

Effects of zeolite and vermiculite addition on exchangeable radiocaesium in soil with accelerated ageing



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ABSTRACT

Soil amendments with zeolite and vermiculite were expected to prevent radiocaesium (¹³⁷Cs) dissolution and uptake from the soil by plants. In this study, we investigated how zeolite and vermiculite added to soil influence the radiocaesium fixation with ageing. Zeolite and vermiculite were mixed with soil (1 wt%) before or after the addition of carrier-free caesium-137 (¹³⁷Cs) to soils with different radiocaesium interception potential (RIP), which is related to the capacity of the soil to fix trace radiocaesium. Then, the soils were exposed for repeated wet and dry cycles to accelerate ¹³⁷Cs immobilization, and its extractability by 1 mol L⁻¹ ammonium acetate was determined before and after 30 dry and wet cycles. Before accelerated ageing (i.e. before dry and wet cycles), when ¹³⁷Cs was adsorbed on the soil before the addition of the amendments, the addition of zeolite and vermiculite caused a decrease in the amount of exchangeable ¹³⁷Cs in low-RIP soils but an increase in the amount of exchangeable ¹³⁷Cs in high-RIP soils. The amount of exchangeable ¹³⁷Cs was significantly decreased after accelerated ageing regardless of the application of amendments. However, radiocaesium fixation with accelerated ageing was partly inhibited by the addition of zeolite, regardless of the RIP values. The ¹³⁷Cs adsorbed on highly selective sites in zeolite is exchangeable by 1 mol L⁻¹ ammonium acetate. Thus, because a portion of the ¹³⁷Cs is selectively adsorbed on highly selective sites in zeolite, the redistribution of ¹³⁷Cs to frayed edge site followed by ageing-induced fixation was likely limited. However, when ¹³⁷Cs was adsorbed on the soil before the addition of the amendments, the addition of zeolite and vermiculite had little influence on the amount of exchangeable ¹³⁷Cs. In conclusion, the use of realistic doses of zeolite and vermiculite as agricultural amendments is not effective in enhancing the immobilization of radiocaesium in soil.

1. Introduction

Caesium-137 (¹³⁷Cs) is an artificial radionuclide that is widely distributed in the environment. The primary source of this radionuclide was atmospheric nuclear weapon testing from the 1950s to the 1970s and accidents at nuclear power plants, such as the Chernobyl nuclear power plant in 1986 and the Fukushima Daiichi nuclear power plant (FDNPP) in 2011. Due to its long half-life of decay (30.2 y), long-term radiation effects associated with chronic uptake of ¹³⁷Cs in food are subjects of concern. After the FDNPP accident, the maximum allowable radiocaesium concentration in general food (except foods for infants) was set to below 100 Bq kg⁻¹ in Japan. The efficiency of countermeasures to reduce radiocaesium absorption by crops was intensively investigated in Fukushima. The application of K fertilizer was found to be the most practical strategy (Yamaguchi et al., 2016) because K

competitively suppresses Cs absorption by plant roots (Zhu and Smolders, 2000).

Plant uptake of hazardous metal(loid)s in soils is suppressed by the application of materials that reduce the metal(loid) concentration in the soil solution through precipitation or adsorption reactions (Bolan et al., 2014). The application of such materials to reduce radiocaesium uptake by plants is effective only for soils with a low capacity of Cs adsorption (Valcke et al., 1997a). This phenomenon is because radiocaesium is rarely dissolved in the soil solution for the following reasons. Radiocaesium becomes selectively adsorbed at negatively charged sites in the wedge zone between the collapsed and expanded interlayers of weathered micaceous minerals, which are referred to as frayed edge sites (FES). After Cs is adsorbed onto the FES, it is strongly fixed by the interlayer collapse and becomes non-exchangeable (Cornell, 1993). Because the number of radiocaesium fixation sites in soil is sufficiently

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large compared with the amount of radiocaesium, which is usually deposited in small amounts in soil, most radiocaesium in soil is fixed and difficult to desorb.

Zeolite is often used as an amendment in agricultural soil to improve water retention and cation exchange capacity. Zeolite is classified into more than 50 species according to morphological characteristics, crystal structure, and chemical composition (Ramesh et al., 2011). Clinoptilolite and mordenite are naturally occurring types of zeolite, and their distinct feature is their great affinity for K^+ and NH_4^+ ions. When applied to soils, natural zeolite slowly releases K^+ to the soil solution. In addition, clinoptilolite and mordenite show very high sorption abilities for radiocaesium (Valcke et al., 1997b) and were therefore used for wastewater treatment after the accident of FDNPP (Hijikata et al., 2014). Zeolite application was found to be effective in reducing radiocaesium uptake by plants grown in organic soil (Paasikallio, 1999; Shenber and Johanson, 1992), by a podzol (Valcke et al., 1997a) and by rice grown in soil with a low clay content (Fujimura et al., 2013). However, Kato et al. (2015) and Kubo et al. (2015) observed no changes in the radiocaesium transfer factor for rice and buckwheat grown in Fluvisols in response to the application of zeolite. The observed differences were attributed to variations in the ability of soils to adsorb radiocaesium relative to zeolite. Valcke et al. (1997c) noted that key factors determining the effectiveness of the added zeolite are the relative radiocaesium adsorption potentials of the soil and the zeolite. According to the evaluation of trace radiocaesium sorption properties of soils based on the radiocaesium interception potential (RIP, Cremers et al., 1988), peat (organic soil) and podzols have a low capacity for radiocaesium sorption (Vandebroek et al., 2012); therefore, the application of zeolite effectively reduces radiocaesium uptake by plants (Paasikallio, 1999; Shenber and Johanson, 1992; Valcke et al., 1997a). Although zeolite can reduce the radiocaesium concentration in the soil solution, the radiocaesium adsorbed on zeolite is reversibly released into the soil solution by cation exchange reactions with alkaline metals (Fan et al., 2014). This process occurs because a large proportion of the Cs adsorbed on zeolite is an outer-sphere complex (Fan et al., 2014). Nonetheless, Parajuli et al. (2016) observed a decrease in the transfer factor for sunflower following the application of zeolite despite the fact that exchangeable Cs was not changed. This was most likely because elevated K concentration inhibited radiocaesium absorption from roots. Kondo et al. (2015) showed that the exchangeable Cs/K ratio is positively related to the transfer factor of Cs in rice. The effectiveness of zeolite in the reduction of radiocaesium uptake by plants is two-fold: the reduction of phytoavailable radiocaesium and the increase in phytoavailable K.

