. In consequence, a kinetic approach is more adequate than an equilibrium one, to describe the distribution of radionuclides between particles and solution ([Nyffeler et al., 1984](#)). Indeed, more recent dispersion models use the kinetic approach ([Periáñez et al., 1996](#); [Margvelashvily et al., 1997](#); [Aldridge, 1998](#); [Piasecki, 1998](#); [Periáñez, 1999, 2000](#); [Abril and Abdel-Aal, 2000](#)).

Some authors have carried out laboratory experiments to determine kinetic coefficients, or rate constants, governing site-specific uptake/release reactions for several radionuclides. In some experiments (for instance [Laissaoui et al., 1998](#)), it was considered that uptake/release of radionuclides was governed by a single reversible reaction. This assumption is also used in the dispersion models cited above. However, there has also been evidence to suggest that uptake takes place in two stages: fast surface adsorption followed by slow migration of ions to pores and interlattice spacings ([Nyffeler et al., 1984](#); [Turner et al., 1992](#); [Turner and Millward, 1994](#)).

Recently, models involving several consecutive and/or parallel reactions between operationally defined compartments have been proposed by different authors to describe uptake/release reactions ([Benes et al., 1992](#); [Oughton et al., 1997](#); [Børretzen and Salbu, 2000, 2002](#); [El-Mrabet et al., 2001](#); [Ciffroy et al., 2001](#)) for a number of radionuclides (^{60}Co , ^{58}Co , ^{134}Cs , ^{54}Mn , ^{59}Fe , ^{110m}Ag , ^{109}Cd and ^{239}Pu). These models have been proposed to fit sorption and desorption laboratory experiments, so that the corresponding specific rate constants for the sediment and water used in the experiment are obtained. Nevertheless, the different models have not been tested in a real marine dispersion model for non-conservative radionuclides. The objective

of this paper consists of carrying out a comparison of the features of the more generally used kinetic models when they are included in a previously validated dispersion model for radionuclides in the English Channel. Artificial radionuclides are released to the Channel by the nuclear fuel reprocessing plant at Cap de La Hague (France). The behaviour of the models will be tested under three typical situations, which correspond to the types of source terms of radionuclides that generally can be found: an instantaneous release (would simulate a large accidental discharge), a continuous release (simulates chronic discharges due to the usual operation of the plant) and the case in which there are not releases, but the sediment is initially contaminated, so that it behaves as a long-term source of previously released waste radionuclides (this would be the situation after the plant stops its operation). Tested models are a 1-step model consisting of a single reversible reaction, a 2-step model consisting of two consecutive reversible reactions and an irreversible model that consists of three parallel reactions, two reversible and one irreversible. The radionuclide used for the comparisons is ^{137}Cs , which is essentially adsorbed by electrostatic attraction between Cs^+ and the negatively charged particle surfaces, and by cation exchange of Cs^+ with K^+ . Nyffeler et al. (1984) suggested that a 1-step model was appropriate for this radionuclide, although Ciffroy et al. (2001) proposed a 2-step model and Børretzen and Salbu (2002) have recently stated that the most suitable approach for this radionuclide is the irreversible model. The differences between these approaches will be assessed when they are included in a real dispersion model for the marine environment.

^{137}Cs is less particle-reactive than other radionuclides, as for instance Pu-isotopes. Indeed, Boust (1999) has found that most of the ^{137}Cs input to the Channel from Cap de la Hague is evacuated by water circulation. However, it has been selected for comparisons since, as commented above, several kinetic models have been proposed by different authors to reproduce the experiments carried out with Cs. Also, its behaviour is non-conservative enough to suffer a significant sorption onto sediments, the marine dispersion model has been previously validated for this radionuclide and, finally, it does not present other problems like being present in the water column in different oxidation states (as for instance happens with Pu), which simplifies the study.

2. The models

2.1. English Channel dispersion model

The model used for the study has been described and tested before (Periáñez, 2003), so only a few details are given here. It is a two-dimensional long-term dispersion model, thus simulations over several years can be carried out. The model is based upon residual (averaged) circulation obtained from a previously validated tidal model of the Channel (Periáñez and Reguera, 1999). The model domain, showing the residual circulation for average wind conditions, is presented in Fig. 1. The position of Cap de La Hague nuclear fuel reprocessing plant is also indicated in the map.

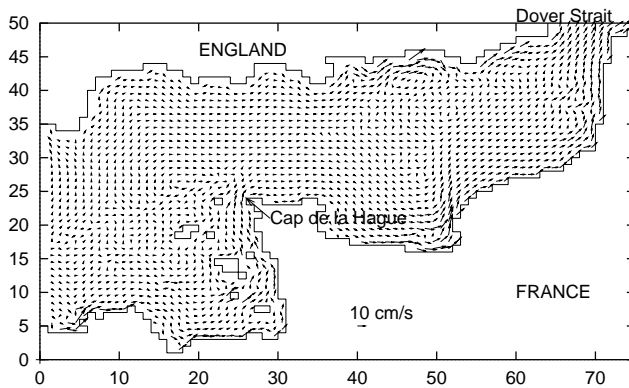


Fig. 1. Residual currents in the model domain for average wind conditions. The position of La Hague reprocessing plant is also shown. Each unit in the x and y axis is 5000 m and corresponds to the coordinates of the grid cells.

