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An Operational Method to Easily Determine the Available Fraction of a Contaminant in Soil and Associated Soil-Solution Distribution Coefficient

Frédéric Coppin, Laureline Février and Arnaud Martin-Garin*

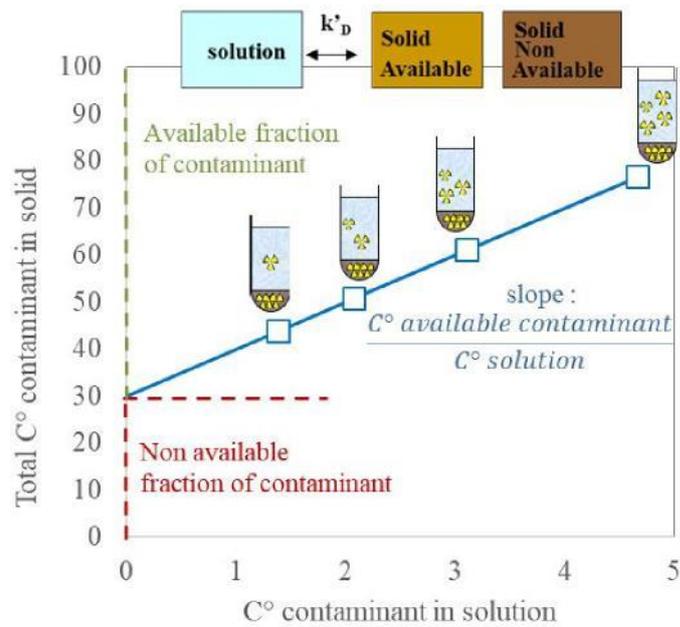
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KEYWORDS : contaminant environmentally available fraction, successive batch extractions, soil, predictive modeling, radionuclide, trace element, pollutant.

ABSTRACT

Well understanding the solid/solution partitioning of a contaminant is of first importance to determine its residence time in the environment, environmental availability, or bioavailability. Currently, parameters of contaminant transfer models are derived from two conceptually different approaches: one considering that the totality of the contaminant is in equilibrium between the solid and the solution and the other one considering that only a part of the contaminant can be transferred from the solid to the solution without considering equilibrium. Our work offers to reconcile these two approaches by assuming that the contaminant associated with the solid is present under two fractions: one available at equilibrium with the solution, and a second one not available and nontransferable to the solution. We propose to use simple operational batch methods (successive desorption batch experiments, or batch desorption conducted at different volume of solution/mass of solid (V/M) ratios) to check this assumption and to determine the real available contaminant fraction (i.e., the contaminant in the solid which can be at equilibrium with the solution) and its associated solid/solution distribution coefficient. The robustness of the proposed method was tested on simulated conditions, on experiments performed to validate the approach, and on the reinterpretation of literature data. Finally, the use of the available contaminant fraction and its associated solid/solution distribution coefficient in transfer models can improve the predictive modeling of contaminant transfer in the soil/solution/plant system.

Graphical Abstract



Synopsis

Interpretation of successive desorption batch experiments to check the equilibrium hypothesis and obtaining soil/solution contaminant transfer parameters independent of the V/M ratio used.

Introduction

Soil is a major compartment at the biosphere/geosphere interface and understanding contaminant behavior in soils is needed to predict its potential dissemination in terrestrial ecosystems. The mechanisms leading to the retention of contaminants in soils (adsorption under outer or inner-sphere complexes, (co)precipitation, bioretention...) as well as carrier phases (minerals organic matter, (micro)organisms...), which partly control their solid/solution distribution, are numerous. Therefore, in the article, the terms sorption and desorption are used as generic terms to qualify any retention of contaminants in soil and any transfer of contaminants from solid to soil_solution, respectively, independent of the chemical process behind this retention or transfer. Well understanding the solid/solution partitioning of contaminants such as trace elements^[1] or radionuclides^[2] is of first importance to determine their residence time in soils^[3], environmental availability^[4] or bioavailability^[5]. To estimate the contaminant transfer from soil to solution two different concepts are usually considered. The first one considers that all the contaminant sorbed onto the solid is available for solution, whereas the second one considers that only a fraction of the contaminant is available and can be transferred to the solution. Within both concepts, the distribution between the available fraction of the contaminant retained on the solid and the soil-solution is assumed to be controlled by reactions at equilibrium. For both concepts, experiments are conducted to obtain the target parameters which are used for predictive modeling. Concerning the first concept, the main target parameter is the soil/solution distribution coefficient (K_D) which can be derived from the concentration ratio between soil and solution (R_D) from sorption^[6] or desorption^[7] batch experiments or from *in situ* measurements^[8]. For the second concept, the target parameter is the percentage of the environmentally available fraction of contaminants (i.e. the fraction transferring from solid to

solution from where it can be taken up by organisms)^[9]. Usually, this fraction is estimated from batch extraction experiments conducted with chemical extractants such as water, acetate or others reagents^[4] and expressed as a percentage of the total contaminant in soil^{[1][10]}. However, for both concepts, the initial main hypotheses (i.e., all the contaminant, or only a part, is available) are rarely checked during the experiments. Both approaches have sometimes been used for the same soil to describe soil/solution contaminant transfer depending on whether sorption or desorption was considered. Sorption experiments are most often interpreted with an equilibrium-based approach and used to derive K_D , whereas desorption experiments are used to derive a finite extraction yield^{[11][12]}. In addition, results showing that K_D or % of the available fraction depends on the volume of solution/mass of solid ratios (V/M) used in batch extraction^{[13]-[15]} may also be a consequence of the wrong use of the initial assumptions. Indeed, if all the contaminant retained on the solid is available and at equilibrium with the solution, K_D has to be independent of V/M. In the same way, if only a % of contaminant retained in the solid is available, this percentage should relate to the intrinsic soil composition only and has to be independent of the experimental protocol used to determine it. A single-step batch extraction often fails to determine it, since it is not sufficient to recover the whole available fraction of the contaminant from the solid. Finally, the main drawback of interpreting experiments without having checked this main hypothesis is to provide transfer parameters that could be uncertain; this is particularly true for K_D . Moreover, experiments conducted to provide only the percentage of contaminant that could be extracted from soil depend on the experimental protocol (e.g., the nature of the extracting solution, V/M ratio...) and do not provide information on the dynamics of solution resupply (i.e., resupply of solution in case of water flux throughout the soil). Thereby, using only the extracted percentage for predictive modeling could be difficult.

Based on the hypothesis that the contaminant associated with the solid is present under two fractions: one available at equilibrium with the solution, and a second one not available and non-transferable to the solution, the objective of this study is to propose simple operational batch

methods to check this hypothesis and to determine the real available contaminant fraction (i.e., contaminant in the solid which can be at equilibrium with the solution) and its associated solid/solution distribution coefficient. Even if a lot of physicochemical properties of soil or solution are known to influence the retention parameters of contaminants in soil (nature of soil and mineralogy, chemistry of the solution, grain size...), the objective of this paper is not to discuss their influence on the targeted parameters. We will demonstrate that two experimental approaches already used for specific conditions in very few studies could provide the same results and be generalizable to determine the available contaminant fraction and its associated distribution coefficient for radionuclides and trace elements. The two selected approaches are batch experiments conducted at different V/M ratio for characterization of Ni retention on clay^[16] and successive batch extractions used to describe organic compounds retention onto soils^[18]. The determination of the available contaminant fraction and its associated contaminant distribution coefficient with these two approaches is first explained from a theoretical point of view. Then, the effectiveness of the two experimental approaches is demonstrated by applying them to various data: either simulated, acquired with different radionuclides or trace elements (Se, Cs, and U), or from literature.