Micaceous minerals, such as vermiculite, biotite and illite, also have the potential to increase phytoavailable K and decrease phytoavailable radiocaesium. In contrast to zeolite, which retains most Cs and K in a reversibly exchangeable form, micaceous minerals irreversibly fix Cs and K in the FES. The micaceous minerals in soil provide a major source of radiocaesium fixation sites (Nakao et al., 2014), and the RIP values of soil are well correlated with the contents of vermiculite (Delvaux et al., 2000). The application of biotite to organic soil (Paasikallio, 1999) and vermiculite to sandy clay soil (Fujimura et al., 2013) was found to be effective in reducing radiocaesium transfer from soil to grass and rice, respectively. However, Kato et al. (2015) reported that vermiculite application did not influence the radiocaesium concentration in rice grains.

In addition to the application of amendments, ageing causes a decrease in the phytoavailability of radiocaesium (Al Attar et al., 2016) due to the progress of radiocaesium fixation. Fujimura et al. (2015) showed that the transfer factor of ^{137}Cs in rice grown in soils contaminated by the FDNPP accident after 2 consecutive years was 30% lower than that in the first year. The fraction of exchangeable ^{137}Cs also decreased, even though the total ^{137}Cs concentration in the soil did not change. Therefore, the decrease in the transfer factor of ^{137}Cs was likely attributable to the increase in radiocaesium fixation. Radiocaesium

immobilization by enhanced fixation with ageing can be promoted by applying wet-and-dry treatment to the soil after the addition of radiocaesium (Roig et al., 2007). The wet-and-dry treatment accelerated the interlayer collapse of 2:1 clay minerals due to dehydration, which was responsible for the radiocaesium fixation in the FES (Hird et al., 1995). In addition, the wet-and-dry treatment was found to create new FES-like sites in soil amended with montmorillonite (Maes et al., 1985) and K-bentonite (Degryse et al., 2004), thereby enhancing radiocaesium fixation and suppressing radiocaesium uptake by ryegrass (Vandenhove et al., 2005). The addition of clay composed of illitic minerals to peat enhanced radiocaesium fixation in association with a wet-and-dry treatment (Rosen et al., 2006). Amendments added to soil can influence the long-term phytoavailability of radiocaesium. The application of zeolite to peat was effective for decreasing the radiocaesium concentration in ryegrass only in the first year of application, whereas the application of biotite continuously reduced radiocaesium uptake for 5 years (Paasikallio, 1999). Because K in zeolite is mostly exchangeable, zeolite can supply K to soil only for a short period. In contrast, biotite can slowly release K, which is fixed in its structure. The different mechanism associated with the release of K was one of the factors explaining the different sustainability of zeolite and biotite as an amendment. Zeolite and micaceous minerals, including biotite, provide sorption sites for radiocaesium in the soil and thereby influence radiocaesium release to the soil solution; however, how they influence radiocaesium immobilization with ageing has not been investigated so far.

The purpose of this study is to investigate the effects of zeolite and vermiculite added to soils on the immobilization of ^{137}Cs due to ageing-enhanced fixation. Two representative farmland soil types in Fukushima, Andosols and Fluvisols, were compared because they have different capacities of ^{137}Cs adsorption. The ageing process was simulated by repeated wet-and-dry treatments, and adsorbed ^{137}Cs was operationally divided into two fractions, exchangeable and fixed ^{137}Cs , by extraction with 1 mol L⁻¹ ammonium acetate solution (AcNH₄). The application of zeolite was recommended in Fukushima after the FDNPP accident to reduce the radiocaesium concentration in crops (Yamaguchi et al., 2016). These results will contribute to evaluating the long-term effects of soil amendments on the immobilization of radiocaesium in soil.