The model solves the advective transport of dissolved radionuclides, which is due to the residual current and wind, turbulent diffusion, and exchanges of radionuclides between water and sediments, that will be formulated following the three kinetic models cited above. Initially (Periáñez, 2003) the model included exchanges with suspended matter particles, deposition of suspended particles and erosion of the sediments. These processes that may cause interference have now been *switched off* since we are interested in testing the behaviour of the kinetic models. Moreover, with the exception of deposition and erosion processes, adsorption/release by suspended matter will be governed by the same kind of processes as bottom sediments (however, kinetic rates may be different depending on the suspended matter concentration). Indeed Li et al. (1984) has pointed out that the sediment–water system can be regarded as a high suspended matter environment.

Equations are solved using explicit second-order accuracy finite-difference schemes with appropriate boundary conditions (Periáñez, 2003). The Channel was divided into 3750 grid cells (forming a matrix 75×50). The grid extends from 4.0° W to 1.5° E and from 48.3° to 51.0° N. The grid cell size is $\Delta x = \Delta y = 5000$ m (x and y measured eastward and northward, respectively) and time step is $\Delta t = 3600$ s.

The full model (including suspended matter processes) was initially tested (using a 1-step model to simulate adsorption/desorption) by comparing observed and computed distributions of ^{137}Cs and $^{239,240}\text{Pu}$ over the Channel, as well as evaluating transit times from La Hague to Dover for these radionuclides and comparing them with those derived from measurements. Observed distributions of ^{137}Cs and $^{239,240}\text{Pu}$ were obtained, respectively, from Herrmann et al. (1995) and Boust et al. (1996). The model was also applied to simulate the dispersion of ^{125}Sb and ^{99}Tc . Results were compared with the data of Herrmann et al. (1995). In general, model results (that will not be repeated here) are in agreement with observations for all radionuclides cited above (Periáñez and Reguera, 1999; Periáñez, 2000, 2003). Thus, it

can be considered that the model is giving a good representation of the English Channel. Now the kinetic model will be modified and differences among the three models will be assessed.

2.2. Kinetic models

Uptake of radionuclides by solid particles depends on the specific surface (surface of particles per water volume unit) which is denoted here as the exchange surface (Periáñez et al., 1996). Rates governing the transfer of radionuclides from solution to the solid phase is proportional to the exchange surface

$$k_i = \chi_i S \quad (2)$$

where k_i is the uptake rate for mechanism i , S is the exchange surface and χ_i is the proportionality constant for uptake reaction i , which has the dimensions of a velocity and is denoted here as the exchange velocity. Assuming spherical sediment particles with a mean radius R , it can be written that (Periáñez et al., 1996)

$$S = \frac{3Lf\phi}{RH} \quad (3)$$

where L is the average mixing depth (the distance to which the dissolved phase penetrates the sediment), f gives the fraction of active (muddy) sediments, since the transfer of radionuclides to sediments is essentially due to small particles (see for instance Bird and Evenden, 1994), H is water depth and ϕ is a correction factor that takes into account that not all the surface of sediment particles is in contact with water since it will be partially hidden by other particles. These concepts have been successfully applied in modelling the dispersion of radionuclides in estuarine (Periáñez, 2002a) and marine (Periáñez, 1999, 2000, 2003) environments, and will also be used in this work for the three kinetic models.

2.2.1. 1-Step model

This model considers that exchanges of radionuclides between water and sediments is governed by a first-order reversible reaction, being k_1 and k_2 the forward and backward rates, respectively. k_1 is given by Eqs. (2) and (3), while k_2 is considered constant since the desorption probability must not depend upon the available particle surface. It is implicitly assumed that sediment surfaces may be treated as a single entity, thereby integrating the relative importance of each component of the sediment surface (Nyffeler et al., 1984; Carroll et al., 1997). This approach is also used in all modelling works: rate constants express mean processes of sorption/release that may be running simultaneously with different sites in the particles. The model is represented in Fig. 2.

