Comparison of 0.1 M Stable CsCl and 1 M NH4NO3 as an Extraction Reagent to Evaluate Cs-137 Mobility in Soils

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To evaluate the mobility and bioavailability of 137Cs in soils, we compared the extraction of 137Cs with stable Cs and ammonium solutions from 137Cs-contaminated minerals and soils. The extraction yields of 137Cs with stable Cs were significantly lower than those with ammonium for minerals with frayed edge sites, but such differences were not observed for minerals without frayed edge sites. The amount of 137Cs extracted with stable Cs from soils was lower than, or equal to, that extracted with ammonium. The above results suggest that stable Cs extracted the 137Cs from easily accessible sites. Plant available 137Cs was assessed using Kochia (Bassia scoparia) cultivated in pots of contaminated soils, and compared with soil parameters including extractable 137Cs and K, and radiocesium intercept potential. The 137Cs/K ratio extracted with stable Cs solution was found to be a potential index for evaluation of the easily mobile and bioavailable fraction of 137Cs in soil.

Keywords Extraction, radiocesium, soil, mineral, stable CsCl, plant uptake

Introduction

Soon after the Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident in March of 2011, a large amount of 137Cs was released into the atmosphere and deposited mainly in the area surrounding Fukushima. In soil, most 137Cs is retained in the surface layer, but a portion is absorbed by plants or leached with water. Because 137Cs has a long half-life (30.2 years), it is essential to evaluate the mobility of 137Cs in soils in farmland as well as forests to enable reliable prediction of its uptake by plants via root systems or leaching to downstream ecosystems. For instance, the ratios of the 137Cs concentrations in plants to those in rhizosphere soils can vary by up to three orders of magnitude, even for the same soil type and plant species. As a result, the factors causing these variations have been studied based on the mobility of 137Cs in soils as well as from other abiotic and biotic perspectives (e.g., water management of paddy fields and potassium fertilization as a strong competitor for uptake). 137Cs adsorbed onto soils can be classified into three forms with different mobility. The first (designated here as RES-137Cs) is bound to nonspecific ion exchange sites (RESs), which exhibit low selectivity for Cs and a lesser extent ammonium and K. If the concentration of these cations is sufficient, their specific sorption in wedge zones induces the collapse of FESs. When FESs collapse, FES-137Cs is fixed and changed to a third form (Fix-137Cs). Because trace amounts of 137Cs due to contamination are rapidly trapped by FESs, RES-137Cs is usually rare in soil. In addition, Fix-137Cs is generally immobile. Therefore, the behavior of FES-137Cs is most important to evaluate the mobility and bioavailability of 137Cs in soil.

The FES capacities in soils are evaluated using the radiocesium intercept potential (RIP), which is defined as RIP = [FES]cFES(Cs-K), where [FES] is the FES capacity and cFES(Cs-K) is the selectivity coefficient of Cs to K in FESs. In most cases, the average cFES(Cs-K) for soils can be approximated as 1000, while the RIP capacity is given by [FES] = RIP/1000. Consequently, 137Cs is more mobile in soil with a lower RIP value; thus, RIP is used to express the potential mobility of 137Cs in soils from the viewpoint of the FES capacity. For instance, plants grown in soils with a lower RIP tend to show higher 137Cs uptake.

