Investigation of cesium adsorption on soil and sediment samples from Fukushima Prefecture by sequential extraction and EXAFS technique

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Previous studies have shown that radiocesium (mainly ^{137}Cs) was retained at the very surface of soils in Fukushima Prefecture. Clay minerals and micas are assumed as the main sorbents for cesium (Cs) in Fukushima, but direct evidence is lacking for this hypothesis. In this study, radiocesium in the natural sample (soil and sediment) from Fukushima Prefecture was investigated through sequential extraction experiment (modified BCR method), which showed that more than 94% of ^{137}Cs was fixed in the residual phase. The results indicated that most of Cs occurred in the interlayer of phyllosilicate minerals. Furthermore, Cs L_{III}-edge extended X-ray absorption fine structure (EXAFS) showed that the Cs species adsorbed on the natural samples were very similar to those adsorbed on clay minerals and micas. This finding provided the direct evidence on the significant contribution of clay minerals or micas to Cs retention in soils from Fukushima Prefecture.

Keywords: cesium, adsorption, clay minerals, sequential extraction, extended X-ray absorption fine structure (EXAFS), Fukushima

INTRODUCTION

The presence of radiocesium in the environment is of great concern because of its high solubility as an alkaline metal ion, its long half-life (30.2 years for ^{137}Cs), and its easy assimilation by living organisms (Cremers *et al.*, 1988; Bostick *et al.*, 2002; Tsukada *et al.*, 2002). The migration and the retention behavior of radiocesium are strongly dependent on the adsorption properties of the solid phase, including mineralogy, pH, ionic strength, competitive cations, and organic matter (Kim *et al.*, 1996; Kim and Kirkpatrick, 1997; Dumat and Staunton, 1999; Takahashi *et al.*, 1999; Cha *et al.*, 2006; Giannakopoulou *et al.*, 2007; Nakamaru *et al.*, 2007; Bellenger and Staunton, 2008; Fan *et al.*, 2012). It is generally considered that the clay minerals in soils and sediments are the major sorbents of cesium (Cs) (Anderson and Sposito, 1991; Kim *et al.*, 1996; Kim and Kirkpatrick, 1997; Choi *et al.*, 2005). The structure of Cs adsorption on montmorillonite and vermiculite was examined with extended X-ray adsorption fine structure spectroscopy (EXAFS), and outer-sphere (OS) and inner-sphere (IS) complexes were determined by Bostick *et al.* (2002). Their study also suggested that EXAFS is a very useful technique to investigate the type of Cs binding in environmental samples and to predict the migration behaviors of Cs.

The Fukushima Daiichi Nuclear Power Plant (FDNPP) accident, which was caused by the catastrophic earthquake and tsunami that occurred on 11 March 2011, led to great emissions of radioactive ^{137}Cs and serious soil contaminations around FDNPP and neighboring prefectures (Kinoshita *et al.*, 2011; Yasunari *et al.*, 2011; Yoshida and Takahashi, 2012). Investigations on vertical profiles showed that radiocesium was mainly retained at the very surface of soils in Fukushima Prefecture, and clay minerals and micas were speculated to be responsible for the high affinity of Cs in soils (Cha *et al.*, 2006; Kato *et al.*, 2012; Ohno *et al.*, 2012; Tanaka *et al.*, 2012; Watanabe *et al.*, 2012). However, no direct evidence exists on the host phase of Cs in such soils to support this hypothesis.

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In this study, radiocesium in the natural sample from Fukushima was investigated through leaching experiments. Moreover, Cs adsorption on clay mineral (vermiculite) and natural samples was also studied by EXAFS technique to examine the fixation mechanism of radiocesium on the soil samples in Fukushima Prefecture. As the concentration of radiocesium in the natural samples is much lower than the level required for EXAFS analysis, we needed to add stable Cs to the samples to measure EXAFS. However, if the Cs added is also fixed in a stable site such as an interlayer of clay minerals, it is most likely that original radiocesium is also most likely retained in the site.

