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Decrease of Cadmium Accumulation in Crops by Zero-valent Iron

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Abstract

Cadmium (Cd) contamination in soils is a serious problem for crop production in the world. Zero-valent iron (Fe(0)) is a reactive material with reducing power capable of stabilizing toxic elements, including heavy metals and metalloids, in a solution. In the present study, we examined the effect of Fe(0) application on Cd accumulation in rice (*Oryza sativa* L. cv. Kirara 397) and spinach (*Pinacia oleracea* L.) plants growing in Cd-contaminated soils under paddy and upland conditions, respectively. The Fe(0) application significantly reduced the Cd concentration in seeds and leaves of rice, and that in shoots of spinach. The forms of Cd in soil were determined by sequential extraction. The potential availability of Cd forms in soils for plant root is: exchangeable > Fe-Mn oxides bound > organic matter bound > free-oxides occluded > residual. In Cd-contaminated paddy soils where rice was grown, the Fe(0) application increased the free oxides occluded Cd content, and decreased the exchangeable and iron-manganese oxides bound Cd content. In Cd-contaminated upland soils where spinach was grown, the Fe(0) application increased the iron-manganese oxides bound and free-oxides occluded Cd content, and decreased the exchangeable and organic matter bound Cd content. Thus, this study clearly showed that the application of Fe(0) is a promising approach for remediation of Cd-contaminated soils under both paddy and upland conditions.

Introduction

Cadmium (Cd) contamination in soils is a significant worldwide environmental problem. The crops cultivated in such contaminated soils often contain significant levels of Cd that can impair human health. Zero-valent iron (Fe(0)) is a reactive material with reducing power and used for decomposition of toxic chemical compounds (e.g. chlorinated hydrocarbons) or stabilization of heavy metals and metalloids (Janda et al., 2004; Lien and Wilkin, 2005; Rangsivek and Jekel, 2005). However, it has not been examined so far whether Fe(0) application decreases Cd accumulation in agricultural crops growing in Cd-contaminated soils. In the present study, therefore, we examined the effect of Fe(0) application on Cd accumulation in rice (*Oryza sativa* L.) and spinach (*Pinacia oleracea* L.) growing in Cd-contaminated soils.

Materials and Methods

Rice

Four levels of Fe(0) (0, 0.5, 1, and 5 g) were individually mixed with 100 g of the Cd-contaminated soil (10 mg kg^{-1} Cd, 0.1 M HCl extractable). The mixed soils were put in a 100-mL test tube and incubated at 23 ^{o}C for 10 days under continuously submerged conditions. Uniform seedlings (shoot height = 5 cm) of rice (*Oryza sativa* L. cv. Kirara 397) were transplanted into the test tubes and cultivated in a growth chamber for 90 days.

Spinach

Surface-sterilized seeds of spinach (*Pinacia oleracea* L. cv. Sunrise) were sown on 300-mL pots containing the Cd-contaminated soils (300 g, 16 mg kg^{-1} Cd, 0.1 M HCl extractable) with or without 1.5 g of Fe(0) application (0.5 g per 100 g soil), and grown in a greenhouse for 30 days. Soils were watered every day so that the water content was 55% of maximum holding capacity.

Analysis

After the treatment, plants were separated into each organ, dried, weighted, and ground for mineral analysis. Cd concentrations in each organ were determined by ICP-AES after wet-digestion. The sequential extraction method reported by Sadamoto et al. (1994) was used to fractionate Cd in the soils (5 fractions). Briefly, soil samples (0.5 g) were shaken with 5 mL of 0.05 M $Ca(NO_3)_2$ at 30 ^{o}C for 24 hours, and then centrifuged at 3000 rpm for 10 min. The supernatant was defined as the exchangeable fraction. The residue was shaken with 5 mL of 2.5% CH_3COOH at 30 ^{o}C for 24 hours, and then centrifuged at 3500 rpm for 15 min. The supernatant was defined as Fe-Mn oxides-bound fraction. The residue was digested with H_2O_2 at 100 ^{o}C until the H_2O_2 evaporated. Then, the residues were shaken with 5 mL of 2.5 % CH_3COOH at 30 ^{o}C for 24 hours, and centrifuged at 3500 rpm for 20 min. The supernatant was defined as the organic-matter-bound fraction. The residue was extracted with 15 mL of acid ammonium oxalate (0.1 M oxalic acid, 0.236 M ascorbic acid, and 0.175 M ammonium oxalate)

at 100 °C for 1 hour, and centrifuged at 15000 rpm for 10 min. The supernatant was defined as the free-oxides-occluded fraction. The residue was vacuum-dried and ground in a mortar. One hundred mg of ground samples were digested with HF-HCl-HNO_3. This fraction was defined as the residual fraction. Cd concentration in each fraction was determined by ICP-AES.

Results and Discussion

In both plant species, the growth was not inhibited by the Fe(0) application (data not shown). The Cd concentration in shoots of rice (seeds and leaves) and spinach grown in Cd-contaminated soils were significantly reduced by the Fe(0) application (Fig. 1). Higher concentration of Cd in spinach may be due to the soil condition (upland condition) because Cd is more available under oxidative conditions. Thus, it has been confirmed that Fe(0) application reduced Cd accumulation in plant grown under both paddy and upland conditions.

