

Modelling Speciation and Distribution of Radionuclides in Agricultural Soils

Volker Hormann

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Abstract The behaviour of radionuclides (and thus their plant availability) in cultivated soils principally depends on soil solution composition and the presence of adsorbing surfaces. Both properties vary with soil type, soil cultivation and climatic conditions. We give an overview of the relevant soil processes and the

V. Hormann (✉)

IUP—Institute of Environmental Physics, University of Bremen, D-28359 Bremen,
Otto-Hahn-Allee 1, Germany

e-mail: vhormann@physik.uni-bremen.de

basic sorption modelling concepts with the emphasis on surface complexation on minerals and humic matter. For estimating speciation and distribution of radionuclides, geochemical codes can be employed. We show an example how modelling can be carried out by using the well-known code PHREEQC and introducing the reference soil concept. Using the example of the UNISECS model, we discuss issues of parametrisation and validation as well as the sources of uncertainty. For selected nuclides, we evaluate the dependence of the distribution coefficient (K_d) on the most important soil parameters.

Keywords Agricultural soils • Speciation • Soil parameters • Sorption • Modelling, PHREEQC • K_d

1 Introduction

Cultivated soils are key entry points for radionuclides into the food chain. Artificial radioisotopes may contaminate those soils by dry and wet deposition as a result of atomic bomb explosions, nuclear accidents (e.g. Chernobyl and Fukushima) or other accidental nuclear releases into the environment. They may also be released from nuclear waste repositories more or less far in the future, migrating through the surrounding rock and subsequently becoming dissolved in groundwater which is frequently used for irrigation and thus introduced into the soil. The groundwater itself may rise carrying the radionuclides to the root zone. Plants are able to incorporate and even accumulate ions and small molecules present in the soil solution via root uptake. Essentials for the amount of activity transferred to plants are not only plant type and activity concentration in the root zone, but also the physicochemical properties of the soil and speciation of the soil solution which play a crucial role because they are governing the bioavailability of the nuclide in question. Sorption and complexation of ions to soil minerals and organic matter are mechanisms which may decrease solution activity and can delay transport drastically. On the other hand, binding of radionuclides to dissolved organic matter (DOM) or colloids in soil solution may enhance their mobility (Tipping 2002; Appelo and Postma 2005).

A lot of these important parameters and processes taking place in soils and on mineral surfaces have already been identified, analysed and quantified. For instance, the solid–liquid distribution coefficient K_d has been experimentally determined (usually in batch experiments) for a variety of nuclides and soil types. The values from the respective publications have recently been compiled and categorised (IAEA 2010). K_d is also being used in risk assessment models like ECOLEGO (Avila et al. 2003) or AMBER (Punt et al. 2005), e.g. to estimate the radiation dose after radionuclide ingestion. Unfortunately, the K_d for a certain nuclide may vary over orders of magnitude even within a single soil category

(IAEA 2010). This could in principle be amended by correlating K_d values with soil parameters like pH or clay content as found experimentally (Gil-García et al. 2009a, b; Vandenhove et al. 2009) and using this correlation for a particular soil. However, this is not feasible if the compiled soil analysis data are not sufficient or only few experimental studies have been performed for a particular radionuclide. Correlations may also be rather poor if additional important soil parameters have not been identified. Moreover, bioavailability is not always well predicted by K_d , for instance, in cases where nuclide speciation is important for plant uptake (Vandenhove et al. 2007b).

In this view, modelling K_d and speciation using geochemical codes may be an attractive alternative to provide data that can be used for estimating plant uptake, thus giving a basis for risk assessment calculations.

2 Important Soil Parameters and Processes

For modelling, it is crucial to identify the soil parameters that largely affect radionuclide distribution and migration. Some parameters may be only relevant for a certain subgroup of nuclides, whereas others are generally important. Physical parameters like porosity or water content have more influence on the migration of the solute than on its solid–liquid distribution unless chemical reactions or surface interactions are taking place on a similar or even slower timescale compared to water flow (Degryse et al. 2009). Here, a short review of the most important parameters is given. Detailed information about soil chemistry and physics can be found in textbooks (Sposito 1989; McBride 1994; Sparks 1999; Scheffer and Schachtschabel 2010).

2.1 Chemical Parameters and Processes

Soils are heterogeneous media, largely composed of a mixture of inorganic minerals, organic matter, water and air.

