Solid-liquid partition coefficients, K_ds: What's the value and when does it matter?

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Abstract. Environmental risk assessments hinge on our ability to predict the fate and mobility of radionuclides and metals in terrestrial soils and aquatic sediments. Solid-solution partitioning (the Kd approach), despite its shortcomings, has been used extensively. Much attention has been devoted to grooming the existing key compendia for values applicable for each nuclear risk assessment carried out worldwide. This appears to be an important task. For example, soil Kd values for a single nuclide can vary over several orders of magnitude, yet the soil Kd value is the most important parameter in the soil leaching model. Similarly, plant uptake depends primarily on the nuclide present in solution phase. Despite this apparent sensitivity, our experience has shown that risk assessors dwell too much on the precision of the Kd value for all nuclides. This paper discusses the effect of the Kd value on the resulting soil concentration during leaching and identifies those radionuclides and assessment conditions where a precise value is required. Only those radionuclides that typically have a soil Kd value of 10 L/kg or less (Tc, Cl, I, As) need be accurately described for timeframes of up to 10,000 years for desired soil model prediction outcomes (soil concentrations within two-fold).

1. INTRODUCTION

Environmental risk assessments of radionuclides and metals are key to acceptance and sustainability of industrial progress and the disposal of industry's wastes, particularly in the nuclear and mining and metal smelting industry. These risk assessments demand the fate and mobility of radionuclides and metals be understood and estimated in terrestrial soils and aquatic sediments. The difficulties of understanding radionuclide behaviour includes the speciation of the radionuclide at source or as it enters the biosphere, and the local chemical interactions such as sorption onto solid mineral surfaces, complexation, chelation, precipitation, interaction with microbes and soil or sediment organic matter to name only a few processes. Further, the plant rhizosphere and plant root exudates add to the complexity and determine the bioavailability of the radionuclide or metal, often the ultimate goal in the foodchain assessment being undertaken.

A surrogate to understanding the complex soil and sediment chemistry is often used. This surrogate is used to partition the radionuclide or metal into that which is associated with the solid phase and that which is free to move via the liquid phase. Solid-solution partitioning or the Kd approach, despite its shortcomings, has been used extensively. It is generally assumed that the use of Kd values is an interim measure until sufficient data is generated for a more complex model.

Several compilations of Kd values for both radionuclides and metals conveniently fill the data requirements [1];[2]. Much attention has been devoted to grooming the existing key compendia for values applicable for each nuclear risk assessment that is carried out worldwide. This appears to be an important task. For example, soil Kd values for a single nuclide can vary over several orders of magnitude, yet the soil Kd value is the most important parameter in the soil leaching model [3];[4]. Similarly, plant uptake depends primarily on the nuclide present in the solution phase.

Despite this apparent sensitivity, our experience has shown that risk assessors dwell too much on the precision of the Kd value for some radionuclides. The relationship between soil Kd and soil concentration is sigmoidal and non-responsive at the tails of the distribution. This paper discusses the effect of the soil Kd value on the resulting soil concentration during leaching and identifies those radionuclides (Kd values) where the precise value is required.

2. APPROACH AND ANALYSIS

The Baes and Sharp model [5] for soil leaching is a simple tool to illustrate the importance of the Kd value in surface soils. The model uses a soil loss term, λs, to describe the loss of an input pulse of radionuclide to the soil of interest. Soil concentration, Cs in Bq/m^2, is expressed as:

$$Cs = I / \lambda s \bullet (1 - \exp^{-\lambda s \bullet t}) \qquad (1)$$

Where I = input flux of radionuclide to the soil surface (Bq/m^2 a),
λs = is the radionuclide loss due to leaching (a^{-1}), and
t = time (a).

Soil leaching loss, λs, is described as:

$$\lambda s = ((Vi / \theta)/zs) \bullet (1 + (\rho b \bullet Kd/\theta)) \qquad (2)$$

Where Vi = net water infiltration rate at the soil surface (m water/a),
θ = soil moisture content (m^3 water/m^3 soil),
zs = soil root zone thickness (m soil),
ρb = soil dry bulk density (kg soil /L soil), and
Kd = soil solid/liquid partition coefficient for the radionuclide of interest (L/kg).