2. Materials and methods

2.1. Soil samples

Soils with and without amendment application were taken from experimental paddy fields in Fukushima in 2012. These experimental fields were used to investigate the effects of zeolite and vermiculite application on the transfer factor of radiocaesium in rice. After harvesting the rice in 2012, control soil (without amendment, soil A-cont) and zeolite- or vermiculite-applied soil (application rate of vermiculite or zeolite: 10 Mg ha⁻¹, soil A-zeo and soil A-vt) were collected from the ploughed layer in paddy field A. Furthermore, control (soil B-cont) and zeolite-applied soils (application rate of zeolite: 1 Mg ha⁻¹, soil B-zeo) were collected from paddy field B. In addition, two contrasting soils with respect to radiocaesium adsorption characteristics were taken from the ploughed layer of upland fields featuring Andosols (soil C) and Fluvisols (soil D), where radiocaesium contamination derived from the FDNPP accident was negligible. From each field, approximately 100 g of soils were collected from five different plots in the field and then mixed well. Then collected soils were sieved through a 2 mm mesh screen and air-dried. Soil classification, relevant soil properties and radiocaesium concentration for soils without application of amendments and X-ray diffractogram of clay fractions collected from soils are shown in Table 1 and supplemental fig. 1, respectively.

Soil amendments applied to soil A and B in Fukushima were commercial zeolite (Iwamilite, Mitsui Mineral Development Engineering

Table 1
Soil properties.

| | Soil classification | Total C | Cation exchange capacity | Coarse sand | Fine sand | Silt | Clay | Total ^{137}Cs | Exchangeable ^{137}Cs |
|---------------------|---------------------|--------------------|--------------------------------|-------------|-------------|---------------|------------|-------------------------|--------------------------------|
| | | | | 2.0–0.2 mm | 0.2–0.02 mm | 0.02–0.002 mm | < 0.002 mm | | |
| | | g kg^{-1} | $\text{cmol}_\text{c kg}^{-1}$ | % | | | | Bq kg^{-1} | % |
| Soil A ^a | Fluvisol | 46 | 15 | 58 | 22 | 11 | 9.0 | 6630 | 8.7 |
| Soil B ^a | Fluvisol | 16 | 13 | 39 | 27 | 17 | 17 | 2160 | 0.21 |
| Soil C | Andosol | 87 | 36 | 19 | 30 | 33 | 19 | – | – |
| Soil D | Fluvisol | 24 | 13 | 27 | 26 | 25 | 22 | – | – |

^a Adapted from Kohyama et al. (2015) except for total C content of soil B.

Co., Ltd., Tokyo, Japan, grain size: 1–3 mm) and vermiculite (Vermitech, Co., Ltd. Gunma, Japan, grain size: 1–2 mm). To investigate the effects of the soil amendments on ^{137}Cs fixation, the same batches of zeolite and vermiculite pulverized and sieved through a 50 μm mesh screen were used for ^{137}Cs sorption-extraction experiments using soil C and D in experiments II and III as described below. Concentrations of exchangeable K were determined by the extraction of soil or amendments with 1 mol L⁻¹ ammonium acetate solution at solid to solution rate of 1:10 for 1 h. The K concentration in the extractant was determined by inductively coupled plasma optical emission spectrometer (ICP-OES, VistaPro, Varian, Palo Alto, USA).

2.2. Radiocaesium interception potential (RIP)

The RIP of the soils (soil A-cont, soil A-zeo, soil A-vt, soil B-cont, soil B-zeo, soil C, soil D) and amendments (zeolite and vermiculite) were determined by the method of Wauters et al. (1996) which simplify the original method by Cremers et al. (1988). In the modified method, Ca²⁺ is used instead of silver–thiourea (AgTU⁺) to saturate regular cation exchange sites before spiking $^{137}\text{Cs}^+$. Soils (1 g) or amendments (0.2 g) were suspended in 5 mL of 0.1 mol L⁻¹ CaCl₂–5 mmol L⁻¹ KCl solution (Ca–K solution) in a dialysis membrane tube (Size 20, Wako Pure Chemical Industries, Tokyo, Japan) and equilibrated with 100 mL of Ca–K solution for 7 days. The Ca–K solution outside the dialysis tube was replaced twice a day. After 7 days of equilibration, 4 k Bq of carrier-free ^{137}Cs was spiked to the Ca–K solution outside the dialysis tube and equilibrated for 5 days with occasional shaking. After 5 days, the ^{137}Cs concentration of the outer solution was determined by an auto gamma counter with an NaI detector (Wizard2480, PerkinElmer Massachusetts, USA), and the adsorption amounts of ^{137}Cs were calculated. The RIP was then calculated according to the following equation:

$$\text{RIP}(\text{mmol kg}^{-1}) = K_d(^{137}\text{Cs}) \times [\text{K}] \quad (1)$$

where K_d is the distribution coefficient of ^{137}Cs in L kg⁻¹ and [K] is the concentration of K in mmol L⁻¹.

2.3. Extraction of ^{137}Cs from soils with amendments before and after wet-and-dry treatment

2.3.1. Experiment I

A carrier-free ^{137}Cs solution (95 kBq mL⁻¹, 100 μL) was added to 1 g samples of soils A and B collected from the experimental paddy fields (soil A-cont, soil A-zeo, soil A-vt, soil B-cont, soil B-zeo). These soil suspensions were well mixed and settled at ambient temperature for 24 h, and then the soils were dried in an oven at 50 °C. Six sets of ^{137}Cs spiked soils were prepared for each soil with and without soil amendments.