The mineral composition varies from site to site and not only depends on the chemistry of the underlying bedrock but also on weathering processes and erosion. Minerals with large surface areas that are capable of sorbing or complexing ions are important for modelling, because in almost all cases the radionuclides will be present in free or complexed form. In this respect, the two most important mineral classes are (1) clay minerals and (2) transition metal (mainly iron) oxides, which make up most of the clay fraction (particle size $<2 \mu\text{m}$) of the soil.

Soil organic matter (SOM) is composed of the decay products of larger organic structures (plant leaves and roots) and is also called ‘humus’. It does not include living organisms like bacteria and fungi which may accumulate radionuclides in

some cases (e.g. Parekh et al. 2008; Akai et al. 2013) and which will not be treated here. SOM is also able to complex cations (Tipping 2002) and can be present either as larger immobile particles, thus contributing to radionuclide retention or in solution as dissolved organic matter (DOM) contributing to nuclide mobility. Some nuclides like ^{131}I can also be bound covalently to organic matter, probably mediated by bacterial activity (Christiansen and Carlsen 1991). SOM can also interact with mineral surfaces, possibly blocking mineral binding sites.

The soil solution is the medium where chemical reactions take place, either at surfaces or in the bulk phase. It also carries ions and molecules that may compete with the binding of radionuclides to surfaces or act as complexants which keep them in solution. The composition of the solution is spatially (there may even be differences in samples from a few metres apart (Campbell et al. 1989)) as well as temporally variable (dilution by rainfall events, concentration effects by evaporation, seasonal variations caused by plant activity).

One of the key parameters is the pH value which largely affects solution chemistry as well as surface properties. The redox potential (pe) is important for the chemical state of certain radionuclides like Se (Ashworth et al. 2008) and U (Langmuir 1997). Changes of pe may lead to reactions involving electron transfer (e.g. $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{e}^-$) and to precipitation or dissolution reactions. For example, as a single (uncomplexed) ion, uranium is usually present in solution as UO_2^{2+} under oxic conditions, while its chemical form is the insoluble U^{4+} if the solution is depleted of oxygen (Langmuir 1997) as it is in the case of flooded soils under stagnant ponding (Sposito 1989).

Generally, the soil pores are not totally filled with water because after a rainfall or irrigation event, the water will redistribute due to gravitational and capillary forces. At the soil surface, water may be also removed by evaporation. In any case, air will penetrate the pore system, leaving it unsaturated. Below the soil horizon, the air may be partly depleted of oxygen and enriched with carbon dioxide due to biological processes (Sposito 1989). This, in turn, will have an impact on the soil redox state and thus on soil solution chemistry.

Air present in small pores will have an effect on water transport due to capillarity effects. Some radionuclides (radon) can also be transported via soil air.

2.2 *Physical Parameters and Processes*

The migration of fallout radionuclides into the root zone is usually mediated by advective flow of water, as the soil solution is the carrier of radionuclides in dissolved or colloidal phase. The vertical water transport velocity depends on a number of physical parameters including soil texture (i.e. clay, silt and sand content), porosity, water content and bulk density. A key parameter is the hydraulic conductivity which can be connected to these parameters by the so-called pedotransfer functions, which have been determined experimentally for a great

number of soils (Weynants et al. 2009). In transport calculations, dispersive and for some nuclides, e.g. ^{137}Cs (Kirchner et al. 2009) also diffusive or diffusion-like effects have to be taken into account. For further reading on soil hydrology, textbooks like Kutilek and Nielsen (1994) are recommended.

2.3 Influence of Agricultural Use

While the parameters and processes described in Sects. 2.1 and 2.2 apply to all soils (including undisturbed), the effects of soil management also have to be taken into account. Ploughing mixes the upper soil layer (usually ca. 15–30 cm) and dilutes the total concentration of slowly migrating radionuclides like Cs in this layer. It also aerates the soil and thus increases the degradation of organic matter. Another effect is that it makes the soil susceptible to erosive processes in certain high slope conditions and inappropriate cultivation practices.

Often, lime is applied to soils in order to increase pH, changing the soil solution chemistry. Fertilisers introduce large amounts of ions that may interact with surfaces, e.g. displacement of Cs^+ from clay surfaces by NH_4^+ (Hormann and Kirchner 2002) or act as complexants (PO_4^{3-} with U).

3 Sorption Modelling Concepts

The interactions of radionuclides with solid and/or particulate surfaces present in the soil strongly depend on the chemical and physical properties of its mineral and organic components. For the estimation of the solid–liquid distribution of these elements, models for element–surface interaction have to be applied.

