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Assessment of the measures for the extraction or fixation of radiocesium in soil

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ABSTRACT

Methods for the remediation of radioactive cesium contaminated soil and for controlling the transfer of ^{137}Cs to plants were assessed in reference to two abundant soil groups in Fukushima region, brown forest soil (BFS) and andosol. The hot acid treatment method, which is found to be effective on extracting substantial amount of Cs from BFS was not effective for andosol. For the remediation of acid treated soil, Komatsuna germination test was performed. Although no successful germination was observed with 100% acid washed soil, the productivity could be improved by lime treatment and mixing with the untreated soil. Targeting the soils like andosol, soils with moderate contamination, or the contaminated soil storage areas, Cs transfer suppression test was performed between 2011 and 2014. In the first planting of sunflower, high concentration of ^{137}Cs is transferred to the plant. It could be successfully suppressed by mixing zeolite or Prussian blue adsorbents onto the soil. Results with nano-Prussian blue mixed soils showed high suppression rate with lowest transfer factor in the first harvest and constantly minimum concentration of exchangeable ^{137}Cs in soil throughout the study.

1. Introduction

The quality of soil is directly related to the quality of life. Heavy metals or the radioactive elements pose deep threat especially on the agricultural land because of continuous risk of their transport to the plants and ultimately to the food chain. Soil remediation is a tough task as the process becomes specific with the type of soil. Moreover, the physicochemical characteristic of the soil plays a major role. In context of cesium (Cs), the major issue is with its long living isotope, ^{137}Cs. There have been numerous works on the Cs decontamination of soil. Peculiar fixation of Cs onto the clay minerals, its mobility in ground water and to the plants, the problem with the extraction, and the difficulty of reproducing the results with soil from different origins, etc. are studied.

Recent Fukushima Daiichi Nuclear Power Plant accident released approximately 1.8×10^{16} Bq ^{134}Cs and 1.5×10^{16} Bq ^{137}Cs contaminating thousands of square kilometers of land (Chino et al., 2011; IAEA, 2012; Stone, 2011). As ^{137}Cs, in particular, possesses strong gamma activity for several years, its existence in the surrounding is a threat (IAEA, 2006; Williams et al., 2004). Therefore, as an immediate relief, topsoil removal is considered. The task of scrubbing the surface soil is certainly difficult and more difficult is long term monitoring of the contaminated soil. According to a report, topsoil removal tested around Fukushima reduced as high as 80% Cs activity, while this process generated 300–400 t/ha waste soil (MAFF, 2011). As a consequence, piles of thousands of tons of removed soil are accumulated around the Tohoku and Kanto area of Japan. In order to find a sustainable solution to the issue of radioactive Cs contamination of soil, we have conducted experiments on the various possible measures. Extraction experiment was carried out targeting the highly contaminated soil groups. For brown forest type soil (BFS), which is the most abundant soil group in the Fukushima region, substantial concentration of Cs could be extracted by hot acid treatment. However, total removal was difficult to achieve (Parajuli et al., 2015, 2013).

In the present work, an assessment on various measures for the extraction of Cs from highly contaminated soil, remediation options of the washed soil, and the results of fixation of Cs using adsorbents in the areas with moderate contamination are discussed. Cs extraction from kuroboku soil (KBS), an andosol found in some areas of Fukushima region, was carried out for comparison using the method optimized for BFS. In addition, as a solution to the safe disposal of the acid washed soil, germination test was performed based on two options: mixing with untreated soil and lime remediation. For the soils with minimal contamination but still posing a threat of enrichment in the crops, Cs fixation study was carried out for total seven cultivations of sunflower throughout 2011 to 2014.

