Mobility and bioavailability parameter values for impact assessment for NORM sites: can they be predicted?

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Abstract
The solid-liquid distribution coefficient and the soil-to-plant transfer factor are two important parameters in the assessment of the dose to man through contamination of the food chain. The solid-liquid distribution coefficient (K_d, L kg^{-1}) determines the mobility of an element (acccumulation in soil versus leaching from soil) and the soil-to-plant transfer factor (TF) indicates the facility of uptake by crops. Both parameters depend on soil characteristics. There is a large variability in K_d and TF values (more than 4 orders of magnitude) with implications for human (and environmental) risk and impact assessment. A possible way to reduce the variability in impact assessment predictions is the development of parameterized K_d and TF values: e.g. by quantifying the influence of soil parameters on radionuclide mobility and bioavailability. Significant relationships are found in large-scale well-defined laboratory experiments between K_d or TF and soil characteristics. However, no such strong correlations were found when considering data compilations such as the database on a.o. K_d and TF developed by IAEA (2010). K_d predictions based on single or multiple parameters failed. Categorizing K_d in function of texture as commonly done, is generally not statistically justified. Also for TFs to specific crops no link with soil parameters could be derived. An important reason for this absence of relationship is in part the lack of systematic recording of relevant soil characteristics during the studies. More information on factors influencing sorption and bioavailability in soils such as pH, cation exchange capacity (CEC), clay content, organic matter (OM) content and concentration of counter ions should be collated. Research is needed to increase the understanding of the mechanisms governing radionuclide-soil-plant interactions. Until we have acquired this increased understanding and improved database for developing parameterized models, the proposed best estimates (as e.g. derived by IAEA 2010) are suitable for screening assessments only, and site specific impact assessment will remain to rely on site specific measurements of K_d and TF instead of on site specific predictions of K_d and TF.

1. Introduction
Naturally occurring radionuclides are present in many natural resources. Human exploitation of these resources may lead to enhanced concentrations of naturally occurring radionuclide materials (NORM) and (or) enhanced potential for exposure to NORM in products, by-products and wastes. Activities involving the extraction, exploitation and processing of materials containing NOR are e.g. the mining and processing of uranium and metal ores, the combustion of fossil fuels, production of natural gas and oil, the phosphate industry. If wastes containing NORs are not properly managed, large areas may become contaminated due to the large quantities of wastes associated with these activities (IAEA 2003). The radionuclides present at these sites can enter the food chain directly via the soil-plant-animal pathway, or indirectly by the use of contaminated groundwater or surface water for irrigation purposes or drinking water. To assess the uptake in the food chain and by wildlife and to predict human

exposure, knowledge on the environmental parameters governing radionuclide mobility and uptake is indispensable. The solid-liquid distribution coefficient, K_d (the ratio of the concentration of the radionuclide in the soil solid phase to the concentration in the (soil) solution, L kg^{-1}), describes the sorption processes that control radionuclide interaction in soils, thus affecting subsequent radionuclide transport in the soil profile and radionuclide accumulation in surface soils. Sorption is element and soil-type dependent, and is affected by soil mineralogy (e.g. clay content and type, iron oxides and hydroxides), organic matter content and soil geochemistry (pH, presence of colloids, presence of counter-ions, …), and by the experimental method used for its quantification.

The processes by which radionuclides can be incorporated into vegetation can either be (1) through interception by external plant surfaces (either directly from the atmosphere or from resuspended material), or (2) through uptake of radionuclides via the root system. Here we discuss the soil-to-plant transfer factor (TF) defined as the ratio of the concentrations of radionuclides in plant (Bq kg^{-1} dry mass) to that in soil (Bq kg^{-1} dry mass). The soil-to-plant transfer factor (TF) depends amongst others on crop type, soil physico-chemical characteristics, climate conditions, …

There is a large variability in K_d and TF values (more than 4 orders of magnitude) with implications for impact assessment. Considering the minimum or maximum K_d values for U (IAEA 2010) in an irrigation scenario leads to a 2000 fold difference in equilibrium soil contamination levels. Considering low or high soil to crop TF values (IAEA 2010) for the naturally occuring radionuclides ^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po and ^{232}Th in a subsistence farming scenario, resulted in dose rates differing 800-fold (Lieve Sweeck, personnal communication). Reducing the variability and uncertainty in these parameter values within a given assessment context will result in more realistic and robust impact assessments.