The equation that gives the time evolution of specific activity in water, C_d (Bq/m^3), is

$$\frac{\partial C_d}{\partial t} = (\text{adv} + \text{dif}) - k_1 C_d + k_2 \frac{A_s L \rho_s f \phi}{H} \quad (4)$$

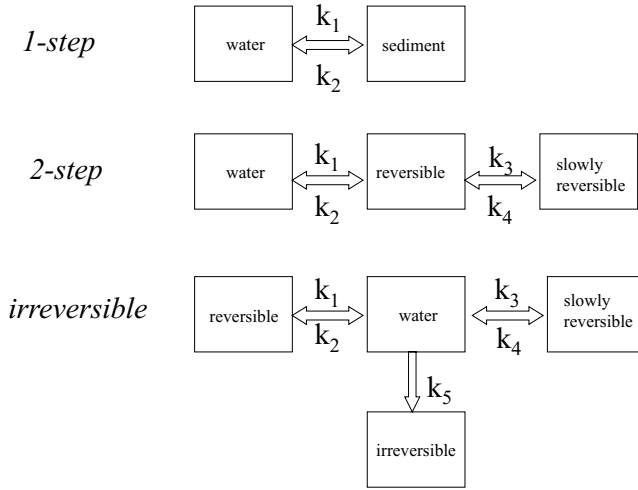


Fig. 2. Kinetic models describing interactions between water and sediments.

where A_s is specific activity (Bq/kg) in the active bottom sediment. Since the model is two-dimensional, it is considered that C_d has a uniform distribution over the water column. The sediment bulk density, ρ_s , is expressed in kg/m^3 and (adv + dif) means advective plus diffusive transport of radionuclides.

The equation for the temporal evolution of specific activity in the active bottom sediment is

$$\frac{\partial A_s}{\partial t} = k_1 \frac{C_d H}{L \rho_s f} - k_2 A_s \phi \quad (5)$$

As commented above, processes involving suspended matter have been removed from the equations. Their full form can be seen in [Periáñez \(2003\)](#).

2.2.2. 2-Step model

This model considers that exchanges are governed by two consecutive reversible reactions ([Fig. 2](#)): surface adsorption is followed by another process that may be a slow diffusion of ions into pores and interlattice spacings, inner complex formation or a transformation such as an oxidation. Thus, sediments are divided in two phases: a reversible and a slowly reversible fraction. This model has been used by [Oughton et al. \(1997\)](#), [Børretzen and Salbu \(2000\)](#) and [Ciffroy et al. \(2001\)](#) to fit their experiments. The model was applied to radioisotopes of Cs, Co, Mn, Fe, Ag and Cd. Earlier evidence of a two-stage sorption also exists ([Nyffeler et al., 1984](#); [Turner et al., 1992](#); [Turner and Millward, 1994](#)). These experiments were carried out with radioisotopes of Cs, Fe, Zn, Be, Mn and Co.

As in the 1-step model, k_1 is given by Eqs. (2) and (3), while the remaining rates are considered constants.

The equation that gives the time evolution of specific activity in water is identical

to Eq. (4) (replacing A_s by A_r , which is specific activity in the reversible fraction). The time evolution of specific activity in the reversible sediment fraction is given by

$$\frac{\partial A_r}{\partial t} = k_1 \frac{C_d H}{L \rho_s f} - k_2 A_r \phi - k_3 A_r + k_4 A_{sr} \quad (6)$$

where A_{sr} is specific activity in the slowly reversible fraction. The equation for its time evolution is written as

$$\frac{\partial A_{sr}}{\partial t} = k_3 A_r - k_4 A_{sr} \quad (7)$$

2.2.3. Irreversible model

According to this model, three types of binding sites are considered: adsorption to surface sites from which radionuclides are generally exchangeable, sorption to wedge sites from which their exchange is limited to ions of similar charge and size and interlattice sites, where radionuclides can be regarded as fixed. The surface sites are considered as reversible binding sites, the wedge sites as slowly reversible binding sites and the interlattice sites as irreversible binding sites (Fig. 2). This model has been recently proposed for Cs by Børretzen and Salbu (2002) and considers that reactions are parallel. Now k_1 , k_3 and k_5 are given by Eqs. (2) and (3) while k_2 and k_4 are considered constants.

The equation for the time evolution of specific activity in the dissolved phase is

$$\frac{\partial C_d}{\partial t} = (\text{adv} + \text{dif}) - (k_1 + k_3 + k_5) C_d + k_2 \frac{A_r L \rho_s f \phi}{H} + k_4 \frac{A_{sr} L \rho_s f \phi}{H} \quad (8)$$

The equations that give the time evolution of specific activity in the three sediment phases are

$$\frac{\partial A_r}{\partial t} = k_1 \frac{C_d H}{L \rho_s f} - k_2 A_r \phi \quad (9)$$

$$\frac{\partial A_{sr}}{\partial t} = k_3 \frac{C_d H}{L \rho_s f} - k_4 A_{sr} \phi \quad (10)$$

$$\frac{\partial A_i}{\partial t} = k_5 \frac{C_d H}{L \rho_s f} \quad (11)$$

for the reversible, slowly reversible and irreversible fractions, respectively. A_i is specific activity in the irreversible sediment fraction.

