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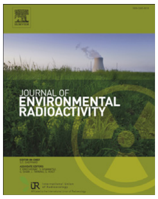

Time-dependent changes of phytoavailability of Cs added to allophanic Andosols in laboratory cultivations and extraction tests

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ABSTRACT

Although it is well known that phytoavailability of radiocaesium is gradually lost after its deposition on the ground by fixation to soil minerals, the decreasing rates during early period after the deposition is not yet quantitatively evaluated. In this study, stable Cs was added to 5 types of soil, including Andosols, a sand-dune regosol and a smectic lowland soil, in a laboratory soil incubation experiment to assess the aging effect of radiocaesium. Aliquots of a soil sample were put into pots and incubated in an artificial climate chamber. Orchardgrass or red clover was cultivated for 28 d in soil pots containing one of the allophanic Andosol samples seven times during about 1200 d using new pots for each cultivation. The soil-to-plant transfer factors of Cs declined exponentially until about 100 d and were almost constant thereafter. The extractabilities of Cs by water and 1 M NH_4OAc solution from this allophanic Andosol soil sample also decreased with time and their decreasing patterns were similar to that of the transfer factor. The temporal changes of extractabilities of Cs in other soil samples were also examined 6 times during about 600 d. Rate of decline for the extracted yield of the added Cs by 1 M NH_4OAc varied widely among all the soil types. Two allophanic Andosol samples showed relatively higher extractabilities in comparison with the other soils throughout the incubation experiment, which may be attributable to the lower contribution of Cs specific sorption sites to total cation exchange capacity of the allophonic Andosol soil samples.

1. Introduction

The radiocaesium isotopes, ^{134}Cs and ^{137}Cs, released from nuclear industries are important for assessment of radiation exposure to the public because of their long half-lives: 2.07 y and 30.2 y, respectively. It is well known that radiocaesium is strongly retained by soil, and its mobility decreases with time after its deposition onto the soil due to the aging effect (Absalom et al., 1995, 1999; Fesenko et al., 1997; Rigol et al., 1999; Roig et al., 2007; Sanzharova et al., 1994). The bioavailability and environmental mobility of the radiocaesium released by the Chernobyl nuclear power plant accident in 1986 have declined markedly in later years, resulting in a decreasing contamination of foodstuffs, vegetation and surface waters (Smith et al., 1999). Understanding of the time-dependent changes in radiocaesium availability in soil is necessary for the prediction of its behavior in surface soil in both the short and long term.

It is well known that Cs^+ is specifically sorbed on frayed-edges sites (FESs) of illitic clay minerals in soils and sediments (Cremers et al., 1988). On the sorption sites, Cs^+ is exchangeable with ions which have a similar hydrated radius, specifically potassium and ammonium ions (Comans et al., 1989). The radiocaesium ions in the sites slowly diffuse into the collapsed interlayer space of phyllosilicates becoming unavailable for direct ion-exchange, and the process is called fixation of radiocaesium to soil minerals (Absalom et al., 1995; Comans and Hockley, 1992).

Andosols, mainly formed on volcanic ejecta, are found in volcanic regions all over the world; their total area is estimated at less than 1% of the global land surface (IUSS Working Group WRB, 2006). However, the Japanese islands are located in the most active part of the Pacific ring-of-fire, and most Japanese soils have been influenced to varying extents by volcanic ejecta. Andosols have some unique properties including a low bulk density, a high water holding capacity and a high phosphate fixing capacity. These soils are the most important for upland farming in Japan, occupying

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about 45% of the total upland fields. Allophanic Andosols, occupying about 70% of the total land area of Andosols, are rich in noncrystalline colloidal materials such as allophane, imogolite, ferrihydrite and Al-humus complexes (Saigusa and Matsuyama, 1998; Nanzyo et al., 1993).

Vandebroek et al. (2009, 2012) compared the radiocaesium interception potential (RIP), which is the indicator of the soil specific retention capacity of Cs, for various soil groups collected worldwide, and found that the Andosols showed one of the lowest RIP values. Since soils with lower RIPs are generally known to show higher Cs transfer to plants (Delvaux et al., 2000a), relatively higher transfer may be observed for Andosols contaminated with radiocaesium. Nakamaru et al. (2007) reported that the soil–soil solution distribution coefficient (Kd) of ^{137}Cs in Andosols is relatively lower than that in other Japanese agricultural soil groups and suggested that soil organic matter could increase the mobility of ^{137}Cs in soils. Ishikawa et al. (2007) investigated the relation between relative content of illite minerals and the strongly fixed proportion of ^{137}Cs tracer in Japanese paddy soils and suggested that mobility of ^{137}Cs was relatively higher in soils with lower illitic mineral content. Although soil-to-plant transfer and vertical transport of fallout ^{137}Cs derived from atmospheric nuclear weapons tests in Japanese soils have been investigated (Kamei-Ishikawa et al., 2008; Komamura and Tsumura, 1994; Tsukada and Hasegawa, 2002; Tsukada et al., 2002, 2008; Uchida et al., 2007), their differences among the soil types are still not clear.

Phytoavailability of radiocaesium in soils with reference to the aging effect and soil characteristics should be understood for management of agricultural fields contaminated with radiocaesium. In particular, the temporal phytoavailability changes of radiocaesium during the early period after the deposition into soil have not been studied quantitatively. In this study, temporal changes in phytoavailability of stable Cs added to allophanic Andosols were investigated on a laboratory scale by pot cultivations and extraction tests to about 1200 d. The time-dependent changes of extractabilities of added Cs in the soil with water and 1 M NH_4OAc were also examined. The temporal changes of extractability with 1 M NH_4OAc in other soil types, including a non-allophanic Andosol, a sand-dune regosol and a smectic lowland soil, were obtained until about 600 d after the Cs addition to investigate effects of soil characteristics on the change. Soil RIP was monitored as a factor influencing extractabilities of the added Cs.