Theoretical Approach

The proposed method is based on the analysis of the mass balance of the contaminant between soil and solution during batch experiments to determine the available fraction of contaminant sorbed onto the solid and its distribution coefficient. Two types of batch experiments can be realized. The first types are batch experiments conducted at different V/M as already done recently for Ni retention on clay^[16]. Basically, solid contaminated material is introduced in a batch and put in contact with a solution. After shaking for a given time, the batch is centrifuged to separate the supernatant from the solid. The supernatant is sampled and analyzed for concentration. The second types are in line with the infinite bath technique which consists in introducing a resin to decrease the element concentration in solution^[17], and successive batch extractions. Such extractions, which have already been used to quantify the release of retained contaminants from soils^{[13][18]}, require a lot of successive steps to recover the totality of the available fraction^[11]. Within successive batch extractions, the first step is similar to the classical batch extraction described above, but the supernatant is renewed after centrifugation and the pellet is resuspended. Then the batch is shaken again. This sequence can be performed several times. For both types of batch experiments, the solid/liquid equilibrium (pH, ion composition...) must be identical between the batches considered in the experiment.

Based on the hypothesis that a fraction of the contaminant sorbed on the solid is available and resupplies the solution while the other fraction remains fixed (nonavailable according to the procedure used) to the solid and never participates in the process of solution resupply, two parameters may be obtained by using successive extractions, or extractions conducted at different V/M ratios: the percentage of the available fraction ($\%_{\text{available}}$) and the distribution coefficient between the contaminant available fraction on the solid and the solution (k'_D). In the successive batch extraction technique, the mass balance of the contaminant in the batch is conserved at each step of the successive extractions and the concentration in the solid can be expressed by the following equations.

$$C_{solid_total_initial} = C_{solid_available_initial} + C_{solid_fixed_initial} \quad (1)$$

$$C_{solid_total_final} = C_{solid_available_final} + C_{solid_fixed_initial} \quad (2)$$

where $C_{solid_total_initial}$, $C_{solid_available_initial}$ and $C_{solid_total_final}$, $C_{solid_available_final}$ are the total and the available concentrations of the contaminant on the solid at the beginning and at the end of the contaminant concentration on the solid at the beginning of the experiment (in Bq kg⁻¹, mol kg⁻¹, mg kg⁻¹...) and it is assumed to be constant throughout the extraction steps.

Equilibrium is assumed between $C_{solid_available}$ and $C_{solution}$ so that,

$$C_{solid_available_final} = k'_D \times C_{solution_final} \quad (3)$$

Where $C_{solution_final}$ is the concentration of the target element in the solution at the end of each extraction step (in Bq L⁻¹, mol L⁻¹, mg L⁻¹...), and k'_D is the distribution coefficient between the solid available fraction and the solution (L kg⁻¹). This coefficient is assumed to be constant.

Merging equation (2) and (3), yields

$$C_{solid_total_final} = k'_D \times C_{solution_final} + C_{solid_fixed_initial} \quad (4)$$

This equation is verified at each step of the extraction. So, by plotting $C_{solid_total_final}$ against $C_{solution_final}$ at each extraction step, we can deduce k'_D (slope of the straight line) and $C_{solid_fixed_initial}$ (y-intercept).

For single-step extractions conducted at different V/M ratios, equation (4) can be applied. Plotting $C_{solid_total_final}$ against $C_{solution_final}$ for each V/M (unit expressed in L kg⁻¹, mL g⁻¹...) provides the same information, if the initial weight of soil is the same in all batches.

Normalizing the two terms of equation 4 by $\frac{C_{solid_total_initial}}{100}$ permits merging different extraction experiments (replication of soil sample; different V/M ratios) to increase the power of the regression or/and directly obtain the percentage of the fixed fraction (equation 5) by plotting

$$\%_{remaining_in_solid} \text{ versus } \frac{C_{solution_final}}{C_{solid_total_initial}} \times 100$$

$$\%_{remaining_in_solid} = k'_D \times \frac{C_{solution_final}}{C_{solid_total_initial}} \times 100 + \%_{solid_fixed_initial} \quad (5)$$

$$\text{where } \%_{remaining_in_solid} \left(\frac{C_{solid_total_final}}{C_{solid_total_initial}} \times 100 \right) \text{ and } \%_{solid_fixed_initial}$$

$\left(\frac{C_{solid_fixed_initial}}{C_{solid_total_initial}} \times 100 \right)$ represent the % of the remaining contaminant in the solid at the end of the

extraction step and the percentage of the initial fixed element in the solid, respectively.

Finally, if the $R_D \left(\frac{C_{solid_total_final}}{C_{solution_final}} \right)$ and the concentration in solution are available in the literature,

k'_D and $C_{solid_fixed_initial}$ can be obtained by dividing equation (4) by $C_{solution_final}$ and plotting

R_D against $\frac{1}{C_{solution_final}}$.

$$R_D = k'_D + C_{solid_fixed_initial} \times \frac{1}{C_{solution_final}} * \quad (6)$$

when all contaminant is available (i.e., $C_{solid_fixed_initial} = 0$), R_D is equal to k'_D , which is equivalent to the classical K_D .

For all the equations, $C_{solid_available_initial}$ can be calculated with equation (1) knowing

$C_{solid_fixed_initial}$ and $C_{solid_total_initial}$.

1. Simulated conditions

To have an overview of the power of the method, Eq(1) to (4) were applied to simulated conditions summarized in **Table 1**. For these simulations, the initial concentration of the contaminant is arbitrarily chosen to be 100 Bq g⁻¹. The k'_D , %*solid_fixed_initial* and V/M ratio ranged from 1 to 1 000 L kg⁻¹, 0 to 99%, and 0.1 to 500, respectively, leading to the simulation of 224 different combinations. The number of extraction steps has been fixed to four, which seems reasonable to obtain a straight line in real conditions. The obtained results for all simulations are available in the supporting information Excel file (Table S1).

Table 1. Simulated initial conditions tested

Range of the tested simulated conditions								
k'_D (L kg ⁻¹)	1	10	100	1000				
% <i>solid_fixed_initial</i> (%)	0	10	30	50	70	90	99	
V/M (L kg ⁻¹)	0.1	0.5	1	5	10	50	250	500

2. Experiments performed to validate the approach

The successive extraction method was tested on different couples of radionuclides and solids and for both in situ contaminated materials and fresh laboratory contaminated ones (either classical batch or dialysis bag experiments). The soil contamination procedure used for spike conditions is available in previous publications^{[19][20]}. The main details of the experimental conditions are given in Table 2, whereas additional details are provided in table S2. Se was chosen because its isotope 79 is of first importance in the study of nuclear waste management

impact, whereas ^{137}Cs is the major radionuclide present in the environment for a long term after nuclear accidents like Fukushima^{[19][20]}.

Table 2. Experimental conditions tested

Elements	Extraction set-up	Contamination	Solid phase	Extractant	V/M (ml/g)	Contact time (h)	Exp.
^{75}Se	Batch	Spike	Silty clay	CaCl_2 ,	5	48,	(1a)
			loam soil (0-20 cm)	0.5 mM	5	480	(1b)
^{137}Cs	Batch	Spike	Andosol (0-20 cm)	*UHQ water	10	24	(2a)
	Dialysis bag	Spike	Andosol (0-20 cm)	*UHQ water	22.5	24	(2b)
^{137}Cs ,	Batch	<i>In Situ</i>	Humus	*UHQ water	26	24	(3)
^{133}Cs	Batch	<i>In Situ</i>	Silty soil (0-10 cm)	*UHQ water	12	24	(4)
	Batch	<i>In Situ</i>	Humus	$\text{C}_2\text{H}_7\text{NO}_2$, 1M	26	4	(5)
	Batch	<i>In Situ</i>	Silty soil (0-10 cm)	$\text{C}_2\text{H}_7\text{NO}_2$, 1M	12	4	(6)

UHQ Water : Ultra high quality water ($>18.2\text{M}\Omega\cdot\text{cm}$).

