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Evaluation of the effects of application of iron materials on the accumulation and speciation of arsenic in rice grain grown on uncontaminated soil with relatively high levels of arsenic

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ABSTRACT

The Codex Committee adopted a maximum level of 0.2 mg kg^{-1} for inorganic arsenic in polished rice at the 37th Session of the Commission (Codex Alimentarius Commission, 2014). It is thus necessary to establish agronomic management practices for reducing the accumulation of As in rice grain even in As-uncontaminated soil. We examined the effect of the application of different kinds of iron (Fe) materials on As uptake in rice plants grown in bottomless concrete frames filled with soil collected from an area surrounding a formerly As-polluted region. We assessed the concentration and speciation of As in soil solution throughout the rice cultivation period. Application of Fe materials had a significant effect on the concentration of arsenite, arsenate, inorganic As (sum of arsenite and arsenate) and total As, in the soil solution. The concentration of these forms of As in soil solution treated with Fe materials was significantly lower than the control. The lowest concentrations of As were observed in the plot to which a metal Fe powder composed mainly of a zero-valence Fe was applied throughout the rice cultivation period. The application of metal Fe powder and Fe oxide material composed mainly of ferrihydrite significantly reduced the amount of available As in the soil. The amount of acid ammonium oxalate extractable Fe was significantly increased by the application of metal Fe powder and Fe oxide material compared to that of the control and converter furnace slag. Concentrations of all forms of As in soil solution showed a significant positive correlation with the amount of available As and a significant negative correlation with the amount of acid ammonium oxalate extractable Fe in soil; this indicated that the increase of acid ammonium oxalate extractable Fe by application of Fe materials retarded the release of As from the soil solid phase to soil solution by fixing As and Fe. The concentrations of arsenite, dimethylarsinic acid (DMA), the sum of As species, and total As in grain with applied metal Fe powder and Fe oxide material were significantly lower than the control, reflecting the concentration of soluble As species in soil solution. These results strongly suggest that the application of metal Fe powder and Fe oxide material effectively reduced As accumulation in rice grain, making it a promising agronomic management practice for reducing the risk of As accumulation.

1. Introduction

In recent years, the levels of heavy metals in foods have been attracting global attention, and arsenic (As) content in rice has been under scrutiny (JECFA, 2010). In 2014, the Codex Committee adopted a maximum level of 0.2 mg kg^{-1} for inorganic As in polished rice at the 37th Session of the Commission (Codex Alimentarius Commission, 2014). The majority of As ingested in Japan is believed to be derived from rice, a staple food. Therefore, identification of agronomic techniques to reduce As concentrations in rice are urgently needed even for regions not polluted by As.

There are many paddy fields in Japan with relatively high As concentrations in areas that have not been subjected to countermeasures because the levels were below the criterion value. It has been reported that a water-saving regimen was remarkably effective in decreasing As concentration in rice grain (Arao et al., 2009). This was because As changes its state depending on the oxidoreduction state of the soil. More specifically, oxidation of the soil due to water-saving efforts retarded the reduction of arsenate to arsenite, which has markedly higher solubility, plant availability,

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and toxicity (Takahashi et al., 2004). However, growing rice under these aerobic conditions caused an increased accumulation of cadmium (Cd) in the rice grains. It may therefore be difficult to simultaneously maintain low Cd and low As concentrations in grains by means of water management alone (Arao et al., 2009).

In addition, the same water-management regimen caused changes in the redox potential of various types of soils because of differences in soil properties, such as microbial status, organic matter content, iron oxides, and minerals and aggregate development. Thus, water management techniques designed to reduce As concentration will not always be effective in different soil conditions.

It was reported that the application of iron (Fe) materials (Yamane, 1989; Liu et al., 2004; Nath et al., 2014) and of silicate (Li et al., 2009a; Seyfferth and Fendorf, 2012) decreased the absorption of As by paddy field rice. Most of these studies on the As transfer from soil or culture solution to plants referred to pot experiments, heavily As-contaminated soils, and culture solution amended with high levels of As. However, most food consumed originates from crops grown in fields that are not heavily contaminated with As. It is thus necessary to study the effects of agronomic practices on As transfer from uncontaminated soil to rice under actual field conditions.

In our previous report (Matsumoto et al., 2015a), we therefore decided to investigate whether the application of commercially available Fe and silicate materials would inhibit the uptake of As by rice as a method applicable to common paddy field farming in unaffected soil with relatively high levels of As. We used soil from an area surrounding a region previously designated as As-polluted under the Agricultural Land Soil Contamination Prevention Law. The concentration of As in the grain was significantly decreased by 30% compared to the control by the application of Fe material produced from converter furnace slag. Meanwhile, no significant difference was observed in As concentration by the application of calcium silicate slag.