3.1 Empirical Models

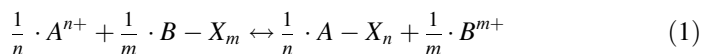
The distribution coefficient K_d is defined as the quotient of the radionuclide activity present in (or sorbed to the surface of) the solid phase S and the respective activity C in the soil solution. Its unit is usually given as l kg^{-1} and can be determined experimentally (Hilton and Comans 2001). Taking K_d as a proportionality factor between S and C , one gets a curve which is called ‘linear isotherm’. In this case, one assumes that adsorption depends exclusively and linearly on solution concentration neglecting all effects originating from surface and soil solution composition. While this may be true for trace concentrations of unionised, hydrophobic organic molecules (Goldberg et al. 2007), for most metal ions and anions (including radionuclides), K_d exhibits a strong dependency on soil parameters like pH or CO_2 partial

pressure (IAEA 2010) and therefore varies spatially as well as temporally. Other relations like Freundlich and Langmuir isotherms (McBride 1994) introduce additional fitting parameters and may account for nonlinearity and saturation effects, but still are only applicable for constant chemical and physical conditions.

3.2 Ion Exchange

In general, soil particle surfaces are charged, and in most cases, there is a contribution by a permanent (usually negative) charge and a variable pH-dependent charge. The binding to permanently charged surfaces is called ‘unspecific sorption’ or ‘ion exchange’, while binding to variable charge surfaces is called ‘specific sorption’ or ‘surface complexation’.

Cation exchange can be described by a simple exchange reaction between two ions A^{n+} and B^{m+} , where n and m are integers:



Here, X is an arbitrary surface group that is capable of binding cations. Usually, the exchange selectivity for an ion A^{n+} is given as the exchange coefficient for sodium (Na):

$$K_{\text{Na}/A} = \frac{[\text{Na} - X][A^{n+}]^{1/n}}{[A - X_n]^{1/n}[\text{Na}^+]} \quad (2)$$

This mechanism is the most important for alkaline and alkaline earth cations and may be relevant for certain trace metal ions like Ni^{2+} , Cd^{2+} and Pb^{2+} (Appelo and Postma 2005), as well as for certain actinides (e.g. Am^{3+} on planar illite sites, Bradbury and Baeyens 2009b). The capability for cation exchange is called ‘cation exchange capacity (CEC)’ and is expressed in meq kg^{-1} soil. Some soil minerals may also exchange anions, but the anion exchange capacity of soils is generally much lower (Scheffer and Schachtschabel 2010).

3.3 Mineral Surface Complexation Models

A way to account for variable charge surfaces is the use of surface complexation models, which include equations for the binding of ions to reactive surface functional groups like S–OH (where S stands for Fe, Al), present on hydrous oxides and clay minerals. Most models include thermodynamic parameters, namely, the surface potential Ψ and the temperature T . An example for such a thermodynamical

equilibrium constant (here: protonation of an S–OH surface group) is given in Eq. (3):

$$K_+ = \left(\frac{[\text{SOH}_2^+]}{[\text{SOH}]\{\text{H}^+\}} \right) \exp\left(\frac{F\Psi}{RT}\right) \quad (3)$$

Here, F is the Faraday constant and R is the molar gas constant. $[\text{SOH}_2^+]$ and $[\text{SOH}]$ are surface group concentrations and $\{\text{H}^+\}$ is the proton activity. Similar expressions exist for the deprotonation of an S–OH surface group and complexation reactions with cations or anions (called ‘complexation constants’), depending on the model. To date, there are various surface complexation models (SCM) making different assumptions concerning the shape of the surface potential and the complexation reactions to be included. While the constant capacitance model (CCM) assumes a linear decrease of Ψ with distance from the mineral surface, other models like the diffuse layer (DLM) and triple layer (TLM) models include one (DLM) or two (TLM) surface layers and a layer of counter ions which is called ‘diffuse layer’. These are so-called two-pK models including two protonation reactions. In the ‘one-pK models’ (e.g. CD–MUSIC by Hiemstra and van Riemsdijk (1996), where multiple surface sites are distinguished), only one protonation reaction is considered. Some of these models also allow for bi- or tridentate binding. For a more extensive discussion of surface complexation modelling, the review articles by Goldberg et al. (2007) and Groenenberg and Lofts (2014) are recommended. A concise treatment of the double layer calculation is given in Appelo and Postma (2005).

The well-known generalised two-layer model by Dzombak and Morel (1990) includes monodentate binding and two separate (‘strong’ and ‘weak’) kinds of sites with different complexation constants. It will be used in the soil model described in Sect. 4.