In Brief, classical batch experiments consisted in mixing contaminated solid materials with a solution containing the selected extractant in centrifuge tubes (first, the solid is introduced into the tube, followed by the solution). The tubes used were 50 mL polycarbonates tubes (1a, 1b and 2a experiments) or 50 mL polypropylene tubes (experiments 3, 4, 5 and 6). The tubes were shaken (300 RPM, orbital agitator) for a given time (**Table 2**), and then centrifuged (10 000 g for 20'). The

supernatant was removed, filtered (PolyterSulfone syringe filters 0.8/0.2 μm) and renewed in each tube. The pellet was again fully dispersed, and the same procedure was reproduced. For dialysis bag experiments^[21], the solid was introduced into a dialysis bag (cellulose dialysis membrane, Visking dialysis tubing MWCO 12-14 kDa), then the extractant was added, and the bag was closed. The filled dialysis bag was introduced into a batch (50 mL polycarbonate tubes) containing the same extractant and shaken. After a given time (**Table 2**), the external extractant was renewed. In order to calculate $C_{solid_total_final}$ at the end of each extraction step it is necessary to take into account the residual solution closely associated with the solid material or that remaining inside the dialysis bag. The $C_{solid_total_final}$ is obtained using the following equation:

$$C_{solid_total_final} = C_{solid_total_initial} - \frac{C_{solution_final} \times V_{final} - C_{solution_added} \times V_{added} - C_{solution_residual} \times V_{residual}}{M_{solid}} \quad \text{where } V_{final}, V_{added} \text{ and } V_{residual} \quad (7)$$

(mL) are the volume at the end of the extraction step, the added volume and the residual one respectively, M_{solid} (g) is the solid mass, $C_{solution_added}$ (Bq mL⁻¹) and $C_{solution_residual}$ (Bq mL⁻¹) are the concentrations of the target element in the added solution and in the residual solution linked to the solid phase after the previous step, respectively. $C_{solid_total_final}$ and $C_{solid_total_initial}$ are the solid concentration (Bq g⁻¹) at the end and at the beginning of each extraction step, respectively.

During these experiments, no unexpected or unusually high safety hazards were encountered.

3. Data from the literature

In order to demonstrate the benefits of this method to the scientific community, works in which enough information was available to be reinterpreted or, for which authors provided complementary information, have been selected. The works conducted by Zheng and Wan

(2005)^[15], Elias et al. (2003)^[22], Nagao *et al.* (2020)^[23] and Rigol *et al.* (1999)^[11] have been reinterpreted using our proposed method. The experimental protocols used by the authors to acquire their data are described here.

Zheng and Wan (2005)^[15] evaluated the impact of V/M ratios on the release of U(VI) from contaminated soils. U(VI) released concentrations are then compared to the solubilities of U(VI)-containing phases of the soil. The extractions have been conducted with NaNO₃ 0.01 M (pH 7.5) and with V/M ratios ranging from 2/1 to 100/1 (L kg⁻¹) for three contact times of 4, 30, and 120 days. Elias et al. (2003)^[22] tested the impact of the V/M ratio and efficiency of a single versus repeated extraction steps on the extraction yield of uranium for U-contaminated sand and clay sediments. One part of this work was focused on the determination of the optimal V/M ratio to reach this objective. The extractions were realized using a 222 mM NaHCO₃ solution (pH 8.3) with V/M ratios ranging from 1/1 to 10/1 (L kg⁻¹). Each extraction was repeated three times. Four sediments were used: fine and coarse sands, clays mixed with weathered Mancos shales from the uranium contaminated Shiprock, NM site and a clay sample from the uranium contaminated Oak Ridge TN site. Nagao *et al.* (2020)^[23] realized successive batch desorption experiments using seawater to extract ¹³⁷Cs from four beach sand cores sampled at a distance of 32 km from the Fukushima Daichi Nuclear power plant at four different depths. The objective of this study was to determine the amount of ¹³⁷Cs which could be transferred with time from sand to seawater. The last example used to test the method on literature data is Rigol *et al.*'s (1999) work^[11]. The objective of their study was to determine the impact of soil ionic status and drying on the interaction of radiocesium with organic soils. After checking the impact of solution composition on K_D of ¹³⁴Cs for sorption experiments on four organic soils, they realized up to 60 successive desorptions to estimate the desorption yield using 1M CH₃COONH₄ or CaCl₂ solutions. CaCl₂ was used to extract ¹³⁴Cs sorbed at the outer surface of clays and humic compounds, whereas CH₃COONH₄ can additionally extract ¹³⁴Cs located in the inter lattice positions at the edges of the clay particles. ¹³⁴Cs sorption experiments were conducted after

having preequilibrated the soils with water (H₂O) or with a Ca + K solution before the addition of ¹³⁴Cs. Then one fraction of the soils preequilibrated with Ca + K was either dried at room temperature (D) or kept in moist conditions (M). These led to three conditions (H₂O-M, PCaKD, and PCaK-M) for which successive desorption experiments were performed.

Results and Discussion 1.

Simulated conditions

The conclusions obtained for the 224 simulations presented in the supporting information (Table S1) are the same whatever the chosen combination of $\%_{solid_fixed_initial}$, k'_d and V/M. As example, some results obtained for the condition with $\%_{solid_fixed_initial}$ equal to 30%, $k'_d=10$ L kg⁻¹ and for the 8 V/M ratios are presented in figure 1 and figure 2. Figure 1 shows the plotting of the $C_{solid_total_final}$ against $C_{solution_final}$ for the four extractions and the eight V/M ratios.

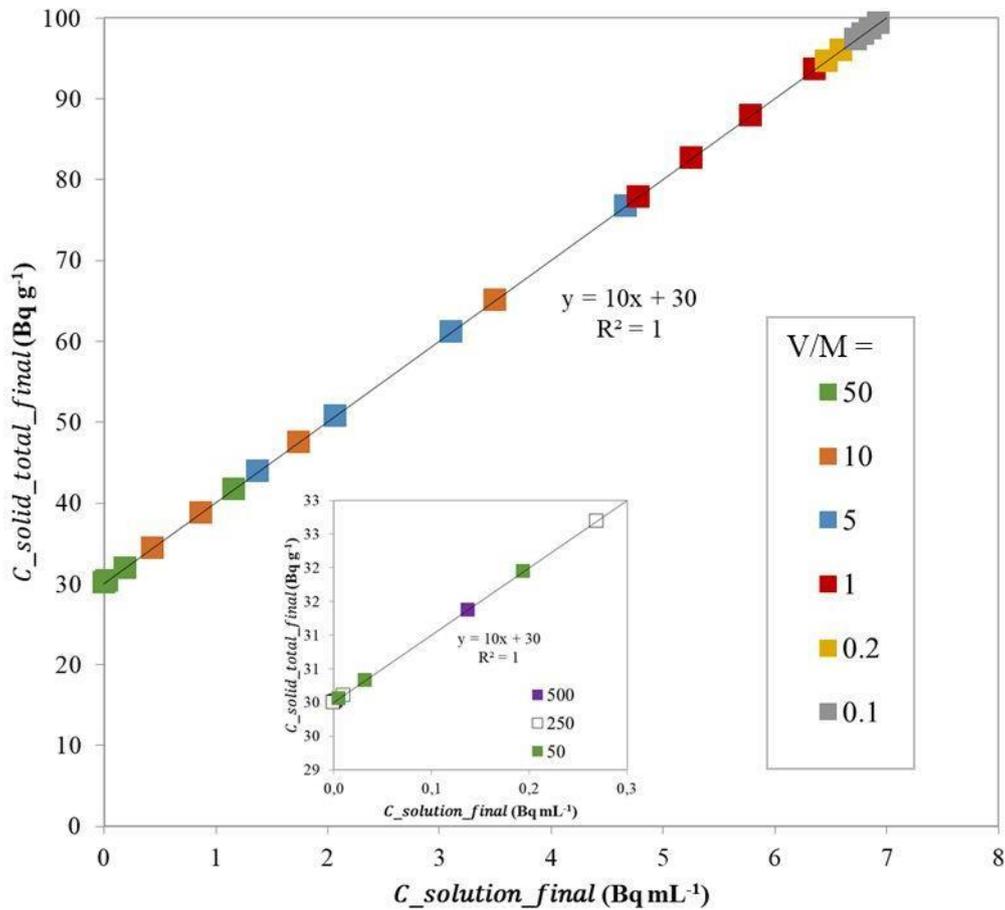


Figure 1. $C_{solid_total_final}$ against $C_{solution_final}$ for the %Solid_{fixed_fraction} of 30% and $k'D = 10 \text{ L kg}^{-1}$ theoretical condition for eight different V/M ratios (the two highest V/M ratios are only presented in the inset plot).

