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Control of cadmium accumulation in topsoil and crops from contaminated farmland

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ABSTRACT

Soil layers in which a charcoal layer and a textile sheet were installed between the topsoil and the cadmium (Cd) contaminated subsoil were developed to prevent crops from Cd contamination. The charcoal layer was designed to protect the topsoil from Cd contamination caused by soil water infiltrating from the contaminated subsoil, and the textile sheet was to block crop root extension into the contaminated subsoil. The effects of the layers developed were examined by pot experiments. The experiments revealed that the charcoal layer could adsorb Cd and interfere with uptake of Cd by soybeans, thereby the Cd content in the soybean seeds were lower than the standard value in Japan.

Keywords: Adsorption; Cadmium; Charcoal; Soybeans

1. Introduction

Recently in Japan, the improvement of technology for farmland development has become important and necessary because of the need for food to be supplied safely and the nation's food self-sufficiency ratio to be improved. On the other hand, farmlands are now often located near industrial land such as refineries and residential areas so the surrounding environment may have harmful effects on the agricultural production area. Eventually the crops may become contaminated with heavy metals. Particularly, cadmium (Cd) is one heavy metal that is difficult to control. If people continue to eat crops grown in soils contaminated with Cd and accumulate trace Cd in the body for a long time, serious illnesses such as itai-itai disease may occur. According to the international standard of the Codex Alimenarius Commission in 2005, the maximum level for Cd is 0.4 mg·kg^{-1} for rice, 0.2 mg·kg^{-1} for wheat, 0.1 mg·kg^{-1} for potatoes, and 0.2 mg·kg^{-1} for stem, root and leafy vegetables [1]. Therefore, it is important to develop technology for remediation and prevention of the contamination of soils with Cd.

Various tests have been carried out for restoration of soils contaminated with heavy metals. Some studies of phyto-remediation have been used for soils contaminated with metals [2–12]. Arao et al. [3, 4] and Ishikawa et al. [5] found a cultivar of rice which can accumulate high concentrations of Cd. Hattori et al. [6] reported that sunflower absorbs Cd from soil contaminated with low levels of Cd. Chen et al. [7] reported that vetiver grass accumulates higher Cd concentrations than *Thlaspi.caerulescens* which is known as a hyper-accumulator. *Polygonum thunbergii*, which is a cadmium-tolerant plant, can accumulate higher Cd concentrations and absorb Cd from soil [11, 12].

Additionally, the method of chemicals application has been used for paddy field soils contaminated with metals. Soil pH level, which has a significant effect on Cd absorption by crops, could be altered by applications

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of an alkaline agent such as autoclaved lightweight concrete or sulfate radical-containing material to Cd-contaminated soil in converted paddy fields [13]. Abmaizar and Smith [14] conducted a test of soil-wash with ethylenediaminetetraacetic acid, and reported that this method efficiently removed Cd from contaminated soil. However, a disadvantage was that EDTA was left in the soil because EDTA is not biodegradable. Makino et al. [15, 16] reported that calcium chloride as a wash chemical could form Cd chloride complexes and enhance Cd extraction from the soil. They also reported that the in situ soil-wash method did not affect rice yield.

We developed technology to improve farmland aimed both at remediating contaminated soils and growing safe crops. In the present study, we designed a layer that controls Cd transportation in the soil to prevent Cd contamination of crops. The system functions during crop growth with Cd being filtered by an adsorbent during the flow of water from the lower layer. The Cd concentrations in the topsoil, the charcoal adsorbent and soybeans were analyzed and the effectiveness of this system to protect against crop intake of Cd from contaminated soil is discussed.

2. Materials and methods

2.1. Structure of soil layers to prevent crops from adsorbing Cd

The structure of the soil layers to prevent crops from absorbing Cd is shown in Fig. 1. The layers are

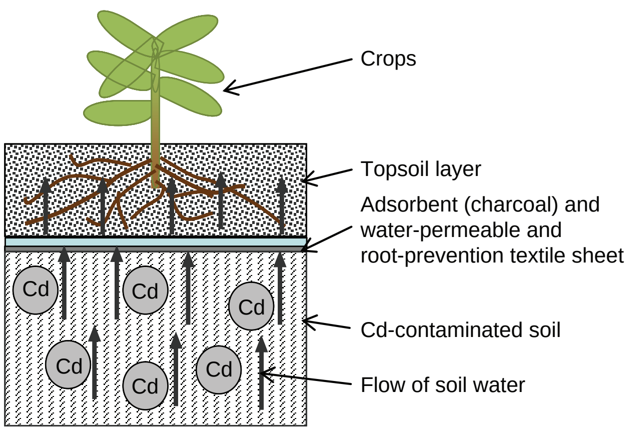

Fig. 1. Structure of soil layers to prevent crops from absorbing Cd.

