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## Reversibility of radiocaesium sorption on illite

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**Abstract**—Adsorption of trace amounts of radiocaesium on NH<sub>4</sub>-, K-, and Na-saturated Fithian illite and subsequent desorption by 1 M NH<sub>4</sub> showed that a substantial amount of radiocaesium (44%, 46%, and 91% for NH<sub>4</sub>-, K-, and Na-illite, respectively) cannot be desorbed after only 5 min of adsorption. Our results suggest that this instantaneous fixation is caused by the collapse of the frayed edges of the clay mineral and the relatively high concentration of radiocaesium building up in solution in the batch desorption experiments. Consequently, commonly applied high-NH<sub>4</sub> extractions underestimate truly exchangeable amounts of radiocaesium in soils and sediments containing illitic clay minerals. The rate of desorption of trace amounts of radiocaesium from the solids using high NH<sub>4</sub> or Cs concentrations has a half-life of about 2 yr, reflecting radiocaesium desorption from (partially) collapsed interlayers. Extraction of radiocaesium from illite after 5 min of contact time with a Cs-selective adsorbent or a 1 × 10<sup>-6</sup> M CsCl solution shows that 100% of the bound radiocaesium is readily available. The desorption rate in the presence of a Cs-selective adsorbent has a half-life of about 0.2 yr. Desorption of radiocaesium from illite using different ammonium concentrations shows that radiocaesium partitioning follows reversible ion-exchange theory if the NH<sub>4</sub> concentration is below 1 × 10<sup>-4</sup> M, and sufficient time (weeks) is allowed for the reaction to proceed. Thus, radiocaesium sorption reversibility in the natural environment is much higher than generally assumed, and equilibrium solid/liquid partitioning may be assumed for the long-term modelling of radiocaesium mobility in the natural environment. In the particular case of anoxic freshwater sediments with very high NH<sub>4</sub> concentrations in the pore waters (up to several mmol.L<sup>-1</sup>), collapse of the frayed edges of illite may occur, influencing radiocaesium partitioning. If collapse occurs before radiocaesium adsorbs to illite, high caesium sorption reversibility as measured by high-NH<sub>4</sub> extraction can be expected because further collapse of the frayed edges during the extraction procedure will be limited. This effect has indeed been observed earlier in the extraction of radiocaesium from anoxic freshwater sediments with high-NH<sub>4</sub> solutions and was as yet unexplained. Copyright © 2004 Elsevier Ltd

### 1. INTRODUCTION

Sorption of trace amounts of radiocaesium on illitic-type clay minerals in the natural environment has often been described as largely “irreversible,” as most of the radiocaesium becomes fixed in the interlayers between the platelets of the minerals (Page and Baver, 1939; Jacobs and Tamura, 1960; Tamura and Jacobs, 1960; Sawhney, 1964; Comans and Hockley, 1992), minimising the transfer of radiocaesium into the ecosystem. However, observations on radiocaesium partitioning in anoxic freshwater sediments (Evans et al., 1983; Comans et al., 1989; Comans, 1999; De Koning et al., 2000) and the persistence of radiocaesium in water, fish, and plants after the Chernobyl accident (Jonsson et al., 1999; Smith et al., 1999; Smith et al., 2000), indicate that radiocaesium sorption must remain at least partly reversible.

These observations on the reversibility of radiocaesium sorption in the natural environment are not corroborated by laboratory studies of radiocaesium sorption reversibility where exchangeability of sorbed radiocaesium was measured against a high (1 mol/L or 0.1 mol/L NH<sub>4</sub>) ammonium concentration (Evans et al., 1983; Comans et al., 1998; Comans, 1999; De Koning et al., 2000). Results of these exchangeability studies

indicate that caesium sorption reversibility is very small. For instance, Comans (1999) found 2 to 7% of the total amount of adsorbed radiocaesium to be exchangeable against 0.1 mol/L NH<sub>4</sub> in the top layers of two freshwater sediments. This discrepancy between observations in the natural environment and those in the laboratory is the subject of the present paper. We show that the small amounts of radiocaesium desorbed from solids by the ion-exchange method are partly caused by the alkali ion sorption behaviour on illitic clay minerals, and we show that caesium sorption reversibility is much greater if measured appropriately.

### 2. Theory

The highly selective sorption of trace amounts of caesium to illitic clay minerals occurs at the frayed edges of these clay minerals (e.g., Jackson, 1968; Sawhney, 1972). The total number of these sites is called the frayed edge site (FES) capacity (Cremers et al., 1988). The specific caesium sorption at the FES is heterogeneous: ~0.5 to 10% of the FES sites have a higher affinity for radiocaesium and are called the high-affinity sites (Wauters, 1994).

A number of similar, but slightly different, approaches have been used to model Cs sorption to illite from trace levels up to high surface loadings, taking the heterogeneous nature of the adsorption process into account. These models differ in the types of sites distinguished, their assumed location on the clay mineral, and preference for Cs relative to other counter ions.

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Table 1. Parameters for the 3-site ion-exchange model used to calculate equilibrium Cs sorption to Fithian illite, at the experimental conditions applied to investigate the reversibility of the sorption process (parameters taken from Bradbury & Baeyens, 2000).

Site type	Site capacity*	Selectivity coefficients
Site I (frayed edge sites)	0.48 $\mu\text{eq.g}^{-1}$	$\log_{\text{K}}^{\text{Cs}}K_C = 4.6$ $\log_{\text{NH}_4}^{\text{Cs}}K_C = 3.5$ $\log_{\text{Na}}^{\text{Cs}}K_C = 7.0$
Site II (intermediate sites)	38.2 $\mu\text{eq.g}^{-1}$	$\log_{\text{K}}^{\text{Cs}}K_C = 1.5$
Site III (planar sites)	152.8 $\mu\text{eq.g}^{-1}$	$\log_{\text{K}}^{\text{Cs}}K_C = 0.5$

\* Site capacities according to Bradbury & Baeyens (2000); Site I = 0.25% of the CEC; Site II = 20% of the CEC; Site III = 80% of the CEC; CEC of 191  $\mu\text{eq/g}$  used for Fithian Illite (Comans et al., 1991).