As expected, based on theoretical hypotheses, for all V/M ratios the same linear regression was obtained with a slope equal to 10 and an intercept equal to 30 which correspond to the theoretical k'_D and %solid_{fixed_initial} respectively for all the experiments. This result implies that whatever the V/M ratio chosen for the successive extractions the same available fraction (calculated from the y-intercept value and eq (1)) was obtained independent of the V/M ratio contrary to the extracted fraction (i.e, the amount extracted at a given step for a given experimental setup) as shown in the calculations presented in Table S1. For high V/M ratios, the total concentration in the solid after the first steps of extraction approaches the “true” nonavailable concentration in the solid (given by the y-intercept). This confirms that extraction with a high V/M ratio better targets the available contaminant fraction^{[14][15]}. However, in these conditions, all extraction steps lead to very close

$C_{solid_total_final}/C_{solution_final}$ values, which make the determination of k'_D difficult. Therefore, intermediate V/M ratios can be a better choice to simultaneously obtain the available fraction and k'_D . Figure 1 also confirms that the available fraction and k'_D may be obtained from the results of single extraction performed at different V/M ratios, but only for the same soil weight, by use of the same plot.

The difference in the recovery of the available fraction between a single-step extraction versus the four steps extraction is given in Figure 2, for the same theoretical condition ($\%_{solid_fixed_initial}$ equal to 30% and the $k'_D=10 \text{ L kg}^{-1}$). For the readability of the figure, the two highest V/M ratios are not presented in Figure 2, with results being available in supporting information Table S1.

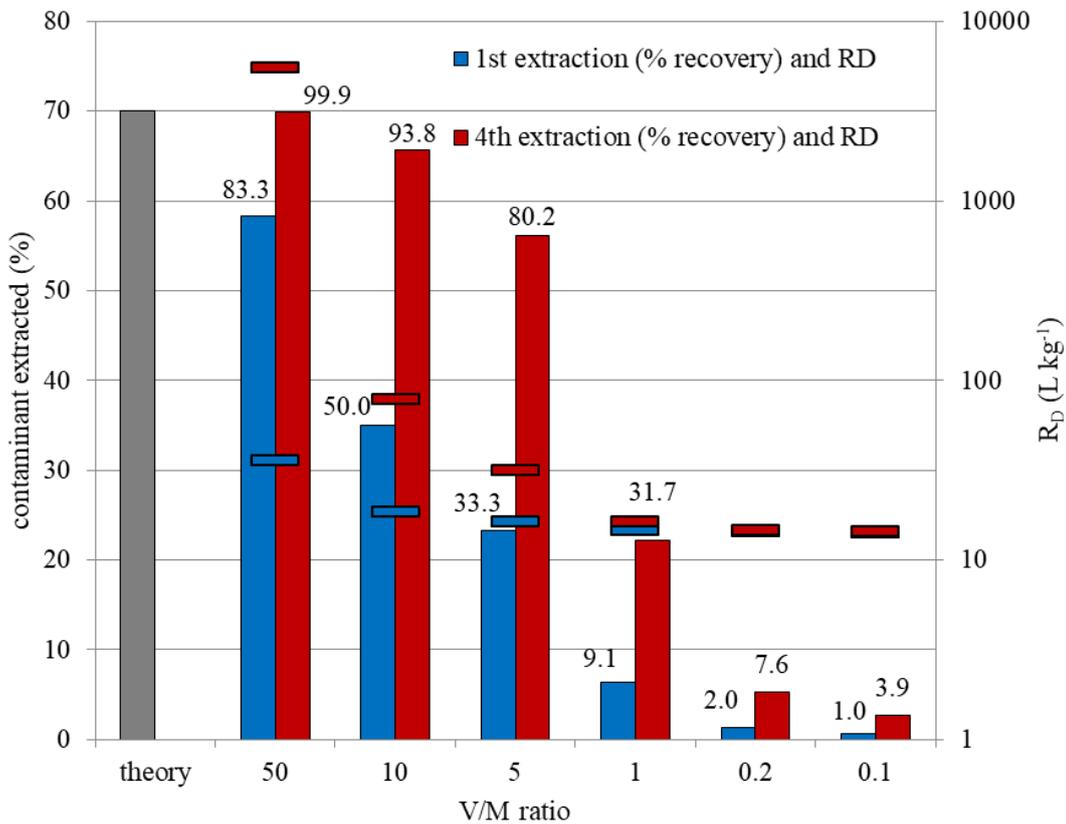


Figure 2. Contaminant extracted (bars) and R_D (rectangles) against V/M ratios for the $\%_{Solid_fixed_fraction}$ of 30% and $k'_D=10 \text{ L kg}^{-1}$ theoretical condition. The data tags correspond to the recovery of the theoretical available fraction (in gray).

The quantity of the contaminant recovered by a single extraction is in any case lower than that recovered by four extraction steps, and lower than the total available quantity (in grey). For the 50, 10 and 1 V/M ratios, the amounts of the recovered contaminant after four steps of extraction represented 99.9, 93.8, and 31.7% of the theoretical available fraction, respectively. For a single extraction, these amounts dropped to 83.3, 50 and 9.1 % respectively. These results showed that for a given contaminated system if the available fraction was estimated by the extracted fraction at the end of the extraction and not the y-intercept the estimation of the available fraction depends on the experimental setup used (number of extractions, V/M ratio) and does not reflect the real value of the available fraction.

For example, only 1% of the contaminant is extracted after one step and 3.9% after four steps for a V/M ratio of 0.1 (representative of an in situ soil water content of 10%) (Figure 2), well below the theoretical available fraction of 70%. This observation showed that: (i) the extracted fraction underestimates the available fraction and (ii) four steps of extraction were not sufficient to deplete the soil available fraction (in this case, after four steps, only 3.9% of available contaminant was extracted, meaning that 66.1 % of the contaminant in the solid is still available). In fact, 700 extraction steps would be necessary to recover 99.9% of the available fraction (results not shown). The results obtained for this combination of parameters are also valid for all tested conditions (Table S1). This result questioned previous estimations of the contaminant available/extractable fraction using only a single extraction step and its transposition from a batch experiment to an in situ situation, for which the real available fraction is certainly underestimated^{[24][25][26][27][28][29]} as already also underlined.

A second interesting point, presented in Figure 2, concerns the calculation of the classical R_D , assimilated by a lot of authors to a K_D value. The calculated R_D , corresponding to the ratio between the solid concentration and the solution concentration at the end of each extraction (in our case $\frac{C_{solid_total_final}}{C_{solution_final}} = \frac{C_{solid_available_final} + C_{solid_fixed_initial}}{C_{solution_final}}$), is reported in Figure 2 for the different V/M ratios and the first and fourth extraction steps. Like the extracted fraction, the R_D value depends also

on the experimental protocol used. For the scenarios illustrated in Figure 2, the R_D values varied over 3 orders of magnitude depending both on whether they were calculated after one or four steps of extraction or at different V/M ratios. This range would even have been higher with more extraction steps (results not shown). For V/M ratios of 50 and 0.1, the R_D values were 36 and 14 ($L\ kg^{-1}$), respectively, for the first step of extraction, whereas they were 5 565 and 14 ($L\ kg^{-1}$) for the fourth step of extraction. The difference in R_D values is due to the fact that in our proposed approach only the solid available fraction is at equilibrium with the solution, whereas in the classical K_D calculation, the total solid concentration of the contaminant is considered to be at equilibrium with the solution. Thus, in our approach, when the solid available fraction decreases, involving a contaminant decrease in solution, the R_D increases due to the $C_{solid_fixed_initial}$ fraction which remains constant. This result can explain the higher R_D measurements obtained from in situ measurements compared to the R_D measurements made in the laboratory from a single batch extraction step,^[13] in line with the difference in V/M ratios. Therefore, assimilating a R_D to a K_D to predict contaminant transfer could generate important bias in the prediction, in the case where only a part of the contaminant sorbed on the solid is available and in equilibrium with the solution (i.e., y-intercept statistically $\neq 0$). R_D values depend on the experimental protocol and/or field conditions (sampling made after rain, after a dry period, and time after contamination...).