To illustrate the concept of which soil Kd values are most important to know accurately, we choose a standard set of input values, other than soil Kd for a set of model simulations. We have chosen parameter values typical of a temperate climate and a medium textured loamy soil under cultivation, similar to the proposed draft reference biosphere case [6] and these are:

I = 1 Bq/m^2a
Vi = 0.5 m/a
θ = 0.2 m^3/m^3
zs = 0.2 m
ρb = 1400 kg/m^3

The soil Kd value was then chosen over the range 1×10^{-6} to 1×10^{6} L/kg. Soil concentration was computed for a variety of simulation durations (1 to 1×10^{6} years).

3. RESULTS AND DISCUSSION

Often safety assessors choose soil Kd values from an established compendium. This is appropriate for a generic safety assessment, for example, to make general conclusions about whether a particular inventory is possible and to get a general impression of which pathways are important for a given suite of radionuclides. However, to refine the key pathways and to create a more site-specific safety assessment, the parameter values for each of the radionuclides have to be chosen to represent the site-specific scenario (soil, crops, lifestyles). At this point assessment modellers review their parameter values and screen them to most accurately represent the soil, climate and crop conditions. Sensitivity analyses tell soil modellers that the two most important parameters are surface water infiltration rate and soil Kd [3];[4];[5]. Soil Kd values vary over several orders of magnitude and infiltration rate only varies between 0.3 and 1 m/a in most climates. Hence, more effort is required to choose the correct soil Kd value.

As a result, modellers scour the literature for the best Kd values available for their site. Much debate has occurred in the literature and at meetings as to whether a particular radionuclide is best represented by a Kd value of 35 or 50 L/kg, or of 30,000 or 40,000 L/kg. Our biosphere simulations with a variety of radionuclides and heavy metals show that this concern is only important in a specific soil Kd value range. The response between soil Kd and soil concentration is sigmoidal and relatively non-responsive at the tails of the distribution for short assessment times (Figure 1). The upper part of the curve is not appropriate because of the short time chosen for this simulation (2 years). The soil concentration at these higher soil Kd values has not reached steady-state. However, at steady-state, some 10^7 years for very high soil Kd values, the soil concentration is linearly increasing above a log soil Kd value of about –2 (0.01 L/kg).

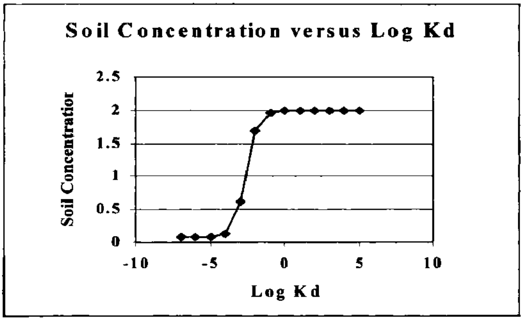

Figure 1 : Plot of soil concentration (Bq/m^2) versus log soil Kd for a very short assessment time (2 years).

Further analysis was carried varying soil Kd over a 7 order of magnitude range and varying assessment times over 6 orders of magnitude, to ensure close to steady-state conditions were reached. This analysis was proposed to determine what soil Kd values are required to be known with the most accuracy? The criteria we used for this analysis was a two-fold change in soil concentration from ten-fold increments in Kd value. This criteria was chosen arbitrarily, but generally much less than a two-fold change in soil concentration is not distinguishable for many radionuclides or metals. This analysis shows the lower soil Kd value remains almost constant (Figure 2). Soil Kd values below 0.0001 L/kg do not cause a two-fold change in soil concentration as they decrease. Actually, values less than 0.001 L/kg are almost not measureable [9]. If you assume no analytical detection limit problems, consider a pipetting error of 0.1% (0.001 change in solution concentration) and optimize the soil:solution ratio for measuring low values (for example a soil:solution ratio of 10:10), then the lowest Kd value measureable is about 0.001 L/kg.

