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Measuring the specific caesium sorption capacity of soils, sediments and clay minerals

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Abstract

Two methods to quantify the specific Cs sorption capacity of soils and sediments, which is generally believed to be associated with the Frayed Edge Sites (FES) of illitic clay minerals, are described in detail and are critically reviewed. The first method is a direct measurement of the FES capacity, while the second quantifies the combined parameter $K_D^{Cs} \times [K^+](= K_C(K \rightarrow Cs) \times [FES])$, i.e. the product of the FES capacity and the affinity of these sites for Cs. Both methods use the bulky AgTU-complex to mask non-specific sorption sites for Cs and are applied to a number of different soils and pure minerals. Measurement of the FES capacity of pure illite is straightforward. It is shown that the measured capacity is independent of the saturating ion, but does depend on particle size. This method could not be successfully applied to a peat bog soil with 90% organic matter, because the necessary correction for non-specific Cs sorption by the large pool of organic exchange sites overpasses the capacity of the small FES fraction. Measurement of the combined parameter $K_D^{Cs} \times [K^+]$ is shown to be more appropriate in such cases. Application of the FES capacity method to the hydrous aluminosilicate mineral allophane, an important soil constituent of Andisols, shows that the AgTU-complex is unable to block all non-specific sorption sites for Cs on this mineral. The $K_D^{Cs} \times [K^+]$ measurements show evidence of a very small number of specific Cs sorption sites on allophane, much smaller than inferred from the FES capacity measurement. The FES capacity of the clay mineral vermiculite is difficult to quantify because the high Cs concentrations that are needed to measure the FES capacity probably cause a collapse of the vermiculite interlayers, thereby creating more high-affinity sites for Cs. The $K_D^{Cs} \times [K^+]$ method, in which only trace concentrations of Cs are used, is shown to be more appropriate for soils containing substantial amounts of vermiculite. It is concluded that both the direct FES capacity measurement and the measurement of the combined parameter $K_D^{Cs} \times [K^+]$ can be very useful methods to isolate and characterise Cs-selective sorption sites in soils and sediments, but that results should be interpreted with great care.

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1. Introduction

Partitioning of Cs in soils and sediments is controlled by sorption to illitic type clay minerals, except for soils and sediments with a very high organic matter content (e.g. Francis and Brinkley, 1976; Valcke and Cremers, 1994). The highly selective sorption of trace amounts of Cs occurs at the frayed edges of the illitic type clay minerals (Sawhney, 1972). At these highly selective sites only other cations with low hydration energies (notably K^+ and NH_4^+) can compete with Cs (Sawhney, 1972). At higher Cs concentrations sorption to less selective sites also becomes important (Brouwer et al., 1983). Different operational ion-exchange models have been developed to describe equilibrium Cs partitioning to clay, clay minerals and soils under different conditions.

A first class of models was developed to predict Cs sorption from very low up to high Cs loadings. These models require a multi-site cation exchange approach, because of the heterogeneous nature of the Cs sorption sites. Important examples of this approach are that of Brouwer et al. (1983) who present a 3 site exchange model for illite, the generalised 3 site sorption model of Bradbury and Baeyens (2000) which can predict Cs sorption to argillaceous rocks based on its illite content only, and the two site model of Liu et al. (2004) which is applicable in solutions with a high ionic strength as encountered in high level radioactive waste.

A second class of models is meant to predict Cs sorption as accurately as possible at trace loading only. Two different methods have evolved to measure the specific Cs sorption capacity in soils and to predict the soil/water partitioning of Cs. The Cs sorption models at the basis of these methods are essentially single site ion-exchange models, but they differ in the way that the capacity and affinity of the highest affinity sites for Cs sorption are assessed. Cremers et al. (1988) and De Preter (1990) have developed a method to measure either the total Cs sorption capacity at the frayed edge sites of illitic type clay minerals (FES) in soils and sediments or the competition between Cs^+, K^+ and NH_4^+ at the frayed edge sites which is explained in more detail by Eq. (1). Konoplev and Konopleva (1999) have presented a method to measure the capacity of the small pool of high affinity sites (HAS) within the FES. Cremers et al. (1988) and De Preter (1990) in principal regard all the frayed edge sites as one homogeneous pool, while Konoplev and Konopleva (1999) focus on the highest affinity sites within the total pool of frayed edge sites.

Because of the different assumptions underlying the above described models, ion-exchange coefficients used in these models cannot be easily compared. In this paper, the closely related approaches of Cremers et al. (1988) and De Preter (1990) will be discussed in detail and the consistency between the methods will be examined. These methods have been selected because they are widely applied to predict trace Cs adsorption in natural environments.

The method of Cremers et al. (1988) and De Preter (1990) is based on a theoretical framework which postulates that the K_D^{Cs} can be related to the sorption capacity of the FES ([FES], μeq g^{-1}) and the selectivity coefficient of the sites for Cs relative to K ($K_C(K \rightarrow Cs)$), according to the relationship:

$$K_D^{Cs} \times [K^+] = K_C(K \rightarrow Cs) \times [FES] \quad (1)$$

To predict trace sorption of Cs to soils, either the FES capacity or the combined parameter $K_D^{Cs} \times [K^+]$ should be known. Experimental procedures have been developed to quantify the FES-capacity (Cremers et al., 1988) or the product $K_D^{Cs} \times [K^+]$ (De Preter, 1990), and are being applied for predicting radiocaesium speciation in soils and sediments (De Preter et al., 1991; De Koning et al., 2000; Comans, 1999). Unfortunately, the experimental procedures and difficulties involved in the FES and $K_D^{Cs} \times [K^+]$ measurements have not been documented in sufficient detail, which hampers their general application and interpretation. Also, to the best of the authors' knowledge, no attempt has yet been made to relate the specific Cs sorption capacity to clay mineral size.