2. Experiments performed to validate the approach

The results presented in this paragraph are not intended to be discussed in detail but are used to highlight the applicability of the method, using different extractants, contaminants or solid materials.

Figure 3 presents the results obtained for different batch or dialysis bag experiments, for two radionuclides (^{75}Se , and ^{137}Cs) and one stable element (^{133}Cs). The experimental protocols are

presented in Table 2, and k'_D and available fraction calculated from linear regression analyses are presented in Table 3. In addition to the two above parameters, the % of recovery after the first and the last steps of extraction compared to the available fraction estimated by the y-intercept is also presented in Table 3.

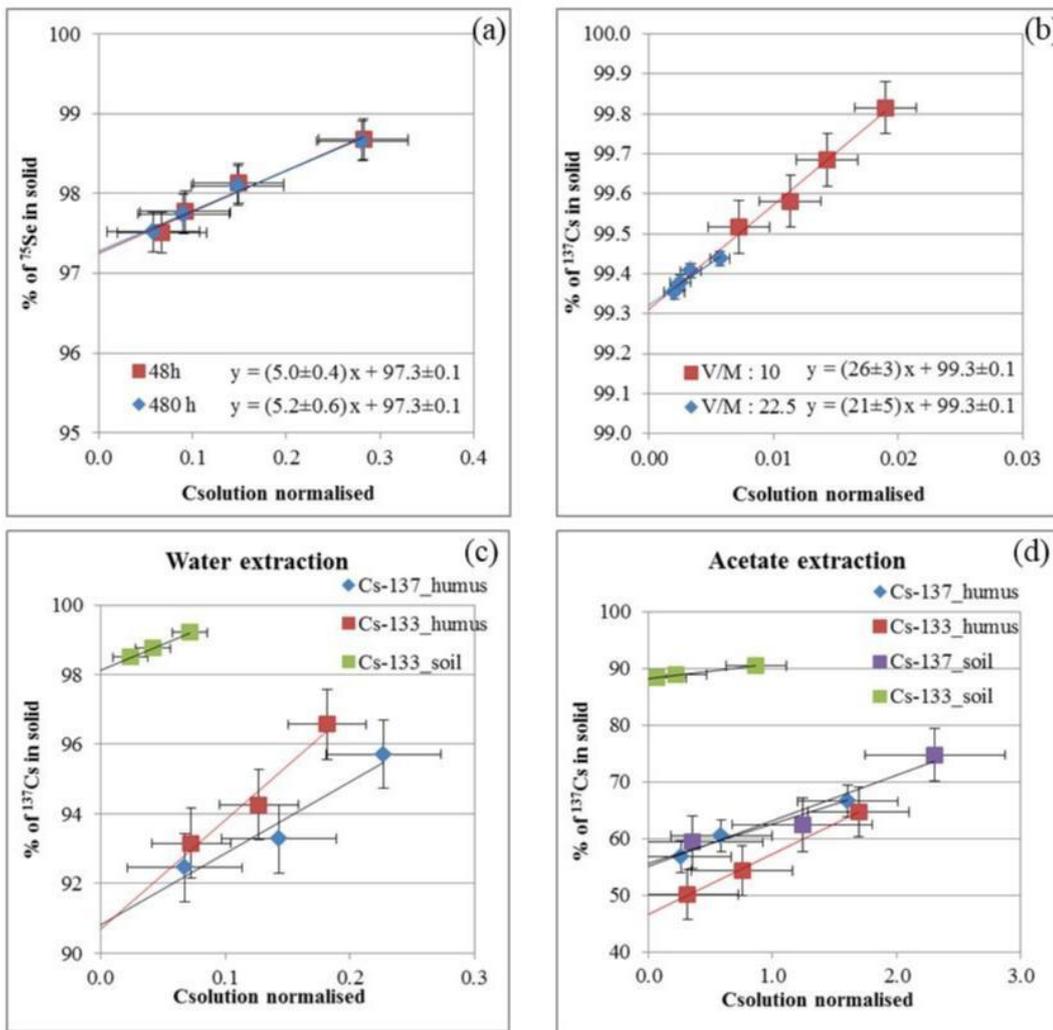


Figure 3. %remaining_in_solid vs $C_{solution_normalized}$ for different experiments : (a) $CaCl_2$ (0.5 mM) extraction of ^{75}Se from contaminated soil using two different contact times, (b) water extraction of ^{137}Cs -contaminated soil using two different V/M ratios, (c) water extraction of in situ ^{137}Cs -contaminated soil and humus layer, and (d) $CH_3COONH_4 - 1M$ extraction of in situ ^{137}Cs contaminated soil and humus layer

The results showed that, in line with the theoretical approach, a linear regression was obtained for all conditions allowing us to calculate k'_D and the available fraction. The recoveries of the available fraction after a single extraction ranged from 27 to 83 %, confirming that a single extraction step was not enough to determine the real available fraction.

Table 3. k'_D and available fraction (in %) deduced from linear regression and recovery after the first and fourth extractions

Exp.	Elements	k'_D (L kg ⁻¹)	% of available fraction	% recovery of 1 st extraction	% recovery of 3 rd (*) or 4 th extraction
(1a)	⁷⁵ Se	5.0 ±0.4	2.7±0.1	49±1%	91±2%
(1b)		5.2 ±0.6	2.7±0.1	48±2%	91±4%
(2a)	¹³⁷ Cs	26.1 ±2.7	0.7 ±0.1	27±2%	70±3%
(2b)		21.2 ±4.7	0.7 ±0.1	83±4%	95±3%
(3)	¹³⁷ Cs	20.5 ±5.2	9.2 ±0.8	47±6%	82±11%*
	¹³³ Cs	31.3±6.2	9.3 ±0.8	37±5%	73±10%*
(4)	¹³⁷ Cs	<LD	<LD	n.d	n.d
	¹³³ Cs	14.9 ±0.3	1.9 ±0.1	43±4%	81±8%*
(5)	¹³⁷ Cs	7.0 ±1.0	44.4 ±1.0	75±8%	97±10%*
	¹³³ Cs	10.6 ±0.3	53.4 ±0.4	66±7%	93±9%*
(6)	¹³⁷ Cs	8.0±2.3	44.9 ±3.5	56±7%	91±11%*
	¹³³ Cs	2.6 ±0.1	11.8 ±0.1	81±8%	99±10%*

Figure 3(a) presents the results obtained for batch extraction (V/M = 5/1) of a ⁷⁵Se(IV)-

contaminated silty clay soil for two different contact times^[19]. No evolution of k'_D and % of available ^{75}Se was observed between the two contact times, suggesting that a steady state was reached faster than 48h. A small percentage of Se(IV) was available for water migration (2.7%) in line with literature data for similar silty clay soils with the same pH^[30]. Adding information on the k'_D (5 L kg^{-1}) of the available fraction will permit the improvement of predictive transfer models by integrating a dynamic approach coupled to water flux compared to just information on the % of available ^{75}Se . Water extraction of a ^{137}Cs -contaminated andosol^[20] by classical batch experiments or dialysis experiments is presented in Figure 3(b). For this set of experiments, after the fourth step of extraction in a classical batch setup, the pellet was introduced in a dialysis bag having a different V/M ratio and a second 4-step successive extraction was conducted using the dialysis bag protocol. Both experiments gave the same results for k'_D and % of available ^{137}Cs (Table 3, experiments 2a and 2b), confirming that these parameters do not depend on the V/M used^[16], although the recovery of the available fraction after the fourth extraction step is clearly different for the two experimental setups (70% and 95% for batch and dialysis bag experiments, respectively).

