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Inhibition of arsenic accumulation in Japanese rice by the application of iron and silicate materials

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ABSTRACT

There are many rice paddy fields with relatively high arsenic (As) concentrations in areas that have not been subjected to countermeasures because the As level was below the criterion value established by the Agricultural Land Soil Contamination Prevention Law in Japan. To reduce the risk of excessive As in rice paddy fields using agronomic methods applicable to common farming practices, we examined the effect of the application of iron (Fe) and silicate materials on As uptake by rice plants in bottomless concrete frames filled with soil collected from an area surrounding a former As-polluted region. Following the application of calcium silicate slag at a rate of 0.5 kg m^{-2}, no significant effect was observed on the As concentration in rice grain or straw, but the available silicate in the soil was increased. The application of Fe materials at a rate of 0.5 kg m^{-2} resulted in a significant reduction of the As concentration in grain and straw, as shown by an analysis of variance. The lowest concentrations of As in both grain and straw were obtained with the application of a metal Fe powder (EM), followed by that with an Fe oxide material (FB), a converter furnace slag (FM), and the control. The EM and FB applications both significantly reduced the 1 M HCl-soluble As concentration in soil compared to the control. The levels of both acid ammonium oxalate extractable Fe ($Fe\text{-}_{ox}$) and citrate–bicarbonate–dithionite extractable Fe ($Fe\text{-}_{CDB}$) in the soil were significantly increased by the application of EM and that of FB compared to the FM and the control. A negative significant correlation was obtained between the amount of 1 M HCl-soluble As and two types of free Fe oxide. These results suggest that the available As in soil was strongly fixed with the Fe oxides that were increased by the application of Fe materials, and that the decrease of available As in the soil induced a decrease in the As uptake by rice plants. The application of Fe materials will thus be effective to lower or prevent the risk of the rice cultivation in paddy fields with relatively high levels of As.

1. Introduction

When the Agricultural Land Soil Contamination Prevention Law was enacted in Japan in 1971, 391 ha in 14 regions of the country were found to require control measures for arsenic (As) pollution. Arsenic is found ubiquitously in rocks, soils and plants (Phillips, 1990) and rarely damages crops as long as the concentration is near the natural values. Contamination of soil accompanied by crop growth inhibition in Japan has rarely been attributed to residues from pesticides that used to contain As (Quazia et al., 2013) or to geological features that are found in South-East Asian countries (Williams et al., 2006). Rather, such contamination and crop inhibition is believed to be caused mostly by As that has eluted due to flooding or spontaneously over a long period of time from muck, slag and pit wastewater from mine development, and then accumulated in agricultural lands (Yamane et al., 1976).

In such As-affected regions, the crop growth inhibition is comparatively mild among dry field crops, but it is known to be severe for paddy field rice (Yamane et al., 1976). This is because As changes its state depending on the state of the oxidoreduction of the soil. More specifically, the reduction of soil by flooding leads to the reduction of the arsenate (a form of As) to the form arsenite, which has markedly increased solubility, plant availability and toxicity (Takahashi et al., 2004). For this reason, water-saving cultivation has been practiced to mitigate damages in paddy fields in As-affected regions (Maejima et al., 2008). However, water-saving cultivation has presented difficulties related to water supply and labor, and the yields were considerably low (Yamane, 1989).

The means to prevent the growth inhibition of rice in As-affected paddy fields include agronomic and civil engineering methods (Yamane, 1989). Civil engineering methods include (1) dilution with additional soil and (2) the removal of contaminated topsoil and replacement with uncontaminated topsoil. Agronomic methods include (1) maintaining soil oxidative by water control and preventing the elution of As, (2) facilitating the formation and precipitation of poorly-

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soluble As compounds by adding materials to the soil, and (3) inhibiting the root uptake by adding a substance that competes with As even when it has been eluted off. Of these, engineering methods have been implemented as permanent measures in As-contaminated areas. By 2008, out of the 391 ha specified by the Agricultural Land Soil Contamination Prevention Law, 324 ha (83%) have been restored through means such as the removal and admixture of soil (Ministry of the Environment, 2010).

However, the international situation regarding As has changed markedly in recent years. The issue of As in food is on the agenda for the Codex Committee. In 1988, the Joint Food and Agriculture Organization/World Health Organization (FAO/WHO) Expert Committee on Food Additives (JECFA) proposed an interim acceptable As intake of 15 μg/kg (body weight)/week (JECFA, 1988), and the discussion is continuing today from an epidemiological point of view (JECFA, 2010).

Compared with other agricultural products, rice contains a particularly high level of As, and rice is believed to be the main contributor of As intake among Japanese people (Takahashi et al., 2004). It is thus necessary to use rice production methods that take into account As concentrations in rice even in uncontaminated regions, and methods to inhibit As uptake in rice are needed.

