

INTERACTIONS OF RADIOACTIVE AND STABLE CESIUM WITH HYDROXY-INTERLAYERED VERMICULITE GRAINS IN SOILS OF THE SAVANNAH RIVER SITE, SOUTH CAROLINA, USA

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Abstract—Sorption and fixation of Cs by the upland soils of the US Department of Energy's Savannah River Site (SRS) have been attributed to micaceous grains consisting mostly of hydroxy-interlayered vermiculite (HIV). Results of experiments to characterize SRS soil samples, to examine aspects of their radiocesium sorption, and to determine how much of their natural Cs is accessible for chemical extraction and isotope dilution are presented in support of mechanistic hypotheses to explain Cs sorption and fixation in HIV grains. The HIV is responsible for most of the soil cation exchange capacity, and concentrations of naturally occurring Cs, Rb, and K in soil samples are closely related to the concentration of HIV. Experiments with ¹³⁷Cs to examine (1) sorption kinetics, (2) blocking of exchange sites with silver thiourea, and (3) susceptibility of sorbed ¹³⁷Cs to chemical extraction, support the idea that added Cs is sorbed at different kinds of cation exchange sites in HIV grains. Sites highly selective for Cs but relatively few in number are inferred to exist in interlayer wedge zones within such grains. Little of the naturally occurring Cs in the soil samples was extractable by chemical agents that would remove Cs from ordinary cation-exchange sites and from within non-silicate soil components. Furthermore, most of the natural Cs was inaccessible for isotope dilution under slightly acidic conditions approximating the natural soil environment. These observations support the idea that most of the Cs in these soils has become effectively fixed in the narrower parts of interlayer wedge zones. Control of Cs uptake and fixation by highly Cs-selective interlayer wedge sites would account for the large distribution coefficients found for ¹³⁷Cs at the low aqueous Cs concentrations typical of environmental systems and also for the relatively large concentrations of stable Cs in the SRS soils.

Key Words—Hydroxy-interlayered Vermiculite, Interlayer Wedge Zones, Isotope Dilution, Natural Cesium, Radiocesium, Savannah River Site, Soil, Sorption.

INTRODUCTION

Sorption of ¹³⁷Cs in soil has been studied widely because it is a major fission product that exists in the environment as a consequence of fallout from nuclear weapon tests, discharges from nuclear facilities, and seepage from radioactive waste basins. Extensive handling and storage of ¹³⁷Cs at the U.S. Department of Energy's Savannah River Site (SRS) has stimulated attempts to predict its retention by soil and the extent of its subsurface movement. Interactions of ¹³⁷Cs with SRS soils and sediments have been studied since soon after plant operations began about 60 years ago (Prout, 1958; NCRP, 2006).

Kaolinite and hydroxy-interlayered vermiculite (HIV) are by mass the predominant clay minerals in the sandy coastal-plain soils of the southeastern U.S. (Harris *et al.* 1992a), including the upland soils that occupy most of the SRS area (Ruhe and Matney, 1980; Kaplan *et al.*, 1996, 1997; Segall *et al.*, 2000). They are also the predominant phyllosilicates in the fine fractions of bottom sediments from SRS streams (Elprince *et al.*, 1977). Favored Cs sorption within interlayer wedge zones of hydroxy-interlayered clay, where expanded interlayers grade into the closed interlayers characteristic of mica, has been considered equivalent to the well known high selectivity for Cs in wedge zones at frayed edges of illite particles (Elprince *et al.*, 1977). In highly weathered micaceous particles that are now mostly HIV [hereinafter, HIV grains], interlayer wedge sites should have much greater affinity for Cs than the sites on or between the planar structural layers, but these interlayer wedge sites are relatively few in number (Rich and Black, 1964; Barnhisel and Bertsch, 1989).

Cs solid-liquid distribution coefficients for five SRS soil samples were determined by Goto *et al.* (2008). The values

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DOI: 10.1346/CCMN.2014.0620301

varied widely, from 2600 dm³ kg⁻¹ to 4.7 dm³ kg⁻¹, with variations in pH, amounts of added Cs and Na, and cation exchange capacity (CEC) of the soil. Equilibrium constants, based on the CEC, ion concentrations in solution, and Freundlich isotherm exponents were the same for all five soils, however, and permitted prediction of distribution coefficients within 50%. The Cs sorption by the SRS soils was inferred by Goto *et al.* (2008) to be primarily by HIV grains and to occur at distinctly different types of ion exchange sites, including relatively few interlayer wedge sites that are highly selective for Cs. The Cs/K ratios in the same five SRS soil samples were found by Wampler *et al.* (2012) to be notably larger than the Cs/K ratio for the upper continental crust and larger than that ratio in soils from other regions of the U.S. Those authors presented evidence that only ~2% of the SRS soil Cs is native to the mica remnants in HIV grains and attributed the high Cs/K ratios to uptake and fixation of naturally occurring Cs in interlayer wedge zones of HIV grains during pedogenesis. K-Ar age values of ~300 million years were determined by Naumann *et al.* (2012) for clay fractions of the same soil samples, providing direct support for the idea (Harris *et al.*, 1992a) that nanoscale remnants of the original mica are present in HIV grains that formed by extensive weathering of detrital mica.

The research reported herein is complementary to the work reported by Goto *et al.* (2008), Wampler *et al.* (2012), and Naumann *et al.* (2012). In the present study, two hypotheses developed during the earlier studies were addressed by establishing the mineralogical character of the soil samples and by examining additional aspects of the behavior of Cs in the soils. The first hypothesis is that sorption of Cs by the SRS soils is primarily by HIV grains at two or more kinds of sites, including highly Cs-selective sites in interlayer wedge zones (Goto *et al.*, 2008). The second is that Cs sorbed by HIV grains becomes fixed by slow migration into the narrower parts of the interlayer wedge zones (Wampler *et al.*, 2012). Specifically described are results of: (1) soil characterization experiments to provide semi-quantitative values for HIV content of the soil clay, so the relationship of Cs, Rb, and K contents to HIV content could be examined; (2) experiments on Cs-uptake kinetics and on the blocking of Cs uptake by silver thiourea (AgTU), to provide insight into the character of the cation exchange sites of HIV grains; (3) sequential extractions of both recently added Cs and naturally occurring Cs, to provide information on how these were distributed in soil materials; and (4) an analysis of published data, to show by isotope dilution the amount of natural Cs in sites accessible to added aqueous Cs.

MATERIALS AND METHODS

Materials

The five near-surface soil samples tested in the present study are from five soil series considered

representative of soil groups that occupy about three-fourths of the SRS area (Rogers, 1990). The samples were collected from uncontaminated site areas in 1996 (Findley, 1998; for locations see Goto, 2001, figure 4-1) from depths that correspond (Looney *et al.*, 1990) to the B horizons of the Fuquay, Orangeburg, and Vacluse series; to the E horizon of the Blanton series; and to the C horizon of the Lakeland series. The soils are acidic and have small clay contents and correspondingly small CEC values (Table 1).