2. Materials and methods

2.1. Soil samples

Soil samples were collected from the plowed layer (0–20 cm depth) of five arable fields in Aomori Prefecture, Japan, and their physicochemical properties are listed in Table 1. The collected samples were dried at 50 °C for a few days and passed through a 2 mm sieve. Two of these soils were allophanic Andosols (AA1 and AA2), and the others were a non-allophanic Andosol (NAA), a sand-dune regosol (SDR), and a gray lowland soil (GLS). Three soil samples (AA1, AA2 and NAA) were rich in organic matter and met the chemical requirements for properties of Andosols (phosphate adsorption coefficient >15 g P_2O_5 kg^{-1} or $Al_o + 1/2\,Fe_o > 20$ g kg^{-1}) (Obara et al., 2011). The AA1 and AA2 soil samples were rich in poorly-crystalline clay minerals as shown by their higher Si_o and they were further classified as allophanic Andosols (Saigusa and Matsuyama, 1998). The allophane contents in AA1 and AA2 estimated by Si_o were 130 g kg^{-1} and 80 g kg^{-1}, respectively (Parfitt, 1990). No clear peaks were observed by X-ray diffraction (XRD) analysis for illitic clay minerals in AA1 and AA2 soil samples (Fig. 1). On the other hand, the NAA sample had a lower Si_o and higher Al_p/

Table 1
Soil samples collected in Aomori Prefecture, Japan.

Sample code	Soil group[a]	Particle size (%)			Total C (g kg^{-1})	Soil pH (H_2O)	CEC (cmol$_c$ kg^{-1})	Exchangeable (cmol$_c$ kg^{-1})				Oxalate extractable (g kg^{-1})			Pyrophosphate extractable (g kg^{-1})		P absorption coefficient (g P_2O_5 kg^{-1})	Crystalline clay minerals[b]
		Sand	Silt	Clay				Na	Mg	K	Ca	Si_o	Al_o	Fe_o	Al_p	Fe_p		
AA1 (Allophanic Andosol)	Silandic Andosols	48	32	20	95	5.8	41.2	0.21	1.6	6.7	16	18.6	44.8	14.4	7.8	4.6	20.2	Vt-Ch > Ch, Kn
AA2 (Allophanic Andosol)	Silandic Andosols	70	18	12	70	5.1	21.7	0.05	0.3	0.4	3	11.5	25.6	8.6	7.4	2.9	15.0	Vt-Ch > Ch, Kn
NAA (Non-Allophanic Andosol)	Aluandic Andosols	19	43	38	63	5.3	30.1	0.36	5.8	0.7	7	1.9	6.9	12.9	5.7	8.0	15.3	Ch, Vt-Ch > Kn, It
SDR (Sand-dune Regosol)	Haplic Aerosols	96	2	2	3	6.0	2.6	0.08	0.8	0.3	2	0.7	0.8	1.1	0.3	0.3	1.5	Ch, Vt-Ch > It, Kn
GLS (Gray lowland soil)	Gleyic Fulvisols	29	48	24	31	5.7	25.6	0.29	3.2	3.7	13	1.8	2.9	11.9	0.8	2.3	8.7	Sm > Ch, It, Kn

Particle size distribution of each soil sample was determined using sieving and sedimentation methods. Total carbon content was measured using a dry combustion method. Soil pH (H_2O) was measured at a soil-to-water ratio of 1:2.5. Cation exchange capacity (CEC) was determined using the semi-micro Schollenberger method. Oxalate-extractable Al (Al_o) and Fe (Fe_o) and pyrophosphate-extractable Al (Al_p) and Fe (Fe_p) were extracted using the methods described by Blakemore et al. (1981) and determined using ICP -AES.

[a] World Reference Base for Soil Resources (2006).

[b] Identified by XRD: Sm, smectite; It, illitic minerals; Kn, kaolinite; Vt-Ch, vermiculite-chlorite intergrade; Ch, chlorite.

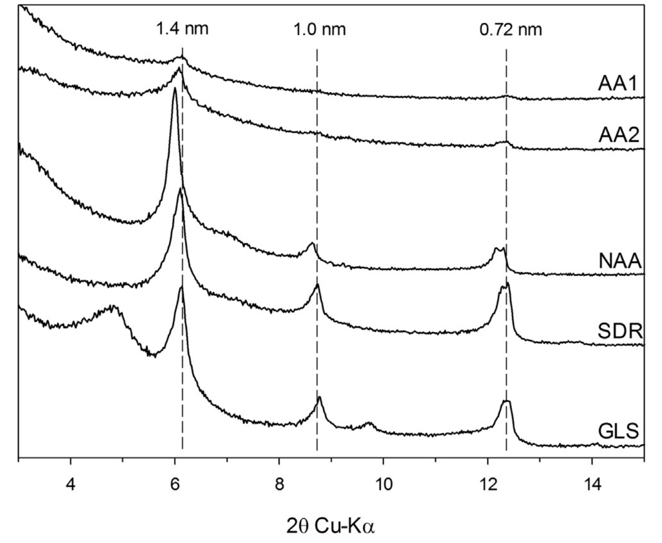

Fig. 1. X-ray diffraction spectra of Mg-saturated clay with the ethylene glycol treatment. Soil samples are indicated on the right.

