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Possible role of organic matter in radiocaesium adsorption in soils

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Abstract

The aim of this review is to examine the hypothesis that organic matter decreases the adsorption of radiocaesium on clay minerals. The factors that determine radiocaesium mobility and bioavailability in soil are briefly outlined to show why a relationship between soil organic matter content and enhanced Cs bioavailability is paradoxical. In all the investigations reviewed the ionic compositions of both the solid and the solution phases have been strictly controlled. We show that the addition of organic matter to reference clay minerals causes decreases of up to an order of magnitude in the distribution coefficient of radiocaesium. Similarly, the chemical removal of organic matter from the clay-sized fraction of soil usually leads to an increase in Cs adsorption. We suggest that the nature of the organic matter and its interaction with mineral surfaces are as important as the amount present. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Radiocaesium; Soil; Organic matter; Adsorption

1. Introduction

There has been renewed interest in the behaviour of radiocaesium in soil–plant systems since the widespread contamination following the accident at the Chernobyl nuclear power plant in 1986. Long-term predictions of the mobility and availability of ^{137}Cs are required because of its relatively long half-life (30 years), and the ease

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with which caesium, which has no known biological role, enters biological systems. Reasonable predictions can only be possible if the underlying mechanisms are well understood. In many agricultural soils, the strong, and possibly irreversible, adsorption of radiocaesium on soil results in very low plant uptake. However, in some ecosystems radiocaesium continues to be bioavailable. In this respect, poor quality upland soils, which often have a large organic matter content, give particular cause for concern. Even years after contamination, radiocaesium continues to be transferred to plants and grazing animals (Absolom, Crout, & Young, 1996; Rigol, Vidal, Rauret, Shand, & Cheshire, 1998; Sanchez, Walters, Singleton, Wood, & Mondon, 1999). An obvious explanation would be that such soils do not contain enough clay, particularly illites, to immobilise caesium. However, careful sample preparation prior to mineralogical analysis indicates that sufficient illite is indeed present to immobilise the trace amounts of radiocaesium present in contaminated soils (Hird, Rimmer, & Livens, 1995). This observation has prompted the hypothesis that organic matter may be responsible for the limited immobilisation. In order to place this hypothesis in its context, a brief review of the factors, which determine the movement of caesium in soil–plant systems, is necessary.

Adsorption plays a determinant role in the mobility and bioavailability of caesium in soils (Livens & Loveland, 1988). Adsorption decreases the solution phase concentration, resulting in very low diffusive fluxes and small transfer by mass flow of soil solution. Clay minerals are known to adsorb Cs very strongly (Sawhney, 1972; Eberl, 1980; Cornell, 1993). Other solid soil constituents, including organic matter, quartz, carbonates and the (hydr)oxides of iron, aluminium and manganese, have much smaller affinities for caesium and hence the extent of adsorption is limited. When the association between Cs and a soil constituent is non-specific, even if it is responsible for a considerable proportion of soil CEC, the extent of adsorption is usually small because of the small relative abundance of Cs with respect to other cations.

Of the various clay minerals, illites and vermiculites have the strongest affinities for caesium, particularly at trace concentrations of the cation, as is the case for even large radiocaesium contamination ($1 \, \mathrm{Bq} \, ^{137}\mathrm{Cs} \equiv 2.3 \times 10^{-15} \, \mathrm{mol}$). This highly selective adsorption is usually attributed to the small hydration energy of caesium and the presence of frayed edge sites (FES) in the minerals (Brouwer, Baeyens, Maes, & Cremers, 1983). These FES account for a tiny proportion (circa 1%) of the cation exchange capacity (CEC) but dominate the adsorption of trace amounts of radiocaesium. Some authors assume that a small number of different sites exist (usually two or three) and calculate selectivities and capacities for each from the concentration dependence of selectivity coefficients (e.g. Brouwer et al., 1983). However, in reality, it is more likely that a broad range of sites exist with differing energies of exchange (Staunton & Roubaud, 1997). Loss of hydration water and partial or complete collapse of the frayed edge accompany adsorption of caesium. The energy of adsorption is therefore large and desorption is energetically unfavourable. While some authors find that adsorption is thermodynamically reversible (Brouwer et al., 1983), others claim that there is some degree of hystereisis, which increases with time (Cheshire & Shand, 1991; Valcke & Cremers, 1994;

Absolom et al., 1996). This process is known as fixation and ageing (Noordijk, Van Bergeijk, Lembrechts, & Frissel, 1992).