Soil characterization

Test portions of the soil samples were treated with Na acetate-acetic acid solution (pH 5) to remove any carbonate cementing agents; Fe oxides were removed by the citrate-bicarbonate-dithionate method (Kunze and Dixon, 1986). The remaining solids were then separated by timed sedimentation into sand (>50 μm), silt (2–50 μm), and clay (<2 μm) fractions on the basis of procedures and settling tables provided by Jackson (1969). The separated fractions were oven-dried at 50°C and then weighed to determine the mass of each relative to the total. [The mass fraction of the clay only was reported by Goto *et al.* (2008).] Potassium was determined on portions of the bulk soil samples (3–5 decigrams, dg) and of the clay fractions (0.5–1.5 dg) by flame atomic absorption spectrophotometry of test solutions prepared after digestion of the silicates in a mixture of HF, HNO₃, and HClO₄. After excess acids had been evaporated from the digestates, each residue was taken up in a weighed amount of an acidic CsCl solution (0.1 mol kg⁻¹ HNO₃, 0.01 mol kg⁻¹ CsCl, both reagent grade). The Cs served as an ionization suppressant in the flame. Readings of absorbance at 766.5 nm for these test solutions were compared with those for reference solutions of known K concentration prepared from standard KCl (SRM 999, US National Institute of Standards and Technology).

A portion of each Na⁺-saturated clay fraction was deposited from slurry onto a glass slide for X-ray diffraction (XRD) measurements after, successively, (1) air drying, (2) ethylene-glycol saturation for 24 h at room temperature, and (3) heating to 550°C for 1 h. Another portion of each clay fraction was saturated with K⁺ (KCl, 1 mol dm⁻³) before deposition on a slide for XRD measurements after, successively, (1) air drying and (2) heating at 300°C for 1 h. CuKα radiation (Philips Model 12045 generator) diffracted by the oriented clay was filtered with a graphite monochromator. A theta-compensating slit was used to maintain constant the area of clay irradiated by the X-ray beam. Diffraction data were recorded from 2 to 32°2θ in steps of 0.02°2θ for either 1.0 s or 2.0 s per step controlled by an MDI Databox (Materials Data, Inc., Livermore, California, USA).

Semi-quantitative values for the proportions of kaolinite, HIV, and quartz in the clay fractions of the

Table 1. Sample properties from previous studies.

Soil series	Sample number*	Depth* (cm)	pH*	Sand* (%)	Silt* (%)	Clay (%)	CEC (cmol kg ⁻¹)	Cs (mg kg ⁻¹)	K ⁺ (g kg ⁻¹)	K in clay [§] (g kg ⁻¹)		
Fuquay	42	122–152	5.29	76	7	18*	17.8 [†]	5.3*	4.5 [†]	4.2 [‡]	1.37	5.9
Orangeburg	46	56–81	5.60	76	8	16*	13.9 [†]	3.8*	3.1 [†]	2.9 [‡]	1.12	5.2
Lakeland	2	51–76	5.06	88	6	6*	8.0 [†]	1.5*	1.1 [†]	1.2 [‡]	0.74	5.6
Blanton	35	25–51	5.13	92	6	2*	1.8 [†]	1.5*	1.5 [†]	1.2 [‡]	0.55	8.3
Vaughan	12	66–91	5.18	96	3	1*	1.6 [†]	0.5*	0.9 [†]	0.5 [‡]	0.29	6.6

* Findley (1998)

† Goto *et al.* (2008)‡ Wampler *et al.* (2012)§ Naumann *et al.* (2012)

SRS soils were calculated from XRD peak heights by solution of three equations for each clay fraction,

$$w_1 = 1.07w_3h_1/h_3, \quad (1)$$

$$w_2 = 0.6w_3h_2/h_3, \text{ and} \quad (2)$$

$$w_1 + w_2 + w_3 + w_4 = 1 \quad (3)$$

where w_i denotes the mass fraction of mineral i in the clay fraction; the subscripts 1, 2, 3, and 4 denote HIV, quartz, kaolinite, and gibbsite, respectively; and h_1 , h_2 , and h_3 are the heights above background of the XRD peaks at 1.4 nm, 0.425 nm, and 0.71 nm, respectively. Equations 1 and 2 are based on equations 10 and 11 of Karathanasis and Hajek (1982), but h_3 was measured at 0.71 nm rather than at 0.70 nm and a factor 0.6 has been added to the right-hand term of equation 2 to correct for the relatively larger area of clay irradiated at 20.9°2θ through the theta-compensating slit used in the present study than through the 1° divergence slit used by Karathanasis and Hajek. To solve the equations for the unknown mass fractions, w_1 , w_2 , and w_3 required a value for w_4 , the mass fraction of gibbsite, for each clay fraction. The values used for gibbsite content were 15% for the Orangeburg clay fraction and 10% for the Blanton clay fraction, as reported by Kaplan *et al.* (1997) for clay fractions from corresponding horizons, and an assumed value of 10% for the clay fractions of the other samples.

Cs-137 uptake kinetics

The rate of ¹³⁷Cs uptake at room temperature by bulk-soil portions of the Fuquay and Vaughan soil samples, added with varying concentrations of stable Cs (¹³³Cs), was determined by shaking 1 g portions of soil with 40 cm³ of 0.005 mol dm⁻³ NaNO₃ solution in closed plastic centrifuge tubes. Each contacting solution initially contained ~180 Bq of ¹³⁷Cs tracer, and ¹³³Cs as the chloride salt in one of the following amounts: (1) 0.62 nmol (the carrier in the ¹³⁷Cs solution); (2) an amount equivalent to ~2% of the cation exchange sites of the soil test portion (0.4 μmol for the Fuquay sample and 0.08 μmol for the Vaughan sample); or (3) an amount equivalent to ~10% of the cation exchange sites (2 μmol and 0.4 μmol, respectively). Shaking was interrupted after periods ranging from 1 h to 175 h to remove a 1 cm³ aliquot from each solution. Each aliquot was replaced with an equal volume of 0.005 mol dm⁻³ NaNO₃ solution. The 0.661 MeV γ-ray activity of ¹³⁷Cs in each aliquot was measured with a Ge detector and spectrometer system (Canberra Industries, Inc., Meriden, Connecticut, USA), calibrated with standard solutions of ¹³⁷Cs.

Blocking cesium sorption with silver thiourea

To determine the degree to which Cs uptake is blocked by the presence of AgTU in the exchange complex (Cremers *et al.*, 1988), 1 g bulk-soil portions of the five soil samples were first saturated with AgTU, each by contact for 4 days in the dark with 40 cm³ of a

solution containing 0.01 mol dm⁻³ AgNO₃ and 0.1 mol dm⁻³ thiourea, SC(NH₂)₂. The solids were then separated by centrifuging, washed with deionized water, and shaken at room temperature in solutions that contained ¹³⁷Cs and ¹³³Cs at the concentrations used in parallel experiments without AgTU described by Goto *et al.* (2008). The solutions, 40 cm³ each, also contained NaNO₃ (0.001 mol dm⁻³), AgNO₃ (0.01 mol dm⁻³), and thiourea (0.1 mol dm⁻³). The amounts of ¹³⁷Cs associated with the solids after 4 days were calculated from the difference between the initial and final amounts in solution, determined by measuring the 0.661 MeV γ -ray activity of solution aliquots with the calibrated Ge detector and spectrometer.

