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Reducing arsenic accumulation in rice grain through iron oxide amendment☆

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ABSTRACT

Effects of soil-arsenic (As), phosphorus and iron oxide on As accumulation in rice grain were investigated. Cultivars that have significantly different sensitivity to As, straighthead-resistant Zhe 733 and straighthead-susceptible Cocodrie, were used to represent different cultivar varieties. The grain accumulation of other elements of concern, selenium (Se), molybdenum (Mo), and cadmium (Cd) was also monitored. Results demonstrated that high soil-As not only resulted in high grain-As, but could also result in high grain-Se, and Zhe 733 had significantly less grain-As than Cocodrie did. However, soil-As did not impact grain-Mo and Cd. Among all elements monitored, iron oxide amendment significantly reduced grain-As for both cultivars, while the phosphate application only reduced grain-Se for Zhe 733. Results also indicated that cultivar type significantly impacted grain accumulation of all monitored trace elements. Therefore, applying iron oxide to As-contaminated land, in addition to choosing appropriate rice cultivar, can effectively reduce the grain accumulation of As.

1. Introduction

Rice is a staple food crop that more than a third of the world's population depends on (Khush, 1997). Arsenic (As) contamination of rice varies globally since the crop might be grown in areas contaminated by As-polluted irrigation water, by various As byproducts due to large mining activity, and by the historic application of pesticides and defoliants containing arsenic (Loebenstein, 1994; Abedin et al., 2002). For example, elevated soil-As levels in the south central United States (U.S.) are the result of monosodium methanearsonate (MSMA) application as an herbicide in this former cotton growing region in the last century, where the majority of paddy rice is produced (Gilmour and Wells, 1980). It was reported that food is the most significant source of inorganic As intake by the U.S. population (Meacher et al., 2002), and the typical Asian–American population, which may consume up to six times more rice than the average consumer in the U.S. (Batres-Marquez et al., 2009), has significantly greater exposure to As. In addition to As, accumulation of other trace elements in rice, such as selenium (Se), molybdenum (Mo), and cadmium (Cd), may also be of concern (Farrow, 2012).

Plant uptake of As is complex, as roots uptake organic and inorganic As species via different uptake mechanisms (Li et al., 2009). Inorganic arsenate (As^{V}) is dominant in aerobic conditions, and is readily available for plant uptake as a phosphate analog via a phosphate transporter pathway (Abedin et al., 2002). However, inorganic arsenite (As^{III}), which has a greater mobility in soil, accounts for the majority of uptake by plants, and is transported into rice roots via glycerol transporting channels (Abedin et al., 2002; Meharg and Jardine, 2003). The uptake and accumulation of As and other elements of concern by plants are influenced by the mobility of these elements in soil, and such mobility can be altered by fertilizers containing phosphate (Wang et al., 2008; Lou-Hing et al., 2011). Peryea (1991) has reported that the addition of phosphate to soils can increase As mobility, phytoavailability, and phytotoxicity through competitive sorption towards available particle surface sites. However, Hua et al. (2011) has reported that phosphate can be easily immobilized by iron oxide, therefore it does not impact As mobility and accumulation by rice grain. Abedin et al. (2002) revealed no significant difference in As concentrations in plants due to increasing phosphate application. The

☆**Capsule:** applying iron oxide to As-contaminated land effectively reduces arsenic accumulation in rice grain.

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conflicting results in previous studies may be due to cultivar specific transporters. Effects of phosphate on the mobility in soil and plant uptake of other elements (Se, Mo, and Cd) have also been reported (Smith et al., 1997; Hopper and Parker, 1999; Waterlot et al., 2011). Because phosphate is an essential fertilizer for rice, its effect on the grain accumulation of trace elements of concern needs to be re-examed using different cultivar types. This information is very important to develop noval nutrient management strategies to control or regulate grain accumulation of trace elements.

Iron is an abundant element and a prevalent sorbent mineral in soil with high adsorption capacities for As^{V}. In an anaerobic environment, the reductive dissolution of Fe-oxide or Fe-hydroxides could result in the release of previously adsorbed arsenic into solution, increasing As bioavailability (Marin et al., 1993). It was also reported that adding ferrous ion (Fe^{2+}) immobilized As in soil and resulted in reduced grain-As accumulation in rice (Hossain et al., 2009). Recent attempts of in situ iron oxide amendment have also resulted in an increase of soil adsorption capacity for As immobilization (Boisson et al., 1999), which may lead to less grain-As accumulation. However, this hypothesis has not been validated. Because iron oxide is economically available, it can be a practical solution to reduce grain-As accumulation from contaminated land if the above hypothesis is validated.

Although As accumulation by rice grain has been extensively studied in recent years, uncertainty remains, and practical solutions to reduce grain-As, other than cultivar selection, are still lacking. The objectives of this research were to determine the effect of soil treatment (phosphate and iron oxide applications) on grain accumulation of As and other selected elements, namely Se, Mo, and Cd, by different cultivars, and to explore practical strategies to reduce grain-As.

