

**Cesium behavior and its relation
to potassium, rubidium and cadmium
in the soil to paddy rice plant system**

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Chapter1 General Introduction

1.1 Environmental pollution by the Fukushima first Nuclear Power Plant accident

1.1.1 Radioisotope pollution

Nearly six years have passed since TEPCO Fukushima Daiichi Nuclear Power Station accident occurred in March 2011. Among the radionuclides released by the nuclear power plant, radioactive cesium (^{134}Cs , ^{135}Cs , ^{137}Cs), strontium (^{90}Sr) and iodine (^{131}I) are the most influential on ecosystems including human beings. ^{131}I has a short half-life of about 8.021 days, so now at least three years have elapsed since the accident, the ^{131}I released at the time of the accident has almost disappeared. However, at the time of the nuclear accident, there were possibilities that many people were exposed to a large amount of ^{131}I . It is necessary to pay attention for health damage by ^{131}I for the time being. At present, the residual in the ecosystem is radioactive cesium with a long half-life (^{134}Cs : 2.05 years; ^{135}Cs : 2.3 million years; ^{137}Cs : 30.3 years) and strontium (^{90}Sr : 29.1 years) (Asami, 2013). However, since radioactive strontium is difficult to analyze, the number of analysis examples is currently low.

In the environment there are natural radionuclides originating in cosmic rays, uranium, thorium and actinium series nuclides in the crust, etc. originally present in nature. The amount of radiation derived from natural radionuclides depends on the geology and topography. Furthermore, 0.0017% of K which is an essential element for living body is radioactive potassium 40 (^{40}K : 1.28 billion years). For example, it contains about 15000 Bq per kg of potassium chloride fertilizer and ^{40}K per 100 kg of soil (Yamaguchi et al., 2012). Also, since adult boys have 2 g of K per kg of body weight, this is equivalent to about 60 Bq kg⁻¹ when converted to a quantity of ^{40}K (Nuclear Encyclopedia, 2004). People take these natural radionuclides through breathing and diet. On the other hand, there are also artificially generated radionuclides (artificial radionuclides). Artificial radionuclides in the environment are contained in radioactive fallout (fallout) released to the atmosphere due to nuclear tests and nuclear power plant accidents to the atmosphere and exhaust gas and cooling water released from nuclear facilities. Like natural radionuclide, it is taken into the body by ingestion of food and drinking and breathing. Among artificial radionuclides, especially important for considering the human body, there is a relatively large amount compared to other nuclides, iodine 131 accumulating in the thyroid gland, almost 100% absorbed from the intestinal tract and absorbed in blood and muscle Cesium 134 (^{134}Cs), ^{135}Cs and ^{137}Cs to migrate, and strontium 90 that accumulates in bone as well as calcium. Since these nuclides of

cesium 137 and strontium 90 have a long half-life and will stay for a long time once released into the environment, the exposure dose is evaluated and it is published in the report of the United Nations Scientific Committee (Yukawa, 2003).

1.1.2 Heavy metal pollution

After the occurrence of The 2011 off the Pacific coast of Tohoku Earthquake, contamination of arsenic, a hazardous heavy metal, was reported from tsunami sediment near the affected area in Miyagi prefecture (Watanabe, 2012). There are arsenic-containing strata upstream of some major rivers in Miyagi prefecture, and there are many mines and deposits (Miyachi, 2013). The possibility that arsenic existing in the stratum was accumulated near the estuary due to long-time river activities, deposited as tsunami deposits on the coastal area, and the possibility that arsenic leaked out from the deposit site of waste ore due to landslides (Watanabe, 2012) have been pointed out. Mines and refining factories that once existed in the catchment area suggested that they have the risk of causing heavy metals to flow out and cause recontamination.

1.2 Characteristics of cesium

Cesium (Cs) exists as non-radioactive stable cesium 133 (^{133}Cs) and radioactive cesium 134 (^{134}Cs half life 2.56), cesium 135 (^{135}Cs half life 2.3 million years) and cesium 137 (^{137}Cs halved Period 30.3 years) (thereafter, nonradioactive cesium is stable Cs; radioactive cesium is collectively referred to as radioactive Cs).

First of all, Cs originally present on the earth is only stable Cs, and it exists in the soil at a median concentration of 4 (0.3 - 20) mg kg⁻¹ (Bowen, 1979). Stable Cs was distributed in soil along with soil formation under the natural environment from the formation of the formation on the earth to the present (Wampler et al., 2012). Stable Cs has no known nutritional role or toxicity to plants and humans (White and Broadly, 2000). On the other hand, all radioactive Cs are anthropogenic, are released into the environment by nuclear bombs and nuclear power plants, and are harmful to the human body because they have radioactivity. Radioactive Cs released into the environment will be newly added to the stable Cs pool in the soil. In the case of Fukushima prefecture (with average value in surface layer soil of 0-15 cm of beach street where Fukushima Daiichi nuclear power station is located), the concentration of radioactive Cs is 5030 Bq kg⁻¹ (Becquerel: number of radioactive nuclei disintegrated per second, radiation Unit representing the strength of Noh). Weight is 1.5×10^{-6} mg kg⁻¹, which is equivalent to 1 / 2,000,000 of stable Cs. Although it is quantitatively less radioactive Cs, its influence on the human body is concerned because it has radioactivity.

1.3 Cesium in minerals

Cesium is a component of three minerals, of which only pollucite, $H_4Cs_4Si_9O_{27}$, containing Cs_2O between 5% and 32%, is of commercial importance. Most Cs, however, is dispersed in some common minerals, like micas and feldspars (Kabata-Pendias 2011).

Mica minerals play important roles in the Cs, K, and Rb supply and in their movement in the soil for two reasons. First, mica minerals are the precursors of expansible 2:1 minerals; the mica minerals can transform into these minerals by replacement of the nonexchangeable interlayer cations (usually K^+) with hydrated exchangeable cations (Fanning 1989); thus, mica minerals can be an important source of Cs, K, and Rb to the soil. Second, mica minerals show the greatest selectivity for Cs and K ions, because the charge density in micas is greater than that in other clay minerals and micas have frayed edges that selectively sorb Cs, K, and Rb (Sawney 1970, 1972). According to Saito et al. (Saito et al. 2014), ^{137}Cs is concentrated in the smaller particle size classes (silt and clay grains), and micaceous minerals are responsible for fixation of ^{137}Cs in the soil.

1.4 Cesium in soil

1.4.1 Negative charge in clay minerals

Most of clay minerals in the soil are layered silicate minerals, which are minerals in which a silicic acid layer and an aluminum layer are bonded. The clay mineral formed by overlapping the silicic acid layer and the aluminum layer one by one is called "1: 1 type clay mineral", and the clay mineral formed by sandwiching the aluminum layer between the two layers of silicic acid is called "2 : 1 type clay mineral ". In 2: 1 type clay mineral, a part of Si^{4+} in the tetrahedron is substituted by Al^{+3} or substitution by Al^{+3} in the octahedron causes a positive charge to be insufficient to generate a negative charge. This is called "negative charge by isomorphous replacement". Further, in all clay minerals, the hydroxyl group bonded to silicon at the end of the crystal structure dissociates at a pH of 9.5 or more to generate a negative charge. This is called "negative charge due to dissociation of silanol group".

1.4.2 Negative charge in the organic matter

Organic matter generated in the soil is called humic substances and occupies most of soil organic matter. In addition to this, nonhuman substances such as polysaccharides, proteins, peptides, lipids, and organic acids produced by plant components and microorganisms are also included, but they are degraded by soil microorganisms, so their abundance is small. Humic substance is a mixture of high molecular weight

organic acids and contains functional groups such as carboxyl group ($-\text{COOH}$) · carbonyl group ($=\text{CO}$) · methoxyl group ($-\text{OCH}_3$) · hydroxyl group ($-\text{OH}$), and contains many carboxyl groups. It is a feature. The carboxyl group dissociates when the pH is neutral or higher to generate a negative charge and attracts cations such as calcium. Humic substances, together with clay minerals, are responsible for a part of the negative charge of the soil.

1.4.3 Constant electric charge and variable electric charge

The negative charge due to isomorphous substitution hardly varies with the pH of the soil, so it is called "constant charge". Since negative charges due to dissociation of silanol groups and carboxyl groups are expressed with pH being neutral or higher, they are called "mutation charges".

1.4.4 Adsorption site of the Cs in soil

Since Cs is a monovalent cation, it is adsorbed to the negative charge in the soil. The negative charge derived from the mutation charge is considered to have lower selectivity to Cs than other cations. Therefore, adsorption is inhibited when a large amount of Ca ion or the like is present, and even if it is once adsorbed, it is easily exchanged by another cation. On the other hand, the tetrahedral substitution type constant charge among the constant charges has a property of attracting interlayer cations more strongly, especially because it is closer to the interlayer cation compared with the octahedral substitution type constant charge, especially Cs + As shown in FIG. The oxygen atom on the base surface of the Si tetrahedral sheet which is in contact with the cations between the layers forms a cavity called a six-membered ring. The size of the six-membered ring (0.29 nm) is almost equal to the ion diameter of Cs ion (Cs^+), potassium ion (K^+), ammonium ion (NH_4^+), rubidium ion (Rb^+) in the unhydrated state (3). The strength (hydration energy) that ions attract hydrated water is proportional to the square of the valence of the ion and inversely proportional to the ion radius. Since the hydration energy of these cations having a valence of 1 and a large ion radius is small, they are easily dehydrated and form a bond (inner sphere complex) that does not interact with the six-membered ring via water. The bonding force is in the order of $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+$ in order of the hydration number.