For instance, Brouwer et al. (1983) assume that two high selectivity sites (Site I and II) are involved in the adsorption of Cs on illite. The authors suggest that both sites are situated at the frayed edges or edge-interlayer positions of the clay mineral. A third adsorption site (Site III) was assumed to be located at the planar surfaces of the clay platelets, the so-called regular exchange sites that exhibit a much lower specific affinity for the  $\text{Cs}^+$ -ion. The capacities and affinities of these sites were found by fitting a three-site ion-exchange model to caesium adsorption isotherms in known electrolyte solutions (Brouwer et al., 1983). For the exchange of caesium against potassium on Morris illite, Brouwer et al. (1983) found that 9.1% of the highly Cs-selective sites (so-called Site I) had a selectivity coefficient ( $\log_{\text{K}}^{\text{Cs}}K_C$ ) of 4.1. The lower affinity sites (so-called Site II) made up 90.9% of the highly Cs-selective sites, with a  $\log_{\text{K}}^{\text{Cs}}K_C$  of 1.4. A somewhat different approach was used by Poinssot et al. (1999) who modelled Cs adsorption at initial Cs concentrations in solution between  $2 \times 10^{-8}$  M and  $7 \times 10^{-5}$  M, using a two-site model. Site I was considered as the FES and Site II was interpreted as an intermediate site. These authors (Poinssot et al., 1999) position this site at the planar clay surfaces, supported by  $^{133}\text{Cs}$  MAS NMR data of Kim et al. (1996). Based on a three-site ion-exchange model similar to that of Poinssot et al. (1999), but including a low affinity/high capacity Site III on the planar illite surfaces, Bradbury and Baeyens (2000) have derived a consistent set of selectivity coefficients for Cs relative to K,  $\text{NH}_4$ , Rb, and Na from the analysis and modelling of a wide range of published Cs sorption data on pure illites. Cs sorption on Fithian illite (Comans et al., 1991), which is used in the present study, was also analysed and well described by their model and parameter set. Finally, Zachara et al. (2002) have recently modelled Cs sorption to micaceous subsurface sediments with a single site for the FES and have found a similar selectivity coefficient ( $\log_{\text{K}}^{\text{Cs}}K_C$ ) of  $4.7 \pm 0.1$  as Bradbury and Baeyens (2000).

Below, we use the model and generic parameter set of Bradbury and Baeyens (2000) to calculate equilibrium Cs sorption to Fithian illite at the different experimental conditions that we have applied to investigate the reversibility of the sorption process. The parameters used are summarised in Table 1. We have adopted this modelling approach to allow for a direct comparison of our experimental results with those of other studies of Cs sorption on illite.

### 3. MATERIAL AND METHODS

#### 3.1. General Setup of the Sorption Experiments

All experiments were performed with Fithian illite, a reference clay mineral, purchased from Ward's Natural Science Establishment Inc. (Rochester, New York). After the clay had been ground, the  $<2 \mu\text{m}$  fraction was separated by sedimentation, mono-saturated with K, Na, or  $\text{NH}_4$ , and stored as suspensions in  $10^{-3}$  M chloride solutions of the saturating ions. Further details on the preparation of the Fithian illite suspensions are similar to those described in Comans et al. (1991). Approximately 1 week before the adsorption/desorption experiments, small amounts of these stock suspensions were diluted to allow for equilibration of the illite at the appropriate background ion concentration used in the experiments.

The caesium concentration used in all adsorption experiments was  $\sim 3.3 \text{ nmol.L}^{-1}$ . Stable Cs concentrations in fresh waters are generally below  $0.15 \text{ nmol.L}^{-1}$  (Hilton et al., 1997), thus our laboratory experiments were performed with Cs concentrations  $\sim 20$  times those found in the natural environment. However, Cs sorption experiments with a range of Cs concentrations have shown that below a Cs concentration in solution of  $10^{-8}$  -  $10^{-9}$  M, sorption to illite occurs at the sites with the highest affinity for caesium (Brouwer et al., 1983; De Preter et al., 1991; Poinssot et al., 1999), and these sites are assumed to control caesium partitioning in the natural environment.

Several experiments were performed to measure radiocaesium desorption from the solid as a function of time, using two different methods: exchange of the adsorbed radiocaesium against a high concentration of a competing ion; or extraction of radiocaesium from the solution with a Cs-selective adsorbent, also referred to as infinite bath desorption (Wauters and Cremers, 1996; Madruga and Cremers, 1997). The general setup of these two types of experiments is discussed below, followed by a detailed description of the individual experiments.  $^{137}\text{Cs}$  adsorption to laboratory materials used in the handling of any solution containing the radiotracer (filters, bottle walls, dialysis membranes, etc.) has been tested and found to be negligible.

#### 3.2. Cs Adsorption Followed by Desorption at High $\text{NH}_4$ Concentrations

The first desorption method, which is commonly used (Schulz et al., 1960; Evans et al., 1983; Konoplev et al., 1996; Smith and Comans, 1996; Rigol et al., 1998), is to exchange the adsorbed radiocaesium from the solid with a high concentration of  $\text{NH}_4$ . In our setup of this experiment, an amount of the appropriate background solution was first prepared and spiked with a known amount of radiocaesium. At the start of the experiment, an amount of preequilibrated illite suspension was added to the solution while the solution was vigorously stirred to promote immediate mixing of illite and the solution. A preequilibration period of approximately 1 week was allowed for the illite suspension before the start of the experiments in  $10^{-4}$  M of the appropriate background solution. During the adsorption and desorption experiments all suspensions were continuously and gently shaken in the dark. After the desired adsorption time, a subsample of approximately 25 mL was taken from the suspension, and 5 mL of this subsample was filtered through a  $0.2 \mu\text{m}$  cellulose acetate filter. The first aliquot was discarded to minimise any influence of the filter on the filtrate, and the radiocaesium activity was counted in the filtrate. The radiocaesium sorption to the solid was calculated from the difference between the initial activity and the activity remaining in solution after adsorption. The remaining approximately 20 mL of the subsample was transferred to acid-cleaned 25 mL polyethylene wide mouth bottles, and within 1 min after taking the subsample from the suspension, an amount of approximately 10 mol/L ammonium acetate ( $\text{NH}_4\text{Ac}$ ) solution was added to the remaining suspension so that the  $\text{NH}_4$  concentration became 1 mol/L. The increased competition caused caesium to be exchanged with  $\text{NH}_4$ . The resulting increase in the concentration of caesium in solution was measured as a function of desorption time. After various desorption times, 5 mL aliquots were taken from the suspension under vigorous stirring to minimise changes in the suspension concentration. The aliquot was filtered through a  $0.2 \mu\text{m}$  cellulose acetate filter and the radiocaesium activity was counted in the filtrate. The amount desorbed was calculated from the difference between the activity in solution and

the activity in solution at the start of the desorption reaction, corrected for the addition of  $\text{NH}_4$  solution.

All activity measurements of this experiment and subsequent experiments were carried out on a LKB Wallac 1282 Compugamma  $\gamma$ -spectrometer with NaI detector.