Triplicate sets of dried ^{137}Cs -spiked soils were shaken with 10 mL of deionized water for 24 h. The soil suspension was centrifuged at 5000 g for 10 min, and the supernatant was filtered through a membrane filter (0.2 μm pore size, Steriflip, Merck Millipore, Darmstadt). The amounts of ^{137}Cs adsorbed on the soil were calculated by subtracting the amount

of ^{137}Cs in the water from the sum of added carrier-free ^{137}Cs and ^{137}Cs contaminated by the accident (Table 1). Subsequently, 10 mL of 1 mol L⁻¹ ammonium acetate solution was added to the soil and shaken for 24 h. The soil suspension was centrifuged at 5000 xg for 10 min, and the supernatant was filtered through a 0.2 μm membrane filter. The concentration of ^{137}Cs in the filtrate was determined by an autogamma counter. The proportion of 1 mol L⁻¹ ammonium-acetate-extractable ^{137}Cs was calculated by dividing the radioactivity of ^{137}Cs extracted with ammonium acetate by the amount of ^{137}Cs that retained in soil. In this study, we define ^{137}Cs extracted by ammonium acetate as exchangeable ^{137}Cs .

The other triplicate sets of ^{137}Cs -spiked soils were subjected to repeated wet-and-dry treatments to enhance ^{137}Cs immobilization. One millilitre of distilled water was added to dried soil after the addition of ^{137}Cs , and the sample was then dried in an oven at 50 °C for 2 days. After standing at ambient temperature for 8 h, 1 mL of water was added again and settled at ambient temperature for 16 h and then placed in an oven at 50 °C. Maximum and minimum water content was 50% and 5%, respectively. This wet-and-dry processes was repeated 30 times. After the wet-and-dry treatment, the amounts of adsorbed and exchangeable ^{137}Cs were determined as described above.

2.3.2. Experiment II

The soil amendments (0.01 g of zeolite and vermiculite) were well mixed with 1 g samples of soils C and D. Then, the carrier-free ^{137}Cs solution (95 kBq mL⁻¹, 100 μL) was added to samples of soils C and D with and without soil amendments. Each soil suspension was well mixed and left to stand at ambient temperature for 24 h. Then, the soil pastes were dried in an oven at 50 °C. Triplicate sets of the ^{137}Cs -spiked soils with the soil amendments were extracted with 10 mL of water and 1 mol L⁻¹ ammonium acetate solution without the wet-and-dry treatment. The other triplicate sets were extracted after 30 cycles of the wet-and-dry treatment. The amounts of adsorbed and exchangeable ^{137}Cs were determined as described above.

2.3.3. Experiment III

A carrier-free ^{137}Cs solution (95 kBq mL⁻¹, 100 μL) was added to soils C and D before the addition of the soil amendments. The soil suspension was well mixed and left to stand at ambient temperature for 24 h. Then, the soil pastes were dried in an oven at 50 °C. After the ^{137}Cs -spiked soil was dry, 0.01 g of soil amendments (zeolite and vermiculite) was added. Triplicate sets of the ^{137}Cs -spiked soils mixed with soil amendments were extracted with 10 mL of water and 1 mol L⁻¹ ammonium acetate solution without the wet-and-dry treatment. The other triplicate sets were extracted after 30 cycles of the wet-and-dry treatment. The amounts of adsorbed and exchangeable ^{137}Cs were determined as described above.

2.4. Statistical analyses

We used the Tukey test to observe the differences in RIP values. One-way ANOVA followed by Games-Howell's test was conducted to

Table 2

Radiocaesium interception potential (RIP) and exchangeable K contents of amendments and soils.

| | Radiocaesium interception potential mmol kg ⁻¹ | Exchangeable K cmol _c kg ⁻¹ |
|-------------|--|---|
| Zeolite | 17006 ± 1095 | 29 ± 0.59 |
| Vermiculite | 5068 ± 167 | 4.4 ± 0.18 |
| Soil A-cont | 312 ± 91.7a | 0.1 ± 0.0073 |
| Soil A-zeo | 736 ± 176b | 1.1 ± 0.20 |
| Soil A-vt | 505 ± 134a | 0.71 ± 0.11 |
| Soil B-cont | 1362 ± 504c | 0.10 ± 0.012 |
| Soil B-zeo | 1490 ± 138c | 0.15 ± 0.0076 |
| Soil C | 659 ± 9.9 | 0.44 ± 0.014 |
| Soil D | 2200 ± 66 | 0.30 ± 0.011 |

Values with different letters for RIP of soil A and B are significantly different according to the Tukey test ($P < 0.05$).

observe differences in the arithmetic means of the adsorption amounts and extraction yields between samples of different experimental treatments. Games-Howell's test was chosen because the homoscedasticity assumption was violated due to the presence of data with large variation. These statistical analyses were performed using SPSS v22.

3. Results

3.1. Radiocaesium interception potential

Table 2 shows the RIP values of the amendments and soils used in this study. The RIP value of zeolite was higher than that of vermiculite, as previously reported (Fan et al., 2014). The RIP values for soil A-cont were lower than those for soil B-cont. The addition of zeolite to soil caused a significant increase in the RIP values for soil A ($P < 0.05$) but did not change the RIP values for soil B. Furthermore, the addition of vermiculite to soil A did not cause a significant change in RIP values. The RIP value of soil C (Andosol) was lower than that of soil D (Fluvisol).

3.2. Soils collected from the fields (experiment I)

Fig. 1 shows the amounts of adsorbed ¹³⁷Cs and the proportion of exchangeable ¹³⁷Cs in soils A and B from experimental paddy fields with and without the application of amendments. More than 99% of the spiked ¹³⁷Cs was adsorbed on the soil, and there were no significant differences among adsorption amounts. Before the wet-and-dry treatment, the proportion of exchangeable ¹³⁷Cs in soil A was not changed by the application of zeolite, whereas the proportion increased in soil B. The application of vermiculite caused a decrease in the proportion of exchangeable ¹³⁷Cs in soil A, although the difference was not significant. After 30 cycles of the wet-and-dry treatment, the amount of exchangeable ¹³⁷Cs decreased significantly, regardless of the application of amendments. The proportion of exchangeable ¹³⁷Cs in zeolite-applied soil was higher than that in the control for both soil A and soil B, whereas the proportion of exchangeable ¹³⁷Cs in vermiculite-applied soil was similar to that in the control.

