

The marine k_d and water/sediment interaction problem

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A B S T R A C T

The behavior of marine distribution coefficients is analyzed with the help of numerical experiments and analytical solutions of equations describing kinetic models for uptake/release of radionuclides. The difficulties in measuring true k_d in a marine environment perturbed by an external radionuclide source are highlighted. Differences between suspended matter and bed sediment k_d are analyzed. The performances of different kinetic models (1-step/2step; single-layer/multi-layer) are studied in model/model and model/experiment comparisons. Implications for the use of models to assess radioactive contamination after an emergency are given; as well as recommendations when k_d data are compiled in order to create a useful database.

1. Introduction

The simplest and most common method of estimating contaminant adsorption on solids is based on partition (or distribution) coefficient, k_d . In turn, the k_d value is a direct measure of the partitioning of a contaminant between the solid and aqueous phases. It is an empirical metric that attempts to account for various chemical and physical retardation mechanisms that are influenced by a myriad of variables. Ideally, site-specific k_d values would be available for the range of aqueous and geological conditions in the system to be modelled. Values for k_d not only vary greatly between contaminants, but also vary as a function of aqueous and solid phase chemistry.

In radioecology, the marine distribution coefficient for a given radionuclide, k_d , is defined (IAEA, 2004) as the ratio between the radionuclide concentration in the solid phase (suspended matter or bed sediment) and the concentration in water (dissolved phase):

$$k_d = \frac{C_s}{C_w} \quad (1)$$

where C_s and C_w are, respectively, radionuclide concentrations in the solid (Bq kg⁻¹) and dissolved (Bq m⁻³) phases. Such concentrations have to be at equilibrium, i.e., after the partition of the radionuclide between phases has reached equilibrium. This k_d is measured in SI units in m³/kg.

This is the simplest method to estimate the concentration of a radionuclide in the solid phase, knowing concentration in the water. It has been implemented in a number of dispersion models, usually long-

term box dispersion models [see for instance Lepicard et al. (2004), Iosjpe et al. (2009), Maderich et al. (2014)], for assessments of radionuclide releases in the marine environment. Consequently, efforts have been done to compile k_d values for a large number of elements in the marine environment, as IAEA (1985). This document was updated in IAEA (2004) and a new revision is in progress in the frame of MOD-ARIA-II (Modelling and Data for Radiological Impact Assessments) program.¹

Presently, there is a trend to use dynamic models, formulated in terms of kinetic rates, instead of equilibrium k_d models, to describe interactions of radionuclides between the dissolved and solid (suspended matter and bed sediment) phases. In the case of an emergency, the use of a k_d model, which assumes equilibrium in the tracer partition between phases, implies that concentration in the sediment will be overestimated in the early stage of the accident. Later, when radionuclides in the water column are washed out from the area by marine currents, the equilibrium approach will underestimate radionuclide concentration in the sediment. However, it is known that a contaminated sediment acts as a long-term delayed source of radionuclides to the water column, as happens in the Irish Sea for instance (Mitchell et al., 1999). This slow redissolution process can only be described by means of kinetic models.

In spite of the limitations of the equilibrium model, the k_d is a very relevant parameter for kinetic models. The reason (details are shown below) is that kinetic rates are related through the k_d ; thus this parameter is used in dynamic models as a constraint for such rates.

Very often concentrations of radionuclides are measured in

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¹ <http://www-ns.iaea.org/projects/modaria/modaria2.asp?s=8&l=129>.

sediment and water, divided, and such ratio is presented as a k_d , without considering if radionuclide partition is at equilibrium. A recent example may be seen in Nagao et al. (2013): in this case the system has been perturbed by the passage of a typhoon, and very hardly it may be assumed that partition of radionuclides between water and sediments will be at equilibrium. In relation with this, the main purposes of this work are:

- 1 To provide some insight on the limitations of the k_d model, due to the fact that the sea is an open environment and, thus, equilibrium conditions are seldom found
- 2 To give some recommendations when k_d are measured in the field in order to create a k_d database
- 3 To compare the performances of different water/sediment interaction models in model/model and model/experiment inter-comparisons in order to investigate the required level of complexity of the model depending on the purposes of the study. In particular, to compare 1-step and 2-step models, and single and multi-layer sediment models.
- 4 Also, some implications with respect to the application of models for the management of nuclear accidents in the sea are given along the document.

Some initial definitions are given in section 1. Later, a discussion on the difficulties in finding equilibrium conditions in the marine environment is presented in section 3. Differences between suspended-matter and bed sediment k_d are presented in section 4. Two-step kinetics and single and multi-layer models are presented in sections 5 and 6 respectively. Comparisons of the performances of these models in the marine environment and laboratory experiments may be seen in sections 7 and 8 respectively. Finally, some suggestions to deal with variable environmental conditions (pH and salinity) in marine dispersion models are introduced in section 9.

2. Initial considerations

Let us consider a closed system consisting of a volume V of water with a given amount of sediment M . A tracer is added in dissolved form at $t = 0$. If adsorption/release is considered to be described by a single reversible reaction (denoted as a 1-step model, see Fig. 1) with rates k_1 and k_2 , respectively, for adsorption and release, the differential equations whose solution gives the time evolution of activity in water and

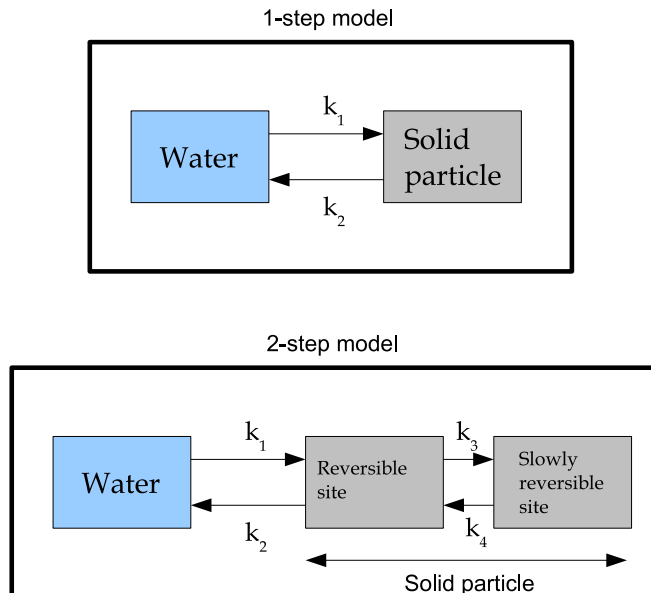


Fig. 1. Scheme representing 1-step and 2-step kinetic models.

$$\begin{aligned}\frac{\partial A_w}{\partial t} &= -k_1 A_w + k_2 A_s \\ \frac{\partial A_s}{\partial t} &= k_1 A_w - k_2 A_s\end{aligned}\quad (2)$$

Note that kinetic rates k_1 and k_2 operationally include all mechanisms for adsorption, like electrostatic attraction, ion exchange etc.

Once the system reaches equilibrium, reaction velocities are the same in both directions and activities in both phases remain constants. Thus, derivatives are zero and the ratio between equilibrium activities is:

$$\frac{A_s}{A_w} = \frac{k_1}{k_2}\quad (3)$$

These activities can be converted into concentrations, C_w and C_s for water and sediment respectively, and related to the k_d defined above (equation (1)):

$$\frac{A_s}{A_w} = \frac{C_s M}{C_w V},\quad (4)$$

thus

$$k_d = \frac{V}{M} \frac{k_1}{k_2} = \frac{1}{m} \frac{k_1}{k_2}\quad (5)$$

where m is the concentration of sediment (mass of sediment per water volume unit).

The equivalent form of equation (2), in terms of radionuclide concentrations, can be obtained using (5):

$$\begin{aligned}\frac{\partial C_w}{\partial t} &= -k_2 m (k_d C_w - C_s) \\ \frac{\partial C_s}{\partial t} &= k_2 (k_d C_w - C_s)\end{aligned}\quad (6)$$

It is known, however, that adsorption depends on the surface of particles per water volume unit at each point and time. This quantity has been denoted as the exchange surface (Periáñez, 2005) or specific surface (Duursma and Carroll, 1996). Thus, the adsorption rate may be written as proportional to such exchange surface S :

$$k_1 = \chi S\quad (7)$$

where the exchange surface has dimensions L^{-1} and χ is a parameter with the dimension of a velocity denoted as the exchange velocity (Periáñez, 2005). If, for simplification, particles are assumed to be spherical, the exchange surface is written as (see references cited above):

$$S = \frac{3m}{\rho R}\quad (8)$$

where R and ρ are particle radius and density respectively. If this expression is included in the definition of k_1 (equation (7)) and then into equation (5), a simple formula is derived for the distribution coefficient:

$$k_d = \frac{\chi}{k_2} \frac{3}{\rho R}\quad (9)$$

In the second fraction we find the dependence of the k_d with the geometry (mean size of the spherical particles and density), and in the first fraction we have the dependence on the geochemical behaviour of the radionuclide and on environmental conditions (salinity, temperature, light etc).