The mobility of 137Cs in soil has also been evaluated by extraction techniques, with ammonium salts solutions commonly used as the extractant. For example, the 137Cs concentrations in trees, shrubs, and grasses were positively correlated with 1 M NH4NO3-extractable 137Cs in Norwegian forests, and 137Cs concentrations in paddy-field rice were correlated with 1 M CH3COONH4-extractable 137Cs/K ratio. Solution of stable Cs salts is also used as an extractant for 137Cs contaminated soils or minerals because excess amounts of stable Cs should be an effective exchanger for trace amounts of 137Cs. Although excess Cs might induce the collapse of FESs, the 10 – 80% of 137Cs was desorbed by a stable Cs solution in some cases, suggesting the
utility of a stable Cs solution as an extractant. This study was conducted to determine if stable Cs-extractable 137Cs is useful for evaluating the mobility of FES-137Cs in soils. To accomplish this, we compared the extraction behavior of 137Cs with 0.1 M stable Cs and 1 M NH₄ solution from 137Cs-contaminated test minerals with or without FES. A similar comparison of 108 farmland soils with wide ranging physicochemical properties (including RIP and mineral compositions) was also conducted. Moreover, we tested whether 0.1 M stable Cs-extractable 137Cs can contribute to a more precise prediction of plant uptake of 137Cs using pot cultivation of Kochia (Bassia scoparia), a potential plant species for phyto remediation of 137Cs from soil.

Experimental

Extraction of 137Cs from artificially-contaminated test minerals

Kaolinite, montmorillonite, mordenite, illite, muscovite, and vermiculite were obtained from distributors (Table S1, Supporting Information). Upon X-Ray diffraction (XRD) analysis, vermiculite produced peaks of micaceous minerals and vermiculite, itself, while illite and muscovite showed peaks of micaceous minerals (Fig S1, Supporting Information). The radio cesium intercept potential (RIP) of the minerals was measured by the Kyushu Environmental Evaluation Association according to the method described by Wauters et al. (details of measured by the Kyushu Environmental Evaluation Association). The RIP was higher in minerals with FESs (illite, muscovite, and vermiculite) than in kaolinite and montmorillonite (Table S1). Although mordenite should contain no FESs, it had the highest RIP. This was likely because mordenite has micropores that specifically adsorb Cs, which may cause an overestimation of RIP.

Preparation of 137Cs-contaminated minerals and subsequent extraction were conducted as described by De Koning and Comans. Briefly, a 50-mg aliquot of the test mineral was mixed with 15 mL of 0.1 mM KCl in a 30-mL polypropylene bottle by shaking (150 rpm) at 25°C for 7 d (n = 10 for each mineral). The potassium adsorption ratio, i.e., $\frac{[\text{K}(\text{mM})]}{\sqrt{[\text{Ca}(\text{mM})] + [\text{Mg}(\text{mM})]}}$, in the aqueous phase of the suspension was found to be above 0.05, regardless of inherent K (Table S1, Supporting Information), indicating that the available FESs were saturated with K, as in the case of soils and sediments described in the literature.

The above mineral suspension was spiked with 15 μL of a 137Cs solution (200 kBq mL⁻¹ containing 0.46 μM 137Cs, 75 μM stable Cs and 0.1 M HCl). Following shaking for 24 h, a 2-mL subsample was taken, passed through a membrane filter (pore size, 0.2 μm; Microsep Advance, Pall, Port Washington, NY, USA), and analyzed for 137Cs. The amount of Cs (stable Cs + 137Cs) in the aqueous phases of the suspensions was below 10⁻³ M after adsorption (Table S1, Supporting Information); thus, FES would not collapse even though most 137Cs should have been adsorbed onto the FESs, as in the case of illite in the literature.

The remaining suspension (13 mL, n = 5 for each reagent) was amended with 7.5 M NH₄NO₃ or 0.75 M stable CsCl (2 mL) to give a final NH₄NO₃ or CsCl level of 1 M or 0.1 M, respectively. For the CsCl solution, 0.1 M was used instead of 1 M because Cs has a greater exchangeability than NH₄, since the selectivity coefficient of Cs to NH₄ in the FES is about 200. After shaking for 24 h, a 2-mL subsample was filtered and subjected to 137Cs analysis. The amount of 137Cs desorbed from the mineral was then calculated from the difference between the radioactivity in the filtrate before and after the extraction procedure. The values obtained were corrected for the dilution by adding 2 mL of the extractants.