Al_o ratio, which showed properties of non-allophanic Andosols (Obara et al., 2011; Saigusa and Matsuyama, 1998). The XRD analysis indicated that the NAA sample had a relatively larger amount of crystalline clay minerals (Fig. 1). The SDR sample had the lowest clay content, organic carbon content and cation exchange capacity. The GLS sample had smectite as its major clay mineral (Fig. 1).

The Cs concentrations in the samples ranged from 1.0 to 7.2 mg kg^{-1}, which was within the concentration range of soils collected throughout Japan (0.12–13 mg kg^{-1}) (Takeda et al., 2004). Extractabilities of Cs in the samples with NH_4OAc and water were 1.3–3.7% and 0.001–0.029%, respectively (Table 2).

The AA1 sample was collected from grassland in Rokkasho, where the first commercial spent nuclear fuel reprocessing plant in Japan is located. Among the five soil samples, the AA1 soil sample was used for a preliminary experiment on carrier effect and the pot cultivations and extraction tests of a long-term laboratory soil incubation experiment. The other four samples were only used in the extraction test of the incubation experiment.

2.2. Preliminary experiment on carrier effect

In this study, stable Cs was used in place of radioactive Cs tracer, because it gives easier handling of the soil samples in the incubation experiment. Since sorption of Cs to soil is influenced by its concentration (Zachara et al., 2002), a preliminary experiment was conducted to investigate the effect of stable Cs concentration on the sorption–desorption process of radioactive Cs tracer. The concentration of stable Cs added to soil samples in the incubation experiment was decided by considering the preliminary experiment results.

Table 2
Concentrations of Cs in soil samples and in extractable fractions.

Sample code	Concentration of Cs in soil sample	NH_4OAc-extractable Cs		Water-extractable Cs	
	(mg kg^{-1})	(μg kg^{-1})	(%)	(μg kg^{-1})	(%)
AA1	2.2	82	3.7	1.07	0.029
AA2	1.0	28	2.7	0.16	0.006
NAA	7.2	97	1.3	0.07	0.005
SDR	1.3	16	1.3	0.01	0.001
GLS	3.0	41	1.4	0.10	0.008

Extractions with deionized water and 1 M ammonium acetate solution (pH 7) were carried out with 1:10 as the ratio of soil sample weight to extract volume.

In the preliminary experiment, the ^{137}Cs tracer was adsorbed onto only the AA1 sample at different carrier concentrations by a batch sorption method to get roughly the carrier concentration which had an effect on the ^{137}Cs sorption behavior. Dried soil sample (2 g) was weighed into a 50-mL centrifuge tube and 20 mL of a ^{137}Cs tracer (18 kBq) solution with stable Cs carrier was added in several different concentrations as $CsNO_3$ (equivalent to 0–5 × 10^2 mg Cs kg^{-1}-soil). After the soil suspension was gently shaken at 20 °C for 7 d, supernatant solution was separated by centrifugation and filtration through a 0.22-μm pore membrane filter. Then, ^{137}Cs activity in the filtrate was measured with a NaI(Tl) scintillation counter (Packard Cobra 5002, Packard), and the soil–soil solution distribution coefficient (Kd) was calculated as follows.

$$\mathrm{Kd} = \frac{^{137}\mathrm{Cs\ concentration\ in\ soil}\ \left(\mathrm{Bq\ kg^{-1}}\right)}{^{137}\mathrm{Cs\ concentration\ in\ solution}\ \left(\mathrm{Bq\ L^{-1}}\right)} \tag{1}$$

Carrier effect on the extractability of spiked ^{137}Cs in the AA1 soil sample with deionized water or 1 M ammonium acetate (NH_4OAc) solution was also investigated under the same extraction conditions as in the incubation experiment. Dried soil sample (1 g) was weighed into a centrifuge tube, and 1 mL solution of ^{137}Cs tracer (10 kBq) and $CsNO_3$ equivalent as 0, 1 or 10 mg Cs kg^{-1}-soil was added also. The concentrations of stable Cs were decided based on the results of the preliminary experiment. The tubes, with the AA1 soil sample and respective tracer solution, were kept without a cap in an artificial climate chamber (17 °C, 70% RH, 30,000 lx, 12 h day length) for 2 d, then extracted with 10 mL of deionized water or 1 M NH_4OAc solution (pH 7) for 1 h at room temperature. The extract was separated using centrifugation and filtration through a 0.22-μm pore membrane filter. Then, ^{137}Cs activity in the filtrate was measured with the NaI scintillation counter. The preliminary experiments were conducted in triplicate samples.

2.3. Soil incubation experiment to investigate aging effect on added Cs in soil

Five soil samples were used in the extraction test and one sample was used in the pot cultivations (Table 1) of the soil incubation experiment. For the extraction test, a dried soil sample (200 g) was placed in each plastic pot (7.7 cm diameter, 10 cm high). An aliquot of $CsNO_3$ solution equivalent to 1 mg Cs kg^{-1}-soil, which was decided by the preliminary experiment, was added to the soil samples. After the sample in each pot was mixed well, all pots were stored in the artificial climate chamber under the same condition as in the preliminary experiment. The water content of the soil was adjusted to 60% of maximum water holding capacity of the soil by adding deionized water every 2 weeks. The soil was almost air-dried at 2 weeks after the addition of water. The soil sample was stirred in the pot every 4 weeks. A control soil sample without Cs addition was also treated in the same way.

