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Physical properties, structure, and shape of radioactive Cs from the Fukushima Daiichi Nuclear Power Plant accident derived from soil, bamboo and shiitake mushroom measurements☆

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ABSTRACT

We conducted an elution experiment with contaminated soils using various aqueous reagent solutions and autoradiography measurements of contaminated bamboo shoots and shiitake mushrooms to determine the physical and chemical characteristics of radioactive Cs from the Fukushima Daiichi Nuclear Power Plant accident. Based on our study results and data in the literature, we conclude that the active Cs emitted by the accident fell to the ground as granular non-ionic materials. Therefore, they were not adsorbed or trapped by minerals in the soil, but instead physically adhere to the rough surfaces of the soil mineral particles. Granular Cs* can be transferred among media, such as soils and plants. The physical properties and dynamic behavior of the granular Cs* is expected to be helpful in considering methods for decontamination of soil, litter, and other media.

1. Introduction

Discharge of radioactive Cs (^{134}Cs and ^{137}Cs, termed Cs*) from the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident triggered by the earthquake and tsunami on 11 March 2011 contaminated a wide area of northeastern Japan (Kinoshita et al., 2011; Yasunari et al., 2011; Yoshida and Takahashi, 2012; Ohkura et al., 2012). Because the Cs* has been found to be non-water-soluble, it has been very difficult to decontaminate contaminated areas (Ohnuki and Kozai, 2013; Kozai et al., 2012). To elucidate the dynamics of transfer of Cs* between soil and flora as well as to ensure that uncontaminated food is protected against future contamination by Cs*, it is critical to establish the physical properties, structure, and shape of the Cs*. Modern techniques of structural analysis such as X-ray crystallography and fluorescent analysis could be used for these purposes, but require minimum picograms or nanograms of Cs* (about 10^{10} atoms of pure Cs*). Spatial concentrations, distributions, and depth profiles of Cs* have been measured to estimate doses (Kato et al., 2012; Tanaka et al., 2012). Those studies determined that the highest concentration of Cs* in the soil was $\sim 10^5$ Bq/kg (Tanaka et al., 2012), equivalent to $\sim 2.3 \times 10^{-10}$ mole/kg. Large-scale equipment is required to collect pure Cs* in the amount required for these experiments from contaminated soil. Even if the experimentally required amount of Cs* could be collected, the radiation level would be on the order of GBq–TBq, which would be challenging to handle in a typical laboratory. Therefore, they tend to use materials that include Cs, but which do not originate from the FDNPP accident. However, we must carefully consider whether these materials are appropriately representative.

Kaneyasu et al. collected Cs* in aerosols 47 days after the FDNPP accident at Tsukuba and measured the activity size distributions of

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^{134}Cs and ^{137}Cs in the aerosols (Kaneyasu et al., 2012). They found that the activity median aerodynamic diameters in the first sample (28 April–12 May) were 0.54 and 0.53 μm, respectively, and those in the second sample (12–26 May) were both 0.63 μm. The activity size distributions of these radiocesium samples were similar to the mass size distribution of non-sea-salt sulfate but not to that of soils (Kaneyasu et al., 2012). The results indicated that the Cs* emitted from the FDNPP accident may have been granular, which is consistent with autoradiography images of contaminated plant leaves using imaging plates (IP) (Sakamoto et al., 2012; Nakajima et al., 2012). Black spots were observed on the contaminated leaves; the origin of the black spots may have been granular radioactive materials such as Cs*. In particular, images showing black spots on the leaves of tall cedar trees indicated that the Cs* fell on the leaves directly from the sky. Therefore, the Cs* likely also fell to the ground as granular radioactive materials. Very recently, Adachi et al. have reported that the shape of the Cs* collected using aerosol sampler was found to be spherical by a scanning electron microscope (Adachi et al., 2013).

In contrast, it has been stated that the Cs* that fell on the ground was adsorbed and trapped in soil minerals, explaining why the Cs* was not soluble in water. There have been many previous reports that radioactive and/or non-radioactive Cs is adsorbed into soil minerals (Tamura and Jacobs, 1989; Sawhney, 1970; Comans et al., 1991; Westrich et al., 1995; Ejeckama and Sherriff, 2005; Saiers and Hornberger, 1999; Ohnuki, 1994; Singh and Tandon, 1977; Hasany and Chaudhary, 2005). However, these papers were published before the FDNPP accident, and according to the mechanism described for Cs adsorption into the soil minerals, the Cs should exist in an ionic or atomic state.

