Rhizosphere Effects on Cesium Fixation Sites of Soil Containing Micaceous Clays

Laura A. Wendling,* James B. Harsh, Carl D. Palmer, Melinda A. Hamilton, Heather M. Dion,
Jeffrey S. Boyle, and Markus Flury

ABSTRACT

Physical and chemical weathering processes in the rhizosphere may lead to the generation of a greater density of Cs-selective frayed edge sites (FES) on rhizosphere soil as compared with bulk soil. This study was undertaken to determine if there are significant differences between bulk and rhizosphere soils from the Idaho National Laboratory (INL) with respect to their ability to bind Cs. The capacity of FES on bulk and rhizosphere soil materials and conditional Cs/K selectivity of FES ($^cK_{ex}^{FES}$) were determined as a function of both soil type and initial exchanger composition. The FES capacity was significantly higher in untreated, Ca-saturated, and K-saturated rhizosphere soil materials as compared with bulk soil materials. Sorption–desorption isotherms were obtained at Cs concentrations between 5×10^{-9} and 5×10^{-6} M. No difference in Cs sorption was observed between bulk and rhizosphere soil materials. The composition of the exchanging solution had the greatest effect on the magnitude of Cs desorption; significantly more Cs was desorbed in the presence of KCl than in either CaCl$_2$ or a mixed-cation soil solution. In addition, Cs desorption was greater from rhizosphere soil materials relative to bulk soil materials. Cesium selectivity with respect to both Ca and K was significantly suppressed by weathering in the rhizosphere. We conclude that enhanced weathering in the rhizosphere increased the Cs sorption capacity of FES, but also reduced Cs selectivity on these sites. Enhanced Cs desorption from rhizosphere INL soils is likely in the presence of actively growing plants and associated microorganisms.

C ESIUM UPTAKE BY PLANTS depends on adsorption–desorption and fixation–release reactions in the soil, as well as on root uptake processes controlled by the plant. The aqueous chemistry of Cs in the environment is controlled by sorption reactions to mineral phases, particularly micaceous clay minerals (Francis and Brinkley, 1976). Micaceous clay minerals are micas and illite or other 2:1 phyllosilicate minerals in which non-exchangeable K can exist in interlayer sites. Phyllosilicate minerals comprise the bulk of the reactive solid phase in low organic matter temperate soils.

Cations with low hydration energy such as K, Rb, Cs, and NH$_4$ can shed part of their hydration shell in the interlayers of phyllosilicate minerals. This permits a close approach to the tetrahedral silicate layers and formation of polar bonds with structural oxygen atoms. Cesium bound to completely dehydrated or "collapsed" inter-

layer sites of high charge phyllosilicates such as micas is not readily exchanged by other cations and is usually considered 'fixed' (Comans et al., 1991).

The strongest association between Cs and the soil solid phase occurs within the collapsed interlayers of micaceous minerals. Cesium may initially sorb at FES of these minerals and diffuse into the more recalcitrant interlayer positions. Weathering of the minerals can serve to open up the mineral edges and increase the exchangeability of adsorbed Cs, K, and other weakly hydrated cations. Thus, soil conditions that enhance the weathering process may increase the number of Cs exchange sites and enhance Cs desorption and availability to plants.

Selectivity of Cs for sorption on either regular (planar) exchange sites or FES can be described using a selectivity coefficient comparing the retention of Cs in relation to another competing ion, such as K or NH$_4$. Exchange on accessible sites of expandable phyllosilicates or soil organic matter occurs easily with relatively small selectivity differences among alkali and alkaline earth cations. Exchange on sites at collapsible interlayers such as those found in micas and vermiculite, on the other hand, show high selectivity for large alkali metals (K, NH$_4$, Cs) over their smaller counterparts (Na, Li) and alkaline earth metals (Ca, Mg). The less negative hydration energy of the large alkali metals allows dehydration and collapse of the interlayer or sites near the edges of collapsed interlayers of micas (FES). As a result, K, Cs, and NH$_4$ can have very high selectivities relative the other metals (see e.g., Wauters et al., 1996). In this paper, we define FES operationally, as those sites that will hold Cs and K against exchange with a large excess of Ca, but not against exchange with NH$_4$ (Wauters et al., 1996).