3. Results and discussion

The values given to parameters involved in the model were presented in Periañez (2000, 2003). In these references a detailed justification of the selections can also be seen, and will not be repeated here. Attention must be paid, however, to the values

given to ^{137}Cs kinetic coefficients in the different models. They are summarized in Table 1. In the case of the 1-step model, χ_1 and k_2 values are those used when the model was calibrated and tested by comparing observed and computed ^{137}Cs distributions (Periáñez, 2000). In the case of the 2-step model, the value given to k_3 is the same that was used when a 2-step model was applied to the Irish Sea (Periáñez, 2002b), since good results are obtained with it. The value is similar to that obtained by El-Mrabet et al. (2001) for marine waters. k_4 is defined as 10 times smaller than k_3 , as suggested by Ciffroy et al. (2001). χ_1 and k_2 are taken as in the 1-step model since they represent fast surface adsorption/release in both 1-step and 2-step models. Børretzen and Salbu (2002) have obtained values for the five kinetic coefficients involved in the irreversible model. However, they cannot be directly used in our model, since they are specific for the experiments. Instead, the ratios between the parameters have been respected. Thus, χ_1/χ_3 in the model must be the same as the ratio k_1/k_3 in experiments of Børretzen and Salbu (2002). Similarly, from ratios k_2/k_4 and χ_1/χ_5 the values of k_4 and χ_5 are obtained, provided that χ_1 and k_2 have the same values as in the 1-step and 2-step models, since they represent equivalent processes. Specific values obtained from experiments carried out with water and sediments collected from the English Channel should ideally be used, although this information is not available in current literature. Nevertheless, the values used in this work seem to be appropriate for carrying out a realistic comparison of the features of the three kinetic models.

As commented before, the three models have been tested under three situations that represent the different environmental sources of radionuclides that can generally be found: instantaneous release, continuous release and redissolution from contaminated sediments.

In the case of an instantaneous release, an input of 5.0×10^{12} Bq was assumed at $t = 0$ at compartment (26, 24) (see Fig. 1), where discharges from La Hague are carried out. Distribution maps obtained 42 days after the discharge with the three models, in water and bottom sediments, are presented in Fig. 3. A patch of radionuclides that moves along the French shore is observed, and bottom sediments are contaminated as the patch of contaminated water travels over them. Transit time from La Hague to Dover, estimated by the cross-correlation function method

Table 1
Kinetic rates used in each model

Rate	Kinetic model		
	1-Step	2-Step	Irreversible
χ_1 (m/s)	2.10×10^{-8}	2.10×10^{-8}	2.10×10^{-8}
k_2 (s $^{-1}$)	1.16×10^{-5}	1.16×10^{-5}	1.16×10^{-5}
k_3 (s $^{-1}$)		1.20×10^{-7}	
k_4 (s $^{-1}$)		1.20×10^{-8}	1.57×10^{-6}
χ_3 (m/s)			1.40×10^{-8}
χ_5 (m/s)			2.05×10^{-9}

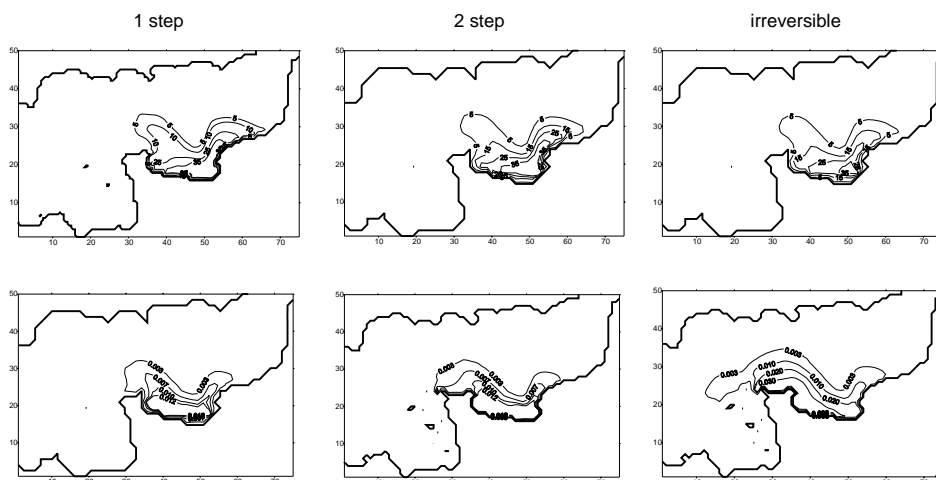


Fig. 3. Distribution of ^{137}Cs in water (Bq/m^3), top line, and sediments (Bq/g), bottom line, computed by the three models 42 days after an instantaneous release from La Hague.