Adsorption is an exchange process and so depends on the relative selectivity of Cs and other cations. Therefore, both adsorption and desorption depend on the cationic composition of the soil solution and the exchange complex. The selectivity sequence for metal cations from the IA group is the same for FES and for the planar or regular exchange sites (RES) of 2 : 1 clay minerals as predicted from the Hard–Soft Acid–Base Theory (Xu & Harsh, 1990), namely $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. However, the difference in selectivity is much more marked for FES than for RES. In soil, the cations that compete most favourably with caesium are potassium and the somewhat similar, non-metallic Lewis acid, ammonium.

In addition to the adsorption properties of soils, plant physiology influences Cs uptake, as indicated by the differences in soil–plant transfer for various species growing on the same soil (Coughtrey & Thorne, 1983, Chap. 7; Desmet, Nassimbeni, & Belli, 1990). Solution culture experiments show that Cs uptake is sensitive to nutritional status and the composition of the external solution (Shaw & Bell, 1991; Smolders, Kiebooms, Buysse, & Merckx, 1996). As for soil adsorption properties, the cations most susceptible to modify Cs uptake are potassium and ammonium. Model simulations confirm the intuitive prediction that uptake is sensitive to both rooting density and root distribution, particularly as a function of depth (Darrah & Staunton, 2000). Shallow rooting plants will be more exposed than deeply rooting plants to radiocaesium, which is concentrated near the soil surface even many years after deposition. Recently, it has also been noted that mechanistic models predict uptake that is much greater than that observed, when realistic input parameters for root absorption, root density and soil adsorption properties are used (Darrah & Staunton, 2000). This strongly suggests either that only a fraction of the root system of mature plants contributes to uptake and so the root absorption parameters obtained in solution culture with young plants are inappropriate or that much of the absorbed Cs is recycled back from the roots to the soil.

There are four approaches to the investigation of the role of organic matter in Cs immobilisation.

- Firstly, for a large number of soils, correlations may be established between Cs adsorption, or soil–plant transfer, and organic matter content (Van Bergeijk, Noordijk, Lembrechts, & Frissel, 1992). While this is an essential step in demonstrating a possible paradox, it is impossible to establish a cause and effect relationship.
- Another approach is the selective extraction of various phases of contaminated soil, thereby releasing Cs into solution, and comparison of the activity concentrations of each extract. This approach is widely adopted for heavy metals, although often criticised. The major drawbacks are that extraction is not as selective as implied and that extracted metals may be readsorbed or precipitated leading to erroneous interpretation and often time-dependent results (Tessier, Campbell, & Bisson, 1979; Beckett, 1989; Sheppard & Stephenson,

1997). This technique is probably best employed to demonstrate changes in speciation with time or following the action of roots (Cheshire & Shand, 1991).
- Some of the inconveniences of the latter approach are avoided by first extracting target phases, then studying the adsorption properties of the residue. This procedure shall be discussed in greater detail below.
- Finally, the adsorption properties of synthetic mineral–organic complexes can be compared to those of the starting materials. Although such complexes, often simple mixtures, may be very different from complex heterogeneous soil material, useful information can be obtained, as will be discussed below.

The objective of this review is to examine the hypothesis that organic matter modifies the adsorption properties of clay minerals in soil, leading to a decreased adsorption and increased plant availability of radiocaesium in organic soils. Other possible reasons, such as the potassium content of the soils or physiological differences including root density and distribution, and adaptation to low potassium status shall not be considered. We shall concentrate largely on our own recent work on reference clay minerals and the clay-sized fraction of soils.