We further compared the ability of different types of Fe materials, including not only converter furnace slag but also an adsorbent of heavy metal-polluted soil and a filter medium, to remove different contaminants in groundwater. Among the Fe materials, metal Fe powder composed mainly of a zero-valence Fe was highly effective in reducing As concentration in the grain compared to the converter furnace slag (Matsumoto et al., 2015b). However, the mechanisms of As stabilization in flooded soils and reduction of As uptake in rice by using Fe-rich materials are still unclear. It is well known that arsenite is the dominant species under paddy conditions, but arsenate, methylarsonic acid (MAA) and dimethylarsinic acid (DMA) are also present in significant quantities (Ultra et al., 2009). It is thought that the application of Fe materials would likely suppress the release of soluble arsenite by the adsorption of arsenate by free Fe oxide, increased by the application of Fe materials. The amount of Fe oxides and hydroxides in the soil plays an important role in regulating the concentration of As species in the soil solution because it affects the surface binding and precipitation of poorly soluble As salts (Ultra et al., 2009). These bio-geochemical processes influence As mobility and availability for uptake by rice. Therefore, it is necessary to study the status of As in soil treated with different kinds of Fe materials to establish farming methods to reduce the risk of arsenic accumulation in rice grain. To this end, we assessed the concentration and speciation of As in soil solution throughout the rice cultivation period. We also evaluated the effect of the application of Fe materials on the speciation of As in rice grain.

2. Materials and methods

2.1. Rice cultivation in concrete frames

In the present study, we conducted a concrete frame experiment rather than a pot experiment to try to reflect possibly as actual field conditions for growing rice (Fig. 1). Bottomless concrete frames ($0.8 \times 0.9 \times 0.6$ m) were used for each replication. The concrete frame experiment was performed in 2013 in a field at Shimane University, Matsue, Japan. Each frame was filled with 400 kg of soil collected from the plow layer (0–15 cm) of paddy fields in an area surrounding a formerly As-polluted region. The tested soil contained 2.3% total C, 0.22% total N, 0.4 mg kg^{-1} total Cd, and 39.5 mg kg^{-1} total As; it had a pH of 5.5. Total As concentration in the soil was higher than the background As concentration in Japanese soil (Iimura and Ito, 1978).

Seedlings of rice (*Oryza sativa* L. cv. Koshihikari) were germinated on soil formulated for seedling growth (Green Soil, Izumo Green Co., Izumo, Japan). Two rice seedlings per hill were transplanted with a spacing of 18 cm $\times$ 16 cm (22.2 hills m^{-2}) in each frame on 17 May 2013. A compound fertilizer containing 2.16 g of N, 0.94 g of P, and 1.79 g of K was supplied to each frame by basal application before the seedlings were transplanted. The application rate of basal fertilizer corresponded to 30 kg of N, 13 kg of P and 25 kg of K per ha, respectively. Ammonium sulfate containing 1.44 g of N was also supplied to each frame by top dressing 45 days after the rice seedlings were transplanted. The application rate of top dressing corresponded to 20 kg of N per ha.

The flooding condition of the frames was maintained from the transplanting to 2 weeks before harvest, except for midseason drainage carried out from June 17–25. Water requirement in depth per day of the soil in the frames was regarded as 44 mm, and the paddy water depth was kept at 30 mm by means of supplying irrigation water. In the present study, although we did not

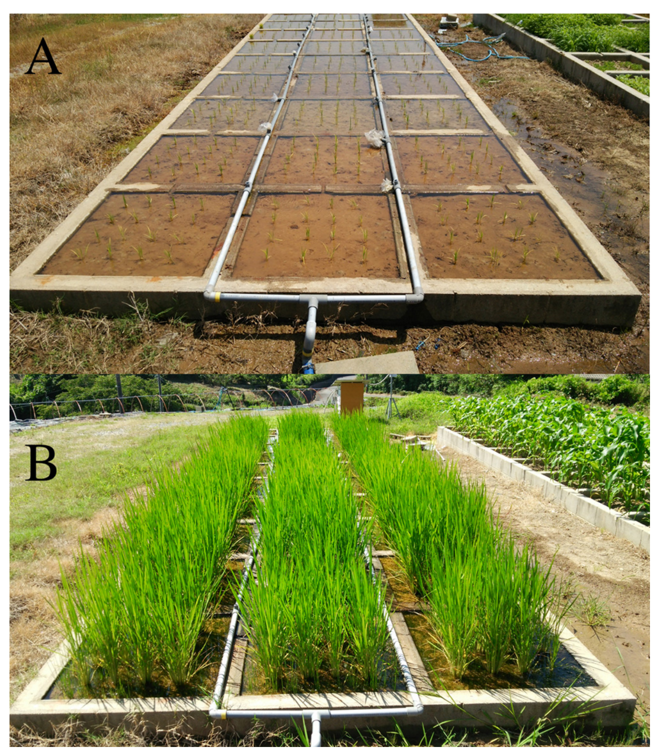

Fig. 1. Rice plants grown in bottomless concrete frames filled with 400 kg of soil collected from the plow layer (0–15 cm) of paddy fields in an area surrounding a former As-polluted region. A: 1 week after transplanting. B: 10 weeks after transplanting.