(Periáñez, 2000), is of the order of 3 months, in agreement with the values obtained from observations (Guegueniat et al., 1994) and models (Salomon et al., 1995). It can be seen that in this case the three models give essentially the same concentrations in the dissolved phase, although values obtained with the irreversible model are slightly lower. With respect to bottom sediments, both 1-step and 2-step models again give very similar concentrations. On the other hand, specific activities produced by the irreversible model are about a factor 2 larger than that of the 1-step and 2-step models. In consequence, specific activities in water produced by the irreversible model must be slightly lower. The irreversible model is giving larger activities in bottom sediments since with this model there are three channels, acting simultaneously, transferring radionuclides to the sediment. With the 1-step model, sediments are cleaned, due to a rapid redissolution, after the patch of contaminated water passes by above them, while with the irreversible model they remain permanently contaminated. This can be observed in Fig. 3 since with the irreversible model the contamination in the sediments extends from La Hague to the east. In the case of the 1-step model the contamination of the sediment is restricted to the area covered by the patch of contaminated water. The 2-step model produces an intermediate result: sediments are partially cleaned, more slowly than with the 1-step model.

In the case of a continuous release, it is assumed that $1.4 \times 10^7 \text{ Bq}/\text{s}$ of ^{137}Cs are introduced at compartment (26, 24). Specific activities computed with the three models after 1 year of release are presented in Fig. 4 for water and bottom sediments. The distribution is different to that of the instantaneous release: now a plume of radionuclides extends from La Hague to Dover, showing decreasing activities away from the French shore. This banded structure has been typically observed in the Channel (Guegueniat et al., 1996). Sediments below this plume are also contaminated. The distribution in water is essentially governed by the high input from the

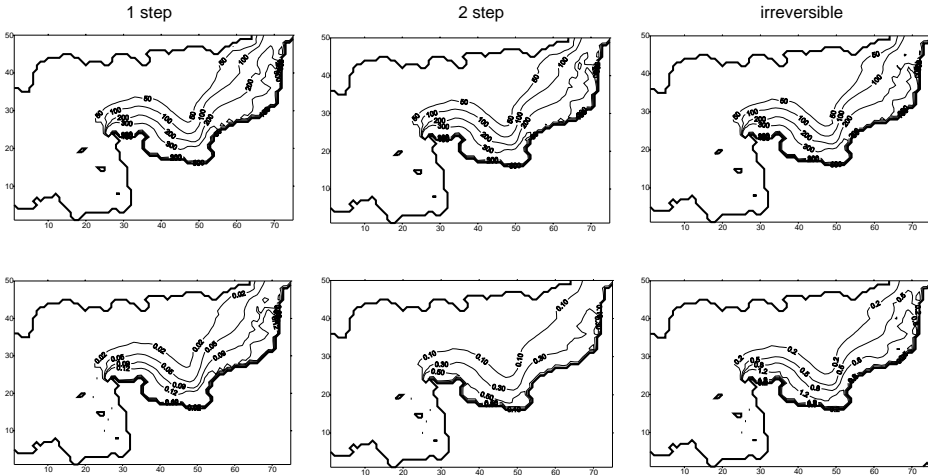


Fig. 4. As Fig. 3, but after 1 year of continuous release.

source and advective transport, thus the three models give essentially the same result for the dissolved phase. However, in the case of bottom sediments results are quite different with the three models. The irreversible model produces the largest concentrations, which as commented above is due to the fact that there are three channels simultaneously transferring radionuclides to the sediment. The 2-step model gives concentrations approximately a factor 2 smaller than those of the irreversible model. On the other hand, the lowest concentrations are produced by the 1-step model (approximately one order of magnitude lower than that of the irreversible model). This is due to the fact, as will be shown below, that the 1-step model produces a high redissolution rate, thus concentrations in the sediment must be shifted to lower values. Differences between the three models become more apparent than in the case of an instantaneous release since contact time between water and sediment is larger now.

To simulate redissolution, an initial specific activity of 10^5 Bq/kg was considered in the active fraction of the bottom sediment (in the slowly reversible fraction in the cases of the 2-step and the irreversible model) in compartment (26, 24), where discharges from La Hague are carried out. Such content implies a total amount of 2.25×10^{13} Bq in the entire compartment. In the rest of the Channel, sediments are assumed to be clean. The distributions of ^{137}Cs in water and sediments after 50 days of redissolution computed by the three models are presented in Fig. 5. The three models are now giving different results for both phases. Generally speaking, due to redissolution, activity goes from the contaminated sediment to the water column above it. Then radionuclides are removed from the area by advective/diffusive processes and they will contaminate initially clean sediments as traced water travels above them. The speed of the redissolution process will govern the distributions obtained in water and bottom sediments as well as activity levels.