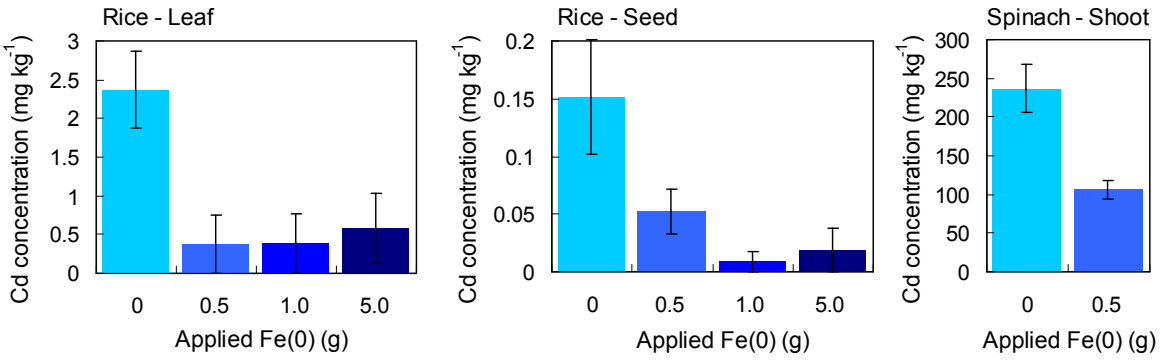

Fig. 1. Cd concentration in rice and spinach grown in Cd-contaminated soils with different Fe(0) application levels. Values are the means of three replicates ± SE. Applied Fe(0) was expressed as g per 100 g soils.

Then, how did the Fe(0) application reduce Cd uptake in rice and spinach? In order to know how the forms of Cd changed in soils with the Fe(0) application, Cd in soil was fractionated by the sequential-extraction method (Sadamoto et al., 1994). The potential availability of Cd forms in soils for plant roots is: exchangeable > Fe-Mn oxides bound > organic matter bound > free-oxides occluded > residual. In paddy soils without the Fe(0) application, the Cd content in each fraction was in the following order: residual >> Fe-Mn oxides bound > exchangeable ≈ free-oxides occluded > organic matter bound (Fig. 2a). By the Fe(0) application, Cd in the exchangeable and Fe-Mn oxides bound fractions, the more bio-available forms, were significantly reduced, whereas the level of Cd in the free-oxides occluded fraction, a less bio-available form, was doubled. In upland soils as well, the Fe(0) application significantly reduced the availability of Cd; decreased the Cd content in exchangeable and organic matter bound fractions (Fig. 2b). In upland soils, however, effect of the Fe(0) application on the

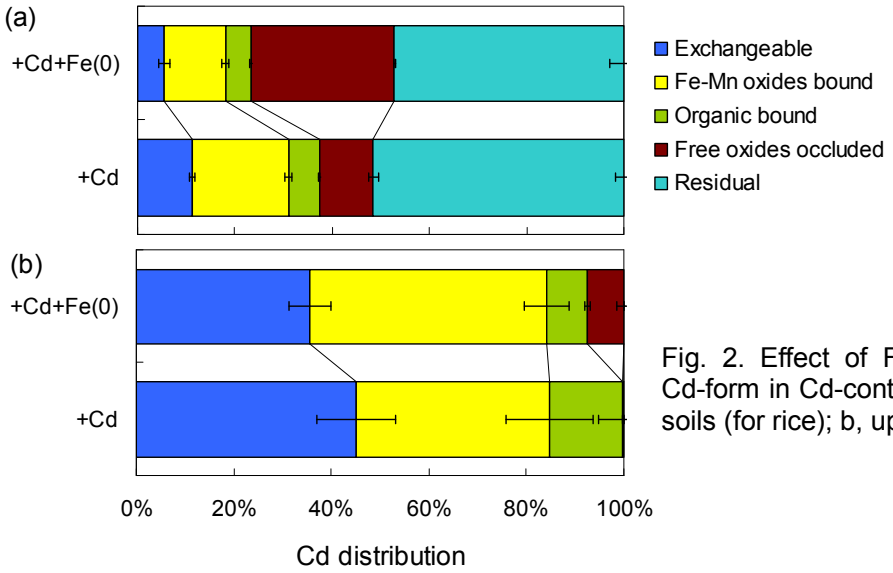

Fig. 2. Effect of Fe(0) application on the Cd-form in Cd-contaminated soils. a, paddy soils (for rice); b, upland soils (for spinach).

reduction of Cd availability was limited, possibly reflecting that Cd concentrations in shoots of spinach was still high in the presence of Fe(0) (Fig. 1).

In conclusion, the present study demonstrated that Fe(0) application significantly reduced more phytoavailable Cd in Cd-contaminated soils, resulting in reduction of Cd accumulation in plant without toxic effects on plant growth, especially under paddy conditions. In general, the inactivation (precipitation) of Cd in soils can be brought about a change in soil pH (Chuan et al., 1996). Since the soil pH after the treatment did not differ between the treatments both in rice and spinach (data not shown), the reduction of phytoavailable Cd was not caused by the changes in soil pH, but presumably caused by the reducing power of Fe(0), directly or indirectly.

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