Interest in the behaviour of the natural radionuclides uranium and thorium and their daughter radionuclides in the terrestrial environment is related to the potential human health and environmental effects from uranium mining, industrial activities extracting and processing materials containing naturally occurring radionuclides and (geological) disposal activities. There is, however, limited information on how soil physico-chemical characteristics and processes in the root environment affect mobility and bioavailability of naturally occuring radionuclides.

Within this paper we will discuss some dedicated experiments to establish relations between the soil physico-chemical characteristics and the soil K_d and TFs. These parametrized K_d or TF can be viewed as a way to reduce variability and increase the robustness of the model predictions. On the other hand we will discuss data compilations for NOR K_d and TF and evaluate if for these databases such parametrized K_d/TF can be derived. To scope, we will concentrate this discussion on uranium and radium.

2. Can we predict mobility from soil parameters?

2.1 The case of uranium

The U behaviour is very complex due to the presence of several U-species and multitude of factors influencing its behaviour: the mineral and organic inventory of the soil and the chemical reaction environment. The mobility of uranium is influenced by sorption and complexation processes on inorganic soil constituents such as clay minerals and oxides and organic matter, and biological fixation and transformation. The system is very complex since many processes act simultaneously.

IAEA (2010) collated K_d values for U for soils grouped according to the texture/OM criterion (Table 1). The ranges within one soil group have a variability of 2 to 5 orders of magnitude, while the GM (geometric mean) differ among soil groups maximum a factor of 40. Clay soils show the lowest K_d (but this can be due to the specific soils conditions in the clay dataset), while the Organic group has the highest (note the limited number of K_d values in the clay and Organic group). The K_d GM are not significantly different between all soil groups, thus suggesting that grouping the K_d based on the texture/OM criterion was statistically not fully justified. Significant amount of variability can be attributed to the fact that uranium sorption is affected by soil properties other than soil texture such as pH, content of amorphous iron oxides, soil organic matter content, cation exchange capacity, and phosphate status (EPA 1999).

EPA (1999) performed an extensive review of K_d (U) values for soils which showed that the sorption of uranium by soils is low at pH values less than 3, increases rapidly with increasing pH from 3 to 5, reaches a maximum in the pH range from 5 to 7, and then decreases with increasing pH at pH values greater than 7. Table 1 also presents the K_d (U) values according to 3 pH-categories. A significant 10-fold higher K_d (U) value is observed for the 5-7 pH range. Though significantly different K_d values can be assigned to the pH categories, data variability was still as high as 3-4 orders of magnitude.

Table 1. K_d (U) (L kg^{-1}) for soils grouped according to the texture/OM criterion and the pH criterion. Number of entries (n), geometric mean (GM), geometric standard deviation (GSD), arithmetical mean (AM), standard deviation (SD), minimum (min) and maximum (max) values and number of references from which entries were extracted (# ref).

Soil group	n	GM	GSD	AM	SD	min	max	# ref
All Soils	178	200	12	200	6700	0.7	66667	22
Sand	50	110^{bc,*}	12	2100	9500	0.7	66667	8
Loam	84	310^{ab}	12	2500	6300	0.9	38710	12
Clay	12	28^{c}	7	120	170	3	480	3
Organic	9	1200^{a}	6	2900	2800	33	7600	7
Unspecified	23	170^{abc}	6	860	1700	16	6200	5
pH<5	36	71^{b,*}	11	540	1200	0.7	6700	16
5≤pH<7	77	740^{a}	8	4000	9800	2.6	66667	17
pH≥7	61	68^{b}	8	450	1100	0.9	6160	14