2. Cs adsorption after removal of organic matter fractions

Dumat, Cheshire, Fraser, Shand, and Staunton (1997) first reported the adsorption properties of the clay-sized fraction ($<2\,\mu m$) of a surface soil from the Tipperty Series (UK), referred to as soil-clay, and various residues of that soil-clay, after extraction of organic matter using a semi-sequential extraction procedure. The soil-clay initially had a CEC of $0.33\,mol_c\,kg^{-1}$, of which about 4% was compensated by potassium, an organic C content of $47.1\,g\,kg^{-1}$ and contained mostly illite, kaolinite and feldspar. The soil-clay was treated with sodium pyrophosphate, then with sodium hydroxide to remove humic and fulvic acids and finally with either hydrogen peroxide or sodium hypochlorite. More experimental details of the full procedure is given in the original article. Organic carbon and nitrogen were lost at each step but no changes were detected in either cation exchange capacity or in mineral content (using XRD). The final residue had a similar organic matter content and almost identical infrared spectrum to soil-clay from the corresponding C horizon. All samples were made homo-ionic in sodium. Cs adsorption, expressed as the distribution coefficient, K_d, was measured in a $0.01\,M$ NaCl background electrolyte at two loadings; $7\,\mu mol\,kg^{-1}$ or $10\,mmol\,kg^{-1}$. Fig. 1 shows the increasing adsorption of Cs with decreasing organic C content of the solid as organic carbon is progressively destroyed. The data are expressed relative to the K_d value of the initial soil-clay at each loading in order to show both data sets on the same scale, despite the strong concentration-dependence of K_d. The trend is similar at both Cs loadings, with a slightly smaller effect for trace Cs. The increase in adsorption is much greater than would be expected simply from the loss of material (organic matter) which contributes little to adsorption. The cleaned soil mineral surface has, therefore, an enhanced affinity for caesium. This strongly suggests that the presence of organic
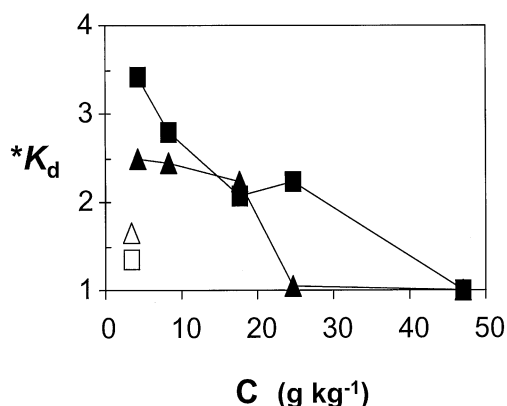
Fig. 1. Effect of progressively removing organic carbon from a surface soil clay on the adsorption of Cs, expressed as K_d relative to that of the initial clay (*K_d) with respect to the C content of the solid for two loadings of Cs [($\blacktriangle$) trace Cs (1 GBq kg^{-1} $\approx$ 7 μmol kg^{-1}), $K_{d,soil} = 33180$ dm^3 kg^{-1}; ($\blacksquare$) 10 mmol kg^{-1} Cs, $K_{d,soil} = 680$ dm^3 kg^{-1}]. Also shown are the relative K_d values of the corresponding subsoil clay (open symbols) at the same Cs loadings (redrawn from Dumat et al., 1997).

matter inhibits adsorption. Another interesting finding is that the clay-sized fraction of the soil from the corresponding C-horizon, with a small organic carbon content (3.3 g kg^{-1}), had a greater affinity for Cs than the initial topsoil clay. This may be attributed to the presence of organic matter in the surface soil. However, the final residue of the surface soil, with a similar organic carbon content to that of the subsoil, had a much greater affinity for Cs. This accords with the greater proportion of weathered minerals in the topsoil, detected by XRD, and suggests that the consequences of the long-term weathering effect of wetting–drying cycles and biological modifications may be important. Confirmation of the increase in Cs retention with increased weathering has recently been reported (Maes, Vielvoye, Stone, & Delvaux, 1999; Maes, Iserentant, Herbauts, & Delvaux, 1999)

