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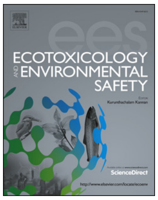

Fenton process-affected transformation of roxarsone in paddy rice soils: Effects on plant growth and arsenic accumulation in rice grain

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ABSTRACT

Batch and greenhouse experiments were conducted to examine the effects of Fenton process on transformation of roxarsone in soils and its resulting impacts on the growth of and As uptake by a rice plant cultivar. The results show that addition of Fenton reagent markedly accelerated the degradation of roxarsone and produced arsenite, which was otherwise absent in the soil without added Fenton reagent. Methylation of arsenate was also enhanced by Fenton process in the earlier part of the experiment due to abundant supply of arsenate from Roxarsone degradation. Overall, addition of Fenton reagent resulted in the predominant presence of arsenate in the soils. Fenton process significantly improved the growth of rice in the maturity stage of the first crop, The concentration of methylated As species in the rice plant tissues among the different growth stages was highly variable. Addition of Fenton reagent into the soils led to reduced uptake of soil-borne As by the rice plants and this had a significant effect on reducing the accumulation of As in rice grains. The findings have implications for understanding As biogeochemistry in paddy rice field receiving rainwater-borne H_2O_2 and for development of mitigation strategies to reduce accumulation of As in rice grains.

1. Introduction

Poultry manure is widely used as an organic fertilizer for crop production (Delgado et al., 2012). Litter from broiler chicken farming frequently contains roxarsone due to the use of roxarsone as a feed additive (Nachman et al., 2005; Fisher et al., 2015). Although roxarsone is of low ecotoxicity, it has been demonstrated that, upon application, chicken manure-borne roxarsone is readily degraded by soil microbes to produce toxic inorganic arsenic species (Mangalgiri et al., 2015). Under anaerobic conditions, it is likely that more mobile and toxic arsenite will be formed, which could inhibit the growth of crop plants and potentially cause accumulation of As in plant tissues (Huang et al., 2014; Zhang et al., 2014; Mangalgiri et al., 2015).

The waterlogging conditions required for paddy rice cultivation are favorable for translocation of As from soils to plants (Zhao et al., 2013). Therefore, rice grains tend to contain more As, as compared to other cereal grains (Sohn, 2014). Excessive consumption of As-containing rice or rice-based foods has been a health concern, especially for infants and young children (Xue et al., 2010; Diamond et al., 2011; Jackson et al., 2012). Rice straw is also commonly used as animal feed in many places (Wanapat, 2009; Dong et al., 2011; Hung et al., 2013). The As-containing rice straw could pose a health risk to animals, and potentially the consumption of As-contaminated bovine meat and milk can affect human health (Abedin et al., 2002).

In theory, input of oxidants into water-inundated soils could enhance oxidation of aqueous trivalent As (As^{3+} as in arsenite) and ferrous iron (Fe^{2+}), and subsequently reduce the bioavailability of As through formation of practically insoluble iron arsenate minerals or adsorption of arsenate to iron oxyhydroxides (Zhao et al., 2010; Zhu et al., 2014). Hydrogen peroxide (H_2O_2) is a strong oxidant that is commonly present in rainwater. It has been demonstrated that H_2O_2 in the concentration range encountered in rainwater had significant effects on transformation of arsenite into arsenate (Ma et al., 2013). In wetland soils like paddy rice soils that favor reductive dissolution of iron compounds, Fe^{2+} in the soil pore water can react with H_2O_2 to trigger Fenton reaction to produce hydroxyl radical (•OH), which may affect degradation of roxarsone via two possible mechanisms: (a) abiotic decomposition of roxarsone using the powerful hydroxyl radical as an oxidant, and (b) impeded biodegradation of roxarsone due to inhibition of microbial activities by hydroxyl radical.

Fenton reaction-driven transformation of roxarsone in paddy soils has implications for understanding As uptake by rice plants in areas receiving abundant rains. Such knowledge will also be useful

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for developing mitigation strategies and techniques (e.g. the use of diluted H_2O_2 as a chemical amendment) for reducing accumulation of As in the rice grains in order to minimize the health risk associated with consumption of As-containing rice and rice-based foods.

In this study, parallel microcosm experiments with and without treatment of the inundated soils with a Fenton reagent (mixed solution of H_2O_2 and Fe^{2+}) were conducted to understand the effects of Fenton reaction on (a) the phase transformation of roxarsone-As in the soils; (b) the growth performance of the rice plants, and (c) the uptake of soil-borne As by the rice plants and accumulation of various As species in the plant tissues.

2. Materials and methods

2.1. The soil used in the experiments

The soil samples used for the microcosm experiments were collected from the paddy rice field of the experimental farm at the South China Agricultural University (Guangzhou, China). The soil samples were air-dried after collection and then ground to pass a 0.25 mm (for soil incubation experiment) or a 2 mm (for plant growth experiment) sieve prior to the uses in the experiments. Some major chemical characteristics of the soils for Experiment 1 and Experiment 2 are given in Table 1.