Sequential extraction

The sequential extraction scheme developed by Miller *et al.* (1986), as applied in the present study, was described by Goto (2001). The reagents and extraction conditions are tabulated with the results, below. Extractions were performed on six 1 g test portions of the Fuquay and Vaucluse soil samples. One of each was untreated bulk soil, one of each had been contacted at room temperature for 4 days with added ¹³³Cs (2.0 μ mol for Fuquay soil and 40 nmol for Vaucluse soil) in 40 cm³ of 0.001 mol dm⁻³ NaNO₃ solution and then separated from the solution, and one of each had been contacted with added ¹³³Cs as just described except that the solutions also contained ¹³⁷Cs (351 Bq). The treated, separated solids were stored moist for ~2 months before extraction. For the soil portions with no sorbed ¹³⁷Cs, the concentration of ¹³³Cs in solution after the original 4 days of sorption, in solutions from each of the seven extraction steps, and in solution after total dissolution of the residual solids, was determined by inductively coupled plasma mass spectrometry (Perkin-Elmer ELAN 5000, Waltham, Massachusetts, USA) against CsCl reference solutions of known Cs content. Measurement relative standard deviation was ~10%. For the soil portions with sorbed ¹³⁷Cs, the activity of ¹³⁷Cs in the solutions from the extractions was determined by measuring the 0.661 MeV

γ -ray activity of solution aliquots with the calibrated Ge detector and spectrometer.

Cesium accessible for isotope dilution

Data from the 4-day Cs sorption experiments of Goto *et al.* (2008) were analyzed to determine how much of the soil Cs (naturally occurring stable Cs in the soil samples) isotopically diluted the radioactive Cs added during those experiments. Considering only the sorption data from those experiments in which added ¹³³Cs was minimal (carrier in the radioactive Cs), the amount of soil Cs accessible for isotope dilution (n_a) was calculated from

$$n_a = n_f A_i / A_f - n_i \quad (4)$$

where the amount (amount of substance) of ¹³³Cs is represented by n and activity (radioactivity) of ¹³⁷Cs is represented by A . The subscripts i and f refer to Cs in solution initially (the added Cs, which was in solution before the soil was introduced) and Cs in solution at the end of the experiment, respectively.

Equation 4 is appropriate for soil that contains no ¹³⁷Cs initially if the added Cs mixes fully and exclusively with the accessible component of the soil Cs, if no Cs isotope fractionation occurs, and if the decrease in amount of ¹³⁷Cs over the course of the experiment is negligible. The accessible fraction of the soil Cs is n_a/n_s , where n_s is the amount of soil Cs. Conversion of n_a to a mass value and division by the mass of dry soil would give an E value, where E , as commonly defined, is the 'isotopically exchangeable' amount of an element in soil, expressed as a mass fraction. No term equivalent to n_i is shown in equation 1 of Smolders *et al.* (1999) because their added radio-cadmium was carrier-free.

RESULTS

Soil characteristics and clay mineralogy

Textural analyses (Table 2) confirmed that the soil samples consist predominantly of sand (75–96% by mass), with more clay than silt except for the Blanton

Table 2. Characteristics of the soil samples determined in the present study.

Sample	Sand (% by mass)	Silt	Minerals in clay fraction*			K – (g kg ⁻¹) –	K in clay
			kaolinite	HIV	quartz		
			——— (% by mass) ———				
Fuquay #42	75.5	6.7	65	25	1	1.36	6.8
Orangeburg #46	78.3	7.8	65	20	0	1.11	5.5
Lakeland #2	86.1	5.9	65	25	0	0.71	6.7
Blanton #35	91.6	6.6	40	45	5	0.57	7.9
Vaucluse #12	95.8	2.6	50	35	2	0.26	7.7

* Because of the semiquantitative nature of the analysis, mineral mass fractions are rounded to the nearest 5% except for the low quartz values, which are rounded to the nearest 1%. As explained in the text, amounts of gibbsite, a fourth mineral in the clay fractions, were estimated to allow calculation of the mass fractions of kaolinite, HIV, and quartz.

and Vaucluse samples. New values for K content (Table 2) confirmed that the clay fractions consistently have <1% K by mass, and that K contents of the quartz-sand-rich bulk-soil samples are even smaller.

The results of XRD analysis showed that the clay fractions of the soils contain kaolinite, HIV, gibbsite, and in some cases quartz. Each of the XRD patterns for oriented, air-dried clay from the soil samples (Figure 1) shows a 1.4 nm peak that indicates the presence of smectite, vermiculite, or chlorite. Peaks at 0.71 nm and 0.36 nm correspond to higher-order basal reflections from the 1.4 nm clay mineral as well as to first- and second-order basal reflections from kaolinite. The large 0.334 nm peak in the pattern for Blanton clay is attributed to quartz because a corresponding 0.425 nm peak is present. A 0.483 nm peak, partially overlapping the third-order peak from the 1.4 nm mineral, indicates the presence of gibbsite in all of the clays. Neither feldspar nor illite was detected.

The XRD patterns obtained after the several chemical treatments of the Orangeburg clay (Figure 2) are typical of the corresponding patterns from all the SRS soil samples. Saturation with ethylene glycol did not cause a noticeable shift in the 1.4 nm peak of any of the clays, eliminating smectite as a possible constituent. Disappearance of the 1.4 nm and 0.71 nm peaks upon heating of the clays to 550°C eliminated chlorite as a possible constituent. Potassium saturation caused no decrease in the basal spacing of the 1.4 nm mineral until

after heating at 300°C, whereupon the basal-reflection peak broadened and shifted to a slightly larger angle to show that the 1.4 nm mineral is HIV (Barnhisel and Bertsch, 1989).

The relatively large 0.71 nm peaks in the XRD patterns of the air-dried clays from the Orangeburg, Lakeland, and Fuquay samples indicate that kaolinite is preponderant in the clay fractions of these samples. Semi-quantitative determinations based on XRD peak-height ratios indicate that HIV makes up ~20% of the Orangeburg clay, 25% of the Fuquay and Lakeland clays, 35% of the Vaucluse clay, and 45% of the Blanton clay (Table 2), provided that estimates of 10% gibbsite in each clay fraction (15% for Orangeburg) are about right. The amounts of kaolinite and HIV found in the Fuquay and Orangeburg clays agree with amounts of these minerals reported by Karathanasis *et al.* (1983) and Kaplan *et al.* (1997), respectively, for clay fractions of samples from the B horizons of these soil series. Kaplan *et al.* (1997) reported 35% HIV in clay from the E horizon of Blanton soil, compared to the 45% found in the present study.

