Initial Interaction of ^{137}Cs with Soils

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Abstract

It is critical to understand the physicochemical behaviour of Cs in soil in order to progress the decontamination of soils which were contaminated by nuclear power plant accident and to improve the reliability of safety assessment of used nuclear fuel disposal. In this paper, the initial interactions of ^{137}Cs with soils, which were sampled in Fukushima 38 days after Fukushima Accident, were investigated with sequential extraction method. It was found that there were fast and slow processes of fixation of ^{137}Cs in clay minerals and that the organic substances might play an important role on kinetics of ^{137}Cs in soils.

1. Introduction

Radionuclides were released into the environment by Fukushima Daiichi Nuclear Power Plant Accident which took place on March 11, 2011. Total amount of ^{137}Cs released into the atmosphere was estimated at approximately 1.3 x 10^{16} Bq [1]. ^{137}Cs released into the atmosphere by nuclear power plant accident is considered to transport as a form of CsI molecule or as aerosols with which ^{137}Cs associates [2] and to stay in the atmosphere at the retention time of approximately 10 days [3]. ^{137}Cs is considered to adhere on the surfaces of trees and leaves, and consequently soil environment becomes a dominant reservoir in two to three years [4]. Previous works elucidated that most of ^{137}Cs released by Chernobyl Accident are retained within several centimeters of the surface soil layer [5], that average transport rates in soils are 0.2 – 3 cm in depth/year [6], and that the transport rate decreases with time [7]. On the other hand, the research on transfer of ^{137}Cs to animals and plants show that absorption from soils to plants is relatively small but the bioavailability becomes larger in organic substance-rich soils [8]. In order to understand the transport behaviour, interactions and bioavailability of ^{137}Cs in soils, it is inevitable to understand which components in soils ^{137}Cs prefers to interact with and what type of mechanism dominate the interaction of ^{137}Cs.

Furthermore, ^{135}Cs is one of key radionuclides which will dominate the long-term annual radiation dose rate in performance assessment and safety assessment of geological disposal of high-level radioactive waste and used nuclear fuel. Therefore, the understanding on physicochemical behaviour of Cs in geosphere and biosphere is an essential challenge for improving the reliability and credibility of the performance assessment and safety assessment.

Previous studies using sequential extraction method suggested that most of ^{137}Cs are trapped by clay minerals in soils [5, 9] and that the fractionation of uptake of ^{137}Cs in clay minerals decreases with increasing the content of organic substances in soils [10]. However, there are only few available studies on how ^{137}Cs interacts and migrates in soils just after its fallout or sedimentation. In order to draw the picture of whole physical and chemical behaviour of Cs in environment, it is necessary to understand the initial interaction of Cs in environment.

The purpose of this paper is to identify the soil components which initially interact with ^{137}Cs and to study the initial interactions. In this paper, soils sampled from an east area of Fukushima Prefecture were used.

2. Experimental

2.1 Soils

Soil samples were collected with a soil sampler (diameter 5 cm, height 5 cm) in an east area of Fukushima Prefecture on April 20, 2011. Soil sampling locations were as follows:

- rice field: 2 points within 2 km from Fukushima Daiichi Nuclear Power Plant (NPP)
  1 point within 20 km from NPP
  2 points within 30 km from NPP
- forest area: 1 point within 30 km from NPP
  1 point within 40 km from NPP
- cultivated field: 2 points within 20 km from NPP
- Minamisoma city: 1point within 20 km from NPP where sea bottom soil was accumulated by Tsunami
- Soma city: 1 point of urban soil (outside of 40 km area)

2.2 Element Analysis on C, N, H and S

After each soil sample was ground with an agate mortar, the contents of carbon, nitrogen, hydrogen and sulphur in 10 mg soil sample were measured by pyrolysis gas chromatography (Elementar vario MICRO cube).

2.3 Sequential Extraction Method

Ho et al [9] studied the interaction of Cs with soils by sequential extraction method. In this paper, referring their method and considering EPA Method 3050B [11], the following sequential extraction procedure was proposed. The liquid phase was separated from the solid phase by centrifugation (22,860G x 1 hour). The each extraction step is as follows.