### 3.3. Cs Adsorption Followed by “Infinite Bath” Desorption

The second desorption method is based on the introduction of a Cs-selective adsorbent into the suspension, which removes radiocaesium from the solution and stimulates the desorption reaction by maintaining a virtually “zero” concentration of radiocaesium in solution. One of the adsorbents suitable for radiocaesium extraction is ammonium ferro hexacyanoferrate ( $\text{NH}_4\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ ). The particular hexacyanoferrate (HCF) used in our experiments is coated on an inert granular substrate and was obtained from Dr. W. Giese (School of Veterinary Medicine, Hannover, Germany). This material has a very high affinity for radiocaesium: we have measured a  $K_D$  of  $2.5 \times 10^4 \text{ L.kg}^{-1}$  in  $1 \times 10^{-4} \text{ M KCl}$  and a  $K_D$  of  $3.9 \times 10^3 \text{ L.kg}^{-1}$  in  $1 \text{ mol/L NH}_4\text{Ac}$ . If sufficient HCF is present in the system, the solution concentration of radiocaesium is extremely low and radiocaesium desorbs from the solid. The rate of radiocaesium uptake by the adsorbent is equal to its intrinsic desorption rate from the solid if three conditions are met: (1) the adsorbent should have sufficient capacity to bind all caesium in the system; (2) the adsorbent should have sufficient affinity for caesium to maintain low caesium concentrations in solution; and (3) the adsorbent (encapsulated in a dialysis membrane) should take up radiocaesium much faster than it is released by the solid, so that the uptake rate by the adsorbent is determined by the desorption rate from the solid. As explained by Madruga (1993) and Wauters et al. (1994), conditions 1 and 2 are met when the amount of adsorbent  $m_a$  (g) with a caesium solid/liquid distribution coefficient of  $K_D^a$  ( $\text{L.kg}^{-1}$ ) is brought into contact with  $m_s$  grams of solid (illite) with a solid/liquid distribution coefficient of  $K_D^s$  ( $\text{L.kg}^{-1}$ ) according to:

$$\frac{K_D^a \times m_a}{K_D^s \times m_s} \geq 10 \quad (1)$$

In our experiments, the ratio was at least 45. The third condition was checked in every experiment by performing a blank experiment to measure the rate of caesium uptake by the adsorbent in a dialysis membrane. The measured uptake rate, expressed in terms of half-life of a first-order reaction, was 8 h maximum.

In view of the boundary conditions discussed above, the general setup of the infinite bath desorption experiment was as follows. After the desired radiocaesium adsorption time, a homogeneous subsample was taken from the illite suspension to measure the radiocaesium adsorbed on the illite particles. Directly afterwards, HCF in a dialysis membrane (Visking 3-20/32", MWCO 12000–14000, pore diameter ca. 25 Å), thoroughly preequilibrated with the electrolyte solution used in the sorption experiments, was introduced into the suspension. The radiocaesium collected on the HCF was measured by taking the dialysis tubing out of the suspension and placing it into a glass tube. The desorbed radiocaesium activity was then measured on a NaI crystal, which took ~10 min, and the dialysis tubing was returned to the same suspension it had been taken from. The procedure could be repeated several times and showed a consistent increase in radiocaesium collected on the HCF as a function of time.

### 3.4. Description and Conditions of Specific Experiments

Four experiments were performed examining radiocaesium sorption/desorption, using one or both of the above desorption methods. The first experiment was aimed at studying radiocaesium sorption and desorption on K-, Na-, and  $\text{NH}_4$ -saturated illite in the presence of  $1 \times 10^{-4} \text{ M KCl}$ , NaCl, or  $\text{NH}_4\text{Ac}$  solution respectively, at a particle concentration ( $\rho$ ) of  $50 \text{ mg.L}^{-1}$  and at ambient temperature ( $15\text{--}30^\circ\text{C}$ ). Solutions were spiked with “carrier-free”  $^{137}\text{Cs}$  tracer, so that the initial activity of  $^{137}\text{Cs}$  in solution was  $\sim 494 \text{ kBq.L}^{-1}$ , corresponding to a caesium mass of  $\sim 3.35 \text{ nmol.L}^{-1}$ . After adsorption times ranging from 5 min to 1400 h, radiocaesium was desorbed from illite by applying 1

mol/L  $\text{NH}_4\text{Ac}$ . Desorption of radiocaesium after each contact time was measured after 15 min, 1 h, 24 h, 2 weeks, and 8 weeks. The maximum adsorption time in the experiment using  $\text{NH}_4$ -saturated illite was only 2 weeks, because it had been found in a separate experiment that the background  $\text{NH}_4$  concentration decreased by 20% in 2 weeks, probably due to (biologic) oxidation.

Further insight into the nature of radiocaesium binding on illite was obtained from three other experiments. The first additional experiment was aimed at measuring radiocaesium adsorption on K-saturated illite ( $I = 1 \times 10^{-4} \text{ M KCl}$ ,  $^{137}\text{Cs} = 494 \text{ kBq.L}^{-1}$ , corresponding to a caesium mass of  $3.35 \text{ nmol.L}^{-1}$   $\rho = 50 \text{ mg.L}^{-1}$ ,  $T = 15\text{--}30^\circ\text{C}$ ) and its subsequent desorption against different concentrations of stable caesium in the range of  $1 \times 10^{-6}$  to  $1 \text{ mol/L CsCl}$ . In this experiment, the adsorbed  $^{137}\text{Cs}$  becomes isotopically diluted (and hence exchanged) by the large amounts of stable caesium in solution. The desorption was studied after 5 min of adsorption. Exchange of  $^{137}\text{Cs}$  was measured after 15 min, 1 h, 24 h, 2 weeks, and 8 weeks. The whole experiment was performed in duplicate.

In a second additional experiment, radiocaesium was adsorbed on K-illite ( $I = 1 \times 10^{-4} \text{ M KCl}$ ,  $\rho = 50 \text{ mg.L}^{-1}$ ,  $T = 21\text{--}23^\circ\text{C}$ ) for 5 min and subsequently desorbed from the illite with  $1 \text{ mol/L NH}_4\text{Ac}$  or with the HCF adsorbent in  $1 \text{ mol/L NH}_4\text{Ac}$ . The desorption of caesium from the illite was followed by measuring the activity of the caesium collected in the dialysis bag with thoroughly preequilibrated HCF. The selectivity of HCF for caesium at  $1 \text{ mol/L NH}_4\text{Ac}$  is still very high ( $K_D \approx 3.9 \times 10^3 \text{ L.kg}^{-1}$ ) compared to illite ( $K_D \approx 2.4 \times 10^2 \text{ L.kg}^{-1}$ ), and the conditions of Equation 1 remain valid. This experiment thus applied the maximum chemical driving force to the illite-adsorbed caesium: a very low concentration of radiocaesium in solution and a high concentration of competing ions in solution. This experiment was performed in triplicate and results were compared with a similar experiment in which exchange was accomplished only by  $1 \text{ mol/L NH}_4\text{Ac}$ .