tri-laminar from the bottom with the Cd-contaminated subsoil layer, an adsorbent layer and topsoil layer. A textile sheet to prevent crop root extension was laid between the topsoil and the adsorbent layer. Soils become oxidative in upland fields so Cd is easily released into the soil water. Soil water contaminated with Cd in the subsoil moves up towards the topsoil. The adsorbent and the textile sheets are expected to prevent crops from uptaking Cd from the water rising through the soil by capillary action. That is, the Cd in the soil water can be adsorbed by the adsorbent as the water passes through the adsorptive layer.

2.2. Adsorbent

Charcoal was used as the adsorbent layer to remove Cd from contaminated soils. The charcoal was made from cedar thinned from the forests and carbonized at 1050°C. The charcoal, produced in a carbonization factory of a forestry cooperative in Japan, was granular with a size of 1 to 5 mm in diameter. The charcoal was used as the adsorption layer after washing with distilled water and air drying at 25°C to remove the charcoal dust. The physical properties of the charcoal are shown in Table 1.

The specific surface area (surface area of charcoal particles per mass) and pore volume were analyzed by the Brunauer-Emmett-Teller method. Our previous laboratory experiments showed that this charcoal successfully removed Cd from a solution containing organic matter at an adsorption rate greater than 60% within 24 h [17].

2.3. Cultivation experiments

The effectiveness of the adsorption layers was tested by pot experiments. We used pots with diameters of ϕ 0.25 m and heights of 0.30 m. The Cd-contaminated soil for the subsoil was collected from a farmland that was Cd-contaminated with smoke discharged from a zinc refiner. The topsoil was collected from a test field in the National Institute for Rural Engineering. The subsoil and the topsoil were loosened before use.

The subsoil, the charcoal and the topsoil were laid in pots from the bottom to the top (Fig. 2). The thickness of the subsoil and the topsoil were 0.15 and 0.07 m, respectively. The charcoal was laid between the subsoil and

Table 1
Physical properties of charcoal used as the adsorbent in this study.

Carbonized temperature (°C)	Mean particle diameter (mm)	Mean pore diameter (nm)	Pore volume ($mL \cdot g^{-1}$)	Specific surface area ($m^2 \cdot g^{-1}$)
1050	1.41	2.7	0.12	224

the topsoil. Three thicknesses of charcoal were tested in Experiments a, b and c, as shown in Table 2. Textile sheets were installed between the soil layers and the adsorbent layer. The experimental pots were irrigated from a Marriott tank connected to the drain hole of the pot so that water was supplied from the subsoil to the topsoil. The Marriott tank was set up outside the pot. The tank sequentially supplied a constant water level in the subsoil. The water level in the pots was adjusted with a water conduit that was open to the atmospheric pressure and connected to the Marriott tank.

The experiments were conducted in a growth chamber. The illumination intensity was alternated between 5 and 0 μmol·m^{-2} every 12 h to simulate daytime and night-time. The air temperature was set at 25°C during the daytime and 20°C at night-time. In order to maintain a constant temperature in the growth chamber, an electric fan was kept on during the experiments to ensure crop pollination.

Cultivation experiments were continuously conducted two times (First-period: June-September, Second-period: October–January) with soybean (*Glycine.max*). The soybeans were treated with fungicide before seeding. Five seeds were planted in each pot. Chemical fertilizer (N: 2.5 kg·(10a)$^{-1}$, P_2O_5:10 kg·(10a)$^{-1}$, K_2O:10 kg·(10a)$^{-1}$) was spread and mixed with the topsoil of each pot during the second time only.

The soils, the charcoal and post-harvest soybeans were sampled after and/or before the experiments. All samples were analyzed by inductively-coupled plasma emission spectrometry.

3. Results and discussion

The initial Cd concentrations of the subsoil ranged from 18.8–22.1 mg·kg^{-1}, and the topsoil ranged from 0.05–0.21 mg·kg^{-1} (0.13 mg·kg^{-1} average). The initial Cd concentrations in the charcoal were at trace levels.