3. The marine environment: distribution coefficients and equilibrium

Many often, k_d s are determined in the field through the collection of a water and a sediment sample, measuring the concentrations of the considered radionuclide in both phases and dividing. Nevertheless, k_d s are defined at equilibrium, thus we must be sure that the partition of

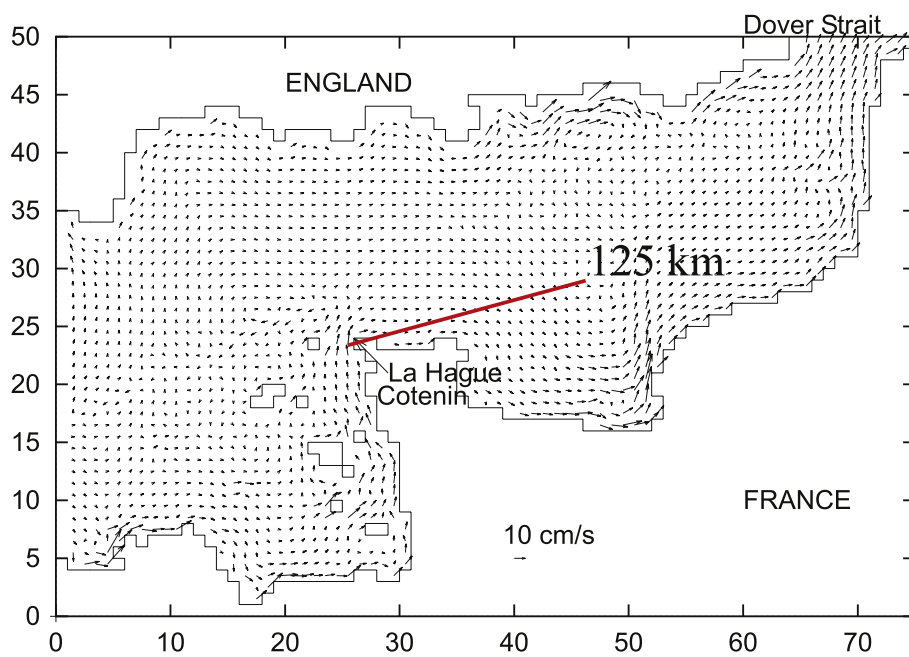


Fig. 2. Steady circulation in the English Channel and location of sampling points at both ends of the red line. Radionuclides are released from La Hague nuclear fuel reprocessing plant. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the radionuclide between sediment and water in the collected samples is effectively at equilibrium. Otherwise, we are not measuring a k_d , but simply a ratio between concentrations in sediment and water, which is meaningless. This ratio might be denoted as an “apparent” k_d .

In fact, it is not easy to determine if partition of a radionuclide between water and sediment is at equilibrium in the marine environment. The reason is that the sea is an open system, continuously perturbed by currents. But even in the extreme simplification of a steady current field, the presence of an external radionuclide source (for instance routine releases from a nuclear facility) prevents the radionuclide partition between water and sediment to reach equilibrium. Even in the simple case that the release is also constant in time, partition between water and sediment will not reach equilibrium. This was demonstrated in [Periáñez \(2003a\)](#), and an example obtained with a dispersion model will be used here to illustrate such problem.

A steady circulation obtained from a hydrodynamic model of the English Channel forced only with the mean wind is shown in [Fig. 2](#). A hypothetical radionuclide release of constant magnitude is introduced at the point where releases from La Hague reprocessing plant (indicated in the map) occur. The dispersion of such radionuclides is then calculated with an Eulerian model including advection, diffusion and interactions of radionuclides with sediments (details may be seen in [Periáñez, 2003a](#)). The model is 2D depth-averaged, thus the water column is assumed to be homogeneous.

The applied model uses a kinetic approach to describe water-sediment interactions. With the selected kinetic coefficients (actually representative of ^{137}Cs), the equilibrium k_d is 140 l/kg. If at a given time along the simulation period we take the calculated concentrations in sediment and water at any point and divide them; the result would be the k_d obtained from the field if a sediment and a water sample are collected at such time and position. The model area is shown in the map; “samples” are collected exactly at the release point and also 125 km downstream such point (the end of the red line).

The result of dividing the resulting concentrations in sediment by the concentrations in water at both locations may be seen in [Fig. 3](#). At La Hague, the system quickly evolves to a steady state (this means that concentrations in water and sediment are constant in time; thus the ratio between them also is). But such ratio is smaller than the true equilibrium k_d (140 l/kg; note that equilibrium k_d is redundant, k_d

implies equilibrium by its definition). Thus, the system is at steady-state (concentrations constant in time) but water-sediment partition is not at equilibrium (the ratio between concentrations in sediment and water is smaller than the k_d). This is due to the external perturbation of the system (the constant release): as contaminated water is introduced, the sediment has no time to “follow” it and a lower k_d results. As a consequence, if you measure radionuclide concentrations in sediment and water and divide them; what you obtain in the vicinity of a source is not a k_d , because the partition of the tracer between sediment and water is not at equilibrium. The situation is even more complicated if the release term and the water currents are not constant in time.

In contrast, 125 km downstream the system again evolves to a steady-state (constant concentrations) which also is equilibrium state (when you divide the concentrations in sediment and water the result is 140 l/kg; the true k_d). Thus, it is relevant to keep in mind that steady-state does not necessarily mean equilibrium in the water/sediment partition of radiotracers.

It is often read in literature that k_d s vary over orders of magnitude. Of course there is natural variability, but we should wonder how much of such variability is due to the fact that many of the provided k_d s are not true k_d s because the system is not at equilibrium.

As an example, reported k_d s for technetium and neptunium in [IAEA \(2004\)](#) are obtained from samples in the Irish Sea. This area is affected by releases from Sellafield and it is not known if partition of radionuclides between water and sediment is at equilibrium and, thus, if such reported numbers actually correspond to k_d s. Very likely, according to the calculations here presented, they do not.

Of course, these calculations were carried out in very simple and idealized conditions: steady water currents and constant radionuclide release rate. These conditions are not found in the real marine environment and consequently the situation is much more complicated, as will be seen below.

4. Suspended matter and bed sediment distribution coefficients

The objective of this section consists of discussing the differences which could be expected if a k_d is measured using either a suspended matter or a bed sediment sample.

For simplicity, it will be assumed that the composition of particles in

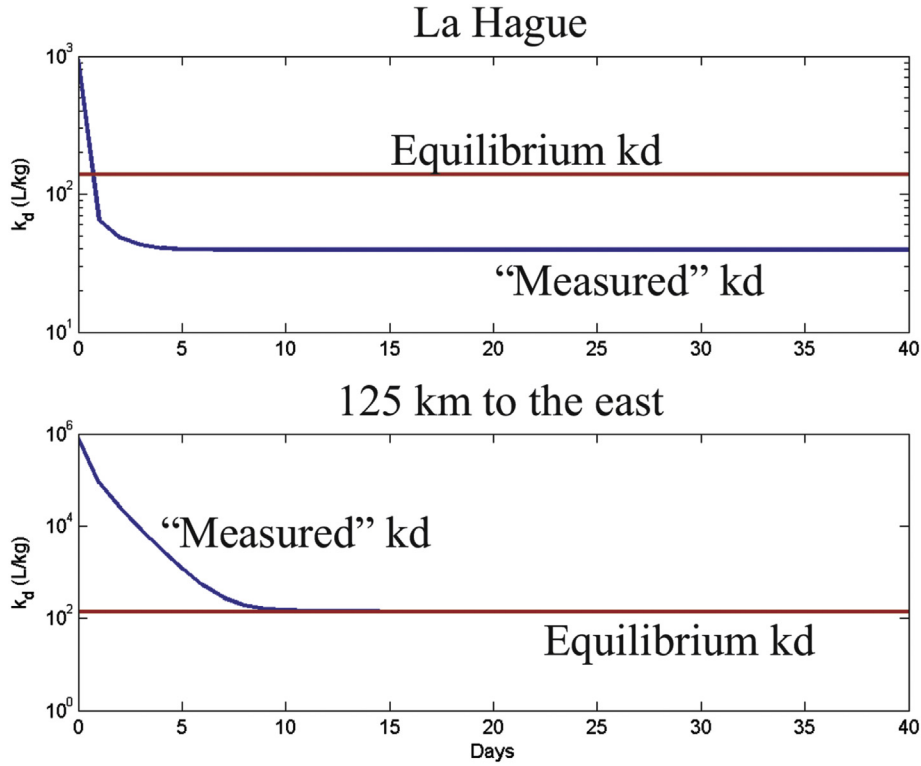


Fig. 3. “Measured” k_d s which would be obtained from sediment and water samples at the release point and 125 km downstream. The true equilibrium k_d (140 l/kg) is given by the red line. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the bed sediment and particles in the water column (suspended matter particles) are the same. Also, for shallow waters it may be assumed that environmental conditions (temperature, salinity, light, oxygen etc) in the water column and close to the seabed are the same. Under these circumstances, the difference between suspended matter and sediments is only due to geometry: in the bed sediment particles are compacted. In this sense, Li et al. (1984) has pointed out that the sediment-water system can be regarded as a high suspended matter environment.