2.2. The rice seedlings

The seeds of rice (*Oryza sativa* cultivar: Tianyou 122) used in Experiment 2 were provided by the Guangdong Academy of Agricultural Sciences. Prior to sowing, the seeds were surface-sterilized by soaking in 30% H_2O_2 for 15 min. The sterilized seeds were then rinsed with deionized water and placed in a container with moistened sands for germination. The pre-germinated seeds were sown into the seed bed that was covered by a plastic sheet to maintain the temperature at 28 ± 2 °C. Healthy seedlings with 4 leaves were selected for the experiment.

Table 1
Major chemical characteristics of the soils used in the microcosm experiment.

Soil parameter	Experiment 1	Experiment 2	Method
pH	6.82	6.52	Bao (2008)
Organic matter (g/kg)	24.7	23.8	Bao (2008)
Total N (g/kg)	1.3	1.06	Bao (2008)
Available N (mg/kg)	127	114	Bao (2008)
Total P (g/kg)	0.87	1.04	Bao (2008)
Available P (mg/kg)	52.3	77.8	Bao (2008)
Total K (g/kg)	23.7	19.6	Bao (2008)
Available K (mg/kg)	135	122	Bao (2008)
Fe^{2+} (mg/kg)	30.9	51.5	Analytical Methods Committee (1978)
Fe^{3+} (mg/kg)	59.8	65.0	Analytical Methods Committee (1978)
Arsenate-As (mg/kg)	2.08	15.6	HPLC-ICP-MS
MMA-As (mg/kg)	0	0	HPLC-ICP-MS
Arsenite-As (mg/kg)	0	0	HPLC-ICP-MS
DMA-As (mg/kg)	0	0	HPLC-ICP-MS
Roxarsone-As (mg/kg)	0	0	HPLC-ICP-MS

2.3. Experiment 1: soil incubation

A 30-day incubation experiment was conducted to observe the changes in different As forms in the soils over time. One control and two treatments were set for the experiment; (a) control (E1C): soil only, (b) Treatment 1 (E1T1): soil with added roxarsone (mixed completely) to obtain an artificially contaminated soils with a concentration of roxarsone-As at 50 mg/kg, and (c) Treatment 2 (E1T2): contaminated soil (formulated as (b) mentioned above) with added Fenton reagent (100 μM H_2O_2:100 μM Fe^{2+}). This Fenton reagent dose was selected after a pre-experimental test that indicated an excellent effect on immobilization of As while not causing damage to soil microbial community. Our work (to be reported somewhere else) suggests that addition of Fenton reagent at this dosage level significantly enhanced the abundance and diversity of the microbiome in the As-contaminated paddy soils due to the reduction in microbial toxicity of arsenic.

Plastic bottles (500 mL) were used as batch reactors. For each reactor, 500 g of a relevant soil sample were placed in the bottle. The experiment commenced following the addition of water (Control and Treatment 1) and Fenton reagent (Treatment 2) to keep the thickness of the overlying water layer at approximately 2 cm. The bottles were capped immediately following addition of the liquids. For Treatment 2, an appropriate amount of standardized H_2O_2 and an appropriate amount of Fe^{2+} solution were simultaneously added to each bottle every 2 days to obtain a theoretical concentration of H_2O_2 and Fe^{2+} both at 100 μM. During the period of the experiment, a small amount (approximately 5 g on a dry weight basis) of soil was taken from each bottle for analysis at the following times: 1, 24, 72, 168, 360 and 720 h.

2.4. Experiment 2: rice plant growth

A greenhouse growth experiment was conducted to observe the growth performance of the rice plants and uptake of As by the rice plants. The experiment lasted for about 9 months, including two continuous crops with a fallow period of about 3 months. The first crop commenced on September 8, 2013 and the rice plants were harvested on January 7, 2014; the second crop commenced on April 3, 2014 and the rice plants were harvested on July 22, 2014.

Like Experiment 1, the soil without added As was used as the control (E2C); Treatments 1 and 2 (E2T1 and E2T2, respectively) were the artificially contaminated soils without and with added Fenton reagent (100 μM H_2O_2:100 μM Fe^{2+}), respectively. The concentration of As in the contaminated soils was the same as that in Experiment 1 (50 mg/kg). The thickness of the overlying water layer was maintained at approximately 2 cm. For Treatment E2T2, an appropriate amount of standardized H_2O_2 and an appropriate amount of Fe^{2+} solution were simultaneously added to each bucket (see below for the details) every 2 days to obtain a theoretical concentration of H_2O_2 and Fe^{2+} both at 100 μM.

Two seedlings were transplanted to a soil column consisting of alternating layers of quartz sand and a relevant soil material. The soil column was contained in a nylon mesh bag (#400 mesh; diameter: 8 cm; depth: 12 cm). Four soil columns were placed in a plastic bucket (Diameter: 22 cm; Height: 15 cm) that was filled with the same soil material. This design allowed the separation of rhizospheric soil from the bulk soil by confining the rice plant roots within the nylon mesh bag or so-called rhizo-bag.

Compound fertilizer (N:P:K=15:15:15) was applied at a rate of 19 g per pot at the 7th day of the experiment. Additional fertilizers were added at a rate of 6.8 g/pot for compound fertilizer and 9.6 g/pot for urea in the early tillering stage of the first crop. In the second crop, 6.8 g/pot and 7 g/pot were added 7 days after