

ADSORPTION OF ^{137}Cs ON MONTMORILLONITE AND ILLITE: EFFECT OF CHARGE COMPENSATING CATION, IONIC STRENGTH, CONCENTRATION OF Cs, K AND FULVIC ACID

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Abstract—A thorough understanding of the capacity of clay minerals to adsorb radiocesium is essential in order to predict the fate of this pollutant in the environment and to interpret routine measurements, such as desorbability. We have investigated the adsorption of radiocesium onto 2 contrasting reference clay minerals in dilute suspensions after a 2-h contact period. The results have been expressed as the distribution coefficient, K_d , or the selectivity coefficient, K_c . The adsorption properties have been studied with respect to various parameters: nature of the charge compensating cation, ionic strength, concentration of Cs, concentration of K and concentration of a soil-extracted fulvic acid.

A Freundlich isotherm has been found to fit experimental data well for levels of adsorbed cesium in the range 10^{-7} to 1 mol kg^{-1} . Evidence of surface heterogeneity is discussed, but it was not possible to deduce the exchange capacities of the groups of exchange sites with differing affinities for Cs, which are thought to exist in illites. The concentration dependence of adsorption upon montmorillonite is postulated to arise from a modification of the exchange complex with increasing presence of Cs, rather than from heterogeneity of exchange sites. Increasing ionic strength caused a decrease in the relative affinity for a trace amount of cesium on both minerals, although mass action led to a fall in K_d . This is thought to indicate a high covalent interaction between Cs and the clay surface.

Potassium caused a smaller decrease in adsorption than stable Cs, which suggests that neither K nor NH_4 plays a decisive role in the immobilization of radiocesium by clay minerals. There was a small decrease in adsorption upon addition of soil organic matter, which may contribute to the poor fixation capacity observed for some soils with a high organic matter content.

Key Words—Cesium, Illite, Ion Exchange, Montmorillonite, Radiocesium, Selectivity, Soil.

INTRODUCTION

One of the radioisotopes of cesium, ^{137}Cs , is relatively long-lived and poses considerable radioecological problems. Various events have led to the introduction of this fission product into the environment, in particular nuclear testing in the 1950s and 1960s, accidental discharges such as the one following the accident at the Chernobyl nuclear power station in 1986, allowed discharges from nuclear plants and waste disposal. Because of its similarity to K, it is mobile in many environmental systems and is easily assimilated by plants and by terrestrial and aquatic organisms. Once ingested, it is efficiently absorbed by mammals from a wide range of foodstuffs (Coughtrey and Thorne 1983). In general, the biological availability of Cs in soils, sediments or surface waters depends to a large extent upon the adsorption capacity of the solid phase (Coughtrey and Thorne 1983; Livens and Loveland 1988; Kirk and Staunton 1989). Clay minerals are known to adsorb Cs and hence restrict its mobility. This factor is also one of the reasons for the use of clays as barriers in the disposal of radioactive waste.

Much is already known about the adsorption of Cs onto clay minerals (Sawhney 1972; Maes and Cremers 1986; Cornell 1993). Among the most important features are the following: 1) Cesium is specifically adsorbed onto micaceous minerals, notably onto the

frayed-edge sites on illite, which account for about 1% of their total cation exchange capacity (CEC) (Sawhney 1972; Francis and Brinkley 1976; Eberl 1980; Brouwer et al. 1983). Adsorption depends to a more limited extent upon CEC. 2) Adsorption depends upon the concentration of Cs. The proportion of Cs adsorbed decreases with increasing concentration. This is thought to arise from the heterogeneity of the surface adsorption sites; as high-affinity sites are progressively saturated, the affinity for Cs of the remaining sites decreases. This phenomenon is seen by decreases (often discontinuous) in the distribution coefficient, K_d , or the selectivity coefficient, K_c . 3) The adsorption of Cs depends upon the cationic composition of the exchange complex. This is because the so-called adsorption reaction is in fact an exchange. Therefore, the adsorption depends upon the relative affinities of Cs and the charge-compensating cations. The order of decreasing affinity is generally reported to be $\text{Cs} > \text{NH}_4 > \text{K} > \text{Na} > \text{Ca}$. Affinity for the highly specific adsorption sites of illite is largely determined by hydration energy; ionic radius is now thought to be less important.

The aim of this study was to carry out a systematic investigation of the adsorption of Cs onto 2 reference minerals under controlled conditions. The effects of 5 parameters have been investigated: charge-compensat-

ing cation, Cs concentration, K concentration, ionic strength and the presence of a soil fulvic acid. The choice of the first 2 parameters is evident from the above discussion. The effect of a small amount of K in a clay saturated in either Na or Ca is of interest, as K competes with Cs for high-affinity sites. These sites may be occupied by K or NH_4 in real situations, even when the dominant cation on the exchange complex is Na or Ca+Mg. The effect of ionic strength has previously received little attention. This lacuna is particularly important in the interpretation of desorption studies. The desorption of Cs is usually measured in solutions of different ionic strength than the solution from which Cs was initially adsorbed. The fraction of Cs that is not desorbed by a given treatment is often described as irreversibly adsorbed, or fixed. Although this may indeed be the case, the conclusion is not valid unless the adsorption of Cs has also been investigated under the same conditions. Finally, the addition of a soil fulvic acid has been studied because many soil studies indicate that organic matter may modify the capacity of clays to immobilize radiocesium (Hird et al. 1996).

Neither the kinetics nor the reversibility of the adsorption reaction has been studied in this investigation. We chose to use a short exchange period in order to avoid any interference from the slow reaction that is known to take place, especially in illites. A 2-h period is sufficient for true ion exchange. The rate and extent of slow reaction are known to depend upon the charge-compensating cation (Comans et al. 1991). Had a longer exchange period been used, the contribution of slow exchange to the measured distribution would have differed for each clay system studied.