A somewhat different approach has been adopted by Rigol et al. (1998). They investigated four soils with contrasting organic matter contents (46–99%) and compositions (relative proportions of fats and waxes, humic and fulvic acids and humin). They compared the K_d of trace Cs on the initial soil, on soil after removal of fats, waxes, humic and fulvic acids, termed the humin + mineral fraction, and on the humin fraction after destruction of minerals with HF. They report K_d values that are nearly 4 times greater for the humin + mineral fractions than for the initial soils for three of the four soils investigated. This is in excellent agreement with the findings of Dumat et al. (1997). The only soil for which no difference was observed had a very small mineral content (1.4% by loss on ignition or 4.2% considering the sum of organic fractions). The NH$_4$-to-K trace selectivity coefficients are also reported for each soil and residue. No NH$_4$/K selectivity would be expected for organic matter, whereas adsorption sites associated with clay minerals, particularly frayed edge sites should exhibit some selectivity (see Section 1). For the humin fractions and the

highly organic soil, no selectivity was observed, as would be expected. However, for the humin + mineral fractions of the other three soils, the selectivity coefficient was about 8, as would be expected for frayed edge sites of illite. Furthermore, the $K_c \times$ (NH$_4$/K) was somewhat enhanced by removal of organic matter, suggesting either that organic matter contributed to adsorption, thereby decreasing the average affinity of adsorption sites, or that the cleaned surfaces had a slightly greater selectivity. The latter possibility is supported by some of the findings that will be reported in the next section.

In contrast, Staunton and Levacic (1999) reported rather small and variable effects on Cs adsorption on the clay-sized fractions of various surface soils and the soils from the corresponding C-horizon when about 75% of organic matter was removed by a single H$_2$O$_2$ treatment. They noted a relative enrichment in organic nitrogen and postulated that amide groups, which are resistant to oxidation (Cheshire, Dumat, Fraser, Hillier, & Staunton, 2000) particularly without a prior pyrophosphate treatment, may play an important role in the decrease in affinity for Cs of mineral surfaces.

3. Cs adsorption on synthetic mineral–organic complexes

A possible criticism of the approach described in the previous section is that the organic matter extraction techniques attack the mineral fraction, thereby altering their adsorption properties, although the authors of these studies tried to ensure that this was not the case. An alternative is to study the adsorption properties of artificial mineral–organic complexes. Such studies have been reported by various authors (Bunzl & Schultz, 1985; Maguire, Pulford, Cook, & Mackenzie, 1992; Staunton & Roubaud, 1997; Dumat & Staunton, 1999; Dumat, Quiquampoix, & Staunton, 2000). The earlier studies are restricted to the investigation of a single humic or fulvic acid on mineral clays at a single Cs loading. They report that, despite the low affinity of Cs for humic substances, the presence of humic or fulvic acid causes a decrease in the affinity of Cs for the mineral surface.

Dumat and Staunton (1999) investigated the effect of humic and fulvic acids from three sources (purchased from the International Humic Substances Society, IHSS) on Cs adsorption at two loadings on each of the two reference clays, an illite and a montmorillonite. These clays were chosen because of their contrasting affinities for Cs. The different additions of Cs were used to distinguish between the possible effect on FES and regular exchange sites (RES). As was outlined in Section 1, at trace loadings of Cs, high affinity FES dominate Cs adsorption on illite, whereas on montmorillonite and for large Cs concentrations on illite, adsorption takes place on planar RES, which have a much weaker affinity for Cs. Despite the small adsorption of the humic substances (HS) on either clay, there is in general a continuous decrease in Cs adsorption, as measured by K_d, with increasing addition of each HS (data not shown). The effect is more marked for illite than for montmorillonite and at the smaller Cs loading. There is up to a tenfold decrease in K_d for trace amounts of Cs (13.4 µmol kg^{-1}) on illite and almost no effect when 10 mmol kg^{-1} Cs was added to

montmorillonite. This suggests strongly that the FES are more sensitive to the presence of humic material than are planar sites.

