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Distribution coefficient Kd of transuranics in soils: Experimental determination and consequences for dose assessment

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Abstract. The distribution coefficient (or Kd) of ^{241}Am between soil and soil solution was estimated on the basis of experiments carried out under controlled conditions for soils displaying pH and organic matter content (which are the relevant parameters for transuranic nuclides sorption ability) found in cultivated soils. In these experiments, designed with five experimental units (batches) per studied contact time, 10 g of dry soil are contaminated with 50 mL of osmosed water containing proper concentrations of the radionuclide. The tracer, initially in nitric form, is neutralized prior to addition with the water, to ensure a constant ionic strength and avoid disturbance of the soil chemistry. After shaking and sedimentation, for each batch, the supernatant is sampled and analyzed by either liquid scintillation or alpha spectrometry. The sorption-desorption kinetic time necessary to reach apparent equilibrium is evaluated (>10 days). Fixation curves, *e.g.* activity of the soil *vs* activity of the solution are established, after measurements, for a single delay representative of the equilibrium, and for a range of several orders of magnitude for radionuclide concentrations. On the basis of several assumptions, Kd values are evaluated by simple linear adjustment. A numerical application to retention half lives in soil is made. Finally, the weight of using site-specific Kd values instead of default parameters, on the doses due to ingestion of terrestrial foodstuffs is discussed for different scenarios.

1. GENERAL SCOPE

Many researches have improved the knowledge of the mechanisms relevant to the mobility of transuranians in the geosphere, aiming at better wastes disposals impact assessments [1-5]. In surface soils americium, usually trivalent and thus expected to have a simple behaviour by comparison with multivalency elements, is still far from being completely elucidated [6,7]; its mobility, connected with the formation of mobile species, either with soluble organic species [8-13] or with small clay particles, producing pseudo-colloids [14,15], is particularly weak. Indeed, because of various phenomena such as hydrolysis, adsorption on clay particles, complexation with carbonates and with most of the humic substances, it tends predominantly to be strongly retained in the upper levels of the soil [8, 16-17]. Although numerous studies have been focused on the sorption desorption processes of transuranics in soil, showing the influence of the global soil-solution parameters such as organics or pH, only few experiments have determined distribution (or partition) coefficients Kd for agricultural soils. The Kd is defined as the ratio of the quantity of the contaminant adsorbed per unit mass of soil to the amount of the contaminant remaining in solution at equilibrium, and is currently expressed in m^3 of solute per kg of dry soil. It is usually obtained from different methods including the laboratory batch or flow-through methods or by field modelling methods. The batch measurement is likely the most simple, yet least robust experimental pattern available. Also, while heterogeneity does typically exist in nature, the Kd value is only valid for the specific set of chemical conditions in which it was measured. In addition, the hypothesis that a) the soil-solute system is at reversible equilibrium and b) adsorption of the radionuclide is independent of its concentration in the aqueous phase are inherent assumptions in this approach, though basically violated. Additionally, values for Kd vary with aqueous and solid phase chemistry in the experiment as well as with several other experimental conditions such as the solution-to-solid ratio, the ionic strength or the impracticality of differentiating between soluble species of the radionuclides that may greatly affect the whole Kd value. Thus, it is not surprising that Kd values measured by different methods or with various experimental conditions will produce very dispersed data. Generic ^{241}Am-Kd used for screening calculations range from about 1 in sandy soils to 110 in organic substrates [19], with lower and upper data being respectively 0.01 to 33000. The common observed trend is a positive correlation of Kd with the organic matter content, for soil having a high (> 25%) organic matter content. For most soils, with mean or low organic matter content, a positive correlation between the soil pH and the sorption intensity is generally observed [18-20]. This apparent relationship does not clearly presume the actual sorption process, which may be controlled by any other soil parameter co-varying with pH. Although these generic values may be useful, they are rather misappropriated for biosphere safety assessment, because data were mainly determined for geosphere, and also for the reason that they largely derive from rather extreme soils or even pure mineral phases. Furthermore, the high uncertainty associated with these Kd values results in a large variability of the predicted residence half-time in the upper layer of the soil, and of the subsequent estimated doses. Our experimental work aimed at such a determination, on seven agricultural soils exhibiting different physico-chemical properties.