Step (1): Water soluble fraction
In this step, ^{137}Cs which could be dissolved in pure water was extracted. After pure water was added to each dry soil sample and the soil/water mixture was stirred for 24 hours at room temperature, the liquid phase was separated from solid phase. The liquid was poured into a storage tube. The solid was washed with pure water, again, and then the liquid was separated and transferred to the same storage tube. The liquid stored in this storage tube is defined as Fraction (1).
Step (2): Ion-exchangeable fraction

In this step, ^{137}Cs which was sorbed on soil by ion-exchange mechanism was extracted. 1 mol/dm^3 ammonium acetate solution (pH 7.0) was added to the solid separated in Step (1). The solid/liquid mixture was stirred for 24 hours. After the solid/liquid separation by centrifugation and the washing of solid as the same procedure as Step (1), the liquid stored in the tube was prepared (Fraction (2)). 1 mol/dm^3 ammonium acetate solution (pH 7.0) was selected in this study, after Cs sorbed by ion-exchange mechanism was confirmed to be desorbed and the solid medium was checked not to be altered by ammonium acetate.

Step (3): Reductive dissolution fraction
In this step, ^{137}Cs that was fixed in the soil components which are reduced and dissolved such as amorphous iron oxide was extracted. 0.04 mol/dm^3 hydroxylammonium chloride - 25 % acetic acid solution (pH 2.0) was added to the solid separated in Step (2), and the mixture was stirred at 80 ± 5 ^{o}C for 24 hours. After the solid/liquid separation and washing, Fraction (3) was prepared.

Step (4) Oxidative decomposition fraction
In this step, ^{137}Cs that was fixed in the soil components which are oxidized and decomposed such as organic substance was extracted. 30 % hydrogen peroxide - nitric acid solution (pH 2.0) was added to the solid separated in Step (3), and the mixture was stirred at 80 ± 5 ^{o}C for 2 hours. After the solid/liquid separation and washing, 3.2 mol/dm^3 ammonium acetate - 20 % nitric acid solution was added to the solid, and the mixture was stirred at room temperature for 1 hour. All liquids after separation were stored in a storage tube (Fraction (4)). The separated solid was collected in a plastic tube and dried.

Step (5) Strong acid dissolution fraction
In this step, ^{137}Cs which was fixed in clay minerals was extracted. Approximately 0.5 g of the solid dried in Step (4) was sampled in a Teflon tube, 5mL pure water was added to the tube, 69 % nitric acid (10mL) was added to the tube, and the solid/liquid mixture was heated at 90 ± 5 ^{o}C. When the volume of liquid phase decreased, 5 mL nitric acid was newly added. The addition of nitric acid was repeated 6 times. Finally, the volume of liquid phase was reduced to approximately 5 mL and then the mixture was cooled. After cooled down, the mixture was poured into 100 mL pure water and the liquid was separated from the solid. The separated liquid was stored in a tube (Fraction (5)). The solid residue was washed with pure water, dried at 90 ^{o}C and stored in a plastic tube (Fraction (6)).

2.4 Preparation of Ion-Exchange Resin for Cs Adsorption

In order to measure the radioactivity of ^{137}Cs in Fractions, the ion-exchange resin for Cs adsorption was used. In this paper, the iron ferrocyanide - supported anion-exchange resin (AG1-X4, 100-200 mesh, chloride form) was prepared after substitution by Cu^{2+}, according to Tanihara's procedure [12]. In order to confirm the performance of the ion-exchange resin obtained, the resin (approximately 1 mL) was added to 10^{-5} mol/dm^3 CsCl solution (300 mL) at various pH , the mixture was stirred for 24 hours, the liquid was separated from the resin, and the Cs concentration in the liquid was measured with ICP-MS (Agilent 7500CX). For the performance confirmation, stable ^{133}Cs was used because ^{133}Cs in soil samples were also measured as mentioned in 2.5. Since the stable and reproducible recovery efficiency was obtained more than 18 house in the resin prepared in this study, the stirred time was decided at 24 hours.

2.5 Measurement of Cs Concentration

After pH in Fractions (1) - (4) were adjusted to pH 0.4 - 1 using 69 % nitric acid, the ion-exchange resin (approximately 1 mL) was added and the mixture was stirred for 24 hours. After the resin was separated by suction filtration and dried, ^{137}Cs radioactivity in the resin was measured by Ge detector. The concentration of ^{137}Cs in Fraction (5) was calculated from the difference of radioactivity among Fraction (4), solid separated in Step (4), and Fraction (6). ^{133}Cs concentration in soil was measured with ICP-MS after a portion was sampled from each Fraction and adequately diluted.