Among these cations, although K^+ has relatively weak bond strength with the six-membered ring, K^+ is overwhelmingly abundant in the crust, so that the six-membered ring that has developed tetrahedral substitution type layer charge To occupy. The penetration of exchangeable cations is hindered in the layer (non-swollen

layer) where the interlayer distance is closed to 1.0 nm by fixing K^+ . The 2: 1 type layered silicate mineral forming the nonswelling layer is called mica. Mica is formed as a constituent material of rocks in the process of magmas and sediments becoming rocks under underground high temperature and high pressure conditions. Since mica which is not subject to weathering maintains the non-swollen layer as the whole structure, the layer charge that permits exchangeable cations can be limited. Eventually, when soil formation of rocks begins at the surface of the earth, the mica will undergo weathering during that process, releasing K^+ little by little from the interlayer of the outer edge portion while maintaining the sheet structure. Between layers where K^+ is released, hydrated ions are retained instead. As a result, a layer (swelling layer or vermiculite layer) having an interlayer distance of 1.4 nm is formed at the outer edge portion of the mica. Since hydrated cations are eliminated due to the spatial restriction in the wedge-shaped layer charge portion (called a flayed edge) located between the swollen layer and the non-swelling layer, the hydration number is the smallest, and the six-membered Cs^+ , which routinely fits the ring, adsorbs with extremely high selectivity and is almost not exchanged by other cations (Figure 1-2). Even when compared with other cations capable of forming inner-zone complexes with six-membered rings, such as the strength of adsorption is about 1000 times on average for K^+ and 200 times on average for NH_4^+ . In fact, this flayed edge is the specific adsorption site of Cs (Cermers et al., 1988; Nakao et al., 2008; Vandebroek et al., 2012; Nakao, 2012; Japan Scientific Reconstruction Association, 2014).

1.4.5 Redistribution of cesium from soil to soil solution

Radioactive Cs flying into the soil is adsorbed to the negative charge in the soil. Then it is redistributed into the soil solution, it is absorbed from the roots of the plant and transfers to the edible part. The amount of radioactive Cs once adsorbed to the soil is redistributed is small. While this minimizes contamination of agricultural crops, it also contributes to making decontamination difficult (Yamaguchi et al., 2012).

1.5 Cesium absorption by plants

1.5.1 Transfer of cesium from soil solution to plant's root surface

Nutrients and other soluble substances move to roots by mass flow induced by the transpiration stream and by diffusion (Ney and Marriott, 1969). Mass flow may supply the root with much of the plant's need for calcium, magnesium, and nitrogen, while usually most of the phosphorus and potassium on many soils must reach the root by diffusion (Barber et al., 1963). Similarly, cesium is transported to the root by mass flow

and diffusion, but it is not known whether it depends on mass flow or diffusion.

1.5.2 Absorption of cesium from the root surface into the plant body

The uptake of mineral elements is mediated by various transporters belonging to different transporter families in phospholipid bilayer of the root, which are membrane proteins (Sasaki et al., 2016). A number of K transporters have been identified in plants, and Cs transport has been demonstrated for several of these K transporters (Fujiwara, 2013).

1.5.3 Cs distribution in plant body

After absorption by roots, Cs is loaded to the xylem to reach the aerial portions of plants; this is followed by phloem transport to reach the grains (Fujiwara, 2013).

1.6 Characteristics of rice (*Oryza sativa*) plant

1.6.1 Classification of the rice by the ecotype

Rice plant is a whole species belonging to Angiosperms, Monocotyledonous plants, Gramineae, Rice. There are 22 species in the rice family, divided into wild rice and cultivated rice. Wild rice is a species that adapts to the natural environment around the world and grows naturally, there are 20 species in total. Cultivated rice is a species that human beings have selected / improved for staple food over a long period of time, and there are two types of "rice cultivated in Asia (*Oryza sativa*)" and "*O. glaberrima* cultivated in Africa". Cultivated rice is one of the world's three largest crops with maize and wheat, it is the most important crop in Asia.

Asian cultivated rice is cultivated in Europe, the Americas, Australia and Africa, mainly in the Asian continent, and has a worldwide distribution area. On the other hand, cultivated rice cultivated in Africa is only locally grown only in West Africa, and the cultivated area is decreasing.

Origin of Asian cultivated rice is presumed to be a mountainous region from Assam, Myanmar, Laos in northern India to northern Thailand to Yunnan Province in the eastern part of India, and it was transmitted to India in the west, Southeast Asia in the south, Eastern China and the Pacific region . Due to the genetically differentiation adaptive to the environment in each region, differentiation of Asian cultivated rice has been advanced at a subspecies level (one classification below the species) level, and furthermore, "Japanese type (Japonica)" "Indian type (Indica)" can be broadly divided. Japanese varieties are generally grown in regions with high cold tolerance and high altitudes, but Indian varieties are often cultivated in areas with low altitude and low

altitude.

Japanese varieties are further classified into two varieties, "Temperate Japanese type" distributed more in Japan and the Korean Peninsula and "Tropical Japanese type" distributed in southern China, Philippines, Indonesia, etc. The latter is referred to as "Java type (Javanica)" (National Agriculture and Biotechnology Specific Industrial Technology Research Organization, 2006). The morphological features of Asian cultivated rice are shown below.

1.6.2 Cultivation environment of the rice

Rice cultivation is called rice production. The land to be cultivated is called a rice field or a rice paddy field, especially a paddy field called a paddy field. Rice cultivated in paddy field, rice plant (field rice) called what was cultivated in rice (field).

Paddy soil is an important soil occupying 30% of agricultural land in tropical Asia and 50% in Japan. By filling the soil with water it is possible to avoid continuous disorder and maintenance of soil fertility and it is advantageous for cultivation. Most of the rice cultivation period is flooded, so it is blocked from the atmosphere and becomes anaerobic, showing reductive properties. However, even in paddy fields where reduction has developed, 5 cm of the surface layer becomes an oxide layer. On the other hand, in upland soil, the soil layer is in oxidation state, and many aerobic microorganisms.

1.6.3 Cs uptake by rice

The absorbed Cs is transported to the aerial part via a conduit and transferred to and accumulated in each tissue (grain, leaf blade, stem, etc). As a result of adding ^{137}Cs to the alluvial soil and cultivating paddy rice in the pod, the ^{137}Cs concentration in each tissue was in order of white rice <brown rice <rice husk \doteq leaf sheath <leaf blade <culm \doteq bran. Similar results are also observed at ^{133}Cs concentrations in paddy cultivated in the field. The same tendency was also observed for K concentration. Differences in behavior of Cs and K in the body can be expressed as a ratio of $^{137}\text{Cs} / \text{K}$ or $^{133}\text{Cs} / \text{K}$ in each organization. The ratio becomes large in the upper leaf blade <culm <husk shell <lower leaf sheath <upper leaf sheath <rice bran <brown rice <white rice <lower leaf blade, K is easy to move to the new leaf body, while Cs accumulates in the old leaf body It's easy to do. The brown rice transition rate (brown rice concentration / whole aerial concentration) depends on cultivation and fertilization conditions, but it is 11-23% in Cs and 8-23% in K. These results also show that in-body behavior (Yamaguchi et al., 2012).

1.7 Objectives of this study

Numerous studies on the behavior of Cs in soil - plant system or paddy system have been made. In particular, the adsorption mechanism against negative charges in soil (Sawhney, 1972; Cornell, 1992; Nakao et al., 2012), the physiological mechanism involved in Cs absorption (White and Broadley, 2000), difference between plant species (Skarlou et al., 1996 ; Broadley and Willey, 1997), differences in accumulated concentration of rice plants by site (Tsumura et al., 1984; Tsukada et al., 2002) and others have been elucidated.

In recent years, it has been reported that there are large varietal differences in Cs absorption even in rice varieties. Fuziwara et al. (2013) conducted field tests using rice varieties of over 100 varieties in Japan and overseas, but reported that there is a maximum difference of 20 times in Cs concentration in brown rice depending on cultivar. Since there are large varietal differences in paddy rice varieties in Cs absorption, it is expected to be used for high absorbance varieties from radioactive Cs contaminated soils for removal of radioactive Cs and for low absorption varieties as encouraging cultivars. There is also the possibility that varieties with improved high and low absorptive capacity may be developed, by breeding high and low absorbing varieties. However, differences between varieties of Cs absorption by various plants such as paddy rice are mostly studied only for the absorption of radioactive cesium and other radioactive nuclides, and alkali metals having physical and chemical properties similar to cesium. There are few studies that dealt simultaneously with the absorption of harmful heavy metals which are also interrelated with "absorption" and "pollution" problem. The absorption of hazardous heavy metals has not been mentioned at all so far, for example, the possibility that Cs low absorption variety is a high absorption type of harmful heavy metal, and conversely low absorption type of hazardous heavy metal is Cs high absorption type. Since it is conceivable, it is necessary to consider at the same time to manage the risk of radioactive Cs.

With respect to Cs absorption from soil to paddy rice, we carried out field experiments (1) to elucidate the relationship among potassium (K) [ionic radius: 0.133 nm] and rubidium [Rb (0.149 nm)] in rice plants and paddy fields, which are similar to Cs ionic radius [0.169 nm] among alkali metals and competitive at adsorption sites in soil; (2) to compare varietal differences of Cs absorption with varietal differences of Cd absorption which is one of hazardous heavy metals and to establish a new variety selection method considering Cs and Cd risk management.

