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Influence of the nonexchangeable potassium of mica on radiocesium uptake by paddy rice

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A pot cultivation experiment was conducted to elucidate the influence of the nonexchangeable potassium (K) of mica on radiocesium (^{137}Cs) uptake by paddy rice (*Oryza sativa* L. cv. Koshihikari), and to evaluate the potential of mica application as a countermeasure to reduce radiocesium transfer from soil to paddy rice. The increase in the exchangeable K concentrations of soils, measured before planting, due to mica (muscovite, biotite, and phlogopite) application was negligible. However, in trioctahedral mica (biotite and phlogopite)-treated soil, the release of nonexchangeable K from the mica interlayer maintained the soil-solution K at a higher level during the growing season in comparison to the control, and consequently decreased the ^{137}Cs transfer factor for brown rice (*TF*). The sodium tetraphenylboron (TPB)-extractable K concentration of the soils, measured before planting, was strongly negatively correlated with the TF, whereas the exchangeable K concentration of the soils, also measured before planting, was not correlated with the *TF*. Therefore, we conclude that TPB-extractable K is more reliable than exchangeable K as a basis of fertilizer recommendations for radiocesium-contaminated paddy fields. Phlogopite-treated soils exhibited higher TPB-extractable K concentrations and lower *TF* values than biotite-treated soils. We thus conclude that phlogopite application is an effective countermeasure to reduce radiocesium uptake in paddy rice.

1. Introduction

Since the Tokyo Electric Power Company's Fukushima Daiichi Nuclear Power Plant (FDNPP) accident in Fukushima Prefecture, Japan, of March 11, 2011, it has become necessary to establish countermeasures to reduce radiocesium uptake by local crops. Potassium (K) application to the soil is one of the most effective countermeasures to reduce the uptake of radiocesium by crops (Zhu and Smolders, 2000). Potassium competes with radiocesium on root uptake by paddy rice; moreover, adequate external K levels inhibit expression of K transporters with high affinity for Cs (Fujimura et al., 2014). Indeed, numerous studies reported that application of potassium chloride (KCl) or K-bearing minerals (i.e., expanded vermiculite and zeolite) reduced radiocesium uptake from soils polluted by the FDNPP accident (e.g. Saito et al., 2012; Fujimura et al., 2013; Kato et al., 2015). Results of urgent experiments conducted in 2011 suggested that the recommended level of soil-exchangeable (1 M CH_3COONH_4-extractable) K, before the usual fertilization, to lower the radiocesium concentration of rice to acceptable levels is 200 mg kg^{-1} (approximately 250 mg kg^{-1} as K_2O; Kato et al., 2015). Accordingly, the Fukushima Prefectural Government recommends improving the amount of exchangeable K in soil to 250 mg kg^{-1} (as K_2O), and to apply a conventional amount of K fertilizer before planting paddy rice (Fukushima Prefectural Government, 2014). For example, when exchangeable K in the soil is 50 mg kg^{-1} (as K_2O), the application of K fertilizer at 300 kg ha^{-1} (as K_2O) improves exchangeable K to 250 mg kg^{-1} (as K_2O); in addition, a conventional amount (i.e., 80–100 kg ha^{-1} as K_2O) of K fertilizer should be applied before

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planting (Fukushima Prefectural Government, 2014). In 2014, the results of inspections on radioactivity levels in 11 million samples of brown rice were within the maximum limit (100 bq kg^{-1}) for general foods (Ministry of Agriculture, Forestry and Fisheries, 2015). This fact would indicate that exchangeable K is a sufficiently reliable indicator of plant available K, at least in order to lower the radiocesium concentration of brown rice to an acceptable level. However, exchangeable K has been suggested to underestimate the plant available K of soils rich in mica (e.g., Jackson, 1985; Mengel and Rahmatullah, 1994), because nonexchangeable K in the mica interlayer is also plant-available (Sparks, 1987).

Mica is a group of 2:1 phyllosilicate minerals with nonexchangeable interlayer cations (normally K^+, Fanning et al., 1989). Mica is further divided into dioctahedral and trioctahedral mica (Fanning et al., 1989). Vermiculite is formed by alteration of mica (Douglas, 1989). Uptake of K by plant roots reduces the K concentration of a soil solution, which facilitates the release of the nonexchangeable K of mica; in laboratory experiments, precipitation of K with tetraphenylboron (TPB) is often used to mimic the process of K uptake by plant roots (Fanning et al., 1989). Paddy rice has the ability to take up nonexchangeable K from the mica interlayer to facilitate the vermiculitization of mica (Nanzyo et al., 1999; Yang et al., 2005; Zhang et al., 2011). However, the influence of the nonexchangeable K of mica on radiocesium uptake by paddy rice has not yet been elucidated. Dioctahedral mica releases nonexchangeable K much less readily than does trioctahedral mica (Fanning et al., 1989). In other words, nonexchangeable K in dioctahedral mica is less plant-available than that of trioctahedral mica. Therefore, the plant-available K of mica-rich soils cannot be evaluated by either exchangeable K or the mica content. Evaluations of plant-available K by TPB extraction have been attempted for crops such as wheat (Cox and Joern, 1999), ryegrass (Wang et al., 2010), and soybean (Fernández et al., 2008); however, no such evaluation has yet been applied for paddy rice.