Table 3
Soil–soil solution distribution coefficient (Kd) values of ^{137}Cs in the AA1 soil sample determined under different concentrations of stable Cs carrier.

Added concentration of Cs (mg kg^{-1} soil)	Kd
0	793 ± 33
5 × 10^{-4}	779 ± 28
5 × 10^{-2}	770 ± 35
5 × 10^{-1}	776 ± 34
5 × 10^{0}	566 ± 27
5 × 10^{1}	297 ± 4
5 × 10^{2}	82 ± 4

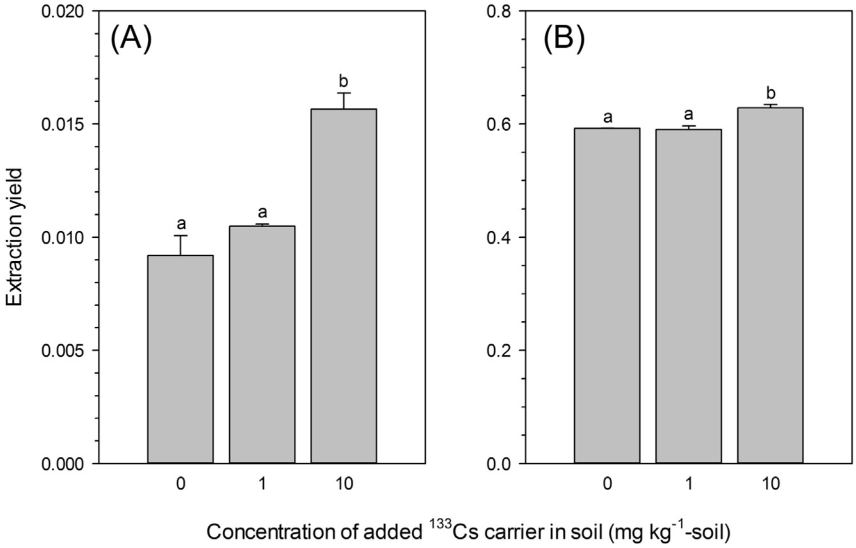

Fig. 2. Extraction yields of added ^{137}Cs tracer in the AA1 soil sample under different concentrations of stable ^{133}Cs carrier. (A) Water extraction; (B) NH_4OAc extraction Small letters indicate a statistically significant difference ($P < 0.01$).

The AA1 soil was used for the pot cultivations. Orchardgrass (*Dactylis glomerata*) and red clover (*Trifolium pratense*) were cultivated in separate pots at 2–29 d, 37–64 d, 86–113 d and 117–204 d, 331–358 d, 569–596 d, or 1185–1212 d after the Cs addition, in the artificial climate chamber mentioned above. The cultivations were carried out in triplicate pots which were not used in former cultivation periods. Twenty germinated seeds of the plants were sowed in each pot. The water content of the soil was adjusted to 60% of maximum water holding capacity of the soil by adding deionized water three times a week during the cultivation period. The aboveground parts of the plants were sampled at 28 d after sowing; they were wiped carefully with paper towels to remove adhered soil particles on the plant surfaces. The plant samples were freeze-dried, finely ground with an agate ball mill, and digested by using the microwave digestion technique with mixed acid (HNO_3, $HClO_4$ and HF). The concentration of Cs in the plant samples was determined with an inductively coupled plasma mass spectrometer (ICP-MS, VG-PQ-Excel, Thermo Elemental). The concentration of added Cs in the plant samples was obtained by subtracting the Cs concentration of the control samples.

Transfer factor (TF) is defined here as follows.

$$\mathrm{TF} = \frac{\text{Concentration of added Cs in abovegroud part of plant } (\text{mg kg}^{-1}\text{ dry plant})}{\text{Concentration of added Cs in soil } (\text{mg kg}^{-1}\text{ dry soil})} \quad (2)$$

The extractability of the added Cs was also investigated in order to get temporal changes of Cs status in soil. An aliquot of the AA1 soil sample was taken from the pot, which was not used for the plant cultivation, at 4 h, 2 d, 9 d, 29 d, 64 d, 113 d, 204 d, 358 d, 596 d or 1212 d after the Cs addition. Soluble fraction was extracted with deionized water or 1 M NH_4OAc (pH 7) and 1:10 of the soil weight to extract volume ratio for 1 h at 20 °C. Extraction with ammonium salt solution is widely used for evaluation of labile Cs in soil (Fesenko et al., 1997; Rigol et al., 1999; Roig et al., 2007; Sanzharova et al., 1994; Takeda et al., 2006; Tsukada et al., 2008). The extract was separated by using high-speed centrifugation, and then filtered through a 0.22-μm pore membrane filter. Aliquots of the four other soil samples (AA2, NAA, SDR and GLS) were also extracted by 1 M NH_4OAc (pH 7) at 1 d, 9 d, 29 d, 113 d, 358 d or 598 d after the Cs addition in the same way.

Extraction with acid oxalate is often used for evaluation of poorly-crystalline clay minerals including allophane imogolite and ferrihydrite (Blakemore et al., 1981). In this study, it was applied to the five soil samples only at 596 d after the Cs addition in order to assess Cs concentration in the poorly-crystalline clay fraction. An aliquot of the soil sample was extracted with 0.2 M NH_4-oxalate solution (pH 3) and 1:100 of the soil weight to extract volume ratio for 4 h at 20 °C. The extracts were separated in the same way as for the 1 M NH_4OAc extraction.