EXPERIMENTAL

Sample collection and analyses

Soil (weathered granite) was collected at Site1 (N 37°34′60″, E 140°43′08″) in the pasture area in Yamakiya District, Kawamata Town in the northern part of Fukushima Prefecture on 29 May 2011. The sample was collected within 5 cm from the surface of the soil, which was not disturbed after the accident. A river sediment sample was collected at Site2 (N 37°34′52″, E 140°32′31″) in Kuchibuto River, Nihonmatsu City also in the northern part of Fukushima Prefecture. The sediment sample accumulated during the sampling period from 17 Sep. to 8 Dec. 2011 was collected with a suspended sediment sampler (Phillips *et al.*, 2000). The collected samples were dried at room temperature. Each sample was sieved with a 2 mm mesh screen and homogenized before it was loaded into a 2.5 cm diameter × 4.5 cm styrol bottle to determine the concentration of ^{137}Cs using a γ-ray spectrometer with a coaxial-type Ge detector (ORTEC, GEM-50195-P). The spectrometer was calibrated with shelf-standard prepared by the Low Level Radioactivity Laboratory of Kanazawa University.

The XRD patterns for the soil and sediment samples were measured by a powder X-ray diffractometer (MultiFlex, Rigaku Co.) with Cu Kα radiation at 40 kV and 20 mA. Each sample was scanned from 4° to 70° with a step interval of 0.02° at a rate of 1.0°/min.

Sequential extraction

The modified BCR procedures proposed by Rauret *et al.* (1999) were used to extract radiocesium (^{137}Cs) in the natural soil and sediment sample. Briefly, soluble and ligand exchangeable (F1), iron and manganese oxyhydroxide associated (F2), and organic matter and sulphide associated (F3) fractions were sequentially extracted by acetic acid (0.11 M), hydroxylammonium chloride (0.5 M), and hydrogen peroxide (8.8 M) + ammonium acetate (1.0 M) solution, respectively. The radiocesium (^{137}Cs) in each fraction was determined with the use of a γ-ray

spectrometer with a well-type Ge detector (GWL-120-16-LB-AWT-HJ-S, Seiko EG&G ORTEC) installed at the National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan (Kanai, 2011). The concentration of ^{137}Cs in the residual fraction (F4) was calculated as the difference between the total ^{137}Cs and the sum of ^{137}Cs in the other three fractions.

Adsorption experiment

The natural samples, including the soil and the sediment from Fukushima Prefecture, and vermiculite (reference sample) were saturated with CsCl solution following methods partly modified from previous studies (Anderson and Sposito, 1991; Bostick *et al.*, 2002). Briefly, the samples were equilibrated once with 0.50 M CsCl solution (1 h), twice with 0.10 M CsCl solution (1 h), and once with 0.050 M CsCl solution (6 h). After the above equilibration, the final suspensions were filtered. Solid phases were rinsed carefully with water to remove the CsCl solution remaining in the sample and were sealed into polyethylene bags for the EXAFS experiment.

EXAFS measurements and analyses

Cesium L$_{III}$-edge EXAFS was collected for Cs in the soil and sediment samples, Cs adsorbed on vermiculite, and Cs$^+$ solution (0.50 M CsCl aqueous solution). Cesium L$_{III}$-edge EXAFS spectra were obtained at BL-12C at KEK Photon Factory (Tsukuba, Japan). X-rays were monochromatized with a pair of Si (111) crystals between two Rh-coated mirrors for collimation and focusing. The adsorbed samples were placed at an angle of 45° from the incident beam and measured in fluorescence mode using a 19-element Ge solid-state detector to obtain their Cs L$_{III}$-edge EXAFS spectra. Energy was calibrated with the first peak of CsCl at 5011.3 eV. Cesium K-edge EXAFS was also measured at BL01B1, SPring-8, but the oscillations in the EXAFS spectra for the reference materials and samples were very weak. This result indicates that Cs L$_{III}$-edge can be more useful than K-edge in obtaining the local structure of Cs by EXAFS technique.