The aim of this paper is to provide a detailed description of the experimental procedures and difficulties involved in the FES capacity measurement, on the basis of measurements on 10 different (clay) mineral and soil samples. In addition, the relation between the particle-size and FES capacity is addressed. The procedure for measuring the product $K_D^{Cs} \times [K^+]$, based on a saturation of the frayed edge sites with K, is also applied and critically reviewed. The separate measurements of the FES-capacity and the combined parameter $K_D^{Cs} \times [K^+]$ on identical samples enables the testing of the extent to which the measured values are mutually consistent. Conclusions and recommendations will be made with regard to the suitability and limitations of the FES-capacity and $K_D^{Cs} \times [K^+]$ measurements for the determination of the specific Cs sorption capacity of soils and sediments.

2. Materials and methods

2.1. Pre-treatment of minerals and soils

Fithian illite, vermiculite and allophane were purchased from Ward's Natural Science Establishment. Fithian illite, a reference clay mineral (Kerr et al., 1950), was finely ground in a tungsten carbide mill (2×30 s.). The fractions <10 μm, <2 μm and <1.5 μm were separated by sedimentation in demineralised water after excess salts were removed by washing repeatedly with demineralised water. Subsamples of the <2 μm suspension were saturated with either Na, K or NH_4 by equilibration with 1 M NaCl, KCl or NH_4Cl, respectively, transferred to dialysis tubing and subsequently dialysed against demineralised water until no Cl^- could be detected. Finally, the clay suspensions were dialysed against the appropriate 1×10^{-3} M NaCl, KCl or NH_4Cl solution after which particle concentration and ion concentration of the suspension were measured. Thus, six different pre-treated illite samples were obtained: 3 K-, Na- and NH_4-saturated samples with a particle size of <2 μm and equilibrated in 1×10^{-3} M chloride solutions (referred to as illite 1, 2 and 3, respectively) and three untreated samples with particle sizes of <1.5 μm, <2 μm and <10 μm (referred to as illite 4, 5 and 6, respectively). Particle size distribution of the six illite samples was measured by laser diffraction with a Malvern 3600 D particle analyser.

The vermiculite was finely ground in a zirconium ball mill, and subsequently saturated with Na. The suspension was then transferred to dialysis tubing and dialysed against demineralised water until no Cl^- could be detected. Finally, the clay suspension was dialysed against 1×10^{-3} M NaCl.

In addition to these clay samples, three other samples were used for this study. A highly organic sample was taken from a peat bog in Cumbria (UK) and was air-dried and ground in a mortar. For a description of the sample site, the reader is referred to Comans et al. (1998). The organic matter content of this sample was 89.9% as determined by loss on ignition (2.5 h at 850 °C). The green clay sample originated from the Savannah River Site (USA). This sample was air-dried and the soil particles were crushed in a mortar and its moisture content was analysed. The allophane from Ward's Natural Science Establishment was finely ground in a Zr ball mill. An overview of the properties of the samples is given in Table 1.

2.2. FES-measurement

The FES analysis is based on measurement of Cs adsorption on the solid sample at different concentrations of Cs in the presence of a 0.015 M silver-thiourea (AgTU) solution. The bulky AgTU complex has a very high ion affinity for the regular exchange sites (Pleysier and Cremers, 1975), i.e. on the planar clay surfaces and organic material, and is used to "mask" those non Cs-specific sites. Although adsorption of the large AgTU molecule to the frayed edge sites can occur, it is strongly

Table 1
Results of the FES capacity measurement on 10 different samples

Sample no.	Background electrolyte	Median particle[b] size (μm)	CEC[a] (μeq g^{-1})	FES (μeq g^{-1})	$K_D^{Cs} \times [K^+]$ (μeq g^{-1})
Illite 1, K-saturated	10^{-3} M KCl	2.69	331	21.0 ± 1.6	
Illite 2, Na-saturated	10^{-3} M NaCl	2.80	406	18.9 ± 0.8	
Illite 3, NH_4-saturated	10^{-3} M NH_4Cl	2.85	368	19.2 ± 0.4	
Illite 4, not mono-saturated		2.03	610	14.3 ± 0.3	16,000
Illite 5, not mono-saturated		2.86	322	25.4 ± 1.3	14,000
Illite 6, not mono-saturated		9.76	165	5.8 ± 1.3	2900
Vermiculite	10^{-3} M NaCl		234	58.1 ± 3.2	
Organic (peat bog) soil			400[c]	<d.l.	412
Allophane			110	10.5 ± 0.7	988
Green clay			405	10.2 ± 0.4	1650

[a] Measured using the AgTU saturation method of Chhabra et al. (1975).
[b] Measured by laser diffraction using a 3600 D Malvern particle size analyser. Values differ from the cut-off sizes used in the separation of the particle fractions <10 μm, <2 μm and <1.5 μm by sedimentation, due to incomplete particle separation and non-ideal particle geometry.
[c] Estimated.

limited by steric hindrance (Wauters, 1994) and the much higher affinity of Cs for the FES relative to AgTU (De Preter, 1990; Wauters, 1994). Thus, at high Cs concentrations the FES become completely saturated with Cs ions, while the regular exchange sites are blocked by AgTU, and the sorption maximum represents the FES capacity of the sediment.