As mentioned, a possible way to reduce the variability in biosphere assessments is the development of parameterized K_d and TF values. Parametrisation entails quantifying the influence of soil parameters on radionuclide mobility and bioavailability. In a laboratory study (Vandenhove et al 2007) we set out to quantify the influence of soil parameters on soil solution uranium concentration and K_d for ^{238}U spiked soils. Eighteen pasture soils were selected such that they covered a wide range for those parameters hypothesised as being potentially important in determining U sorption. Maximum soil solution uranium concentrations were observed at alkaline pH, high inorganic carbon content and low cation exchange capacity, organic matter content, clay content, amorphous Fe and phosphate levels. Except for the significant correlation between the solid-liquid distribution coefficients and the organic matter content (R^2=0.70) and amorphous Fe content (R^2= 0.63), there was no single soil parameter significantly explaining the soil solution uranium concentration (which varied 100-fold). Above pH=6, log(K_d) was linearly related with pH [log(K_d) = -1.18 pH + 10.8, R^2=0.65] (Fig. 1). Echevarria et al (2001) found no significant effect of clay or organic matter. However, they did find a significant relation between soil K_d and pH. For soils in the 5.5 tot 8.8 pH range they deduced a linear relationship: log K_d = -1.29 (±0.17) x pH + 11.0 (±1.2), R^2=0.76]. Sheppard et al (2006) found a similar correlation for soils with pH ranging from 5.5 to 8.8: log K_d = -1.07 (±0.13) x pH + 9.8 (±0.9), R^2=0.41. This clearly points to the importance of pH in ruling U-mobility.

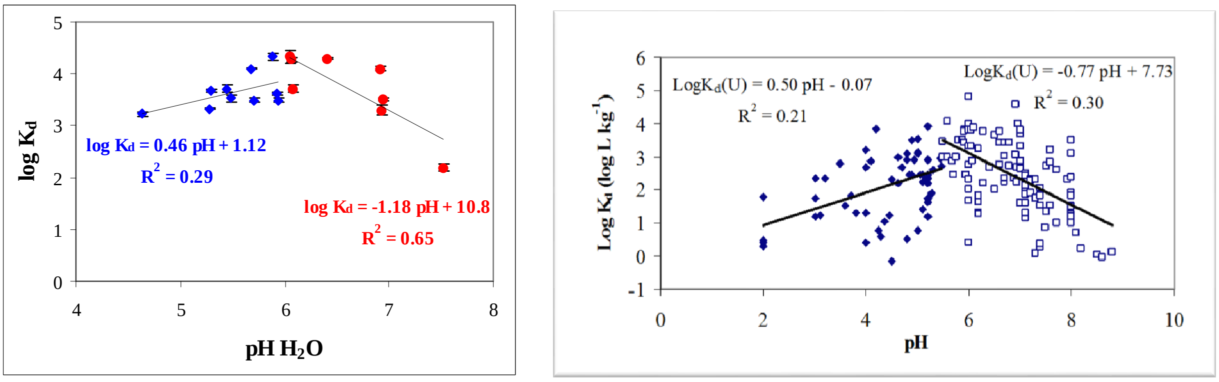

Figure 1: Log K_d(U) (L kg^{-1}) as function of pH according to Vandenhove et al. (2007a) and based on data collected for the IAEA (2010) database

For the IAEA (2010) compilation, pH only explained 30 % of the variation in the higher pH range (pH≥5.5) and only 20 % in the low pH range. No relationship with organic matter or oxalate extractable Fe was found. Sheppard (2011) reported K_d relationships as a function of soil characteristics and found statistically significant relationships for U-K_d: Log(K_d) = 9.05 − 0.989·(pH) + 0.00290·(clay)·(pH) where pH ≥ 5.5; Log(K_d) = 1.75 + 0.0145·(clay)·(pH) where pH < 5.5 (R^2 not given). However if we applied these relationships to the IAEA (2010) dataset, comparing recorded K_d with K_d calculated based on the Sheppard (2011) equation using the respective soil characteristic, R^2 was only 0.2 (Fig. 2, left).

The fact hat very significant correlations are found in large-scale experiments with many soil characteristics reported while such strong relationships disappear for K_d compilations (mostly no relevant soil characteristics were recorded), calls for a more methodical soil characterisation in order to be able to deduce the processes ruling uranium sorption and to allow for prediction of K_d(U) from soil parameters for robust impact assessments.