The third additional experiment involved the desorption of radiocaesium from illite using a range of ammonium concentrations. This experiment was performed in essentially the same manner as the CsCl desorption experiment discussed above. The radiocaesium adsorption times were 5 min and 2 weeks. The desorption reaction was followed for two weeks and the concentrations of ammonium used were 1, 0.01, 0.001, and 0.0001 mol/L  $\text{NH}_4\text{Ac}$ .

## 4. RESULTS

### 4.1. Radiocaesium Sorption and Desorption on K-, Na-, and $\text{NH}_4$ -illite

Results of the caesium adsorption and desorption experiments on K-, Na-, and  $\text{NH}_4$ -saturated illite are shown in Figure 1. The amount of rapidly adsorbed caesium increases in the order  $\text{NH}_4 < \text{K} < \text{Na}$ -saturated illite, consistent with the decreasing competitiveness of the counter-ions. The adsorption and desorption show an initial rapid uptake/release within the first 15 min sampling interval, followed by a much slower process, continuing over weeks to months. Adsorption of  $^{137}\text{Cs}$  on Na-illite decreases somewhat after 800 h of reaction time and is probably related to a slow release of potassium from the illite edge interlayers, causing a noticeably greater competition for Cs adsorption. This hypothesis is corroborated by the findings of Poinsot et al. (1999) who reported the release of potassium from Na-saturated illite at near-neutral pH. Although the trace Cs adsorption-desorption data on the Na-saturated illite are probably influenced by a slow potassium release, they clearly show the effect of a less competitive environment on the adsorption of Cs.

The equilibrium concentrations of  $^{137}\text{Cs}$  adsorbed on K- and  $\text{NH}_4$ -, and Na-saturated illite in the presence of  $10^{-4} \text{ M}$  of  $\text{K}^+$ ,  $\text{NH}_4^+$ , and  $\text{Na}^+$  have been calculated using the 3-site ion-exchange model and generic parameter set of Bradbury and

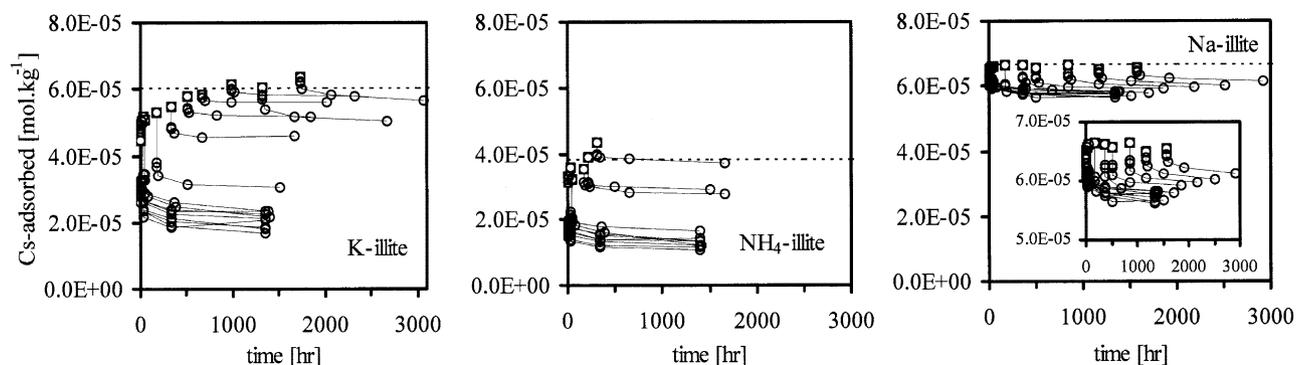


Fig. 1. Adsorption of radiocaesium on K-, Na- and  $\text{NH}_4$ -saturated Fithian illite in  $1 \times 10^{-4}\text{M}$  KCl, NaCl or  $\text{NH}_4\text{Ac}$  background electrolyte (■). Subsequent desorption of  $^{137}\text{Cs}$  was accomplished by exchange against 1 mol/L  $\text{NH}_4\text{Ac}$  (○). Broken lines indicate predicted equilibrium concentrations of  $^{137}\text{Cs}$ , based on ion-exchange calculations using parameters from Table 1.

Baeyens (2000). The parameters used are summarised in Table 1 (only the frayed edge sites, Site I, are involved at the experimental conditions). The predicted values are shown in Figure 1 and compare well with the measured amounts of Cs sorbed to illite in these electrolyte solutions after long reaction times.

The amount of rapidly desorbed radiocaesium decreases with the adsorption time, in accordance with earlier observations of a progressively stronger binding between Cs and illite with increasing reaction time (e.g., Mundschenk, 1983; Comans et al., 1991; Absalom et al., 1995). The slow rate of desorption, operationally defined as the desorption occurring after more than 24 h desorption time, was interpreted in terms of a first order process. The rate of desorption was calculated from the slope of the line fitted through the linearised desorption data (three examples are shown in Fig. 2). The average rates of slow desorption, determined after 5 min to 1400 h adsorption are 1.0, 2.5, and 3.9 yr for  $\text{NH}_4$ -, K-, and Na-illite, respectively (note that desorption rates given in Figure 2 are for 168 h adsorption).