Chapter2 Concentrations of Cs, K, and Rb in rice

(*Oryza sativa*) cultivated under paddy and upland conditions

1. Introduction

Cesium, an alkali metal, has both stable (^{133}Cs) and radioactive (^{134}Cs , ^{135}Cs , and ^{137}Cs) forms. Originally, cesium was present in soil only in its stable form, at an average concentration of 4 mg kg^{-1} (ranging from 0.3 to 20 mg kg^{-1}) (Bowen et al. 1979). The modern distribution of stable cesium (Cs) in soils represents the result of soil evolution under ambient natural conditions over geological time periods (Wampler et al. 2012). In contrast, radioactive cesium (*r*-Cs) has a long half-life by human standards, so any that is present in the soil is artificial, and was emitted from nuclear bombs and nuclear power plants, and has only been recently added to the soil Cs pool. Movement of the stable form therefore serves as a long-term indicator of *r*-Cs movement in ecosystems (Tsukada et al. 2002; Uchida et al. 2007; Cook et al. 2007). After the March 2011 Fukushima nuclear accident in Japan, the abundance of ^{137}Cs near the Fukushima Daiichi Nuclear Power Plant from the soil surface to a depth of 15 cm was 5030 Bq kg^{-1} (Yamaguchi et al. 2012), which is equivalent to $1.6 \times 10^{-3} \text{ } \mu\text{g kg}^{-1}$. Since Cs averages 4 mg kg^{-1} in the soil, ^{137}Cs amounts to $4 \times 10^{-6} \%$ of the Cs content in the soil. However, even at these low levels, it is important to pay attention to *r*-Cs because of its long half-life and its potential to harm the human body.

Dietary intakes of Cs and *r*-Cs in Japan are limited to 9.1 ng and 61 mBq per person per day (Shiraishi et al. 1999). The main sources of Cs in the human diet are uptake by crops through foliar adsorption from the air and root absorption from the soil (Yamagata et al. 1965; Tsumura et al. 1985). When *r*-Cs is present in the air after being emitted from a nuclear power plant, foliar adsorption and root absorption should therefore be carefully considered. As the *r*-Cs concentration in the air decreases, the contribution of root absorption increases (Tsukada et al. 2011). The nutritional role of cesium in plants is unknown, but it does not appear to be phytotoxic at solution culture concentrations exceeding $200 \text{ } \mu\text{mol L}^{-1}$ (White and Broadley 2000). This, in turn, suggests that plants can accumulate high levels of cesium without disturbing normal growth (Adams et al. 2015). The *r*-Cs deposited in soils via fallout appears to be more mobile and more easily absorbed by plants than Cs because the *r*-Cs has not yet been immobilized in the soil (Uchida et al. 2007). However, Kamei-Ishikawa et al. (2011) reported that Cs and *r*-Cs were taken up by rice (*Oryza sativa*) at a rate proportional to the plant-available fraction

in the soil. To decrease the concentration of *r*-Cs in crops, we therefore need to understand the behavior of both *r*-Cs and Cs in the soil–plant system. This includes elucidation of the mechanisms for input of cesium to the soil, cesium entry into the soil solution, and cesium uptake by plants (Yamaguchi et al. 2012). Researchers would benefit from studying the movement of Cs from the soil into the plant because Cs is so much more abundant than *r*-Cs.

At least four factors affect cesium uptake by plants: the potassium (K) status of the soil, the abundance of 2:1 clay minerals, the plant species, and the plant's growth rate (Cook et al. 2009). K is also an alkali metal, and reacts similarly to cesium in physicochemical reactions. When soil K is readily available to plants, cesium uptake will be relatively low. However, when K is relatively unavailable, cesium uptake will increase, and can be reduced by the application of K (Nishita et al. 1962; Smolders et al. 1997; Zhu and Smolders 2000). Clay minerals, and especially 2:1 clay minerals, lock up cesium ions in the inter-layer spaces between the minerals (Sawney 1972; Cornell 1992; Nakao et al. 2008). Finally, cesium uptake by plants varies widely among plant species, including crops (Skarlou et al. 1996; Yamaguchi et al. 2012). To decrease human dietary intake of *r*-Cs, this suggests that a practical approach would take advantage of cultivars that accumulate less Cs in their grains (Fujiwara 2013).

The physicochemical properties of K could also be similar to those of rubidium (Rb), which is also an alkali metal, so Rb is frequently used as a tracer of K in soils and plants (Tyler 1997). It may partly substitute for K at binding sites in plants, although it cannot substitute for K in metabolic roles (Kabata 2011). Similarly, cesium competes with K for the same binding sites in essential plant proteins (Hamptom et al. 2004). K competes with cesium not only for uptake by plants but also at the same sites within plants (Isaure et al. 2006). These facts suggest that cesium could compete with both K and Rb for root uptake and at certain binding sites in plants. On the other hand, soil cations with low hydration energy, such as K, NH₄, Rb, and cesium ions, readily become fixed in the spaces between layers in 2:1 clays since these cations fit closely into hexagonal cavities in the basal oxygen planes (Sawney 1972). This suggests that cesium could compete with K and Rb for binding to clay sites in the soil and for entry into the soil solution. However, few researchers have studied the interaction of cesium with both K and Rb in the soil and in plants. This information is important, since it will improve our understanding of the mechanisms of cesium accumulation from the soil to plants. Thus, the interactions of cesium with both K and Rb during their transfer from the soil into plants should be studied.

In Asian countries, consecutive paddy rice cultivation has been conducted for many

years. Paddy fields are flooded for 3 to 4 months, with occasional drainage during a cultivation period, resulting in a drastic switch between paddy and upland conditions (Okada et al. 2011). However, the effect of these conditions on cesium uptake by rice has rarely been studied in the field.

The objective of the present study was to elucidate Cs, K, and Rb concentrations and their interactions in the soil and the resulting content in brown rice under paddy and upland conditions. To provide this knowledge, we carried out a field experiment with paddy and upland rice.

2. Materials and methods

2.1 Field experiment

2.1.1 Study site

The experimental field is located in Nonoichi (36° 30'N, 136° 36' E), in Ishikawa Prefecture of north-central Japan, which has a Japan Sea Climate (equivalent to the Cfa Climate in the Köppen climate zone classification). There is much snow in the winter and more than 2800 mm of precipitation per year. The study area has an annual mean temperature of 14.8 °C, with mean monthly temperatures ranging from 3.8 °C in January to 27 °C in August (Nonoichi City 2015). Most of the land is a rice paddy field, with Gray Lowland Soils (Hapludepts), and part of it lies within the Tedorigawa River alluvial fan. The soils of this area range from clay loams to silty clay loams, with a minor component of round medium gravels in the standard Krumbein classification scale (i.e., ranging from 8 to 16 mm in diameter) (National Institute of Agricultural Sciences 1969; Ministry of Land 2015).

2.1.2 Experimental design

Half of the experimental paddy field has been cultivated under upland conditions (for soybean [*Glycine max*] in 2006; Japanese mustard spinach [*Brassica rapa*] in 2007; wheat [*Triticum aestivum*] and soybean in 2008; soybean and spinach [*Spinacea oleracea*] in 2009; eggplant [*Solanum melongena*], Chinese cabbage, Japanese mustard spinach, and carrot [*Daucus carota*] in 2010; Japanese mustard spinach in 2011; Welsh onion [*Allium fistulosum*] in 2012; and taro [*Colocasia esculenta*] in 2013); these crops were cultivated for 8 years after switching this part of the field from paddy conditions to upland conditions. The other half of the field was maintained as paddy rice during this period.

In this study, the field experiment with rice was carried out under both paddy and upland conditions. Table 1 summarizes the soil characteristics in the experimental field. Both soils are clay loams dominated by fine sand. The primary soil minerals are feldspar and quartz, and biotite is easily visible using an MT9300 microscope (Meiji Techno Co., Ltd., Saitama, Japan) under both normal and polarized light (Fig. 1). Figure 2 shows that the secondary clay minerals include kaolinite (peak C), a mica-type clay (peak B), and aluminum-vermiculite (peak A).

We used 13 varieties of rice, including five temperate *japonica* and eight tropical *japonica*, in the field experiment. All 13 cultivars were planted under paddy conditions, but only 9 of the 13 cultivars were planted under upland conditions (Table 2). Each plot was 1 m × 1 m under paddy conditions and 0.3 m × 2 m under upland conditions. There were three replicates in each plot. Thus, we used 39 plots (39 m²) under paddy conditions and 27 plots (16.2 m²) under upland conditions, with the plots arranged completely randomly in each experimental field. Transplanting of seedlings was carried out on 26 May 2014. Harvesting aboveground parts of the rice plants was done on 28 September. During a cultivation period, the field under paddy conditions was constantly submerged and the field under upland condition was watered using watering pot when the soil dried.

2.1.3 Soil and brown rice samples

We evenly sampled about 500 g of the soil from the plow layer (to a depth of 15 cm) at five points in each field on 28 September. The soil samples were stored separately, then were dried at 70 °C for 48 hours in a forced-air oven and ground with a grinder (SSM-2, Fujihira Industry CO., LTD, Tokyo, Japan) until they could pass through a 2-mm sieve. They were then stored in glass screw-top bottles. The aboveground parts of the rice plants were harvested and then threshed to retrieve the grains. The rice husk was removed to obtain samples of brown rice. These samples were dried at 70 °C for 48 hours in a forced-air oven. The brown rice samples were stored in glass screw-top bottles.