EXPERIMENTAL METHODS

The clay minerals used in this investigation were a Wyoming montmorillonite with a CEC of $0.94 \text{ mol}_c \text{ kg}^{-1}$ and a Le Puy illite with a CEC of $0.30 \text{ mol}_c \text{ kg}^{-1}$ (Tessier and Pedro 1987). The size fraction $< 2 \mu\text{m}$ was separated by sedimentation and samples of each mineral made homoionic in either K, Na or Ca by repeated washing in 1 M solutions of their chloride salts, then washing with deionized water until the AgNO_3 test was negative. The resulting salt-free clays were stored, refrigerated, as suspensions containing approximately 20 g dm^{-3} until required.

The isotope ^{137}Cs was obtained from Amersham International (370 MBq in 1.04 mL, $0.32 \text{ g Cs dm}^{-3}$) and used without further preparation. 1 Bq of ^{137}Cs is equivalent to $2.3 \times 10^{-15} \text{ mol}$; the presence of a small amount of stable, or carrier, Cs adds a further 4.4 mol. The fulvic acid was extracted from a sandy loam soil using the method of Goodman et al. (1991).

Triplicate suspensions were prepared by pipetting appropriate volumes of salt-free clay suspension, electrolyte solution and a solution of ^{137}Cs and stable Cs,

if required. The resulting suspensions contained, unless otherwise specified: 1 g dm^{-3} clay mineral, $10^{-2} N$ chloride salt of the charge-compensating cation (K^+ , Na^+ or Ca^{2+}), $1 \text{ MBq dm}^{-3} \text{ }^{137}\text{Cs}$ (equivalent to $6.8 \times 10^{-9} M$). The initial Cs concentration in solution was varied in the range 1.4×10^{-9} to $4 \times 10^{-4} M$ using both ^{137}Cs and stable Cs. In the range 0.2–10 MBq $\text{dm}^{-3} \text{ }^{137}\text{Cs}$, no stable Cs was added. In one series of experiments, small concentrations of K were added to the suspensions of Na and Ca clays. The initial concentration of K in solution was varied in the range 10^{-7} to $4 \times 10^{-4} M$ by adding KCl to $10^{-2} N$ solutions of NaCl or CaCl_2 , respectively. Suspensions were also prepared containing 10–250 mg dm^{-3} of fulvic acid, equivalent to 1–25% by weight of clay.

The suspensions were shaken end-over-end at 20°C for 2 h, then centrifuged at 20,000 g for 30 min. Preliminary trials were run to ensure that phase separation was complete. Triplicate samples of the clear supernatant solution were taken and counted by liquid scintillation in a Beckman LS 5801.

DATA TREATMENT

The results are expressed either as the distribution coefficient, K_d , as the Freundlich adsorption isotherm or as the selectivity coefficient, K_c . The solution Cs concentration is calculated from the measured activity of the supernatant solution and the known specific activity of the initial solution. The quantity adsorbed per unit mass of clay, x_{Cs} , is calculated from the solid:liquid ratio and the difference in Cs concentration between a standard solution, to which no clay was added, and the supernatant solution of the suspension.

The distribution coefficient, K_d , is defined as the ratio of concentrations of Cs in the adsorbed x_{Cs} (mol kg^{-1}) and solution $[\text{Cs}]$ (mol dm^{-3}) phases:

$$K_d = \frac{x_{\text{Cs}}}{[\text{Cs}]} \quad [1]$$

The Freundlich isotherm can be expressed as follows:

$$x_{\text{Cs}} = a[\text{CS}]^b \quad [2]$$

where a and b are empirical parameters and $0 < b < 1$. The parameters a and b are obtained from the linear regression of the plot of $\log x_{\text{Cs}}$ against $\log [\text{Cs}]$, where b is the gradient and a is calculated from the intercept.

The selectivity coefficient, K_c , is defined using the Gaines-Thomas convention as follows:

$$\frac{z_{\text{Cs}}}{z_{\text{M}}} K_c = \frac{z_{\text{Cs}}^n \gamma_{\text{M}} [\text{M}^{n+}]}{z_{\text{M}} \gamma_{\text{Cs}}^n [\text{Cs}^+]^n} \quad [3]$$

where z_{Cs} and z_{M} are the equivalent fractions of Cs and M^{n+} on the exchanger surface; γ_{Cs} and γ_{M} the activity coefficients of the cations in solution; and n the valence of the cation exchanged. No account is taken of

Table 1. K_d ($\text{dm}^3 \text{kg}^{-1}$) values for montmorillonite and illite saturated in K, Na or Ca. Standard deviations are calculated from replicates. $[^{137}\text{Cs}] = 1 \text{ MBq dm}^{-3} = 6.8 \times 10^{-9} \text{ M}$; $[\text{Cl}^-] = 10^{-2} \text{ N}$; $[\text{clay}] = 1 \text{ g dm}^{-3}$.

	K	Na	Ca
Montmorillonite	713 ± 6	2636 ± 31	1405 ± 15
Illite	4350 ± 90	33700 ± 800	244000 ± 6000

differences in surface phase activity coefficient, or fugacity.

The value z_{Cs} is calculated from the amount of Cs adsorbed per unit weight of clay (mol kg^{-1}) and the CEC of the clay ($\text{mol}_e \text{kg}^{-1}$) and $z_{\text{M}} = 1 - z_{\text{Cs}}$. No account has been taken of the possible variation of CEC with the saturating cation. The activity coefficients are calculated from the Davies equation:

$$\log \gamma = -An^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad [4]$$

where I is the ionic strength (M) and A (20°C) = 0.507.

RESULTS

Table 1 shows values of K_d obtained for trace concentrations of Cs ($[\text{Cs}]_{\text{initial}} = 6.8 \times 10^{-9} \text{ M}$) on the 2 minerals initially homoionic in each of the cations studied. Cesium is adsorbed more strongly onto illite than onto montmorillonite, despite its lower CEC. The K_d value on illite depends greatly on the charge-compensating cation and indicates that the order of relative affinity of the surface for the cations decreases in the order $\text{Cs} > \text{K} > \text{Na} > \text{Ca}$. This effect is less marked for montmorillonite and appears to be reversed for Na and Ca.