Those extractions were conducted with triplicate aliquots of the soil sample from each pot. The concentrations of Cs in the extracted solutions were also determined with the ICP-MS. Temporal changes of transfer factor and extraction yield of the added Cs were analyzed by a nonlinear regression method with Sigma Plot 12 (Systat Software Inc.).

2.4. Radiocaesium interception potential

The radiocaesium interception potential (RIP) has been established as a quantitative indicator of frayed edge sites (FESs) in soil which adsorb specifically radioactive Cs (Cremers et al., 1988). In this study, soil RIP both before the incubation experiment and at 596 d after the Cs addition was measured. The RIP value is defined by the product of the selectivity coefficient of trace Cs to K of the FES ($K_{c(Cs-K)}^{FES}$), and the concentration of the FESs ([FES]) (Wauters et al., 1996). This product is calculated from the solid/liquid distribution coefficient for ^{137}Cs in a solution with specific K^+ and Ca^{2+}

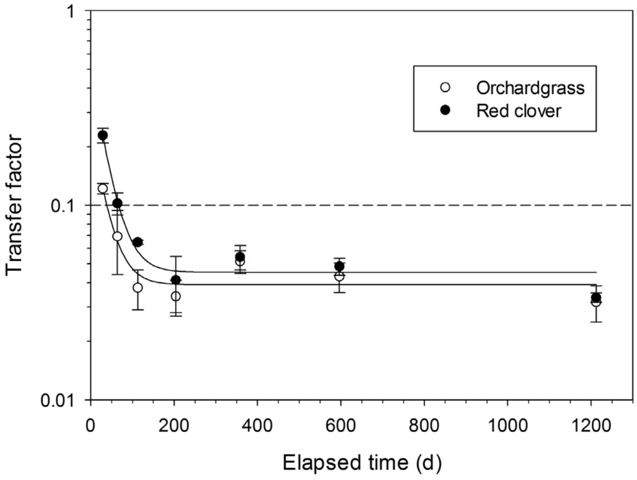

Fig. 3. Temporal changes of soil-to-plant Cs transfer factor in the pot cultivations with the AA1 soil sample. Curves are fitting curves for time-dependent changes of transfer factors. Error bars indicate standard deviations.

ionic strength (K_D^{Cs}), and the K concentration in the solution (mK). The basis of this calculation was given by Cremers et al. (1988).

$$\mathrm{RIP} \ = K_{c(Cs-K)}^{FES} \ [\mathrm{FES}] \ = K_D^{Cs} \ \mathrm{mK} \left(\mathrm{mol\ kg^{-1}}\right) \tag{3}$$

To evaluate the RIP, 1.0 g of soil was put into a dialysis bag along with 5 mL of 0.1 M $CaCl_2$ and 0.5 mM KCl solution. The dialysis bag was transferred to a 125 mL plastic bottle containing 100 mL of 0.1 M $CaCl_2$ and 0.5 mM KCl solution, and then shaken for 2 h twice a day during 5 d. The outer solution was renewed each time before shaking to maintain the desired condition. After 5 d dialysis, the bag was put into a new 125 mL plastic bottle with 100 mL of a mixed solution of 0.1 M $CaCl_2$, 0.5 mM KCl and 10 kBq of carrier-free ^{137}Cs, and the bottle was shaken for 2 h twice a day during 5 d. Then, ^{137}Cs activity in the outer solution was measured with a NaI scintillation counter, and the distribution coefficient of Cs (K_D^{Cs}) calculated from the depletion of ^{137}Cs in the solution. The concentration of K in the solution (mK) was assumed to be 0.5 mM. The RIP was measured in triplicate for each soil.

3. Results and discussion

3.1. Carrier effect

The results of the preliminary experiment done by the batch sorption method using ^{137}Cs tracer under various concentration of stable Cs are shown in Table 3. When the added stable Cs was less than 0.5 mg kg^{-1}-soil, Kd values of ^{137}Cs were constant and did not differ from the Kd values under the carrier-free condition. On the other hand, Kd values drastically decreased with increasing concentration of stable Cs above 5 mg kg^{-1}-soil, indicating the saturation of Cs adsorption sites in the soil solid phase.

Based on those results, extraction yields of ^{137}Cs added to the soil with different stable Cs concentrations was examined and they are shown in Fig. 2. Addition of stable Cs at 10 mg kg^{-1}-soil increased the extractability of ^{137}Cs from the soil both by water and NH_4OAc. However, statistically significant differences in the extraction yields were not observed between the soil sample with 1 mg kg^{-1}-soil of added stable Cs and the carrier-free condition. Therefore, we decided the addition of Cs at 1 mg kg^{-1}-soil as the suitable concentration for the long-term soil incubation experiment, which was carried out as alternative to a radioactive Cs tracer experiment.

3.2. Time-dependent changes of phytoavailability in allophanic Andosols

The concentration of added Cs in orchardgrass and red clover was relatively lower in the later stage compared to that soon after the Cs addition to the soil. The soil-to-plant transfer factor, which is defined as Equation (2), decreased with time: from 0.12 to 0.043 for orchardgrass and 0.23 to 0.034 for red clover during 1212 d (Fig. 3). Red clover absorbed a relatively larger amount of Cs than orchardgrass at an earlier stage in the experiment; however, their decreasing rates of the transfer factor were quite similar. The transfer factors of Cs rapidly decreased with time up to the third cultivation, and did not show any remarkable decrease thereafter. Temporal changes of the transfer factor of Cs were expressed by the following regression equation:

$$Y \ = \ ae^{-\lambda_1 t} + be^{-\lambda_2 t} \tag{4}$$

where Y is the soil-to-plant transfer factor, t is elapsed time since the Cs addition at the end of the cultivation (d), a and b are constants, and λ_1 and λ_2 are rate constants (d^{-1}). In this case, decline in the later period is so slow that cannot be quantified, and λ_2 is not significantly different from 0. Therefore the second exponential term can be regarded as a constant. Each parameter was estimated with less than 31% standard error by nonlinear regression analysis (Table 4).