2.2 Instruments for determinations of Cs, K, and Rb

We applied inductively coupled plasma mass spectrometry (ICP-MS) using an X SERIES II spectrophotometer (Thermo Fisher Scientific, Massachusetts, USA) for measurements of Cs and Rb contents, which were calculated by determination of ¹³³Cs and ⁸⁵Rb, respectively. The working standard was prepared from a series of SPEX Multi-Element Plasma Standards (XSTC289 and XSTC622) supplied by SPEX

Industries, Inc. (Metuchen, NJ, USA). The interface compartment of the ICP-MS was made of nickel sampler and skimmer cones (with openings 1.0 and 0.7 mm in diameter, respectively). The ion lens compartment was equipped with a hexapole collision cell (CC), and the instrument's software could rapidly switch from standard mode (no gas, cell vented to the mass analyzer chamber) and CC mode. The mass separation compartment contained a quadrupole mass spectrometer. The ICP-MS operating conditions were as follows: setting, standard mode; RF incident power, 1400 W; plasma argon flow rate, 13 L min⁻¹; auxiliary argon flow rate, 0.92 L min⁻¹; resolution, standard; dwell time, 10 ms; sweeps, 100; number of readings per replicate, 3.

Atomic absorption spectrophotometry (AAS) was performed using an AA-6300 spectrophotometer (Shimadzu, Kyoto, Japan) for the K measurements. The AAS measurement conditions were as follows: flame aspiration method, normal lamp, wavelength, 766.49 nm; slit width, 0.7 nm; light mode, non-background gas; lamp electric current low, 16 mA; lamp electric current high, 0 mA; burner height, 7 mm; burner angle, 0°; flame type, Air-C₂H₂; fuel gas flow, 1.8 L min⁻¹; and supporting gas flow, 15.0 L min⁻¹.

2.3 Determinations of Cs, K, and Rb in soil, mica, brown rice, and certified reference materials

2.3.1 Soil

To determine the total Cs, K, and Rb concentrations in soil, we ground 200 mg of the soil samples with an agate mortar and pestle, then transferred the soil into a platinum melting pot. We then added 2 g of sodium carbonate and mixed the solids. Finally, we covered the mixture with a small amount of sodium carbonate, then capped the pot. The melting pot and cap were then heated to 900 °C for 60 minutes in an oven, and cooled overnight to room temperature in a desiccator. The solidified material was placed in a 200-mL beaker, and 50 mL of 2.26 mol L⁻¹ hydrochloric acid was added, little by little, while heating and dissolving the materials on a hotplate. The volume was then adjusted to 100 mL by adding ultrapure water. The resulting solution was then filtered through a Dismic-25hp 0.45-µm membrane filter (Advantec, Tokyo, Japan) and diluted to 10% of its initial volume by adding ultrapure water. Cs and Rb concentrations in the solutions were determined by means of ICP-MS, and the K concentration was determined by AAS. ICP-MS and AAS were performed as described in section 2.2.

Moreover, two single-extraction methods were applied to the soil samples. First, to

determine the exchangeable Cs, K, and Rb concentrations, we added 3 g of the soil samples to 30 mL of 1 mol L⁻¹ ammonium acetate solution, then shook the solution with a reciprocating shaker for 30 minutes at 20 °C. We filtered the solution through a 0.45- μ m membrane filter and diluted it to 1% of its initial volume by adding ultrapure water. Second, to determine the water-soluble Cs, K, and Rb concentrations, we added 3 g of the soil samples to 30 mL of ultrapure water, then shook the solution with a reciprocating shaker for 24 hours at 20 °C. We filtered the solution through a Dismic-25hp 0.45- μ m membrane filter. Cs and Rb concentrations in the solution were determined by means of ICP-MS, and the K concentration was determined by AAS. ICP-MS and AAS were performed as described in section 2.2.

2.3.2 Mica

Mica minerals play important roles in the Cs, K, and Rb supply and in their movement in the soil for two reasons. First, mica minerals are the precursors of expandable 2:1 minerals; the mica minerals can transform into these minerals by replacement of the nonexchangeable interlayer cations (usually K⁺) with hydrated exchangeable cations (Fanning 1989); thus, mica minerals can be an important source of Cs, K, and Rb to the soil. Second, mica minerals show the greatest selectivity for Cs and K ions, because the charge density in micas is greater than that in other clay minerals and micas have frayed edges that selectively sorb Cs, K, and Rb (Sawney 1970, 1972). According to Saito et al. (Saito et al. 2014), ¹³⁷Cs is concentrated in the smaller particle size classes (silt and clay grains), and micaceous minerals are responsible for fixation of ¹³⁷Cs in the soil. In our experimental field, the presence of biotite and mica-type clays in the soil (Fig. 1, 2) suggests that Cs could be easily fixed in the soil.

In this study, we determined the Cs, K, and Rb concentrations in four types of mica (biotite from Bancroft, Ontario, Canada; phlogopite from the Parker Mica Mine, Quebec, Canada; lepidolite from Minas Gerais, Brazil; and muscovite from Ishikawa town, Fukushima, Japan) as reference materials. We then compared the Cs, K, and Rb concentrations in the mica minerals with those in the soil. Figure 3 shows the four types of micas observed using an MT9300 microscope under both normal and polarized light. Figure 4 shows the X-ray diffraction patterns of the four types of micas obtained using a MiniFlex X-ray diffractometer (Rigaku, Tokyo, Japan). The decomposition of the mica was performed as described in section 2.3.1. Cs and Rb concentrations in the solution that resulted from the decomposition were determined by means of ICP-MS after diluting the solution to 0.1% of its initial volume by adding ultrapure water. The K concentration was determined by AAS after diluting the solution to 1% of its initial

volume by adding ultrapure water. ICP-MS and AAS conditions were performed as described in section 2.2.

2.3.3 Brown rice

To determine the Cs, K, and Rb concentrations in brown rice, we placed 0.5 g of the brown rice samples in a 50-mL conical beaker, and then added 6 mL of 13.1 mol L⁻¹ nitric acid. The mixture was then heated and dissolved at 100 °C on a hotplate for 1 hour. The resulting solution was then diluted with ultrapure water to a total volume of 50 mL and filtered through a Dismic-25hp 0.45-µm membrane filter. Cs and Rb concentrations in the solution were determined by means of ICP-MS. The K concentration was determined by AAS after diluting the solution to 1% of its initial volume by adding ultrapure water. ICP-MS and AAS were performed as described in section 2.2.

2.3.4 Certified reference material

We analyzed a certified reference material (pine needle, NIST 1575a) from the National Institute of Standards and Technology (Gaithersburg, MD, USA) to calibrate the Cs, K, and Rb measurements. The certified value was 238 ± 9.00 µg kg⁻¹ (mean ± SD) for Cs, 4170 ± 136 mg kg⁻¹ for K, and 16.5 ± 0.200 mg kg⁻¹ for Rb. The digestion of the samples and determination of the Cs, K, and Rb were carried out as described in section 2.3.3.

2.3.5 Statistics

Data analysis used Student's *t*-test and Pearson's correlation coefficient *r*, with significance at *p* < 0.05 in both tests. We used version 10 of the JMP software (www.jmp.com) for all analyses.

3. Results

3.1 Soil Cs, K, and Rb concentrations

Table 3 summarizes the total and extracted (exchangeable plus water-soluble) Cs, K, and Rb concentrations in the paddy and upland soils. Total and exchangeable (ex-) Cs were 11% lower and 53% higher, respectively, in the paddy soil. Total and ex-K were 29% higher and 44% lower, respectively, in the paddy soil. Total Rb did not differ greatly between the two soils, but ex-Rb was 13% higher in the paddy soil. The water-soluble (ws-) Cs, K, and Rb concentrations were 38, 59, and 26% higher,

respectively, in the upland soil. All of these differences were statistically significant (*t*-test, $p < 0.05$) except for total Rb and ex-K concentrations.

Table 4 presents the values of Pearson's correlation coefficient (*r*) for the relationships among the various combinations of the three elements in the paddy and upland soils. The ex-Cs, ex-K, and ex-Rb were significantly positively correlated in the paddy soil; however, only ex-K and ex-Rb were significantly correlated (positively) in the upland soil. All four correlations were strong ($r > 0.8$, $p < 0.05$). The ws-Cs, ws-K, and ws-Rb were not significantly correlated, except for a negative correlation between ws-K and ws-Rb in the upland soil ($r = -0.97$, $p < 0.001$). The extracted Cs, K, and Rb concentrations clearly revealed different patterns under paddy and upland conditions. This suggests that the movement of Cs, K, and Rb in the soil changes easily under management regimes with different moisture conditions.

3.2 Cs, K, and Rb concentrations in mica

Table 5 shows the Cs, K, and Rb concentrations in the four mica minerals. Cs was highest in lepidolite (2 303 mg kg⁻¹) and lowest in phlogopite (7.65 mg kg⁻¹). K was highest in muscovite (86 700 mg kg⁻¹) and lowest in phlogopite (66 695 mg kg⁻¹). Rb was highest in lepidolite (13 939 mg kg⁻¹) and lowest in phlogopite (353 mg kg⁻¹). Cs contents varied most (by three orders of magnitude), and K contents were similar in all four minerals.