Effect of Concentration in Cs

Figure 1 shows the effect of initial concentration of Cs in solution on K_d over a range of concentration that extends from a level of radioactivity which provides a convenient compromise between counting time, and hence number of samples, and accuracy, to the concentrations usually required for detection of the stable isotope. The overall normality of the electrolyte solution was not significantly modified by addition of Cs. In general, the values of K_d decrease with increasing concentration in Cs. The effect is more marked for illite than montmorillonite. In illite, the order of decreasing K_d $\text{Ca} > \text{Na} > \text{K}$ -clay is observed at all levels of Cs or K. It should be noted that a log scale has been used because of the magnitude of the decrease in K_d : 3 orders of magnitude in the case of Ca-illite. There are 2 unusual features in the trends observed for Ca-montmorillonite: 1) the value of K_d is lower than for Na-montmorillonite for all levels of Cs and 2) the K_d falls rapidly upon addition of Cs to a value lower than that of K-montmorillonite, which remains fairly constant.

The variation of K_d with initial Cs concentration shows that the adsorption isotherm is not linear. Figure 2 shows these data with the amount of Cs adsorbed per unit weight of solid, x_{Cs} (mol kg^{-1} clay), plotted against the resulting solution phase concentration on a log-log scale. Although the K_d decreases with increasing $[\text{Cs}]$, the amount adsorbed continues to increase.

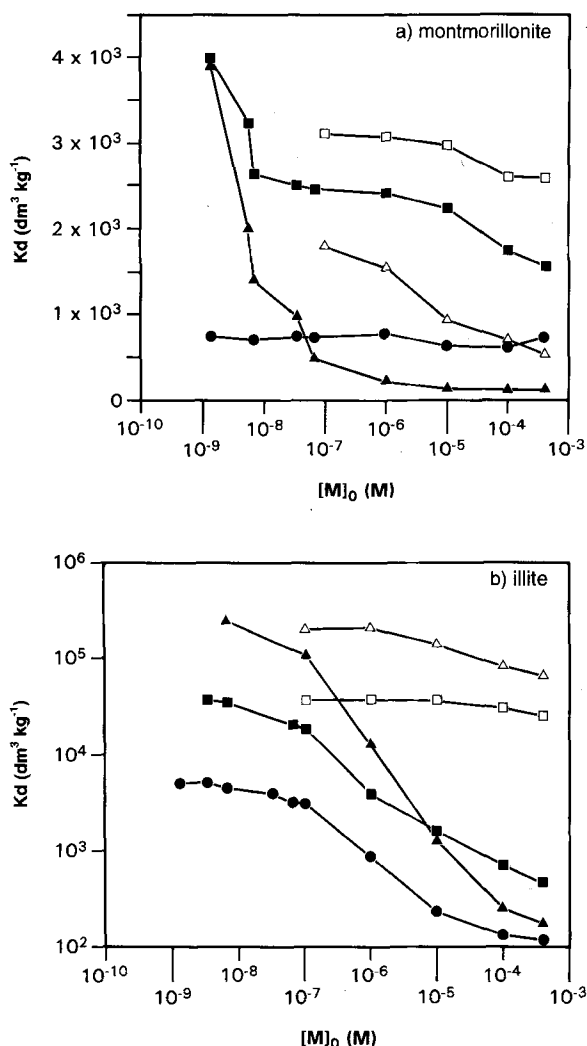


Figure 1. Distribution coefficient with respect to the initial solution concentration of CsCl (closed symbols) or KCl (open symbols) at constant concentration of the chloride salt of the charge-compensating cation (10^{-2} N) for montmorillonite (a) and illite (b), saturated in K (●), Na (■, □) or Ca (▲, △).

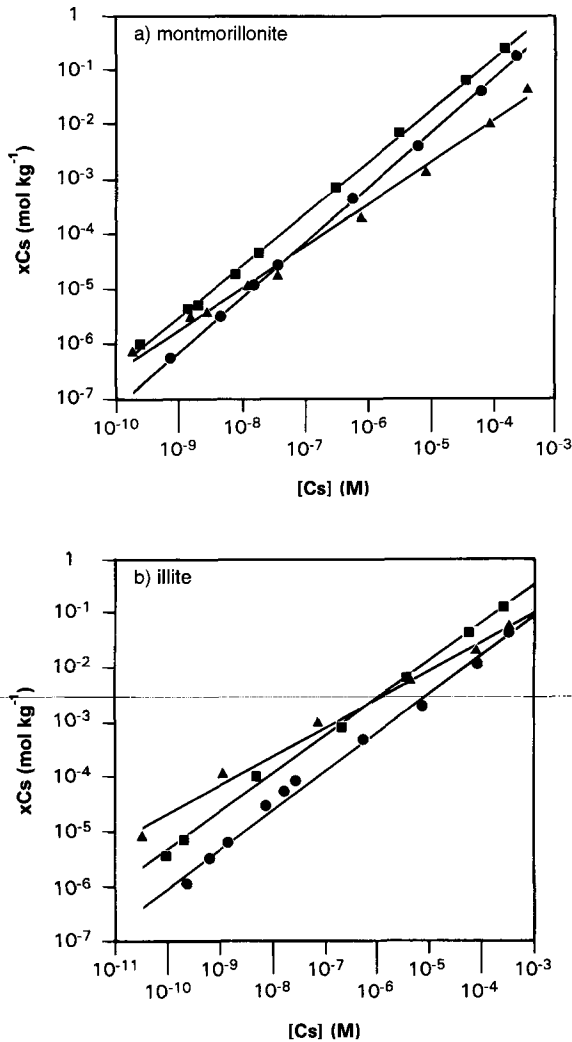


Figure 2. Adsorption isotherm of Cs on montmorillonite (a) and illite (b), saturated in K (●), Na (■) or Ca (▲).