3.4 Ion Binding of Organic Matter

In many soils and other natural systems, organic matter (OM) plays a significant role for transport and retention of radionuclides. While SCMs for minerals usually include just two or three kinds of surface sites, modelling complexation to OM has to take into account the great complexity of the material. There are two basic approaches to this: (1) assuming a continuous distribution of binding strengths (the NICA–Donnan model by Benedetti et al. 1996) and (2) using an assemblage of discrete binding sites (the humic ion-binding (HIB) model VI (Tipping 1998)). In both cases, only cation binding is considered because the OM surfaces exhibit negative charge at all pH values (Tipping 2002).

While the NICA–Donnan model gives the amount of a bound species in a closed analytical form with fitted parameters, model VI assumes two site types A and B, where each type has a distribution of sites with complexation constants K given by

$$\log K(i) = \log K_{MA} + \frac{2i - 5}{6} \Delta LK_{A1} \quad (4)$$

with $i = 1 \dots 4$ for site type A (associated with carboxyl groups) and

$$\log K(i) = \log K_{MB} + \frac{2i - 13}{6} \Delta LK_{B1} \quad (5)$$

with $i = 5 \dots 8$ for site type B (associated with phenolic groups). K_{MA} and K_{MB} are intrinsic equilibrium constants different for each cation. ΔLK_{A1} and ΔLK_{B1} are fitting parameters, which were shown to be equal for all metals (Tipping 2002). These formulas only describe monodentate binding; for bi- and tridentate binding, additional expressions are given, introducing an additional metal-specific fitting parameter ΔLK_2 . In total, there are 80 binding sites, each having its own abundance. Equilibrium constants and fitting parameters for a number of cations have been derived for binding to both fulvic and humic acids. Electrostatic interaction is accounted for by a factor $\exp(2PZ \log(I))$, where Z is the charge on the humic substance in eq g^{-1} , I is the ionic strength of the solution and P is an adjustable coefficient. For details, see Tipping (2002).

3.5 Model Parametrisation

In principle, the complexation constants for a model have to be determined experimentally for each mineral phase to be considered. This is done by fitting the amount of adsorbed activity to either pH or to the activity concentration in solution at constant pH. If there are no experimental data, complexation constants can often be estimated by so-called linear free energy relationships (LFER). For example, in the case of transition metal cation complexation described by the model by Dzombak and Morel (1990) (see above), linear relationships between surface complexation constants $\log K_i$ and the ions' first hydrolysis constants $\log K_{OH}$ (for the reaction $M^{n+} + OH^- \leftrightarrow MOH^{(n-1)+}$, where M^{n+} is the metal cation) have been found both for weak and strong sites. If $\log K_i$ has not been determined for a specific transition metal cation, it may be estimated by using the respective LFER if $\log K_{OH}$ is known. For further information, see Appelo and Postma (2005) and Tipping (2002).

The density of surface sites is one of the most important modelling parameters. It can either be calculated by the use of crystal dimensions if a pure phase is modelled or be determined experimentally by a wide range of methods including tritium exchange, acid–base titration and analysis of sorption isotherms (Davis and Kent 1990). As an example, the estimation of site densities on montmorillonite surfaces is described in Baeyens and Bradbury (1997). Surface areas are usually determined by the Brunauer–Emmett–Teller N_2 adsorption method (McBride 1994).

3.6 *Assemblage Models*

For solid–liquid distribution modelling, it has to be considered that each soil has its own characteristic mineral and organic composition. There are two basic concepts to model assemblages: the *general composite* (GC) approach and the *component additive* (CA) approach.

The GC approach is the most useful for predictive purposes if a specific field (sampling) site has to be considered and a large set of experimental data (titration and adsorption curves for the relevant radionuclides) is present. In this case, one can define ‘generic’ surface groups which represent the average soil surface properties, and the chosen model can be parametrised. Within the range of chemical conditions where the experimental data have been taken, predictions should be valid. However, for other field sites and/or chemical conditions, they will be questionable.

Following the CA approach, one assumes that the behaviour of a soil can be described by the sum of its most active pure components. If models and sufficient thermodynamic databases for these pure components exist, it is technically possible to predict the behaviour of the total assemblage. This is most convenient in cases where it is not possible to do extensive experimental work or to make estimations for a broader range of soil types. The main disadvantage is that interactions between the components (e.g. binding of humic material to mineral surfaces, thus reducing the mineral’s number of accessible binding sites) are not taken into account. Moreover, in many natural systems, one finds a broad variety of minerals that often have not been investigated yet. Even so, by taking well-characterised minerals and organic substances as proxies for the most important soil components, one may predict the K_d of radionuclides for a certain soil type under given conditions with much higher accuracy than those listed in documents such as IAEA (2010) for general soil types like sand or clay. In the next paragraph, it will be shown how this can be accomplished.