The general procedure for measuring the frayed edge site capacity was taken from Madruga (1993), and was slightly modified. For the solid samples, an amount of approximately 0.2 g of air dried soil or mineral was transferred to small (10 mL) Teflon FEP centrifuge tubes. For the illite and vermiculite suspensions, an amount of the suspension with an equivalent mass of about 0.2 g solid material was transferred to the FEP tubes. Then, the suspensions were centrifuged (30 min, 20,000*g*) and the supernatant was carefully removed. Further handling (i.e. adding the 0.015 M AgTU solution, see below) of the originally suspended and solid samples was then the same.

Particular care is required in the preparation of a stable AgTU solution. A 500 mL of 0.015 M AgTU solution was prepared by first dissolving 3.806 g of thiourea in 250 mL demineralised water in a 500 mL volumetric flask. 1.274 g of $AgNO_3$ were dissolved in about 150 mL demineralised water and this solution was slowly added to the thiourea solution while stirring vigorously. Finally, demineralised water was added to a total volume of 500 mL. A slightly different way of preparing an AgTU solution (of 0.010 M) is given by Chhabra et al. (1975). The 0.015 M AgTU solution is unstable above approximately pH 8. Therefore, if the FES capacity is to be measured for a soil or sediment with a pH of >8, the soil has to be acidified to lower the pH to <8.

Five mL of 0.015 M AgTU solution was added to the solids in the centrifuge tubes and the samples were shaken for 24 h. Then, samples were centrifuged (30 min, 20,000*g*) and the supernatant was discarded. This pre-equilibration step is needed to ensure that in the next step that 0.015 M AgTU is present in the solution. Then, 5 mL of ^{137}Cs-spiked Cs solutions in the concentration range of 5×10^{-5}–5×10^{-2} M $CsNO_3$, in a background of 0.015 M AgTU solution, was added to the samples. After shaking the samples for 24 h and centrifuging (30 min, 20,000*g*), the remaining ^{137}Cs-activity in the supernatant was measured on a LKB Wallac 1282 Compugamma γ-spectrometer with NaI detector. Although the adsorption of a small fraction of Cs has been shown to continue after this equilibration period (De Koning and Comans, 2004), this process has a minor effect on the total measured FES capacity. Therefore, the authors have adopted for this purpose the 24 h equilibration period from the original work of Madruga (1993). All measurements were carried out in duplicate. Caesium adsorption was calculated from the difference between the initial and remaining ^{137}Cs-activity in solution.

Although in this procedure virtually all regular exchange sites (RES) are saturated by the strongly adsorbing AgTU-complex, a small number of these sites can be occupied by Cs ions, depending on the Cs–AgTU ion-exchange coefficient of the RES and the Cs and AgTU concentration in solution. For a correct assessment of the FES-capacity, the amount of Cs adsorbed on the RES should be subtracted from the total Cs adsorption. The adsorption of Cs at the regular exchange sites can be calculated on the basis of a Cs–AgTU selectivity coefficient for the RES of 0.022 (Cremers et al., 1988) and the overall cation exchange capacity (CEC). Most preferably, the CEC used in the correction is measured by the AgTU saturation method (Chhabra et al., 1975), as this CEC value would be closest to the number of RES that are occupied by AgTU in the FES measurement. CEC values that were measured with the AgTU saturation method are given in Table 1. Using these measurements, the maximum correction for the mineral samples ranges from 15% for illite No. 5 to 60% for illite No. 6. For the organic peat soil the correction is >100%, which means that more than 50% of all adsorbed radiocaesium is adsorbed on the RES and not on the FES.

The results are plotted as adsorption isotherms, i.e. Cs adsorbed on the FES versus the Cs concentration in solution. To determine the total Cs sorption capacity at the FES, a Langmuir adsorption isotherm is fitted to the measurements using a non-linear regression routine that minimises the sum of square errors. The sorption maximum of the Langmuir adsorption isotherm is taken as the FES-capacity.

As has been shown by Brouwer et al. (1983) and Konoplev and Konopleva (1999), a small fraction of the FES sites have an even higher affinity for Cs. In the above procedure, the FES sites with a relatively low affinity for Cs are ultimately all saturated with Cs. As the Cs binding heterogeneity of the relatively low-affinity sites is small (>90% of the FES sites are low affinity sites, Brouwer et al., 1983; Wauters, 1994) it is justified to estimate the total Cs sorption capacity of the FES with a single Langmuir isotherm.

2.3. $K_D^{Cs} \times [K^+]$ measurement

The $K_D^{Cs} \times [K^+]$ measurement quantifies the affinity of the high affinity sites for Cs as a function of the K concentration by measuring the K_D of trace Cs levels on the solid samples at a range of K concentrations in solution. If the K concentration is high enough to fully saturate the frayed edges, it is shown by Eq. (1) that the product of $K_D^{Cs} \times [K^+]$ is constant, and is equal to the product of the parameters $K_C(K \rightarrow Cs) \times [FES]$ (De Preter, 1990). This constant $K_C(K \rightarrow Cs) \times [FES]$ product can be used to predict the K_D^{Cs} in environments with different K concentrations.