The good linear regressions that can be fitted to these log-log plots for all sets of data (Table 2) demonstrate that the adsorption isotherms conform to Freundlich isotherms over this range of concentrations for both clays and for each saturating cation.

The same data have been reanalyzed to calculate the selectivity coefficients, K_c . The variation of K_c with final Cs concentration is shown in Figure 3. The contrast between heterovalent (Ca-Cs) and homovalent exchange is enhanced when data are expressed as K_c rather than K_d (compare Figures 1 and 3). At low [Cs], there are 4 orders of magnitude difference between ${}_{Ca}^{Cs}K_c$ and ${}_{K}^{Cs}K_c$ in montmorillonite and 7 orders of magnitude in illite. For both montmorillonite and illite, the selectivity coefficients show the expected trend ${}_{Ca}^{Cs}K_c > {}_{Na}^{Cs}K_c > {}_{K}^{Cs}K_c$ at every concentration of Cs. The apparent nonconformity to the usual trend in selectivity for montmorillonite suggested by the values of K_d

Table 2. Parameters of the Freundlich isotherm fitted to the adsorption isotherms of Cs on montmorillonite and illite saturated in K, Na or Ca. $[Cs]_{initial} = 1.4 \times 10^{-9} - 4 \times 10^{-4} M$ [salt] = $10^{-2} N$; $x_{Cs} = a[Cs]^b$.

	K	Na	Ca
Montmorillonite			
<i>a</i>	$0.621 \pm .050$	$0.982 \pm .107$	$0.0109 \pm .004$
<i>b</i>	$0.991 \pm .006$	$0.944 \pm .008$	$0.755 \pm .023$
Illite			
<i>a</i>	$0.0094 \pm .0033$	$0.0359 \pm .0079$	$0.0038 \pm .0014$
<i>b</i>	$0.694 \pm .023$	$0.690 \pm .015$	$0.522 \pm .026$

was clearly and simply an artifact, illustrating the inadequacy of K_d , which fails to take the stoichiometry of the exchange reaction into account. The trends within a series are the same for K_c and K_d : decrease

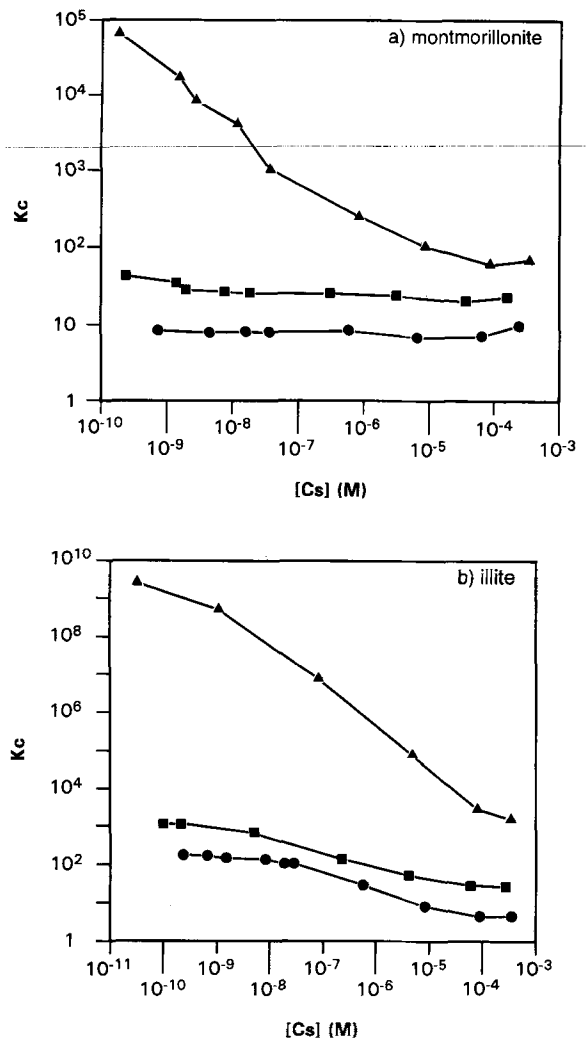


Figure 3. Variation of the selectivity coefficient to the final solution concentration of Cs on montmorillonite (a) and illite (b), saturated in K (●), Na (■) or Ca (▲).

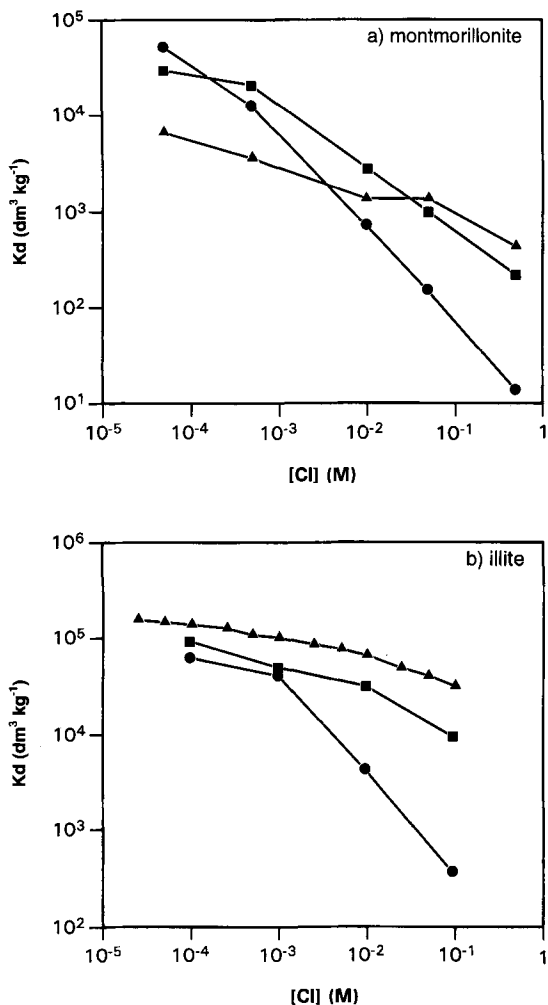


Figure 4. Distribution coefficient with respect to the concentration of the chloride salt of the charge-compensating cation in the electrolyte solution for montmorillonite (a) and illite (b), saturated in K (●), Na (■) or Ca (▲).