3.3. Soils mixed with amendments before ¹³⁷Cs adsorption (experiment II)

Fig. 2 shows the amounts of adsorbed ¹³⁷Cs and the proportion of exchangeable ¹³⁷Cs in soils C and D in which amendments were mixed before the addition of ¹³⁷Cs. Similar to soils A and B, in which amendments were applied in the field, mixing amendments with soils C and D did not influence the amount of adsorbed ¹³⁷Cs in soil C. For soil C, which had a low RIP value, the proportion of exchangeable ¹³⁷Cs was

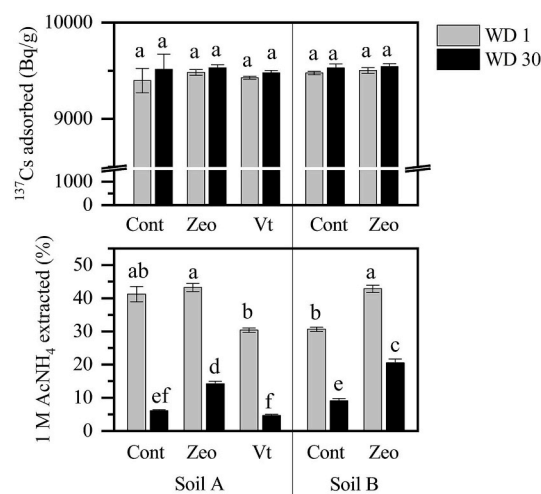


Fig. 1. Amounts of adsorbed ¹³⁷Cs and the proportions of exchangeable ¹³⁷Cs in soils A and B from experimental paddy fields with and without the application of amendments. Cont: control, Zeo: zeolite, Vt: vermiculite, WD1: 1 cycle of the wet-and-dry treatment, WD30: 30 cycles of the wet-and-dry treatment. Error bars indicate one standard deviation. Bars with different letters are significantly different according to the Games-Howell test ($P < 0.05$).

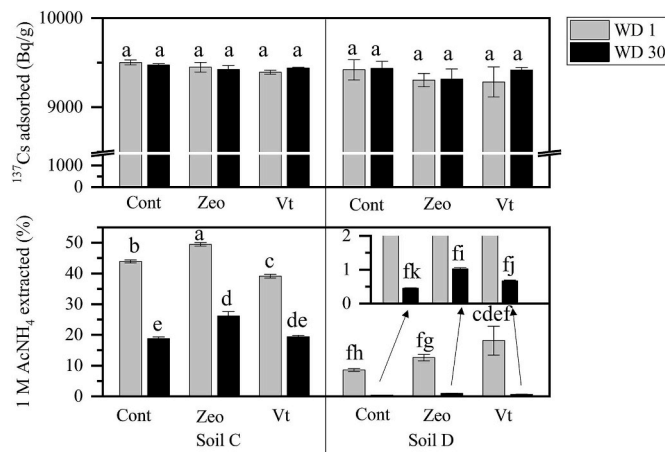


Fig. 2. Amounts of adsorbed ¹³⁷Cs and the proportions of exchangeable ¹³⁷Cs in soils C and D in which amendments were mixed before the addition of ¹³⁷Cs. Cont: control, Zeo: zeolite, Vt: vermiculite, WD1: 1 cycle of the wet-and-dry treatment, WD30: 30 cycles of the wet-and-dry treatment. Error bars indicate one standard deviation. Bars with different letters are significantly different according to the Games-Howell test ($P < 0.05$).

higher in the zeolite-added soil than in the control, whereas the proportion was lower in the vermiculite-added soil than in the control before the wet-and-dry treatment. Furthermore, the proportion of exchangeable ¹³⁷Cs was lower in soil D, which had a higher RIP value, than in soil C, regardless of the addition of amendments. The proportion of exchangeable ¹³⁷Cs tended to increase in the order of Cont < Zeo < Vt in soil D before the wet-and-dry treatment. After 30 cycles of the wet-and-dry treatment, the proportion of exchangeable ¹³⁷Cs decreased significantly in both soil C and D, regardless of the addition of amendments. The proportion of exchangeable ¹³⁷Cs in soils with vermiculite was not different from that in the control, whereas the proportion of exchangeable ¹³⁷Cs in zeolite-added soil was significantly higher than that in the control ($P < 0.05$). For soil D, the proportion of exchangeable ¹³⁷Cs was less than 1% after the wet-and-dry treatment, and that in the zeolite-added soil was significantly higher than that in the control. Large differences were observed among the three replicates for adsorption amount and extraction yield for soil D-Vt.