3.1 First cultivation

The results for the first cultivation are shown in Figs. 3 and 4. The Cd concentrations of the topsoil in Experiments a-1, b-1 and c-1 after the first cultivation were 0.40, 0.31, and 0.30 mg·kg^{-1}, respectively (Fig. 3). These results suggest Cd moved from the subsoil to the topsoil as the soybeans grew in the pots. The Cd concentrations in the topsoil without the charcoal layer were higher than those with charcoal. The Cd concentrations

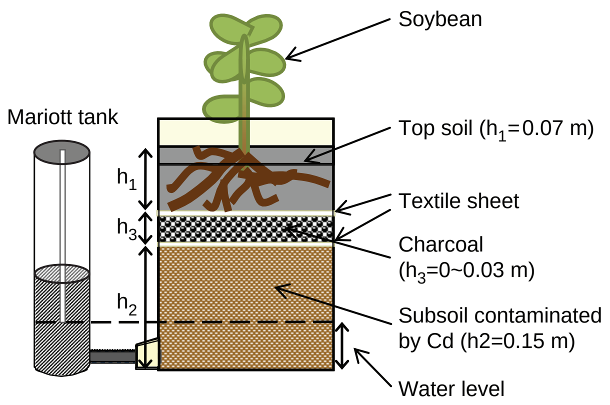

Fig. 2. Schematic of cultivation experiments using pots and a Marriott tank.

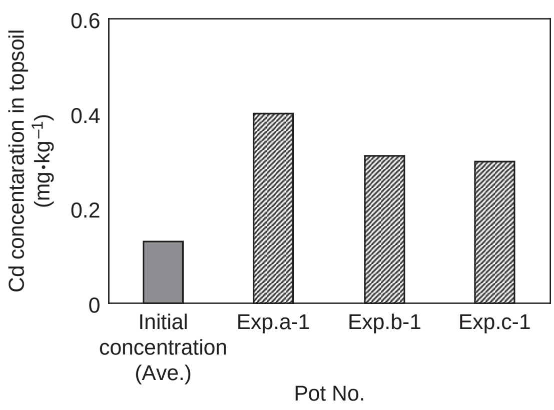

Fig. 3. Cd concentrations in topsoil before and after the first experiment.

Table 2
Schedule cultivation experiments and thicknesses (m) of soil layers and charcoal layer.

Cultivation	Pot No.	Thickness of Cd contaminated soil	Thickness of top-soil	Thickness of adsorbent (charcoal)
First	Exp.a-1	0.15	0.07	0
(Jun.–Sep.)	Exp.b-1			0.01
	Exp.c-1			0.03
Second	Exp.a-2	Continuous use	Continuous use	Continuous use
(Oct.–Jan.)	Exp.b-2			
	Exp.c-2			

in the 0.01 m charcoal layer were slightly higher than in the 0.03 m charcoal layer.

The Cd concentrations in the soybeans in the pots without the charcoal layer were 1.07 mg·kg^{-1} and exceeded the 0.5 mg·kg^{-1} standard value proposed by Japan (Fig. 4), while, the Cd concentrations in the soybean seeds for Experiments b-1 and c-1 with the charcoal layers were 0.13 and 0.11 mg·kg^{-1}, respectively. These Cd concentrations are below the standard value by Japan (0.5 mg·kg^{-1}). Moreover, the Cd concentrations in the pot with 0.01 m of charcoal were higher than the 0.03 m charcoal.

The textile sheet prevented the soybean roots from growing into the subsoil in each pot. However, this sheet could not prevent Cd from moving into the topsoil with the soil water. Moreover, in spite of the charcoal layers in Experiments b-1 and c-1, the Cd concentrations in the topsoil increased 0.25–0.35 mg·kg^{-1} higher than before the experiment (Fig. 3). This suggests the Cd moved from the lower layer into the topsoil. If the adsorbent layer cannot adsorb enough Cd from the soil solution, the Cd can move into the topsoil, so repeated cropping may cause Cd accumulation in the topsoil. Accordingly, the subsoil, the topsoil and the charcoal layers used in the first cultivation were used in repeated cropping experiments as a second cultivation.