4 Constructing a CA Soil Model

To perform calculations for K_d estimations, three basic components have to be chosen and assembled:

- A physicochemical speciation code for solving the set of equilibrium speciation equations
- A suitable combination of model components
- An appropriate set of thermodynamical data

The components have to be then implemented in the code (the interface is usually given as an input file) and have to be properly parametrised to give an optimal representation for the system to be modelled. If a code (e.g. PHREEQC (Parkhurst and Appelo 2004)) allows for performing user defined calculations using

simulation data, this is convenient for direct calculation of the distribution coefficient.

4.1 *Speciation Code and Representative Soil Components*

Assuming that it is neither intended to write the necessary codes ‘from scratch’ nor to do the experimental work for calibrating surface complexation models, one has to assemble the necessary tools from the literature. Before starting, it is not only important to get a clear picture of the model’s intended use in the immediate future, but also to think of possible applications further ahead. In the case of the CA model developed by Hormann and Fischer (2012, 2013) on behalf of the German Federal Agency of Radiation Protection (henceforth called ‘UNISECS¹ model’), two properties have been emphasised: (1) easy expandability for the inclusion of further nuclides and (2) options for doing transport calculations or for being coupled to hydrological transport codes. For these purposes, one starts by looking for a speciation code that includes (or is able to include) various thermodynamical databases that may be modified and expanded in order to perform the appropriate solution chemistry calculations. The code also has to be capable of including surface complexation and exchange models for doing solid–liquid distribution estimations. Some popular codes are FITEQL (Herbelin and Westall 1996), ECOSAT (Keizer and Van Riemsdijk 1998), Visual Minteq (Gustafsson 2010) and PHREEQC (Parkhurst and Appelo 2004).

Before choosing the speciation code, the key components of the model system and models that describe sorption on these components have to be determined. For the UNISECS model, four components, their representative materials and respective models (given in parentheses) have been identified:

- Soil clay (illite, Bradbury and Baeyens 2000, 2009a, b)
- Hydrous oxides (ferrihydrite, Dzombak and Morel 1990)
- Immobile organic matter (humic acid, Tipping 1998)
- Dissolved organic matter (fulvic acid, Tipping 1998)

Clay minerals and hydrous oxides are significant soil components and have both high sorption capacities and large specific surface areas. On the other hand, it is probable that larger particles like quartz grains make only minor contributions to the sorptive capacity of a soil. The required models for illite and ferrihydrite (two-pK non-electrostatic model and diffuse double layer model, respectively) are already implemented in the geochemical code PHREEQC and can be readily parametrised.

¹ Because it had originally been developed to estimate the distribution of the long-lived radionuclides ²³⁸U, ⁶³Ni, ⁷⁹Se and ¹³⁵Cs in agricultural soils (Hormann and Fischer 2012).

Organic matter will be present in the immobile form (e.g. as coatings or attached to soil particles) or in solution (dissolved organic matter, DOM). As humic acids have a larger average molecular weight than fulvic acids, they will tend to accumulate in the immobile phase (e.g. by coagulation). Thus, it seems to be appropriate to phase-separate these two humic substances as a first approximation. The humic ion-binding model can be included in PHREEQC by using the diffuse double layer model implementation and by replacing the electrostatic interaction factor described above by the Boltzmann factor from Eq. (3) (Appelo and Postma 2005).

4.2 *Thermodynamical Data*

Geochemical speciation codes are usually equipped with a database containing the thermodynamical constants for reactions in solution and on surfaces. The quality of a database depends on careful selection of data from the literature and on a thorough check for chemical consistency. PHREEQC provides several databases from different sources, but the authors emphasise that these data have not been checked for consistency and consider them as preliminary (Parkhurst and Appelo 2004). Especially when modelling radionuclides, it is possible that not all relevant reactions for a certain radionuclide are included in the database. In this case, these data have to be taken from the literature and added to the input or database file.

For the UNISECS model, we chose the NAGRA/PSI database (Hummel et al. 2002), which was assembled to support the safety assessment of a nuclear waste repository and also includes, as the authors state, ‘elements commonly found as major solutes in natural waters’. It contains a large amount of radionuclide data, has been checked for consistency and is supplied in a format compatible with PHREEQC.