Mica, or mica-bearing rocks, has been examined as a potential slow-release K fertilizer or as an amendment to improve soil K status (Manning, 2010). When the mica amendment is exhausted of plant-available K, the K-depleted mica (i.e., the vermiculite) is expected to exhibit high radiocesium selectivity (Komarneni and Roy, 1988; Guivarch et al., 1999; Maes et al., 1999; Cho and Komarneni, 2009). Muscovite (a common dioctahedral mica), biotite (a common trioctahedral mica), and phlogopite (an Mg-rich trioctahedral mica) are commercially available; hence, application of these micas can be an effective countermeasure to reduce radiocesium transfer from the soils of plants. Sreenivasa Chari et al. (2011, 2012) suggested that application of waste mica (dominantly muscovite) could reduce the radiocesium uptake of spinach, lettuce, green gram, and soybean. Paasikallio (1999) indicated that biotite application reduced the radiocesium uptake of Italian ryegrass from peat soil, and the effect lasted for at least 5 y.

In this study, we conducted a pot cultivation experiment of paddy rice using radiocesium-contaminated soil treated with muscovite, biotite, or phlogopite. The objective of the pot cultivation experiment was to elucidate the influence of the nonexchangeable K of mica on the radiocesium uptake by paddy rice, and to evaluate the potential of mica application as a countermeasure to reduce radiocesium transfer from soil to paddy rice. We also cultivated paddy rice using soil treated with KCl or zeolite for comparison, or treated with vermiculite prepared from phlogopite to determine the residual effect of K-depleted (vermiculitized) mica amendment. Moreover, we attempted to measure the reliability of TPB-extractable K as a basis of fertilizer recommendations for radiocesium-contaminated paddy fields.

2. Materials and methods

2.1. Soils

Radiocesium-contaminated soil was sampled from an upland field converted from a paddy field in Odaka-ku Minamisouma City, Hama-dori region, Fukushima, Japan. The soil was classified as Gleyic Fluvisol (IUSS Working Group WRB, 2006); this type of soils comprises more than 50% of paddy soils in the Hama-dori region (Fukushima Prefectural Government, 2006). The field has not been cultivated since the FDNPP accident. The soil was air-dried and passed through a 4 mm screen. Selected soil properties of <2 mm fractions are summarized in Table 1. The soil showed high exchangeable K levels that were approximately double the recommended level (Fukushima Prefectural Government, 2014). The radiocesium interception potential (*RIP*) can be used as a measure of the high-affinity site for radiocesium. The distribution coefficient (K_d) of added ^{137}Cs was measured in a mixed solution of 0.1 M $CaCl_2$ and 0.5 mM KCl, according to the method of Wauters et al. (1996). The *RIP* value was calculated by multiplying the K_d of ^{137}Cs by the K concentration in the equilibrated solution.

2.2. Mineral amendment preparation

Muscovite (Indian; Yamaguchi Mica, Aichi, Japan), biotite (Indian; Yamaguchi Mica, Aichi, Japan), and phlogopite (Finnish; Repco, Tokyo, Japan) were dry-ground using a laboratory blender (Wonder Blender WB-1, Osaka Chemical, Osaka, Japan). The dry-ground micas were dispersed into water by vigorous shaking by hand without any other physical or chemical treatment, and then 10–20 μm fractions were separated by sedimentation. Vermiculite was prepared from phlogopite by potassium depletion using TPB (Smith and Scott, 1966). A 50 g aliquot of the 10–20 μm phlogopite fraction was placed in 1 L of 0.2 M Na-TPB/1.7 M NaCl/0.01 M 2Na-EDTA solution for 3 d, and then filtered. The residues were shaken in 500 mL of a 60:40 (v/v) acetone-water solution containing NaCl (0.5 mol L^{-1}) for a few minutes to dissolve the K-TPB precipitates, and filtered. The residual vermiculite was washed with fresh NaCl-acetone-water, then with water, and dried at 50 °C. Zeolite (clinoptilolite, Japanese; Mitsui Mineral Development Engineering, Tokyo, Japan) was dry-ground, and then wet-sieved through 53 μm mesh. Selected properties of the prepared amendments are summarized in Table 2.

Table 1
Selected properties of soil (<2 mm fraction) used in pot experiments.

$w_{K(ex)}$ as K_2O[a] (mg kg^{-1})	*RIP*[b] (mol kg^{-1})	Clay (g kg^{-1})	Silt	Sand	Clay mineralogy[c]	^{137}Cs concentration (Bq kg^{-1})
517	0.82	341	164	495	Kt > HIV > Mi, Vr	5200

[a] Exchangeable K at soil solution ratio of 1:20.
[b] Radiocesium interception potential (Wauters et al., 1996).
[c] Determined by X-ray diffraction; Kt, kaoline; HIV, hydroxy interlayed vermiculite; Mi, mica; Vr, vermiculite.