One of the most striking results of our experiments is that after only 5 min of contact between caesium and illite, no

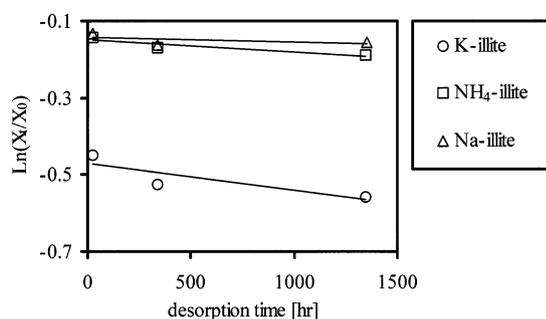


Fig. 2. Three examples of the linearised desorption data of  $^{137}\text{Cs}$  from K-, Na-, and  $\text{NH}_4$ -saturated Fithian illite after approximately 168 h adsorption time. The desorption curves have been linearised by plotting the natural logarithm of the fraction of  $^{137}\text{Cs}$  remaining adsorbed to illite ( $\ln X_t/X_0$ ) as a function of the desorption time. The rate of desorption was derived from the slope of the linear regression lines. The fitted regression lines are for K-illite  $Y = -7.0 \times 10^{-5}X - 0.47$ ,  $R^2 = 0.75$ ;  $\text{NH}_4$ -illite  $Y = -3.1 \times 10^{-5}X - 0.49$ ,  $R^2 = 0.89$ ; and Na-illite  $Y = 1.3 \times 10^{-5}X - 0.14$ ,  $R^2 = 0.32$ ; corresponding to desorption half-lives of 1.1, 2.5 and 5.9 yr, respectively.

complete exchange of radiocaesium against 1 mol/L  $\text{NH}_4\text{Ac}$  is observed. For  $\text{NH}_4$ -, K-, and Na-saturated illite, the amount remaining adsorbed after 8 weeks of desorption was 44%, 46%, and 91%, respectively, of the initial amount adsorbed. The “equilibrium” concentrations of  $^{137}\text{Cs}$  adsorbed on K- and Na-illite in a 1 mol/L  $\text{NH}_4\text{Ac}$  solution were measured in an 800 h adsorption experiment and were found to be  $9.30 \times 10^{-7}\text{mol.kg}^{-1}$  and  $6.65 \times 10^{-7}\text{mol.kg}^{-1}$ , respectively. These results indicate that the desorption reaction is still far from equilibrium after 8 weeks of reaction in 1 mol/L  $\text{NH}_4\text{Ac}$ . Incomplete exchange of caesium against 0.1 mol/L  $\text{KNO}_3$  after only short caesium adsorption times (0.5 d) has also been observed by Zachara et al. (2002) for Na-saturated micaceous subsurface sediments from the Hanford site.

The apparent irreversibility of radiocaesium sorption as measured by ion exchange has been attributed to the slow migration of caesium into the interlayers of the illite clay mineral, from where it can only be slowly removed (Evans et al., 1983; Comans et al., 1991; Comans and Hockley, 1992). Our present observation that the radiocaesium sorbed after only 5 min is already largely nonexchangeable is inconsistent with this hypothesis, because interlayer migration is a very slow process. De Haan et al. (1965) measured an interlayer migration distance of  $^{40}\text{K}$  of  $\sim 4 \text{ \AA}$  in 2 yr for two illite-containing clays.

Two hypotheses have been postulated in the literature to explain the apparent irreversibility of radiocaesium sorption after relatively short adsorption times. The first is that the frayed edge site structure of the clay minerals collapses under the influence of high concentrations of adsorbed alkali metal ions, thus preventing the further release of radiocaesium (Madruca, 1993; Absalom et al., 1995; Absalom et al., 1996). Alternatively, Sparks (1989) argued that when the ion-exchange method is used in a batch procedure, a relatively high concentration of the desorbed species (i.e.,  $^{137}\text{Cs}$ ) builds up in solution, which could inhibit further adsorbate release from the solids. A similar mechanism has been found for the extraction of interlayer potassium from micas, where the presence of very small amounts of potassium in the solution inhibited the further extraction of interlayer potassium (Hanway et al., 1957; Scott et al., 1960).

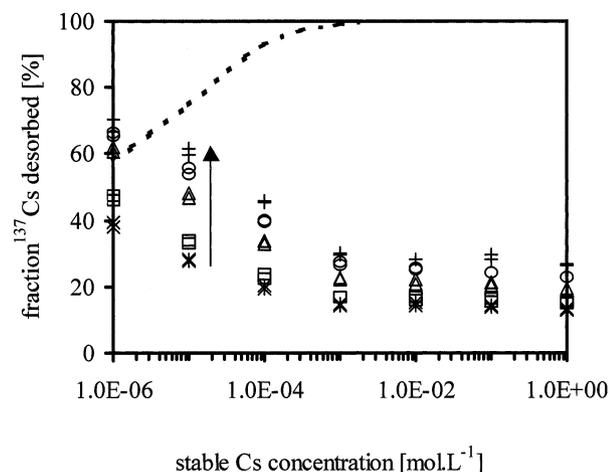


Fig. 3. Exchange of  $^{137}\text{Cs}$  adsorbed on K-saturated illite in a background of  $1 \times 10^{-4}$  M KCl against stable caesium. Concentrations of stable caesium in the experiment ranged from  $1 \times 10^{-6}$  to  $1 \text{ mol/L}$ . Desorbed radiocaesium is shown as a fraction of the initially adsorbed amount after 15 min (\*), 1 h ( $\square$ ), 24 h ( $\Delta$ ), 2 weeks ( $\circ$ ) and 8 weeks (+) as a function of added stable caesium concentrations in the experiment. The broken line indicates predicted values for  $^{137}\text{Cs}$  desorption from illite resulting from isotopic exchange with stable Cs, based on ion-exchange calculations using parameters from Table 1 (see text for further details). Desorption time increases in the direction indicated by the arrow.

#### 4.2. Exchange of Adsorbed Radiocaesium Against Different Concentrations of Cs

To test the hypothesis that high concentrations of alkali metals sorbed on the frayed edges may hinder the radiocaesium desorption reaction, its desorption was measured by exchange with “high” concentrations of stable caesium ( $^{133}\text{Cs}$ ). We used stable caesium because the stable isotope should be able to fully exchange with  $^{137}\text{Cs}$ , so that rather low levels of stable Cs in solution could, in principle, lead to 100%  $^{137}\text{Cs}$  desorption. The caesium mass present in the system during the adsorption reaction was approximately  $3.35 \text{ nmol.L}^{-1}$ , whereas the lowest stable caesium concentration during the desorption reaction was  $1 \text{ }\mu\text{mol.L}^{-1}$ . However, sorption of stable caesium on illite significantly reduces the caesium concentration in solution at the lower radiocaesium concentrations applied. Thus, assuming that all radiocaesium is isotopically exchangeable, nearly complete desorption can only occur at added stable caesium concentrations of  $1 \times 10^{-3}$  M and higher, because even when all planar exchange sites are occupied by caesium, 98% of all caesium will be in solution at these concentrations.