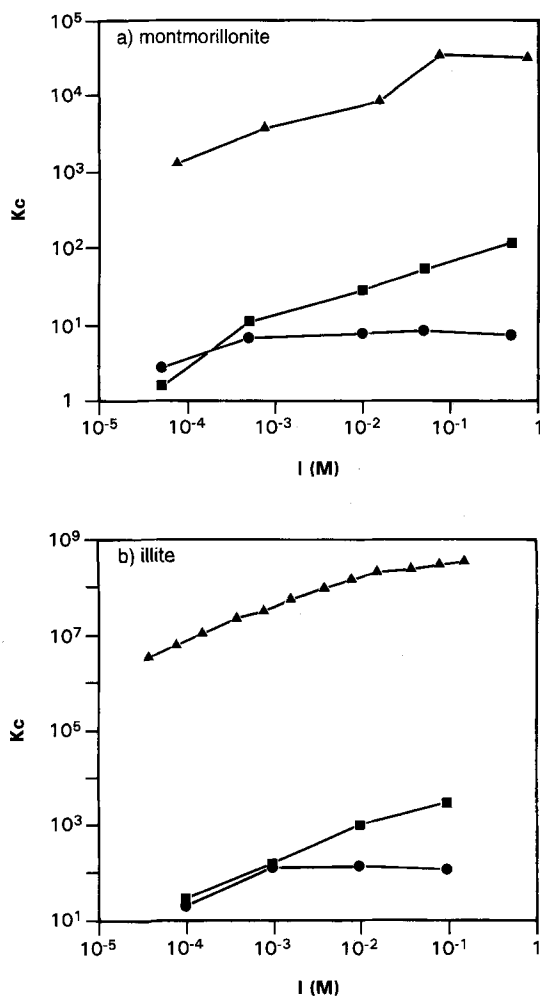


Figure 5. Relationship of the selectivity coefficient to the ionic strength for the adsorption of trace amounts of Cs on montmorillonite (a) and illite (b), saturated in K (●), Na (■) or Ca (▲).

in K_c with increasing $[\text{Cs}]$ for both Ca-clays and to a lesser extent for Na- and K-illite; constant value of K_c for K-montmorillonite.

Effect of Concentration in K

Figure 1 also shows the effect of varying concentration of K (10^{-7} to $4 \times 10^{-4} \text{ M}$) for the Na and Ca clays with a constant initial concentration of ^{137}Cs (1 MBq dm^{-3}) and of the salt of NaCl or CaCl_2 , respectively (10^{-2} M). The overall normality of the electrolyte solution was not significantly modified by addition of K. No attempt was made to determine the extent of exchange between K and the charge compensating cation. In general the values of K_d decrease with increasing K concentration, but to a lesser extent than was observed for Cs.

Effect of Salt Concentration

Figure 4 shows the decrease in K_d values of trace concentrations of Cs on each of the clays, saturated in either K, Na or Ca with increasing salt concentration. For both minerals, the slope of the curves is greatest for K-clay and least for Ca-clay. It is interesting to note that, for montmorillonite, the expected trend in K_d values is observed at high salt concentrations; the Ca- and Na-curves cross at $[\text{Cl}^-] = 2 \times 10^{-2} \text{ N}$. This is another illustration of the fact that the order of selectivity implied by the K_d values for montmorillonite should be treated with some caution.

When the same data are expressed as the selectivity coefficient against ionic strength on a log-log scale (Figure 5), the selectivity coefficient generally increases with increasing ionic strength, whereas the opposite trend was observed when K_d was plotted against salt

Table 3. Linear regression coefficients for log K_c vs. log I obtained for the adsorption of a trace amount of Cs on montmorillonite and illite saturated in Na or Ca.

	Na	Ca
Montmorillonite		
gradient	0.444 ± .056	0.365 ± .058
intercept	2.286 ± .177	4.689 ± .185
Illite		
gradient	0.679 ± .050	0.558 ± .033
intercept	4.249 ± .112	9.200 ± .132

concentration (Figure 4). For both montmorillonite and illite, the increase in log K_c with log I is roughly linear when the saturating cation is Na or Ca. The slopes are similar for the Na and Ca forms, and slightly greater for illite than for montmorillonite (Table 3). For the K forms of both clays, the value of K_c increases slightly with I at low values of the latter, but reaches a plateau level at $I = 10^{-3} M$. The slight fall in K_c at the highest value of I studied in Ca-montmorillonite is probably an artifact, since the Davies equation is at the limit of validity at this ionic strength.

Effect of Organic Matter

Clay minerals under natural conditions are associated with varying amounts of organic matter. Figure 6 shows the effect of the addition of a soil-extracted fulvic acid to each clay preparation. Only a small proportion of the fulvic acid was adsorbed by the minerals so that the organic matter content of the clay-fulvic complex never exceeded approximately 2%. Since the adsorption of fulvic acid onto the Na- and K-clays was at the limit of detection, we preferred to present the data with respect to the initial concentration of fulvic acid in solution rather than the final content in the solid phase. The K_d is calculated with respect to the mass of clay, no account being taken of the additional weight of adsorbed fulvic acid. The latter correction, had it been made, would have lowered the values of K_d still further. The presence of fulvic acid lowered the pH, but no attempt was made to readjust pH, since preliminary trials had shown that K_d was not sensitive to pH for uncoated clays. It should be noted that a semi-log scale has been used to present the illite data. The addition of fulvic acid has no effect on the values of K_d observed in K-clays; there is a small but measurable decrease in the Na-clays, and more marked decreases in the Ca-saturated clays, particularly for illite. The effect is greatest at low ratios of fulvic acid to clay, 1–5%.