The general procedure for the measurement of the $K_D^{Cs} \times [K^+]$ was taken from De Preter (1990). Known amounts of solid samples (about 0.2 g) are equilibrated with 5 ml of 0.015 M AgTU solutions containing K concentrations in the range of 0.5–50 mmol L^{-1}. After pre-saturation (two times, 24 h) phase separation was accomplished by centrifugation (30 min, 20,000*g*) and the solids were equilibrated with the appropriate K/AgTU solutions spiked with ^{137}Cs. After 24 h the K_D^{Cs} was calculated from the remaining ^{137}Cs activity in solution. Results are plotted as $K_D^{Cs} \times [K^+]$ versus the potassium concentration in solution. $K_D^{Cs} \times [K^+]$ measurements have been made for organic matter, organic peat bog soil and green clay.

3. Results and discussion

3.1. FES capacity measurements of illite

Fig. 1 shows the FES measurement of the six different pre-treated illite samples together with the fitted Langmuir isotherm (solid line) and sorption maximum (broken line). The values of the FES capacity are given in Table 1. For all illite samples a well-defined adsorption plateau is reached at an equilibrium Cs concentration in solution of 5–10 mmol L^{-1}. The illite samples from the same size fraction but with different saturating ion (illite 1, 2 and 3) all have the same FES-capacity within the experimental error, which shows that the saturating cation has no great influence on the measured FES capacity. Illite samples 4, 5 and 6 show that the FES capacity of the illite does vary with its median particle size, which is further discussed below.

Wauters (1994) noted that the FES capacity and the illite content of a soil or sediment do not show a strong correlation. This lack of correlation might be due to variability in illite particle size, which would lead to differences in the specific edge surface

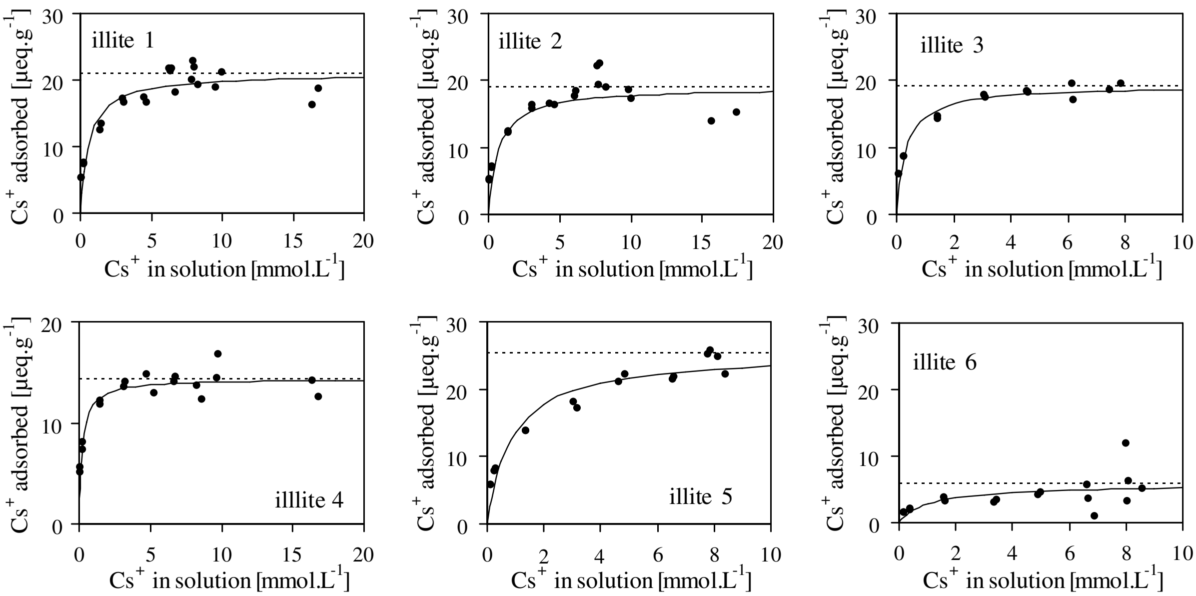

Fig. 1. Results of the frayed edge site measurement on illite 1–6. The measured adsorbed Cs (μeq g^{-1}) corrected for Cs adsorption at the regular exchange sites as a function of the equilibrium Cs concentration in solution (mmol L^{-1}) is indicated by the black dots. The fitted Langmuir adsorption isotherm is indicated by the solid line, and the adsorption maximum derived from the fitted Langmuir adsorption isotherm by the broken line.

area. The ratio of specific edge surface areas ($S_{edge,a}/S_{edge,b}$) of two clay particles having different radii (r_a and r_b) are related according to $S_{a,edge}/S_{b,edge} = r_b/r_a$, assuming that the particles are perfectly disk shaped. Assuming that the specific edge surface area of illite particles is linearly related to the FES capacity, the ratio of the FES should be as follows: illite 4:illite 5:illite 6: = 4.8:3.4:1. The measured ratio of the FES for illite 4:illite 5:illite 6 = 2.5:4.4:1. These results show that the relation between particle size and FES capacity is not as simple as presented above, because illite 4 with the smallest median particle size does not have the highest FES capacity. Although these results show that particle size is an important parameter, its precise relation with the FES capacity is not yet completely understood. Nevertheless, the observed effect of illite particle size on FES capacity may well explain at least part of the variability that has been observed in the relation between illite content and FES capacity of environmental samples (Wauters, 1994).