A number of studies have shown that the exudates of both plant roots and rhizosphere bacteria enhance the weathering of phyllosilicate minerals (Boyle et al., 1967; Boyle and Voigt, 1973; Boyle et al., 1974; Hinsinger and Jaillard, 1993; Leyval and Berthelin, 1991; Mojallali and Weed, 1978). Biological and chemical weathering processes in the rhizosphere can account for the loss of more than 20% of elements from clays, micas, and feldspars on a weight basis (Robert and Berthelin, 1986). Specifically, the exudates of plant roots and rhizosphere bacteria may enhance Cs bioavailability by accelerating weathering at frayed edges of phyllosilicate minerals, thereby releasing Cs sorbed to frayed edge and interlayer sites and making the ion available for plant uptake. Wendling et al. (2004) have recently shown that treatment of illite with oxalate increases the number of

L.A. Wendling, USDA-ARS, P.O. Box 646120, Washington State Univ., Pullman, WA 99164-6120; J.B. Harsh, J.S. Boyle, and M. Flury, Dep. of Crop and Soil Sciences and Center for Multiphase Environmental Research, P.O. Box 646420, Washington State Univ., Pullman, WA 99164-6420; C.D. Palmer and M.A. Hamilton, Idaho National Lab., P.O. Box 1625, Idaho Falls, ID 83415; H.M. Dion, Los Alamos National Lab., P.O. Box 1633, Los Alamos, NM 87545. Received 25 Aug. 2004. *Corresponding author (lawendling@wsu.edu).

Abbreviations: AAS, atomic absorption spectrophotometry; FES, frayed edge sites; INL, Idaho National Laboratory; XRD, X-ray diffraction; $^cK_{ex}^{FES}$, conditional Cs/K selectivity of FES; $^cK_{ex}$, Vanselow conditional exchange coefficient.

FES and the quantity of Cs sorption while lowering the selectivity of Cs with respect to Ca and Mg ions.

The INL was established in 1949 as the National Reactor Testing Station and was once the site of the world's largest concentration of nuclear reactors. A large portion of the area that is now the INL was used as a gunnery and bombing range by the U.S. Navy and U.S. Army during World War II. Soil contamination at the INL is limited to areas of localized accidents or spills, and where releases or disposal have occurred (Bowman et al., 1984). According to a report prepared by the U.S. Department of Energy, a number of radionuclides and metals have been released to the soil at the INL (DOE-ID, 2001). One event resulting in the release of radionuclides to the local environment occurred in January 1961 when the SL-1 reactor located in the Auxiliary Reactor Area (ARA) in the south-central portion of the INL was destroyed by a nuclear accident. Over the past several decades, atmospheric dispersion has spread ^{137}Cs contamination resulting from the 1961 SL-1 reactor accident and from ongoing ARA operations over local surrounding surface soils (Holdren, 1995).

Recent surveys at the INL have shown that ^{137}Cs levels in the top 30 cm ranged from non-detectable to more than 3.7 Bq (100 pCi g^{-1}) (Melinda A. Hamilton, Idaho National Laboratory, Idaho Falls, ID, unpublished data, 2002). Total Cs mean concentration measured in representative INL soils was approximately 0.02 mmol kg^{-1} soil and the radiocesium activities measured in contaminated soils were on average five orders of magnitude less than the total Cs concentration (Melinda A. Hamilton, Idaho National Laboratory, Idaho Falls, ID, unpublished data, 2002).

The objective of this work was to determine if there are significant differences between bulk and rhizosphere soils at the INL with respect to their ability to bind Cs. We chose crested wheatgrass (*Agropyron desertorum)* as the model plant species for this study after field surveys of ^{137}Cs levels at the INL showed that more than 90% of the ^{137}Cs accumulation in aboveground biomass was associated with this species (Melinda A. Hamilton, Idaho National Laboratory, Idaho Falls, ID, unpublished data, March 2002).

MATERIALS AND METHODS

Eight 25-cm (10-inch) diameter core samples, each containing a single crested wheatgrass plant and root-associated soil (coarse-silty, mixed, frigid, Xeric Haplocalcid), were collected from a non-contaminated portion of the SL-1 area in the south-central part of the INL in June 2003. Crested wheatgrass is a drought-tolerant perennial bunch grass that begins growth early each spring. Soil separated from among the fibrous roots in the root ball of each plant to a depth of approximately 15 to 20 cm (6–8 inches) was composited and mixed. Eight core samples (15 to 20 cm [6–8 inches] deep) from non-vegetated areas within 1 m of the location of wheatgrass cores were collected, composited, and mixed. Both rhizosphere and bulk soil materials were air-dried, lightly crushed to pass a 2-mm sieve, and mixed thoroughly.