DISCUSSION

Although K_d is widely used to describe the capacity of clay minerals to adsorb Cs, this parameter is not a sensitive measure of the relative selectivities of a clay for various cations. A clear demonstration of this is

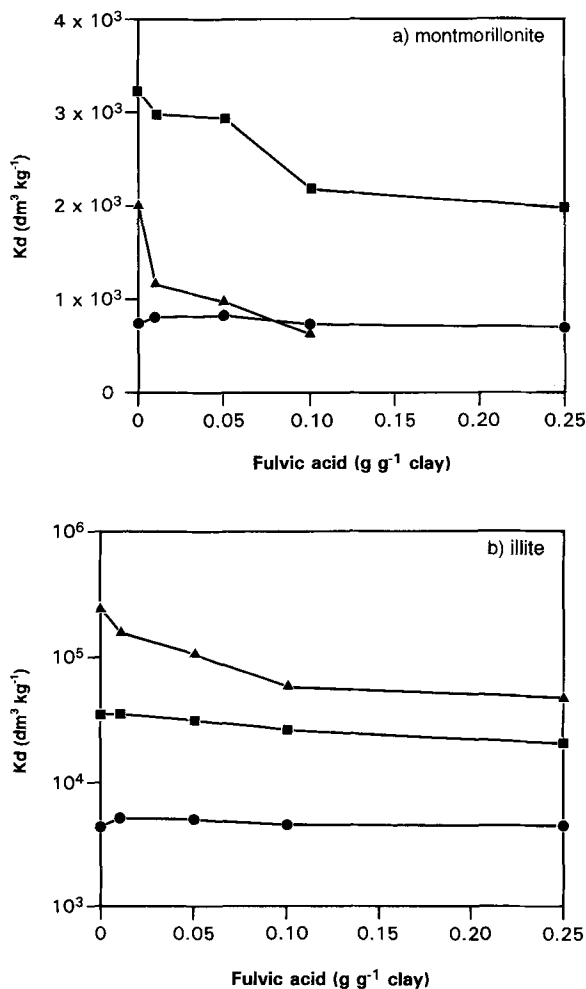


Figure 6. Distribution coefficient of a trace amount of Cs with respect to initial solution concentration of fulvic acid for montmorillonite (a) and illite (b), saturated in K (●), Na (■) or Ca (▲).

the cross-over of curves of K_d against $[Cs]$ or $[salt]$ for different charge-compensating cations (Figures 1 and 4), which implies a change in the order of affinity of the surface for the cations studied. When selectivity coefficients are calculated, the expected order of affinity—namely that of the Hofmeister or lyotropic series, $Cs > K > Na > Ca$ —is always observed. This is due to the failure to take the activity coefficients and, more importantly, the stoichiometry of the exchange, into account in K_d .

The observed trend in selectivity is well-known and has been discussed by several authors (Sawhney 1972; Bolt 1979; Goulding 1984; Sposito 1984; Maes and Cremers 1986). The difference in selectivity is more marked for illite than for montmorillonite. This is because the adsorption of Cs onto illite is thought to be determined by a small proportion of exchange sites that have a very high affinity for Cs. In montmorillonite-

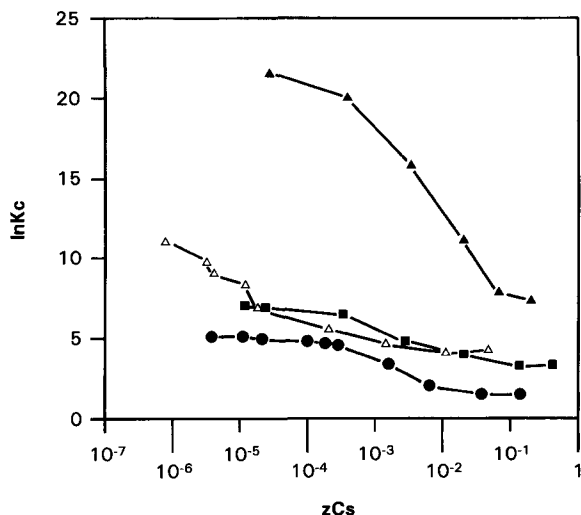


Figure 7. Relationship of the selectivity coefficient to the equivalent fraction of adsorbed Cs on Ca-montmorillonite (Δ) and illite saturated in K (\bullet), Na (\blacksquare) or Ca (\blacktriangle).

ite, selectivity differences arise mainly from the extent to which inner-sphere complexes are formed (Sposito 1984; Xu and Harsh 1990).

Surface Heterogeneity

The variation of the selectivity coefficients of illite with Cs concentration is often taken as an indication that the surfaces are heterogeneous, containing sites with differing affinities for Cs. The sites that are most selective for Cs are thought to be preferentially occupied by Cs and, as these become saturated, the role of less selective sites increases, thereby decreasing Kc. Our data suggest that the surface of illite, and possibly that of montmorillonite, is heterogeneous. Brouwer et al. (1983) and Comans et al. (1991) interpreted similar data, using the multi-site ion exchange model developed by Barrer and Klinowski (1972) for zeolites to assign intrinsic selectivity coefficients to a small number of different sites. The most highly selective sites for Cs, as for K, are associated with the frayed-edge, or wedge, sites of illite (Bolt et al. 1963; Sawhney 1972; Goulding 1987). The planar, or regular exchange, sites of illite, like those of montmorillonite, do not have a very high relative affinity for Cs. These groups of site account for varying proportions of the total CEC; in general, the frayed-edge sites (FES) are not thought to account for more than about 1% of the CEC. Differences between exchange sites are not clearly identified for montmorillonite. External and interlayer sites may have differing affinities, and so observed affinity will depend on the size of and the ordering within quasi-crystals. Other differences may arise from charge location and the heterogeneity of charge density. Our data show little change in Kc for Na- and K-montmorillonite, indicating a fairly uniform

surface, whereas the value of Kc for Ca-montmorillonite decreases progressively with increasing [Cs]. This contrast between clays saturated in divalent and monovalent cations suggests that the change in Kc may not necessarily be due to the presence of discrete sites. The effect may be due, at least in part, to changes in entropy as Cs occupies an increasing fraction of the exchange complex. Cesium loses most of its water of hydration upon adsorption and also causes collapse, or partial collapse, of clay layers. The importance of entropy in Ca-K exchange on montmorillonite has been highlighted by Inoue and Minato (1979).