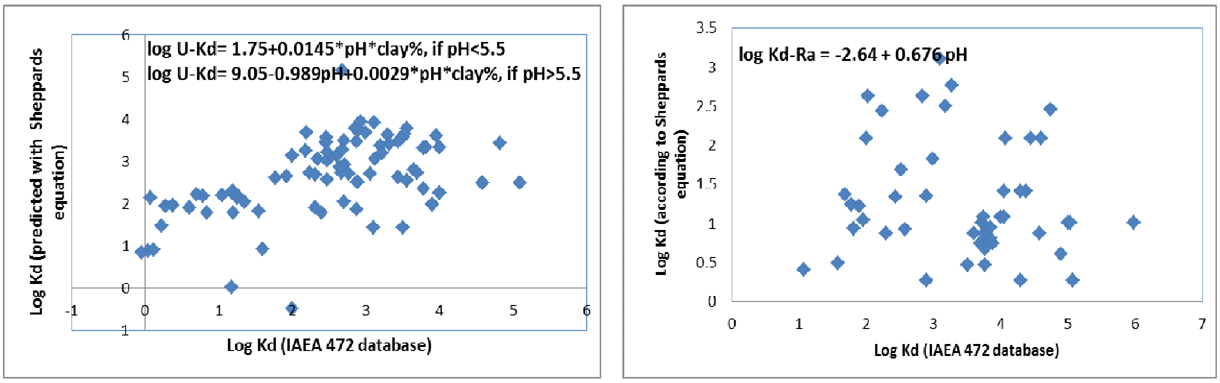

Figure 2: Relation Log K_d (U) (L kg^{-1}) (left) and Log K_d (Ra) U) (right) from the IAEA (2010) compilation (X-axis) and estimated using the equation by Sheppard (2011) based on the soil characteristics in this IAEA (2010) database.

2.2. The case of radium

Only 7 references were identified that reported suitable K_d (Ra) values (total of 47 entries) for soils following the constraints set to compile the IAEA (2010) dataset. Table 2 shows geometric means for K_d (Ra) were highest for Clay soils and lowest for Loam soils.

Table 2. K_d (Ra) (L kg^{-1}) for soils grouped according to the texture/organic matter criterio. Number of entries (n), geometric mean (GM), geometric standard deviation (GSD), arithmetical mean (AM), standard deviation (SD), minimum (min) and maximum (max) values and number of references from which entries were extracted (# ref).

Soil group	n	GM	GSD	AM/value	SD	min	max	# ref
All soils	47	1800	10	11000	21000	12	100000	7
Sand	20	3100^{ab}	8	9600	12000	49	40000	4
Loam	17	710	14	8600	20000	12	80000	4
Clay	4	13000	10	41000	47000	696	100000	2
Organic	1			200				1
Unspecified	4	1200	1	1300	500	785	1890	1

Considering the high affinity of Ra for the regular exchange sites (Simon and Ibrahim, 1990), the higher K_d (Ra) value observed for Clay soils than for Loam soils can be explained by the generally higher CEC of clay soils, which thus have a higher sorption capacity. K_d (Ra) estimates were generally not significantly different between soil groups, due to a variability of 2 to 5 orders of magnitude. For Clay soils and especially for Organic soils the K_d data are scarce which makes it difficult to deduce best estimates for these groups.

Simon and Ibrahim (1990) reported that organic matter sorbs about ten times as much radium as clay. Vandenhove and Van Hees (2007) exploring the effect of soil properties on the radium availability in a small-scale study covering 8 soils, concluded that K_d (Ra) could be predicted by CEC [K_d (Ra) = 0.71 x CEC – 0.64, R^2=0.3] (Fig. 3) and soil organic matter content [K_d (Ra) = 27 x OM - 27, R^2=0.4]. However, these correlations were not significant with the K_d (Ra) values of the IAEA (2010) compilation (Fig. 3). Multiple regression analysis also did not result in significant regressions.