3. Results

3.1 Performance of Ion-Exchange Resin for Cs Absorption

It was found that more than 95 % of Cs were recovered by the ion-exchange resin in the pH range of 0.4 to 1.0. Hence, this ion-exchange resin was used to measure ^{137}Cs radioactivity in Fractions (1) - (4) in this pH range.

3.2 ^{137}Cs in Each Fraction

Figure 1(a) shows the ^{137}Cs distribution in fractions of the soil which was sampled from a rice field of Futaba town (within 2 km from NPP). Figure 2 illustrates the distribution of ^{137}Cs in the fractions of all soil samples. In Figure 2, error bar represents the standard deviation of ± 2.7 σ, and red circle represents the extremely higher or lower values. In many soil samples, the strong acid dissolution fraction (Fraction (5)) retained 50% or more ^{137}Cs, and followed by the residue (Fraction (6)) and ion-exchangeable fraction (Fraction (2)). This means that approximately 50 % of ^{137}Cs were trapped by clay minerals only

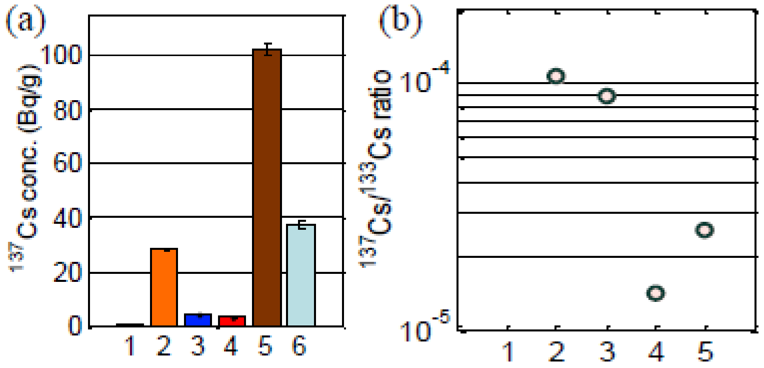

Figure 1 ^{137}Cs concentration (a) and ^{137}Cs/^{133}Cs ratio (b) in fractions of soil sampled from a rice field of Futaba town

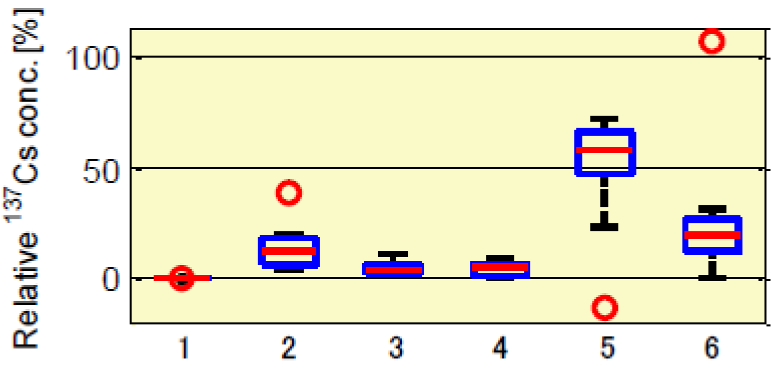

Figure 2 ^{137}Cs content in each fraction of all soil samples.
Error: ± 2.7 σ. Red circle represents extremely higher or lower values.

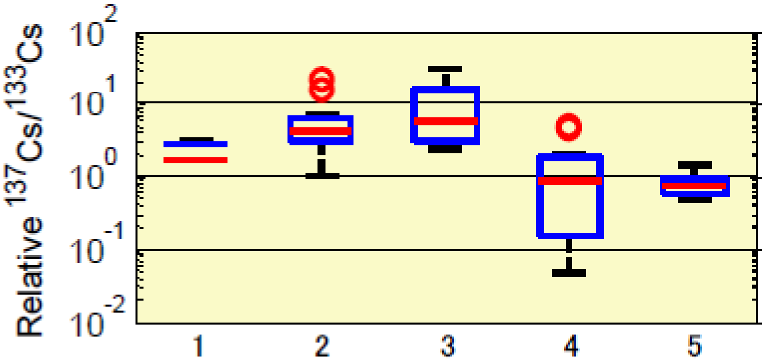

Figure 3 ^{137}Cs/^{133}Cs ratio in each fraction of all soil samples

38 days after the accident. On the other hand, only few ^{137}Cs was present in the water soluble fraction (Fraction (1)). Most ^{137}Cs in soil sampled from the forest (within 40 km) could not be extracted by the sequential extraction method and remained in the residue.