In order to compare with the suspended matter case, an expression for the bed-sediment k_d can be derived from equations (5) and (7), assuming as before spherical particles. The exchange surface for the bed sediment is (Periáñez, 2005):

$$S = \frac{3Z(1-p)\phi}{RH} \quad (10)$$

where Z is the sediment layer thickness (sediment layer which interacts with the water), p is sediment porosity and H is the thickness of the water layer above the sediment which interacts with the sediment. The thickness of this layer is related to water turbulence. But it may also be related to sediment properties as particle size and porosity. Finally, ϕ is a correction factor that takes into account that part of the sediment particle surface may be hidden by other sediment particles. Consequently, the exchange surface is smaller than if particles were suspended in the water column and the k_d should also be smaller. If the mass of sediment per water volume unit is:

$$m = \frac{Z\rho(1-p)}{H} \quad (11)$$

then the resulting k_d is:

$$k_d = \frac{\chi}{k_2} \frac{3\phi}{\rho R} \quad (12)$$

The difference with respect to the suspended matter k_d is the factor ϕ . The sediment k_d is ϕ times smaller than the suspended matter k_d if all conditions are the same. Parameter ϕ is often calibrated in models and

typical values in the range $10^{-1} - 10^{-3}$ are given (Periáñez, 2005).

As a conclusion, it is essential to provide information, when k_d data is provided, about the origin of such value: suspended matter or bed sediment. The compactation of sediments may lead to significantly different k_d s.

5. Two-step kinetic models

There has 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; Ciffroy et al., 2001; El-Mrabet et al., 2001). Thus, a 2-step model has been included in some marine radionuclide dispersion models. Such kinetic model considers that exchanges are governed by two consecutive reversible reactions: 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. k_3 and k_4 are forward and backward rates for this second reaction (Fig. 1). Thus, radionuclides adsorbed by sediments are divided into two phases: a reversible and a slowly reversible fraction. It has been shown that the 2-step model reproduces both the adsorption and release kinetics of ^{137}Cs in the Irish Sea, where it is released from Sellafield nuclear fuel reprocessing plant (Periáñez, 2003b).

The equations which describe the 2-step kinetics are:

$$\begin{aligned} \frac{\partial A_w}{\partial t} &= -k_1 A_w + k_2 A_r \\ \frac{\partial A_r}{\partial t} &= k_1 A_w - k_2 A_r - k_3 A_r + k_4 A_{sr} \\ \frac{\partial A_{sr}}{\partial t} &= k_3 A_r - k_4 A_{sr} \end{aligned} \quad (13)$$

where A_r and A_{sr} denote the activities in the reversible and slowly reversible sediment phases. If equilibrium is achieved, then temporal derivatives are zero and the ratio between equilibrium activities in the sediment and water are:

$$\frac{A_t}{A_w} = \frac{k_1}{k_2} \left(1 + \frac{k_3}{k_4} \right) \quad (14)$$

where $A_t = A_r + A_{sr}$ is the activity in the whole sediment. If activities are converted into activity concentrations, then:

$$k_d^{tot} = \frac{1}{m} \frac{k_1}{k_2} \left(1 + \frac{k_3}{k_4} \right) \quad (15)$$

The first term in this equation is the k_d defined by equation (5), and k_d^{tot} means that it refers to the whole sediment (reversible plus slowly reversible fractions). If the k_d defined in equation (5) is denoted as a *fast* k_d , then:

$$k_d^{tot} = k_d^{fast} \left(1 + \frac{k_3}{k_4} \right) \quad (16)$$

Since, k_3 is about one order of magnitude larger than k_4 (Ciffroy et al., 2001), k_d^{tot} is also about 10 times larger than k_d^{fast} . Therefore it is essential to know, when a k_d is measured (both in the field or laboratory experiment), if the slowly reversible fraction has been extracted and measured in the sediment sample, or only the radionuclide content in the reversible phase has been measured. In IAEA (2004), k_d s are derived assuming that 10% of the total pelagic clay abundance represents the proportion of exchangeable phase particulate element (if no data exists about this). However, it is not specified if exchangeable means only what we call reversible, or if it also includes the slowly reversible phase (which, after all, is also exchangeable).

6. Single layer and layered sediment models

6.1. Single layer models

In this model (Periáñez, 2005), it is considered that the sediment consists of a single well-mixed layer of thickness Z which is able to interact with the overlaying water. The thickness of the overlaying water later (also assumed to be well mixed) which interacts with the sediment is denoted as H . If a 1-step kinetic is assumed for simplicity, the equation which gives the time evolution of the tracer concentration in the sediment, C_s , is (Periáñez, 2005):

$$\frac{\partial C_s}{\partial t} = k_1 C_w \frac{H}{\rho_s Z} - k_2 \phi C_s \quad (17)$$

where C_w is concentration in water, ρ_s is sediment bulk density (dry mass per wet volume, thus related to porosity) and ϕ is the correction factor defined in equation (10) to take into account that part of the sediment particle surface is not available for exchanging radionuclides with water. The kinetic coefficient k_1 is defined as in equation (7), taking into account that the exchange surface is given by equation (10). An equivalent form for equation (17) can be obtained (e.g. Margvelashvily et al., 1997; Kobayashi et al., 2007) from (17) using (11 and 12) as

$$\frac{\partial C_s}{\partial t} = k_2 \phi (k_d C_w - C_s). \quad (18)$$

This model may be easily extended to include a 2-step kinetics. Note that erosion and deposition fluxes, as well as radioactive decay, have not been considered for simplicity.

6.2. Layered sediment models

Maderich et al. (2017) have recently described a radionuclide dispersion model for the marine environment in which the bed sediment is approximated by a number of well mixed layers to describe the vertical migration of radionuclides within the seabed due to erosion/deposition, molecular diffusion and bioturbation. Also, several sediment fractions with different sizes are considered.

The layered sediment model, schematically presented in Fig. 4,

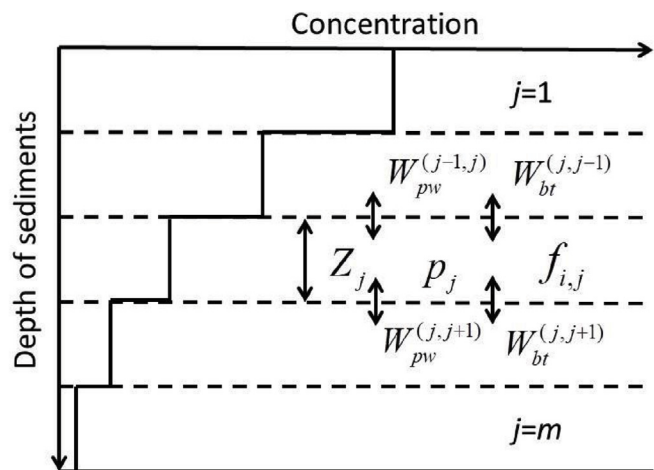


Fig. 4. Structure of the bottom sediment layers in the model in Maderich et al. (2017).

considers that radionuclides in each layer exists in three phases: pore water, a reversible sediment phase and a slowly reversible sediment phase (thus, a 2-step kinetic model is applied). Equations are then written for each phase and layer (details are given in Maderich et al., 2017). Transfers of radionuclides between layers are described in terms of exchange rates of pore water between layers j and $j - 1$, $W_{pw}^{j-1,j}$ and bioturbation exchange between layers, $W_{bt}^{j-1,j}$, p_j is porosity of layer j , Z_j is layer thickness and $f_{i,j}$ is the volume fraction of sediment class i in layer j .