Since the HS used were anionic, the reason for decreased Cs adsorption clearly cannot be competition for the same adsorption sites. It is more likely that anion exchange sites are close to the FES and the presence of organic macromolecules impedes the collapse of frayed edges. A somewhat similar explanation for the reduced selectivity of soil clays has been postulated by Hird et al. (1995). If the reduced selectivity were the result of steric hindrance, then the size of the organic molecule would be important. This prompted the comparison of pairs of humic and fulvic acids from the same origin. There is no consistent trend distinguishing humic acids from the smaller fulvic acids (Fig. 2). Similarly, a simple model of the physical effect on FES would predict that the extent of the effect of HS would depend on the amount adsorbed. This is the case for a given humic + clay couple, adsorption decreasing with increasing HS added (data not shown), and the greater effect for illite than montmorillonite accords with the larger adsorption of HS on the former. However, when the effect of a fixed addition of different humic substances, which adsorb to different extents on clay, are compared, as in Fig. 2, or when the effect on illite relative to that on montmorillonite is compared to the relative HS adsorption on the two clays (data not reproduced here), then no trend is observed. It appears that the action of organic macromolecules on the surface properties of clays is complex and cannot simply be attributed to steric hindrance.
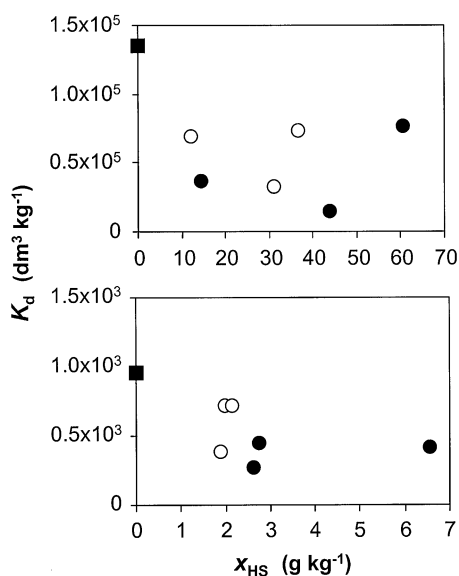
Fig. 2. Distribution coefficient of trace Cs on illite (top) and montmorillonite (bottom) with ($\bigcirc$, $\bullet$) and without ($\blacksquare$) addition of a fixed amount (0.25 g g^{-1}) of humic ($\bullet$) or fulvic ($\bigcirc$) acids from different sources as a function of the adsorption of the humic substance on clay.

Since the reduction in the affinity of clays for Cs by humic substances seems to be a general effect, we postulated that other organic macromolecules, typical of those present in soil, might have a similar effect (Dumat et al., 2000). We chose to investigate the effect of an anionic soil polysaccharide and a model protein, bovine serum albumin (BSA) that has an isoelectric point of 4.8. The effects of these two very different organic molecules are strikingly similar to that of humic substances: (i) there is a continuous decrease in K_d with increasing addition of the organic polymer; (ii) the effect is greater for illite than for montmorillonite and for trace Cs than for the larger Cs loading; and (iii) there is no correlation between the decrease in K_d and the amount of organic polymer adsorbed when data from all experiments are pooled. It is interesting to note that soil polysaccharide reduces the adsorption of trace amounts of Cs to the same extent as the bulky thiourea, used to block planar sites (Cremers, Elsen, De Preter, & Maes, 1988) and hence determine the adsorption capacity of illite FES.