2. EXPERIMENTAL DETERMINATION OF KD

2.1 Soils

Among the seven soils (Ap horizons) used, six are commonly found in French agricultural landscapes, and have rather mean properties as regard to pH, organic matter content, texture, cationic complex saturation; an additional tropical cultivated soil (TH1), which has a specific high matter content and no mineralogical clay was also used as a comparison point.

Table I: Main characteristics of the tested soils (Values given as g $kg^{-1}_{dry\ sieved\ soil}$ unless other precision).

	CAD01	LHA01	PAL01	TRI01	BEL01	NCY01	TH1
Rough sand	7	23	2	3	73	9	13
Fine sand	32	22	43	16	7	4	8
Rough silt	25	22	39	21	6	18	6
Fine silt	19	16	9	30	8	36	38
Clay	17	18	7	30	6	33	35
O.M.	37	71	11	32	15	31	340
pH_{water}	8.4	5.6	5.4	7.3	4.1	7.6	4.1
C.E.C. cmol kg^{-1}	56	107	66	106	37	18	280
Gross Ca	265	0	0	127	0	3	0
Saturation %	100	89.1	92	100	60	85	8.5

Rough sand: 200-2000 µm; Fine sand: 50-200 µm; Rough silt: 20-50 µm; Fine silt: 2-20 µm; Clay: < 2 µm; O.M.: organic matter; C.E.C.: cationic exchange capacity.

2.2 Experimental feature

Primarily, equilibrium time was established with the LHA01, PAL01, TRI01 soils: five replicates of 2 g d.w. of soil were weighted in polyethylene batches. Osmosed water was added 24 hours before the contamination in order to allow soil-solution balancing. ^{241}Am, as carrier-free americium nitrate in 1N HNO_3 was used. Each sample was spiked with a 200 µL aliquot of 1000±10 Bq, neutralized to pH 6.4 with 113 µL of 1M Na_2CO_3, immediately before addition to the batch; the final volume was adjusted to 20 mL (^{241}Am concentration: 0.39 µg L^{-1}). Batches were squeezed by hand to obtain homogenous contamination of the samples. Then, samples were left, with periodical shaking by hand, at room temperature (20 °C) and 1 mL of each supernatant was sampled after 1, 2, 7, 15 and 30 days. The sampled solution was then hot-acidic mineralized. Measurements were performed by liquid scintillation and, where necessary, *e.g.* for samples under detection limits, by alpha spectrometry. At the end of the experiment, all containers and residual soils were measured to appreciate losses of radioactivity due to sorption on experimental devices. Sorption isotherms were afterwards determined in a similar manner with the following differences: a) soil was spiked with a range of ^{241}Am aliquots including 100, 500, 1000, 5000 and 10000 Bq, per sample and b) 1 mL of each supernatant was sampled after the equilibrium time previously determined. Samples were then treated and measured as described before.

2.3 Data interpretation

The sorption isotherms (massic activity sorbed on the soil *vs* volumic activity remaining in solution, Bq g^{-1} per Bq mL^{-1}) were drawn and the experimental points fitted to a linear curve, the slope being the value of Kd. Then the theoretical retention in soils was evaluated with the Baes and Sharp model classically used in assessment calculations [20, 21] and described thereafter:

$$R=\frac{1}{\lambda_r+\lambda_w} \tag{1}$$

$$\lambda_w=\frac{Fe}{H\times(\theta+\rho\times Kd)} \tag{2}$$

$$C_{soil}(t)=C_{soil}(0)\times e^{-t/R} \tag{3}$$

with:

