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Radiocesium sorption in relation to clay mineralogy of paddy soils in Fukushima, Japan

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HIGHLIGHTS

- RIP was measured for 97 paddy soils from Fukushima to assess ^{137}Cs retention ability.
- The dominant clay mineral was smectite, but this did not control RIP.
- RIP was positively correlated with native K content.
- Micaceous minerals were found to control the ^{137}Cs retention ability of the soil.

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ABSTRACT

Relationships between Radiocesium Interception Potential (RIP) and mineralogical characteristics of the clay fraction isolated from 97 paddy soils (Hama-dori, $n = 25$; Naka-dori, $n = 36$; Aizu, $n = 36$) in Fukushima Prefecture, Japan were investigated to clarify the mineralogical factors controlling the ^{137}Cs retention ability of soils (half-life 30.1 y). Of all the fission products released by the Fukushima accident, ^{137}Cs is the most important long-term contributor to the environmental contamination. The RIP, a quantitative index of the ^{137}Cs retention ability, was determined for the soil clays. The composition of clay minerals in the soil clays was estimated from peak areas obtained using X-ray diffraction (XRD) analyses. The predominant clay mineral was smectite in soils from Hama-dori and Aizu, while this was variable for those from Naka-dori. Native K content of the soil clays was found to be an indicator of the amount of micaceous minerals. The average RIP for the 97 soil clays was 7.8 mol kg^{-1}, and ranged from 2.4 mol kg^{-1} to 19.4 mol kg^{-1}. The RIP was significantly and positively correlated with native K content for each of the geographical regions, Hama-dori ($r = 0.76$, $p < 0.001$), Naka-dori ($r = 0.43$, $p < 0.05$), and Aizu ($r = 0.76$, $P < 0.001$), while it was not related to the relative abundance of smectite. The linear relationship between RIP and native K content not only indicate a large contribution of micaceous minerals to the ^{137}Cs retention ability of the soil clays, but also could be used to predict the ^{137}Cs retention ability of soil clays for other paddy fields in Fukushima and other areas.

1. Introduction

The accident at the Fukushima Daiichi Nuclear Power Plant (NPP) in March 2011 has turned attention to the fate of radionuclides in terrestrial environments. Of all the fission products released by the NPP accident, ^{137}Cs is the most important long-term contributor to the environmental contamination because of its high release rate, estimated at 1.3×10^{16} Bq (Chino et al., 2011), and longer half-life (30.1 y) than ^{131}I (8 d) and ^{134}Cs (2 y). Fukushima prefecture was highly contaminated, especially to the northwest of the NPP, where ^{137}Cs concentrations at 0 to 5 cm soil surface were above 1000 Bq kg^{-1} (Yasunari et al., 2011). Understanding the fate of ^{137}Cs in soil is particularly important for establishing proper strategies to manage the farmland contaminated by ^{137}Cs. Paddy fields are a primary target to investigate, since rice is the main component of the diet in Japan.

In soils, ^{137}Cs is strongly adsorbed on 2:1 phyllosilicates (Sawhney, 1972) whereas it is weakly adsorbed in an exchangeable state on other soil constituents (Rigol et al., 2002). Basal oxygen surfaces bounding the structural layers of expansible 2:1 phyllosilicates, if negatively charged, can form strong inner-sphere complexes with monovalent cations with low hydration energy, such as K^+, NH_4^+, Rb^+, and Cs^+ (Sposito, 1999). Because of its lowest hydration energy, Cs^+ is adsorbed onto the basal oxygen surfaces with the highest selectivity among these four ions. Previous studies have shown that micaceous minerals adsorb Cs^+ with