3.2. Second cultivation

The results of the second cultivation are shown in Figs. 5 and 6. The Cd concentrations in the topsoil in this second cultivation were also detected at levels comparable with the first cultivation. The Cd concentrations in the topsoil were 0.36, 0.28 and 0.29 mg·kg^{-1} in Experiments a-2, b-2 and c-2, respectively (Fig. 5). The concentrations did not increase compared to those before the second experiments. The Cd concentrations in the topsoils from the end of the first cultivation to the end of the second cultivation decreased 0.04, 0.03 and 0.01 mg·kg^{-1} in Experiments a-2, b-2 and c-2, respectively. These results suggest continuous cultivation has a low potential for Cd concentration increasing in the topsoil.

The Cd concentrations in soybean seeds were lower in the second cultivation than the first cultivation except for Experiment b-2 (Fig. 6). The Cd concentrations in Experiments a-2, b-2 and c-2 were 0.93, 0.16 and less than 0.05 mg·kg^{-1}, respectively (Fig. 6). The concentrations in the pots with a 0.03 m-thick charcoal-adsorbent layer were higher than in the 0.01 m-thick charcoal as also seen in the first cultivation. Moreover, the Cd concentrations in the soybean seeds from Experiment a-2 exceeded the standard value proposed by Japan (0.5 mg·kg^{-1}). However, the Cd concentrations in the

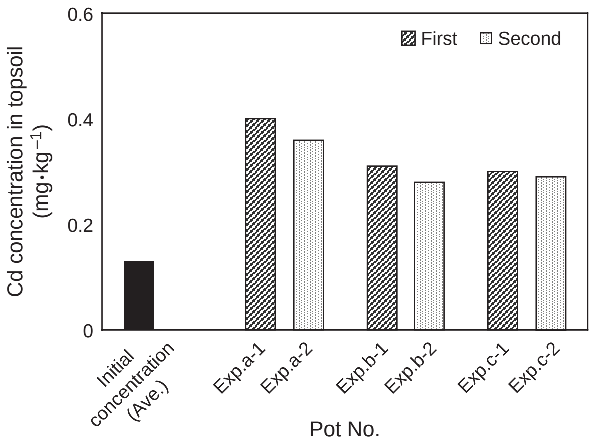

Fig. 5. Cd concentrations in top-soil during the first and second cultivation experiments.

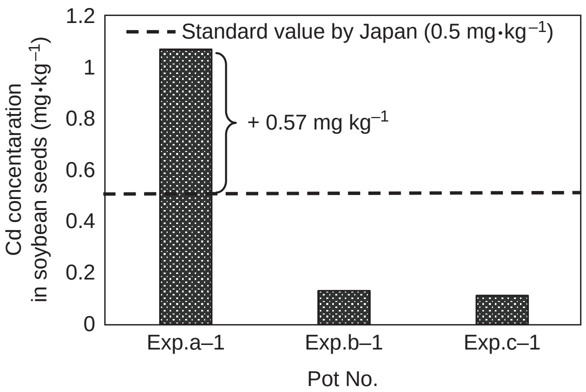

Fig. 4. Cd concentrations in soybeans after the first experiment.

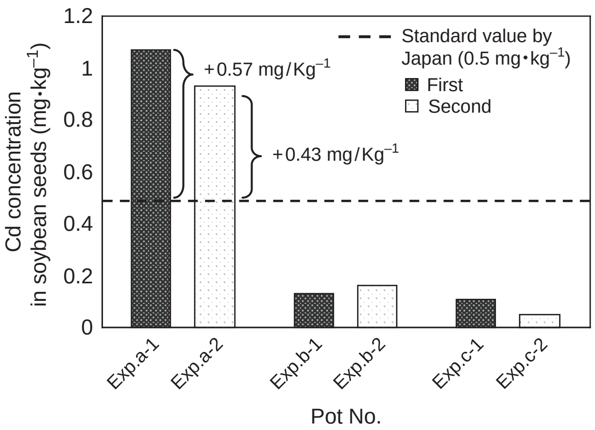

Fig. 6. Cd concentrations in soybean seeds in the first and second experiments.

soybeans of Experiments b-2 and c-2 did not exceed the standard value by Japan.

The Cd concentrations in the charcoal adsorbent layer were directly analyzed to confirm the Cd adsorption effect in the second cultivation. The Cd concentrations in the charcoal increased from trace levels to 2.6 mg·kg^{-1} in Experiment c-2, indicating the charcoal can adsorb Cd from the soil water, and prevent crops from uptaking Cd from the contaminated subsoil.