The half-times ($\ln 2/\lambda_1$) of rapid decline in the earlier period were 21 d and 22 d for orchardgrass and red clover, respectively. To our knowledge, no rapid decrease of the Cs transfer factor in a period of several months has been reported previously. Smith et al. (1999) summarized the reported values for the decline rate of ^{137}Cs in vegetation during the years after the Chernobyl accident. They reported a mean half-time of 2.0 y ranging between 1 and 4 y Sanzharova et al. (1994) reported the average half-times of decreasing soil-to-grass transfer factors after the Chernobyl accident were 3.5 y in 1986–1989 and 17 y in 1989–1991; Fesenko et al. (2009) also reported that the half-times of decreasing transfer factors for perennial grasses after the Chernobyl accident were 2.3–2.6 y in 1987–1989 and 4.6–21 y in 1989–1999, and the average half-times ranged from 4.0 to 17.3 y in 1987–1999. When we expressed the temporal changes of the transfer factor of Cs in this study by a double exponential decline, the half-times of the second phase were 15 y and 6 y for orchardgrass and red clover, respectively, without being statistically significant. The lower limits of the 95% confidence interval were 1.6 y and 1.7 y for orchardgrass and red clover, respectively, and not inconsistent with the other results previously reported.

The water-solubility of Cs in the soil decreased with time after its addition (Fig. 4). Extraction yield of the added Cs by water at 1212 d after the addition was 0.16%, while it was 1.3% in the first extraction at 4 h after the addition. The extractability of Cs with 1 M NH_4OAc also decreased with time from 72% to 22% during the incubation period. The extraction yield of the added Cs rapidly decreased with time up to approximately 100 d after the Cs addition, and did not show any remarkable decrease thereafter. Decreasing patterns of the extraction yields of Cs both with water and NH_4OAc agreed with that of its transfer factors. Temporal changes of the extraction yield of Cs also showed exponential decline at an early period and the decline was expressed by Equation (4), where Y is an extraction yield of the added Cs. The second exponential term can be regarded as a constant as well as the case of the transfer factor (Fig. 3). Each parameter was estimated with less than 26% standard error by nonlinear regression analysis (Table 4).

Table 4
Parameters in the regression curves for the temporal changes of the soil-to-plant transfer factors and extraction yield of the added Cs in the soils.

	a	λ_1	b	λ_2
Transfer factor[a]				
Orchardgrass	0.22 ± 0.07[b]	0.033 ± 0.010	0.039 ± 0.004	0
Red clover	0.46 ± 0.06	0.032 ± 0.004	0.045 ± 0.004	0
Extraction yield[a]				
Water extraction				
AA1	0.010 ± 0.001	0.029 ± 0.006	0.0015 ± 0.0004	0
NH_4OAc extraction				
AA1	0.46 ± 0.01	0.026 ± 0.002	0.23 ± 0.01	0
AA2	0.37 ± 0.03	0.044 ± 0.010	0.31 ± 0.02	0
NAA	0.33 ± 0.04	0.018 ± 0.006	0.11 ± 0.02	0
SDR	0.25 ± 0.01	0.133 ± 0.010	0.26 ± 0.00	0.00092 ± 0.00006
GLS	0.16 ± 0.02	0.010 ± 0.001	0.21 ± 0.02	0.0010 ± 0.0002

Temporal changes of the transfer factor and extractability of Cs are expressed by one of the following regression equation; $Y = a \exp(-\lambda_1 t) + b \exp(-\lambda_2 t)$.

[a] Pot cultivation with the AA1 soil.

[b] ± indicates standard error.

The half-times of extraction yield in the first rapid decline were 24 d for water extraction and 27 d for 1 M NH_4OAc extraction. The decreasing rate constants in the transfer factor (21–22 d) agreed with those of the extraction yields, especially for the extraction yield with water. The results suggested that the extractable Cs could be a good indicator of time-dependent changes of Cs phytoavailability in the soil.

The results suggested that fixation of the added Cs was very slow about 100 d after the Cs addition. Tsukada et al. (2008) reported that the percentage of fallout ^{137}Cs from weapon testing in the NH_4-extractable fraction was 12 ± 5% for some agricultural soils (nine Andosols and two Fulvisols) collected in 1991–2004 in Aomori Prefecture, Japan. In our laboratory extraction test, the extraction yield of the added Cs by NH_4OAc was 22% at 1212 d after the addition, which was still higher than that for fallout ^{137}Cs after aging for several decades. The results imply that the phytoavailability of Cs would decrease gradually with further elapse of time. A drying–wetting cycle is known to affect the rate of aging (Roig et al., 2007). Although the soil samples were exposed to the drying–wetting cycle, their condition in the laboratory differed from that in the field, regarding such point as plant root and microbial activities, seasonal changes in temperature, and degree of drying. We would suggest that those factors are important for the fixation of Cs. Further study is required for clarifying the fixation process.