The Kc values of the illite samples seem to tend towards constant values at high concentrations. However the step-wise decrease in Kc with increasing levels of Cs is much less marked than for the data presented by Brouwer et al. (1983). The observed form of the data in Figure 6 is not appreciably modified if the data are presented as $\ln Kc$ against z_{Cs} (Figure 7). It is, however, possible to compare the limiting values of Kc at trace levels of Cs in this work with those found by Brouwer et al. (1983). The latter found limiting values of $\ln Kc$ of 3.6, 8 and 20 for exchange of Cs with K, Na and Ca, respectively, whereas we find values that are slightly different: 5, 7 and 22 (taking the maximum value of Kc as the plateau value for Ca). It should be noted that the values of Kc given by Brouwer et al. (1983) are averages of values obtained at ionic strengths of 0.001 and 0.04 N for heterogeneous exchange or obtained at 0.005 N for homogeneous exchange.

We consider that it is not reasonable to determine intrinsic selectivity coefficients, nor indeed to certify the existence of 2 or 3 distinct groups of sites using most available data sets, including the present one. Indeed, fairly good linear regressions may be fitted to the log-log plots of Kc against [Cs] ($r^2 > 0.95$ for the illites in this work). The slope of the linear regression of $\log Kc$ against $\log [Cs]$ is analogous to the value of the b parameter of the Freundlich isotherm. It may therefore be taken as a measure of the heterogeneity of the adsorption sites (see below); the more negative the gradient, the more heterogeneous the surface appears to be.

Freundlich Adsorption Isotherm

The linear regressions fitted to the log-log plots of x_{Cs} against [Cs] and the standard deviations of the calculated parameters a and b , given in Table 2, indicate that the Freundlich isotherm provides a good description of the data. Other workers have also found that a Freundlich isotherm describes Cs adsorption over a large concentration range; for example, Filipovic-Vincekovic et al. (1989), Konishi et al. (1988) and Comans and Hockley (1992). Comans and Hockley (1992) report a similar value of b for a K-saturated

Fithian illite, but a lower value for the Ca-saturated clay ($b = 0.3$). Filipovic-Vincekovic et al. (1989) and Liang et al. (1993) report a relatively high value of b for montmorillonite (0.9), but the dominant cation on the exchange complex was not determined and the ionic strength varied with Cs concentration in both studies. Bond (1995) has used a similar empirical approach to obtain an empirical constant, which is equivalent to b from selectivity data; the same trend for K, Na and Ca was observed.

Although the Freundlich isotherm is largely empirical, Sposito (1984) has shown that the parameter b is a measure of the heterogeneity of the surface; the nearer b is to unity, the more homogeneous is the surface. The values of b calculated in this study follow the expected trend of surface heterogeneity with respect to Cs adsorption as discussed above; b (illite) $< b$ (montmorillonite), and b decreases with the cation on the exchange complex in the order $K > Na > Ca$. The near-unity slope for the K-montmorillonite, reflecting the nearly linear adsorption isotherm and the nearly constant value of K_d , indicates that all of the surface exchange sites of montmorillonite have the same relative affinities for Cs and K. The contrast between the values of b reported here for Le Puy illite and by Comans and Hockley (1992) for Fithian illite implies that the surface of the former is less heterogeneous; this may be related to its greater CEC or to differing degrees of weathering of edge sites.

Effect of K Concentration

The effect of increasing the concentration of K in Na- or Ca-saturated clays was studied for 3 reasons: 1) The selective adsorption sites for Cs also have a high affinity for K, and both cations cause interlayer collapse in swelling clay minerals (Eberl 1978; Sawhney 1972); 2) Potassium fertilizer is often recommended as a countermeasure to reduce the bioavailability of ^{137}Cs in soil (Coughtrey and Thorne 1983 and references therein); 3) Potassium and NH_4 are thought to have similar effects on the adsorption of Cs by clay minerals, and the latter has been postulated to play an important role in the remobilization of Cs from sediments (Evans et al. 1983; Comans et al. 1989; Pardue et al. 1989; Davison et al. 1993). A decrease in K_d with increasing $[\text{K}]$, analogous to the effect of increasing $[\text{Cs}]$, was expected, since K is selectively adsorbed on the same sites and therefore competes with Cs. This would result in a decrease in the capacity of contaminated solids to immobilize ^{137}Cs .

The small effect of $[\text{K}]$ is surprising. Even in Ca-illite, for which the greatest effect was observed, the highest concentration of K, $4 \times 10^{-4} M$, equivalent to about 1% of the total charge-compensating cation present, only produces a fourfold reduction in K_d . Insofar as these clay minerals may be regarded as adequate models of soil minerals, this finding suggests

that the addition of K may not significantly reduce the adsorption of ^{137}Cs . Neither will the depletion of K from the exchange complex modify Cs adsorption, although mineral weathering that may result from severe K-depletion may be significant.

Effect of Ionic Strength

Decreases in K_d with increasing salt concentration have been observed for various exchange systems (Wahlberg and Fishman 1962; McBride 1979; Di Toro et al. 1986). However, no systematic investigation of the effect of ionic strength and charge-compensating cation has hitherto been reported. When the trends in K_d and K_c are compared, it is seen that the effect of salt concentration arises largely from dilution as the equivalent fraction of Cs in the initial solution decreases. This is particularly marked for the K-clays that showed the most marked decreases in K_d and no dependence on I above $10^{-3} M$.

