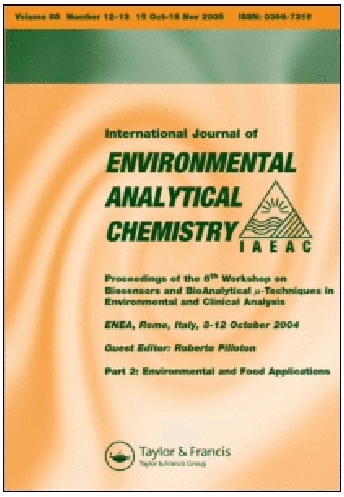

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LABORATORY EXPERIMENTS TO STUDY RADIOCAESIUM INTERACTION IN ORGANIC SOILS

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The total concentration of a pollutant in a given environmental compartment is often used for risk assessment. However, the real impact of the pollutant also depends on its toxicity and mobility. In soils, pollutant mobility is strongly related to its interaction with the different sites. The mechanisms and dynamics of this interaction may be studied by adsorption and desorption approaches. Adsorption experiments based on the measurement of the pollutant solid-liquid distribution coefficient (K_D) determine the interaction capacity of the soil and identify the nature of the sites involved. Desorption experiments based on single, sequential or consecutive extractions show the reversibility of the adsorption process (soil fixation capacity) and how it might be affected by changes in field conditions. They also predict changes in reversibility over time. In this work, the study of radiocaesium interaction in organic soils is used to illustrate these statements. In this study, the combined use of adsorption and desorption experiments shows that, even in highly organic soils, the specific sites of clay materials may govern radiocaesium behaviour.

Keywords: Soil, pollutant, radiocaesium, adsorption, desorption, interaction

INTRODUCTION

There is increasing interest in the fate of inorganic pollutants after an accidental release to the environment. While early efforts attempted to quantify the total content or the acid-extractable fraction of a trace element, more recent studies have focused on speciation. This is because it is difficult to predict the impact of pollution on the basis of contamination levels alone. Environmental studies today deal with the different patterns of behaviour shown by the various *species* of a

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given element. These species may have contrasting geochemical cycles and interactions, which would eventually determine their incorporation into the food chain through soil-to-plant transfer or contamination of groundwaters. However, they may differ not only in their mobility in the environment but also in their toxicity.

In the soil-plant system, the mobility of a pollutant (root uptake, vertical migration, run off) depends on its distribution between the soil solution and the solid phase, which may be affected by different factors such as pH, redox potential, and concentration of organic complexing ligands and chelating agents[1]. But the term "speciation" refers not only to the chemical forms in the soil solution, but also to the type of interaction between the pollutant and the solid phase: sorption by Fe and Mn oxides, coprecipitation with carbonates, complexation with organic matter compounds (humic and fulvic acids), and specific interaction with clay minerals, with or without additional coating by precipitated compounds. The type of interaction in the solid phase actually affects the equilibrium between the solid phase of the soil and its soil solution, thus controlling the level of the pollutant in the soil solution that eventually may be transferred to the plant or may migrate down to the groundwater. Moreover, the knowledge on the pollutant-soil interactions is essential for a suitable design of restoration strategies to decrease its impact on humans[2].

Although for most heavy metals the potential contamination of groundwaters is often considered more relevant than root uptake, for some radionuclides such as radiocaesium and radiostrontium, root uptake is the way of contamination of major concern[3], since after an accidental release of these radionuclides, the concentration levels in plants easily exceed the intervention limits. Moreover, radiocaesium and radiostrontium, which may be released in a nuclear accident, have similar chemical properties to potassium and ammonium, and calcium and magnesium, respectively, which are macronutrients for plants, this fact favouring their root uptake. In the case of these radionuclides, especially of radiocaesium, speciation should not be considered in relation to different chemical species, but from the point of view of interaction, since sites with extremely different specificity for radiocaesium may be found in the solid phase of soils[4].

In this paper we review some results from previous works, as an example of how the use of laboratory experiments provides information on the interaction of radiocaesium in organic soils, and thus predicts its mobility in the soil-plant system. Two main groups of soils are considered: organic soils containing a certain amount of clays (*organic-clay*) and organic soils with a negligible content of clay materials (*organic*).