2. Experimental

2.1. Extraction of Cs from contaminated soil

Two kinds of soil samples collected from Koriyama city: brown forest soil (BFS) with 36.5 kBq/kg total Cs activity and andosol kuroboku (KBS) with 37.6 kBq/kg total Cs activity were studied for Cs extraction

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in the conditions which were found to be effective for BFS in our previous work (Parajuli et al., 2015, 2013). 1 mol/l HNO_3 solution was used as solvent. Taking 1:200 soil to solvent ratio (g/ml), extraction experiment was performed at 95 °C under reflux or pressurized heating at 200 °C using specially designed stainless steel reactor. The extract was separated using suction filtration through the 0.45 μm membrane filter. The extraction rate was evaluated based on the total concentration of ^{137}Cs and ^{134}Cs released to the solution phase. For this SEIKO EG&G Multichannel Analyzer with ORTEC GEM25P4-70 Germanium Semiconductor Detector (Ge-Detector) was used. Rigaku ZSX Primus II X-ray Fluorescence Spectrometer (XRF) and PANalytical model X'Pert PRO MPD X-ray Defractometer (XRD) were used for studying the soil properties before and after extraction.

2.2. Productivity test of acid washed soil

The possibility of reusing acid washed soil was studied by germination test of Komatsuna (*Brassica campestris* L.) seeds at various conditions. BFS and KBS soils were washed with 0.5 mol/l sulfuric acid at 95 °C at 1:10 ratio, for 1 h and then rinsed till the pH of wash water reached 3. The treated soils were used for a comparative seeding experiment. For each soil types, total five patterns were prepared: untreated soil as control, a mixture of 67% untreated soil and 33% acid washed soil, and acid washed soil only. The latter two were subdivided into lime conditioned and unconditioned specimens. All five sets of soils for KBS and BFS separately were filled in Petri disk in triplicates. Ten Komatsuna seeds per disk were planted and were monitored for the germination followed by cotyledon development. Average of the triplicates was used for discussion. In addition, soil pH, nitrogen and phosphorus content, soil cation exchange capacity (CEC), exchangeable potassium, etc. were measured using standard techniques.

2.3. Suppression of Cs transfer

The experiment was conducted inside a glass greenhouse in the Fukushima Agricultural Technology Centre (Koriyama, Fukushima). The experiment was started on 8 July, 2011. Sixteen 4 l wagon pots filled with 2.0 kg KBS were prepared and were divided into four groups. The first group of four pots was set as the control and was mixed with 500 ml tap water, each. The second group of four was mixed with 200 g (= 10 kg/m^2) of clinoptilolite (1–3 mm, distributed by Zeeklite Co., Yamagata, Japan) and 500 ml tap water. The third group of four was mixed with 2 g (= 100 g/m^2) of n-PB (Kanto Chemicals, Japan) and 500 ml tap water. The fourth group of four was mixed with 2 g (100 g/m^2) of PB dye — Milori Blue 905 (Dainichi Seika, Japan) and 500 ml tap water. The final ^{137}Cs concentration in the respective group in average for the dry soil was 8860 Bq/kg in the control soil, 8110 Bq/kg in the soil with zeolite, 8960 Bq/kg in n-PB mixed soil, 8940 Bq/kg in PB dye mixed soil. During the filling, all 16 pots were fertilized with magnesium lime (200 g/m^2) and ammonium sulfate (N 0.21 g/m^2). CDU (N 2 g/m^2) was added after confirming the germination in each pot.

Sunflower (*Helianthus annuus* L. cv. F1 Sun. Rich Orange sold by Takii & Co., Ltd.) cultivation was performed for total seven harvests. First seeding was performed on July 9, 2011. Two cultivations per year were performed between 2012 and 2014. Eight seeds per pot were seeded, which after germination were reduced to four seedlings per pot. The harvest was carried out at the time of sunflower blossoming by cutting 2 cm above the soil level.