3.2. $K_D^{Cs} \times [K^+]$ measurement of allophane, peat bog soil and green clay

The frayed edge site capacity measurements on green clay, allophane, vermiculite and peat bog soil did not yield straightforward results for reasons discussed below. Therefore, the product $K_D^{Cs} \times [K^+]$ was also measured for allophane, peat bog soil and green clay (vermiculite will be discussed further in the next section). These measurements then allow comparison with the FES measurements, as both should ideally give the same information about the affinity of these samples for Cs. The results of the $K_D^{Cs} \times [K^+]$ measurements are shown in Fig. 2. Although Eq. (1) shows that a constant value of $K_D^{Cs} \times [K^+] = K_C(K \rightarrow Cs) \times [FES]$ should be obtained when the frayed edge sites are fully saturated with K, no exact $K_D^{Cs} \times [K^+]$ plateau is measured at the higher concentrations of K applied in the experiments, particularly for green clay. It is, therefore, not certain whether mono-saturation of the frayed edge sites with K was truly accomplished.

At decreasing K concentration, the $K_D^{Cs} \times [K^+]$ product decreases and indicates that the frayed edge sites are increasingly occupied by other ions than K. This other competing ion might be AgTU (which is present at 0.015 M), as suggested by De Preter (1990), or ions such as Al^{3+}, Ca^{2+}, Mg^{2+}, Na^+ and H^+ that are already present at the frayed edges at the start of the experiment. However, this would mean that the unknown ions present on the FES are not easily replaced by K, which can be concluded from the results of the $K_D^{Cs} \times [K^+]$ measurements shown in Fig. 2. Three pre-equilibration periods with 20 mmol L^{-1} K/0.015 M AgTU solution is apparently not sufficient to fully saturate the FES, indicating that the unknown competing ion must have a high affinity for the FES, relative to K. Alternatively, this ion would have to be present at a high concentration after the pre-equilibration, but this explanation seems unlikely.

The sites not occupied by K are most probably occupied by AgTU. It has been shown by Wauters (1994), that it is possible to extract substantial amounts of adsorbed radiocaesium (3.1–26.3%) from the FES with a 3 × 24 h 0.015 M AgTU extraction. Because the affinity of Cs for the FES is much higher than that of AgTU (De Preter, 1990), interference of AgTU with Cs sorption on the frayed edge sites is small. As the affinity of K for the FES is much lower than that of Cs ($K_C(K \rightarrow Cs) \approx 1012$; Wauters et al., 1996) K is much more easily exchanged by AgTU. On the other hand, it has been proven that access of the AgTU-ion to the FES is partly sterically hindered (De Preter, 1990), which implies that AgTU would not be able to exchange all K and Cs from the FES. It would be interesting to measure K exchange against AgTU to verify that AgTU is indeed able to compete with K ions adsorbed on the FES, and to which extent AgTU has access to the FES, but this is beyond the scope of the present study.

Assuming that AgTU is indeed able to compete with Cs and K on the FES, the K_D of Cs as a function of the K concentration in the $K_D^{Cs} \times [K^+]$ measurement can be described more accurately by the following equation, derived from ion-exchange theory for the ternary system Cs–K–AgTU:

$$K_D^{Cs} = \frac{[FES] \times K_C(K \rightarrow Cs) \times K_C(AgTU \rightarrow Cs)}{[K^+] \times K_C(AgTU \rightarrow Cs) + [AgTU] \times K_C(K \rightarrow Cs)} \quad (2)$$

Using Eq. (2), the values of FES, $K_C(K \rightarrow Cs)$ and $K_C(AgTU \rightarrow Cs)$ were fitted using a non-linear regression routine minimising the relative sum of squares between the measured K_D^{Cs} and K_D^{Cs} calculated according to Eq. (2). Using the fitted values, the fraction of sites occupied by K can be calculated. In Fig. 2 the fitted line is shown together with the derived value of the parameter $K_C(K \rightarrow Cs) \times [FES]$. Also shown is the fraction of the FES occupied by K, as a function