A knowledge of the effect of ionic strength on Cs adsorption is essential for the interpretation of many desorption studies. Adsorbed Cs that is not desorbed by a given treatment is often assumed to be irreversibly adsorbed and referred to as "fixed." Unless adsorption and desorption isotherms are compared, there is no reason to assume that nondesorbed Cs is fixed. Furthermore, even if hysteresis is detected, it may be a result of experimental techniques, as has been discussed by Verburg and Baveye (1994), and may not reflect the dynamics of Cs in a real clay system.

Purely electrostatic considerations predict that increasing ionic strength should decrease the selectivity for a monovalent cation in heterogeneous exchange (Bolt 1979). The reverse is observed. There is no electrostatic reason for selectivity in homogeneous exchange to vary with ionic strength. Bond (1995) notes no consistent variation in the thermodynamic exchange coefficient at different ionic strengths for Na-K, Ca-K and Ca-Na binary exchange. Brouwer et al. (1983) observed a similar effect of ionic strength on homogeneous exchange on Morris illite, but made little comment on its possible origin.

One effect of ionic strength that may account for some of the observed change in selectivity is the increase in tactoid size with increasing ionic strength, as suggested by van Bladel and Laudelout (1967). Tactoids are smaller in the presence of monovalent cations and when the electrolyte concentration is low (Schramm and Kwak 1982; Barak 1989; Verburg and Baveye 1994). Therefore, increasing ionic strength increases the proportion of interlayer exchange sites in montmorillonite with the possibility of partial collapse of interlayers. A similar effect may occur in illite, increasing the proportion of edge sites, but these would not be high-affinity FES. The K form of both clays exhibits an effect only when $I < 10^{-3} M$; this reflects the lower dispersion power of K. The K_c of Na-mont-

morillonite falls to almost unity ($K_c = 1.53$) when $I = 5 \times 10^{-3} M$; indeed, this value is lower than that of K-montmorillonite. The Na-clay is probably so highly dispersed that all the exchange takes place at external planar sites which are known to have very low selectivity. The K-clay is less highly dispersed.

However, the above considerations are unlikely to fully explain the observations. McBride (1979) points out that variation in selectivity with ionic strength may reflect entropy changes. However, he used his argument to explain the opposite trend; namely, a decrease in preference of montmorillonite for K relative to Na at higher ionic strength.

We postulate that the phenomenon arises because of the covalent, or inner-sphere, nature of the Cs-clay interaction. The trend in selectivity for homogenous exchange between the alkali metals follows that of polarizability and Misono softness (Sullivan 1977; Xu and Harsh 1990). This illustrates the increasing importance of covalent interactions with increasing atomic number. Cesium exchange is not controlled by mass action; it takes place at highly selective sites, particularly in the case of illites. Purely electrostatic considerations are insufficient to understand these exchange reactions. Furthermore, it should be remembered that the data presented here are for exchange of a trace amount of Cs. Nonselective sites therefore contribute little to the adsorption of trace amounts of Cs. An additional indication that exchange at these sites is not controlled by electrostatic interaction comes from the calculation of the Ca-Na selectivity coefficient. If exchange is considered to be reversible, then:

$$\frac{C_a}{C_Na} K_c = \frac{C_s}{C_Na} K_c^2 \quad [5]$$

Since both $\frac{C_s}{C_a} K_c$ and $\frac{C_s}{C_Na} K_c$ decrease with increasing I , and at similar rates, then $\frac{C_a}{C_Na} K_c$ decreases. This is contrary to electrostatic theory.

Effect of Organic Matter

The presence of a soil-extracted fulvic acid has a marked effect on the capacity of these clays, particularly Ca-illite, to adsorb Cs. Similar findings are also reported for heavy metals (Lo et al. 1992), but this is usually attributed to the formation of complexes in solution. It is unlikely that the reduction in adsorption is due to the formation of stable complexes between Cs and fulvic acid in solution. Cesium may be associated with the CEC of organic matter in soils, but this adsorption is non-specific. A more probable explanation is that the fulvic acid has a high affinity either for the selective adsorption sites or for adjacent sites, thereby impeding access of Cs to the former. This is supported by the observation that the effect is greater in illite than montmorillonite, that adsorption onto K-saturated clay is not modified by addition of fulvic acid and that in illite the effect is greatest when the charge-compen-

sating cation is Ca. Other authors have reported decreased adsorption onto clays in the presence of organic matter, under different experimental conditions (Bunzl and Schultz 1985; Maguire et al. 1992; Hird et al. 1995; Hird et al. 1996). This important finding, if found to be a general effect, has profound consequences on the prediction of the adsorption properties of soils and sediments from their clay mineralogy.

CONCLUSIONS

Accurate, reliable laboratory measurements of adsorption of radiocesium on both reference minerals and field samples obtained under controlled conditions are essential for the prediction of bioavailability. However, if there are differences in certain key parameters, such measurements may not be directly extrapolated to field conditions. The most important parameters are clay mineralogy, Cs concentration, cation composition and ionic strength. The roles of organic matter and K concentration (less than 1% CEC) appear to be much less determinant. The decrease in adsorption with increasing organic matter content suggests that the high bioavailability observed in organic soils may not simply be due to the low clay content.

Although the value of K_d provides useful information, trends in its value may be misleading. For example, the decrease in K_d with increasing salt concentration is a mass action effect; the selectivity coefficient, K_c , which can only be calculated when the composition of the exchange complex is known, tends to increase with ionic strength. This trend is taken as evidence of the covalent nature of the Cs-clay interaction at high-affinity sites.

The slope of the log-log plot K_c against Cs concentration, and the value of the Freundlich b parameter, appear to be good indicators of the degree of heterogeneity of the mineral surface. However, dependence of the selectivity coefficient on Cs concentration is not in itself proof of the existence of discrete surface sites. It was not possible to calculate the exchange capacities and individual selectivity coefficients for the various surface sites.

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