Figure 3c,d exhibits the results obtained for batch extractions with water and ammonium acetate (1 M) of ^{137}Cs and ^{133}Cs from humus and sandy soils, sampled close to the Chernobyl area. Due to the sampling campaign schedule, only three successive extractions were realized. As expected,^{[20][31][32]} the acetate available fraction was higher than the water available fraction for both Cs isotopes ranging from 12% (for ^{133}Cs in soil) to 53 % (^{133}Cs in humus).

This paragraph illustrates that the proposed method could be used to macroscopically describe the mobility of different radionuclides and stable elements in soils, whatever the chemical processes that have led to their retention in soils (adsorption, reduction, precipitation...). For all experiments, the obtained straight line permits to determine k'_D and % of the available contaminant. By comparison to the estimated available fraction, the % of recovery after the first extraction step (Table 3) confirmed that using a single extraction protocol could underestimate the

real available fraction, from 19 to 72% in the presented examples, even with ammonium acetate (1 M) which is classically used to obtain the exchangeable fraction of a contaminant using a single extraction.

3. New light on some literature data

the work of Zheng and Wan (2005)^[15] on U(VI) release from soils showed that R_D and aqueous schoepite dissolution could be the controlling factor for U release. This assumption was based on the comparison of the observed aqueous U(VI) concentrations with simulated aqueous U(VI) concentrations in equilibrium with schoepite at pH 7.5 for the different V/M ratios. However, the simulation was not entirely satisfactory with a slight underestimation of simulated aqueous U(VI) for the lowest V/M ratio and an overestimation increasing with V/M ratios for the other ones. As their simulation relied only on schoepite dissolution/precipitation, the authors attributed their unperfect simulations to the involvement of potential other mechanisms in U(VI) release that could be dependent on the V/M ratio (ion exchange, dissolution, desorption...). By analyzing their results with our proposed methodology, we will demonstrate that another explanation can be proposed. Because the obtained results showed that the steady state was not reached at 4 and 30 days and only R_D and aqueous U(VI) concentration data were reported, equation (6) was used for the reinterpretation of data obtained for 120 days of contact time. The results presented in Figure 4(a) show a linear correlation between R_D and the inverse of U(VI) concentration in solution for the different V/M. Using the proposed method, we can estimate that $62 \pm 3 \%$ of U(VI) is available (calculated from equation (1) knowing the slope (*i.e.* $C_{solid_fixed_initial}$) and the total initial concentration of U: 206 mg.kg^{-1}) with a k'_D of $11 \pm 7 \text{ L kg}^{-1}$ whatever the V/M considered. As shown in the previous parts of this work, the observed dependence of R_D with the V/M ratio by Zheng and Wan^[15] can thus easily be explained by the fact that only a part of U(VI) retained on soil

is available and at equilibrium with the solution. The percentage of available U(VI) estimated with our proposed method is close to the sum of U(VI) in the water-soluble form, exchangeable form, carbonate-associated or bound to the organic ($55 \pm 7\%$) determined by the authors with a sequential extraction procedure. This observation can suggest that these forms may constitute the reservoir of U available forms in their soil. Interestingly, a single distribution coefficient (k'_D of $11 \pm 7 \text{ L kg}^{-1}$) could thus be used to model the uranium transfer to solution in this sediment even if the available fraction of U is constituted by different U forms.

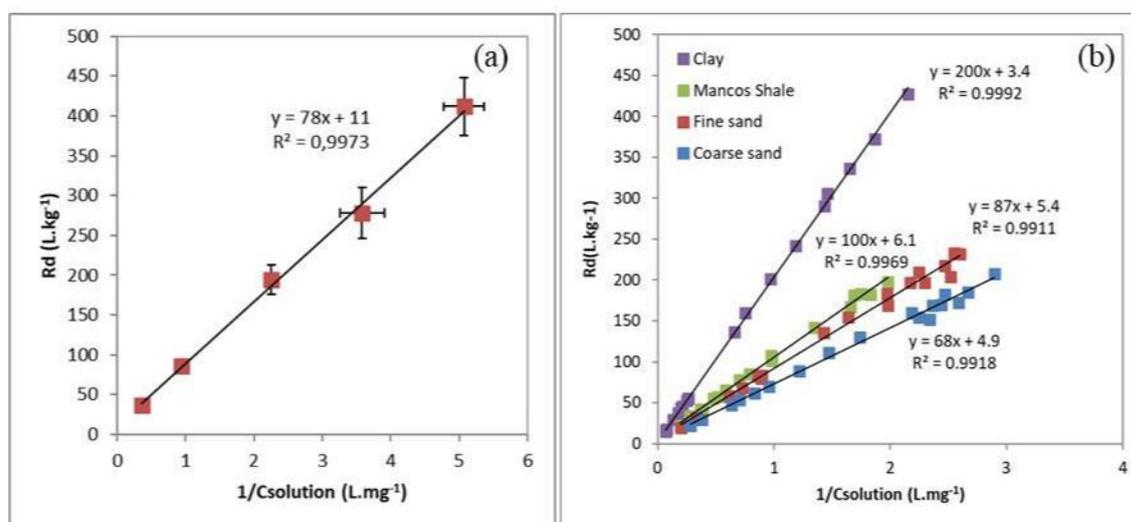


Figure 4. Interpretations of literature data : equation(6) applied to Zheng and Wan (2005)^[15] data (a) and to Elias et al. (2003)^[22] (b).

In the same way, Elias et al. (2003)^[22] tried to determine the optimal V/M to quantify the sorbed U(VI) pool in their contaminated sediments with a 222 mM acetate solution. They observed that the optimal V/M depended on the sediments. For the fine sand sediment, the amount of extracted U increased from V/M 1/1 to 10/1, whereas for the three other sediments no increase was observed for V/M ratios higher than 6/1 or 8/1. Based on this result no real conclusion was provided by the authors on the choice of the optimal V/M to use to estimate the complexed U(VI) pool in sediments. The use of our proposed method demonstrates that the complexed U(VI) pool estimation could be obtained

based on the combination of V/M ratios or successive extractions for a given V/M realized by the authors. Finally, no estimation of optimal V/M was necessary. Their data were re-interpreted using equation (6). As the authors did not conduct their experiments to estimate the proportion of U available fraction but only to estimate the amount of complexed U(VI) extracted from sediments, the total U in the sediments was not analyzed in raw samples (personal communication from authors). So, we had to use an estimated U total concentration to use equation (6). Of course, the R_D value and $C_{solid_fixed_initial}$ depend on the total initial chosen concentration (range tested from 5 times the maximum of extracted U to 100 times). However, the available fraction (calculated from equation (1) knowing the slope (*i.e.* $C_{solid_fixed_initial}$) and the total initial concentration) and k'_D given by equation (6) are independent of the initial chosen concentration (same results for all total U concentration tested, results not shown). The results obtained for the four sediments, the 6 V/M ratios, a $C_{solid_initial}$ corresponding to 5 times the maximum amount of extracted U by the authors and the three extractions steps are reported in Figure 4b. The figure shows that for a given sediment all the points are on the same line, permitting the calculation of the U(VI) extractable by a 222 mM acetate solution and its k'_D . Considering uncertainties, k'_D is very close for all sediments (ranging from 3.4 ± 1.4 to 6.1 ± 1.5). Concerning the available fraction (calculations are provided in Table S3), it ranges from 13 ± 1 to $47 \pm 1 \mu\text{g g}^{-1}$ (coarse sand 13 ± 1 , fine sand 15 ± 1 , Mancos Shale 26 ± 1 and clay 47 ± 1), which is close to the value obtained by the authors after one extraction for the higher V/M. The reinterpretation of these data makes it possible to understand the dependence of the quantities of U(VI) extracted according to the V/M ratios observed by the authors.