3.3 Concentrations of Cs, K, and Rb in brown rice

Table 6 shows the concentrations of Cs, K, and Rb in brown rice under paddy and upland conditions. The K concentration in brown rice was 13% higher under paddy conditions, whereas Cs and Rb concentrations in brown rice were 29% and 6% higher, respectively, under upland conditions. All differences between paddy and upland conditions were statistically significant (*t*-test, $p < 0.05$). No significant correlations were observed among the K, Rb, and Cs concentrations in brown rice of the cultivars cultivated under paddy and upland conditions. This suggests that all three elements follow different paths from soil to rice under the two sets of soil conditions, and therefore accumulate differently in brown rice.

3.4 Accuracy of the Cs, K, and Rb determinations

Table 7 shows the concentrations of Cs, K, and Rb in the certified pine needle

sample (NIST 1575a). The results agreed well with the reference values. The accuracies (the measured value divided by the certified value) were 99.6% for Cs, 94.2% for K, and 87.9% for Rb. Thus, ICP-MS and AAS performed well for quantifying Cs, K, and Rb concentrations.

4. Discussion

4.1 Concentrations of Cs, K, and Rb in the soil and mica samples

The proportion of the total concentration accounted for by the extracted concentration was low (<8% for the ex- concentrations and <0.1% for the ws- concentrations) for all elements and all soils (Table 3). In the paddy soil, the ratio of ex-K to total K was only half that in the upland soil, but the same ratios were approximately equal for Rb, and the ratio for Cs in the paddy soil was nearly twice that in the upland soil. These values were similar to those reported by Romheld and Kirkby (2010) for K and by Kondo et al. (2015) for Cs. The ratio of ws- concentrations to total concentrations was higher in the upland soil than the paddy soil for all elements.

The soils contained much lower levels of K, Rb, and Cs than existed in the mica minerals (Table 5). The total Cs, K, and Rb concentrations in the mica minerals were 6 times (phlogopite) to 9 times (muscovite) those in the soils for K, 3 times (phlogopite) to 128 times (lepidolite) those in the soils for Rb, and 7 times (phlogopite) to 368 times (lepidolite) those in the soils for Cs. These results suggest that the mica minerals can potentially supply large quantities of Cs, K, and Rb to a soil that contains these minerals.

4.2 Relationships among Cs, K, and Rb concentrations in the soil and brown rice

Our results showed that ex-Cs, ex-K, and ex-Rb were positively correlated with each other under paddy and upland conditions (Table 4); all correlations were significant for the paddy soil, but only the ex-K versus ex-Rb correlation was significant under upland conditions. These observations suggested that Cs, K, and Rb shared the same exchange sites in the soil. On the other hand, Cs, K, and Rb were not significantly correlated in brown rice. The relationships among Cs, K, and Rb in plants are not completely understood. In previous studies, Rb and Cs were strongly and significantly positively correlated in the needles of Norway spruce (*Picea abies*) (Tobler et al. 1994; Wyttenbach et al. 1995). In addition, Cs, K, and Rb tend to be positively correlated in the tissues of plants, mosses, and fungi in natural ecosystems (Cao et al. 2008; Vinchuk

et al. 2011). However, Yamagata et al. (1958) reported that the tissues of 50 species of plants growing under natural conditions plants showed no significant correlation between Rb and Cs or between K and Cs, but that K and Rb were typically positively correlated. Chu et al. (2015) recently reported positive correlations between Cs and Rb in *Amaranthus* shoots, but no correlation between K and Cs. In a solution culture experiment, increasing the solution K and Rb concentrations decreased Cs uptake by barley (*Hordeum vulgare*) roots (Handley et al. 1961) and decreased Cs transport to the wheat (*Triticum aestivum*) shoot (Jackson et al. 1966). These reports suggest that K and Rb compete with Cs for root uptake.

From the results of Yamagata et al. (1965) and Wallace (1968), rice and bush bean (*Phaseolus vulgaris*) show different distributions of Cs, K, and Rb in their leaves, stems, and roots. In rice plants, K was most abundant in young leaves, whereas Cs was most abundant in old leaves in a field experiment (Tsukada et al. 2002b). Others have found a significant negative relationship between the Cs concentration in aerial parts and the root K concentration and between the Cs concentration in brown rice and the stem K concentration, which suggests that high K concentrations in plants impede Cs translocation from the roots to the aerial parts and from the stems to the brown rice (Kondo et al. 2015b). The lack of clarity in the relationships among Cs, K, and Rb in plant tissues may result from their different distribution and translocation patterns, which may in turn derive from differences among growth stages and species.

4.3 Influence of paddy and upland conditions on Cs, K, and Rb uptake by rice

Our field experiment showed that field conditions (paddy vs. upland conditions) influenced Cs, K, and Rb uptake by the plants. Cs and Rb concentrations in brown rice were significantly higher under upland conditions than under paddy conditions (t -test, $p < 0.05$), whereas significantly more K accumulated in brown rice under paddy conditions (t -test, $p < 0.05$). These results differ from those of Tensho et al. [48], who found higher absorption of Cs by rice under paddy conditions and concluded that this resulted from the form of nitrogen under paddy conditions (i.e., ammonium, versus nitrate under upland conditions). However, the upland conditions defined by Tensho et al. (1961) in their laboratory experiment maintained soil moisture continuously at about half the maximum water-holding capacity, which differs from the conditions in our field experiment. Upland conditions in the present study involved wetting and drying cycles rather than constant moisture levels.

Shalhevet (1973) reported that the effect of moisture content on Cs uptake by plant roots was controlled by two main soil factors: ion diffusion and the ion concentration.

Shalhevet (1973) showed that when the soil moisture content remained constant, Cs uptake was controlled by its rate of diffusion and therefore increased as moisture content increased. On the other hand, when moisture changed in a wetting and drying cycle, Cs uptake was controlled by its concentration: the drier the soil, the higher the Cs uptake due to the increased Cs concentration in the soil solution as a result of evapotranspiration during dry periods. In agreement with this hypothesis, our field results show that the ws-Cs, ws-K, and ws-Rb concentrations in the soil were all higher under upland conditions than under paddy conditions (Table 3). That is, root uptake of Cs under paddy and upland conditions in our field experiment appeared to have been controlled by ion diffusion and ion concentration, respectively. On the other hand, Cs uptake by roots under paddy and upland conditions in the experiment of Tensho et al. (1961) appeared to have been controlled only by ion diffusion, so that higher Cs absorption occurred under paddy conditions.

For K and Rb, higher moisture content increased root uptake of K (Kuchenbuch et al. 1986) and of Rb (Place et al. 1964) under constant moisture levels because root uptake of K and Rb would be controlled by ion diffusion under those conditions. However, additional research on K and Rb uptake by plants under the changing moisture contents that occur with wetting and drying cycles will be needed to clarify these mechanisms.

In our field experiment, the ion concentration could be a stronger factor than ion diffusion for increasing Cs and Rb uptake by roots because the Cs and Rb concentrations in brown rice under upland conditions were higher than those under paddy conditions, in which soil moisture remained relatively constant; these conditions would increase ion diffusion but would not increase the ion concentration. Rosen et al. (2006) found that wetting and drying of peat soil after liming increased the uptake of Cs by perennial ryegrass (*Lolium perenne*), which agrees with the present results. However, we found no research that compared Rb uptake by plants under wetting and drying cycles with uptake under constant moisture levels.

In contrast with Cs and Rb, ion diffusion could be a stronger factor for increasing K uptake by roots, because the K concentration in brown rice under paddy conditions was higher than that under upland conditions, which produced a high ws-K concentration. This suggests that plant roots absorb K from the soil preferentially compared with Cs and Rb by means of ion diffusion. In agreement with this result, Zeng and Brown (2000) showed that maintaining constant soil moisture levels increased K uptake by corn (*Zea mays*) compared with uptake under a wetting and drying cycle.

Table 1 The characteristics of the soil from the field used for the field experiment, with part of the field under paddy conditions and the other part under upland conditions. CL, clay loam; EC, electrical conductivity; TC, total carbon; TN, total nitrogen.

	Clay (%)	Silt (%)	Fine sand (%)	Coarse sand (%)	Field texture	TC (mg kg ⁻¹)	TN (mg kg ⁻¹)	pH	EC (mS m ⁻¹)
Paddy condition	23	28	41	8.2	CL	1.74	0.17	5.11	4.23
Upland condition	24	28	39	9.4	CL	1.53	0.14	6.07	4.18

Table 2 Rice (*japonica*) cultivars used in the field experiment, their origin, and their ecotype

Paddy field	Upland field	Origin	Ecotype
Cultivar name	Cultivar name		
Koshihikari	Koshihikari	Japan	Temperate
Kinuhikari	-	Japan	Temperate
Yumemizuhō	-	Japan	Temperate
Notohikari	-	Japan	Temperate
Nipponbare	Nipponbare	Japan	Temperate
Kalenayan Gabreno	Kalenayan Gabreno	Philippines	Tropical
Homay	Homay	Philippines	Tropical
Karemon	-	Philippines	Tropical
RC66	RC66	Philippines	Tropical
Kaluis	Kaluis	Philippines	Tropical
Sarokot	Sarokot	Philippines	Tropical
Kalenayan Labong	Kalenayan Labong	Philippines	Tropical
Basilanon Sept	Basilanon Sept	Philippines	Tropical

Table 3 Total and extracted (exchangeable and water-soluble) Cs, K, and Rb concentrations (mean \pm SD, $N = 5$) in the soil under paddy and upland conditions. All differences between paddy and upland conditions were statistically significant (t -test, $p < 0.05$) except for total Rb and exchangeable K concentration.