The EXAFS data were analyzed with REX2000 software (Rigaku Co. Ltd.) and FEFF 7.02 (Zabinsky *et al.*, 1995). After extracting EXAFS oscillation by spline smoothing method to obtain $\mu(0)$, the $\chi(k)$ function weighed by k^3 was Fourier transformed (FT) to obtain a radial structure function (RSF) with a *k*-range of approximately 1.8–7.0 Å^{-1}. The distinct shells of the RSF were then back-transformed to *k*-space for spectral simulation with the use of the parameters extracted by the FEFF 7.02. The backscattering amplitudes and phase-shift functions for Cs–O in this calculation were extracted from the structure of cesium hydroxide (CsOH). The Debye-Waller factor (σ^2) was constrained at 0.015, and ΔE_0 was constrained to the same value for each shell, as reported by Bostick *et*
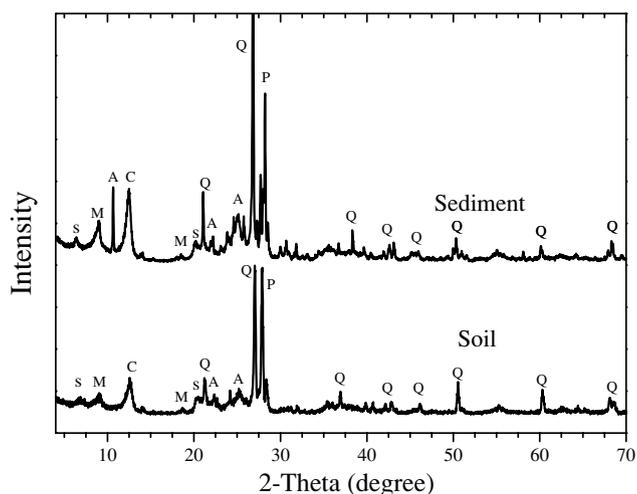
Fig. 1. XRD patterns for the soil and sediment sample from Fukushima Prefecture. S, smectite; M, mica; C, chlorite; A, anorthite; Q, quartz; P, plagioclase.

Table 1. ^{137}Cs *in different fraction in the soil and sediment sample (Bq/g)*

Sample	F1	F2	F3	F4
Soil	0.047 (0.10)	1.34 (2.81)	1.45 (3.02)	45.0 (94.1)
Sediment	0.0006 (0.01)	0.070 (1.13)	0.037 (0.60)	12.4 (98.3)

Value in parentheses indicates the relative percentage of each fraction (%).

al. (2002). The quality of the fit was given by the goodness of fit parameter, *R* factor, as expressed by the following formula:

$$R = \sum \left\{ \chi_{\text{obs}}(E) - \chi_{\text{cal}}(E) \right\}^2 \Big/ \sum \left\{ \chi_{\text{obs}}(E) \right\}^2$$

where $\chi_{\text{obs}}(E)$ and $\chi_{\text{cal}}(E)$ are the experimental and calculated absorption coefficients at a given energy (*E*), respectively.

RESULTS AND DISCUSSION

XRD pattern

Similar XRD patterns were observed for both the soil and sediment sample (Fig. 1). Two lager peaks at 27° and 28°, which correspond to quartz and plagioclase, respectively. The diffractions at 6.9°, 8.9° and 12.5° were assigned to the characteristic peaks of smectite, mica, and chlorite, respectively. This result suggested that clay minerals and micas are present in the natural samples from Fukushima Prefecture.

Radiocesium in the natural sample

The total concentration of ^{137}Cs in the soil and sediment sample was 48.0 ± 3.62 Bq/g and 6.28 ± 0.20 Bq/g, respectively, after correction based on its half-life (corrected on 11 March 2011). This finding suggests that the samples have been severely contaminated because of radiocesium emission from the FDNPP accident. The results from sequential extraction experiment showed that only small parts of ^{137}Cs were released into the aqueous phases (Table 1). Less than 0.1% of the total ^{137}Cs in the

natural sample was extracted in the first step, which implies that extremely small amounts of ^{137}Cs can be found in the soluble and exchangeable species in the soil and the sediment. A lower percentage of soluble ^{137}Cs was observed in the sediment compared with that of the soil, which is possible because most of the soluble ^{137}Cs in the sediment has been released into the river. A relatively larger amount of ^{137}Cs was observed in F2 and F3 fractions, but it was still significantly lower than those normally reported for other metals (such as Zn, Pb, Cu) in these fractions (Mossop and Davidson, 2003). The results indicated that most of ^{137}Cs was not adsorbed on iron and manganese oxyhydroxide, organic matter, and sulphide. More than 94% of ^{137}Cs still remained in the residue fraction after the three-step extractions for the soil and the sediment from Fukushima Prefecture. This finding can be explained by the fact that most of Cs occurs in the interlayer or frayed edge sites (FES) of clay minerals (Choi *et al.*, 2005).