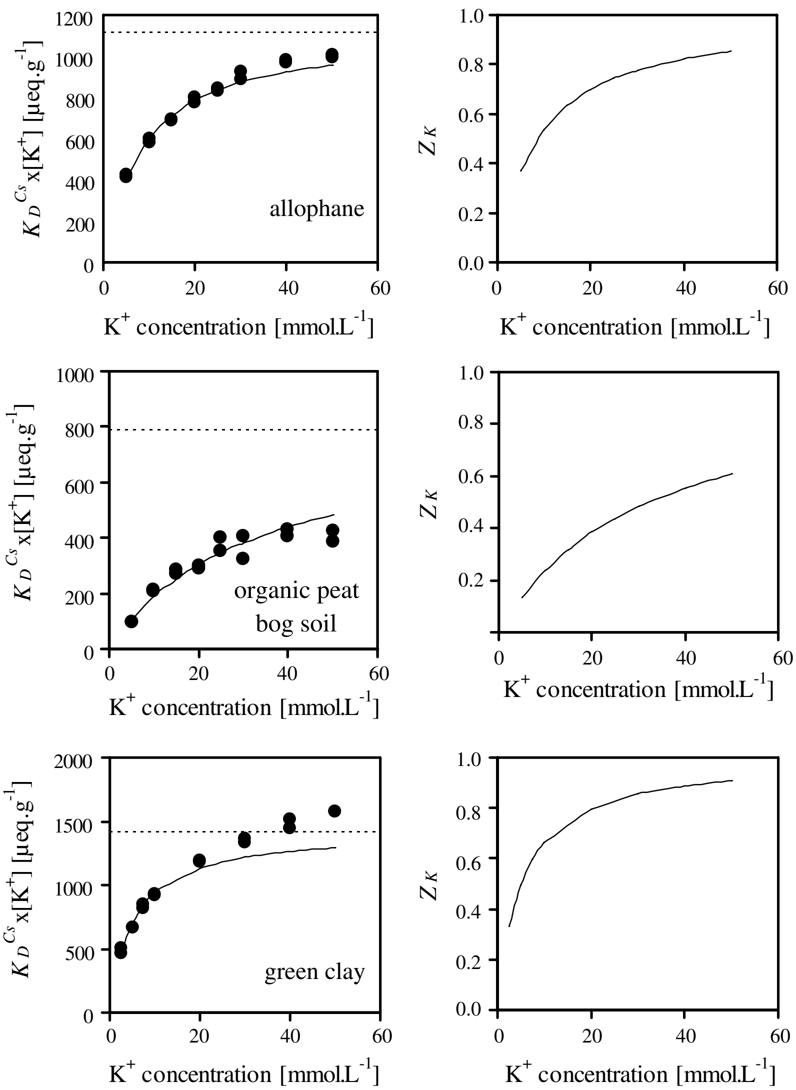

Fig. 2. Results of the $K_D^{Cs} \times [K^+]$ measurement on allophane, organic peat bog soil and green clay. The measured product of $K_D^{Cs} \times [K^+]$ ($\mu eq\ g^{-1}$) indicated by the black dots is given as a function of the $[K^+]$ concentration ($mmol\ L^{-1}$) in the left-hand graphs. The fitted $K_D^{Cs} \times [K^+]$ values according to Eq. (2) are also shown (solid line). The broken line indicates the value of the combined parameter $K_C(K \to Cs)$ [FES], derived from the fitted parameters. The right-hand graphs show the calculated fraction of frayed edge sites occupied by K as a function of the K concentration in solution.

of the K concentration in solution. Numerical results of this fit are shown in Table 2.

Table 2 shows that the fitted $K_C(K \to Cs)$ value for green clay, organic soil and allophane are in the range of values measured on various soils, sediments and clay minerals (164–2276; Wauters, 1994). Caesium adsorption is also preferred over AgTU on the FES of green clay, organic soil and allophane. The fitted value of the $K_C(AgTU \to K)$, 0.5–3.0 (Table 2), suggests that K and AgTU are about equally competitive. The calculated occupancy of the FES by K (Fig. 2) shows that complete saturation of the sites with K is indeed not reached. This lack of K-saturation results in a fitted value of the parameter $K_C(K \to Cs) \times [FES]$ that is slightly different from the value that would be derived from the maximum $K_D^{Cs} \times [K^+]$ measured.

In the following sections it will be shown that, with an explicable exception for allophane, the FES capacities fitted on the basis of Eq. (2) ($1.86\ \mu eq\ g^{-1}$ for green clay, $0.37\ \mu eq\ g^{-1}$ for the organic soil and $1.28\ \mu eq\ g^{-1}$ for allophane) are consistent with those measured directly. The authors believe, therefore, that Eq. (2) allows for a

Table 2
Results of fitting equation (2) to the measured K_D^{Cs} measurements as a function of the K concentration

Sample	Fitted parameters			Derived parameters	
	FES (μeq g^{-1})	$K_C(AgTU \rightarrow Cs)$	$K_C(K \rightarrow Cs)$	$K_C(K \rightarrow Cs) \times [FES]$ (μeq g^{-1})	$K_C(AgTU \rightarrow K)$
Green clay	1.86 ± 0.05	2267 ± 59	765 ± 60	1423 ± 118	3.0 ± 0.2
Organic peat bog soil	0.37 ± 0.04	1000 ± 159	2139 ± 81	791 ± 91	0.5 ± 0.08
Allophane	1.28 ± 0.01	1533 ± 25	876 ± 26	1121 ± 34	1.8 ± 0.06

From the fitted values of the parameters [FES], $K_C(K \rightarrow Cs)$ and $K_C(AgTU \rightarrow Cs)$, the values of $K_C(K \rightarrow Cs) \times [FES]$ and $K_C(AgTU \rightarrow K)$ are calculated.

robust approach of deriving the product $K_C(K \rightarrow Cs) \times [FES]$, even at conditions of incomplete K-saturation of the FES.

3.3. FES measurement of allophane, organic peat bog soil, green clay and vermiculite

Fig. 3 shows the FES measurements of allophane, organic peat bog soil, green clay and vermiculite. The FES measurement of allophane suggests that a Cs sorption capacity of 10.5 μeq g^{-1} is present, in spite of the absence of illitic clay minerals as detectable by X-ray diffraction. Allophane is a hydrous aluminosilicate mineral consisting of hollow, irregularly shaped particles with a diameter of 3.5–5 nm (Wada, 1989). It is likely that large organic cations such as AgTU do not have full access to all exchange sites in allophane, depending on structure and size, while the smaller Cs ion has. This hypothesis is corroborated by measurements of the adsorption of alkyl-ammonium cations on allophane, which decreases with increasing molecular size of the cations (Birrell, 1961; Theng, 1972). These findings show that solely a measured Cs sorption capacity in the presence of AgTU is, therefore, not necessarily direct evidence for the presence of illitic frayed edge sites with a very high selectivity for Cs. However, the $K_C(K \rightarrow Cs)$ value of 1533 for allophane that was obtained from the $K_D^{Cs} \times [K^+]$ measurement (Eq. (2) and Table 2), i.e. at low Cs concentrations, suggests that a fraction of the measured Cs sorption capacity may indeed