The harvest was dried at 75 °C for 72 h and ground. The powder form was filled in U-8 container for ^{137}Cs measurement using Ge detector. After each harvest, the soil was removed from the pot and air dried for analyzing the concentration of ^{137}Cs. In this case also, U-8 container was used. The concentration of exchangeable ^{137}Cs was analyzed by mixing the air dried soil with 1 mol/l ammonium acetate at 1:10 soil to solution ratio and shaking for 1 h. The extracted amount was counted as the exchangeable concentration. Measurement time of ^{137}Cs using Ge-detector was 20–70 min for soil, 30–90 min for dried sunflower, and 50–1290 min for the ammonium acetate extract.

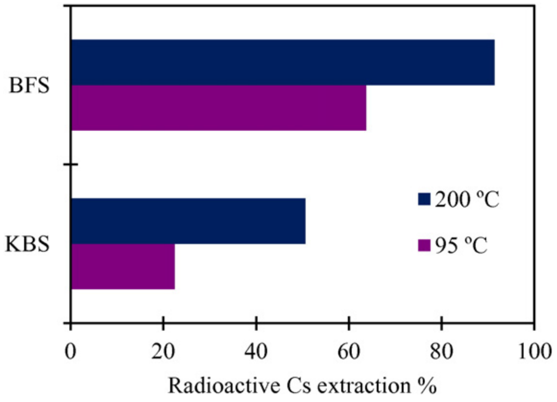

Fig. 1. Extraction of radioactive Cs from contaminated soil samples with 1 mol/l HNO_3 at different temperatures. 1:200 ratio, 3 h.

3. Result and discussion

3.1. Extraction of radioactive Cs

In our study on the extraction of Cs from brown forest type soil collected in Fukushima region showed the combined role of acid concentration, temperature, time, and the solvent volume (Parajuli et al., 2015). In the present study, the results were compared with another soil type KBS, an andosol group soil abundant in the same region. As shown in Fig. 1, the difference in the extraction rate is distinct between the two samples. Cs extraction from KBS is less promising. Heating under reflux for 1 h at 95 °C with 1 mol/l HNO_3 released over 50% Cs from BFS, but only around 20% was released from KBS. The results were similar with 1 mol/l H_2SO_4. Under pressurized heating at 200 °C BFS released over 91% Cs and about 50% Cs was extracted from KBS.

Particle distribution and composition of crystalline clay evaluated from semi-quantitative analysis of XRD patterns of BFS and KBS are given in Table 1. XRD patterns taken before and after treating with 1 mol/l HNO_3 at 200 °C are given in Fig. 2. BFS is sand rich while KBS contains a substantial portion of clay. Commonly known Cs adsorbing clay, vermiculite is found in both the samples. However, the proportion of mica is much higher in BFS. As per the XRD profiles, the major units of BFS are quartz, albite, and anorthite. Those in KBS are quartz, cristobalite, magnetite, and anorthite. The patterns of acid treated samples show sharper peaks, which is due to the dissolution of soil organics leading to the enrichment of insoluble matrices. Though the patterns for BFS are not significantly different, distinct difference is observed around 10, 29, and 60° of KBS. Past study supports the presence of vermiculite in

Table 1
Particle distribution and composition of crystalline clay evaluated from semi-quantitative analysis of XRD patterns.

Particle distribution (%)

	Sand (<2 mm)	Silt (<0.02 mm)	Clay (<0.002 mm)
BFS	86.4	9.6	4.7
KBS	44.3	31.0	22.5

Clay composition (based on semi-quantitative analysis of XRD patterns)

	Vr	Sm	HIV/HIS	Ch	Mi	Mi–Vr/Mi–	Kt	Crystalline part (%)
BFS	+	+	+	−	+++	+	+++	97
KBS	+	+	++	++	+	+	++	68

Vr: vermiculite; Sm: smectite; HIV/HIS: 2-1-2:1 (hydroxy-interlayered Vr/Sm); Ch: chlorite; Mi: mica mix-layered minerals; Kt: kaolinite.
−: absent; +: 1–10%; ++: 10–35%; +++: 35–60%.