Radioactivity of ^{134}Cs was also determined in some selected samples (F1 and F2 fractions in the soil and the sediment samples, respectively). The activity ratios of $^{137}Cs/^{134}Cs$ were 1.03 ± 0.07 and 0.98 ± 0.12 (corrected on 11 March 2011) for the samples, respectively. The values were within the range of 0.8 and 1.1, which were similar to those reported for the other samples affected by the FDNPP accident (Kinoshita *et al.*, 2011; Kato *et al.*, 2012; Honda *et al.*, 2012). This result shows that the radiocesium in our samples also originated from the accident.

Cs L_{III}-edge EXAFS

EXAFS analyses have been successfully conducted to explore the local structures of Cs adsorption on clay minerals (Bostick *et al.*, 2002; Nakano *et al.*, 2003) and crown ethers (Kemner *et al.*, 1996; Antonio *et al.*, 1997). Figures 2A and B show the k^3-weighted $\chi(k)$ spectra of Cs L_{III}-edge EXAFS and their radical structural functions (RSF, phase shift not corrected) for CsCl solution, Cs-adsorbed vermiculite, and Cs adsorbed on the natural samples.

The $k^3\chi(k)$ of Cs adsorbed-vermiculite showed significantly different oscillations in frequencies and amplitudes compared with those for CsCl solution (Fig. 2A),

Table 2. The structural parameters for Cs-adsorbed samples obtained by curve-fitting analysis of EXAFS data

Samples	Shell	CN	R (Å)	ΔE_0 (eV)	σ^2 (Å^2)	R factor (%)	N_O/N_I*
CsCl solution	Cs–O (OS)	2.8	2.98	8.2	0.015	5.5	
Vermiculite	Cs–O (OS)	3.4	3.01	3.8	0.015	5.6	0.23
	Cs–O (IS)	15	4.14		0.015		
Soil	Cs–O (OS)	1.8	3.14	7.6	0.015	8.4	0.32
	Cs–O (IS)	5.7	4.21		0.015		
Sediment	Cs–O (OS)	1.7	3.14	6.9	0.015	8.0	0.22
	Cs–O (IS)	7.7	4.19		0.015		

OS, OS complexes; IS, IS complexes.
*Ratio of Cs–O coordination numbers of OS to IS complexes.
CN, coordination number; R, interatomic distance; ΔE_0, threshold E_0 shift; σ, Debye–Waller factor.
Errors in the fitted parameters were estimated to be generally ±0.02 Å for R, ± 20% for N, and 20% for σ^2 (O'Day et al., 1994).
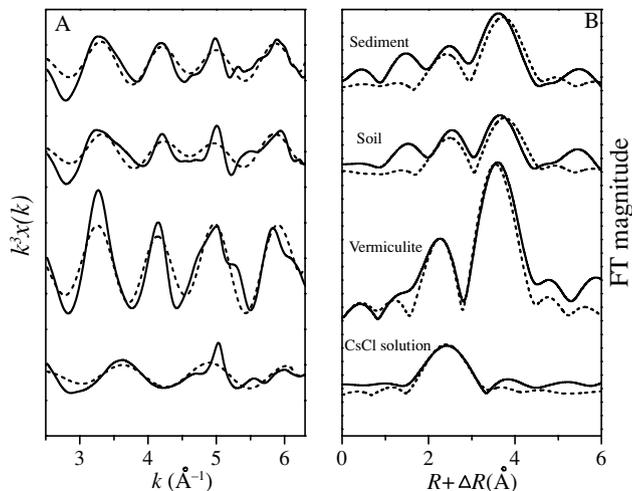
Fig. 2. Cesium L_{III}-edge EXAFS spectra of reference material, Cs-adsorbed samples. (A) k^3-weighted $\chi(k)$ spectra, and (B) RSF of (A) (phase shift not corrected). Solid lines are spectra obtained by experiments and dotted lines are fitted spectra by curve-fitting analysis.

indicating that some inner-sphere complexes have been formed when Cs was adsorbed on vermiculite. RSF confirmed the differences between the $k^3\chi(k)$ spectra. In comparison with the RSF of CsCl solution, another obvious peak at $R + \Delta R = 3.5$ Å was observed in vermiculate aside from the first peak at $R + \Delta R = 2.4$ Å (Fig. 2B). The first peak in the RSF of vermiculite and CsCl solution was well fit with a Cs–O shell at a distance of 3.01 Å and 2.98 Å, respectively (Table 2). The similar Cs–O distance suggested the same coordination environment, in which Cs carries some hydrated water molecules even when adsorbed on vermiculite to form OS complexes. The sec-

ond peak in vermiculite RSF was fit with a larger Cs–O shell at a distance of 4.14 Å (Table 2), which is similar to Cs adsorbed on vermiculite, montmorillonite, and clinoptilolite (Bostick *et al.*, 2002). The longer Cs–O distance was attributed to the formation of IS complexes, which are partially or fully dehydrated Cs coordinates with siloxane groups at the FES or within the interlayer of vermiculite and other clay minerals (Kim *et al.*, 1996; Bostick *et al.*, 2002).

