The marine $kd$ and water/sediment interaction problem

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ABSTRACT

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 $kd$ in a marine environment perturbed by an external radionuclide source are highlighted. Differences between suspended matter and bed sediment $kd$ are analyzed. The performances of different kinetic models (1-step/2-step; 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 $kd$ 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, $kd$. In turn, the $kd$ 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 $kd$ values would be available for the range of aqueous and geological conditions in the system to be modelled. Values for $kd$ 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):

$$ k_d = \frac{C_s}{C_w} \tag{1} $$

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 m$^3$/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), Iosipe et al. (2009), Maderich et al. (2014)], for assessments of radionuclide releases in the marine environment. Consequently, efforts have been done to compile $kd$ 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 MODARIA-II (Modelling and Data for Radiological Impact Assessments) program.

Presently, there is a trend to use dynamic models, formulated in terms of kinetic rates, instead of equilibrium $kd$ 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 $kd$ 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
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 intercomparisons 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 sediment, \( A_w \) and \( A_s \), are:

\[
\begin{align*}
\frac{dA_w}{dt} &= -k_1A_w + k_2A_s \\
\frac{dA_s}{dt} &= k_1A_w - k_2A_s
\end{align*}
\] (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:

\[
\frac{A_w}{A_s} = \frac{k_1}{k_2}
\] (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)):

\[
\frac{A_w}{A_s} = \frac{C_w}{C_s} = \frac{C_w}{V} \cdot \frac{V}{k_d}
\] (4)

thus

\[
k_d = \frac{V}{k_d} = \frac{1}{k_d}
\] (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):

\[
\begin{align*}
\frac{dC_w}{dt} &= -k_1m(k_2C_w - C_s) \\
\frac{dC_s}{dt} &= k_2(k_1C_w - C_s)
\end{align*}
\] (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 \( S \):

\[ k_1 = \chi S \] (7)

where the exchange surface has dimensions \( L^{-1} \) and \( \chi \) 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):

\[
S = \frac{3m}{\rho R}
\] (8)

where \( R \) and \( \rho \) 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:

\[
k_d = \frac{\chi}{k_2} \frac{3}{\rho R}
\] (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, \( k_d \) 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, \( k_d \) are defined at equilibrium, thus we must be sure that the partition of
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