Subsamples of untreated bulk and rhizosphere soil materials were analyzed for selected chemical properties and particle-size distribution. Particle-size distribution of bulk and rhizosphere soil materials was characterized using a Malvern Mastersizer S (Malvern Instruments Ltd., Worcestershire, UK). Samples were pretreated with sodium acetate and hydrogen peroxide to dissolve soil carbonates and oxidize soil organic matter before analysis. Soil pH and electrical conductivity (EC) were measured in saturation paste extracts, as were soluble cations. The cation composition of saturated paste extracts from bulk and rhizosphere soils were determined using atomic absorption spectrophotometry (AAS). Total soil C was quantified using a LECO CNS2000 dry combustion analyzer (LECO Corp. St. Joeseph, MI). We quantified NO$_3$–N and NH$_4$–N in 2 M KCl extractant colorimetrically using a Lachat 8000 QuickChem AE (Lachat Instuments, Milwaukee, WI). Exchangeable K, Ca, Mg, and Na were quantified via Ba exchange followed by AAS analysis of supernatant solutions. Cation exchange capacity (CEC) was determined by Ba/Mg exchange (Sumner and Miller, 1996). The mineralogy of silt and clay fractions of untreated bulk soil was determined by x-ray diffraction (XRD).

Frayed Edge Site Measurement

Frayed edge site capacity and Vanselow Cs/K selectivity coefficients for FES ($^{c}K_{ex}^{FES}$) were determined for untreated, Ca-saturated and K-saturated bulk and rhizosphere soils using a modification of the work by Wauters et al. (1996). First, 0.25-g soil samples were equilibrated at room temperature with 25 mL aliquots of a 100 mM CaCl$_2$/0.5 mM KCl mixed solution several times over a 24-h period to saturate planar surface cation exchange sites with Ca and FES with K. The suspensions were mixed for 4 h (t = 4 h), centrifuged, and supernatant solutions discarded. Three subsequent washings were mixed for 4, 8, and 12 h, respectively, before centrifuging and discarding the solution phase.

The samples were then rinsed twice with 25 mL of 100 mM CaCl$_2$ to remove any K on planar sorption sites. Each rinse step involved resuspension of the soil pellet through minimal vortexing and 5 min of mixing followed by centrifugation. In each case the rinse supernatant was discarded.

The Ca/K saturated soil samples were equilibrated with a 100 mM CaCl$_2$/0.5 mM KCl/0.05 mM CsCl mixed solution over a 24-h period in the same manner as the K/Ca washing then extracted several times with 100 mM CaCl$_2$ to remove any Cs or K on planar sorption sites. Supernatant solutions were saved for analysis of K and Cs.

Following equilibration and washing, soil samples were extracted with 1 M NH$_4$Cl to remove K and Cs from FES. Solution phase Cs and K were determined by AAS. Total FES abundance was assumed equal to the sum of extractable Cs and K.

Vanselow conditional selectivity coefficients for Cs/K exchange on FES ($^{c}K_{ex}^{FES}$) were calculated from the Cs-K binary cation exchange reaction illustrated here:

$$KX_{(s)} + Cs^+_{(aq)} \Leftrightarrow CsX_{(ex)} + K^+_{(aq)}$$

$$^{c}K_{ex} = \frac{N_{CsX}\,(K^+_{(aq)})}{N_{KX}\,(Cs^+_{(aq)})}$$
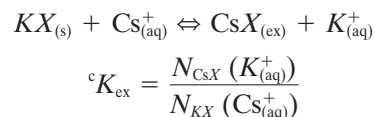
where $(Cs^+_{(aq)})$ and $(K^+_{(aq)})$ are the activities of the soluble ions and N represents the mole fraction of the exchangeable species. Because all K and Cs extracted with NH$_4$ are assumed to come from FES, such sites are operationally defined. We distinguish Cs/K exchange on FES from exchange on the whole soil with the 'FES' superscript (i.e., $^{c}K_{ex}^{FES}$). Activities of ions in solution were estimated with the Davies equation (Sposito, 1994).