R	y	mean residence time of the radionuclide in the considered soil layer
λ_r	y^{-1}	radioactive constant $\lambda=\ln 2/T$ (for ^{241}Am T = 432.7 y)
λ_w	y^{-1}	constant for soil weathering
$C_{soil}(t)$	Bq kg$^{-1}{}_{dw}$	soil concentration of radionuclide t years after contamination at $t=0$
Fe	m y^{-1}	water flux leached through the upper layer of soil (estimate: 0.5)
H	m	soil depth (estimate: 0.2)
ρ	kg m$^{-3}{}_{dw}$	*in situ* soil volumic mass (estimate: 1400)
θ	m$^{3}{}_{water}$ m$^{-3}{}_{soil}$	soil moisture (estimate: 0.4)
Kd	m^{3} kg$^{-1}{}_{dw}$	distribution coefficient

These categories of relationship are convenient for modeling, however they postulate implicit assumptions that controvert their validity; for instance, in contradiction with equation (2), it is likely that the Kd value varies as a function of the volumetric water content because as a soil dehydrates the aqueous phase in contact with the soil surfaces increases in the smallest pores and the ionic strength of the solution tends to extent closer to the clay surfaces.

3. RESULTS AND DISCUSSION

3.1 Determination of Kd values

The sorption of ^{241}Am on the soils begins rapidly; the equilibrium is expected to be achieved after 200 hours. At that time, more than 99 % of the initial radioactivity is sorbed on the soil (Figure 1). The "sorption isotherms" are thus established for a contact time of 250 hours.

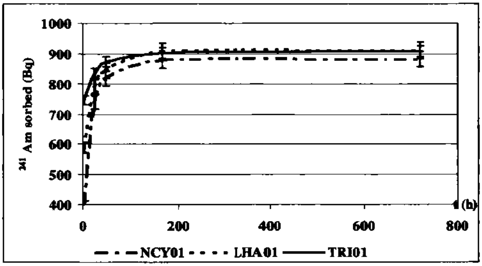

Figure 1: Determination of equilibrium time: radionuclide sorbed on the soils, *vs* contact time *t*. Batches of 2 g d.w. of soil and 20 mL of solution spiked with 1000 Bq of ^{241}Am at $t = 0$. Fixation on the bucket is 117±23 Bq.

An example of the curves that were obtained for each soil is shown (Figure 2). The constant slope suggests that the number of available sorption sites remains constant throughout the whole range of concentrations and attests that the saturation is not reached. This model explicitly considers dependency of the partition coefficient on the solution concentration of ^{241}Am only and neglects dependence on other parameters that can influence adsorption. The Kd values are equal to the slope of the line fitted to the experimental points (Table II). These results are consistent with default values usually applied in risk assessments and with the general known behaviour of americium in soil: a high positive correlation ($R^2 = 0.967$) of Kd values *vs* pH is observed except for the very specific TH1 soil. In this case, we can suppose that the complexation of the radionuclide with the organic matter is so important that it masks any other soil parameters' influence.

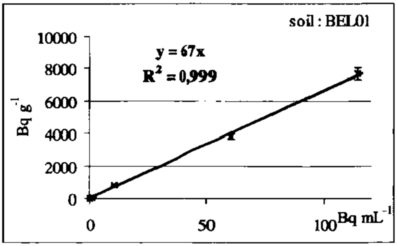

Figure 2: Example of sorption isotherm: experimental points and linear adjustment.

Table II: ^{241}Am distribution coefficient Kd (arithmetic mean ± standard deviation), in Bq $kg^{-1}_{dry\ soil}$ per Bq $m^{-3}_{soil\ solution}$, for a contact time of 250 h. Experimental points fit a linear regression; the correlation coefficient R^2 is indicated in italic letters.