The classification of K_d values by soil group does not result in significant differences between the soil classes. However, a more suitable parameter for classifying K_d values (pH, CEC, OM) could not be suggested either. Sheppard (2011), however, established following relation between $\log K_d$-Ra and pH [Log $K_d = -2.64 + 0.676 \cdot (\mathrm{pH})$] yet applying this relationship to the IAEA (2010) K_d and related soil characterisation data, an R^2 of only 0.01 was obtained. Hence proposed equations by Sheppard are hence not universally valid.

As for U, a more methodical soil characterisation is advised in order to be able to deduce the processes ruling radium sorption and to allow for prediction of K_d(Ra) from soil parameters. Additional research to collate K_d(Ra) values, especially for clayey and organic soils is recommended.

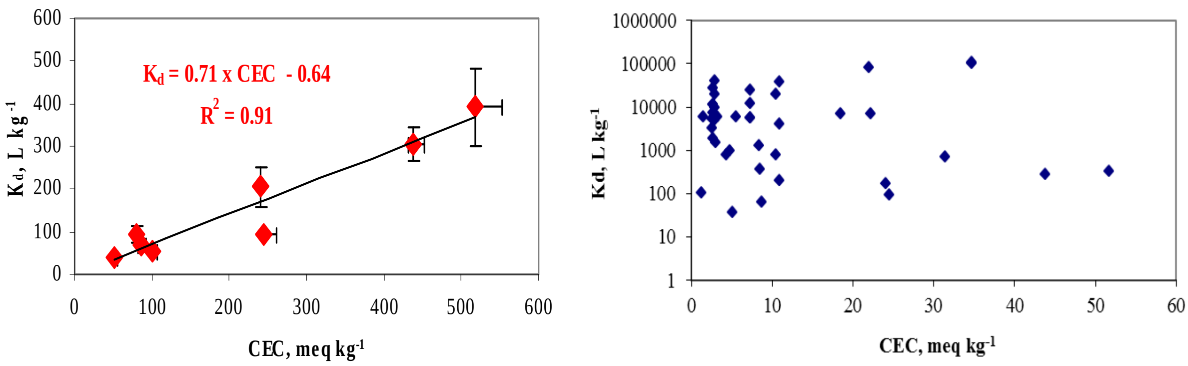

Figure 3: K_d(Ra) (L kg^{-1}) as function of CEC according to Vandenhove and Van Hees (2007) (left) and based on the IAEA (2010) database (right)

3. Can we predict soil-to-plant transfer from soil parameters

As mentioned, an important pathway for human exposure is via ingestion of food crops and animal products. One of the key parameters in environmental assessment is therefore the soil-to-plant transfer factor to food and fodder crops. Transfer factors depend on plant type, the plant part concerned, soil characteristics, climate conditions, agricultural practice, time since contamination, …. Transfer factors are hence highly variable and it is not straightforward to capture the causes of the variation observed.

For risk assessment purposes, transfer factors are generally reported by plant group. In this context, IAEA (2010) compiled soil-to-plant transfer factors a.o. for uranium, thorium, radium, lead, and polonium. Transfer factor estimates were presented for following major crop groups (Cereals, Leafy vegetables, Non-leafy vegetables, Root crops, Tubers, Fruits, Herbs, Pastures/grasses, Fodder). Each crop group exists of several plant species – e.g. green vegatables consists of lettuce, spinach, chinese cabbage, …. each with different properties leading to specific transfer factors. Transfer factors within a given crop group were obtained for specific soils, specific fertilizer regimes, …. In order to allow for users of assessment models to apprais the dependency of the TF on global soil characteristics, the transfer factors' dependency on specific soil characteristics was evaluated.

3.1. The case of uranium

Figure 4A gives the TF-U estimates for selected crop groups derived by IAEA (2010). Fodder, Pastures/grasses, and Herbs showed the highest TF-U (2.3-6.5 10^{-2} kg kg^{-1}), and Legumes, Cereals and Tubers had the lowest TF-U (2.2-6.2 10^{-3} kg kg^{-1}). Derived TF-U values were not always significantly different between crop groups with typical ranges within a crop group being 1 to 5 orders of magnitude. Significant differences were observed in TF based on texture/OM criterion only for a few crop groups (Fodder, Leafy vegetables, Tubers). No significant correlations (overall or per crop group) were found between single soil parameters (pH, CEC, OM, Clay content, Amorphous Fe) and TF-U which may be in part due to the fact that only in few cases (< 50 %) soil characteristics were recorded next to the U-TF.