Equations for the top sediment layer include erosion and deposition fluxes and the transfer of radionuclides from the water column to pore water in such top layer. Transfers between pore water and fast and slow sediment phases are essentially described in the form of equation (13).

The exchange rate $W_{pw}^{0,1}$ between dissolved radionuclides in the water column and pore water in the top sediment layer is estimated from boundary layer theory and corrected for surface roughness (Shaw and Hanratty, 1977; Dade, 1993):

$$W_{pw}^{0,1} = 0.1778u_* Re^{-0.2} Sc^{-0.604} \quad (19)$$

where u_* is friction velocity and Re and Sc are Reynolds and Schmidt numbers respectively.

This model has been compared with a laboratory experiment on the uptake of ^{134}Cs by lake sediments (Smith et al., 2000). Details may be seen in Maderich et al. (2017). It is interesting to note that a 1-step kinetics was also tested with this layered configuration. It was found that the 2-step model describes the profiles of ^{134}Cs in sediments and concentration in overlaying water better than the 1-step model for time scales larger than months.

6.3. Equivalence between models

Apart from the obvious different number of layers, models described above present a relevant difference: in Periáñez (2005) model there is a direct adsorption of radionuclides from overlaying water on sediment particles. However, in Maderich et al. (2017) model there is a transfer from overlaying model to pore water and then from pore water to sediment.

As shown in Maderich et al. (2017), the equilibrium time between pore water and sediment is much shorter than the other involved time scales. Thus, the equation for pore water can be simplified. After this (details may be seen in the given reference) and also reducing the model to a single layer, a single sediment size and 1-step kinetics for simplicity, the equation which gives the time evolution of radionuclide concentration in the sediment is:

$$\frac{\partial Z C_s}{\partial t} = a_{bds} Z (k_d C_w - C_s) \quad (20)$$

where a_{bds} is defined as:

$$a_{bds} = \frac{k_2 W_{pw} \phi}{W_{pw} + k_2 Z \rho (1 - p) k_d \phi} \quad (21)$$

where W_{pw} is the exchange rate between overlaying water and pore water. Note that through this simplification, equation (20) includes transfers between overlaying water and sediment, without pore water concentration appearing in an explicit form.

In the limits in which $Z \rightarrow 0$, and also when $W_{pw} \rightarrow \infty$, then $a_{bds} = k_2 \phi$. It can be seen from (18) that in this case equation (20) is exactly the same as equation (17). Thus, both models are the same in these two extreme situations.

Consequently, the role of pore water could be neglected when the sediment thickness is very small, and also in very turbulent flows, with high friction velocities and consequently high W_{pw} values (equation (19)). Notice, however, that simplification of the equation for pore water does not mean that the pore water is in a local equilibrium with sediment (5) as assumed in different models (e.g. Smith et al., 2000; Lepicard et al., 2004; Iosjpe et al., 2009) due to the fluxes of activity through the layer upper surface.

7. Comparison of models in the marine environment

7.1. Comparisons of 1-step and 2-step models

The predictions of 1-step and 2-step models are compared in the example that follows, involving Fukushima Daiichi nuclear power plant accident. Models have been applied (Periáñez et al., 2015) to simulate the dispersion of ^{137}Cs in the Pacific Ocean immediately after the accident (during the first three months after it). These models have been used to calculate the concentration of ^{137}Cs in deep water (the deepest water, which is in contact with the sediment) in a point some km offshore Fukushima. The result of such calculations is shown in Fig. 5. Since calculations only cover 90 days and we are interested on a longer scale, it is assumed that ^{137}Cs concentration decreases in time until reaching a typical background concentration of 2 Bq/m^3 , which remains constant. The exact shape of the curve describing such reduction is not relevant for our discussion.

These ^{137}Cs concentrations are used to solve equations of the 1-step and 2-step models (equation (2) and (13) respectively) in a single-layer configuration. The equations are re-written in terms of concentrations instead of total activities and the first equation (for the dissolved phase)

is not solved since concentration in water is imposed as a boundary condition.

Results are presented in Fig. 6. There are several interesting points in this graphic. With respect to concentrations in sediments; 1-step and 2-step model produce the same results in the early contamination stage (until approximately day 20), since in this time there has not been yet a significant transfer of ^{137}Cs to the slowly reversible phase of the sediment (concentration in this phase is orders of magnitude lower than in the reversible phase). From this moment, concentration in water starts to decrease and the 1-step model and the reversible fraction in the 2-step model follow this decreasing trend. However, concentration in the slowly reversible fraction is still increasing (fed by the reversible one). At about 150 days, concentrations in the 1-step model and in the reversible phase of the 2-step model start to diverge. The 1-step model continues the decreasing trend in water, reaching a background steady level simultaneously with water. However, a transfer of ^{137}Cs from the slowly reversible to the reversible phase starts to be significant and as a consequence, the decrease in the reversible phase concentration is much slower than in the 1-step model. About 20–30 years are required to elapse until concentrations in the 1-step model and in the reversible phase converge. Concentrations in the total sediment predicted by the 1-step and 2-step models are however significantly different due to the fact that the slowly reversible phase is retaining ^{137}Cs , which is not easily redissolved.

The resulting distribution coefficients are plotted in the bottom panel of Fig. 6. It must be pointed out that the kinetic coefficients used in the present numerical experiment correspond to the k_d recommended by IAEA (2004) for Cs: $2 \text{ m}^3/\text{kg}$ [note that kinetic rates and k_d are related; equations (5) and (9)].

It may be seen that the 1-step model achieves a steady state k_d as soon as water stabilizes in the background level (at day 300 approximately). This steady k_d is also a true equilibrium k_d , since its value is exactly $2 \text{ m}^3/\text{kg}$, the value which has been used to define the kinetic rates. The situation is completely different with the 2-step model. In this case about 3 decades are required to achieve equilibrium due to the slow redissolution from the slowly reversible phase. After some 30 years, the fast k_d is the same as in the 1-step model, indicating true equilibrium in the partition of the radionuclide, and the total k_d is one order of magnitude larger than the fast k_d , as predicted by equation (16). Results indicate that contaminated sediments actually are very long-term delayed sources of radionuclides. Note that the 30 year time here found would be the “optimum” situation since concentration in water remains at background levels (because a strong current of clean water is continuously washing out from the area the redissolved radionuclides). In a more closed environment, with a long water

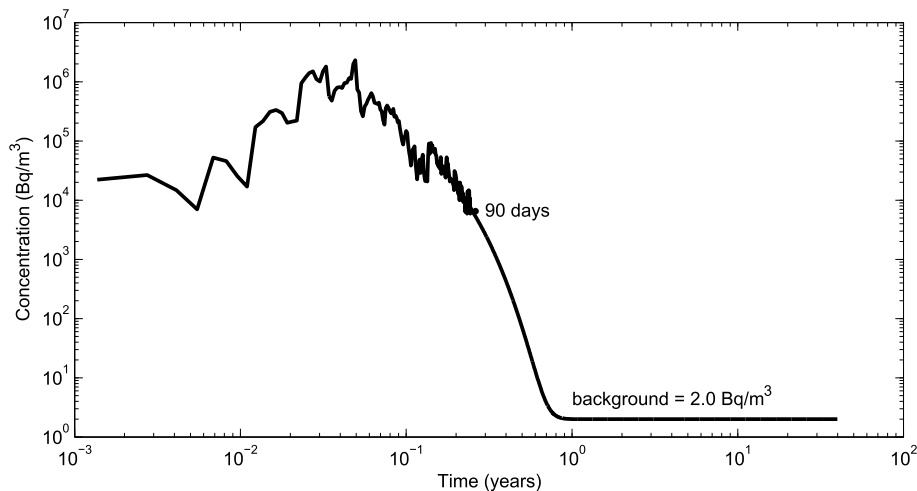


Fig. 5. Time evolution of ^{137}Cs concentration in deep water offshore Fukushima. Until day 90 after March 11th, 2011, it is calculated by the dispersion models. From day 90 on, a progressive reduction to background is specified.