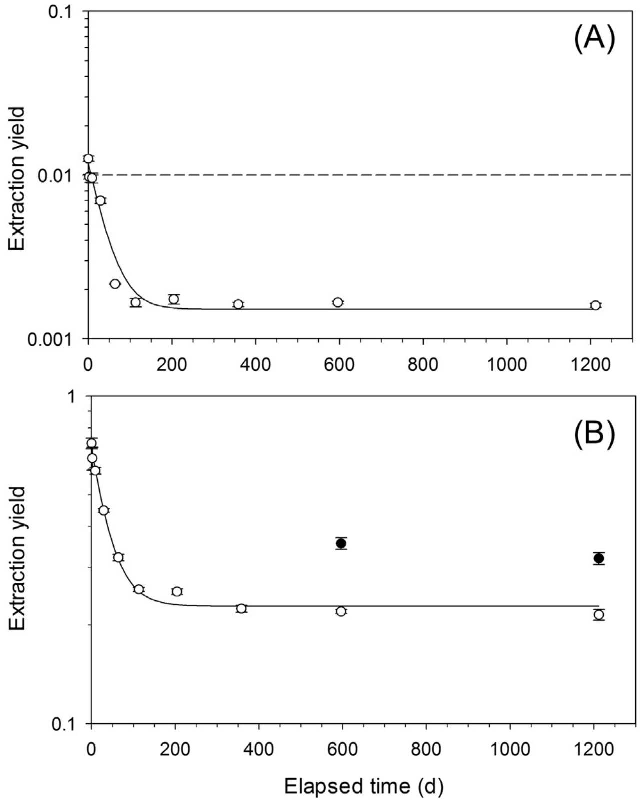

Fig. 4. Temporal changes of the extraction yield of the added Cs from the AA1 soil sample by (A) pure water and (B) NH_4OAc solution. Curves are fitting curves for time-dependent changes of transfer factors. Black circles indicate the extraction yield by the oxalate solution at 596 d and 1212 d after the Cs addition. Error bars indicate standard deviations.

3.3. Extractabilities and clay minerals

The extractability change of the Cs added to the different soil samples during 596 d is shown in Fig. 5. Extraction yield of the added Cs by NH_4OAc solution in all samples decreased with time. Two allophanic Andosols (AA1 and AA2) retained relatively higher extractabilities than the other samples throughout the incubation period (Figs. 4 and 5). More than 60% of the added Cs was extracted just after the Cs addition, and 22–30% of the added Cs was extracted from 358 d after the addition to the end of the incubation experiment in AA1 and AA2 samples. On the other hand, the nonallophanic Andosol (NAA) and the smectic soil (GLS) showed lower extractability throughout the incubation period. Extraction yield of the added Cs at 596 d after the Cs addition for the NAA, SDR and GLS samples was 11–15%.

As shown in Figs. 4 and 5, relatively larger amounts of the added Cs were extracted by the NH_4-oxalate than the NH_4OAc in each soil at the end of the incubation period. The percentage of the oxalate-extractable added Cs in the allophanic Andosols, AA1 and AA2, which were rich in poorly-crystalline clay minerals, was relatively higher than the percentages in the other soils (Table 1, Figs. 4 and 5). More than 60% of the added Cs still existed as a non-extractable form in the allophanic Andosols, implying that crystalline clay minerals play an important role for retaining Cs in these soils.

Temporal changes of the extraction yield of Cs by NH_4OAc solution in these soil samples were expressed by Equation (4), where Y is an extraction yield of the added Cs. The extraction yield in the SDR and GLS samples showed double exponential decline, while the second exponential term can be regarded as a constant for the AA1, AA2 and NAA samples. Parameters obtained by the regression analyzes are listed in Table 4. The half-times of rapid decline in the early period ($\ln2/\lambda_1$) varied largely between 5 and 72 d. The half-times of slow decline in the later period ($\ln2/\lambda_2$) observed for SDR and GLS samples was 1.9–2.1 y, which is in accordance with reported values for transfer factor and exchangeability of ^{137}Cs during

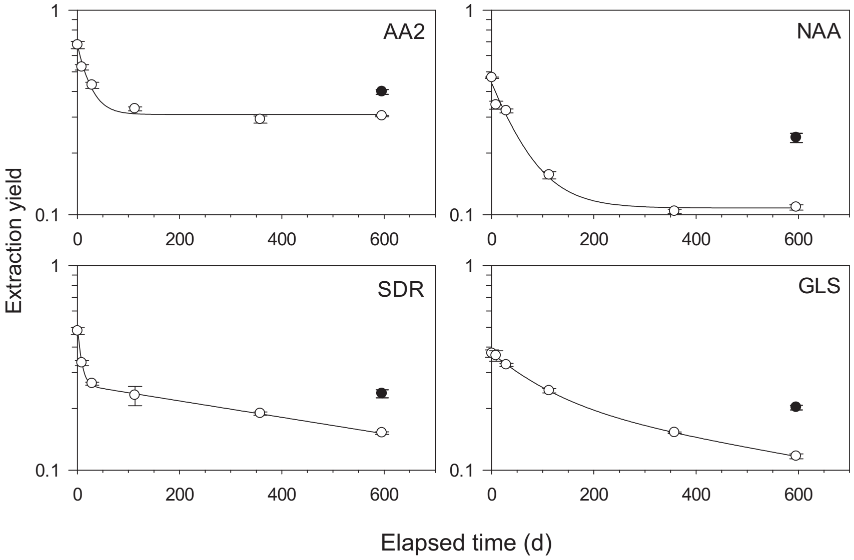

Fig. 5. Temporal changes of the extraction yields of the added Cs from AA2, NAA, SDR and GLS soil samples. Open circles indicate the extraction yield by the NH_4OAc solution. Curves indicate fitting curves for time-dependent changes of the extraction yield by NH_4OAc solution. Closed circles indicate the extraction yield by the oxalate solution at 596 d after the Cs addition. Error bars indicate standard deviations.

a few years after the Chernobyl accident (Smith et al., 1999; Fesenko et al., 2009).