BASIC KNOWLEDGE OF THE RADIOCAESIUM-SOIL INTERACTION

Radiocaesium mobility in soils is a function of several parameters that may be grouped in the following classes: ionic composition of the soil solution, environmental conditions affecting its interaction with the solid phase of the soil, and the type of interaction in the solid phase. The first is related to the concentration of elements competing for root uptake (mainly potassium and ammonium), and the plant physiological processes involved (selectivity, dilution effect)[5,6]. The second group of parameters indirectly affects the interaction of radiocaesium in the solid phase (*e.g.* hydric regime)[7,8]. Finally, the third is the most significant. It includes the adsorption capacity of the solid phase, the reversibility of adsorption, and the changes of both adsorption and desorption processes with time that may determine radiocaesium behaviour in the short and long-term after a pulse of contamination[9–13].

Whereas for most trace elements and macronutrients the pH and the total Cation Exchange Capacity (CEC) of the soil are basic parameters governing adsorption[14,15], this is not the case for radiocaesium. Because of its low concentration (lower than trace level) with respect to the potential active sites in the solid phase, some specific sites in the frayed edges of illitic clay minerals control its adsorption, although these sites represent less than 0.5 % of the total CEC[9,16]. This specific adsorption is based on the low hydration energy of monovalent cations, the selectivity sequence being $Cs > NH_4 > K$. This pattern explains why traditional soil parameters affecting trace element transfer to plants, such as CEC, pH and carbonate content, have less influence on radiocaesium transfer. Questions arising are whether in soils with a low mineral content, such as organic soils, the specific sites in the mineral phase still control radiocaesium adsorption, and how reversible this adsorption is, especially considering the large soil-to-plant transfer rates that may push contamination levels in food above the intervention limits.

Therefore, there is a need of robust analytical methods capable of obtaining information on mechanisms and dynamics of the pollutant-soil interaction. Two approaches may be followed: adsorption and desorption experiments. The first are based on calculating the solid-liquid distribution coefficient in several solution compositions, which measures the interaction capacity of the soils, and identifies the sites involved. This type of approach is less used in predictions of mobility, although it provides information on the equilibrium between the solid phase and the soil solution. Complementary, desorption experiments measure the reversibility of the adsorption (fixation capacity of the soils) by means of the quantification of the exchangeable fraction of radionuclide using mild extractants (salt solutions or complexing agents)[17,18]. Although this fraction only represents the pool of pollutant participating in the equilibrium between the solid phase and the soil solution, it can be used for mobility predictions[19,20] and for the study of dynamics, i.e. how the reversibility of the adsorption process changes with time[13]. The information derived from both adsorption and desorption studies is operational, but as is shown along this work this information is extremely useful for comparison purposes either between soils or for the same soil at different times after a contamination event.

ADSORPTION METHODS

In soils, the adsorption pattern of radiocaesium, as well as of other trace elements, depends on two parameters: the solid-liquid distribution coefficient (K_D), and the selectivity coefficient versus other elements with similar chemical properties. The solid-liquid distribution coefficient of an element A is defined as the equilibrium concentration ratio of the element in the solid and liquid phases:

$$K_D(A)(\text{ml g}^{-1}) = \frac{(A)_{\text{Solid}}}{(A)_{\text{Liquid}}} = \frac{Z_A \cdot [\text{sites}]}{m_A}$$

where Z_A is the fraction of element adsorbed in a group of sites of a given concentration *[sites]* in meq kg^{-1} and m_A the concentration of the element in the equilibrium solution expressed in meq l^{-1}. In fact, this coefficient responds to *pseudo*-equilibrium between the liquid and the solid phases, which depends on the experimental conditions. However, this parameter provides reliable and comparable information when dealing with known experimental conditions.