Cesium-137 uptake kinetics

About half of the added ^{137}Cs was taken up by the Fuquay sample in the first hour (Figure 3) but only ~18% was taken up in that time by the Vaucluse sample, which has a much smaller CEC than the Fuquay. The amount of added ^{133}Cs had little effect on the fraction of ^{137}Cs

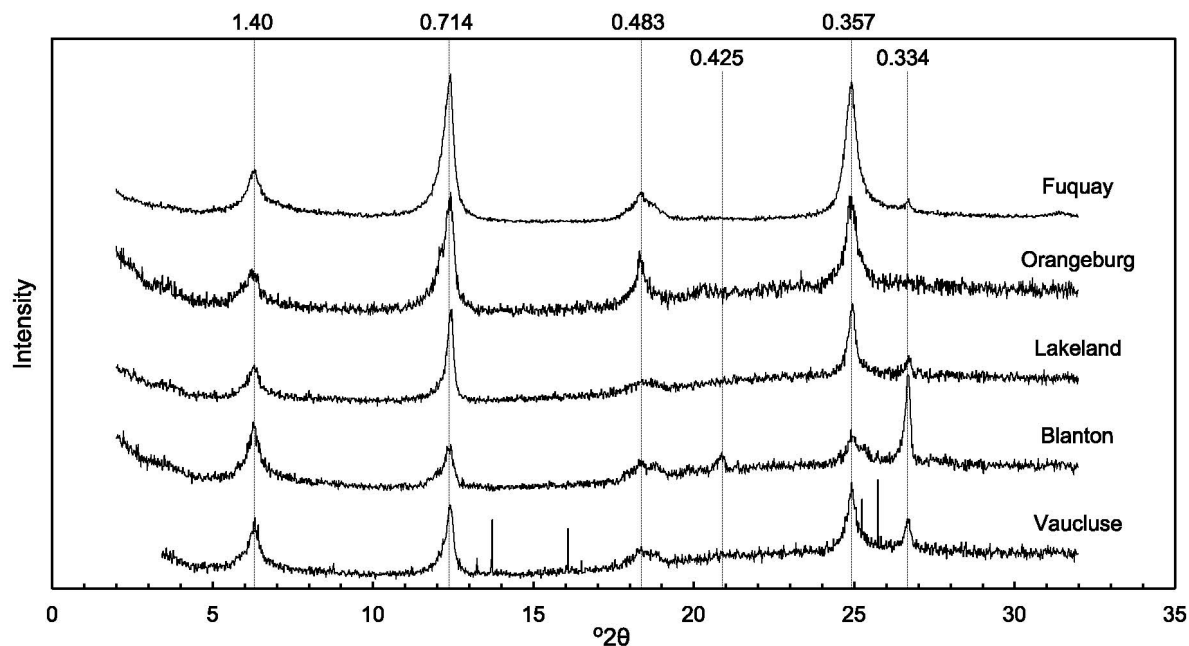


Figure 1. XRD patterns from oriented, air-dried portions of Na^+ -saturated clay fractions of SRS soil samples. The vertical lines represent specific values of d/n from the Bragg equation, each labeled with its value in nanometers. Plotted values for the Fuquay clay are $\frac{1}{4}$ the measured intensities. The narrow spikes near 14° , 16° , and $26^\circ 2\theta$ in the Vaucluse pattern are instrument artifacts probably caused by power surges.

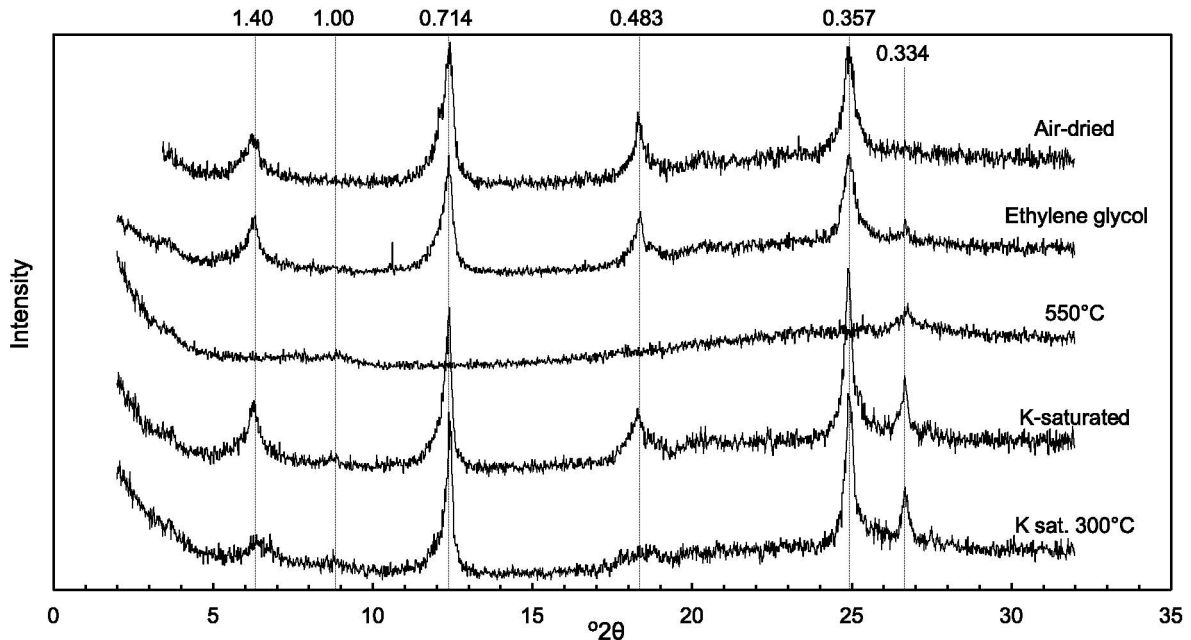


Figure 2. XRD patterns from oriented Orangeburg clay after various treatments. The vertical lines represent d/n with values in nanometers.