Soil concentration maximums are reached under steady-state conditions as sorption increases expanding the range of Kd values that cause this two-fold soil concentration change with simulation duration (Figure 2). For short timeframes, up to 100 years – typical of low-level radioactive waste assessments and present-day metal ecotox assessments, the most important Kd values to know accurately are those that fall in the 0.0001 to 0.1 L/kg range. For longer timeframes, 100 to 1000 years – timeframes typical of intermediate radioactive waste assessments, the most important soil Kd values to know accurately are those values less than 1 L/kg. For long-term or high-level radioactive waste assessments, it becomes important to know soil Kd values between 0.0001 and 10,000 L/kg accurately. Above a soil Kd value of 10,000 L/kg – typical of a soil half-time of about 4 million years – it doesn't really matter how much larger than 10,000 the value gets. More importantly, for assessments of 10,000 years, considered by some to be the longest timespan we can estimate what the biosphere will look like, the most accurate soil Kd values required are those with a value less than 10 L/kg (Figure 2).

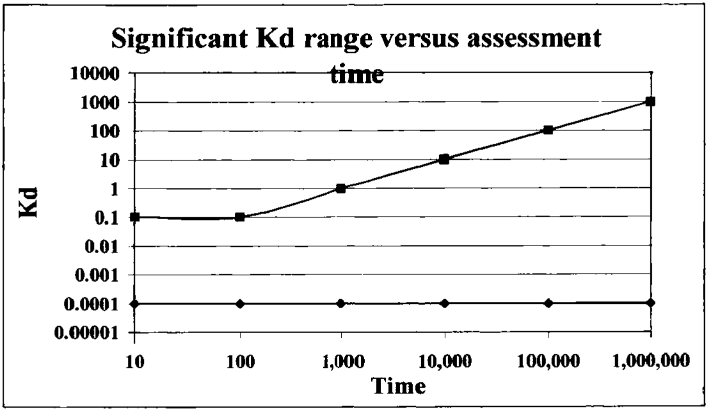

Figure 2 : Plot showing the Kd (L/kg) with assessment time (years) that causes a two-fold change in soil concentration.

To put this analysis into perspective for metals and radionuclides, we have prepared a list of metals and radionuclides that fall in this envelope of soil Kd values that require very careful attention to accuracy below a stated value (Table 1). It is easy to see from Table 1 that great accuracy in soil Kd values for most radionuclides is only required in longer-term assessments. Even at 10^3 years, few radionuclides need be known with a lot of precision. Beyond 10^3 years, the list lengthens and radionuclides such as Ac, Ce, Cm, Co, Cs, Hf, Pa, Pb, Pu, Ra, Th, Zn, and Zr are not even listed until well beyond an assessment time of 10^6 years. Of course, these nuclides are only discussed with respect to a specific compendium [7]. Site-specific values for some nuclides may place them in a different class.

4. CONCLUSIONS

Although detailed sorption isotherms are the preferred route for understanding the fate and migration of radionuclides and metals, this detail may be absent or unattainable for the porous media and nuclide of interest. In this case and for generic or scoping safety assessments, the soil solid/liquid partition coefficient or soil Kd value is the default approach. Since many of these values make their way eventually to compendia, adequate soil characterization data should always accompany the values. The key point we make in this work is to direct the correct amount of effort in choosing the default Kd value for the radionuclide or metal of concern and the assessment duration required. Only those radionuclides and metals that typically have a soil Kd value of 10 L/kg or less (Tc, Cl, I, As) need be accurately described for timeframes of up to 10,000 years for desired soil model prediction outcomes (soil concentrations within two-fold).

Table 1 : Selected metals and radionuclides (from the IAEA Handbook, 1994) requiring the most accurate soil Kd values in a loam soil (based on expected or Geometric Mean values) for 100 to 10^6 year durations.

100 years ≤ 0.1L/kg	10^3 years ≤ 1 L/kg	10^4 years ≤ 10 L/kg	10^5 years ≤ 100 L/kg	10^6 years ≤ 1000 L/kg
Cl*	Cl*	As*	As*	Ag
Tc	Tc	Cl*	Br	Am
		I	Ca	Be
		Tc	Cd	Bi
			Cr	Fe
			I	Ho
			Np	Mn
			P	Mo
				Nb
				Ni
				Pd
				Po
				Rb
				Ru
				Sb
				Se
				Si
				Sn
				Sm
				Sr
				Ta
				U

* As and Cl were not included in the IAEA compendium (values come from[1] and [9])

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