The radioactivity of 137Cs was measured using a NaI detector (Wallac1480, PerkinElmer, Waltham, MA, USA). Potassium, Ca, and Mg were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES; ICP750, Thermo Fisher, Waltham, MA, USA), while stable Cs was measured using an inductively coupled plasma mass spectrometer (7500 cx, Agilent, Santa Clara, CA, USA).

Extraction of 137Cs from contaminated farmland soils

Farmland soils from depths of 0 to 15 cm were sampled at 108 sites (63 paddy fields, 14 buckwheat fields, and 31 soybean fields) in Fukushima Prefecture from September to November 2014. The samples were air-dried, passed through a 2-mm sieve and homogenized. Sampling, pretreatment, and measurement of the total 137Cs concentration, RIP and XRD of soils were conducted by the Ministry of Agriculture, Forestry, and Fisheries of Japan. The RIP ranged from 0.19 to 7.03 mol kg⁻¹. Additionally, an XRD analysis revealed that all samples contained kaolinite and micaceous minerals. Among 60 samples with smectite, eight contained vermiculite, 12 contained chlorite, and 40 contained vermiculite and chlorite. Among the remaining 48 samples without smectite, one contained vermiculite, 13 contained chlorite, and 32 contained vermiculite and chlorite. The XRD peak intensities of soils were classified into four groups (−: not detected; ±: scarce; +: common; ++: abundant).

Twelve grams of soil were extracted with 120 mL of each extractant (0.1 M CsCl or 1 M NH₄NO₃) in a 250-mL polypropylene bottle by shaking (150 rpm) at 25°C for 48 h. The suspension was then centrifuged at 1660g for 10 min to obtain the extract, which was passed through a cellulose filter (pore size, ca. 2.5 μm; Whatman No. 42, GE Healthcare, Chicago, IL, USA), then packed into 100 mL polypropylene containers (50 mm inner diameter, 62 mm height) to measure the radioactivity. The extraction yield of 137Cs was calculated as [137Cs (Bq mL⁻¹)] in extract × 120 (mL)/{[initial 137Cs (Bq g⁻¹) in soil] × 12 (g)}.

The radioactivity of 137Cs was measured using a P-type coaxial HPGe detector (GEM65P4-83, ORTEC, Oak Ridge, TN, USA) equipped with the Gamma Studio software (DSP200/W32, SEIKO EG&G, Tokyo, Japan). Calibration was conducted using MX033U8PP standard sources (The Japan Radiisotope Association, Tokyo, Japan).

Pot cultivations of Kochia using a 137Cs contaminated soil

Surface soil (0 – 5 cm in depth, soil type: Andosols) contaminated by the FDNPP accident was collected in July of 2011 from a farm in Ibaraki Prefecture, air-dried and stored. The dominant constituents of the soil were allophane and ferrihydrite, and XRD peaks corresponding to gibbsite, quartz, and kaolinite were detected, as well as lesser amounts of chlorite, vermiculite, hydroyx-Al interlayered vermiculite and micaceous minerals. The RIP of the soil was 0.99 ± 0.03 mol kg⁻¹; this value is comparable to the RIP values for Andosols in Fukushima and the surrounding areas (mean RIP = 0.98 mol kg⁻¹), yet this is relatively smaller than those in other soil types (e.g., mean RIP in Fluvisols = 1.79 mol kg⁻¹). Other characteristics of the soil have been reported elsewhere.

To modify the mobility of 137Cs in the soil, mordenite-type zeolite (the same mordenite as the test mineral in the previous section) or exfoliated vermiculite (Vermitech Corporation, a different product from the vermiculite used as the test mineral)
was mixed with the soil. Zeolite and exfoliated vermiculite were selected because they have been applied to farmlands in Fukushima to examine their ability to reduce the Cs uptake by plants. Among zeolites, mordenite selectively adsorbs Cs inside micropores because the size of micropores and the Al/Si ratio are suitable for the adsorption of Cs. The RIP of mordenite is high (73 mol kg⁻¹ in this study), but the adsorption sites of mordenite do not fix Cs to the same degree as FESs.