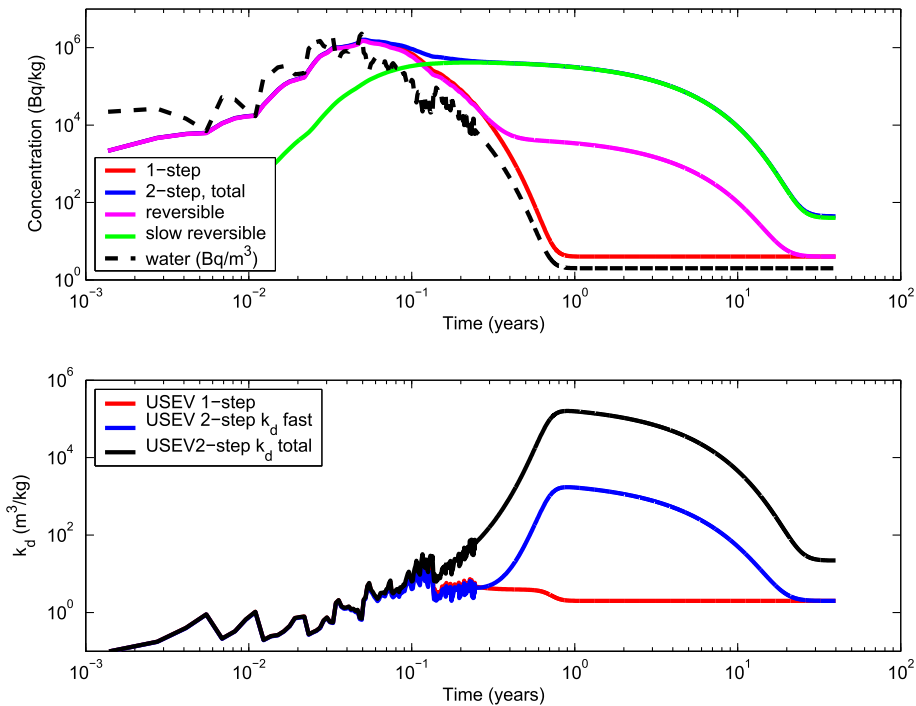


Fig. 6. Time evolution of calculated ¹³⁷Cs concentration in sediments and resulting *k_d*s. In the case of the 2-step model, concentrations in reversible and slowly reversible are shown, as well as the total. Total and fast *k_d* are also plotted.

residence time (like the Baltic Sea, where it is some 30 years [Leppäranta and Myberg, 2009]), the role of sediments as a delayed radionuclide source would be even longer.

We can then summarize in the following essential points:

- 1 In the initial contamination stage, 1-step and 2-step models produce the same results. Thus, for rapid radioactive assessments after emergency situations a 1-step model may be safely applied. However, the 2-step model should be used for long-term calculations. This is in agreement with Maderich et al. (2017), who compared 1-step and 2-step models in adsorption experiments and found that the 2-step kinetics performs better than the 1-step for time scales longer than months (see section 6.2).
- 2 After an accidental radioactive release in the sea, as in the case of Fukushima accident, equilibrium in the partition of radionuclides between water and sediments is not quickly achieved. If radionuclide kinetics is governed by a 2-step model, as generally seems to be the case, decades are required to achieve equilibrium, time during which the apparent *k_d* will slowly decrease from its maximum. This maximum *k_d* is delayed with respect to the maximum concentration in water.

7.2. Comparisons of single layer and layered models

Calculated concentrations of ¹³⁷Cs in deep water offshore Fukushima described in the previous section have now been used to compare the outputs of single-layer and layered models. However, only the first 90 days have been used. All the applied models include 2-step kinetics. They are the USEV model (Periáñez, 2005; single layer) and I/K (IMMSP/KIOST) model (Maderich et al., 2017) in both single and multi-layer configurations.

Fig. 7 (top panel) shows the time evolution of ¹³⁷Cs in the sediment (top layer in the case of multi-layer model) along such 90 days. There are significant differences between the multi-layer model and both single-layer models. These differences are due to the different parameterization of the exchange processes between water and bottom sediments in the models. In particular, Fig. 7 shows that better agreement

between I/K and USEV models is obtained for I/K multi-layer model. Other factors resulting in differences are parameterization of the turbulent exchange and effect of *k_d* in equation (21). However, such differences reduce in time since by the end of the simulation calculated concentrations by all models are within the same order of magnitude.

Both USEV and I/K models include parameter ϕ (see equation (10)), which takes into account that not all the sediment particle surface is available to adsorb radionuclides. This parameter is not measured, but specified after model calibration. A sensitivity study has been carried out with USEV model and results are presented in Fig. 8. Model results are shown for several ϕ values and compared with I/K multi-layer model. The conclusion is that a calibration of the single-layer model can lead to results in very close agreement with those of the multi-layer model (see green line in Fig. 8). Nevertheless, although a proper calibration can produce very similar results for radionuclide concentration in the surface sediment, the single-layer model cannot predict correctly the inventory in a sediment core, as shown in Maderich et al. (2017).

The use of single or multi-layer approaches would depend on the objectives of the particular modelling study. A multi-layer model is required to evaluate sediment inventories of radionuclides and radionuclide profiles in sediment cores, of course; but a single-layer model may produce satisfactory results for radionuclide concentrations in the surface sediment. Since single-layer models are simpler and require less computational efforts, they can consequently be more appropriate for fast assessment after emergencies.

8. Model comparisons with laboratory experiments

Experiments have been carried out to evaluate the transfer of radionuclides from water to sediments and to estimate kinetic rates from numerical fitting of the adsorption curves. In particular, the experiments described in Børretzen and Salbu (2000) for ¹⁰⁹Cd and ⁶⁰Co, and the described in Børretzen and Salbu (2002) for ¹³⁴Cs will be used as a relatively simple case in which models can be compared with experiments. These experiments are examples of a closed system, not subjected to external perturbations as in the case discussed in section 3.

Details on the experiments may be seen in the cited papers. Briefly,

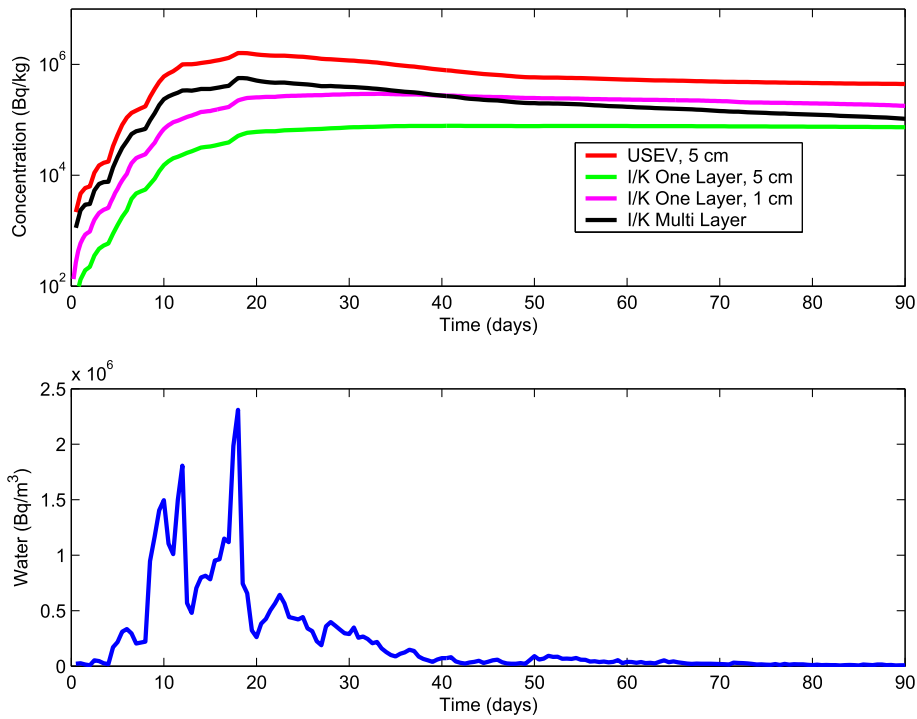


Fig. 7. Calculated time evolution of ^{137}Cs in the sediment (top layer in the case of multi-layer model) along 90 days after Fukushima accident. Layer thickness is given in the legend in the case of single layer models. Concentrations in deep water are shown in the bottom panel for illustration. These are the same as in Fig. 5 but only until day 90.

water and sediments were collected from Novaya Zemlya. Sediments were sieved through 2 mm mesh size prior to the experiments. They were mostly silty sediments. Temperature was 4 °C and water salinity 33. Amount of sediment was 2 g (dry weight) and the amount of water 20 ml. Water was not agitated during the experiment. Tracers were added to the dissolved phase and the fractions of tracer in water, reversible and slowly reversible sediment phases were measured at several times after tracer addition. The apparent k_d was also provided. Since both sediment phases are measured, the provided k_d actually corresponds to the total k_d given by equation (16). The temporal evolution of the apparent k_d was fitted by the authors of the experimental work to curves of the form:

$$k_d(t) = k_d(1 - e^{-\beta t}) \quad (22)$$

where $k_d(t)$ is the apparent k_d (changes with time, thus it is not a true k_d but a simple ratio between concentrations in sediment and water) and

Table 1

k_d in the experiments by Børretzen and Salbu (2000, 2002) obtained from numerical fitting to functions in the form of equation (22).

	k_d (m^3/kg)
^{134}Cs	0.295
^{109}Cd	0.512
^{60}Co	19.3

k_d is the true equilibrium coefficient at equilibrium ($t \rightarrow \infty$). These values are listed in Table 1.