Desorption of  $^{137}\text{Cs}$  was measured after 5 min of  $^{137}\text{Cs}$  adsorption on K-illite in a background of  $1 \times 10^{-4}$  M KCl. As was argued above, we expected that the slow migration of radiocaesium into the interlayers after such a short adsorption time would not play a significant role, and thus, that all radiocaesium was accessible for (isotopic) exchange against  $^{133}\text{Cs}$ . Figure 3 shows the fraction of  $^{137}\text{Cs}$  desorbed from illite after 15 min, 1 h, 24 h, 2 weeks, and 8 weeks as a function of the Cs concentration added at the start of the desorption experiment. Clearly, the greatest displacement of  $^{137}\text{Cs}$ , 68% after 8 weeks of desorption, is measured at the lowest added stable Cs con-

centration, i.e.,  $1 \times 10^{-6}$  M. The smallest fraction desorbed is measured at added stable Cs concentrations between  $1 \times 10^{-4}$  and  $1 \text{ mol/L}$  and is approximately 28% after 8 weeks of desorption. This amount is comparable to what has been found for the desorption of  $^{134}\text{Cs}$  from illite-containing suspended matter from the river Rhine, using  $1000 \text{ mg.L}^{-1}$   $\text{Cs}^+$  and 0.1 h contact time, (31%; Mundschenk, 1983).

This result indicates that high concentrations of caesium prevent the release of radiocaesium from the frayed edge sites, possibly by inducing a collapse of the expanded illite edges, that are believed to be hydrated (Jackson, 1968). The fact that hydrated interlayer spacings of clay minerals can dehydrate and collapse due to the sorption of large amounts of caesium has been observed for vermiculite. Vermiculite is a normally expanded clay mineral with 14 Å interlayer spacing, and with Mg and Ca sandwiched between the clay platelets (Douglas, 1989). It has been observed (Jacobs and Tamura, 1960; Coleman et al., 1963) that caesium sorption increases the affinity of the vermiculite clay for caesium due to collapse of the vermiculite lattice and reduction of the interlayer spacing to  $\sim 10$  Å, the dehydrated interlayer spacing. This mechanism of caesium sorption on vermiculite is corroborated by  $^{133}\text{Cs}$  MAS NMR data, which show that at high concentrations sorbed on vermiculite, caesium is present in dehydrated form (Weiss et al., 1990a; Weiss et al., 1990b).

The desorption pattern of  $^{137}\text{Cs}$  under the influence of high Cs concentrations is similar to that at high ammonia concentrations, with most of the  $^{137}\text{Cs}$  exchange taking place within 15 min, and slow desorption continuing for over 8 weeks. This slow  $^{137}\text{Cs}$  release, between 24 to 1344 h at a high concentration ( $1 \times 10^{-3}$  to  $1 \text{ mol/L}$ ) of stable Cs in solution, has a half-life ( $\pm$  standard deviation, based on duplicate measurements) of  $1.57 \pm 0.17$  yr, which is of the same order as the rate of radiocaesium desorption from K-, Na-, and  $\text{NH}_4$ -saturated illite in  $1 \text{ mol/L}$   $\text{NH}_4$ . This observation supports the idea that a high  $\text{NH}_4$  concentration induces a collapse of the frayed edges and that the slow rate of exchange from the collapsed sites has a half-life of the order of two yr. At a CsCl concentration of  $1 \times 10^{-4}$  M, the half-life of the reaction rate decreases to  $0.94 \pm 0.02$  yr, and at  $1 \times 10^{-5}$  M CsCl even to  $0.87 \pm 0.04$ . At these concentrations, some of the frayed edges may still be collapsed because not all radiocaesium is immediately exchanged, but the higher exchange rates suggest that the collapse is less pronounced.

Using the 3-site ion-exchange model and generic parameter set of Bradbury and Baeyens (2000), we have calculated the amount of  $^{137}\text{Cs}$  that is expected to desorb as a result of isotopic exchange by the amount of stable Cs that adsorbs at the applied concentration range to K-illite in a background of  $1 \times 10^{-4}$  M KCl. The parameters used are summarised in Table 1. The predicted values are indicated by the broken line in Figure 3. Clearly, the measured desorption at high stable Cs concentrations is far less than predicted if all adsorbed  $^{137}\text{Cs}$  would be able to participate in the isotopic exchange with stable Cs. The hysteresis between the predicted and measured desorption decreases towards lower stable Cs concentrations. At  $1 \times 10^{-6}$  M CsCl, the predicted desorption by isotopic exchange is  $\sim 60\%$ , rather than 100%, because a significant amount of the added stable Cs is adsorbed at the frayed edge sites. Compared to the calculated 60%, a maximum of 68% of the sorbed radiocaesium

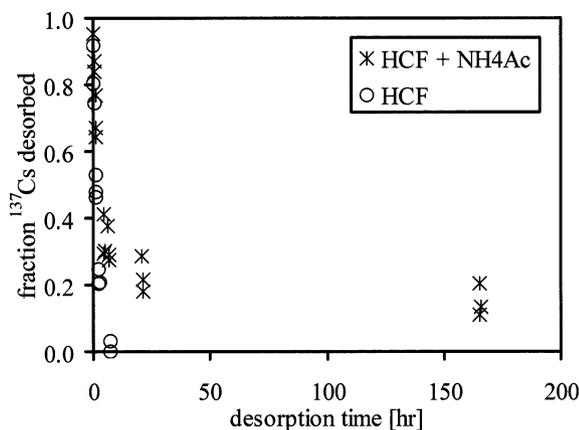


Fig. 4. Desorption of  $^{137}\text{Cs}$  from K-saturated illite after 5 min of adsorption in  $1 \times 10^{-4}$  M KCl in the presence of a Cs-selective HCF resin (○) (background of  $10^{-4}$  M KCl) and using both HCF resin and 1 mol/L  $\text{NH}_4\text{Ac}$  (\*). Desorbed radiocaesium is shown as the fraction remaining in suspension as a function of time.

was exchanged in this experiment at  $1 \times 10^{-6}$  M CsCl, indicating that collapse of the frayed edges no longer hindered  $^{137}\text{Cs}$  desorption. We believe, therefore, that all radiocaesium is exchangeable against stable caesium within 8 weeks (and largely within 2 weeks) at the applied concentration of  $1 \times 10^{-6}$  M CsCl.

#### 4.3. Radiocaesium Reversibility Measured by HCF and HCF + 1 mol/L $\text{NH}_4\text{Ac}$

The cause of the apparent rapid “fixation” process of radiocaesium was also examined using a Cs-selective hexacyanoferrate (HCF) resin to stimulate desorption of  $^{137}\text{Cs}$  adsorbed on illite. The hypothesis that rapid “fixation” of radiocaesium can also be induced by high concentrations of  $\text{NH}_4$  was explicitly investigated by a parallel experiment in which desorption was initiated by adding both HCF and 1 mol/L  $\text{NH}_4$ . Figure 4 shows that radiocaesium adsorbed on illite in 5 min can indeed be rapidly and completely removed, i.e., is reversibly bound. However, when 1 mol/L  $\text{NH}_4$  is present, a substantial fraction (15%) of the radiocaesium is retained by the clay and can apparently only be very slowly desorbed. Initial release also seems slower in the presence of 1 mol/L  $\text{NH}_4$ . As indicated in the methods section, the capacity and affinity of the HCF in 1 mol/L  $\text{NH}_4$  is sufficient to desorb all radiocaesium from illite in this experiment.