Table 1. Soluble Ca, Mg, Na, and K in bulk and rhizosphere soil saturated paste extracts.

Cation	Bulk soil	Rhizosphere soil
	mmol L^{-1}	
K	0.21	0.26
Na	0.29	0.21
Mg	0.58	0.56
Ca	1.15	1.21

Sorption Experiments

To examine the relative significance of Ca and K competition with Cs for binding sites in bulk and rhizosphere soils, subsamples were left untreated or treated three times with 0.5 M CaCl$_2$ or 1 M KCl solutions to achieve saturation of the solid phase with Ca or K, respectively. The excess saturating solution was removed by washing the samples three times with deionized water. Cesium sorption isotherms were obtained on 0.25 g untreated, K-saturated, and Ca-saturated bulk and rhizosphere soils in 10 mL 0.23 mM KCl/0.25 mM NaCl/0.57 mM MgCl$_2$/1.18 mM CaCl$_2$ mixed-cation, 5.725 mM KCl, and 1.908 mM CaCl$_2$ solutions, respectively, at Cs concentrations between 5×10^{-9} and 5×10^{-6} M. The concentrations of Ca, Mg, Na, and K of the mixed solutions and the ionic strength of the KCl and CaCl$_2$ solutions used in the exchange experiments were based on those determined in saturated paste extracts of the collected soils (Table 1). Cesium concentrations were kept low to restrict Cs sorption to FES and to stay in a range of realistic concentrations at the INL site. At Cs concentrations of 5×10^{-9} and 1×10^{-8} M, ^{137}Cs was used alone; at concentrations above 1×10^{-8} M, Cs solutions contained 1×10^{-8} M ^{137}Cs mixed with stable Cs as CsCl to achieve total Cs concentrations of 5×10^{-8} M, 1×10^{-7} M, 5×10^{-7} M, 1×10^{-6} M and 5×10^{-6} M.

The suspensions were shaken in 30-mL polycarbonate centrifuge tubes on a reciprocal shaker at 20°C for 48 h and the liquid phase separated by centrifugation at 5000 $\times$ g for 30 min. Sample mass was determined before and following Cs sorption to account for any ^{137}Cs solution remaining in subsequent desorption experiments. The ^{137}Cs in the aqueous phase was determined by scintillation counting and adsorbed Cs determined indirectly as the difference between initial and final Cs concentrations or calculated by isotopic dilution analysis.

For isotopic dilution analysis at initial Cs concentrations between 5×10^{-8} and 5×10^{-6} M, we used the following equation to determine Cs in solution following sorption ([Cs$_{(aq)}$]):

$$[Cs_{(aq)}] = [Cs_T]/[^{137}Cs] \times [\text{measured } ^{137}Cs]$$

where [Cs$_T$]/[^{137}Cs] is the initial solution ratio, and [measured ^{137}Cs] is the ^{137}Cs concentration determined by scintillation counting. This equation is based on the assumption that the sorption sites show no preference for ^{137}Cs or Cs over the other so that the solution ratio does not change with sorption.

Desorption Experiments

At the conclusion of the sorption experiments, the centrifuged soils, without drying, were equilibrated with a mixture of 2.30 mM KCl/2.50 mM NaCl/5.70 mM MgCl$_2$/11.80 mM CaCl$_2$ mixed-cation, 57.25 mM KCl, or 19.08 mM CaCl$_2$, corresponding to the solution used for Cs sorption. Solid-liquid phase separation and determination of aqueous ^{137}Cs concentration were as described above. The equilibration time for sorption–desorption experiments was 48 h as similar experiments on mica-containing sediments from the Hanford Reser-

vation indicated that constant solution concentrations were reached in this period (Zachara et al., 2002).

For each point on the desorption isotherm, Vanselow conditional exchange coefficients ($^cK_{ex}$) for Cs/K and Cs/Ca exchange on highly selective FES were calculated from the binary cation exchange reactions following Cs sorption (Sposito, 1994). Using the desorbed Cs concentration in solution determined above, the quantity of Ca or K sorbed was determined by assuming a one for one exchange with FES Cs on a charge basis. Changes in K and Ca concentrations in solution were not possible to determine directly ($<0.05\%$). We assumed that at the low Cs concentrations used in sorption experiments, between 5×10^{-9} and 5×10^{-6} M, Cs sorption occurred only on highly selective FES. The mole fractions of each cation on FES were calculated and used in $^cK_{ex}$ calculations.