On the other hand, the K_D of a given element may be understood with respect to the K_D of a competitive element with similar adsorption behaviour. Thus, radiocaesium K_D may be written as:

$$K_D(\text{Cs}) = K_D(X) \cdot K_C(\text{Cs}/X)$$

where X is a competitive element such as NH_4 or K, and K_C (Cs/X) is the Cs-to-X selectivity coefficient. Therefore, the K_C (Cs/X) is a constant value that relates the two K_D, and depends on the competitive element and on the nature of the sites, since for radiocaesium different adsorption selectivity is observed for the specific sites located in the clay interlayers, and the non-specific sites, mainly planar sites on clays and organic matter sites. The non-specific sites may be estimated by the CEC and have similar selectivity for all monovalent elements[21,22]. In contrast, the specific sites seem to be associated with several clay minerals such as illite or vermiculite and show large differences of selectivity among Cs, NH_4 and K[23,24].

Identification of sites involved in radiocaesium adsorption

Several methods have been proposed to determine the concentration of specific sites and the selectivity coefficient of Cs versus K or NH_4, either individually[10,16] or as a combination of the two[9]. These methods are based on the determination of K_D in several media with different concentrations of K and NH_4.

For a homoionic composition of K or NH_4 on the specific sites and at low concentrations of caesium the product between the K_D and the concentration of a competitive element in solution (m_X) reaches a constant value, which can be used to measure the radiocaesium adsorption capacity of soils. This parameter is called Radiocaesium Interception Potential (RIP) and it can also be defined by the product of the concentration of specific sites and the selectivity coefficient versus the corresponding competitive element according to the following expression[9]:

$$[K_D^{\text{specific sites}}(\text{Cs}) \cdot m_X] = K_C^{\text{specific sites}}(\text{Cs/X}) \cdot [\text{specific sites}] = \text{RIP}_X$$

Considering that the K_C (Cs/X) is an adimensional parameter, the RIP is expressed as concentration of sites. In contrast with CEC, RIP is not influenced by changes in pH, but it has been demonstrated that it depends on the concentration and nature of the monovalent species present, being higher in K than in NH_4 medium. Moreover, its magnitude allows the evaluation of radiocaesium interaction in soils, other parameters such as carbonate or oxide content being of less relevance. Such a specific parameter has not been found for the adsorption of other trace elements, for which the pH and CEC are the reference parameters.

Taking into account that the concentration of specific sites in the soil is independent of the competitive element present in solution (NH_4 or K), the differences in RIP are attributable to differences in the selectivity coefficient. Therefore, the specific sites are more selective for NH_4 than for K. In soils that contain clays the NH_4-to-K selectivity coefficient takes values between 4 and 8[10,11], which can be used as a fingerprint of specific adsorption. Thus, the response of the radiocaesium solid-liquid distribution coefficient to NH_4 addition in a medium that also contains K, allows the identification of the soil phase that controls radiocaesium adsorption. A method was developed following this premise[25], which is summarised in Figure 1.

If the specific sites control radiocaesium adsorption, increasing concentrations of NH_4 decrease radiocaesium K_D, since NH_4 is much more competitive than K

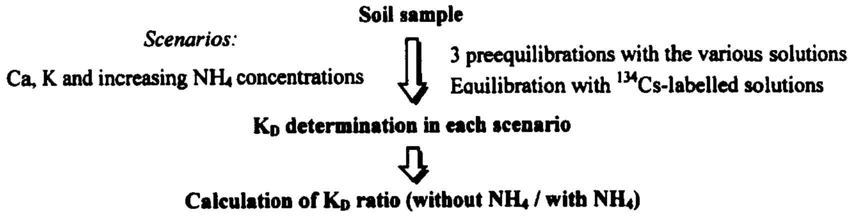

FIGURE 1 Method for the identification of the nature of the sites involved in radiocaesium adsorption

for these sites. In this case the ratio of the K_D in a medium without ammonium versus a medium with ammonium increases. The higher the contribution of the specific adsorption the higher this increase. In contrast, if non-specific sites control radiocaesium adsorption, increasing concentrations of NH_4 do not affect radiocaesium K_D and a unit value of the K_D ratio is obtained for all the solution compositions. This approach has been useful for the identification of the sites that control radiocaesium adsorption in organic soils, since the number of specific sites is much lower than the number of non-specific sites in this type of soil[12,26].