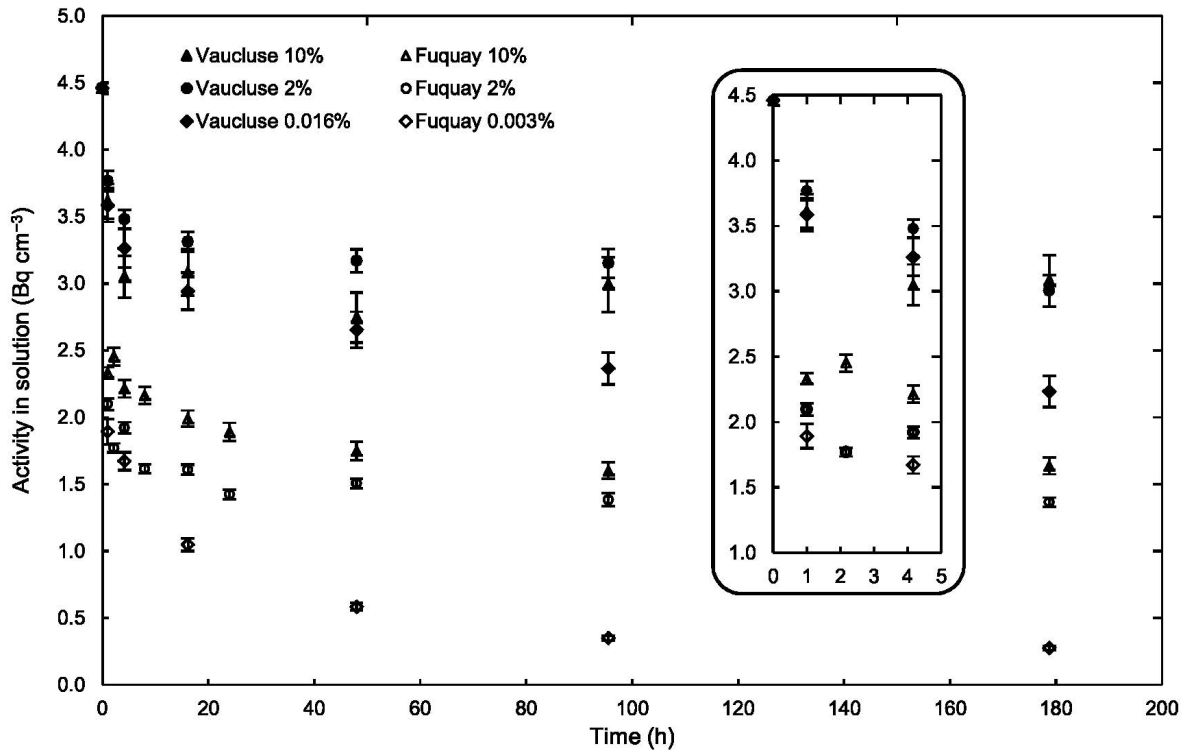


Figure 3. Time profile of ^{137}Cs uptake by 1 g portions of two SRS soils in 40 cm^3 0.005 mol dm^{-3} NaNO_3 solutions. Each solution initially contained ^{137}Cs in the equivalent ratio to the soil cation exchange sites shown in the legend as a percentage. The initial ^{137}Cs activity was the same, 4.45 Bq cm^{-3} , in all six experiments. Vertical bars represent the counting error as the standard deviation. The time scale is expanded in the inset portion to show more clearly the uptake during the first 4 h.

taken up in the first hour. Uptake continued much more slowly afterward. At the higher levels of added Cs, ^{137}Cs uptake was practically complete after 4 days. At the lowest level of added Cs (the very small amount of carrier in the ^{137}Cs solution), continued uptake of ^{137}Cs was evident throughout the 7-day period of the experiment.

Effects of silver thiourea on ^{137}Cs uptake

When added Cs was equivalent to $\sim 0.03\%$ of the cation exchange sites, the presence of AgTU reduced sorption of ^{137}Cs by only $\sim 10\%$ for the Fuquay, Orangeburg, and Lakeland samples and by 30% and 40% for the two other soil samples (Figure 4). At higher added Cs concentrations, the reduction of ^{137}Cs sorption in the presence of AgTU was much larger, except for the Blanton sample, averaging $\sim 70\%$ at the highest Cs level.

Sequential extractions

Less than 5% of the ^{133}Cs originally in the soils was removed in seven steps of sequential extraction of untreated portions of the Fuquay and Vaucluse soil samples (Table 3). Nearly all of the Cs remained with the solid phase until the final, total-dissolution step. In contrast, radioactive and stable Cs that had been sorbed by portions of these soil samples 2 months earlier were extracted readily, most appearing in the first two extraction steps. Much smaller, gradually decreasing, amounts were extracted in the subsequent extraction steps, until only $\sim 3\%$ of the recently sorbed Cs remained with the solids when they were dissolved in the final step.

Accessible original cesium

Isotope dilution of added radioactive Cs by the accessible natural Cs in soil, n_a , causes the specific activity, A/n , of Cs in the contacting solution to decrease, as shown by rearranging equation 4:

$$n_a = A_i(n_f/A_f - n_i/A_i) \quad (5)$$

where the right-hand expression must be positive if $n_a > 0$. In the work reported by Goto *et al.* (2008), the specific activity of Cs in solution decreased substantially over 4 days of contact of added Cs with portions of the Fuquay and Orangeburg samples (Table 4). The calculated amounts of accessible Cs for these samples are nearly 20% (on average) of the soil Cs. Little or no change in specific activity of Cs in solution for the other samples indicated little or no dilution of the added ^{137}Cs by soil Cs under acidic conditions. Under neutral conditions, the specific activity of Cs in solution decreased for all samples. The calculated amounts of accessible Cs range from near 10% of the soil Cs for the Blanton and Vaucluse soils to as much as 77% for the Fuquay soil.

DISCUSSION

Sorptive capacity of HIV in SRS soils

The XRD analyses showing HIV to be a substantial constituent of the clay fractions of the SRS soil samples are consistent with previous studies that show HIV to be widespread in highly weathered soils of the southeastern U.S. (Kirkland and Hajek, 1972; Harris *et al.*, 1992a).

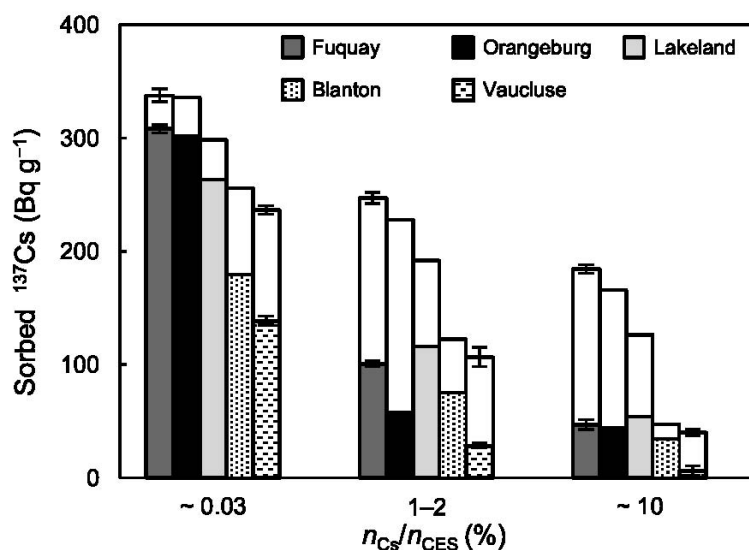


Figure 4. Cesium-137 sorbed by soil in the presence of AgTU (filled bars) compared to that sorbed in corresponding experiments without AgTU (larger values represented by the full height of each bar, filled plus open; from Goto *et al.*, 2008) at three levels of ^{133}Cs , indicated as the equivalent ratio of ^{133}Cs (aqueous plus sorbed) to cation exchange sites, $n_{\text{Cs}}/n_{\text{CES}}$, in percent. Results for the Fuquay and Vaucluse samples are averages of results from duplicate portions. The ends of the 'error bars' represent the results for the individual portions.

Table 3. Stable Cs (^{133}Cs) and ^{137}Cs removed from untreated and Cs-treated soils by sequential extraction.