In November 2012, 57 kg of air-dried soil was divided into three portions, one 19 kg portion was mixed with 1 kg of exfoliated vermiculite (hereafter referred as EV soil), another 19 kg portion was mixed with 1 kg of mordenite (MZ soil), and the other 19 kg portion was used as is (NC soil). The proportion of soil amendments in this study (5%) was comparable to those applied in some field experiments, yet it was higher than those actually applied to amend farmlands in Fukushima (0.3%, unpublished data). Soil (2.2 kg of EV, MZ or NC) was placed in a plastic pot (surface area: 0.02 m²; volume: 0.003 m³) without drain outlets; five pots were prepared for each soil. Fifteen pots were placed under the roof and kept flooded by adding tap water weekly for five months with the expectation that Cs would be redistributed in the soil. After discarding excess water, the soil in the pots was allowed to dry for 2 weeks. The soil was then stirred in the pots, after which a seedling of Kochia (Bassia scoparia) that was purchased from a domestic test was transplanted into each pot. Chemical fertilizer (nitrogen: 64 mg, phosphorus: 64 mg, potassium: 40 mg) was applied to each pot. The pots were then placed under the roof and tap water was supplied as appropriate for growth of the Kochia. The aboveground parts of the plants were sampled at 115 d after planting, at which time they were rinsed carefully with tap water to remove adhered soil. The plant samples were then dried in an oven (80°C), weighed, pulverized with a titanium mill, and packed into 100 mL polypropylene containers to measure the radioactivity using a P-type coaxial HPGe detector.

Soil in the pots after cultivation was air-dried, passed through a 2-mm sieve, and homogenized. Next, 50 g of soil were extracted with 500 mL of each extractant (0.1 M CsCl, 1 M NH₄NO₃) and tap water was supplied as appropriate for growth of the Kochia. The aboveground parts of the plants were sampled at 115 d after planting, at which time they were rinsed carefully with tap water to remove adhered soil. The plant samples were then dried in an oven (80°C), weighed, pulverized with a titanium mill, and packed into 100 mL polypropylene containers to measure the radioactivity using a P-type coaxial HPGe detector.

Results and Discussion

Extraction of ¹³⁷Cs from artificially-contaminated test minerals

For the test minerals without FES (kaolinite, montmorillonite, and mordenite), more than 83% of the ¹³⁷Cs was extracted with both extractants (Fig. 1). For kaolinite and montmorillonite, the extraction yields obtained with 0.1 M CsCl were equal to those with 1 M NH₄NO₃. These results indicate that both 0.1 M CsCl and 1 M NH₄NO₃ are effective extractants for trace amounts of RES-¹³⁷Cs from these test minerals. For mordenite, the extraction yield with 0.1 M CsCl (100% extraction yield) was higher than that with 1 M NH₄NO₃ (83% extraction yield); this result indicates that micropores of mordenite selectively adsorb Cs, although because this reaction is reversible, they can be considered as RESs.

In contrast, for micaceous minerals with FESs (vermiculite, illite, and muscovite), extraction yields with 0.1 M CsCl (vermiculite: 6%; others: 19 – 31%, Fig. 1) were consistently lower than those with 1 M NH₄NO₃ (vermiculite: 9%; others: 55 – 73%, Fig. 1). For muscovite, extraction yields for the clay fraction were lower than those for the silt fraction, likely because RIP was higher, and more ¹³⁷Cs was adsorbed as Fix-¹³⁷Cs in the former fraction (Table S1, Supporting Information). In addition, the extraction yields from muscovite (clay fraction) with 1 M CsCl (23 – 24%, n = 2) were not higher than the extraction yields with 0.1 M CsCl (22 – 27%, n = 5, Fig. 1), suggesting that they would not increase even if the concentration of CsCl was higher than 0.1 M. For vermiculite, extraction yields with 0.1 M CsCl and 1 M NH₄NO₃ were lower than those for illite and muscovite, probably because FES of vermiculite collapsed more easily and more ¹³⁷Cs was adsorbed as Fix-¹³⁷Cs.