The 1-step model produces the quickest redissolution, thus specific activities in

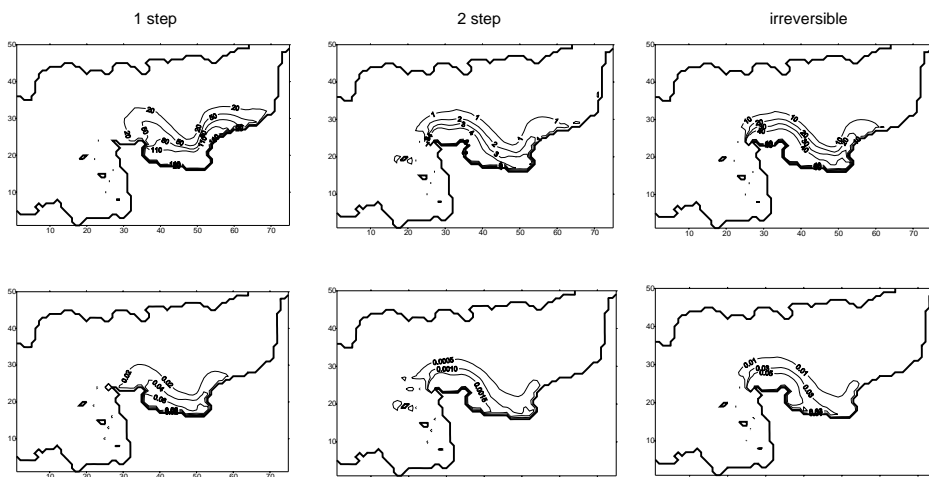


Fig. 5. As Fig. 3, but after 50 days of redissolution of ^{137}Cs from sediments of the area of La Hague.

water are also the highest ones. Since specific activities in water are high, sediments will also be considerably contaminated. Sediment halving time (which is defined as the time in which specific activity in the sediment decreases in a factor of 2 due to redissolution) obtained with the 1-step model is 7.009 ± 0.016 days. Redissolution from the sediment is so fast that its effect can be compared with an instantaneous discharge: in both cases a patch of contaminated water that moves along the French shore is obtained (compare with Fig. 3).

The 2-step and irreversible models produce a slower redissolution. Sediment halving times are 793.3 ± 1.0 days and 51.477 ± 0.004 days with the 2-step and the irreversible models, respectively. It can be seen that the slowest redissolution is produced by the 2-step model. As a consequence, this model also gives the lowest activity levels in water and sediments. Specific activities in water with this model are about a factor of 20 smaller than with the 1-step model. Results from the irreversible model lies between the 1-step and 2-step models: specific activities in water are a factor of 2 smaller than those obtained with the 1-step model. It is interesting to notice that, due to the decrease in the rate of redissolution, with the 2-step and irreversible models sediments are really behaving as a long-term source of waste radionuclides. Indeed, distribution maps are similar to those presented in Fig. 4 for a continuous release: a plume extending from La Hague to the east is obtained. This plume would reach Dover if a longer simulation is carried out.

At this point, the three models are generally giving different results, and it is difficult to decide which can be the most appropriate approach, that is, which is giving the most realistic output. However, redissolution from the sediment produced by the 1-step model seems to be too fast (halving time of some 7 days compared with 51 and 793 days of the 2-step and irreversible models, respectively). In a previous modelling work (Periáñez, 2002b), it was found that the halving time for plutonium in Irish Sea sediments computed with a 1-step model was two orders of

magnitude smaller than that estimated from observations. On the other hand, halving time computed with a 2-step model was of the same order of magnitude as the observed value. Thus, although the 1-step model is the simplest approach, with the advantages that few (just 2) rates are required and that it is computationally cheaper than the other two models, it is not adequate for simulating redissolution of radionuclides from contaminated sediments. Nevertheless, if the model has been designed for decision-making purposes (for instance in the case of an accident) a 1-step approach may be enough, specially if a rapid response is required. Indeed, it can be seen that specific activities in water are essentially the same with the three models in the cases of instantaneous and continuous releases (Figs. 3 and 4), although some differences become apparent for sediments.

A more detailed comparison of the 2-step and the irreversible model has been carried out. The time evolution of specific activities in water and sediment at La Hague (grid cell (26, 24)) in the case of a 1 year redissolution is presented in Figs. 6a and b for the 2-step and the irreversible models, respectively (activity is considered to be initially in the slowly reversible fraction in both models). The time evolution of specific activities in the different sediment fractions is also shown. Both models produce an initial increase of specific activity in water. Activity in water then decreases due to advective/diffusive transport, that removes radionuclides from the area. Activity in the reversible fraction, in the 2-step model, initially increases as radionuclides are transferred from the slowly reversible fraction to the reversible