Step	Targeted form	Reagents	Time (h)	Fuquay sample		Vauluse sample	
				Untreated ^{133}Cs (mg kg $^{-1}$)	Treated ^{137}Cs (Bq g $^{-1}$)	Untreated ^{133}Cs (mg kg $^{-1}$)	Treated ^{137}Cs (Bq g $^{-1}$)
1	Water soluble	Water	16	<0.01	36	<0.01	56
2	Exchangeable	0.5 M Ca(NO $_3$) $_2$	16	<0.01	56	<0.01	87
3	Acid soluble	0.44 M CH $_3$ COOH	8	0.1	9	<0.01	19
		0.10 M Ca(NO $_3$) $_2$					
4	Manganese oxide occluded	0.01 M NH $_2$ OH.HCl	0.5	<0.01	6	<0.01	11
		0.1 M HNO $_3$					
5	Organically bound	0.01 M Na $_4$ P $_2$ O $_7$	24	<0.01	4	<0.01	8
6	Held by amorphous iron oxide	0.175 M (NH $_4$) $_2$ C $_2$ O $_4$	4	<0.01	3	<0.01	5
		0.1 M H $_2$ C $_2$ O $_4$					
7	Held by crystalline iron oxide	0.15 M Na $_3$ C $_6$ H $_5$ O $_7$	0.5 (50°C)	<0.01	<1	<0.01	2
		0.05 M H $_3$ C $_6$ H $_5$ O $_7$					
8	Structurally bound	HF/HNO $_3$	Sum Expected value	4.3	8	0.8	4
				4.4	123	0.8	191
				4.5*	174 ‡	0.9*	180 ‡

* Natural Cs from Goto *et al.* (2008) ‡ Sum of natural Cs determined by Goto *et al.* (2008) and sorbed added Cs determined in the present study from the difference between the amount added and the measured amount in solution at the end of the sorption period. ‡ Sorbed ^{137}Cs from Goto *et al.* (2008)

Table 4. Results of isotope dilution determination of accessible soil Cs.

Soil sample	NaNO ₃ in solution (mol dm ⁻³)	Solution mass (g)	Solution volume (cm ³)	¹³³ Cs in solution* (nmol dm ⁻³)	¹³⁷ Cs in solution* (Bq cm ⁻³)	– Accessible Cs [†] – (μmol kg ⁻¹)	(%)
Acidic mixtures							
Fuquay	0.001	1.030	40.1	5.7	0.227	7.4±0.9	22±3
		0.989	39.5	2.7	0.272	2.3±0.4	7±2
	0.005	0.981	40.2	10.4	0.342	9.6±1.1	28±4
		1.000	40.2	6.6	0.390	4.7±0.6	14±2
Orangeburg	0.001	1.010	40.0	4.5	0.291	4.2±0.6	18±3
		1.020	40.1	4.4	0.297	3.9±0.6	17±3
Lakeland	0.001	1.000	40.0	7.0	1.28	0.7±0.2	8±3
		1.000	40.1	4.7	1.51	–0.2±0.2	–2±2
Blanton	0.001	1.020	39.6	10.4	2.24	0.4±0.2	4±2
		1.000	40.1	9.5	2.39	0.2±0.2	1±2
Vaucluse	0.001	1.020	40.1	10.8	2.63	0.2±0.2	3±3
		1.010	40.0	11.2	2.91	0.1±0.2	2±3
		1.010	40.1	11.6	3.13	0.1±0.2	1±3
		1.010	40.2	10.6	3.25	–0.1±0.2	–1±3
Neutralized mixtures							
Fuquay	0.001	1.010	40.2	19.8	0.250	28±3	77±11
		1.010	40.2	27.5	0.576	16±2	45±7
Orangeburg	0.001	1.020	40.2	5.1	0.136	12.2±1.4	51±8
		1.050	40.1	4.9	0.169	9.0±1.1	37±6
		1.020	40.2	9.3	0.317	9.3±1.1	39±6
	0.005	1.040	40.2	10.7	0.311	10.9±1.3	45±7
		1.020	40.1	3.4	0.314	2.7±0.4	31±6
Lakeland	0.001	1.020	40.1	3.4	0.314	2.7±0.4	31±6
		1.050	40.2	4.2	0.670	1.0±0.3	11±3
Blanton	0.001	1.030	40.0	3.4	0.533	1.0±0.3	9±2
		1.010	40.2	5.9	0.988	0.9±0.3	8±2
Vaucluse	0.001	1.020	39.9	5.4	0.831	1.1±0.3	15±4
		1.020	40.0	6.4	1.09	0.9±0.3	12±4
		1.000	40.2	8.9	1.77	0.6±0.2	8±3
		1.030	40.2	6.6	1.68	0.2±0.2	2±3

* From Goto *et al.* (2008); ¹³³Cs concentration and ¹³⁷Cs activity concentration are as determined at the end of the experiment. The measurement standard deviation was 10% for ¹³³Cs and 2% for ¹³⁷Cs. The activity of added ¹³⁷Cs was 351 Bq for acidic mixtures and 364 Bq for neutralized mixtures and the amounts of added ¹³³Cs were 1.28 nmol and 1.32 nmol, respectively. [Table footnotes of Goto *et al.* (2008) gave the unit for added ¹³⁷Cs as kBq by mistake, and the amounts of added ¹³³Cs were slightly more than the nominal 1.24 nmol listed in those tables.]

† Amounts of accessible Cs, expressed here as specific amounts in dry soil, were calculated as described in the 'Materials and Methods' section. In the last column, the calculated amount of accessible Cs is expressed as a percentage of the naturally occurring soil Cs. The error values are based on the measurement standard deviations for ¹³³Cs and ¹³⁷Cs.

The shift to a slightly larger angle and broadening of the HIV basal-reflection peak upon heating K-saturated clay at 300°C suggest substantial filling of the HIV interlayer with hydroxy-Al polymers (Barnhisel and Bertsch, 1989) and are similar to behavior that Harris *et al.* (1992a) described as typical of HIV in Florida soils. The relatively large amount of HIV in the clay fraction of the shallowest sample (Blanton) is consistent with numerous observations that HIV is particularly abundant in near-surface horizons (Harris *et al.*, 1992a). If the CEC of the HIV is ~50 cmol kg⁻¹, the mean of values reported by Kirkland and Hajek (1972) for HIV in

Alabama, there is sufficient HIV in the clay fraction (Table 2) to account for most of the CEC (Table 1) of each SRS soil sample.