The RIP values obtained both in initial soils before the experiment and in control soils incubated without Cs addition at 596 d are shown in Table 5. The RIP values in initial soils ranged between 0.31 and 6.4 mol kg^{-1}. The RIP value is known to be affected by both content and weathering degree of illitic clay minerals (Nakao et al., 2008, 2009). The allophanic Andosols, AA1 and AA2, had relatively lower RIP values which were similar to those of Andosols reported by Vandebroek et al. (2009, 2012). The clay content of the SDR sample was only 2% (Table 1), and its RIP value was similar to those of allophanic Andosols. The NAA and GLS samples showed relatively higher RIP values, which were significantly increased during the incubation. Especially, GLS showed a remarkable increase of RIP from 6.4 to 8.4 mol kg^{-1}. The increase may be caused by the repetition of air drying and rewetting of the smectic soil sample throughout the incubation period. Highly selective Cs sorption sites in smectite are known to be generated by drying–wetting cycle (Degryse et al., 2004; Maes et al., 1985). Effect of the drying–wetting cycle on the Cs fixation process is reported to be different among the soil types (Rigol et al., 1999; Roig et al., 2007; Rosén et al., 2006). Nakao et al. (2011) indicates drying–wetting cycle with K saturation enhances Cs sorption in smectic soils but not in allophanic soils. Extractability of the added Cs in GLS tended to continue to gradually decrease (Fig. 5 and Table 4), which could be partly influenced by increasing the number of Cs selective sites in smectite during the incubation.

Table 5
Radiocaesium interception potential (RIP) in soil samples before the incubation experiment and 596 d after the Cs addition.

Sample code	RIP (mol kg^{-1})[a]		Hypothetical [FES][b] (% in CEC)
	Initial	After 596 d	
AA1	1.20 ± 0.03	1.35 ± 0.06	0.29
AA2	0.31 ± 0.01	0.25 ± 0.02	0.14
NAA	2.32 ± 0.06	2.75 ± 0.03	0.77
SDR	0.71 ± 0.03	0.63 ± 0.03	2.72
GLS	6.42 ± 0.22	8.35 ± 0.91	2.51

[a] Mean value ± standard deviation ($n = 3$).
[b] Estimated by using initial RIP value and $K^{FES}_{c(Cs-K)} = 10^3$.

Hypothetical [FES] was calculated from the RIP value divided by 10^3, a reference value of $K^{FES}_{c(Cs-K)}$ (Wauters et al., 1996). Allophanic Andosols (AA1 and AA2) had high CEC (Table 1); however, the percentage of [FES] to the CEC was only <0.3%. On the other hand, SDR had the lowest CEC but a high percentage of [FES] to the CEC as did GLS (both were >2.5%) (Tables 1 and 5). The ratio of the added Cs adsorbed in the regular exchange sites (RESs) to that in the FESs is an important factor for its mobilization in soil, because Cs sorbed on RESs is reversibly exchangeable (Valcke and Cremers, 1994; Wauters et al., 1994; Delvaux et al., 2000b). The Cs in the allophanic Andosols would be more labile than in other soils, possibly because of the smaller proportion of Cs that was adsorbed to the FESs.

Factors controlling aging process of Cs in allophanic soils are still not clear. Surface soils in Japan are influenced to varying degrees by deposition of aeolian dust including illitic clay and other 2:1 type clay minerals (Inoue and Naruse, 1987). Although contribution of the aeolian dust for radiocaesium retention in the allophanic soils has not been investigated, it can play an important role for controlling Cs behavior in the soil environment. Joussein et al. (2004) investigated specific retention of ^{137}Cs in African volcanic ash soils devoid of micaceous clay minerals and suggested there were ^{137}Cs specific adsorption sites present in halloysitic soils. Although halloysite is not commonly present in the surface layer of volcanic ash soil (Saigusa et al., 1978), it can also contribute to the retention of radiocaesium in soil.

4. Conclusions

A laboratory soil incubation experiment with addition of stable Cs was carried out to assess the aging effect on Cs phytoavailability, especially during the early period after the addition. The soil-to-plant transfer factors for orchardgrass and red clover and the extraction yield of Cs in the allophanic Andosol rapidly decreased with time up to about 100 d after its addition, and were almost constant thereafter. The decreasing pattern of the extraction yields of Cs with water and 1 M NH_4OAc solution resembled that of the transfer factors.

The extractability of Cs in 5 different soils was also examined. The temporal changes of the extractability by NH_4OAc were expressed by a single or a double exponential decline. In comparison among the soils, allophanic Andosols showed relatively higher extractability throughout the study period of 20 months, which may be attributable to their lower capacity of specific Cs retention. Partitioning of the Cs between RESs and FESs would be one of the important factors for its aging process. Detailed information for clay mineralogy and specific retention capacity for Cs in surface soil in many regions are required both for better management of contaminated soils and for better prediction of Cs transfer to crops.

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