Collectively, these results suggest that some of the FES-¹³⁷Cs in micaceous minerals cannot be extracted with stable Cs, but is extractable with NH₄. This might seem counterintuitive because Cs adsorbs more strongly to micaceous minerals than NH₄ under hydrated conditions; however, the relationship might be different under the dehydrated conditions within vermiculite interlayers in which the ionic radius of NH₄⁺ (1.4 Å) is smaller than that of Cs⁺ (1.65 Å). Sawhney proposed that adsorption of Cs in vermiculite decreases the interlayer distance, but not enough to prevent Cs ions from diffusing into the interlayers and replacing the Cs ions. Because the NH₄ ion has a similar ionic radius and thermodynamic properties, e.g., hydration enthalpy (NH₄: 364 kJ mol⁻¹; K: 393 kJ mol⁻¹), to those of K, we propose that the interlayer distance in vermiculite with adsorbed Cs is large enough to permit NH₄ ions to diffuse in and replace the Cs ions. Ions bound to FES or interlayers are not hydrated; therefore, NH₄ in the interlayers diffuses more readily than does Cs and may replace the ¹³⁷Cs bound to FESs at the end of the interlayers. The ¹³⁷Cs extracted with 1 M NH₄NO₃ may have contained
mobile and less-mobile fractions of FES-137Cs, but that with 0.1 M CsCl only contained a mobile fraction. Therefore, 0.1 M CsCl should be a better extractant for estimating the easily-bioavailable 137Cs in soil than 1 M NH4NO3. To examine this hypothesis, we provide the results from two experiments in the following sections.

Extraction of 137Cs from contaminated farmland soils

The yields of 137Cs extracted from the 108 farmland soils with 0.1 M CsCl (E Cs) or those with 1 M NH4NO3 (E NH4) were negatively correlated with RIP (Fig. 2). Because the E Cs, E NH4, and RIP of the sampled farmland soils had non-normal distributions (Shapiro-Wilk test), they were analyzed using Spearman’s rank correlation. These results reflect that 137Cs in soils with lower RIP is more easily extracted. Vandebroek et al.21 also found a strong negative correlation between the square root of RIP and logarithm of the extraction yields with 0.1 M HCl from artificially-contaminated soils. They interpreted that the release of trace 137Cs from soils exposed to 0.1 M HCl-extraction reflected the susceptibility of the minerals to weathering.21 Because the extraction process in this study (ion-exchange reaction) was different from that used in Vandebroek et al.21 (washing with weak acid), a comparison of the results using the same soils will provide more useful information for evaluating the mobility of 137Cs in soil.

The E Cs values were ≤ the E NH4 values (Fig. 3) and the average ratio of E Cs to E NH4 (R Cs/NH4) was 0.7. This suggests that 0.1 M CsCl extracted the 137Cs from easily accessible sites in soil, and such 137Cs was inferred to be more mobile. There was no significant correlation between RIP and R Cs/NH4 (r s = –0.1, p > 0.1, Spearman’s rank correlation), implying that the variation in R Cs/NH4 was affected by slight differences in the
binding structure of FES-\(^{137}\)Cs. The farmland soils contained micaceous minerals, which should affect the mobility of \(^{137}\)Cs in soil. However, because the XRD peak intensities of micaceous minerals in 103 of the 108 soils were ranked into the same group (+: common), the extractabilities of \(^{137}\)Cs could not be examined based on the abundance of micaceous minerals.