Single- and multi-factor analyses of variance (ANOVA) and paired t test statistical analyses were obtained using SAS 8.0 for Windows (SAS Institute, Inc., Cary, NC). In all cases, statistical significance is reported at the 5% level of significance ($\alpha = 0.05$).

RESULTS

Soil Physical and Chemical Properties

Both bulk and rhizosphere soil materials are silt loam soils (Table 2). X-ray diffraction analyses indicated that mica (illite), smectite, vermiculite, kaolinite, quartz, chlorite, and feldspars were the predominant minerals in the clay (<2.0 μm) fraction of bulk INL soil materials. Total K analysis indicated the clay fraction of bulk INL soil materials contained about 30% mica (illite) (Bernas, 1968). This indicates that illite will supply an abundance of FES relative to the amount of Cs used in these experiments. Quartz, feldspars, and mica were the primary minerals identified in the silt (2–50 μm) fraction of bulk INL soil materials.

Frayed Edge Site Capacity and $^cK_{ex}^{FES}$ (Cs/K)

We observed significant differences in FES capacity between bulk and rhizosphere soil materials and among soil treatments (Table 3). In the untreated INL soils, FES capacity was 19% higher in the rhizosphere than in the bulk soil material. Relative to bulk soil material, FES capacity was 12 and 4% greater in rhizosphere Ca-saturated and K-saturated soil materials, respectively. We suggest that the rhizosphere soil materials are more weathered by root exudates than the bulk soil materials in agreement with simulated weathering experiments in the laboratory (Wendling et al., 2004). The relative increase in FES capacity in rhizosphere soil materials indicates that there are more sites for selective Cs fixation in rhizosphere soils. In the long term (e.g., years to decades), this may reduce Cs availability to plants or leaching. In the short term (e.g., weeks to months), creation of FES via mineral weathering may be releasing Cs and K into the root vicinity.

We observed greater capacities of FES on both bulk and rhizosphere soil materials that were K-saturated as compared with untreated or Ca-saturated soil materials. This may be due to K saturation of vermiculite and high charge smectite (Onodera et al., 1998) mineral interlayers in these soil materials. Potassium bound in vermicu-
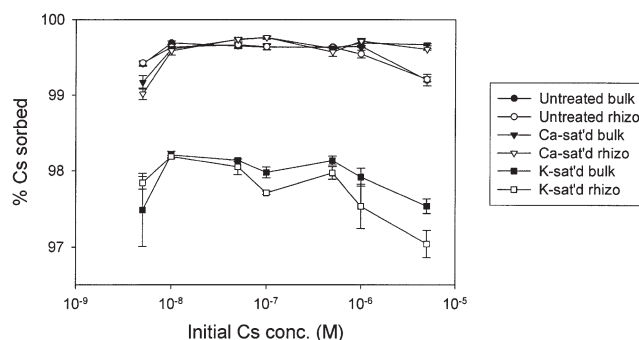
Table 2. Selected physical and chemical properties of bulk and rhizosphere soil materials.

Property	Bulk soil	Rhizosphere soil
Physical		
Particle size distribution, g kg^{-1}		
Sand	226.8 ± 22.7	254.5 ± 8.0
Silt	556.5 ± 13.8	525.5 ± 9.1
Clay	216.7 ± 10.1	220.0 ± 5.1
Chemical		
pH	7.3	7.6
EC, dS m^{-1}	0.42	0.44
Total C, %	0.96	1.11
CaCO$_3$, %	0.2	0.2
CEC, cmol$_c$ kg^{-1}	25.2	25.6
NO$_3$–N, mmol kg^{-1}	0.25	0.14
NH$_4$–N, mmol kg^{-1}	0.23	0.17
K, mmol kg^{-1}	12.1	13.2
Ca, mmol kg^{-1}	92	93
Mg, mmol kg^{-1}	25	25
Na, mmol kg^{-1}	1.8	1.3

Fig. 1. Percentage of initial Cs in solution sorbed by bulk and rhizosphere soils.

lite and high charge smectite interlayers may not be easily replaced by Ca ions during equilibration in the CaCl$_2$/KCl/CsCl mixed solution. If K ions in vermiculite and smectite interlayers were replaced by NH$_4$ during the final step in FES measurement, these interlayer sites would be included in FES calculations.