We take the findings in Figures 3 and 4 as strong indications that high concentrations of alkali metals and ammonium “trap” the illite-bound radiocaesium by collapsing the frayed edge sites of the illite clay. However, results in Figures 1 and 4 also show that the increased  $^{137}\text{Cs}$  concentration in solution during a batch ion-exchange experiment can limit the desorption of radiocaesium from illite, as argued by Sparks (1989). A comparison of the experiment in which  $^{137}\text{Cs}$  was adsorbed on K-illite and subsequently desorbed by applying 1 mol/L  $\text{NH}_4\text{Ac}$  (Fig. 1), and that in which both the HCF adsorbent and 1 mol/L  $\text{NH}_4\text{Ac}$  were used for the desorption reaction, (Fig. 4) shows that a significantly greater amount of radiocaesium was

desorbed in the latter experiment (85% using HCF + 1 mol/L  $\text{NH}_4\text{Ac}$  vs. 59% using only 1 mol/L  $\text{NH}_4\text{Ac}$ ) in which the build up of  $^{137}\text{Cs}$  in solution was prevented.

#### 4.4. Exchange of Adsorbed Radiocaesium Against Different Concentrations of $\text{NH}_4$

The above experiments show that both high concentrations of  $\text{NH}_4$  and Cs solutions can cause a collapse of the frayed edges of illite. Since in the natural environment rather high levels of ammonium can occur in the pore water of anoxic freshwater sediments (e.g., up to  $6.7 \text{ mmol.L}^{-1}$  was measured by Smith and Comans, 1996), it is important to know to what extent these concentrations may induce frayed edge-site collapse and hinder in situ desorption from contaminated sediments. It is equally important to know the concentrations of alkali metals where frayed edge site collapse does not take place and exchange between Cs and the alkali metal is fast and reversible. Therefore, radiocaesium desorption from illite was measured as a function of time and ammonium concentration.

Figure 5 shows the desorption of radiocaesium from illite as a function of time at 1, 0.01, 0.001, and 0.0001 mol/L  $\text{NH}_4\text{Ac}$  after adsorption times of 5 min and 2 weeks. Figure 5 also shows predicted amounts of radiocaesium sorbed on the illite sample at the various  $\text{NH}_4$  concentrations used, based on the 3-site ion-exchange model and generic parameters of Bradbury and Baeyens (2000). The parameters used are summarised in Table 1 (only the frayed edge sites, Site I, are involved at the experimental conditions).

There are no great differences between caesium desorption at 1 and 0.01 mol/L  $\text{NH}_4\text{Ac}$ . Approximately the same amounts of radiocaesium are desorbed at the same rate. At 0.001 mol/L  $\text{NH}_4\text{Ac}$ , slightly more radiocaesium desorbs from the clay, although the calculated equilibrium Cs concentration is much higher. At  $1 \times 10^{-4}$  M  $\text{NH}_4\text{Ac}$  the desorption of radiocaesium quickly attains the calculated equilibrium Cs concentration. This suggests that radiocaesium solid/liquid partitioning below  $1 \times 10^{-4}$  M of competing ions follows reversible ion exchange according to the 3-site ion-exchange model and generic parameters of Bradbury and Baeyens (2000), if sufficient reaction time (weeks) is allowed. These findings also suggest that a limited reversibility of Cs sorbed on illite can be induced by the high pore water  $\text{NH}_4$  concentrations in anoxic sediments.

## 5. DISCUSSION

Our results show that the highly selective binding of radiocaesium to illite is a reversible ion-exchange reaction as long as alkali metal concentrations in solution do not exceed a critical level, which is  $\sim 1 \times 10^{-4}$  M for  $\text{NH}_4$  and  $8 \times 10^{-7}$  M for Cs. At higher concentrations of these ions frayed edge site collapse may be induced, resulting in an apparent fixation of adsorbed radiocaesium. Although we have not demonstrated this effect for potassium, this alkali metal may have a similar effect on the reversibility of radiocaesium sorption to illite. Although this would need to be experimentally verified, the critical potassium level may be somewhat higher than that of  $\text{NH}_4$ , given the one order of magnitude lower affinity of K for the frayed edge sites, relative to  $\text{NH}_4$  ( $\log_{\text{K}}^{\text{NH}_4} K_{\text{C}} = 1.1$ ; Bradbury and Baeyens, 2000).