Vandenhove et al (2007b) set out to evaluate if the influence of soil characteristcis on U-tranfer to ryegrass could be derived. Ryegrass transfer factor was studied for 18 uranium-spiked soils, differing greatly in characteristics. Soil-to-plant transfer factors for ryegrass ranged from 0.0003 to 0.0340 kg kg^{-1}. There was no significant relation between the U soil-to-plant transfer and the uranium concentration in the soil solution or any other soil factor measured, nor with the U recovered following selective soil extractions. It was concluded that pH≥6.9 is generally conducive to higher transfer. The influence of uranium speciation on uranium uptake observed was featured: UO_2^{2+}, uranyl carbonate complexes and $UO_2PO_4^-$ seem the U species being preferentially taken up by the roots and transferred to the shoots. Though an improved correlation was obtained between mentioned U species and the observed TF, correlation is still rather poor (r=0.65). The lack of simple relationship between U-TF and soil properties, even for controlled experiments highlights the complex behaviour of U. For more robust predictions of U availability based on soil properties, future studies on soil-to-plant TF in laboratory or field, should also include detailed information on soil properties.

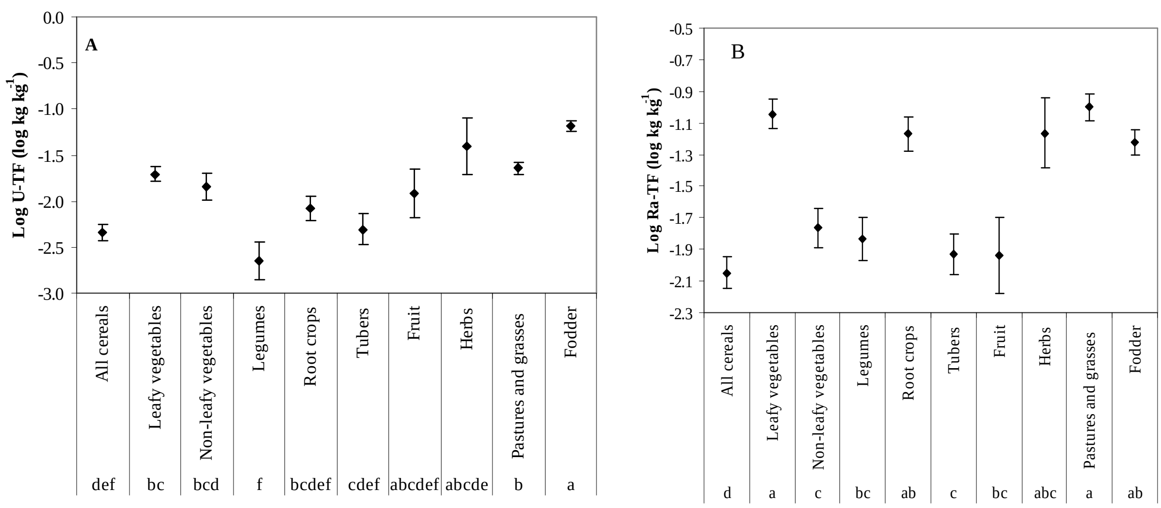

Figure 4: Logarithm of the U (A), Ra (B) soil-to-plant TF [Log TF, log (kg kg^{-1})] for the different broad plant groups. Error bars denote residual SE after analysis of variance accounting for the effect of plant type. Values followed by the same letter are not significantly different (P<0.05).