After the FDNPP accident, there were also several reports that the Cs* was adsorbed into the soil minerals (Kogure et al., 2012; Kozai et al., 2012; Ohnuki and Kozai, 2013). For example, Kogure et al. carried out x-ray diffraction and high-resolution transmission electron microscopy experiments of the Cs ions trapped in new vermiculite clay. They showed that “ionic Cs” was fixed in the centers of hexagonal rings in the upper and lower silicate tetrahedral sheets (Kogure et al., 2012). However, they used commercially available $CsNO_3$ for the Cs^+ ions in the samples (Kogure et al., 2012). It is not yet clear whether the Cs* emitted from the FDNPP was actually in an ionic state and thus, the experiment of Kogure et al. may not have simulated actual conditions. Ohnuki et al. studied the adsorption behavior of radioactive Cs by non-mica minerals, including kaolinite and 5 other minerals. For the Cs, they used commercially available radioactive and non-radioactive CsCl. This type of radioactive Cs and normal Cs are present in water in an ionic state and would be expected to be adsorbed into non-mica minerals (Ohnuki and Kozai, 2013). This experiment was also not intended to simulate the behavior of the Cs* emitted from the FDNPP accident. Kozai et al. examined the Cs* fallout on soils collected in Fukushima, Japan and characterized them with desorption experiments using appropriate reagent solutions (Kozai et al., 2012). They used contaminated soils containing Cs* emitted from the FDNPP accident, but analyzed all the obtained data assuming that the Cs* was adsorbed into the matrix of the soil minerals.

Because there are reports that the Cs* was in the form of an aerosol (Kaneyasu et al., 2012) and was observed as black spots in IP autography images (Sakamoto et al., 2012; Nakajima et al., 2012), additional experiments are required to determine whether the Cs* has been adsorbed into soil minerals. Based on the IP autoradiography of the leaves of tall trees (Sakamoto et al., 2012) and the activity size distributions of the aerosols (Kaneyasu et al., 2012), we may assume that granular Cs* fell onto the trees as well as on the ground. The physical and chemical characteristics of the Cs* need to be examined using soils contaminated with Cs* from the FDNPP accident and moreover, we must consider whether the Cs* is present inside or outside the soil minerals, because it has not yet been clarified whether granular Cs* can be adsorbed into soil minerals. Therefore, in this study, we characterized the desorption behavior of Cs* in soil from the FDNPP accident using various reagent solutions. In addition, we considered autoradiography results for soils, plants, and other materials to determine the dynamic behavior of Cs*.

2. Experimental

2.1. Water washing of soils contaminated by the FDNPP accident

Contaminated soils from the playground of a primary school in Fukushima prefecture were collected on 5 May 2012. The place of the primary school is indicated in the map as shown in Fig. 1. Twenty grams of soil were immersed in 30 ml water while stirring at 200 rpm for 3 h at 20 °C and filtered through a 0.5 μm mesh filter. The radioactivities of the soil residues and filtrates were measured by a Ge-semiconductor detector, (CANBERRA GC4020: Energy resolution at 1.33 MeV is smaller than 2.0 keV.) termed Ge-measurement below.

2.2. Washing of soils contaminated by the FDNPP accident with Cs^+ ion excess aqueous solution

After water washing, 20 g of the soils were immersed in 30 ml 0.1 M $CsNO_3$ aqueous solution while stirring at 200 rpm for 3 h at 20 °C and filtered through a 0.5 μm mesh filter. The radioactivities of the soil residues and filtrates were measured using Ge-measurement.

2.3. Washing of soils contaminated by the FDNPP accident with various reagent solutions

After water washing, 10 g of the soils were immersed in 30 ml of various aqueous solutions, including HCl (1 M), H_2SO_4 (1 M), CH_3COOH (1 M), $(NH_4)_2SO_4$ (1 M), NH_4Cl (1 M) while stirring at 200 rpm for 3 h at 20 °C and filtered through a 0.5 μm mesh filter. The radioactivities of the soil residues and filtrates were measured using Ge-measurement.

2.4. Autoradiography of contaminated soils, bamboo shoots, and shiitake mushrooms with imaging plates

The distributions of Cs* in soils, bamboo shoots, and shiitake mushrooms contaminated by the FDNPP accident were measured using imaging plates (IPs; BAS-SR 2040, 200 mm wide × 400 mm long). The IPs were inserted into 12 μm thick aluminum foil. The samples were placed on 12 μm thick aluminum foil and sandwiched by IPs. The samples and IPs were stored in a shielding house constructed of lead bricks, a 0.5 mm thick Cd sheet, and 200 mm thick water layer for shielding from environmental radiation (gamma rays and neutron beams). The environmental radiation background was reduced to 0.004 μSv/h from 0.103 μSv/h. IP readings were conducted with a Fuji Film BAS-2500, termed IP measurement.

Shiitake mushrooms were harvested at a cultivation field in Yokokawa, Takahagi about 84 km south of the FDNPP on 14 November 2012. Bamboo shoots were harvested from a bamboo forest in Nihonmatsu, about 30 km west of the FDNPP on 19 May 2012. The places of Yokokawa and Nihonmatsu are indicated in the map (Fig. 1). Although Yokokawa locates at 80 km south from FDNPP, the deposition densities of total of cesium −134 & 137 at

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