Element	Soil condition	Total concentration (T)	Exchangeable concentration (ex)	Water-soluble concentration (ws)	(ex/T) \times 100 (%)	(ws/T) \times 100 (%)
Cs (mg kg ⁻¹)	Paddy	6.26 \pm 0.202	0.491 \pm 0.0153	0.00389 \pm 0.000736	7.8	0.06
	Upland	6.93 \pm 0.269	0.322 \pm 0.0208	0.00537 \pm 0.000385	4.6	0.08
K (mg kg ⁻¹)	Paddy	12434 \pm 1467	58.1 \pm 29.5	2.94 \pm 0.781	0.5	0.02
	Upland	9614 \pm 1378	103.0 \pm 42.2	4.68 \pm 0.539	1.1	0.05
Rb (mg kg ⁻¹)	Paddy	110 \pm 3.71	1.14 \pm 0.600	0.0315 \pm 0.00169	1.0	0.03
	Upland	109 \pm 3.53	1.01 \pm 0.370	0.0397 \pm 0.00150	0.9	0.04

Table 4 Correlation coefficients (Pearson's r) between K and Rb, K and Cs, and Rb and Cs under paddy and upland soil conditions

	Exchangeable (ex-)		Water soluble (ws-)	
	Paddy soil	Upland soil	Paddy soil	Upland soil
K and Rb	0.98 ***	0.84 *	0.33	-0.97 ***
K and Cs	0.89 *	0.18	-0.11	-0.61
Rb and Cs	0.81 +	0.69	0.55	0.70

*** $p < 0.001$ * $p < 0.05$ + $p < 0.1$

Table 5 Cs, K, and Rb concentrations in the four types of mica

Mica	Cs (mg kg ⁻¹)	K (mg kg ⁻¹)	Rb (mg kg ⁻¹)
Biotite	46.4	72 414	412
Phlogopite	7.65	66 695	353
Lepidolite	2 303	76 108	13 939
Muscovite	45.4	86 700	1 212

Table 6 Concentrations of Cs, K, and Rb in brown rice under paddy and upland condition. All differences between paddy and upland conditions were statistically significant (*t*-test, *p* < 0.05).

Field condition	Cs ($\mu\text{g kg}^{-1}$)	K (mg kg^{-1})	Rb (mg kg^{-1})
Paddy (<i>N</i> ^a = 13)	9.44 \pm 1.32 ^b	2890 \pm 380	6.45 \pm 0.600
Upland (<i>N</i> = 9)	12.2 \pm 1.41	2550 \pm 170	6.82 \pm 0.370

^a Number of cultivars ^b Mean value \pm SD

Table 7 Analysis of the certified reference material (pine needle, NIST 1575a) and comparison with the reference values by means of ICP-MS and AAS

Sample	Element	Reference value ^c	Measured value (<i>n</i> = 3) ^c	Precision ^d (%)	Accuracy ^e (%)
NIST 1575a	Cs ^a ($\mu\text{g kg}^{-1}$)	283 \pm 9.00	282 \pm 4.29	1.5	99.6
	K ^b (mg kg^{-1})	4170 \pm 136	3930 \pm 136	3.5	94.2
	Rb ^a (mg kg^{-1})	16.5 \pm 0.200	14.5 \pm 0.204	1.4	87.9

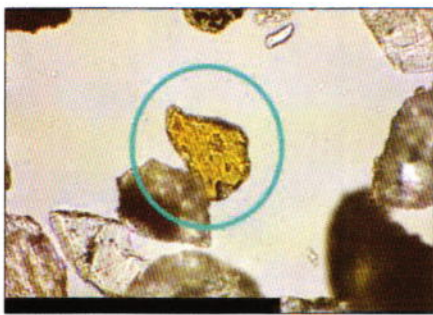
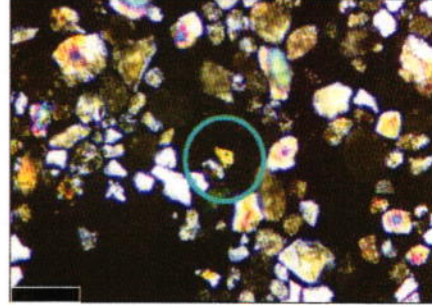
^a ICP-MS determination ^b AAS determination ^c Mean value \pm SD ^d The coefficient of variation ^e Measured value divided by the certified value

(a) Normal light



100 × magnification; bar = 100 μm

(b) Polarized light



400 × magnification; bar = 100 μm

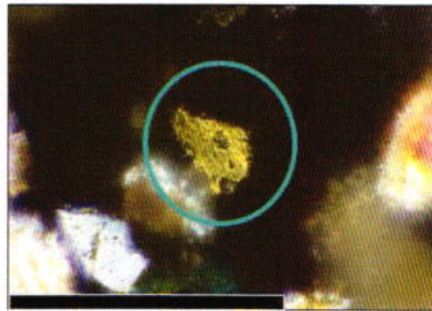


Fig. 1 Photographs of black mica (biotite, inside the circles) in the 25- to 250-μm fraction of the experimental field soil, observed using an MT9300 microscope (Meizi Techno Co., Ltd.) under (a) normal and (b) polarized light (100× magnification; bar = 100 μm).

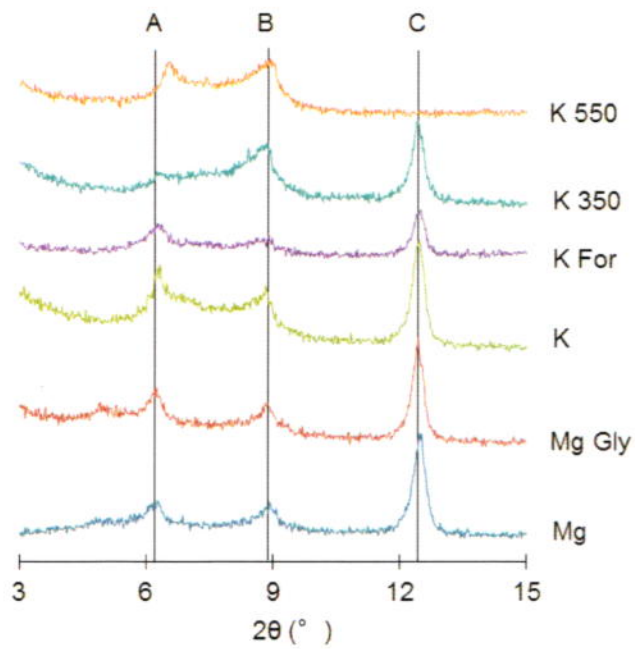
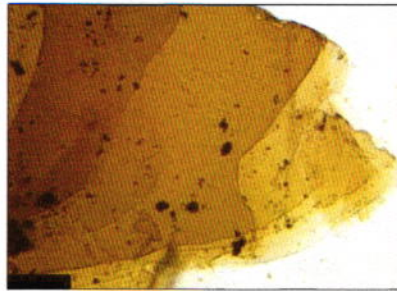


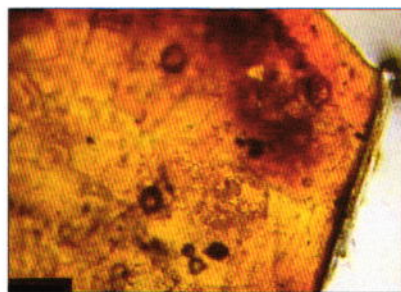
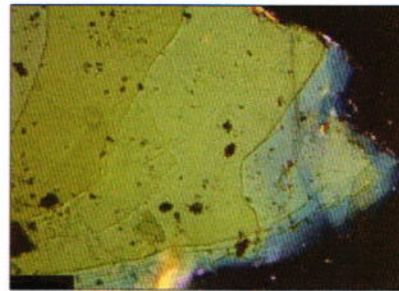
Fig. 2 X-ray diffraction results for the soil from the experimental field under paddy conditions. Peaks are for Cu $K\alpha$ radiation: A, $2\theta = 6.2^\circ$ (aluminum-vermiculite); B, $2\theta = 8.9^\circ$ (a mica-type clay); and C, $2\theta = 12.6^\circ$ (kaolinite). K, saturated by K; K 350, saturated by K and heated to 350°C ; K 550, saturated by K and heated to 550°C ; K For, saturated by K and treated with formamide; Mg, saturated by magnesium (Mg); Mg Gly, saturated by Mg and treated with glycerol.