3.2. The case of radium

IAEA (2010) recorded following best estimates for the radium soil-to-plant tarnsfer factor: Pastures/grasses, Leafy vegetables, Root crops, Fodder and Herbs showed the highest TF-Ra (6 10^{-2} – 10^{-1} kg kg^{-1}), Cereals, Non-leafy vegetables, Legumes, Tubers and Fruits showed the lowest (9 10^{-3} – 2 10^{-2} kg kg^{-1}) (Fig. 4B). Variation within a crop group was 1 to 5 orders of magnitude and significant differences in TF-value between crop groups were rarely observed. A significant effect of soil texture/organic matter content on TF-Ra was observed for only a few crop groups (Non-leafy vegetables, Root crops). Following linear regression analysis, clay content and TF-Ra were not correlated (neither overall, nor for specific crop groups). Though a significant correlation between OM and TF-Ra could not be derived considering all crop groups, a significant negative dependency of TF-Ra on OM content was found for Legumes (R^2=0.42), Leguminous fodder (R^2= 0.62), and Natural pastures (R^2=0.27).

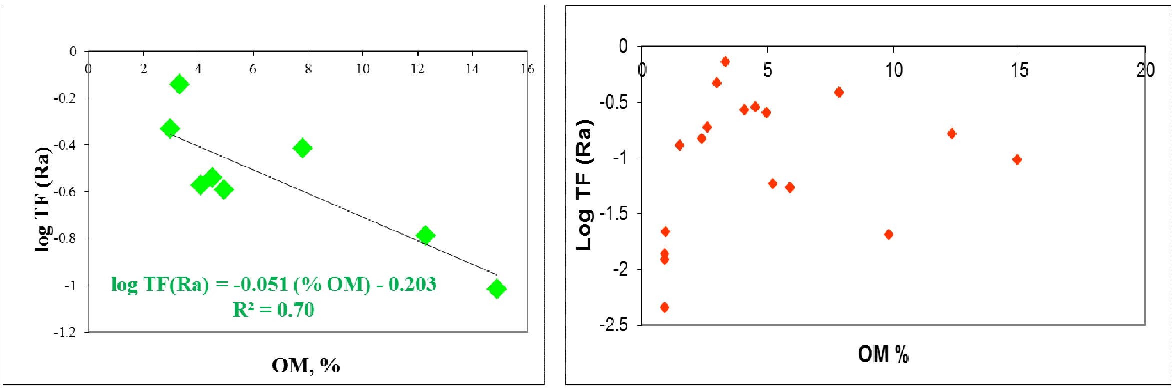

Figure 5: Log TF (Ra) in function of soil organic matter content (%) for a specific experiental set-up (Vandenhove et al. 2007) or for the IAEA (2010) TF compilation (right).

Vandenhove and Van Hees (2007) conducted a radium spiked soil experiment (8 soils with diverging characteristics) with the soil-to-plant TF ranging from 0.054 kg kg^{-1} to 0.385 kg kg^{-1} for ryegrass and from 0.034 kg kg^{-1} to 0.565 kg kg^{-1} for clover. The soil-to-plant transfer factor was significantly affected by the soil type. TF (or Log(TF)) was related to K_d , to CEC, OM) and the calcium concentration in the soil solution (for both plants if excluding one soil) (Fig 5). For the IAEA compilation, no such relationship was found. (Fig. 5).

4. Conclusions

Significant differences in the K_d estimates between textural classes were observed only in a few cases. For the radionuclides considered, K_d is hence largely texture-independent and grouping based on soil texture classes should be discouraged. K_d prediction could be significantly improved by a more thorough description of the soil characteristics. More specifically, information on factors influencing sorption such as pH, CEC, clay content, OM content and concentration of counter ions should be collated and detailed reporting of research data to increase the understanding in the mechanisms governing radionuclide-soil interaction is encouraged. Large-scale laboratory based experiments show clear dependency of K_d on soil characteristics and parametrized K_d could be deduced. Such approach can only be applied to compilations if information of soil characteristics is available.

The dependency of soil-to-plant transfer factors of naturally occuring radionuclides U and Ra on soil characteristics would also only be derived within controlled experiments. The influence of soil characteristics on the soil-to-plant transfer was also evaluated for the IAEA (2010) compilation but no significant relationship was found. A striking observation was that the majority of soil-to-plant TF data were reported without information on soil properties.

Only about 50 % of the entries contained information on soil type. Information on pH, CEC or OM was generally even less frequently recorded.
There is hence a call for a methodological approach to soil characteristics analysis to allow for prediction of NOR Ra/U K_d and TF from soil properties.

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