Arao et al. (2009) reported that a water-saving regimen was remarkably effective for decreasing the As concentration in rice grain, whereas growing rice under 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. In addition, the same water-management regimen caused different changes in the redox potentials of various types of soils because of differences in soil properties, such as microbial status, contents of organic matter, iron oxides and minerals and aggregate development. 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 that of silicate (Li et al., 2009; Seyfferth and Fendorf, 2012) decreased the absorption of As by paddy field rice. The possible effects of the application of Fe materials include: (1) the increased deposition of Fe oxide in an oxidized band around rice roots and within rice roots and the inhibition of the penetration of As into the roots, (2) co-precipitation around neutral pH when the ratio of Fe to As increases, and (3) suppression of the release of soluble arsenite by the adsorption of arsenate by Fe.

The application of silicate was expected to prevent As uptake by paddy field rice competitively because of the chemical similarities between As and silicate. However, most of the above-cited studies were conducted in As-contaminated soil or with culture solution to which a high concentration of As was added. Those studies were not designed based on the As uptake by rice in normal paddy field farming, and further examinations are needed to determine whether those studies' findings are directly applicable to the current paddy field cultivation methods.

The application of Fe and silicate materials is a common practice in rice production systems in Southeast Asia. In Japan, most of the Fe and silicate materials applied to the paddy rice fields are produced from converter furnace slag and calcium silicate slag, respectively. The concentration of Fe in the commercially available Fe-containing soil conditioners is typically within the range of 14 to 21%. The guaranteed available silicate (0.5 M-HCl extractable silicate) in silicate fertilizer is regulated to be at least 20% by the Fertilizers Regulation Act in Japan.

In our previous report (Matsumoto et al., 2015), 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. Toward this end, we used soil from an area surrounding a former As-polluted region previously designated under the Agricultural Land Soil Contamination Prevention Law. The concentration of As in the grain was significantly decreased by 30% by the application of Fe material that was produced from the converter furnace slag compared to the control while no significant difference was observed in the concentration of As in the grain by the application of calcium silicate slag. Although these results indicate that converter furnace slag is effective in decreasing As accumulation in rice grain, the comparative effects of different types of Fe materials and combination use of Fe materials and calcium silicate slag on concentrations of As in rice grain are still unclear. In the present study, to clarify the interaction of Fe material and calcium silicate slag and different type of Fe materials, therefore, we conducted two-way experimental design using calcium silicate slag and three types of Fe materials.

2. Materials and methods

2.1. Rice cultivation in the concrete frame experiment

Bottomless concrete frames ($0.8 \times 0.9 \times 0.6$ m each) were used for each replication. The concrete frame experiment with three replications was performed in 2012 at the field of Shimane University, Matsue, Japan. Each concrete frame was 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. The soil tested contained 2.3% total C, 0.22% total N, 0.4 mg kg^{-1} total Cd, and 39.5 mg kg^{-1} total As, and it had a pH of 5.5. The 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 raising seedling culture soil (Green Soil, Izumo Green Co., Izumo, Japan). Two rice seedlings per hill were transplanted at the spacing of 18 cm by 16 cm (22.2 hills m^{-2}) in each frame on 30 May 2012. 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 a midseason drainage carried out from June 30 to July 10. The heading days occurred between August 5 and August 10. After the seeds had matured, the stems of the plants were cut at 2 cm above the soil surface on September 14.

2.2. Application of materials

Three types of commercially available Fe-containing materials were used in this experiment: (1) metal Fe powder (EM) (ECOMEL, Kobe Steel, Kobe, Japan) which is composed of mainly a zero valent Fe (Fe% > 99%) and which has been successfully used as a filter medium to remove different contaminants in groundwater; (2) Fe oxide material (FB) (FIXALL, Ishihara Sangyo Kaisha, Osaka, Japan) which is composed of mainly ferrihydrite (Fe% ≑ 56%) and which has been used as an adsorbent of heavy metal-polluted soil; and (3) converter furnace slag (FM) (FM GOLD, Yoneda Industry Co., Okayama, Japan) which was obtained as Fe manufacturing waste and has been used as an agricultural soil conditioner (Fe% ≑ 20%). The application rates of these Fe materials were 0.5 kg m^{-2} (5 Mg ha^{-1}) with six respective replicates. Frames without the application of Fe materials were used as the control.

Calcium silicate slag (guaranteed available SiO_2% ≑ 30%) was also applied at the rate of 0 and 0.5 kg m^{-2} (5 Mg ha^{-1}) with 12 replicates, including of the frames in which Fe materials were applied. These materials were applied to the soil in the concrete frames 14 days before the transplanting of rice seedlings, and then the soils were immediately plowed. The soils were sufficiently flooded and tilled for the