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much higher selectivity than expansible 2:1 phyllosilicates, such as smectite (Sawhney, 1972; Staunton and Roubaud, 1997; Zachara et al., 2002). Micaceous minerals, as this term is often used arbitrarily, are 2:1 phyllosilicates having 1.0 nm basal spacing. These include illite and muscovite and remnants of these minerals that are mostly vermiculite or hydroxy-interlayered vermiculite. Interlayer sites at the weathering front of micaceous minerals, termed as frayed edge sites (FES), are not accessible by hydrated cations with large effective ionic radii, but are accessible by easily dehydrated cations such as Cs^+ (Zachara et al., 2002). Once Cs^+ is adsorbed on FES, it is hardly exchanged by the common base cations (Brouwer et al., 1983). Because of the selective adsorption of Cs^+ on FES, ^{137}Cs would be concentrated on micaceous minerals in natural environments. This has been shown by X-ray diffraction (XRD) analysis, and ^{137}Cs activity measurement of finely fractionated ^{137}Cs-contaminated river sediments (Francis and Brinkley, 1976), and suggested by autoradiography of mica flakes fractionated from sediments in a ^{137}Cs-contaminated vadose zone (McKinley et al., 2001). However, few studies have quantitatively related the ^{137}Cs retention ability to the amount of micaceous minerals in soils (cf. Nakao et al., 2009a, 2012). In some cases, the ^{137}Cs retention ability of soils has been found to be associated with the amount of vermiculitic clay minerals (i.e. Maes et al., 1999a,b; Delvaux et al., 2000).

An extensive survey of the mineralogical composition of paddy soils in Fukushima (Sano et al., 2010) found that smectites were the most abundant clay minerals, while micaceous minerals were relatively minor. Although smectites adsorb Cs^+ with lower selectivity than micaceous minerals (Maes et al., 1985; Staunton and Roubaud, 1997), their adsorption selectivity for Cs^+ is larger than that of the other soil materials (e.g. kaolinite, silicate minerals and aluminum oxides, and organic matter), particularly if smectite has a higher charge per half unit cell (Degryse et al., 2004). Since adsorption depends on the number of adsorptive sites as well as on their selectivity, the amount of smectites may control the mobility of ^{137}Cs in paddy soils in Fukushima. However, the relationship between the ^{137}Cs retention ability and clay mineralogy is not clear for paddy soils in Fukushima because of the lack of analytical data.

The objectives of this study were to determine the ^{137}Cs retention ability of soil clays in paddy soils in Fukushima by measuring the Radiocesium Interception Potential (RIP; Wauters et al., 1996), and to clarify the mineralogical factors controlling variances in the RIP values in this region. Our research hypothesis was that the ^{137}Cs retention ability of soil clays is largely controlled by the amount of micaceous minerals even though they are not dominant clay minerals. To elucidate the relationship between RIP and clay mineralogy, we used soil clays fractionated from soils after decomposing organic matter and destroying aggregates rather than soil samples for the determination of the RIP values. These treatments were to avoid possible under estimation of the ^{137}Cs retention ability of clay minerals owing to organic matter coatings on clay surfaces (Dumat et al., 1997) or to soil aggregation. This information will be useful to those growing crops on soils impacted by the Fukushima disaster.

2. Materials and methods

2.1. Soil samples

Lowland areas in Fukushima Prefecture are divided from east to west into three geographical regions, namely Hama-dori, Naka-dori, and Aizu (Fig. 1), by the Abukuma and Ou mountain ranges, which run from north to south. Basement rocks are mainly Tertiary sandstone or mudstones with tuffs in the Hama-dori region, granite, Tertiary sandstone or mudstones with tuffs and andesitic lavas in the Naka-dori, and Tertiary sandstone or mudstones with tuffs and andesitic lavas in the Aizu regions. Most of the paddy soils in these regions are classified as Fluvisols or Gleysols (IUSS Working Group WRB, 2007). Soils were collected from paddy fields distributed in the respective regions, with 25 sites in Hama-dori, 36 sites in Naka-dori, and 36 sites in Aizu, and then air dried. As they were collected before March 11, 2011 for the Soil Conservation Measures Project by the Fukushima Agricultural Technology Centre, they were not contaminated by the ^{137}Cs fallout from the NPP accident. Hence, sample preparation and most of the experiments described below were carried out under ordinary laboratory conditions (i.e. outside of a radioisotope center).