The work of Nagao *et al.* (2020) [23] was devoted to assessing ^{137}Cs availability contained in beach sands. For their 4 samples, they concluded, after 12 or 16 desorption steps with seawater, that 58, 19, 37 and 51 % of ^{137}Cs were available in samples labeled St1, St4, St5a and St5b, respectively. After the calculation of ^{137}Cs concentration in solid and solution at each desorption step, based on their figure showing the extracted percentage at each extraction step, equations (4) and

(6) were used to calculate the available ^{137}Cs and its associated k'_D . Equations (4) and (6) lead to the same values, only results obtained for equation (6) are presented in table S4 and Figure S1. The available fraction of ^{137}Cs (calculated from equation (1) knowing the slope (*i. e.* $C_{\text{solid_fixed_initial}}$) and the total initial concentration) obtained for St1, St4, St5a and St5b are 61, 25, 41 and 56 %, respectively. As expected, these results are slightly higher than those obtained by Nagao *et al.* (2020)^[23], mainly for sample St4 for which Nagao *et al.* (2020)^[23] underestimated the available ^{137}Cs fraction by 30%. This higher underestimation of the available fraction of ^{137}Cs for sample St4 may be explained by the higher values of k'_D obtained for this sample compared to the others (38, 77, 51 and 43 L kg⁻¹ for St1, St4, St5a and St5b, respectively). The higher the k'_D , the higher the number of extractions needed to recover the totality of the available fraction. This directly points out another argument in favor of the proposed method, which is the gain of time for a good estimation of k'_D and ^{137}Cs available fraction (four extractions being enough). Additionally, even if the pool of available ^{137}Cs in sand that can be extracted by seawater was well determined by Nagao *et al.* (2020)^[23] for the majority of sands, this information is not sufficient to model the dynamics of recontamination of seawater. This sort of modeling is classically realized using a K_D model. However, as already explained, this approach considers that all the contaminant in the solid is available. Our approach permits integrating the dynamic release of the real fraction of available ^{137}Cs only. As an example, simulated results of predictions made by a K_D model or by our model are presented in Figure S2 for St4. For these simulations, the K_D value was set equal to the R_D measured at the first desorption step (322 L kg⁻¹), whereas % of available ^{137}Cs and k'_D were those presented above for St4. The water content of sand was provided by Nagao *et al.* (2020)^[23], the contact time used for desorption (48h) was used as the time of solution renewal, and the radioactive decay of ^{137}Cs was considered. The results showed that our model predicts a release of ^{137}Cs in interstitial water 2 orders of magnitude lower than the K_D model after 10 years and 7 orders of magnitude lower after 40 years. On the opposite, after 40 years, ^{137}Cs remaining on the sand is 2 orders of magnitude lower for the K_D simulation. This result

illustrates the difference in the prediction of solid/solution distribution using one model considering that all the contaminant present in the solid is available for solution transfer against another considering that only one part of this contaminant is available.

The last example used to test the method on literature data was Rigol *et al.*'s (1999)^[11] work. In this paragraph, we compared the yield of extraction obtained by the authors with those obtained using equations (4) and (6). The objectives of this comparison were to determine (1) if the proposed method can permit decreasing the number of extraction realized by the authors (from 8 with CH₃COONH₄ up to 60 with CaCl₂) to determine the ¹³⁴Cs available fraction and (2) if the number of extractions realized by the authors is enough to recover the totality of the ¹³⁴Cs available fraction. The results obtained for calculation using equation (4) for the extractions conducted with CH₃COONH₄ are presented in Figure 5, whereas those obtained using equations (4) and (6) for the extractions conducted with CaCl₂ are presented in Figure 6.

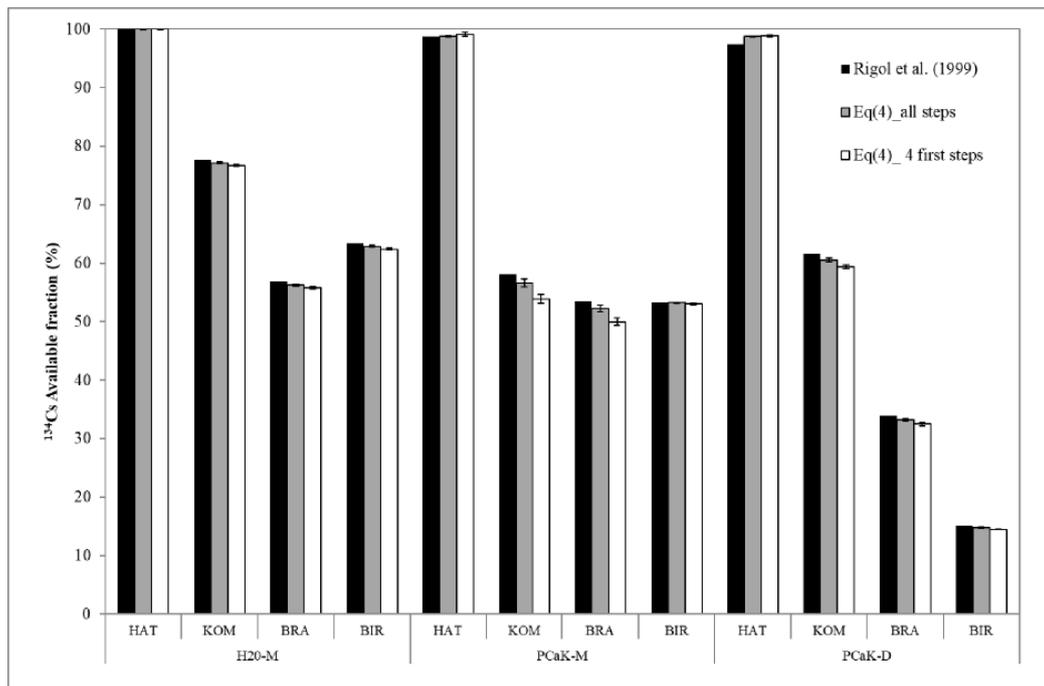


Figure 5. CH₃COONH₄ available fractions of ¹³⁴Cs obtained by Rigol *et al.* (1999)^[11] and calculated using equation 4 for the eight extraction steps or using only the four first extraction steps

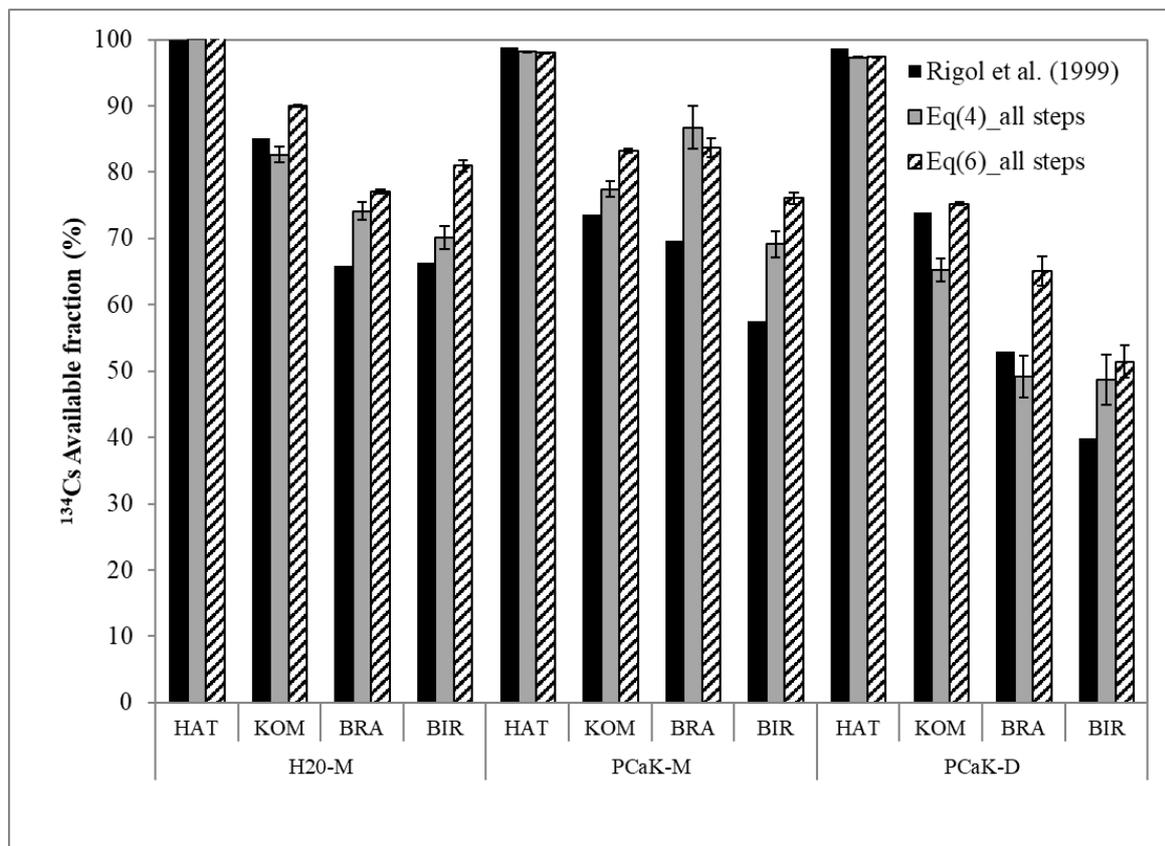


Figure 6. CaCl_2 available fractions of ^{134}Cs obtained by Rigol et al. (1999)^[11] and calculated using equations (4) and (6).