2. Materials and methods

2.1. Soil collection and preparation

The base soil used in this study was obtained from the USDA-ARS Dale Bumpers National Rice Research Center near Stuttgart, Arkansas in winter 2009. Two control soils in the soil-As experiment were native soil and MSMA-amended soil, obtained from the experimental rice field. The MSMA-amended soil has been treated with MSMA at a rate of 6.7 kg MSMA per hectare in alternate years since the 1980s to evaluate straighthead resistance among various rice cultivars in breeding programs (Yan et al., 2008). The native soil was from a field adjacent to the MSMA-amended soil, where there is no history of MSMA amendment. Both soils were homogenized using an industrial concrete mixer (Lancaster Concrete Mixer, Type SW, Year 1942, no. 153, Lancaster, PA), and air dried prior to distributing to each planting pot at 3 kg per pot. The soil moisture contents in different pots ranged from 0.9% to 9.0%, with an average of 5.00% and a standard deviation of 0.02%. After distribution, the native soil was subsequently amended in the laboratory with inorganic As^{V} solution (from sodium hydrogen arsenate heptahydrate; $Na_2HAsO_4 \cdot 7H_2O$) to achieve variable total As concentrations for soil-As impact studies. For phosphate and iron oxide impact studies, the native soil was amended with inorganic As^{V} solution to achieve the similar total As concentration as the MSMA-amended soil.

2.2. Treatment factors for rice cultivation

Multiple plots were set up in the Chester Baker Greenhouse at the Missouri University of Science and Technology (Missouri S&T), Rolla. Between February 2010 and January 2012, three studies

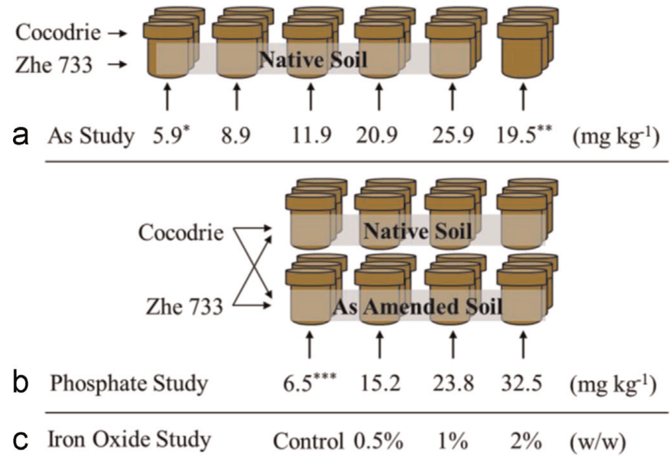

Fig. 1. Experimental design of soil-As (a), phosphate (b) and iron oxide (c) studies; *, **, *** indicate native soil, monosodium methanearsonate (MSMA)-amended soil and background phosphate, respectively. The native and MSMA-amended soils were from Stuttgart, Arkansas, the former representing a rice paddy in the southern states and the latter specifically for straighthead evaluation with application of MSMA.

were conducted: soil-As impact, phosphate impact, and iron oxide impact on total element accumulations in rice grain (Fig. 1). Two rice cultivars with significantly different sensitivity to soil-As, Zhe 733 and Cocodrie, which are resistant and susceptible to straighthead disease, respectively, were used in this study (Yan et al., 2008). All studies were completed in triplicate, including a control, unless stated otherwise.

The primary focus on this research is to reduce grain-As. However, other trace elements could also impact human health. For example, rice is the major source of Cd exposure in Asian countries (Sun et al., 2014). For this research, we also monitored grain- Se, Mo, and Cd, and to determine if the factors used for As study can impact their uptake.

The soil-As impact study, Fig. 1a, included two control soils (native and MSMA-amended) and four additional soil-As levels amended with inorganic As^{V} in lab. Prior to seeding, 1 L As^{V} solution was added during soil homogenization within the pot to achieve total soil-As concentrations of 8.9, 11.9, 20.9, and 25.9 mg/kg, covering the practical concentration range from that in uncontaminated native soil to slightly greater than that in the MSMA-amended soil of 19.5 mg kg^{-1}.

The phosphate impact study, Fig. 1b, included native and lab As-amended soils. These two soils were treated with calcium dihydrogen phosphate $Ca(H_2PO_4)_2$ solution rather than common fertilizers, to avoid addition of other nutrients such as potassium and ammonia along with phosphate addition. Because phosphate can mobilize As in soil, it may positively or negatively impact As uptake by rice plants. Therefore, relatively higher concentrations than the background level are needed to test this physical–chemical effect. After the plants had five to six leaves, 15.2, 23.8, and 32.5 mg P/L were applied as solutions in 50 mL increments every two weeks to achieve phosphate concentrations (w/w) of up to five times of the background level.

The iron oxide impact study, Fig. 1c, included the same soil treatments as the phosphate impact study. The iron oxide used in this experiment was obtained as a milling byproduct from an iron ore production facility in the U.S. The byproduct, also known as fines (500 mesh or 0.025 mm), was composed of 80% magnetite (Fe_3O_4) and 20% hematite (Fe_2O_3), and the total iron content was approximately 72%. Based on the feasibility of application, iron oxide application rates were 0.5%, 1.0%, and 2.0% (w/w), respectively.

Rice plants were consistently maintained in flood throughout