\(^{137}\)Cs concentration in plant and extractable \(^{137}\)Cs in the pot cultivation experiment

The \(^{137}\)Cs concentrations of plants (Kochia) grown in the mordenite mixed soil (MZ plot: 43 ± 6 Bq kg\(^{-1}\)) did not differ significantly from those in control soil (NC plot: 51 ± 13 Bq kg\(^{-1}\)), but were higher than those in the exfoliated vermiculite mixed soil (EV plot: 20 ± 2 Bq kg\(^{-1}\)). The \(^{137}\)Cs concentrations in Kochia did not show clear relationships with concentrations of total \(^{137}\)Cs, 0.1 M CsCl-extractable \(^{137}\)Cs, 1 M NH\(_2\)NO\(_3\)-extractable \(^{137}\)Cs, 1 M CH\(_3\)COONH\(_4\)-extractable \(^{137}\)Cs in soil or RIP (Fig. S2, Supporting Information). According to an investigation of paddy-field rice,\(^8\) the \(^{137}\)Cs concentrations in the plants showed no clear relationship with the total \(^{137}\)Cs or 1 M CH\(_3\)COONH\(_4\)-extractable \(^{137}\)Cs concentrations in soil, but were positively correlated with 1 M CH\(_3\)COONH\(_4\)-extractable \(^{137}\)Cs/K ratios. Similarly, in this study, the \(^{137}\)Cs concentrations in Kochia had a significant positive linear correlation with 0.1 M CsCl-extractable \(^{137}\)Cs/K ratios (\(R^2 = 0.76\), \(p < 0.001\)) (Fig. 4a), although the correlation was poor when 1 M NH\(_2\)NO\(_3\)-extractable \(^{137}\)Cs/K or 1 M CH\(_3\)COONH\(_4\)-extractable \(^{137}\)Cs/K ratios were used as explanatory variables (\(R^2 < 0.50\)) (Figs. 4b and 4c). These results are consistent with our previous hypothesis that \(^{137}\)Cs extracted with 0.1 M CsCl is relatively mobile in soil and more available for plants than that extracted with 1 M NH\(_2\)NO\(_3\) or 1 M CH\(_3\)COONH\(_4\).

The parameter 1/[Exchangeable K], where 1 M CH\(_3\)COONH\(_4\)-extractable K was used as exchangeable K, may be another important variable to explain \(^{137}\)Cs concentrations in plants because K competes with \(^{137}\)Cs and inhibits the uptake of \(^{137}\)Cs in the course of nutrient absorption by plants.\(^6\)\(^8\)\(^9\)\(^10\)\(^11\) Actually, the concentrations of \(^{137}\)Cs in Kochia were positively correlated with 1/[Exchangeable K] (Fig. 4d), but the plots scattered similarly to those in Figs. 4b and 4c and the coefficient of determination was still low (\(R^2 = 0.49\)). In addition, RIP is a well-known index for evaluation of the immobility of \(^{137}\)Cs in soil as described before, and the parameter, 1/[RIP [Exchangeable K]], has been used to evaluate the uptake of \(^{137}\)Cs by soybeans.\(^3\) However, the relationship between the concentrations of \(^{137}\)Cs in Kochia and 1/[RIP [Exchangeable K]] was very weak, as shown by the low coefficient of determination (\(R^2 = 0.19\)) (Fig. 4e).

As a result, 0.1 M CsCl-extractable \(^{137}\)Cs/K ratios were the best variables to explain the concentrations of \(^{137}\)Cs absorbed by Kochia. Because the change in the mobility of \(^{137}\)Cs in soil and subsequent plant uptake can be attributed to various factors (e.g., soil types, application rate of soil amendments, plant species), further research is required for a more detailed prediction. Nevertheless, our study demonstrated that 0.1 M CsCl extraction might be a good method for predicting the plant uptake of \(^{137}\)Cs during short-term cultivation as well as that from soil amended with zeolite (mordenite).

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Supporting Information

Basic properties (Table S1) and XRD patterns (Fig. S1) of test minerals, relationship between \(^{137}\)Cs concentration in plants and \(^{137}\)Cs concentration or extractable \(^{137}\)Cs in soil (Fig. S2), and the method of RIP measurement. These materials are available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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