Large-ion alkali metals in HIV grains and mica

Amounts of the large-ion alkali metals, Cs, Rb, and K, found in the five soil samples are correlated with the mass fraction of clay-sized HIV (Figure 5), the latter calculated as the product of the mass fractions of HIV in the clay (Table 2) and of clay in the soil (the average of values in Table 1). The K content of the clay fraction, as a mass fraction relative to the mass of dry soil ('Clay K'

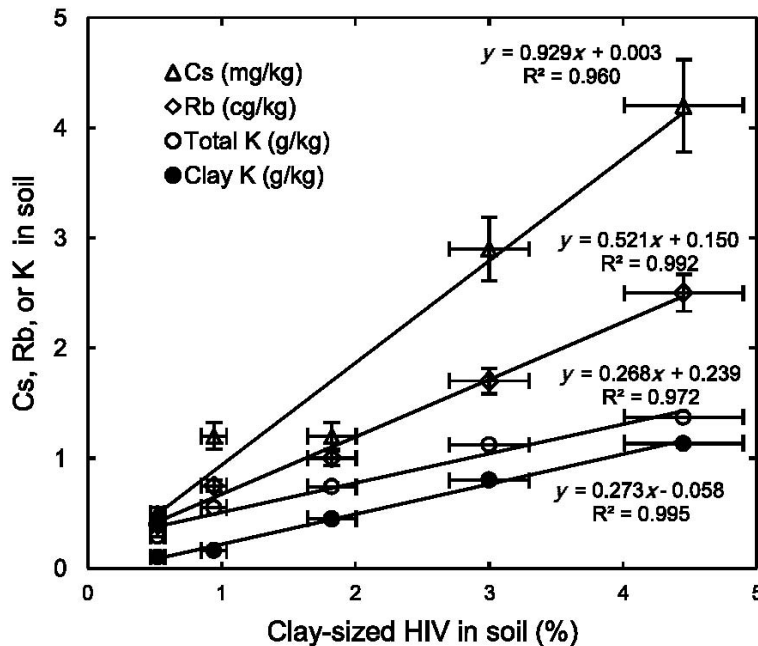


Figure 5. Correlations of mass fractions of Cs and Rb (from Wampler *et al.*, 2012) and K (averages of values in Tables 1 and 2) in SRS soil samples with the mass fraction of clay-sized HIV. The legend gives the units for element mass fractions. The ‘Clay K’ values are of the mass of K in the clay fraction relative to the mass of dry soil. Relative error in HIV content is estimated as $\pm 10\%$. Error values for Cs and Rb content are from Wampler *et al.* (2012). Errors in K values are smaller than the symbols for the values.

in Figure 5), is closely proportional to the mass fraction of clay-sized HIV in the soil, indicating that the K in the soil clay is in HIV grains. The ‘total K’ includes any K in micaceous grains larger than clay (HIV or mica), so the values are greater than those for ‘Clay K,’ an effect greatest for the Blanton sample, which has a high ratio of silt to clay. For three of the five samples, Cs content is nearly proportional to the mass fraction of clay-sized HIV in the soil. The Blanton Cs value is elevated, probably because of Cs in silt-sized HIV grains. The distinctly low Cs value for the Lakeland sample may be due to a shorter time for Cs fixation in the relatively young Lakeland soil (an Entisol) than in the other soils studied (Ultisols). The relationship of Rb content to clay-sized HIV is consistent with the inference of Wampler *et al.* (2012) that Rb occurs in the HIV grains as a native constituent of mica (as does K) and also as a result of its selective sorption in interlayer wedge zones (as does Cs).

Cesium-137 uptake kinetics

The kinetics experiment was intended to find the time necessary for added Cs to reach exchange equilibrium with SRS soils, but the results have value beyond that original purpose. The continued, slow uptake of ^{137}Cs after the first day at the lowest level of added ^{133}Cs is reminiscent of uptake of ^{137}Cs by Fithian illite from solutions having similar initial ^{133}Cs concentration ($\sim 10^{-8}$ mol dm^{-3} ; figure 1 of Comans *et al.*, 1991). After relatively large ^{137}Cs uptake during the first few

hours, the Fithian illite continued to sorb ^{137}Cs slowly during the next twelve days. The early (≤ 4 h) ^{137}Cs uptake by illite was about twice as great as in a parallel experiment (Comans *et al.*, 1991, figure 1) in which the initial ^{133}Cs concentration was 20 times greater, which indicates that Cs ions had prompt access to sites on illite that are highly Cs-selective but low in abundance, consistent with the view that these sites are at the particle edges.

In contrast, wide variation of initial ^{133}Cs concentration had relatively little effect on ^{137}Cs uptake by the two SRS soils during the first 4 h of contact, which indicates that sites highly selective for Cs but low in abundance played only a minor role in the short-term uptake. The effects of the different amounts of ^{133}Cs added became apparent over longer times. At the lowest ^{133}Cs level, sorption increased gradually over the entire week of the experiment until amounts of sorbed ^{137}Cs were distinctly greater than in corresponding experiments with more added ^{133}Cs . These results are evidence that SRS soil has low concentrations of highly Cs-selective sites and that added Cs cannot reach most such sites quickly.

These observations are consistent with the inference that uptake of Cs by SRS soils is primarily by HIV grains that have abundant sites on planar surfaces and relatively few highly Cs-selective interlayer wedge sites (Goto *et al.*, 2008). Furthermore, the results support the structural model of Rich and Black (1964) in which the interlayer wedge zones are well within interlayers

partially filled by hydroxy-Al polymers, which would cause the pathways for interlayer diffusion to be narrow and tortuous (Harris *et al.*, 1992b).

Blocking cesium uptake with silver thiourea

At the lowest level of added ^{133}Cs , most sorbed Cs should have reached highly Cs-selective sites after 4 days. That such sites are not blocked by AgTU effectively explains the small influence of AgTU on ^{137}Cs sorption at that level. The results do not allow quantitative calculation of the fraction of sites blocked by AgTU, because the acidity of thiourea caused enhanced competition by H ions for exchange sites that would take up Cs^+ .

At the higher ^{133}Cs concentrations, in the absence of AgTU most of the Cs sorption should have been on planar surfaces of HIV. The observed large reductions in ^{137}Cs uptake in the presence of AgTU at these ^{133}Cs concentrations, except for the Blanton sample, indicate that AgTU blocked large fractions of the planar-surface sites that otherwise would have held Cs^+ . The anomalous response of the Blanton sample to the presence of AgTU may have arisen from the relatively large size of the HIV grains in that E-horizon sample. This issue cannot be resolved with the data available now, but it points to a need for study of HIV grains from different size fractions.

Sequential extraction

The sequential extraction results are consistent with the expectation that the uptake of recently sorbed ^{137}Cs and ^{133}Cs was predominantly by ion exchange. The generally decreasing amounts of ^{133}Cs and ^{137}Cs removed in steps 3 to 7 can be attributed to continued, progressively more complete, replacement of sorbed Cs^+ by Na^+ rather than to responses by the specific solid phases targeted in these steps. The relative amounts of recently sorbed ^{133}Cs and ^{137}Cs extracted in each step are broadly consistent with one another, even though the totals indicate losses that may be due to loss of clay during repeated phase separations by centrifugation and decantation (Goto, 2001).

The results for the untreated soil portions confirm earlier work by Findley (1998) and show that very little of the Cs originally in the soils is at ordinary ion-exchange sites or is bound in organic matter or Fe and Mn oxides. The much greater extractability of the recently added Cs in comparison to the natural Cs is consistent with the observation by Clark *et al.* (1996) that ^{137}Cs recently introduced to the environment at the SRS is much more labile than the ^{133}Cs originally present.