As shown in Figure 2, even in some soils with a high organic matter content, the adsorption pattern is very similar to that of illite. Therefore, in spite of the high content of organic matter in these soils, the presence of clay materials such as illite or vermiculite leads to specific adsorption. The non-specific sites only control radiocaesium adsorption in soils with a negligible content of these materials. These differences in behaviour may also be explained by radiocaesium K_D, since different values of this parameter are obtained for the two types of soil.

Effect of the ionic status of the solution on radiocaesium adsorption

An important aspect to be considered in adsorption experiments is the ionic composition of the solution chosen[27–29]. One option is the use of the soil solution composition that best simulates the environmental conditions, but in this case the information obtained depends on the soil studied. Another option is the use of a fixed ionic composition, which allows the comparison between different soils.

Table I shows the values of the radiocaesium solid-liquid distribution coefficient (K_D) obtained for soils with different organic matter content (%O.M.). These K_D values were obtained following the protocol shown in Figure 1, with several solution compositions. High differences of K_D are observed depending

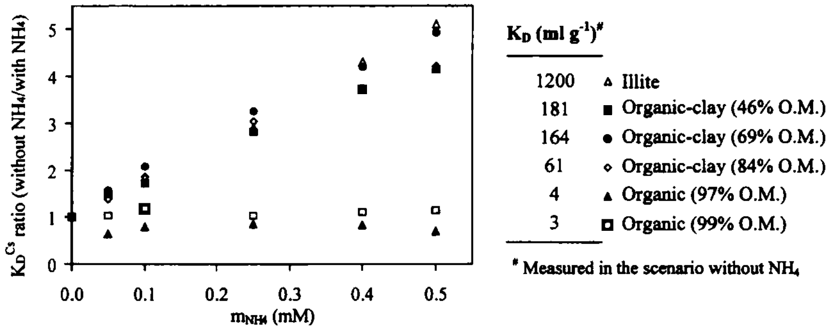

FIGURE 2 Adsorption pattern of various organic soils in terms of K_D values and dependence on increasing concentrations of NH_4

on the composition of the solution used for the determination of this parameter. These differences provide information on interaction mechanisms.

TABLE I Radiocaesium solid-liquid distribution coefficients measured in different solution compositions* (mean ± standard deviation)

Soil (%O.M.)	K_D (ml g^{-1})		
	K	*Ca*	H_2O
Organic-clay (46)	198 ± 7	1357 ± 37	2519 ± 282
Organic-clay (69)	183 ± 9	1654 ± 124	1900 ± 177
Organic-clay (84)	83 ± 4	296 ± 12	354 ± 29
Organic (99)	41 ± 1	6.9 ± 0.2	210 ± 14

**K*: 10mM K; *Ca*: 100mM Ca; *H_2O*: Deionized water.

In water the K_D takes the highest values, which is attributed to the low level of competitive elements for the specific and the non-specific sites. Moreover, in the *organic* soils *Ca* solution leads to lower radiocaesium K_D values than *K* solution. This demonstrates that the non-specific sites control radiocaesium adsorption in this type of soil, and Ca due to its higher charge is more competitive than K for these sites, as could also be expected for other pollutants such as heavy metals. In contrast, in *organic-clay* soils the *K* solution gives the lowest radiocaesium K_D, and a specific adsorption of radiocaesium can be assumed in these soils, with K being more competitive than Ca, since it is able to interact with the specific sites.

From adsorption experiments it can be concluded that the identification of the parameters that affect pollutant adsorption is essential, and the design of specific experiments for each specific interaction is required. Whereas the ionic composition of the solution, especially in terms of NH_4 and K concentrations, is extremely important in radiocaesium behaviour, for other trace elements (*e.g.* heavy metals), other parameters such as pH and CEC are of more relevance.

DESORPTION METHODS

Once the pollutant has been adsorbed in the soil, desorption methods can be used to determine the reversibility of the adsorption in terms of the pool of adsorbed pollutant that may participate in the equilibrium between the soil and the soil solution. These methods give operational information and do not explain absolute values of mobility. However, they are excellent tools for comparative purposes either between soils or in the same soil at different times after the contamination event.