4.3 *Model Parameters*

Once the thermodynamical data have been implemented, the physicochemical characteristics of the system have to be specified. The most important are:

- Number of surface binding sites
- Soil solution composition
- Redox state and oxygen content
- Solid phases
- CO₂ pressure

In most of the surface binding models, the surface density of binding sites (in sites per m²) and the specific surface area (in m² g⁻¹) are given for specific

minerals. These values must be treated with caution because they usually have been determined in the laboratory using model substances which may not have the same properties like the respective minerals present in the soil. Moreover, the number of sites blocked by other soil components (humic substances on mineral surfaces) may not be negligible. If the geochemical code requires the number of surface sites n_w per kg soil solution, but only the number n_d per kg dry mass is known, one can calculate n_w with the help of the dry soil density ρ and the water-filled porosity ϕ :

$$n_w = n_d \cdot \frac{\rho}{\phi} \quad (6)$$

If not known, ρ and ϕ may be calculated from soil texture data using the so-called pedotransfer functions (Rawls et al. 1982; Saxton et al. 1986).

When modelling with a geochemical code, the composition of the solution is highly important for the following reasons:

1. The surface charge in surface complexation models usually depends on the ionic strength and the pH of the solution.
2. Ions in solutions will compete for surface binding sites (thus binding constants for major ions such as Fe^{3+} on humic acid or PO_4^{3-} on hydrous oxides should be available).
3. Some dissolved species may form complexes with the radionuclide in question that are not or only weakly bound to surfaces.

If the soil solution composition is not available, it can be estimated using values from the literature (Scheffer and Schachtschabel 2010). If a radioactive contamination is introduced, in many cases, the activity² is given in Bq kg^{-1} soil. As the geochemical code usually requires a mass or concentration as input, this has to be converted using the specific activity for the respective nuclide. The oxygen content and thus the redox state of the solution will have an influence on chemistry and oxidation state of many ions (see above) and therefore has to be specified. In PHREEQC, *pe* can be adjusted, for instance, by consumption of dissolved oxygen by organic matter (Appelo and Postma 2005).

For dynamical simulations (e.g. *pe* changes and/or transport), solid phases may have to be defined, because they may remove ions from solution by precipitation or introduce new ions by dissolution. Selenium in solution, for example, will be precipitated as elemental selenium or selenide when submitted to anoxic conditions (Ashworth et al. 2008, Masscheleyn et al. 1990). The definition of solid (non-sorptive) phases is also useful for determining the concentration of major ions (e.g. equilibration of the solution with gibbsite for estimating the aluminium concentration). Carbonate and hydroxycarbonate are important major ions that act as a buffer and form complexes with cations. The concentration of these ions varies with the CO_2 pressure which itself depends on biological activity.

²Not to be confused with the chemical activity.

4.4 Calculating the Distribution Coefficient

When all soil parameters have been adjusted, the simulation can in principle be started. Usually, one would first equilibrate the surface ensemble with the uncontaminated soil solution to create ‘standard conditions’ in the sense that a realistic equilibrium distribution of major ions on the surfaces is calculated. Then, depending on the scenario, the contamination is introduced and a new equilibrium calculation is performed. The distribution coefficient K_d can be calculated by

$$K_d = \frac{\Phi}{\rho} \cdot \frac{\sum_i a_{i,\text{solid}}}{\sum_j a_{j,\text{solution}}}, \quad (7)$$

where Φ is the water-filled porosity and ρ is the dry soil density. $a_{i,\text{solid}}$ and $a_{j,\text{solution}}$ are the activities of the radionuclide in its chemical form i associated with the solid phase and j in solution, respectively. This definition is somewhat ambiguous as the term ‘solid phase’ is not clearly defined. If a fraction of the activity has been precipitated during the equilibration, it is generally not clear, whether it is present in particulate or colloid form in solution (and thus transportable) or bound to the soil solid. If K_d is experimentally determined, frequently the activity of the extracted soil solution is measured; thus, precipitates may be attributed to the liquid phase, leading to a different distribution coefficient. In the UNISECS model, all precipitates have been assigned to the solid phase.

Note that in this case, K_d is calculated for the state of equilibrium. In most cases, it is assumed that the kinetics of the sorption/complexation reactions is fast (meaning in the order of milliseconds or seconds), a condition that is usually met in soils (Scheffer and Schachtschabel 2010). Still, in some cases, the reaction may be slow and diffusion controlled, like the exchange of alkali ions on clay minerals, which is in the order of hours (Sparks 1999).

