Title
Decrease of Cadmium Accumulation in Crops by Zero-valent Iron

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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 (*Pinnacia 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 °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 (*Pinnacia 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 °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\(_3\)COOH at 30 °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\(_2\)O\(_2\) at 100 °C until the H\(_2\)O\(_2\) evaporated. Then, the residues were shaken with 5 mL of 2.5 % CH\(_3\)COOH at 30 °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-HNO₃. 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.

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
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.

References