2.2. X-ray diffraction analysis

Soil clays (<2.0 μm) were prepared from the 97 soil samples. After decomposing the soil organic matter with 10% H_2O_2 solution, the clay fraction was dispersed by adjusting pH of the suspended solution from 10 to 11 by adding 1 mol L^{-1} NaOH or from pH 3.5 to 4.0 by adding 1 mol L^{-1} HCl. Because some soils containing non-crystalline minerals were not dispersed at alkaline pH, they were dispersed at pH 3.5 to 4.0 after renewing supernatant solution several times. The clay content was determined by extracting 10 mL of the dispersed clay suspension by the pipet method, and then the rest of the clay suspension was collected by siphoning. The clay suspension was stored until use after pH had been adjusted to 5 to 6.

The clay minerals in the soil clays were identified by XRD analysis (MiniFlex, Rigaku, Japan) with Ni-filtered Cu K_α radiation produced at 30 kV and 15 mA. Free iron oxides were removed by dithionite–citrate–bicarbonate (DCB) method (Mehra and Jackson, 1960) to reduce background emission of X-ray fluorescence from Fe atom. The X-ray diffraction patterns were obtained from the clays oriented on glass slides by sedimentation after a fraction of the clay suspension was saturated with either Mg^{2+} or K^+. Two different slides, one with Mg-saturated clay and one with K-saturated clay, were dried at 25 °C for each of the soil clay with no replication. The Mg-saturated clay was glycerol-solvated on the slide after the XRD pattern had been obtained. The K-saturated clay was heated at 550 °C on the slide after the XRD pattern had been obtained. The slides were step-scanned from 2° to 15° (2θ) in steps of 0.02° at a scan speed of 2° min^{-1}. The software package JADE (Materials Data Inc., Livermore, CA, USA) was used for spectrum smoothing, background subtraction, peak separation, and peak area measurement. The relative abundances of the clay minerals were estimated from their respective peak areas by calibrating the relative peak intensity of clay minerals (Egashira et al., 1995). We classified the soil clays into 8 groups on the basis of the relative abundances of clay minerals. Soil clays showing no clear diffraction peak were classified as amorphous. Soil clays having >50% smectite, vermiculite, micaceous minerals, chlorite, or kaolinite were classified respectively as smectitic, vermiculitic, micaceous, chloritic, or kaolinitic. Soil clays with no one clay mineral type predominant were classified as semi-smectitic if smectite was >25% and otherwise were classified as mixed.

2.3. Radiocesium Interception Potential (RIP)

Radiocesium Interception Potential is defined (Cremers et al., 1988; Wauters et al., 1996) as the product of the limiting value of the Cs to K selectivity coefficient at frayed edge sites (FES) as Cs loading approaches zero, $K_c(Z_{Cs} \rightarrow 0)$, and the specific FES content of the solid material, n_{FES}/m_s, where n_{FES} stands for the FES content and m_s stands for the mass of dry soil. This product is calculated from the solid/liquid distribution coefficient for carrier-free ^{137}Cs in a specific K^+–Ca^{2+} ionic background (K_D^{Cs}) and the K concentration in solution (c_K).

$$\mathrm{RIP} = K_c(Z_{Cs} \rightarrow 0) \cdot n_{FES}/m_s = K_D^{\;Cs} \cdot c_K. \tag{1}$$

As $K_c(Z_{Cs} \rightarrow 0)$ is assumed to be a constant, $K_D^{Cs} \cdot c_K$ is regarded as being proportional to the FES content of the soil.

To evaluate the RIP, soil clays (<2.0 μm) were separated from the soils after organic matter had been decomposed with 10% H_2O_2 solution