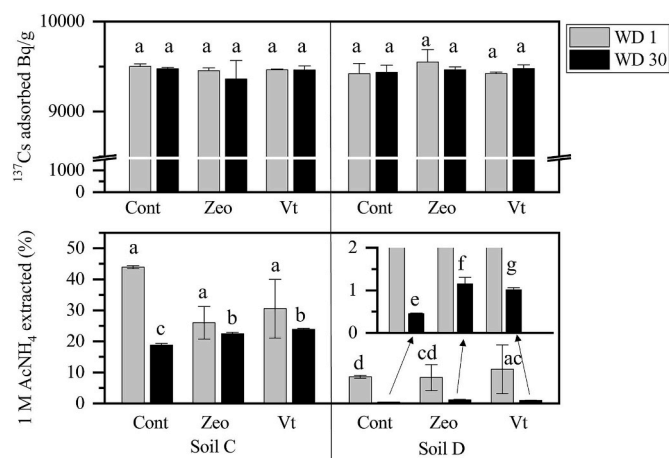


Fig. 3. Amounts of adsorbed ^{137}Cs and the proportions of exchangeable ^{137}Cs in soils C and D in which amendments were mixed after the addition of ^{137}Cs . Cont: control, Zeo: zeolite, Vt: vermiculite, WD1: 1 cycle of the wet-and-dry treatment, WD30: 30 cycles of the wet-and-dry treatment. Error bars indicate one standard deviation. Bars with different letters are significantly different according to the Games-Howell test ($P < 0.05$).

3.4. Soils mixed with amendments after ^{137}Cs adsorption (experiment III)

Fig. 3 shows the amounts of adsorbed ^{137}Cs and the proportion of exchangeable ^{137}Cs in soils C and D in which amendments were mixed after ^{137}Cs was adsorbed on the soil. Mixing amendments with soils C and D after the addition of ^{137}Cs to the soil did not influence the amounts of adsorbed ^{137}Cs . The proportion of exchangeable ^{137}Cs tended to decrease with the addition of zeolite and vermiculite before the wet-and-dry treatment for soil C. For soil D, the proportion of exchangeable ^{137}Cs was not changed by the addition of amendments before the wet-and-dry treatment. After the wet-and-dry treatment, the proportion of exchangeable ^{137}Cs decreased in both soil C and soil D, regardless of the addition of amendments. In soil C, the proportions of exchangeable ^{137}Cs in the zeolite- and vermiculite-added soils were higher than that in the control. A similar trend was observed for soil D. The exchangeable ^{137}Cs showed large variance in both soil C and soil D before the wet-and-dry treatment when zeolite and vermiculite were added.

4. Discussion

4.1. Effects of the wet-and-dry treatment on the extraction yield of ^{137}Cs

The ^{137}Cs adsorbed at FES is fixed following interlayer collapse of the vermiculated layers of weathered micaceous minerals (Cornell, 1993). The ^{137}Cs fixed at FES is hardly desorbed by cation exchange reaction, thus it is not extracted by 1 mol L^{-1} ammonium acetate solution. With respect to the proportion of exchangeable ^{137}Cs , the soils without the addition of amendments exhibited the order of Soil D < Soil B < Soil A < Soil C, and this order was in accordance with the decreasing order of RIP values, except for the order of soil A and C. By definition, RIP is the product of the selectivity coefficient of ^{137}Cs over K and the number of FES in the soil. Assuming that the selectivity coefficient of trace ^{137}Cs over K at FES is 1000 (Brouwer et al., 1983), the number of FES in soils was calculated to be 310–2200 mmol/g based on the measured RIP values (Table 2). Since the ^{137}Cs radioactivity value of 95 kBq added to 1 g of soil is equivalent to 2.2×10^{-8} mmol, the soils used in this study have enough FES to fix all ^{137}Cs atoms experimentally added to the soil. Therefore, more than 99% of the added ^{137}Cs atoms were adsorbed on the soils regardless of the addition of amendments (Figs. 1–3). Although a sufficient number of FES for ^{137}Cs fixation were likely present in the soil in our

experimental conditions, 10–40% of the ^{137}Cs adsorbed on the soil remained exchangeable before the wet-and-dry treatment (Figs. 1–3). This result suggested that ^{137}Cs is not instantaneously fixed by the soil. After 30 cycles of the wet-and-dry treatment, the extraction yield of ^{137}Cs was significantly decreased, although the adsorption amounts had not changed. This result indicated that the fixation of ^{137}Cs was enhanced by the wet-and-dry treatment of the soils. Repeated application of the wet-and-dry treatment may increase the quantity of FES, as suggested by previous studies on bentonite (Degryse et al., 2004) and soils (Rigol et al., 1999; Roig et al., 2007). In addition to the increase in sites for fixation, repeated wet-and-dry treatments likely induced redistribution of exchangeable ^{137}Cs to sites that are highly selective for ^{137}Cs , i.e., FES. Once ^{137}Cs is adsorbed at FES, drying the soil induces the dehydration of clay minerals and thereby induces interlayer collapse and fixation of ^{137}Cs .

4.2. Effects of zeolite and vermiculite added to soil before ^{137}Cs adsorption on the proportion of exchangeable ^{137}Cs

The RIP values of amendments used in this study were larger for zeolite than vermiculite (Table 2). However, these results did not mean that zeolite possesses a larger number of FES than vermiculite. RIP is an index for the relative comparison of ^{137}Cs selectivity over K among soils and minerals when cation exchange sites, except FES, are occupied by Ca^{2+} or Ag^+ . The RIP value of zeolite was high because sites with higher selectivity for ^{137}Cs over K and Ca were present. Valcke et al. (1997b) showed that the selectivity of trace level of radiocaesium over K increased with increasing Ca loading in zeolite (clinoptilolite and mordenite). Because we determined RIP under the condition that most of the cation exchange sites of zeolite are occupied by Ca^{2+} , the calculated selectivity of ^{137}Cs over K may be larger than the realistic value upon mixing with soil. The steric feature of highly selective sites for ^{137}Cs in zeolite is not like that of FES because zeolite does not have a layered structure, such as that of 2:1 aluminosilicate minerals. Therefore, the ^{137}Cs adsorbed at highly selective sites in zeolite is not strongly fixed because interlayer collapse does not occur.