The $k^3\chi(k)$ of Cs adsorbed on the soil and sediment samples from Fukushima also showed complex oscillations in k-space (Fig. 2A). Two principal coordination peaks were observed in the RSF of the natural samples at a similar position to those for Cs on vermiculite (Fig. 2B). Furthermore, the first shell was also fit with a Cs–O distance of 3.14 Å, whereas the latter one was fit with a Cs–O distance at 4.21 Å and 4.19 Å for the soil and sediment samples, respectively. The distances of the two Cs–O bonds in the soil and sediment samples were very similar to those in clay minerals (Bostick *et al.*, 2002), indicating that the adsorption for Cs on the natural samples from Fukushima can mainly be ascribed to the contribution of clay minerals or micas. Both OS and IS complexes can exist in the Cs-adsorbed natural samples.

A previous study suggested that the ratio of coordination numbers for each Cs–O shell (N_O/N_I) can be used to identify the fraction of OS and IS complexes, and a larger N_O/N_I value indicated the presence of relatively more OS complexes formed in the sample (Bostick *et al.*, 2002). The N_O/N_I value of the sediment sample (0.22) is almost the same as that of vermiculite, which reflected the dominance of the IS complexes as reported by Bostick *et al.* (2002). A larger N_O/N_I was observed in the soil sample (0.32), which suggested the higher fraction of OS complexes for Cs in the soil sample. Their difference can be

explained by at least two reasons. Firstly, organic matter in natural samples may play an important role in preventing the coordination of Cs with siloxane groups to form IS complexes, since organic matter has been suggested to influence their affinity for Cs (Dumat and Staunton, 1999). The effect of organic species was also speculated from the result of ^{137}Cs in F3 fraction in the sequential extraction experiment, but the effect can be minor because of the low values in the F3 fraction. Second, different types of clay minerals may occur in different natural samples. Formation of OS and IS complexes for Cs is strongly dependent on the mineralogy and the associated crystal chemistry of clay minerals and micas. Compared with vermiculite and illite, montmorillonite tends to generate OS complexes with Cs ion (Kim *et al.*, 1996; Bostick *et al.*, 2002). It is possible that the mineralogy of the soil sample is responsible for the larger N_O/N_I value of the soil sample in this study.

As stable Cs shows similar geochemical behavior as radioactive Cs in the environment (Tsukada *et al.*, 2002; Giannakopoulou *et al.*, 2007), the retention of radiocesium in natural samples should be expected to be the same as that in Cs adsorption experiment. As discussed in the sequential extraction section, the fact that more than 94% of ^{137}Cs was found in the residual phase suggested that radiocesium was strongly adsorbed on clay minerals and micas, which agrees with the EXAFS results for the stable Cs adsorbed on the samples. It must be noted that the present study shows direct evidence on the formation of IS complexes for stable Cs added to the natural samples. The same formation can explain the low solubility of radiocesium found in our sequential extraction experiments.

Strictly speaking, IS complexes are probably the only dominant complexes in the environment that have very low concentrations of Cs, or radiocesium (Kim *et al.*, 1996; Zachara *et al.*, 2002), which cannot be detected by EXAFS technique (Bostick *et al.*, 2002). However, the fact that IS complex was found for stable Cs added to the natural samples in EXAFS analysis can be a direct evidence that radiocesium in the natural samples also formed IS complexes possibly in the interlayers of clay minerals and micas, because (i) the IS complex is more stable than the OS complex and (ii) Cs at a lower concentration should be preferentially adsorbed as the IS complex (= more stable species).

Finally, it is suggested that we can use the EXAFS spectra of Cs adsorbed on any soil or sediment samples to characterize natural samples in terms of the potential of Cs fixation. For example, samples with relatively large IS peaks in the EXAFS for adsorbed Cs can immobilize Cs efficiently because of the larger stability of the IS complexes of Cs in the natural samples.

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