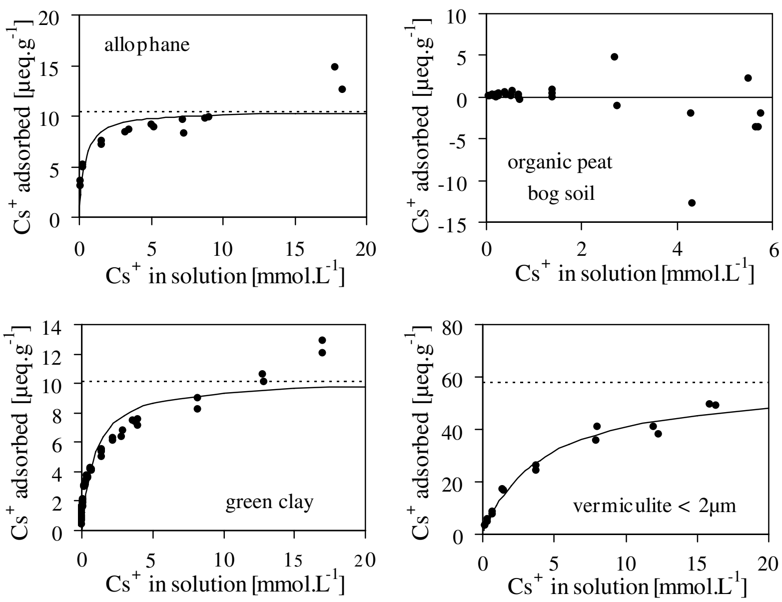

Fig. 3. Results of the frayed edge site measurements on allophane, organic peat bog soil, green clay and vermiculite. The measured adsorbed Cs (μeq g^{-1}), corrected for adsorption at the regular exchange sites, as a function of the equilibrium Cs concentration in solution (mmol L^{-1}) is indicated by the black dots. The fitted Langmuir adsorption isotherm is indicated by the solid line, the adsorption maximum derived from the fitted Langmuir adsorption isotherm by the broken line. No meaningful Langmuir isotherm could be fitted to the organic peat bog soil.

consist of sites with a very high selectivity for Cs. The exact nature of these binding sites is at present unclear, but the high Cs-selectivity is supported by experiments of Mon et al. (2005) who found that about 20% of Cs^+ incorporated in allophane could only be desorbed by K and not by Ca. The FES capacity of 1.28 μeq g^{-1} obtained from the $K_D^{Cs} \times [K^+]$ measurement (Table 2), suggests that about 12% of the sites on allophane that are accessible to Cs but not to AgTU (10.5 μeq g^{-1}) consist of sites with a high Cs-selectivity.

The FES measurement of the organic peat bog soil (89.9% organic matter) shows that it is not possible to obtain FES capacity measurements for soils where this capacity is very small compared to the total cation exchange capacity (CEC). The correction for adsorption of Cs on the regular exchange sites becomes very large. The calculated FES is the result of the subtraction of two large numbers (measured total amount adsorbed on solid – calculated amount adsorbed on regular exchange sites) and is, therefore, unreliable. This is shown in Fig. 3 were a negative Cs adsorption on the FES is calculated. It is still possible that frayed edge sites are present in this soil with a capacity below the detection level of the FES measurement procedure. Indeed the fitting procedure used to obtain the $K_D^{Cs} \times [K^+]$ indicated that the organic soil contains a very small FES capacity of ≈0.37 μeq g^{-1} and the fitted value of the parameter $K_D^{Cs} \times [K^+]$ (791 μeq g^{-1}) shows that frayed edge sites may indeed be present in this organic soil (Fig. 2). Small values for $K_D^{Cs} \times [K^+]$ in the range of 0.065–0.31 μeq g^{-1}were also found by Valcke and Cremers (1994) in soils with a similar organic matter content.

Measuring the FES capacity of the green clay soil did not succeed well as no adsorption maximum was obtained at Cs concentrations in solution of up to 20 mmol L^{-1}. The green clay soil contains vermiculite clay as detected by X-ray diffraction. Possibly, the expanding vermiculite clay mineral is responsible for the anomalous FES measurement. To test this hypothesis, a FES measurement was made on pure Na-saturated vermiculite clay. As shown in Fig. 3, Cs sorption on vermiculite in the presence of 0.015 M AgTU-complex did also not reach a sorption plateau.

Vermiculite is an expanded clay mineral with Mg and Ca sandwiched between the clay platelets (Douglas, 1989). Possibly, upon sorption of large quantities of Cs, the clay layers start to dehydrate (collapse) and in the wedge zone between hydrated and dehydrated clay layers new high affinity sites are formed. This process could potentially cause further adsorption of Cs until the vermiculite interlayers are completely collapsed and the CEC is saturated with Cs. This mechanism of Cs sorption on vermiculite is corroborated by ^{133}Cs MAS NMR data, which show that Cs sorbed on vermiculite at high concentrations is present in dehydrated form (Weiss et al., 1990a,b). Jacobs and Tamura (1960) and Sawhney (1965) have also noted an increase in Cs sorption affinity on vermiculite at higher Cs concentrations in solution. Thus, FES measurements on soils or sediments containing a substantial amount of vermiculite are very likely to show continuous Cs sorption.

In view of the above, it is assumed that Cs adsorption on green clay soil in the presence of 0.015 M AgTU is governed by adsorption at frayed edge sites and subsequently by further adsorption at collapsing vermiculite interlayers. Therefore, the authors have examined if Cs adsorption data on green clay soil can be described by a two-site Langmuir adsorption isotherm. The results of this examination are shown in Fig. 4 and Table 3. The two-site Langmuir isotherm (sum of squares error = 31.2) describes the data much better than the single site Langmuir isotherm (sum of squares error = 496). These results suggest that the green clay soil contains one site with a low capacity and high affinity and a second site with a high capacity and low affinity. Most probably, the high affinity site is associated with the true FES capacity and is about 1.42 μeq g^{-1}. This FES capacity is very similar to the FES capacity found by fitting equation (2) to the $K_D^{Cs} \times [K^+]$ data (1.86 μeq g^{-1}, see Fig. 2 and Table 2).