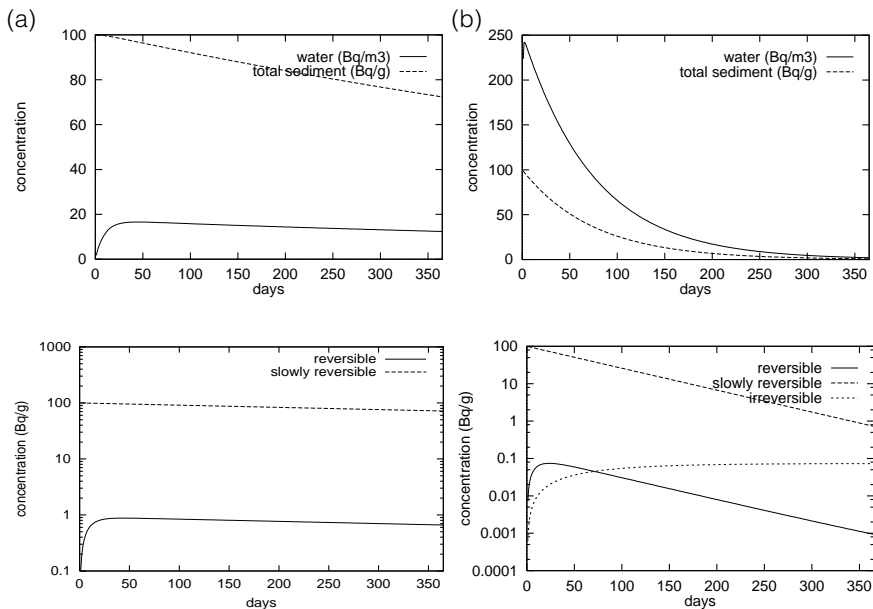


Fig. 6. Time evolution of specific activities in water (Bq/m³) total sediment (Bq/g) and each sediment fraction (Bq/g) during 1 year of redissolution obtained with the 2-step model (a) and with the irreversible model (b) at grid cell (26, 24).

fraction, that with this model is an intermediate step towards redissolution. Afterwards there is a slow decrease as redissolution proceeds. With the irreversible model, activity in the slowly reversible fraction decreases with time as radionuclides are directly redissolved, but there is a partial readsorption by the sediment since concentrations in the reversible and irreversible fractions increase. After some 20 days, activity in the reversible fraction also decreases due to the redissolution process from this phase, but there is a continuous increase in concentration in the irreversible fraction.

Such continuous increase in specific activity in the irreversible fraction can also be clearly observed in the case of a continuous release from La Hague (Fig. 7). Although concentrations in both reversible fractions reach a stationary state, this is not the case with the irreversible fraction. The continuous increase in specific activity of the irreversible fraction constitutes a problem. Indeed, if a closed system is simulated by means of an irreversible model (removing advective and diffusive terms in Eqs. (8) to (11), typical laboratory adsorption/desorption experiments would be simulated), it can be clearly seen from the equations that the only possible steady state is that in which all radionuclides are in the irreversible fraction. This is obviously a non-realistic situation. Although Børretzen and Salbu (2002) could fit their sorption laboratory experiments with this model, experiments were carried out over a relatively short time scale (150 days). If time-integration of the model is continued, it can be seen that after approximately 900 days all the phases (water and both reversible fractions of the sediments) are totally clean of radionuclides, being all the activity present in the irreversible sediment fraction. This effect was already noticed by El-Mrabet et al. (2001). Indeed, after a long contact time, the fraction of occupied sites in the irreversible phase becomes a non-negligible fraction of the total available sites. Thus, saturation has to be considered. This can be easily modelled by introducing a correction factor to the k_5 coefficient (El-Mrabet et al., 2001):

$$k_5 = k_5^0 \left(1 - \frac{A_i}{A_i^{\text{sat}}} \right) \quad (12)$$

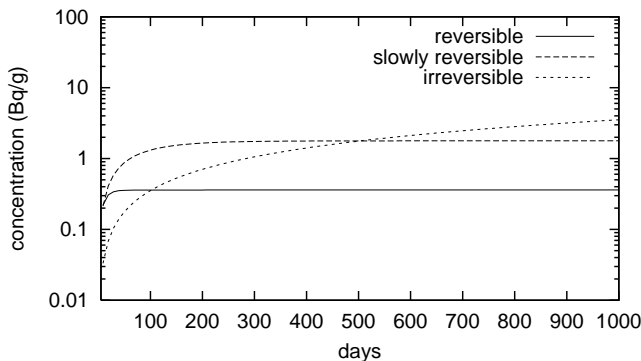


Fig. 7. Time evolution of specific activity in each sediment phase (Bq/g) considered in the irreversible model during 1000 days of continuous release at grid cell (26, 24).

where A_i^{sat} , is the maximum possible concentration in the irreversible fraction, corresponding to all sites occupied and k_5^0 is the kinetic coefficient corresponding to the situation of all sites being unoccupied.