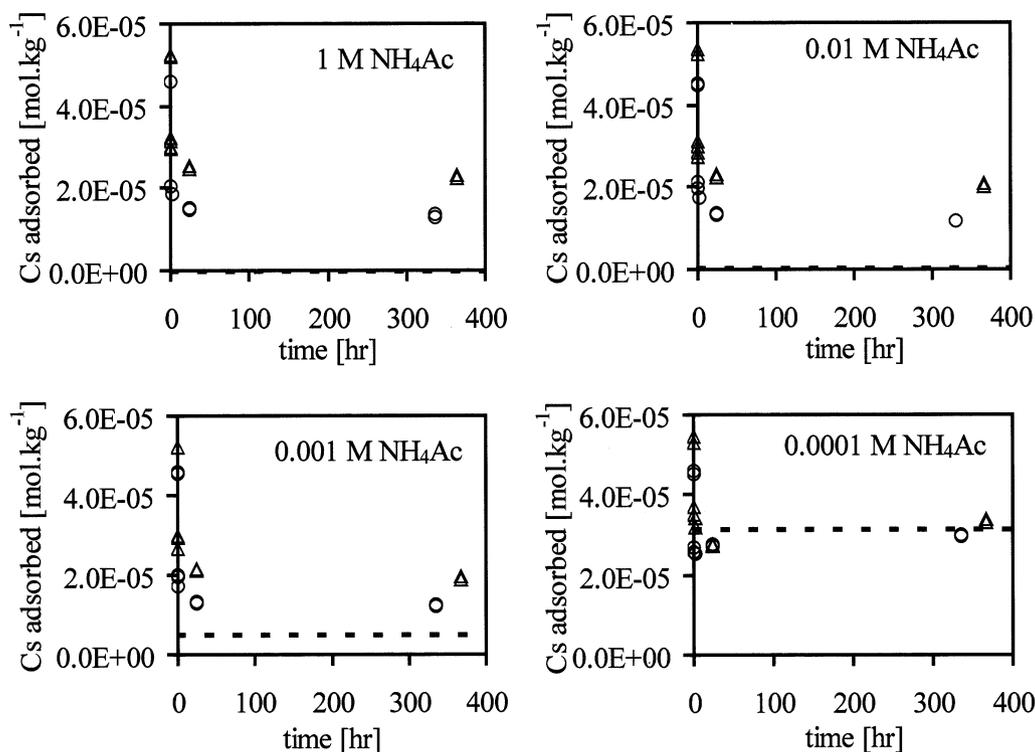


Fig. 5. Radiocaesium desorption from K-saturated illite after 5 min (○) and two weeks (Δ) of contact time between caesium and illite, applying different concentrations of NH<sub>4</sub>Ac. Replicate measurements are shown. The amount of caesium adsorbed on illite is shown as a function of time. Broken lines indicate predicted equilibrium concentrations at the given ammonium concentration, based on ion-exchange calculations using parameters from Table 1.

Similar observations of a high degree of radiocaesium sorption reversibility were provided by Grütter et al. (1990), who studied caesium sorption/desorption on grain size fractions (<2 mm) of quaternary glaciofluvial deposits containing substantial amounts of illite. They found that at low caesium surface loading of the samples (Cs concentration <1 × 10<sup>-8</sup> M), and after 7 d of adsorption, complete desorption of caesium was possible in weeks to months using successive equilibration with caesium-free solutions. Loading the solid with a low caesium concentration (Cs concentration 1 × 10<sup>-8</sup> M) and subsequent exchange against solutions containing nonlabelled caesium in the concentration range 1 × 10<sup>-8</sup>-1 × 10<sup>-7</sup> M for 7 d showed that all caesium was exchangeable within the experimental error. At higher caesium loading of the samples, desorption was found to be incomplete, in agreement with our proposed mechanism of caesium fixation by a collapse of the frayed edges.

Given our findings that NH<sub>4</sub> concentrations of ~10<sup>-4</sup> M and higher affect the reversibility of radiocaesium sorption on illite by inducing a collapse of the frayed edges, it is quite possible that this process is effective in anoxic sediments. Ammonium concentrations in pore water from these environments may exceed several mmol.L<sup>-1</sup> and thus affect in situ radiocaesium reversibility. Indications for this in situ collapse have come from Smith and Comans (1996), who noticed that the lower parts of anoxic sediments, where NH<sub>4</sub> concentrations were very high, also showed very high radiocaesium sorption reversibility (23% to 31% of the particle-bound radiocaesium, compared to 0.5 to 9% in the upper sediment layers), as measured with 0.1 mol/L NH<sub>4</sub> extraction. Smith and Comans (1996) ascribed

these observations to changing properties of the lower sediment layers. However, later observations on four freshwater sediments from The Netherlands and the United Kingdom (Comans, 1998) showed that the high reversibility of radiocaesium in the lower part of anoxic sediments is a more general, and to date, unexplained phenomenon. We believe that our present observations enable a mechanistic explanation of these findings. In the lower layers of these sediment cores, radiocaesium must have originated and migrated downward from the peak reflecting the primary contamination event, e.g., fallout from Chernobyl and/or nuclear weapons testing, and thus have adsorbed to illite in a high-NH<sub>4</sub> environment. If the collapse of the frayed edges occurred before radiocaesium adsorption, a high sorption reversibility, as measured by 0.1 mol/L NH<sub>4</sub> extraction, is expected. A further collapse of the frayed edges during the extraction procedure will be limited, resulting in a relatively high <sup>137</sup>Cs sorption reversibility, as observed by Smith and Comans (1996) and Comans (1998).

In general, we believe that our new experimental results and mechanistic interpretation bridge the apparent inconsistency between laboratory findings and in situ observations with regard to radiocaesium sorption reversibility that was discussed in the introduction. In particular, our mechanistic interpretation of the competitive ion-exchange of radiocaesium, ammonium, and potassium on illite is consistent with (in situ) observations of reversible sorption behaviour of radiocaesium in aquatic sediments (Evans et al., 1983; Smith and Comans, 1996; Comans, 1999), as well as the observed persistence of this radionuclide in water and food products (fish and vegetation) for

many years following the Chernobyl accident (Smith et al. (2000) discuss the relationship between radiocaesium sorption reversibility on illite and uptake in food products in more detail). It also explains the recent observations by Zachara et al. (2002) of incomplete exchange of caesium against 0.1 mol/L  $\text{KNO}_3$  on Na-saturated micaceous subsurface sediments from the Hanford site after only short caesium adsorption times.

## 6. CONCLUSIONS

Laboratory experiments showed that radiocaesium desorption, after only 5 min of adsorption, is incomplete when induced by high concentrations of alkali metals in a batch experiment, but is complete when induced by an "infinite bath" procedure using a Cs-selective adsorbent. The incomplete exchangeability of radiocaesium, that is generally observed when extracting contaminated mineral sediments with high-concentration  $\text{NH}_4$  solutions, is believed to be caused by  $\text{NH}_4$ -induced collapse of the frayed edges of illite clays where radiocaesium is adsorbed, and the build up of relatively high concentrations of (desorbed) radiocaesium in the solution. Consequently, the commonly applied high- $\text{NH}_4$  extractions underestimate true exchangeable amounts. An "infinite bath" procedure using a Cs-selective adsorbent is to be preferred.

Radiocaesium sorption in natural waters with less than  $1 \times 10^{-4}$  M of  $\text{NH}_4$  follows reversible ion exchange if sufficient reaction time (weeks) is available. Since  $\text{NH}_4$  concentrations above  $1 \times 10^{-4}$  M can collapse the frayed edges of illite, and these concentrations can occur in anoxic freshwater sediments, the effect of frayed edge site collapse may influence partitioning of radiocaesium in anoxic freshwater sediments.

In general, the results of this study bridge the apparent earlier inconsistency between laboratory experiments and in situ observations with regard to radiocaesium sorption reversibility, in particular, the largely reversible sorption behaviour of radiocaesium in aquatic sediments and the observed persistence of this radionuclide in water and food for many years following the Chernobyl accident. Based on these findings, we believe that radiocaesium sorption reversibility in the natural environment is much higher than generally assumed and that equilibrium solid/liquid partitioning may be assumed for the long-term modelling of radiocaesium mobility in the natural environment.

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