The combined parameter $K_D^{Cs} \times [K^+]$ for the green clay soil is measurable ($K_D^{Cs} \times [K^+] = 1423$ μeq g^{-1}) because in this procedure the soil is not subjected to high Cs concentrations that cause collapse of the clay structure (Fig. 2). Using the measured $K_D^{Cs} \times [K^+]$ and the FES capacities based on the single and two-site Langmuir isotherm, the ion-exchange coefficient of Cs relative to K ($K_C(K \rightarrow Cs)$) on the FES can be calculated for these two different FES estimates. The $K_C(K \rightarrow Cs)$ value based on the interpretation of the measurements with a single site Langmuir isotherm (FES = 10.2 μeq g^{-1}) is 145, and based on the two-site isotherm (FES = 1.42 μeq g^{-1}) is 1042. The former very low value indicates that the FES capacity is truly overestimated, while the latter value is close to values measured on pure illite (≈1480; Wauters, 1994), which suggests that this FES value is associated with the true Cs-specific sorption capacity of

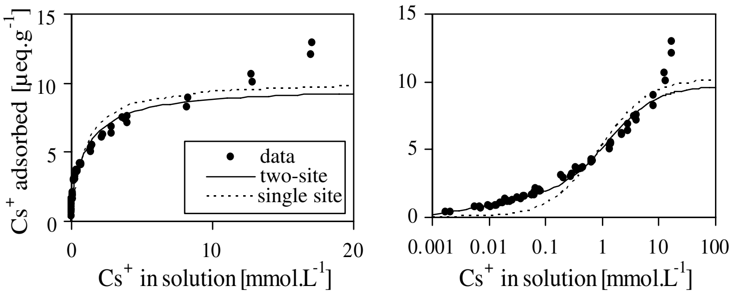

Fig. 4. Two-site and single-site Langmuir isotherm fitted to Cs adsorption data on green clay soil. Symbols indicate measurements; the black line denotes the two-site Langmuir adsorption isotherm, the broken line indicates the single-site Langmuir adsorption isotherm. The fitted parameter values for the two-site Langmuir isotherm are given in Table 2. Results are shown on a linear (left) and logarithmic (right) scale for the Cs concentration in solution.

Table 3
Parameter values of the two-site Langmuir isotherm fitted to the Cs adsorption data for green clay soil in the presence of 0.015 M AgTU

Parameter	Value ± Standard deviation
K_1	145 ± 42
Q_1 (µeq g^{-1})	1.42 ± 0.17
K_2	0.79 ± 0.22
Q_2 (µeq g^{-1})	8.36 ± 0.86

the green clay soil. Therefore, fitting of a two-site Langmuir adsorption isotherm seems an appropriate method for the detection of the FES capacity of soils with a high vermiculite content.

In principle, the investigated methods to measure the specific Cs sorption capacity can both be used to predict equilibrium Cs partitioning in the environment, even when the concentrations of competing ions such as NH_4^+ vary strongly (e.g., De Koning et al., 2000). However, as shown and explained above, the FES-capacity measurement may give results for specific minerals that are not representative for the partitioning of Cs at trace levels. Therefore, the measurement of the $K_D^{Cs} \times [K^+]$ is more generally applicable for prediction of the in-situ partitioning of Cs in the environment. Nevertheless, quantifying the FES capacity provides further insight in the coordination environment of the Cs ion and can contribute to advance the understanding of the mechanisms of Cs sorption.

4. Conclusions

The following conclusions are drawn from this study with respect to measurement of Cs-selective sorption sites in soils and sediments:

- In general, both the direct FES capacity measurement and the measurement of the combined parameter $K_D^{Cs} \times [K^+](= K_C(K \rightarrow Cs) \times [FES])$ can be very useful methods to isolate and characterise Cs-selective sorption sites in soils and sediments, but results should be interpreted with great care.
- The FES capacity of illite clay is dependent on particle size but does not depend on the saturating cation.
- Measurement of the FES capacity is not successful when this capacity is small relative to the overall CEC, as a result of the large correction that is required to account for Cs sorption on regular (non-selective) exchange sites. Measurement of the combined parameter $K_D^{Cs} \times [K^+]$ is more appropriate in such cases.
- The $K_D^{Cs} \times [K^+]$ measurement gives more reliable results when interpreted in terms of a ternary ion-exchange process between Cs, K and AgTU, compared to binary exchange between only Cs and K.
- The bulky AgTU-complex is probably unable to block all non-selective adsorption sites of allophane. Therefore, the sorption capacity of Cs in the presence of AgTU in soils or sediments may not always be quantitatively related to frayed edge sites on illite clays.
- Measurement of the FES capacity for soils or sediments containing substantial amounts of vermiculite is difficult and may be unsuccessful. The high concentrations of Cs needed in the experiment can induce a partial collapse of the vermiculite interlayers and thereby create more sites with a high affinity for Cs. Better results are obtained with this method when a two-site Langmuir adsorption isotherm is applied to the data.

Measurement of the combined parameter $K_C(K \rightarrow Cs) \times [FES]$, in which method only trace concentrations of Cs are used, is more appropriate for soils containing substantial amounts of vermiculite.

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