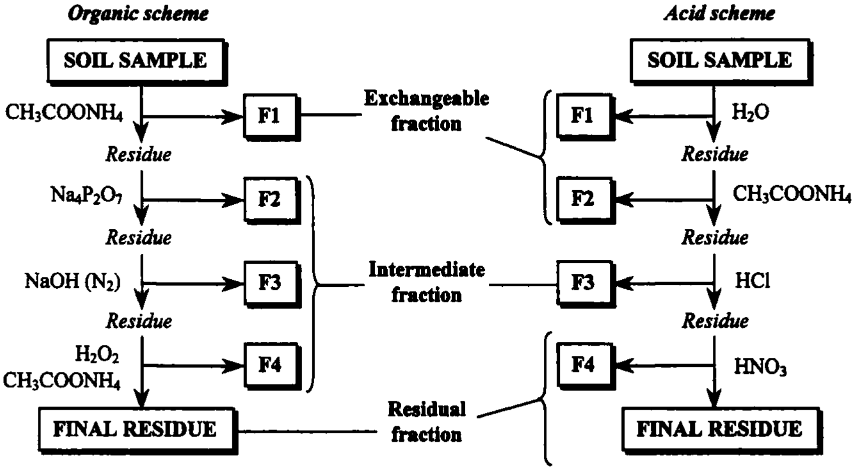

FIGURE 3 Sequential extraction schemes for radiocaesium

In the short-term a rapid pollutant-soil interaction can be expected, in which the pollutant is distributed between an exchangeable and an irreversibly adsorbed fraction. Moreover, in the long-term an ageing process may occur, which is defined as an increase in the irreversibly adsorbed fraction with time. Ageing mostly depends on the pollutant, soil characteristics, environmental and experimental conditions. For radiocaesium, ageing is partially attributed to solid-state migration into the specific sites in the interlattice positions of illitic clay materials and subsequent fixation due to interlayer collapse[30,31]. Thus, if specific sites control radiocaesium adsorption, a certain ageing of this radionuclide is expected. In contrast, no ageing should be observed in soils with non-specific adsorption.

Up to now, several desorption methods such as single, consecutive and sequential extractions have been used, which follow different approaches and give complementary information. Single extractions with different reagents allow the estimation of the fraction of pollutant remobilised by ionic exchange (*e.g.* $CaCl_2$, CH_3COONH_4), or by other processes such as complexation (*e.g.* EDTA) or acidification (*e.g.* CH_3COOH). Consecutive extractions allow the definition of the fraction of pollutant remobilisable by a continuous addition of fresh extractant that avoids pollutant saturation of the extractant solution. These extractions may give information about pollutant-soil interaction mechanisms and side-effects of extractant reagents. Sequential extractions provide additional information on those soil fractions that only release the pollutant by drastic changes in soil properties or environmental conditions such as acidification or redox processes.

Single extractions for the estimation of the radiocaesium exchangeable fraction

Mild extractants such as Ca and NH_4 salts are the most frequently applied for the estimation of the exchangeable fraction, usually at concentrations close to 1M, at liquid/solid ratios between 10 and 40 ml g^{-1}, typically using overnight extractions [17,18]. For radiocaesium, in contrast with other pollutants such as heavy metals, single extractions with Ca and NH_4 solutions give different information since the two cations involved have contrasting desorption characteristics. Whereas Ca only can desorb radiocaesium associated with the non-specific sites, NH_4 enters clay interlayers and desorbs radiocaesium in the specific sites[12,25,29].

TABLE II Radiocaesium desorption yields obtained by single extractions

Soil (%O.M.)	*RCs desorption yield (%)*		
	1M CH_3COONH_4		*1M $CaCl_2$*
Organic-clay (46)	49.6	>>	5.8
Organic-clay (69)	46.1	>>	3.3
Organic-clay (84)	49.4	>>	10.7
Organic (88)	87.1	>	67.7
Organic (97)	92.1	≈	92.8
Organic (99)	88.8	≈	88.2

Table II compares radiocaesium desorption yields obtained with the two extractant solutions. As seen in this table, for the *organic-clay* soils, which have specific adsorption, desorption yields with NH_4 are much higher than those with Ca. In contrast, similar yields are obtained for the *organic* soils, indicating non-specific adsorption. Therefore, single extractions with these two cations give an idea of the exchangeable fraction, but also supply information on interaction mechanisms such as radiocaesium distribution between specific and non-specific sites in the soil.