A *t* test showed that FES of Ca-saturated bulk soil materials exhibited significantly greater Cs/K selectivity than similarly treated rhizosphere soil materials ($P =$ 0.0406). *t* tests also indicated that FES of K-saturated bulk and rhizosphere soil materials exhibited significantly higher Cs/K selectivity than untreated bulk and rhizosphere soil materials ($P =$ 0.0408 and 0.0080, respectively). A series of *t* tests indicated no significant difference in $^cK_{ex}^{FES}$ overall between bulk and rhizosphere soil materials when soil treatments were grouped, or between untreated and Ca-saturated soil treatments when $^cK_{ex}^{FES}$ for bulk and rhizosphere soil materials of each treatment were grouped. In addition, *t* tests showed that when $^cK_{ex}^{FES}$ for bulk and rhizosphere soil materials of each treatment were grouped K-saturated soil materials exhibited significantly greater Cs/K selectivity than untreated ($P =$ 0.0002) or Ca-saturated ($P =$ 0.0085) soil materials.

Overall, these results suggest that the Cs selectivity of FES in the INL soils is influenced to a large degree by the cations present, as well as by weathering in the plant rhizosphere as indicated by the quantity of FES. Although differences in $^cK_{FES}$ between grouped bulk and rhizosphere soil materials were not statistically significant, the lower values for $^cK_{FES}$ in Ca-treated rhizosphere soil materials relative to Ca-treated bulk soil materials observed here is similar to results obtained by Wendling et al. (2004, 2005) who observed a decrease in $^cK_{ex}^{FES}$

(Cs/K) of illite weathered by citrate, oxalate or exudates from rhizosphere bacteria for 16 d. Potassium treatment might have masked these differences by creating "frayed edge sites" of a different nature than those in the Ca system, where collapse of high charge clays should be precluded. Also, the quantity of illite present in the INL soils may have been insufficient to exhibit statistically significant changes in $^cK_{FES}$ (Cs/K) between bulk and rhizosphere soil materials.

Cesium Sorption–Desorption

In all treatments, Cs sorption to soil materials increased with greater initial aqueous Cs concentration; however, significantly more Cs was sorbed by untreated and Ca-saturated soil materials than by K-saturated soil materials (Fig. 1). In every soil and treatment and at every initial Cs concentration, nearly 100% of Cs in solution was sorbed by the soil materials during the 96-h equilibration period, strongly suggesting that Cs was adsorbed only at high affinity sites. Several studies have demonstrated that on time scales of a few days or less Cs sorption is limited to external planar surfaces and interlayer edges, and that the magnitude of Cs sorption depends on aqueous Cs concentration and the relative affinities of Cs and other cations in solution for accessible exchange sites (Comans and Hockley, 1992; Francis and Brinkley, 1976; Sawhney, 1966; Staunton and Roubaud, 1997). Micas and vermiculites are known to preferentially sorb trace quantities of Cs from solution, and some research indicates that Cs adsorption to the soil solid phase is largely determined by the quantity of illite present (Francis and Brinkley, 1976; Staunton and Levacic, 1999).

Cesium desorption as a function of soil and desorbing solution at each initial Cs concentration is illustrated

Table 3. Measured capacity of frayed edge sites (FES) and Vanselow conditional Cs/K selectivity coefficients of FES ($^cK_{ex}^{FES}$) on bulk and rhizosphere soils that were untreated and treated with either 0.5 *M* CaCl$_2$ or 1 *M* KCl.