The RIP value of soil A amended with zeolite in the field was higher than that of the control. However, the addition of vermiculite to soil A and zeolite to soil B did not cause significant changes in the RIP values compared with the control soil (Table 1). This lack of change of RIP is because the highly selective sites for ^{137}Cs supplied to soil by the addition of amendments were small compared with the soil without amendment. Although the RIP values in soil A were increased by the application of zeolite, the proportion of exchangeable ^{137}Cs did not differ from that of the control before the wet-and-dry treatment (Fig. 1). In contrast, the addition of zeolite to soil B under field conditions (experiment I) caused an increase in the extraction yield of ^{137}Cs , even though the RIP did not change. When zeolite was mixed with soils C and D before the addition of ^{137}Cs under laboratory conditions (experiment II), the proportions of exchangeable ^{137}Cs were higher than that of the control. The ^{137}Cs added to soil with zeolite was likely preferentially distributed to the highly selective sorption sites on zeolite rather than the FES in the soil. Because the highly selective sites on zeolite cannot fix ^{137}Cs , the adsorbed ^{137}Cs was extracted by 1 mol L^{-1} AcNH_4 through the cation exchange reaction.

After 30 cycles of the wet-and-dry treatment, it is evident that the addition of zeolite to the soil caused a significant increase in the extraction yield of ^{137}Cs . Due to the high selectivity for ^{137}Cs adsorption, zeolite inhibited ^{137}Cs distribution to the FES in the soil, thereby retarding ^{137}Cs fixation.

Increased amounts of exchangeable K due to the addition of zeolite may also influence the changes in exchangeable ^{137}Cs (Table 2). The distribution coefficient of ^{137}Cs was decreased when K was added before the addition of ^{137}Cs because the adsorption of ^{137}Cs competed with K (Absalom et al., 1995). However, K supplied from zeolite did not have any influence on the amounts of adsorbed ^{137}Cs in our

experimental conditions because the amount of ^{137}Cs added to the soil was much lower than the number of FES. Absalom et al. (1995) also showed that the distribution coefficient of ^{137}Cs was increased when K was added after the addition of ^{137}Cs because the interlayer collapse of micaceous minerals was enhanced by the addition of K. Nonetheless, our results showed that the proportion of exchangeable ^{137}Cs was higher for zeolite-added soil than for the control after the wet-and-dry treatment. It was likely that the K supplied by the zeolite to the soil was not high enough to enhance the interlayer collapse of micaceous minerals in the soil under our experimental conditions.

The proportion of exchangeable ^{137}Cs before the repeated wet-and-dry treatment was decreased by the addition of vermiculite to soils A and C, which had lower RIP values (Figs. 1 and 2). When the highly selective sites for ^{137}Cs in the soil were rare, ^{137}Cs was likely distributed to more selective sites in vermiculite, and then part of the ^{137}Cs distributed to the FES in vermiculite was fixed due to the interlayer collapse after a single drying step. This result was corroborated by the study of Park et al. (2018) showing that Cs adsorbed on vermiculite bearing soil is distributed to the interlayer of vermiculite as an exchangeable fraction initially, and wet-and-dry treatment induced Cs fixation due to the interlayer collapse of vermiculite. The repeated wet-and-dry treatment induced the redistribution of ^{137}Cs to FES, and the extraction yield of ^{137}Cs for the control soil and vermiculite-added soil became similar. The amounts of adsorbed and exchangeable ^{137}Cs varied in the three repeated experiments when vermiculite was added to soil D; therefore, it was difficult to compare how vermiculite influenced these parameters in soil D, which had high RIP values. An additional experiment involving three replicates also showed large variance. It was likely that vermiculite caused a heterogeneous distribution of radiocaesium to sorption sites in the soil and vermiculite. In our experimental conditions, the FES supplied to soil by the addition of vermiculite represented less than 10% of the original FES in the soil, even for soils with low RIP values, based on the RIP-based estimation assuming that the selectivity coefficient of Cs over K at FES is 1000 (Brouwer et al., 1983). Our results showed that agriculturally realistic amounts of vermiculite (less than 1 Mg ha^{-1}) applied to soil were not effective in reducing the proportion of exchangeable ^{137}Cs in the soil, especially after ageing.

4.3. Effects of zeolite and vermiculite added to soil after ^{137}Cs adsorption on the proportion of exchangeable ^{137}Cs

When zeolite and vermiculite were added to ^{137}Cs -adsorbed soil, the proportion of exchangeable ^{137}Cs tended to decrease in soil C but remained unchanged in soil D before the repeated wet-and-dry treatment (Fig. 3). After ^{137}Cs was already distributed to highly selective sites in the soil, zeolite and vermiculite adsorbed a portion of the ^{137}Cs , which was then extracted from low-RIP soil C with the 1 mol L^{-1} ammonium acetate solution. However, only small amounts of ^{137}Cs were extracted from high-RIP soil D with the 1 mol L^{-1} ammonium acetate solution; therefore, zeolite and vermiculite did not act as additional sorption sites for ^{137}Cs . The addition of zeolite and vermiculite to the soil caused large variation among the three replicates of extraction yield of ^{137}Cs with 1 mol L^{-1} ammonium acetate, as was also observed when vermiculite was added to soil D before the addition of ^{137}Cs . Furthermore, smaller amounts of ^{137}Cs that had desorbed from the unequilibrated soil before the wet-and-dry treatment were distributed between the soil and the amendments in experiment III (in which amendments were added to ^{137}Cs -adsorbed soil before the wet-and-dry treatment) than in experiment II. This observation may explain the large fluctuations in the triplicate data.

