

CUMULATIVE DISTRIBUTION FUNCTIONS TO DESCRIBE URANIUM SOLID-LIQUID DISTRIBUTION COEFFICIENTS IN SOILS

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Keywords: soil; sorption; distribution coefficient; uranium; cumulative distribution functions

Introduction

The solid-liquid distribution coefficient (K_d) of pollutants (e.g., heavy metals; radionuclides) in soils is a parameter frequently used in risk assessment to estimate pollutant retention in soils. However, the quantification of the K_d is extremely affected by the methodology used for its determination and the properties of soils, which in turn affect pollutant speciation. This leads to large variability in the reported K_d values for a target pollutant that hampers to suggest a single best estimate K_d value. An approach to better describe and decrease K_d variability and to suggest representative K_d best estimates is to group data on the basis of the properties related to methodological and soil factors.

Cumulative Distribution Functions (CDFs) permit to continuously describe the K_d values of a given pollutant over a set of soils. It is a preferable option to represent a K_d population than to use simple K_d descriptors, such as minimum, maximum and mean values. CDFs not only give information on the most probable K_d value, corresponding to the 50th percentile, but also account for all the range of potential values, with an indication of their probability of occurrence. Besides, confidence intervals of K_d values can also be established by calculating the corresponding percentile ranges (e.g., the 90% confidence interval corresponds to the 5th - 95th ranges).

Regarding radionuclides (RNs) with a high environmental relevance as pollutants, such as uranium (U), the proposal of reliable K_d values with a statistical description of its variability is still an unresolved issue. Whereas soil factors affecting $K_d(U)$ have been already partially tested to decrease $K_d(U)$ variability (Vandenhove et al. 2009), the effect of the methodology in terms of sorption dynamics (elapsed time since contamination) on $K_d(U)$, the potential use of analogue geological matrices to fill gaps in soil datasets and a full statistical description of $K_d(U)$ variability with CDFs have not yet been examined.

Methods

Soil $K_d(U)$ data coming from field and laboratory experiments were compiled, along with the soil properties and the methodology followed to obtain the $K_d(U)$ values. $K_d(U)$ data from other geological materials, such as subsoil, gytja and till samples, were also considered but treated separately to decide whether could be included within the soil dataset. $K_d(U)$ dataset was formed by 197 entries for soils, and 86 for other geological matrices.

The $K_d(U)$ values were grouped according to various criteria: 1) methodology in terms of sorption dynamics (short-term and long-term incorporated radionuclides); 2) organic matter (OM) content and texture (organic (> 20% OM) and mineral soils, these latter being also classified based on sand and clay percentages (sand, loam and clay soils)); 3) pH as a factor governing U speciation and sorption in soils (pH < 5; 5 ≤ pH < 7; and pH ≥ 7). Data groups were fitted to a probability function (tested as lognormal for all cases), CDFs were constructed, and geometric mean (GM) along with 5th and 95th percentiles were derived to propose best estimates and related data variability, respectively.

Results

The overall $K_d(U)$ for soils was around 310 L kg^{-1} , with a variability of near 5 orders of magnitude. Whereas a statistically significant but minor effect of the sorption dynamics was observed (long-term GM was only two-fold higher than short-term GM), the $K_d(U)$ CDFs for organic soils substantially differed from that of the mineral soils (Figure 1a), with a GM for organic soils around one order of magnitude higher. On the other hand, no statistical differences among mineral soil textural subgroups were observed. These findings confirmed the relevant role of the organic matter, which increases uranium sorption in soils, whereas the effect of soil texture on U sorption can be considered as negligible.

When grouping data by pH, the three populations created on the basis of the U speciation were significantly different (Figure 1b). An increase in $K_d(U)$ was observed when increasing soil pH, reaching maximum values within the 5-7 pH range, in agreement with the competition of the uranyl cation with protonated sites at low pH values. At higher pH, $K_d(U)$ decreased due to the formation of weakly sorbing uranyl carbonate complexes (Payne et al., 2011). The simultaneous use of the two criteria (pH and OM) led to the creation of 5 groups with CDFs that did not generally overlap (Figure 1c). The derived GMs followed the main trends observed when applying solely the OM and the pH criteria and the related 5th-95th percentile ranges generally comprised $K_d(U)$ values varying only one to two orders of magnitude.

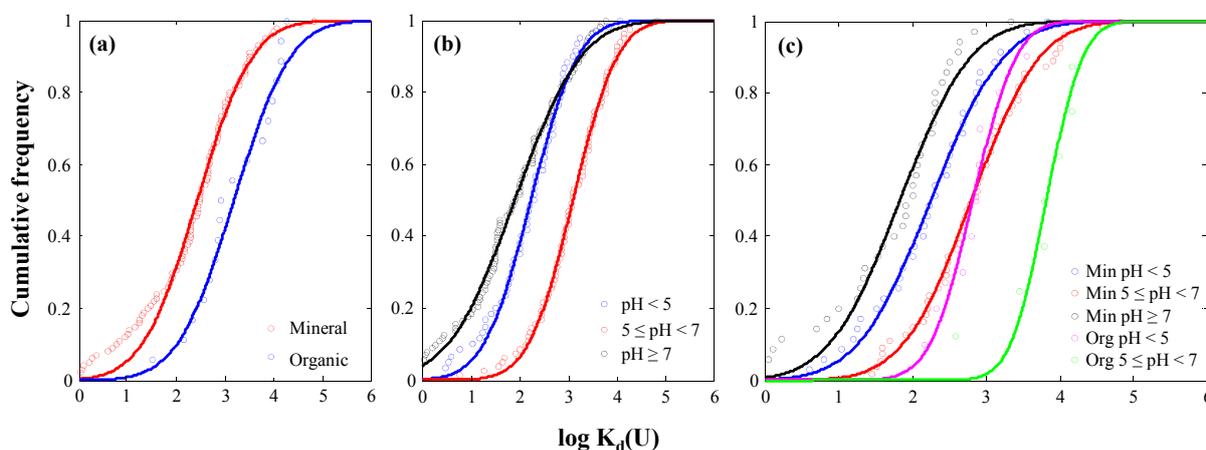


Figure 1. $K_d(U)$ CDFs created according to different grouping criteria: (a) OM, (b) pH and (c) pH+OM.

Finally, some geological materials, such as subsoils or tills, had $K_d(U)$ GM similar to that of soils, and they could be incorporated into the soil dataset, if required for soil groups with less data.

Conclusion

Whereas sorption dynamics had a minor effect on $K_d(U)$, OM content and pH were confirmed to be key properties to group $K_d(U)$ data. When grouping soils based on pH and OM criteria, $K_d(U)$ best estimates were derived with a much lower associated variability and, thus, more reliable and useful for radioecological assessments. The present study provides end-users with $K_d(U)$ CDFs for different soil types, allowing them to properly foresee the interaction of U in a given soil by selecting the CDF of the soil group that better fulfills the target scenario in terms of pH and/or OM soil properties.

References

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