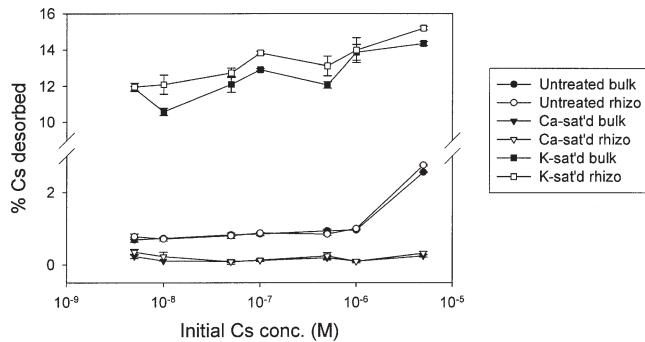| Soil	Treatment	FES (mmol$_c$ kg^{-1})	Cs occupied FES (mole fraction)	$^cK_{ex}^{FES}$ (Cs/K)
Bulk	None	5.75 ± 0.20	0.27	4.92 ± 0.08
Rhizosphere	None	6.86 ± 0.01	0.26	4.71 ± 0.05
Bulk	CaCl$_2$	5.38 ± 0.39	0.27	5.05 ± 0.17
Rhizosphere	CaCl$_2$	6.05 ± 0.65	0.25	4.53 ± 0.32
Bulk	KCl	7.26 ± 0.23	0.26	5.52 ± 0.28
Rhizosphere	KCl	7.59 ± 0.29	0.26	5.39 ± 0.18

Fig. 2. Amount of Cs desorbed from bulk and rhizosphere soils as a percentage of total Cs sorbed.

in Fig. 2. A multi-factor ANOVA indicated significant differences in Cs desorption as a function of the desorbing cation at all initial Cs concentrations. Cesium desorption in bulk versus rhizosphere soils was first examined using a multi-factor ANOVA at each initial Cs concentration, where all desorbing cation treatments were grouped. This indicated that Cs desorption from rhizosphere soil was significantly greater than desorption from bulk soil at initial Cs concentrations 1×10^{-8}, 1×10^{-7}, and 5×10^{-6} M. Each desorbing cation treatment was then examined separately using a single-factor ANOVA at each initial Cs concentration.

In the untreated soils, Cs desorption from rhizosphere soils in the presence of mixed-cation solution was significantly greater than desorption from bulk soils at initial Cs concentrations 1×10^{-6} and 5×10^{-6} M. There was no significant difference in Cs desorption between Ca-saturated bulk and rhizosphere soils at any initial Cs concentration examined. Cesium desorption from K-saturated rhizosphere soils was significantly greater than desorption from K-saturated bulk soils at 1×10^{-8}, 1×10^{-7}, 5×10^{-7}, and 5×10^{-6} M initial Cs concentrations. The higher desorption from the K-saturated rhizosphere soil is consistent with the lower Cs/K selectivity observed for the FES in the rhizosphere soil. Although the difference was small, it was apparently sufficient to allow more K for Cs exchange.
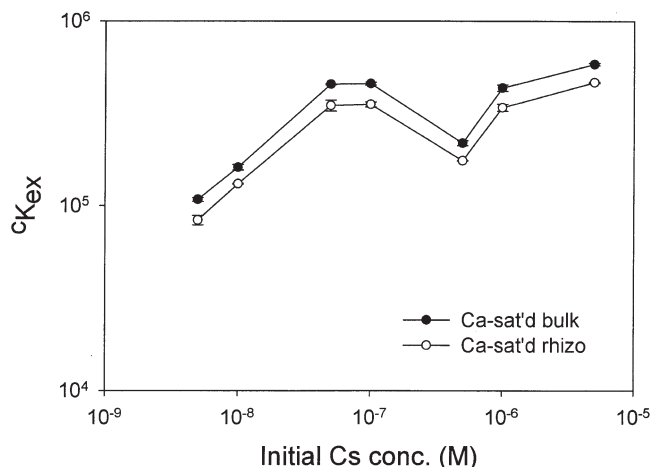

Fig. 3. Vanselow conditional exchange coefficients ($^c K_{ex}$) calculated from binary Cs/Ca exchange on Ca-saturated bulk and rhizosphere soils.
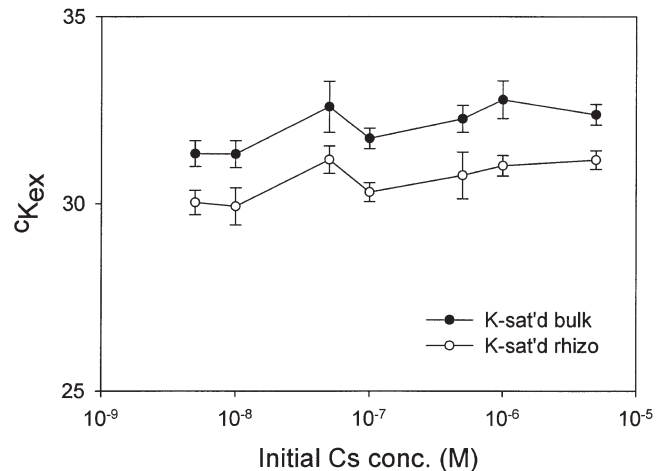