Accessible original cesium

Experiments with carrier-free ^{137}Cs can mislead if the amount of accessible natural Cs in soil is not known (Grütter *et al.*, 1990). Very little of the natural Cs in SRS

soils is inaccessible because it remains in residual primary minerals (Wampler *et al.*, 2012). The rest of the Cs in soil has participated in mineral–water reactions as pre-existing materials have been converted into the soils existing today. In concept, one might divide such Cs into: (1) Cs that has become ‘fixed’ in some way and is no longer accessible for isotope dilution and (2) Cs that is accessible for isotope dilution as exchangeable cations or in a soluble form. Slow fixation of small amounts of radiocesium by illite and illitic sediments, over periods of weeks to months, has been reported by a number of investigators (Comans and Hockley, 1992). The relatively small amounts of natural Cs found in the present study to be accessible for isotope dilution under acidic conditions, 20% or less of the soil Cs, indicate that most of the natural Cs in the upland SRS soils is effectively fixed. The ~20% of soil Cs found to be accessible in the Fuquay and Orangeburg samples was probably in cation exchange sites highly selective for Cs, because only a few percent of the soil Cs was removed by sequential extractions.

After neutralization of the soil suspensions, substantially more of the soil Cs was found to be accessible in all five of the samples. Under the assumptions used in calculation, these greater amounts of accessible Cs would require that neutralization converted some previously inaccessible Cs into accessible Cs. An alternative view, based on the common observation that *E* values increase with increasing contact time owing to kinetically limited dilution of an added radioisotope by the natural element in some soil compartments (Diesing *et al.*, 2008), is that the isotope dilution process was not complete in either case but was more rapid and thus more extensive in the neutralized soils. If most of the natural Cs in the SRS soils is effectively fixed in the narrower parts of interlayer wedge zones, where steric hindrance to cation exchange is to be expected (Wampler *et al.*, 2012), the effect of neutralization on the conformation of the interlayer wedges zones may have influenced the rate of isotope dilution. Interlayer hydroxy-Al polymeric cations prevent expansion of HIV (Meunier, 2007), but neutralization of these polymeric ions would have eliminated their electrostatic attraction to the clay layers and may thus have allowed some interlayer expansion. Such expansion may have widened interlayer wedge zones enough that the rate of isotope dilution of added Cs by natural Cs that was in the narrower parts of the wedge zones could increase substantially.

Synthesis

The findings reported above point clearly to HIV grains as the hosts of the naturally occurring Cs, Rb, and K in the upland soils of the SRS. The XRD analyses show that HIV is a major constituent of the soil clay, second only to kaolinite. The recalcitrance of nearly all of the soil Cs to the sequential extractions shows that

most such Cs is either fixed or is in cation exchange sites that are extremely selective for Cs ions relative to Na and H ions. In contrast to HIV, kaolinite has little CEC (Lim *et al.*, 1980) and no highly Cs-selective sites (Nakao *et al.*, 2008), and the same is true of quartz and gibbsite. Elimination of soil materials other than HIV grains as hosts is consistent with the observation that the Cs, Rb, and K contents of these soils are closely related to their HIV content.

By similar reasoning, the experiments in the present study on Cs sorption by SRS soil samples were effectively tests of Cs sorption by the HIV grains. The distinct differences in sorption kinetics and in the effects of AgTU at different levels of added ^{133}Cs support the hypothesis of Goto *et al.* (2008) that HIV grains have different kinds of sites for Cs sorption. By this hypothesis, when only traces of ^{133}Cs were present, Cs sorption occurred mostly on the relatively few sites highly selective for Cs. That AgTU did not block these sites and that added Cs did not promptly reach most of these sites supports the idea that they are stereoselective sites mostly well inside HIV grains (Rich and Black, 1964). In contrast to its behavior at trace levels, Cs in larger concentrations was sorbed mostly on abundant planar-surface sites that are not especially selective for Cs, accounting for the ready extraction of most of the recently sorbed Cs and for the extensive reduction of Cs sorption in the presence of AgTU. The distinction between these two site types allows prediction that ^{137}Cs retention from aqueous discharges onto HIV-containing soil will be most effective when stable cesium concentration in solution is lowest.

The evidence presented by Goto *et al.* (2008) and in this study for the presence of highly Cs-selective sites in HIV grains is contrary to an inference by Maes *et al.* (1998) and Nakao *et al.* (2009) that the hydroxy-Al polymers in such particles block radiocesium access to the Cs-specific sites and to a finding by Dion *et al.* (2005) of very low Cs selectivity for HIV-bearing sandy sediment from the SRS. More-detailed study of soil clays in which HIV grains are the sole host for sorbed Cs is needed to resolve the conflict.

The much greater chemical extractability of recently added radiocesium than natural, stable Cs emphasizes important differences between the interaction of SRS soils with Cs in large amounts over short times and their interaction with trace amounts of Cs over long times. That the natural Cs does not occupy ordinary cation exchange sites is shown by its observed resistance to chemical extraction (Findley, 1998; this study). Most of the soil Cs did not isotopically dilute the added ^{137}Cs under acidic conditions, indicating effective fixation of most of the soil Cs in sites where Cs atoms either were inaccessible or were accessible only very slowly. These observations support the mechanistic interpretation that most of the Cs in these soils has become effectively fixed in the narrower parts of interlayer wedge zones

where steric hindrance to exchange of large cations is great. The predicted gradual shift of sorbed ^{137}Cs inward within such zones may be a key factor in the soil's ability to hold radiocesium.

CONCLUSIONS

Findings in the experiments described and information from the cited references were synthesized to conclude the following:

In the upland soils that cover most of the SRS, HIV is a major constituent of the clay, second only to kaolinite, and is the major ion-exchange medium. The HIV grains host the naturally occurring Cs, Rb, and K in these soils.

The HIV grains hold Cs at three types of sites: (1) numerous ion-exchange sites that do not discriminate strongly among ions in favor of Cs; (2) a small fraction of ion-exchange sites that hold Cs strongly during exchange with other ions in solution; and (3) sites that hold Cs and do not exchange it readily with ions in solution, be they Cs or other ions.

A physical mechanistic model is proposed that associates sites of the first type with planar surfaces and sites of the second and third types with interlayer wedge zones. Sites of the third type are deep within interlayer wedge zones where Cs ions are effectively inaccessible for cation exchange. The first and second site types are analogous to the regular exchange sites and frayed-edge sites, respectively, of illite. Most of the natural Cs in SRS soils is effectively fixed in sites of the third type.

ACKNOWLEDGMENTS

This research was supported in part by ERDA Project GA 00-64 of the Westinghouse Savannah River Company. D. Kaplan of the Savannah River National Laboratory provided valuable support and advice. Helpful comments by P. Ryan and other reviewers, by the editors, and by A. Meunier and others who reviewed earlier manuscripts about this work are gratefully acknowledged.

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(Received 30 June 2013; revised 6 June 2014; Ms. 784; AE: J.W. Stucki)