5 Verifying and Validating the Model

Once a model has been implemented, it has to be checked for consistency, and it has to be made sure that it meets all of its specifications. This procedure is called verification and it should be performed before the validation process. Typical verification procedures may involve summing the activity of all species used for calculation of the K_d (which should result in the added activity) or checking for charge balance, pH and redox state after the equilibration.

Validating the model includes testing its ability to reproduce experimental results achieved in the laboratory under controlled conditions. This means that preferably all input data for the simulation should be known. As this is not always the case (if it is not feasible to perform experiments by oneself), there are several possible levels of validation, depending on the number of unknown parameters. In the following subsections (5.1 and 5.2), two validation procedures performed for the UNISECS model will be presented. More information about these procedures including an additional test for cesium modelling can be found in Hormann and Fischer (2013).

5.1 Comparison of Simulations with Averages of Experimental K_d Values for Two Soil Types

In the IAEA Technical Reports Series No. 472 (IAEA 2010), the best estimates of solid–liquid distribution coefficients are given for a number of radionuclides. These values have been derived from field and laboratory studies and are given as the geometric mean for four generic soil types. In most cases, the ranges of the K_d values span one or two orders of magnitude. The validity of a model may be checked by finding the physicochemical properties of a ‘typical’ or ‘representative’ soil type, simulating the distribution under ‘normal’ conditions using a soil solution composition derived from average field values and comparing the result with the best estimate for the respective nuclide.

The Refesol (reference soil) concept (Kördel et al. 2009) developed for establishing a reference system for chemical testing of soil presents an attractive possibility of choosing soils which are taken as representative for some of the soil types used in the IAEA report. The Refesols are well characterised and provide all the input parameters necessary for simulation, except for the soil solution composition, which can be derived by average values given in Scheffer and Schachtschabel (2010).

Using these parameters and the database as well as the complexation constants discussed in the previous sections of this chapter, K_d values have been calculated for a typical loamy soil (Refesol No. 2) and a typical sandy soil (Refesol No. 4). In Fig. 1, these values are compared with the best K_d estimates and the corresponding experimental ranges given in IAEA (2010). The calculated values are close to the best estimates, the deviations being always considerably less than an order of magnitude. Considering the ranges of experimental values, the simulations are fitting remarkably well. This demonstrates the model’s ability of performing meaningful equilibrium K_d estimations at least for the elements U, Ni, Se and Cs in two generic soil types.

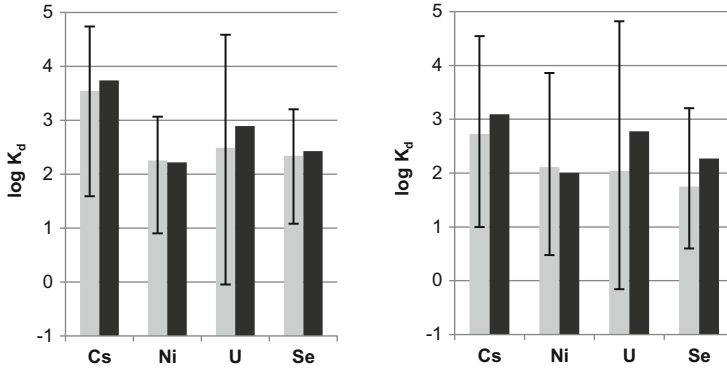


Fig. 1 Comparison of the IAEA best K_d estimates (light grey) and their ranges (whiskers) for Cs, Ni, U and Se with results calculated using the UNISECS model (dark grey) for a loamy soil (left) and a sandy soil (right) (Adapted from Hormann and Fischer 2013)

5.2 Simulating Experimental Uranium Distributions in Batch Experiments with Several Specified Soils

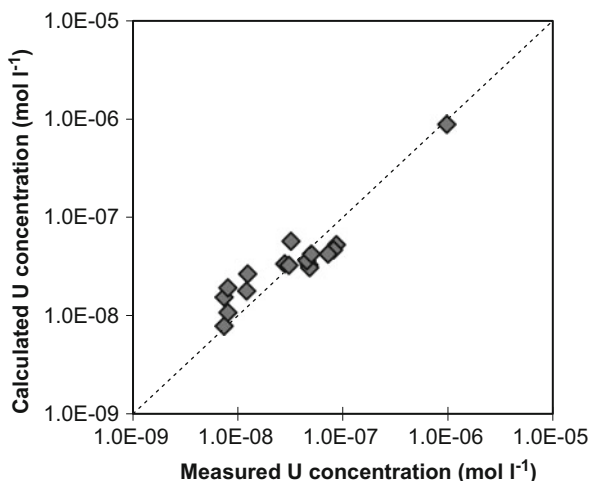
Having shown the general predictive capability of the UNISECS model, the next question is whether it is also able to estimate the solid–liquid activity distribution in specified soils. Uranium is an element that interacts with all model components, and the high variability of its distribution coefficient makes it particularly suitable for validating the model. Thus, a study has been chosen where 18 thoroughly characterised soils were used for determining the distribution of uranium after contamination of soil samples in batch experiments (Vandenhove et al. 2007a). These soils covered a wide range of soil parameters affecting K_d , such as pH, Fe and Al oxide and hydroxide content, clay content and organic carbon. The soil solutions had been extracted after 4 weeks of equilibration and subsequently analysed for uranium.