Consecutive extractions for the evaluation of the side-effects of extractant reagents

Consecutive extractions with Ca or NH_4 differ from single extractions in two main aspects: the continuous addition of the extractant cation and a radiocaesium level in solution near to zero because of the addition of fresh extractant.

TABLE III Radiocaesium cumulative desorption yields (%) after a certain number of consecutive extractions

Soil (%O.M.)	*1M CH_3COONH_4*			*1M $CaCl_2$*				
	n° 1	*n° 3*	*n° 8*	*n° 1*	*n° 8*	*n° 20*	*n° 40*	*n° 60*
Organic-clay (46)	58.3	62.4	63.4	9.8	30.7	52.3	68.0	77.3
Organic-clay (69)	51.8	55.8	56.8	6.5	26.8	48.0	67.4	74.9
Organic-clay (84)	71.3	76.6	77.7	22.6	56.2	76.3	85.6	89.1
Organic (99)	94.3	99.8	100	94.5	100	–	–	–

Table III shows the desorption yields obtained after different number of extractions for several organic soils[29]. Both extractant solutions show an increase in the radiocaesium desorption yield by increasing the number of extractions, this pattern being more evident for the extractions with Ca solution. On the other hand, for the *organic-clay* soils, an opposite side effect is observed for the two extractant solutions. Desorption yields reach a plateau when using NH_4, whereas a slow and continuous desorption is observed for extraction with Ca. An explanation for these different desorption patterns is that NH_4 collapses clay interlayers preventing radiocaesium diffusion from the specific sites to the solution, whereas Ca, due to its high hydration energy can not collapse but may expand clay interlayers[30–32] favouring the diffusion of radiocaesium into the solution, even overcoming desorption yields obtained with NH_4. This collapse with NH_4 has also been observed using lower concentration levels of this cation[26]. In contrast, for the *organic* soils, the same desorption pattern is obtained for the two extractant reagents, suggesting radiocaesium interaction with the non-specific sites of the regular exchange complex.

Sequential extraction schemes for the study of radiocaesium dynamics

The origin of sequential extraction schemes goes back to early works of Tessier et al.[33], which studied the interaction of heavy metals in sediments, and several schemes have been used since then with the same aim[34]. When moving to soils, there was a need of introducing a first step that defined the exchangeable fraction, and for radiocaesium, even additional modifications of the usual schemes became necessary because of its characteristic interaction in soils[13,35–37].

Radiocaesium in soils can be mostly found as an exchangeable fraction and an irreversibly adsorbed fraction. As the exchangeable radiocaesium may be associated with specific sites, a monovalent cation with similar characteristics (*e.g.* NH_4) is required for the determination of the exchangeable fraction. On the other hand, a first extraction with water is useful to evaluate the most reversible fraction of radiocaesium, whereas this step was never considered in the early schemes, because of its low capacity of desorbing heavy metals from sediments. Moreover, the application of extractant reagents targeting phases such as carbonates (*e.g.* CH_3COOH) or oxides (*e.g.* $NH_2OH{\cdot}HCl$) has less sense for radiocaesium, since desorption of radiocaesium with these two extractant solutions is more attributable to the breaking of coatings existing between clays and carbonates or oxides than to a direct interaction of radiocaesium with these two phases[13]. On the contrary, for organic soils, some extractant reagents able to dissolve organic matter may be useful to establish the role of this phase on radiocaesium behaviour. Figure 3 shows two schemes widely used to study radiocaesium distribution in soils, which introduce some changes with respect to those used for heavy metals in sediments. Both schemes use CH_3COONH_4 to desorb the exchangeable radiocaesium and, whereas the *organic* scheme attempts to obtain information on the organic fraction by desorption with $Na_4P_2O_7$, NaOH or H_2O_2, the *acid* scheme, widely used in NIS (New Independent States) countries, is more focused on the irreversibly adsorbed fraction by the use of strong acids. For the two schemes, three groups of fractions have been considered: an exchangeable fraction, an intermediate fraction and a residual fraction, and they have also been applied with the aim of predicting radiocaesium dynamics in soils.