Normal light

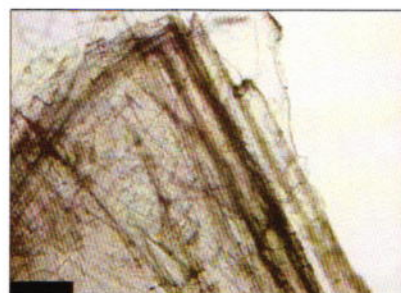
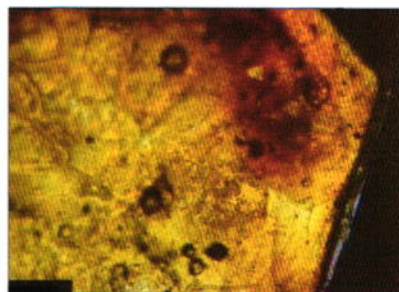


(A) Biotite

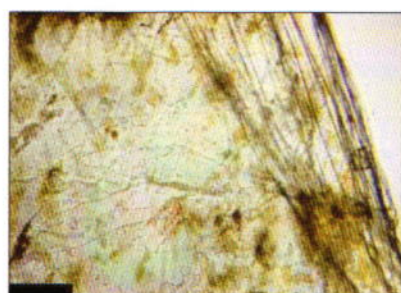
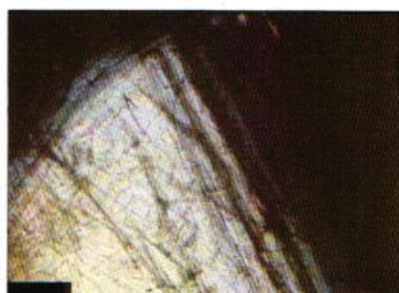
Polarized light



(B) Phlogopite



(C) Lepidotite



(D) Muscovite

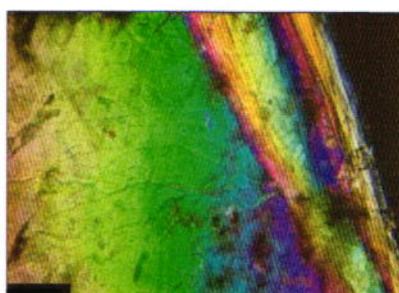


Fig. 3 Photographs of the four types of mica observed under (left) ordinary light and (right) polarized light using an MT9300 microscope (Meizi Techno Co., Ltd.) under (a) normal and (b) polarized light (100× magnification; bar = 100 μm).

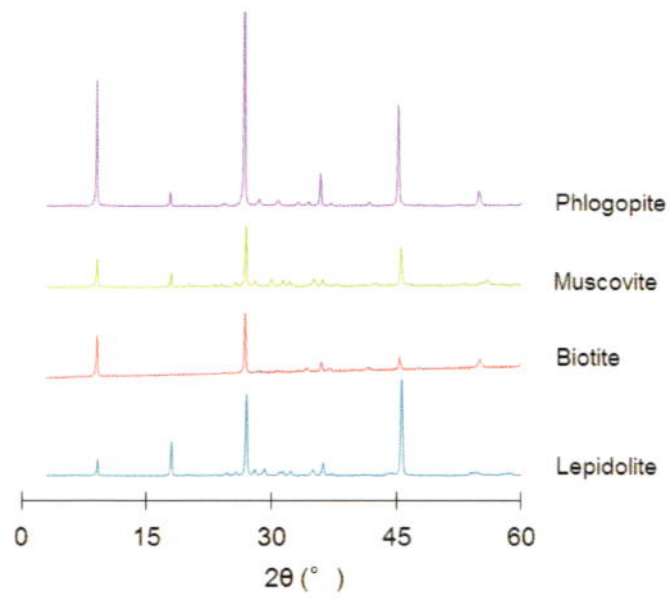


Fig. 4 The X-ray diffraction patterns of the four types of micas obtained by means of X-ray diffraction (MiniFlex, Rigaku). Peaks are for Cu $K\alpha$ radiation.

Chapter3. Varietal difference of Cd and Cs concentrations in brown rice among different japonica cultivars(*Oryza sativa*)

3.1 Introduction

Several heavy metals, including iron (Fe), zinc (Zn), manganese (Mn), and copper, are essential for plants and affect crop yield and quality (Ogo et al., 2013). On the other hand, of all the non-essential heavy metals, cadmium (Cd) is perhaps the metal which has attracted most attention in soil science and plant nutrition due to its potential toxicity to man and the relative mobility in the soil-plant system (McLAUGHLIN and Singh, 1999). Recently, many researchers studied varietal differences of Cd uptake for rice (*Oryza sativa*) so that the cultivars with high Cd uptake ability can be utilized for rehabilitation in soil and the cultivars with low Cd uptake ability can decrease dietary intake of Cd for human.

After the occurrence of The 2011 off the Pacific coast of Tohoku Earthquake, contamination of arsenic, a hazardous heavy metal, was reported from tsunami sediment near the affected area in Miyagi prefecture (Watanabe, 2012). There are arsenic-containing strata upstream of some major rivers in Miyagi prefecture, and there are many mines and deposits (Miyachi, 2013). The possibility that arsenic existing in the stratum was accumulated near the estuary due to long-time river activities, deposited as tsunami deposits on the coastal area, and the possibility that arsenic leaked out from the deposit site of waste ore due to landslides (Watanabe, 2012) have been pointed out. Mines and refining factories that once existed in the catchment area suggested that they have the risk of causing heavy metals to flow out and cause recontamination.

However, relationship of heavy metal with cesium in crops has not been clear at all. The objective of this study was to elucidate the variation of cadmium (Cd) and stable cesium (Cs) levels in grains of rice (*Oryza sativa*) among different japonica cultivars. To provide this knowledge, we carried out a field experiment with paddy and upland rice, and investigated the necessity of selecting suitable cultivars for Cs and Cd risk management by quantifying the concentration of hazardous heavy metal Cd in soil and brown rice and comparing it with Cs concentration in rice brown rice.

3.2 Materials and Method

3.2.1. Rice cultivars

Total 13 japonica cultivars of two ecotypes were used in the field experiment, including 5 temperate japonica cultivars and 8 tropical japonica cultivars. The temperate japonica cultivars were 'Koshihikari', 'Kinihikari', 'Yumemizuhō', 'Notohikari', and 'Nipponbare', which originated in Japan. The tropical japonica cultivars (local variety) were Kalenayan Gabreno, Hōmay, Karemon, RC66, Kaluis, Sarokot, Kalenayan Labong, and Basilanon, which originated in the Philippines. Rice seeds were submerged in a water bath for about 48 h at room temperature and germinated under moisture condition at 32°C for another 30 h. The germinated seeds were grown in a nursery paddy soil till 30-day old since plantation.

3.2.2 Experimental design

The field experiment was carried out at a rice paddy field of Ishikawa Prefectural University located in Nonoichi in Ishikawa Prefecture of north-central Japan. Figure X shows the abundance of total elements accounted by an element every soil horizon to the depth of 100 cm in the experimental field, which included SiO₂, Al₂O₃, Fe₂O₃, K₂O, Na₂O, MgO, CaO, TiO₂, P₂O₅, and MnO. Influence of paddy condition on the abundance of Fe₂O₃ and MnO were observed from this figure. MnO was more included in the horizon of 56-69 cm and Fe₂O₃ was more abundant in that of 45-56 cm, because Mn²⁺ was easy to be resolved and migrate downward in comparison with Fe³⁺.

Half of the experimental paddy field has been cultivated under upland conditions for 8 years after switching this part of the field from paddy conditions to upland conditions. The other half of the field was maintained as paddy rice during this period. In this study, the field experiment with rice was carried out under both paddy and upland conditions. Each plot was 1 m × 1 m under paddy conditions and 0.3 m × 2 m under upland conditions. There were three replicates in each plot. Thus, we used 39 plots (39 m²) under paddy conditions and 27 plots (16.2 m²) under upland conditions, with the plots arranged at completely random in each experimental field. The Cd concentration in the soil ranged from 0.200 mg kg⁻¹ to 0.273 mg kg⁻¹ for paddy field and 0.206 mg kg⁻¹ to 0.304 mg kg⁻¹ for upland field. The Cs concentration in the soil ranged from 6.03 μg kg⁻¹ to 6.55 μg kg⁻¹ for paddy field and 6.59 μg kg⁻¹ to 7.29 μg kg⁻¹ for upland field.

Fertilizer management followed conventional practices for the study area, with 30 kg ha⁻¹ for N (quick-release nitrate), 75 kg ha⁻¹ for P, and 48 kg ha⁻¹ for K as basal fertilizer, and 40 kg ha⁻¹ for N (slow-release nitrate), 12 kg ha⁻¹ for P, and 20 kg ha⁻¹

for K as top-dressing at the heading stage. The growing period of the cultivars was 156 d. During the period, the field under paddy condition was constantly submerged and the field under upland condition was watered by spiking cans when the soil was drying.

The aboveground parts of the rice plants were harvested and then threshed to retrieve the grains. The rice husk was removed to obtain samples of brown rice. These samples were dried at 70 °C for 48 hours in a forced-air oven. The brown rice samples were then ground with the grinder (MM301, Verder Scientific Co., Ltd, Tokyo, Japan) and stored in glass screw-top bottles.

3.2.3 Cd and Cs determination in brown rice

To determine the Cs, K and Rb concentrations in brown rice, we placed 0.5 g of the brown rice samples in a 50-mL conical beaker, and then added 6 mL of 13.1 mol L⁻¹ nitric acid. The mixture was then heated and dissolved at 100 °C on a hot plate for 1 hour. The resulting solution was then filled with extra pure water to 50 mL and filtered through a 0.45-µm membrane filter. Cs and Cb concentrations in the solution were determined by means of ICP-MS.