Finally, we divided the materials from each pot, and investigated the ability of the textile sheet to block root extension and the distribution of soybean roots in the topsoil after the experiments. No roots were found penetrating the sheet on the side of the absorbent layer in each pot. The roots of the soybeans were densely distributed in the topsoil.

3.3. Evaluation of the soil layer with adsorbent

From the results of both the first and second cultivations, it was found that the soil layer including the adsorbent layer works efficiently as a countermeasure for contaminated soils and crop intake of Cd from the soil solution. The Cd concentrations in the topsoil in the second cultivation decreased compared to the first cultivation. Since the difference in Cd concentrations in the topsoil between the first and second cultivations ranged from 0.01–0.04 mg·kg^{-1} and based on the lower limit of 0.05 mg·kg^{-1}, these values are insignificant. Moreover, irrespective of the thickness of the charcoal layer, the Cd concentrations in the topsoil of each pot with charcoal were lower than the pot without charcoal in the second cultivation as well as in the first cultivation. Therefore continuous crop cultivation does not necessarily cause Cd to accumulate in the topsoil.

Additionally, the textile sheet for blocking the crop root extension into the subsoil could not prevent Cd from moving with the soil solution, since the difference of Cd concentrations in the soybeans between the pots with and without textile sheet differed greatly in the first and second cultivations.

3.4. Estimation of the useful life span of the charcoal layer

We estimated the useful life span for the charcoal layer when applied in the field. We assumed that the charcoal can adsorb only Cd contained in the contaminated subsoil. The conditions for the estimation of the useful life span are shown in Table 3.

The useful life span was estimated under the following conditions: The equilibrium for the amount of Cd adsorbed in the charcoal as obtained by a batch test in the laboratory was 1.6×10^3 mg·kg^{-1} [17]; the thickness of the adsorbent layer was 0.01 m; and the volume of upward moving soil water was 2.5×10^{-3} m·d^{-1}. The equilibrium for Cd adsorption was regarded as the maximum amount of adsorption during the estimated useful life span. Additionally, the time required to pass through the Cd-adsorbent layer averaged four days, which is a long enough contact time between the soil water and the charcoal.

From the results of Experiment c-2, the Cd concentration adsorbed by the charcoal was 2.59 mg·kg^{-1} for the continuous 2 cultivations (240 days). The amount of Cd adsorbed onto a unit volume of charcoal in Experiment c-2 was 3.2×10^4 mg·m^{-3} derived from a filling rate of the charcoal at 1.7×10^2 mg·m^{-3} (Table 3).

The estimations indicate this type of soil layer is efficient for a useful life span of 134 years under continuous cultivation. Moreover, if the adsorbent is replaced in 25 years, an adsorbent layer 1.8×10^{-3} m thick will satisfy the conditions of estimation.

4. Conclusions

We developed soil layers in which a charcoal layer and a textile sheet were installed between the topsoil and the cadmium contaminated subsoil to prevent contamination of crops with Cd. The charcoal layer as an adsorbent was efficient in preventing the contamination of crops. The results obtained from the cultivation experiments with pots were as follows:

1. Irrespective of the thickness of the charcoal layer used, the charcoal layer decreased the Cd concentrations in the soybeans grown with Cd-contaminated subsoil.
2. Cd contamination in soybeans grown in pots with the charcoal layer did not exceed the international standard, 0.5 mg.kg^{-1} proposed by Japan.
3. Charcoal as an adsorbent prevented the accumulation of Cd in the topsoil with repeated cropping.

Table 3
Conditions for the estimations of the useful life span for the charcoal adsorbent.

Filling rate for charcoal	Equilibrium adsorbent amount from the previous test	Soil water upward movement	Thickness of adsorbent layer
1.7×10^2 mg·m^{-3}	1.6×10^3 mg·kg^{-1}	2.5×10^{-3} m·d^{-1}	0.01 m

4. The textile sheet could not prevent both crop root extension and Cd moving upward with the soil water at the same time.
5. The useful life span of the 0.01 m thick charcoal layer installed in the soil layers was estimated at 134 years.

In order to practically apply the method in this study to future studies, we need to consider the most effective adsorbent material and development of a textile sheet with the ability to adsorb Cd in situ.

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