Figure 4 shows, as an example, some radiocaesium distributions and their dynamics in two different soils. Moreover, for the same soil, samples of different origins are compared. Some samples were directly contaminated by the Chernobyl fallout (6Y), and the other were contaminated in the laboratory and analysed at different times after contamination. A set of these later samples was stored at constant humidity and temperature (4D, 1M, 8M, 12M, 17M, 20M and 25M) and the rest were subjected to drying-wetting cycles (12M*, 17M*, 25M* and 30M*), which better simulates environmental conditions. Information on different mechanisms can be obtained from the application of these schemes.

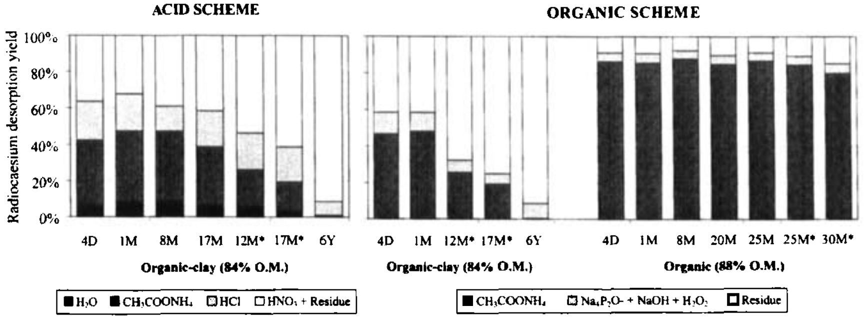

FIGURE 4 Radiocaesium distribution and dynamics obtained with the organic and acid schemes for two soils of contrasted characteristics (D-day, M-month, *application of drying-wetting cycles, Y-year)

For the *organic-clay* soils, the irreversibly adsorbed fraction of radiocaesium is higher than the exchangeable fraction, especially for the samples aged in field conditions. Moreover, at constant humidity and temperature, radiocaesium fixation does not increase with time, which does not explain the distribution obtained for the 6-year samples. However, the use of drying-wetting cycles leads to a radiocaesium distribution close to that obtained in field conditions, since these cycles favour collapse of clay interlayers. Therefore, a certain ageing of radiocaesium can be predicted in this type of soil by the application of drying-wetting cycles. This agrees with the decrease with time in radiocaesium soil-to-plant transfer observed in these soils[38,39].

In contrast, for the *organic* soils, a completely different distribution is observed, characterised by an exchangeable fraction close to 100% and no effect of drying-wetting cycles. This predicts a high and constant exchangeability of radiocaesium, which also agrees with data on soil-to-plant transfer[38,40].

Moreover, for the different soils, the use of the organic scheme demonstrates a poor association of radiocaesium with the organic phase. Finally, the comparison of radiocaesium distributions obtained when applying the same scheme to two soils with similar organic matter content, indicates that it is the illitic clay content and not the organic matter content that controls radiocaesium interaction in organic soils.

As shown by the results obtained, desorption experiments based on several approaches are useful to evaluate the reversibility of the adsorption process of a given pollutant in the short- and long-term, and how it is affected by changes in field conditions. However, the extractant solutions must be adapted to the characteristics of the pollutant taking into account the solid phases involved in its adsorption.

CONCLUSIONS

Both adsorption and desorption methods are advisable for the study of the interaction mechanisms and dynamics of a pollutant in soils or sediments. Although adsorption studies allows the characterisation of a soil in terms of interaction capacity with pollutants and the identification of the adsorption sites, desorption methods are required to know the fraction of this pollutant that is able to participate in the equilibrium between the solid phase and the soil solution, that is, the fraction of pollutant that may be considered mobile and can be incorporated to plants or waters.

Adsorption and desorption experiments must be designed taking into account the characteristics of the pollutant, the components of the solid phase involved in the interaction, and the factors that may affect this interaction. This requires a previous evaluation of all these factors and a subsequent control during the development of experiments.

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