The models which have been tested are the 2-step models described in Periañez (2003b) and Maderich et al. (2017). In this case, transfer processes can be described in frame of the system of equation (13). The analytical solutions of these equations, rewritten for concentrations in

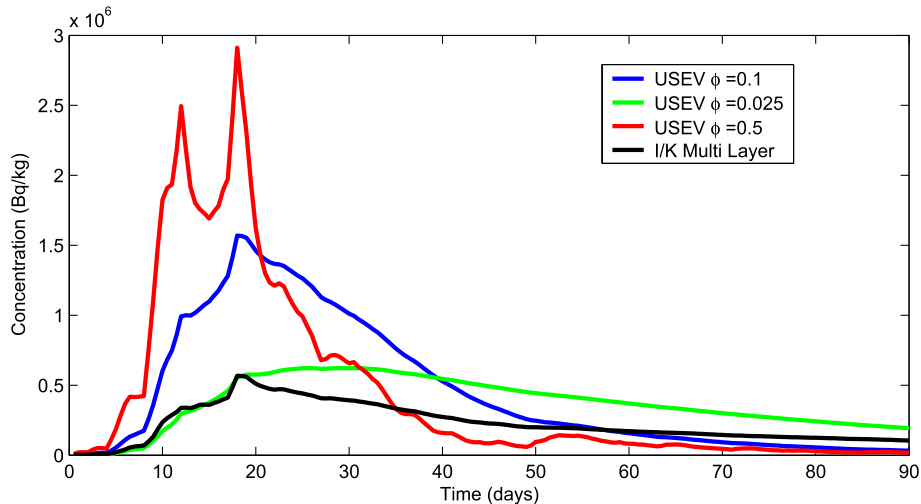


Fig. 8. USEV single-layer model sensitivity to parameter ϕ and results of I/K multi-layer model. 2-step kinetics is used in all cases.

different phases are:

$$C_w(t) = A \exp(-r_1 t) + B \exp(-r_2 t) + C, \quad (23)$$

$$mC_r(t) = k_2^{-1}((k_1 - r_1)A \exp(-r_1 t) + (k_1 - r_2)B \exp(-r_2 t) + C), \quad (24)$$

$$mC_{sr}(t) = C_{w0} - C_w(t) - mC_r(t), \quad (25)$$

where

$$A = \frac{k_1 - r_2}{r_1 - r_2} C_{w0} + \frac{r_2}{r_1 - r_2} C,$$

$$B = -\frac{k_1 - r_1}{r_1 - r_2} C_{w0} - \frac{r_1}{r_1 - r_2} C,$$

$$C = \frac{C_{w0}}{1 + \frac{k_1}{k_2} \left(1 + \frac{k_3}{k_4}\right)},$$

where C_{w0} is the initial value of concentration in the dissolved phase and $r_{1,2}$ are the roots of the quadratic characteristic equation

$$r^2 - pr + q = 0. \quad (26)$$

Here, $p = k_1 + k_2 + k_3 + k_4$, $q = k_2 k_4 + k_1 k_3 + k_1 k_4$.

In both models, the adsorption rate k_1 is deduced from the equilibrium k_d in Table 1, the concentration of sediments and the desorption rate k_2 , from equation (15). The kinetic coefficient k_2 is $1.16 \times 10^{-5} \text{ s}^{-1}$ according to the experiments in Nyffeler et al. (1984), value that has been used in other modelling works (Perianez, 2003b, 2004). As described in Nyffeler et al. (1984), k_2 is very similar even for radionuclides with a rather different geochemical behaviour, being k_1 the essential parameter describing the tracer geochemical behaviour. Thus, the same k_2 is applied to all radionuclides. Kinetic rates for the slow reactions were calibrated in the case of I/K model (Maderich et al., 2017). In the case of USEV (Perianez, 2003b) they were taken as follows: El-Mrabet et al. (2001) have measured a value of $1.4 \times 10^7 \text{ s}^{-1}$ for k_3 in their experiments carried out with sea water from the southwest of Spain. k_4 is defined as 10 times smaller than k_3 , as suggested by Ciffroy et al. (2001). These values have been used in previous modelling works in the Irish Sea (Perianez, 2003b) and to simulate Fukushima Daiichi releases in the Pacific Ocean (Perianez et al., 2012) and are used in this application as well. A summary of kinetic rates used in each 2-step model and for each radionuclide is shown in Table 2.

Temporal evolution of the apparent k_d for the three radionuclides obtained from the experiments and models are presented in Fig. 9. Solutions (23)–(25) are here corrected for radioactive decay. Of course, I/K model produces results in better agreement with observations than USEV model since in the former kinetic rates were calibrated, while fixed values (used in previous works) were applied in USEV model. Nevertheless, it has to be noted that such values gave very bad results in the case of ^{60}Co and, consequently, k_3 for this radionuclide was also calibrated in USEV model. However, the ratio $k_4 = k_3/10$ was retained. The increasing trend in apparent k_d is generally well described by the models. For the purpose of environmental assessment in the case of releases to the sea, even the model with fixed parameters could be

Table 2
Kinetic rates (s^{-1}) used in each 2-step model for each radionuclide.

	k_1	k_2	k_3	k_4
I/K				
^{134}Cs	5.7×10^{-5}	1.16×10^{-5}	1.0×10^{-6}	2.0×10^{-7}
^{109}Cd	5.4×10^{-5}	1.16×10^{-5}	1.0×10^{-6}	1.0×10^{-7}
^{60}Co	2.22×10^{-4}	1.16×10^{-5}	1.0×10^{-6}	4.0×10^{-8}
USEV				
^{134}Cs	3.11×10^{-5}	1.16×10^{-5}	1.4×10^{-5}	1.4×10^{-6}
^{109}Cd	5.4×10^{-5}	1.16×10^{-5}	1.4×10^{-5}	1.4×10^{-6}
^{60}Co	2.03×10^{-3}	1.16×10^{-5}	5.0×10^{-7}	5.0×10^{-8}

safely used without involving too large errors in the predictions. Exceptions may be extremely reactive radionuclides like Co isotopes.

Results obtained with a 1-step model are also shown in Fig. 9 (red lines). Of course, results are not realistic since the k_d provided by the experiment is the total k_d (including the slowly reversible sediment phase), which cannot be accounted for in a 1-step model. The fast k_d should be used if a 1-step model is to be applied. The purpose of showing these results with a 1-step model is to clearly point out that it is essential to communicate, when k_d data are provided, if they correspond to fast or to total k_d . Otherwise, large errors in predictions may be expected when such k_d is used for assessments after emergencies if the wrong assumption is done.

Temporal evolutions of the fraction of tracer in water, both sediment phases and the total sediment may be seen in Figs. 10–12 for the three tracers. The calibrated model, as should be expected, produces results in better agreement with observations than USEV model, not calibrated. However, some general trends are provided by both models. For instance, in the case of ^{60}Co there is an extremely fast adsorption (Fig. 12): virtually all the tracer is instantaneously removed from water and fixed in the sediment particles. Adsorption is slower in the case of the less reactive ^{134}Cs and ^{109}Cd , but most of both tracers is in any case fixed in the sediment. This is due to the extremely high ratio sediment mass/water volume used in the experiments.

The main conclusions of these comparisons may be summarized in the following points:

1. It is essential to know, if a k_d dataset is provided, if such k_d s correspond to fast or to total k_d . Otherwise, large errors in predictions are expected when they are used for assessments after emergencies.
2. Although in a relatively long scale (over some 50 days) both calibrated and non-calibrated models produce similar tracer fractions in water and sediment, this is not generally the case for shorter time scales. Thus, for radioactive assessments after emergencies, which imply short temporal scales, it should be recommended to have site-specific values for kinetic rates which could be used in dispersion models. In other words, as it is the case with water circulation, that a careful selection of the ocean model is needed and should be done after a detailed comparison with local measurements of currents in an area potentially exposed to an accident (Perianez et al., 2016), kinetic rates should also be as well characterized as possible for areas where accidents could occur. As commented above, natural variability in the sea could mask differences between models, but this should be verified.