Fig. 4. Vanselow conditional exchange coefficients ($^c K_{ex}$) calculated from binary Cs/K exchange on K-saturated bulk and rhizosphere soils.

Conditional Cesium/Calcium and Cesium/ Potassium Exchange

Vanselow conditional exchange coefficients were calculated from binary Cs/Ca exchange (Fig. 3) and Cs/K exchange (Fig. 4) on the FES of both bulk and rhizosphere soils following Cs sorption to Ca-saturated or K-saturated soils. Conditional Cs/Ca exchange coefficients for both bulk and rhizosphere soils are significantly greater than Cs/K exchange coefficients at all initial Cs concentrations. These results show that sorbed Ca was more easily exchanged by Cs on both bulk and rhizosphere soils than was K; however, the results also suggest that either Ca is displaced from high affinity FES sites, which should not have sorbed Ca, or that some of the Cs is exchanging with Ca at low affinity sites. Given the high Cs/Ca selectivity coefficient, it appears that Cs is displacing at least some Ca from high affinity sites. We were unable to determine how much K was displaced in the Ca treatments.

Multi-factor ANOVAs indicated that both $^c K_{ex}$ (Cs/Ca) and $^c K_{ex}$ (Cs/K) are significantly greater overall for bulk soils than for rhizosphere soils. The change in Cs/Ca selectivity is in agreement with a laboratory study by Wendling et al. (2004) that showed illite reaction with oxalate lowered Cs selectivity with respect to Ca. That result was attributed to an increase in the number of low affinity sites relative to FES.

DISCUSSION

Our results indicate that Cs in the soil rhizosphere may be more available for plant uptake than previously indicated by studies on pure minerals and bulk soils. Mineral weathering mechanisms are primarily related to the production of acids and complexing compounds by plants and soil microbes, as well as exchange and uptake of elements among soil minerals, the soil solution, and plants (Leyval and Berthelin, 1991). Our work demonstrates that exudates from crested wheatgrass roots and the associated microbial communities are likely to enhance weathering of micaceous phyllosilicate min-

erals and increase the quantity of bioavailable Cs. This indicates that phytoremediation could potentially be utilized for the successful removal of ^{137}Cs from contaminated surface soils at the INL. The experiments described here do not adequately represent all of the processes and interactions that occur in the plant rhizosphere in a living system. In such a dynamic system, the uptake of K and Cs from the soil solution would likely accelerate desorption of these ions from FES of micaceous phyllosilicate minerals and further enhance uptake.

Both the type of soil material (i.e., bulk vs. rhizosphere soil) and the cation composition of the desorbing solution significantly affected Cs desorption from INL soil. Rhizosphere soils exhibited a greater proportion of Cs-selective FES than did bulk soils, and demonstrated significantly greater Cs desorption as compared to bulk soils at aqueous Cs concentrations between 5×10^{-9} and 5×10^{-6} *M*. As expected, both KCl and the mixed-cation solutions containing K were more effective at desorbing Cs from bulk and rhizosphere soils than was the CaCl$_2$ solution.

Increased weathering in the rhizosphere is likely to alter Cs bioavailability in INL rhizosphere soils as compared with bulk soils at environmentally relevant Cs concentrations. Cesium phytoavailability will be determined by the ability of a plant to extract Cs from the FES at the time of uptake. Both K availability and the location of ^{137}Cs within micaceous minerals will affect the success of remediation technologies dependent on the weathering of minerals to release 'fixed' Cs. Trace quantities of Cs will sorb selectively to the FES of micaceous phyllosilicate minerals. Over time, Cs may diffuse into mineral interlayers and become less available; however, such "fixed" Cs presents little danger for transport or unintended uptake by living organisms.

ACKNOWLEDGMENTS

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