This formulation has been tested taking k_5^0 equal to the value given before for k_5 in the irreversible model without saturation effects (from χ_5 given in Table 1 and Eqs. (2) and (3)) and $A_i^{\text{sat}} = 0.20$ Bq/g, selected after a calibration exercise. It has been observed that, over short time scales (150 days), results of the irreversible model without saturation are reobtained when simulating adsorption and desorption laboratory experiments. The 2-step and the irreversible models (with and without saturation) give very similar results for activities in water and the total sediment (adding all phases considered in each model), although the irreversible model produces a faster variation in the first 10 days. However, the irreversible model produces, as expected, a continuous increase in sediment activity if saturation is not considered. This does not occur if saturation effects are included. In this case, the solutions of the irreversible and the 2-step models stay close to each other: essentially the same steady state is reached with both models.

If saturation is included in the English Channel model, there are no differences with the earlier irreversible model in the cases of instantaneous release and redissolution from the sediment. However, concentrations in the sediments are slightly lower, approaching the 2-step model values, in the case of a continuous release. In this situation water–sediment contact time is larger and thus saturation effects become more evident. Fig. 8 shows the time evolution of specific activities in the irreversible fraction (with and without saturation) at grid cell (26, 24) in a continuous release situation. It can be seen that with saturation effects, a steady concentration is reached in the irreversible fraction, that does not increase continuously now. Indeed, it corresponds to the saturation concentration, which is reached after a time of the order of 200 days.

It is clear that the inclusion of saturation effects avoids the continuous increase of activity in the irreversible fraction. However, it is worth noticing that there are still differences in the outputs of the irreversible and 2-step models when they are

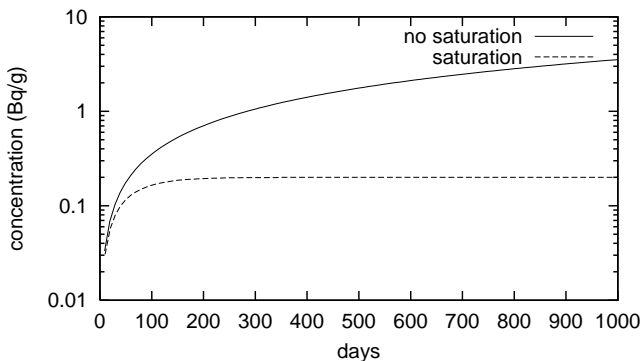


Fig. 8. Time evolution of specific activity (Bq/g) in the irreversible fraction of the sediment during 1 year of release at grid cell (26, 24) with and without saturation effects.

compared in a real situation (English Channel in our case), although their solutions are very similar if they are used to simulate laboratory experiments. It seems that differences between models, that may be rather small in the laboratory, are drastically amplified when they are used in the real marine environment. Major differences appear in the cases of continuous releases, when sediment–water contact times are larger, and in the case of redissolution of radionuclides from a contaminated sediment, when the desorption kinetics is governing the future behaviour of radionuclides.

It is not possible at this moment to give a clear conclusion about which can be the most suitable approach, but the author hopes that this work serves to point out how critical the selection of the kinetic model describing adsorption/release processes is to the model output. Probably, any of the models presented here can reproduce measured concentrations in water and sediments in the marine environment through an appropriate calibration of kinetic coefficients. However, time scales of the processes (for instance redissolution) would still remain very different.

4. Conclusions

Three kinetic models have been incorporated into a real marine dispersion model for radionuclides previously developed and validated for the English Channel. The kinetic models have been tested for ^{137}Cs under three situations that correspond to the types of source terms that can generally be found: instantaneous release, continuous release and redissolution of radionuclides from initially contaminated sediments.

Differences between the models are clearer when contact times between water and sediments are larger, like in the case of a continuous release from the source, and when redissolution of radionuclides from a contaminated sediment is the dominant process. In the case of an instantaneous release, outputs from the three models are more similar.

The 1-step model produces a too fast redissolution of radionuclides from the sediments. However, this approach could be useful for models developed for decision-making purposes, since it is simple, only two rates are required, and is computationally cheap. Indeed, in the case of an instantaneous release, its output is similar to that of the other two models.

The irreversible model produces a continuous increase of activity in the irreversible fraction, which does not correspond to a realistic situation. This problem may be solved incorporating saturation effects in the irreversible phase.

Outputs from the 2-step and irreversible models are similar when they are applied to laboratory experiments. However, differences become evident (in both activity levels in water and sediments and in the redissolution velocity from sediments), if they are applied in the real marine environment. A clear conclusion about which can be the most suitable approach cannot be given at this moment. Although the irreversible model (including saturation of the irreversible phase) is the more detailed approach, this also has the inconvenience that many (5) kinetic rates are required, as well as the saturation concentration. Also, initial conditions for running the model

are more difficult to define since specific activities in three sediment phases should be given over all the model domain. Probably, a 2-step model represents a compromise between ease and level of detail of the description, but clearly further work is required.

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