3.3. Results and discussion

3.3.1 varietal variations of Cs uptake and Cd uptake by rice in paddy field

The Cd concentration of brown rice for 13 cultivars ranged from 0.145 to 0.781 mg kg⁻¹ with a median of 0.395 mg kg⁻¹. The Cs concentration ranged from 7.49 to 12.2 µg kg⁻¹ with a median value of 9.48 µg kg⁻¹. The variability coefficients of Cd and Cs concentrations in brown rice for 13 rice cultivars were 48.5% and 14.7%, respectively. Apparently, there was much higher variability with Cd than Cs among 13 cultivars. This indicated that Cd concentration in brown rice for the japonica cultivars showed wide variation, but the Cs concentration in brown rice exhibited narrow variation. Figure 2 shows Cd and Cs concentrations in brown rice for 13 rice cultivars under paddy conditions. The Cd and Cs concentrations in the brown rice clearly formed different patterns. These results suggest that Cd and Cs follow different paths from soil to brown rice. The uptake of mineral elements is mediated by various transporters belonging to different transporter families [4]. Cs is taken into plants through K transporter. After absorption by roots, Cs is loaded to the xylem to reach the aerial portions of plants; this is followed by phloem transport to reach the grains (Fujiwara 2013). In the case of K, the loading of K is mediated by SKOR; however, its involvement in Cs transport has not been demonstrated. Nobori et al. (2014) suggested that (1) Cs is transported from roots

to leaves but can be remobilized via the phloem to the grain and (2) Cs is transported from roots to the aboveground parts via the xylem, and xylem-to-phloem transfer carries Cs into the brown rice without passing through the leaves. This, in turn, suggests that the estimation of both Cs and Cd concentration in rice grain is demanded to utilize high uptake rice for rehabilitation and low uptake rice for food with respect to Cs, because the high Cd and low Cs uptake rice or the low Cd and high Cs rice can exist.

3.3.2 Absorption capacity of Cs and Cd in 13 rice varieties

Cs in brown rice showed narrow concentration range, difference between varieties was small, Cd in brown rice showed wide concentration range of low to high concentration, showing a large difference between varieties.

The mean value of Cs transition coefficient was 2.17×10^{-3} [range: 1.71×10^{-3} (Kaluis) - 2.78×10^{-3} (Karemon)] in paddy field cultivation. The average value of radioactive Cs concentration in brown rice which was calculated assuming the radioactive Cs concentration in soil to be 5000 Bq kg^{-1} is $10.9 \text{ Bq kg}^{-1} \text{ DW}$ (range: $8.53 - 13.9 \text{ Bq kg}^{-1} \text{ DW}$) in paddy cultivation. It was. Radioactive Cs concentration in brown rice calculated for $114 \text{ Bq kg}^{-1} \text{ DW}$ ($100 \text{ Bq kg}^{-1} \text{ FW}$), which is the new reference value of radioactive Cs that took effect on April 1, 2012, is 10 minutes of the reference value. Since the radioactive Cs concentration in the brown rice which was calculated assuming that it was grown in contaminated soil was about 1/10 of the reference value, 13 varieties of paddy used in this study are low absorbable cultivar which hardly accumulates Cs in brown rice. It was positioned as.

Considering the standard deviation in 13 varieties of paddy rice, three varieties whose Cd concentration in brown rice in paddy field cultivation exceeds $454 \mu\text{g kg}^{-1} \text{ DW}$ ($400 \mu\text{g kg}^{-1} \text{ FW}$) which is the standard value based on the Food Sanitation Law Cd high absorption variety. Considering the standard deviation, the Cd concentration in the brown rice of RC 66, which may exceed the reference value, is considered to be a medium absorption variety and the one showing a significant difference is set as the low absorption type. The two low-absorbent varieties were classified as Yume Mizuho and Noto Hikari. It was revealed that 13 types of paddy rice had low absorbance varieties with Cd high absorption variety and Cd concentration in brown rice below $100 \mu\text{g kg}^{-1} \text{ DW}$.

It is clarified that Cd high absorbance varieties exist in Cs low absorption variety to brown rice, and there is a need to establish a new variety selection method taking account of Cd accumulation in brown rice for Cs risk management. Have been shown. In

addition, among the 13 varieties of paddy rice used in this study, the lowest Cs and Cd risk to human beings was "Noto Hikari" and "Yume Mizuho" which had little accumulation of Cs and Cd in brown rice, so Cs and Encourage cultivation as low absorption rice of Cd.

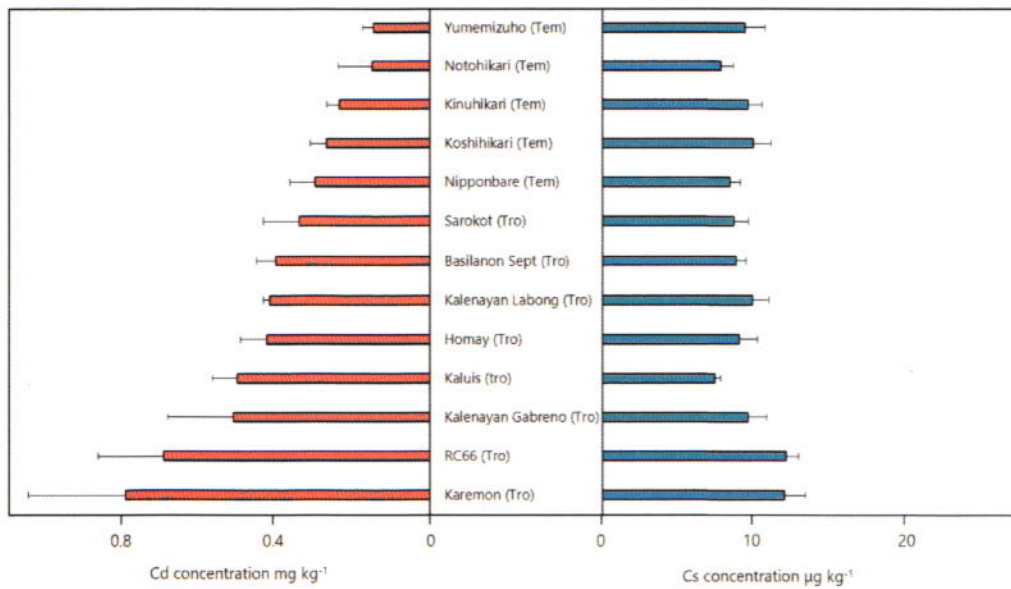


Fig.5 Cs and Cd concentrations in brown rice among 13 rice cultivars

Chapter4. General discussion

4.1 The mechanisms of Cs uptake by rice from soil under upland and paddy conditions.

Based on the results of the Cs, K, and Rb concentrations in the soil, mica, brown rice, and certified reference materials that we obtained by means of ICP-MS and AAS, we have the following conclusions. The soils contained much lower levels of Cs, K, and Rb than existed in the mica minerals. The mica minerals can potentially supply large quantities of K, Rb, and Cs to a soil that contains these minerals. The reason for a lack of clarity in the relationships among Cs, K, and Rb concentrations in rice tissues results from differences in their translocation and subsequent distribution in the plant, which may result from differences among growth stages and cultivars. Land use (here, paddy vs. upland conditions) strongly affected Cs, K, and Rb concentrations in the soil and their subsequent accumulation in rice plants. Differences in ion concentrations in the soil solution between the two conditions may have affected (increased) Cs and Rb uptake by roots more strongly than ion diffusion. In contrast, ion diffusion more strongly affected (increased) K uptake by roots. From the above results, Cs behaves more like Rb than K in soil - paddy rice system and concluded that the change in moisture state in soil is greatly related to Cs absorption.

In future research, details of Cs, K, and Rb uptake by the rice plants should be studied, perhaps by monitoring changes in the distribution of each element within the rice plants as they mature, to provide additional insights into uptake of these elements under different field conditions. This information could be enhanced by laboratory tests to compare uptake by each cultivar when uptake is limited by ionic diffusion versus ionic concentrations.

4.2 A study on a new variety selection method for paddy rice considering Cs and Cd risk management

The brown rice of the japonica cultivars exhibited wide variation of Cd concentration in low and high levels, and showed narrow variation of Cs concentration in paddy field. This suggests that some rice cultivars for less absorbing Cs can highly concentrate Cd in brown rice.

For the ^{137}Cs deposited on the soil by atmospheric nuclear test conducted in the 1950 - 1960 's, the geometric mean value of the Cs transition coefficient obtained from the measurement results of soils and brown rice collected from various parts of Japan after several decades since deposition was 4.7×10^{-3} (range: 0.57×10^{-3} to 33×10^{-3})

(Tsukada et al., 2011). The Cs transition coefficient in our field experiments was the same value as the average value in this report. The average value of the radioactive Cs concentration in brown rice which was calculated assuming the concentration of radioactive Cs in the soil at 5000 Bq kg⁻¹ was 10.9 Bq kg⁻¹ DW in paddy cultivation. Radioactive Cs concentration in brown rice calculated for 114 Bq kg⁻¹ DW (100 Bq kg⁻¹ FW), which is the new reference value of radioactive Cs that took effect on April 1, 2012, is 10 minutes of the reference value. Based on this calculations, 13 kinds of paddy rice used in this study is a low absorbance variety hard to accumulate Cs in brown rice. It was positioned. For 13 varieties of paddy rice, even in customary cultivation, the high absorbance variety exceeding 400 µg kg⁻¹ FW (454 µg kg⁻¹ DW) which is the standards based on the Food Sanitation Law and the Cd concentration in brown rice falls below 100 µg kg⁻¹ DW. It was revealed that low absorption variety existed.

It is clarified that Cd high absorbance varieties exist in Cs low absorption variety to brown rice, and there is a need to establish a new variety selection method taking account of Cd accumulation in brown rice for Cs risk management. It was shown. In addition, among the 13 varieties of paddy rice used in this study, the lowest Cs and Cd risk to human beings was "Noto Hikari" and "Yume Mizuho" which had little accumulation of Cs and Cd in brown rice, so Cs and Encourage cultivation as low absorption rice of Cd.

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