9. Changes in environmental conditions

In some marine environments, close to river discharges and in estuaries, there may be significant changes in salinity and even pH if there is industrial waste disposal. It is therefore relevant to have a formulation which describes the effects of these changes in the kinetics of radionuclides.

The formulation given in Laissaoui et al. (1998) for the dependence of the exchange velocity upon salinity, S , which is deduced from the theory of Abril and Fraga (1996), can be used:

$$\chi = \chi^0 (1 - \delta) \quad (27)$$

where

$$\delta = \frac{S}{S + S_0} \quad (28)$$

In these equations χ^0 is the freshwater value of the exchange velocity and S_0 is the salinity value at which 50% of saturation occurs (Laissaoui et al., 1998). It must be noted that as salinity increases, the transfer of radionuclides to the solid phase decreases due to competition effects of radionuclides with ions dissolved in water. The relations given above have been tested through laboratory experiments

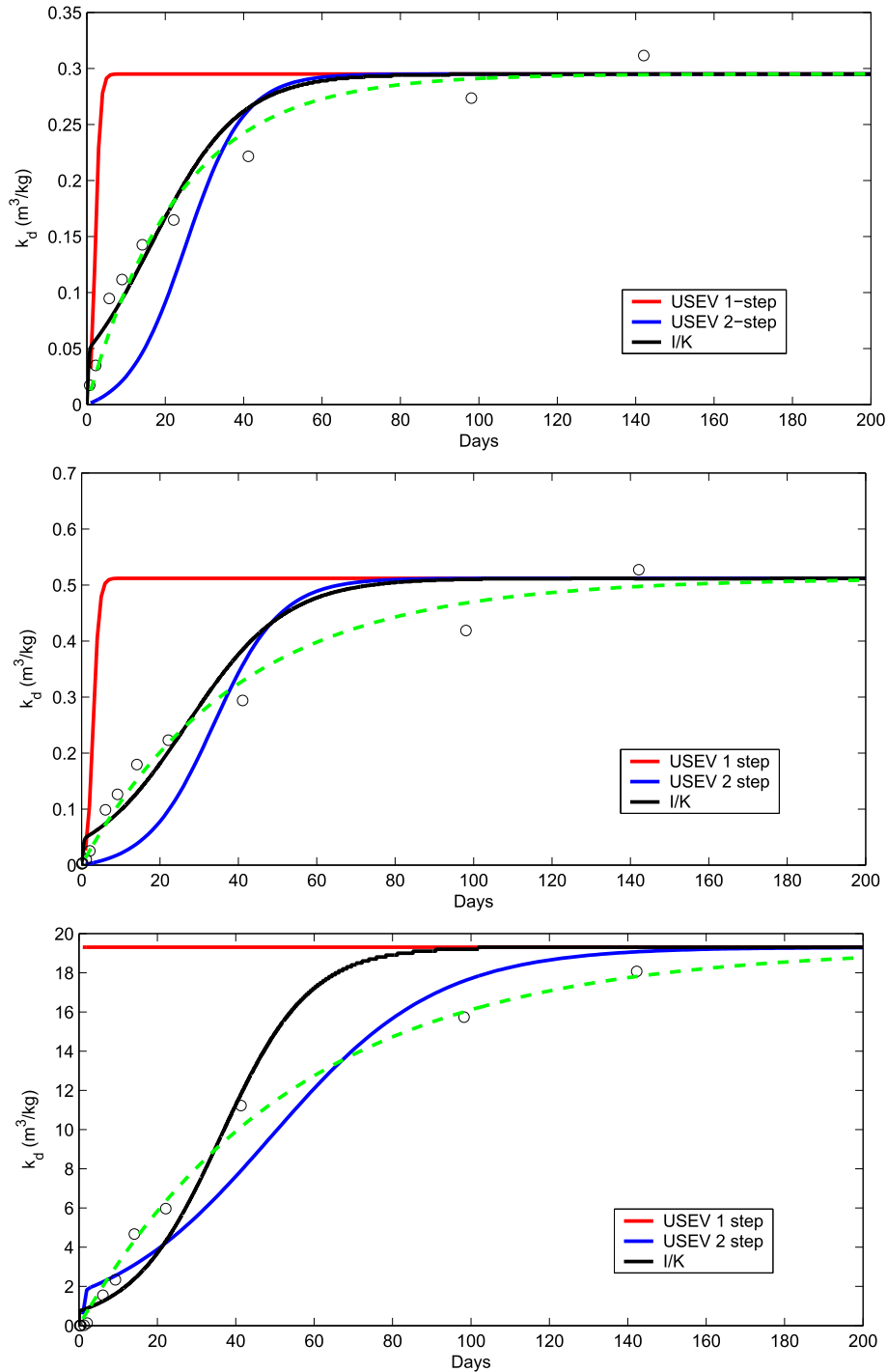


Fig. 9. Time evolution of calculated and measured (black circles) apparent k_d s for ^{137}Cs , ^{109}Cd and ^{60}Co (top to bottom). The green line is the numerical fitting to equation (22). The application of a 1-step model is also shown (red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

(Laissaoui et al., 1998). Indeed, the best agreement with experiments is obtained with $S_0 = 15.8$. This value was also used in a practical test of the present formulation (Perinez et al., 2013).

It is also possible to describe the dependence of the exchange velocity with pH. Since k_1 and the sediment-water distribution coefficient, k_d , are proportionally related, we may base on the fact that the k_d increases with increasing pH (USEPA, 1999), which was also deduced by Abril and Fraga (1996). A mathematical function $g(\text{pH})$, ranging between 0 and 1, which modulates the observed behaviour of k_d with pH (USEPA, 1999) was constructed. It has the form:

$$g(\text{pH}) = \frac{1}{\exp[-\alpha(\text{pH} - \beta)] + 1} \quad (29)$$

where β is the pH at which some 50% of precipitation occurs and α controls how abrupt is the k_d increase with pH increase. These parameters were fitted to reproduce the observations in USEPA (1999) and it was found $\alpha = \beta = 5$.

Thus, the final dependence of the exchange velocity with salinity and pH (note that the k_d is proportional to rate k_1 as mentioned above) is written as follows:

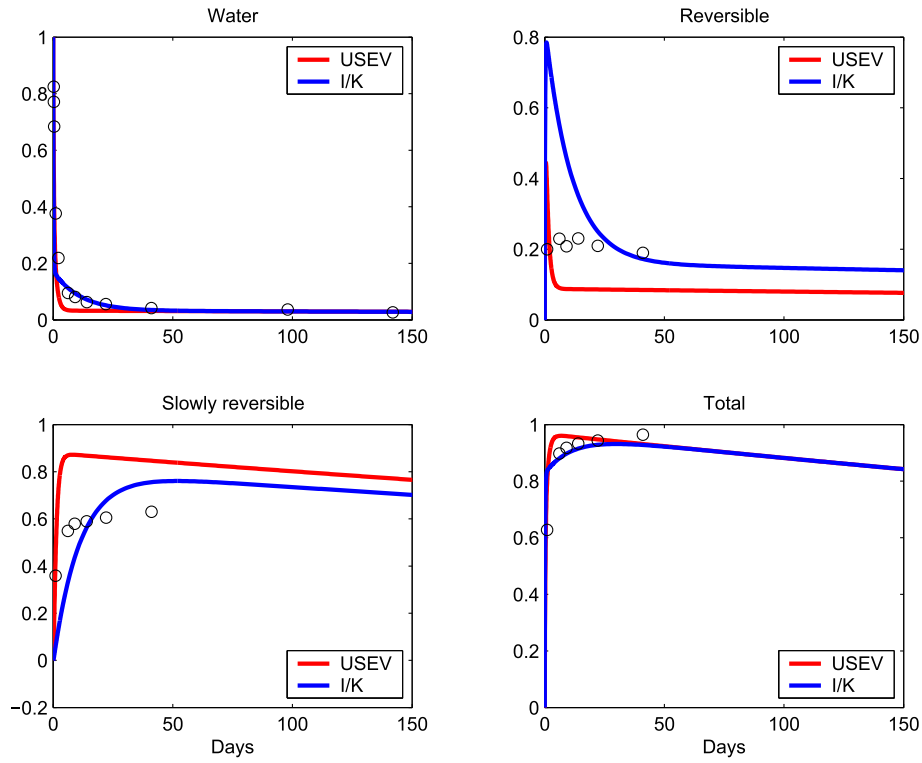


Fig. 10. Time evolution of calculated ^{134}Cs fraction in water, both sediment phases and total sediment. Black circles are measured values.