For each soil, the uranium concentration has been calculated by the UNISECS model using the soil component and soil solution data given in the experimental study. As shown in Fig. 2, the UNISECS estimations are quite close to the experimental results, and the largest deviation is by a factor of 2.4, which is again remarkable considering the fact that CO₂ pressure and dissolved organic matter content are not given in the experimental study and therefore have to be estimated.

5.3 Sources of Uncertainties

Even if validation efforts give promising results as shown above, a model still has to be used with caution. As soils are very complex systems, in many cases, their

Fig. 2 Comparison of measured (Vandenhove et al. 2007a) U concentration in soil solution with results from simulations with the UNISECS model (Hormann and Fischer 2013, with permission from Elsevier)



chemical composition and behaviour may not be adequately taken into account, especially if unconsidered minerals are present in the soil that also have strong complexing abilities but different relative selectivities concerning the relevant nuclides. Considerations under which circumstances certain minerals will precipitate (e.g. oversaturation of gibbsite) may also be an issue.

Another source of uncertainty is the parametrisation of the model component. As an example, the number of surface sites is usually assumed to be constant. In real soils, the actual composition of the sorbent and thus its surface structure may be different. Moreover, a significant fraction of these sites may be blocked by other soil components (e.g. organic matter) and thus not be accessible for sorption. The surface sites themselves may be affected by the mineral's interior structure, allowing sorbed ions to diffuse into the crystallite, thus rendering the sorption partially irreversible as is the case with Cs on illite (Comans and Hockley 1992). However, these effects may only be significant after longer times (weeks or months).

Of course, the assumed soil composition is also a source of uncertainty, and thus, incorrect parametrisation with respect to soil parameters may cause misinterpretations of the simulation results. This is especially important if a parameter has to be estimated or if it is sensitive to climatic conditions. To give an overview, Table 1 qualitatively shows the most significant effects of parameter variation on the distribution coefficient.³ Parameter ranges occurring in cultivated soils (Scheffer and Schachtschabel 2010) are compared to the calculated corresponding K_d variations for the Refesol 2 and the elements U, Ni, Se and Cs, respectively. Details are given in Hormann and Fischer (2013).

³ Corresponding calculations were performed for clay, ferrihydrite, pCO₂, pH, DOM and organic matter.

Table 1 Simulated soil parameter ranges and corresponding K_d ranges

Element	Parameter and range	K_d range ^a	Correlation
U	pCO ₂ (1.5–3.5)	80–5900	Positive
	pH (4–8)	30–1200	Non-monotonous ^b
Ni	pH (4–8)	35–1000	Positive
	Organic C (0–5 %)	50–500	Positive
	DOM (0–200 mg l ⁻¹)	400–1000	Negative
Se	Ferrihydrite (0–14 mg kg ⁻¹)	0–700	Positive
	pH (4–8)	15–950	Non-monotonous ^c
	pCO ₂ (1.5–3.5)	100–600	Positive
Cs	Clay content (2–50 %)	550–19,000	Positive

^aValues given in l kg⁻¹

^bMaximum at pH = 6

^cMinimum at pH = 4.5

It is obvious that the four elements exhibit different sensitivities toward the individual parameters reflecting the unique behaviour of each element in the pedosphere. If two or more parameters are varied, the effects may in some cases be potentiated, and in other cases, they may cancel each other out.

6 Conclusion

In summary, we have shown that it is possible to perform reasonable predictions of the solid–liquid distribution of radionuclides in agricultural soils, especially if generic soil types are considered. However, physicochemical parameters as well as thermodynamical data for these elements and for the most significant soil components must be available. The composite model should be extensively checked for consistency and validity. Still, one always has to be aware of the sources of uncertainty and their consequences for K_d estimation. For the simulation of individual soils and the interpretation of the results, even more caution is advised.

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