Soil	BEL01	LHA01	PAL01	NCY01	TRI01	CAD01	TH1
Kd	67×10^{-3} $\pm 5 \times 10^{-3}$	411×10^{-3} $\pm 28 \times 10^{-3}$	988×10^{-3} $\pm 188 \times 10^{-3}$	2691×10^{-3} $\pm 585 \times 10^{-3}$	2695×10^{-3} $\pm 1100 \times 10^{-3}$	4103×10^{-3} $\pm 1140 \times 10^{-3}$	8204×10^{-3} $\pm 63 \times 10^{-3}$
R^2	*0.999*	*0.999*	*0.996*	*0.953*	*0.90*	*0.986*	*0.976*

3.2 Evaluation of ^{241}Am residence time in soils

The mean ^{241}Am residence time is evaluated (equation 1) using either the experimentally measured Kd values (Table II) or the default values chosen according to their corresponding "soil type" [20, 19]; experimental and theoretical values are then compared (Table III). Depending on the soil, there may be large differences between both results, most of experimental values being lower than the default ones. This may be attributed to the fact that the definition of the theoretical soil types, mainly based on textural criteria, are poorly adapted to americium, the behaviour of which depends more on other soil parameters than on its texture.

Table III: Residence time of ^{241}Am in soil, evaluated from either experimental data or generic (default) values.

Soil	Residence time calculated from experimental Kd (y)	Theoretical soil type and corresponding default Kd ($m^3\ kg^{-1}$)	Theoretical residence time calculated from default Kd (y)
BEL01	38	sand (2.0)	1120
NCY01	151	clay (8.1)	4536
LHA01	230	loam (0.99)	555
PAL01	553	loam (0.99)	555
TRI01	1509	clay (8.1)	4536
CAD01	2298	loam (0.99)	555
TH1	4594	organic (110)	61600

In order to evaluate the importance of selecting a particular value of Kd, we used equations (1-3) to determine the significance of modifying Kd on the ratio $C_{soil}(t)/C_{soil}(0)$ for t varying from 10 to 500 years (Figure 3). For a given isotope, and thus a given radioactive decay, the importance of Kd depends not only on t value, but also obviously on the range of Kd itself: for instance, in the case of ^{241}Am, for t=10 y, using an overestimated Kd value ($m^3\ kg^{-1}$) of 10^{-1} instead of 10^{-2} overestimates approximately five times the ratio $C_{soil}(10)/C_{soil}(0)$, but using a Kd of 10 instead of 1 has rather no influence on this ratio.

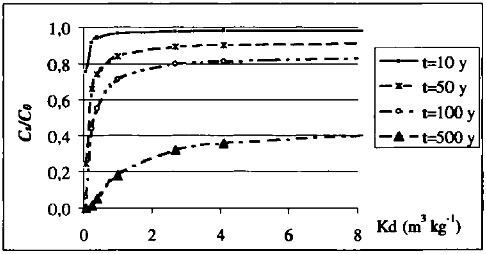

Figure 3: Variation of $C_{soil}(t)/C_{soil}(0)$ evaluated with equations (1-3), function of ^{241}Am Kd values, different times after contamination.

4. CONCLUSION

Generic or default partition coefficient values can result in significant uncertainties when predicting the impact of radionuclide migration. Using more suitable Kd values is more important for radiosotopes with longest radioactive period. For a given radioactive decay, the weight of Kd increases with the time scale considered and also when soils exhibit low distribution coefficients. Therefore, depending on these three main circumstances, partition coefficient values measured on site-specific soil are either wanted or not needed at all, for improved assessments. This supposes anyway that the simplified models using the Kd for evaluating the radionuclide retention time in soil can be appropriate regarding the aim of the evaluation. Intrinsic limits to the Kd concept, measurement and utilization favor the wish of mechanistic or semi-mechanistic models that would explicitly accommodate the dependency of radionuclide sorption on true chemical speciation. But, to be operational, these means require intensive modelling attempt sustained by a large data collection effort that will unlikely be possible in the immediate future.

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