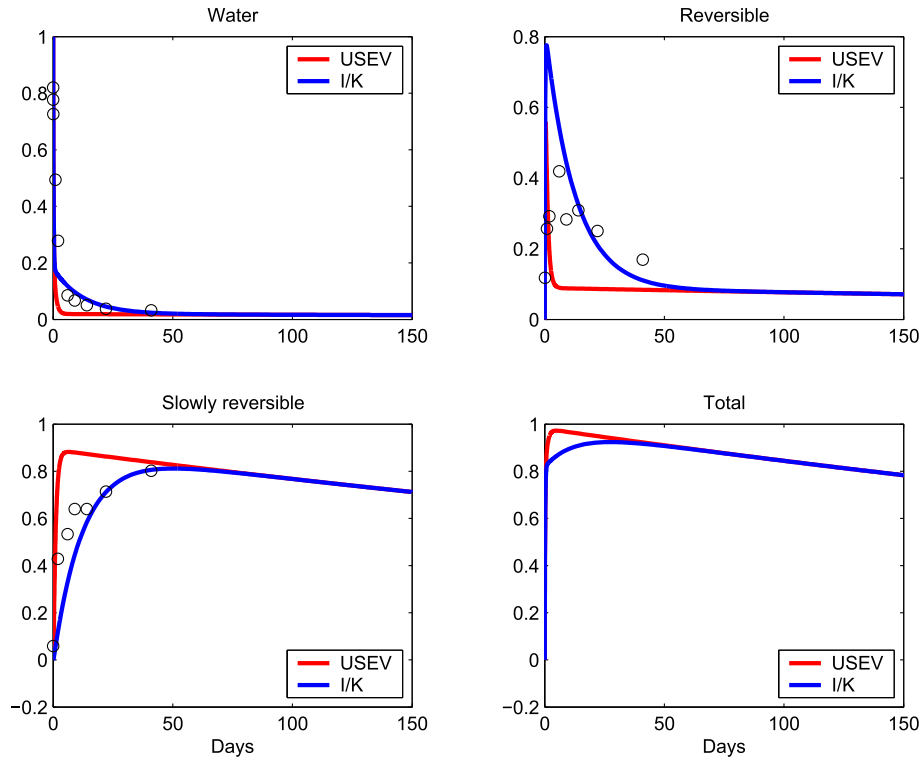


Fig. 11. Time evolution of calculated ^{109}Cd fraction in water, both sediment phases and total sediment. Black circles are measured values.

$$\chi = \chi^0 F(S, pH) = \chi^0 \left(\frac{S_0}{S + S_0} \right) \max[g_{min}, g(pH)] \quad (30)$$

$g_{min} = 0.001$ is just a threshold value to avoid $\chi \approx 0$ at low pH. A graphical representation of the function F , modulating the freshwater exchange velocity, may be seen in Fig. 13.

This formulation was successfully tested in simulations of ^{226}Ra behaviour in an estuarine system in southwest Spain (Periáñez et al., 2013), where this radionuclide was released by a phosphate fertilizer processing plant.

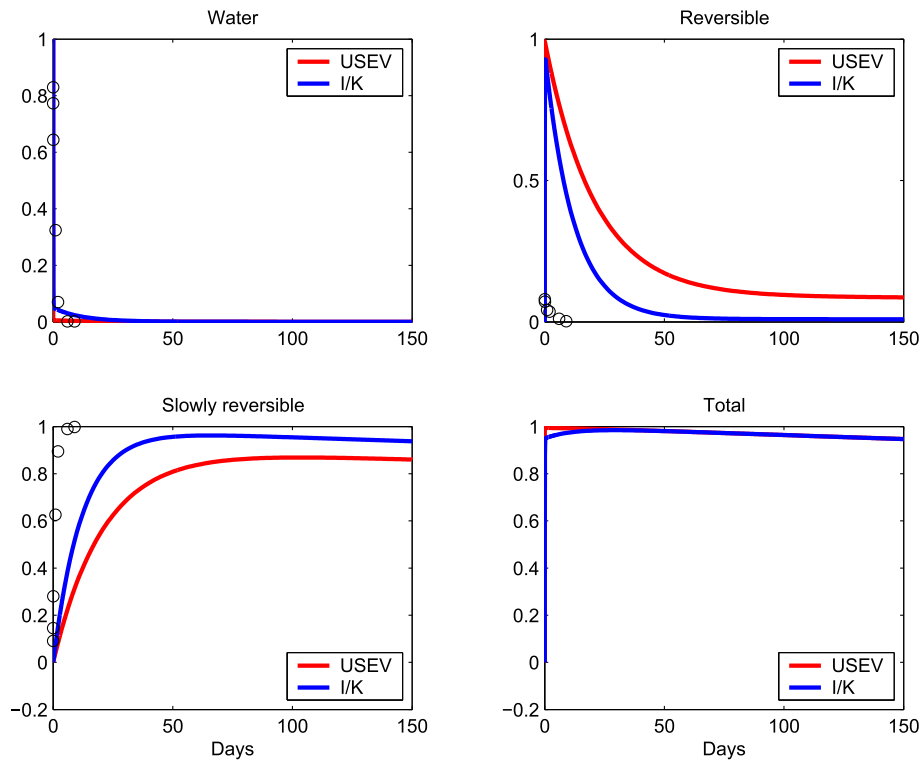


Fig. 12. Time evolution of calculated ^{60}Co fraction in water, both sediment phases and total sediment. Black circles are measured values.

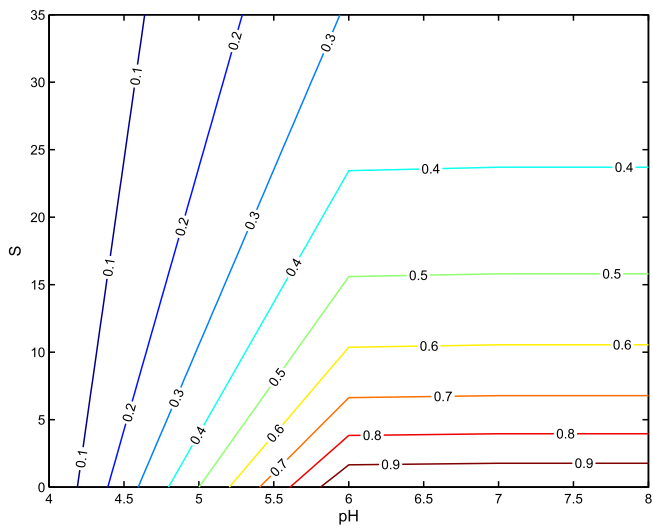


Fig. 13. Function $F(S, \text{pH})$, modulating the freshwater exchange velocity with salinity and pH.

10. Conclusions

The main conclusions derived from this study may be summarized in the following points:

- 1 The marine environment is an open system affected by external perturbations. As a consequence, steady-state does not necessarily mean equilibrium in the partition of tracers between the liquid and solid phases. When k_d s are measured in the sea, samples should be taken as far as possible from points of radionuclide release.
- 2 When k_d data are provided, it is essential to know if they correspond to suspended water/water or bed sediment/water, since they may vary in orders of magnitude being all the conditions identical.
- 3 In an initial contamination stage, 1-step and 2-step models produce

the same results. Thus, for rapid radioactive assessments after emergency situations a 1-step model may be safely applied. However, the 2-step model should be used for long-term calculations.

- 4 After a radioactive release in the sea, as in the case of Fukushima accident, equilibrium in the partition of radionuclides between water and sediments is not quickly achieved, if radionuclide kinetics is governed by a 2-step model, as generally seems to be the case, decades are required to achieve equilibrium.
- 5 The use of single or multi-layer approaches would depend on the objectives of the particular modelling study. A multi-layer model is required to evaluate sediment inventories of radionuclides; but a single-layer model, adequately tuned, may produce satisfactory results for radionuclide concentrations in the surface sediment.
- 6 It is essential to know, if a k_d dataset is provided, if such k_d correspond to fast (only reversible sediment phase) or to total (reversible plus slowly reversible phases are measured) k_d . Otherwise, large errors in predictions are expected when they are used for assessments after emergencies.
- 7 For radioactive assessments after emergencies, which imply short temporal scales, it should be recommended to have site-specific values for kinetic rates which could be used in dispersion models. Kinetic rates should be as well characterized as possible for areas where accidents could occur.

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