The available fractions of ^{134}Cs obtained for $\text{CH}_3\text{COONH}_4$ extractions using equation (4) are the same as those obtained by Rigol *et al.* (1999)^[11]. Interestingly, the results obtained using the four first extraction steps gave the same results as others, showing that for this kind of extractant, a lot of successive extractions are not necessary to determine the real available fraction (Tables S5 and S6).

The results concerning the CaCl_2 available fraction of ^{134}Cs reported in Figure 6 show that for the HAT soil, in which almost all the ^{134}Cs is available, the results obtained using equations (4) or

(6) are similar to those obtained by Rigol *et al.* (1999)^[11]. For the other soils (KOM, BRA, and BIR), the available fractions calculated using equations (4) and (6) are a bit different, with results obtained by equation (6) being higher than those obtained by equation (4) and higher than those proposed by Rigol *et al.* (1999)^[11]. This difference can be explained by the fact that the values proposed by Rigol *et al.* (1999)^[11] were obtained after a maximum of 38 extraction steps, whereas the plateau was still not reached. In this case using equation (6) permitted us to really determine the available fraction even for experiments in which the plateau was not reached. The slight difference in the % of available ¹³⁴Cs obtained with equation (4) and the one obtained with equation (6) can be explained by the fact that for the CaCl₂ experiments reporting C_{solide} versus C_{solution} does not always lead to a straight line, whereas with the RD versus 1/C_{solution} representation the break in the slope is not observable (Figure S3). This poor alignment of C_{solide} versus C_{solution} suggests that processes involved in the ¹³⁴Cs extraction cannot be simplified using a model considering a single ¹³⁴Cs available fraction at equilibrium with the solution and a non-available ¹³⁴Cs fraction. Rigol *et al.* (1999)^[11] already suggested the existence of two available fractions: one immediately available and another one whose availability is diffusion limited. Moreover, CaCl₂ is supposed to extract ¹³⁴Cs sorbed on the outer surface of clays and humic compounds. The sorption of Cs on the surface of clay minerals can occur under inner-sphere or outer-sphere complexes^[33] and under outer-sphere complexes on organic compounds^[34]. As outer-sphere complexes are highly available compared to inner-sphere complexes, we can suppose that the pool of outer-sphere complexes was removed with the first extraction, whereas the inner-sphere complexes pool was recovered with the following ones. The results obtained using equations (4) and (6) applied to the complete data set, the data set minus the four first extraction steps, and those to the four first extraction steps are available in the Supporting Information (Tables S5 and S6). The estimation of the ¹³⁴Cs available fraction using the entire data set is similar to the one using the data set minus the four first extraction steps for equation (6). Differences appear only for some soils using

equation (4) (maximum 15% for BRA soil after PCaK-D treatment). The results obtained using the four first extraction steps showed that the estimated available fraction and k'_D were lower than those obtained from the entire data set, except for HAT soil for which the results were the same. This result confirms that the CaCl_2 available fraction can be subdivided into two fractions: one highly available and another one less available. For this experiment, using equation (6) for the full data set is a better way to estimate the global available fraction. The reinterpretation of Rigol *et al.*'s (1999)^[11] work permitted us to go further into the validation and criticism of the proposed method, by underlying the limitation of the proposed method, if the available fraction of a contaminant is a combination of different sub-fractions with different availabilities which cannot be described by a single k'_D .

4. Conclusions

The results obtained under simulated conditions, from experiments performed to validate the approach, and from the reinterpretation of the literature showed the robustness of the proposed method.

In this paper, the technique of successive desorption has been seen in a new light. Compared to previous studies, in which only the extracted fraction was determined, the proposed method permits determining the real percentage of the available fraction and its associated distribution coefficient (k'_D). We demonstrated that using successive desorption or experiments conducted at different V/M can provide the same parameters. One of the main advantages of the “successive desorption” method is that the obtained parameters do not depend on the V/M ratio used for the extraction, which permits comparing the results obtained with different experimental protocols. The % of the available contaminant and k'_D can then be used to calculate the time needed to leach the available fraction of contaminated soil in natural environments, by knowing the *in situ* soil humidity, precipitation level, and infiltration rate.

Moreover, this method (1) confirms that using a single-step extraction can underestimate the

real available fraction and (2) provides information on the use of R_D as K_D in modeling: if the available fraction is about 100 %, k'_D is equal to R_D and can be assimilated to K_D .

The proposed method relies on the assumption that soil/solution system can be represented by a two-site model: one site at equilibrium with the solution and another site which does not interact with the solution. However, some limitations can be underlined for this operational and simple assumption. For example, very slow kinetic reactions may control the release in the solution of the second pool (which cannot be considered as “fixed” anymore), or different sorption sites having different equilibrium or kinetic constants may lead to different pools released at different extraction steps. In this case, a first conceptual simplification could be proposed: k'_D represents the fractionation of the contaminant between the soil/solution for the sites having equilibrium or kinetic constants permitting the transfer from solid to solution with the experimental protocol used and the non-available fraction represents the sites with higher equilibrium or lower kinetic constants conducting to non-significant desorption due to the experimental protocol used. In case where this simplification is not satisfactory, more complex models (kinetics, geochemists...)^{[33][35]} need to be used to describe the contaminant transfer from contaminated material to the solution. Nevertheless, in most cases, the method is interesting from an operational point of view to predict the transfer of contaminants in soils being easy to apply and more realistic than the K_D classical approach. One perspective of this work would be to better link this macroscopic method to the process that controls the retention of contaminants in soil and to determine the influence of the soil's physicochemical parameters on the available fraction and its distribution coefficient, based on specific experiments or reinterpretation of existing literature.

Supporting information

Table S1 (Results obtained for the 224 simulated initial conditions), Table S2 (Additional information concerning the experiments performed to validate the approach), Table S3 (Calculation of available fraction for Elias et al. (2003) work), Table S4 (Estimation of available fraction (%) and its associated $k'd$ using equation (6) from Nagao et al. (2020) data), Table S5 (Estimation of available fraction (%) and its associated $k'd$ using equation (4) from Rigol et al. (1999) data), Table S6 (Estimation of available fraction (%) and its associated $k'd$ using equation (6) from Rigol et al. (1999) data), Figure S1 (^{137}Cs extraction with seawater for the four sand cores: R_d vs $1/C_{\text{solution}}$ (data from Nagao et al. (2020)), Figure S2 (Estimation of the evolution of ^{137}Cs concentration in interstitial water for the St_4 core (35-40 cm) (a) and remaining in sediment (b). Considered parameters : water content of sediment 22.7%, renew of solution 2 days (data from Nagao et al. (2020)), Figure S3 (^{134}Cs extraction with CaCl_2 (1M) for the KOM soil: C_{solid} vs C_{solution} (a) and R_d vs $1/C_{\text{solution}}$ (b) (data from Rigol et al. (1999)).

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. The authors contributed equally.

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