A more recent, unpublished study shows that dissolved organic carbon (DOC) extracted from a muck soil also decreases the K_d of Cs on illite. In order to modify the amount and nature of DOC extracted (Zsolnay, 1996), the temperature, ionic strength and soil:solution ratio were varied. Fig. 3 shows the K_d value of trace Cs on illite in a simple electrolyte solution (1 or 10 mM CaCl$_2$) or the same solution containing DOC extracted at either 20°C–40°C with a soil:solution ratio of 1:2 or 1:10 g ml^{-1}. Data are expressed as K_d relative to that of the bare clay at the appropriate ionic strength. There is a tendency for adsorption to decrease on addition of organic carbon. If all the data are considered, the response appears to be curvilinear. However, a closer examination suggests that the reduction depends on the temperature and ionic strength. To illustrate this, lines have been drawn between pairs of data points corresponding to the same ionic strength and temperature of extraction. For each pair, more carbon is extracted
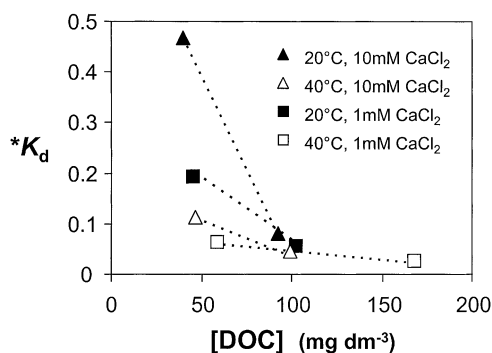

Fig. 3. Distribution coefficient of trace Cs on illite in the presence of DOC extracted from a soil, relative to that of the bare clay (*K_d) as a function of the total DOC concentration. DOC concentration varied with the experimental conditions used to extract it (see key and text).

in the more concentrated suspension $(1:2\,\mathrm{g\,ml^{-1}})$ and the corresponding $^*K_d$ is smaller. A more detailed study of the DOC (not shown) suggests that for a given DOC concentration, K_d decreases with increasing fluorescence efficiency and decreasing relative fluorescence and absorptivity. The conditions of the extraction modify not only the amount of organic carbon retrieved but also its composition and its subsequent effect on Cs adsorption sites of illite. This variant of the methodology used in the other similar studies described above is particularly interesting because the interactions with mineral clay are more likely to be the same in soil and in the synthetic complex on account of the non-aggressive extraction technique.

4. Conclusions and perspectives

We have illustrated that, despite the weak, non-specific interaction between soil organic matter and Cs, the former decreases the affinity of clay minerals, thereby reducing their ability to immobilise Cs in soil. This is one of the factors that contributes to the small immobilisation of radiocaesium in organic soils and hence to its large availability to plants and other soil biota. It could also contribute to the differences in Cs adsorption in the rhizosphere and bulk soil observed by Guivarch, Hinsinger, and Staunton (1999), in addition to the effect of potassium depletion, because of the accumulation of organic exudates. The effect is much greater on highly selective sites, namely the frayed edge sites of illites, than on the less selective planar sites of both illite and montmorillonite. Although the mechanism is not fully elucidated, it is not due to a simple steric effect, since the size and amount of organic molecule adsorbed do not determine the reduction in affinity.

We have not considered the consequences of organic matter on the reversibility of Cs adsorption. There are as yet very few data on the effect of organic matter on the reversibility of Cs adsorption. Rigol et al. (1998) found a slightly smaller ammonium acetate desorption yield for trace Cs adsorbed on soil from which humics had been removed than for the initial soil. Thus, although the adsorption is enhanced fourfold, the proportion of adsorbed Cs that is apparently fixed is barely affected by organic matter.

Both destruction of soil organic matter and addition of organic macro-molecules to mineral clays give broadly similar results. However, small differences, such as the relative effect at different Cs loadings, indicate that simple synthetic mixtures do not reproduce the full complexity of soil organo-mineral complexes. Further work is also needed to distinguish between the immediate, short-term effect of organic matter on the surface properties of clay minerals and longer-term weathering effects. More elaborate methods of preparing synthetic organo-mineral complexes should also be investigated, including wetting–drying cycles, which are known to fix Cs (Rigol, Vidal, & Rauret, 1999) and also to modify dissolved organic matter and less aggressive methods of removal of soil organic matter are clearly called for.

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