3.3 ^{137}Cs/^{133}Cs Ratio in Each Fraction

^{137}Cs/^{133}Cs ratio in a rice field of Futaba town is shown in Figure 1(b), and the ratios in all soil samples are shown in Figure 3. It was found that the ratio in the strong acid dissolution fraction (Fraction (5)) was smaller than the ratios in the ion-exchangeable fraction (Fraction (2)) and the reductive dissolution fraction (Fraction (3)) in all soil samples. Furthermore, the ratio in the oxidative decomposition fraction (Fraction (4)) was smaller than the ratios in the ion-exchangeable fraction and the reductive dissolution

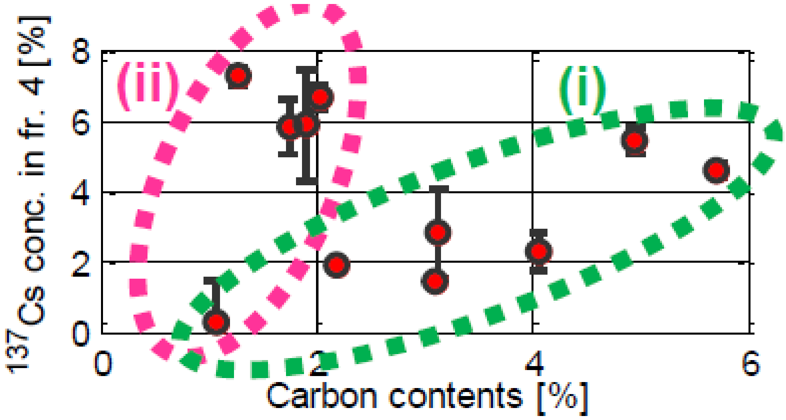

Figure 4 Correlation between ^{137}Cs content in oxidative decomposition fraction and carbon content in soil

fraction in many soil samples, and smaller than the ratio in the strong acid dissolution fraction in some samples.

3.4 Correlation with Carbon Content of Soil

Figure 4 shows the correlation between the carbon content and the ^{137}Cs concentration in oxidative decomposition fraction (Fraction (4)) in soil samples. This figure suggests there are 2 groups; one is that fixation of ^{137}Cs gradually increased with the carbon content (group (i)) and the other is that ^{137}Cs was fixed in the small carbon content (group (ii)).

4. Discussion

The experimental results of sequential extraction method indicated that more than half of ^{137}Cs in the soil was trapped by clay minerals in the short elapsed time and most ^{137}Cs could not be desorbed by water and ion exchangeable cation.

The distribution of ^{137}Cs/^{133}Cs ratio suggests a presence of sorption process of ^{137}Cs which is slowly transferred to clay minerals from other components with time. This may be consistent with the previous study [13] which proposed that Cs is sorbed on clay minerals by fast and slow processes. The smaller ^{137}Cs/^{133}Cs ratio in oxidative decomposition fraction suggests a slow sorption process to which the organic substances are related.

All soils, in which the ^{137}Cs/^{133}Cs ratio in the oxidative decomposition fraction was smaller than the ratio in the strong acid dissolution fraction, were classified into group (i), suggesting that the interaction with organic substances also consists of both the fast and the slow fixation processes, and that the difference in the interaction kinetics contributes to the presence of two groups (i) and (ii). However, there is a possibility that ^{137}Cs was dissolved out when the crystalline minerals in the soil were dissolved by oxidative decomposition, and hence the element analysis in extraction liquids will be required.

5. Conclusions

Sequential extraction method was applied to the soils sampled from an east area of Fukushima Prefecture, and the initial interactions of ^{137}Cs with the soils were studied. The following conclusions were drawn:

- It was found that most ^{137}Cs were trapped in clay minerals and the sequential extraction residue 38 days after NPP accident, followed by ion-exchangeable forms, and that only few ^{137}Cs could be desorbed by water.
- Since the ratios ^{137}Cs/^{133}Cs in strong acid dissolution fraction in sampling soils were smaller, the presence of slow sorption process in clay minerals was confirmed.
- It was suggested that the interaction of organic substances with Cs consisted of the fast and the slow fixation processes.

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