The proportions of exchangeable ^{137}Cs after the repeated wet-and-dry treatment of ^{137}Cs -spiked soil with zeolite and vermiculite were higher than those of the control for both soil C and soil D. However, the difference was not as great as that in the results of experiment II when the ^{137}Cs was added after the amendments were mixed with soil C

(Figs. 2 and 3). When the ^{137}Cs was added to the soil before the soil was mixed with zeolite, the added ^{137}Cs was first distributed to highly selective sites in the soil. After zeolite was added, a portion of the ^{137}Cs that desorbed from the soil was redistributed between sorption sites on the zeolite and the soil during the process of the repeated wet-and-dry treatment. Therefore, as in the case of high-RIP soil D, the effects of zeolite on the proportion of exchangeable ^{137}Cs after repeated wet-and-dry treatment were small even for low-RIP soil C.

4.4. Implications for the mitigation of radiocaesium-contaminated-soil with zeolite and vermiculite

Zeolite and vermiculite are effective adsorbents for removing radiocaesium from water (Hijikata et al., 2014; Ishikawa et al., 2017; Kobayashi et al., 2016). As a countermeasure to reduce radiocaesium absorption by rice, the application of zeolite in addition to K fertilizer was recommended in Fukushima prefecture in 2011, the year of the FDNPP accident. Fujimura et al. (2013) showed that the application of vermiculite and zeolite effectively reduced the radiocaesium concentration in brown rice harvested in 2011 and 2012. In contrast, another field survey showed that the radiocaesium concentration was not significantly decreased by the application of vermiculite (5 Mg ha^{-1}) and zeolite (10 Mg ha^{-1}) for brown rice (Kato et al., 2015) or by zeolite (1 Mg ha^{-1}) for buckwheat (Kubo et al., 2015). Mixing zeolite with soil (10 kg m^{-2}) caused a decrease in the transfer factor of ^{137}Cs for sunflower, although the amount of exchangeable ^{137}Cs in soil was not changed (Parajuli et al., 2016). These inconsistent results were likely attributable to different K statuses in the soils, which influence Cs uptake for plant physiological reasons. Among the factors controlling the radiocaesium transfer from soil to plant, the efficiency of K was found to be more important than the soil adsorption potential. Both zeolite and vermiculite can supply K to soil. The application of zeolite was promised to contribute to the increased concentration of exchangeable K in the soil. When soil has enough exchangeable K for plant growth, the application of amendments to soil is effective only in soils with low radiocaesium adsorption potential, such as podsols (Valcke et al., 1997a).

Among the major soil types used for crop production in the area affected by the radiocaesium released from the FDNPP, Andosols have the lowest capacity of radiocaesium fixation (Yamaguchi et al., 2017). When zeolite and vermiculite were mixed with Andosols containing adsorbed radiocaesium, exchangeable radiocaesium was decreased only before the wet-and-dry treatment (Fig. 3). When the soil has enough sites to fix radiocaesium, as in Fluvisols with high RIP values, additional sorption sites supplied by amendments did not influence the exchangeability of radiocaesium in the soil before ageing. Instead, zeolite interfered with radiocaesium fixation in the soil during ageing due to the presence of highly selective adsorption sites without the ability to fix radiocaesium. We applied a wet-and-dry treatment to mimic the long-term stabilization of radiocaesium in soil. Paddy soils are flooded during rice growth, and the soil does not experience dry conditions. In such situations, radiocaesium fixation at FES due to the interlayer collapse of clay minerals does not occur, and the negative influence of zeolite application may not be critical.

Although the ability of zeolite and vermiculite to provide K to plants is effective in reducing radiocaesium uptake through plant roots, these amendments lack the ability to enhance radiocaesium fixation in contaminated soils.

5. Conclusions

When ^{137}Cs was added to soil mixed with zeolite or vermiculite, zeolite caused an increase in exchangeable ^{137}Cs , whereas vermiculite caused a decrease in exchangeable ^{137}Cs before ageing. When zeolite or vermiculite was mixed with soil that already contained adsorbed ^{137}Cs , zeolite and vermiculite did not have a significant influence on

exchangeable ^{137}Cs in high-RIP soils before ageing. When combined with ageing, the addition of zeolite caused retardation of radiocaesium fixation in both Andosols and Fluvisols, whereas the effects of vermiculite on ^{137}Cs fixation varied depending on the experimental conditions. Once ^{137}Cs is trapped by a highly selective site on zeolite, the redistribution of ^{137}Cs to FES in soil was inhibited, and ^{137}Cs remained exchangeable. Our results provide evidence that the application of realistic doses of zeolite and vermiculite to soil as agricultural amendments does not enhance the immobilization of radiocaesium despite their good performance in removing radiocaesium from water.

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Appendix A. Supplementary data

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