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# Effects of water management on arsenic and cadmium speciation and accumulation in an upland rice cultivar

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## ABSTRACT

Pot and field experiments were conducted to investigate the effects of water regimes on the speciation and accumulation of arsenic (As) and cadmium (Cd) in Brazilian upland rice growing in soils polluted with both As and Cd. In the pot experiment constant and intermittent flooding treatments gave 3–16 times higher As concentrations in soil solution than did aerobic conditions but Cd showed the opposite trend. Compared to arsenate, there were more marked changes in the arsenite concentrations in the soil solution as water management shifted, and therefore arsenite concentrations dominated the As speciation and bioavailability in the soil. In the field experiment As concentrations in the rice grains increased from 0.14 to 0.21 mg/kg while Cd concentrations decreased from 0.21 to 0.02 mg/kg with increasing irrigation ranging from aerobic to constantly flooding conditions. Among the various water regimes the conventional irrigation treatment produced the highest rice grain yield of 6.29 tons/ha. The As speciation analysis reveals that the accumulation of dimethylarsinic acid (from 11.3% to 61.7%) made a greater contribution to the increase in total As in brown rice in the intermittent and constant flooding treatments compared to the intermittent-aerobic treatment. Thus, water management exerted opposite effects on Cd and As speciation and bioavailability in the soil and consequently on their accumulation in the upland rice. Special care is required when irrigation regime methods are employed to mitigate the accumulation of metal(loid)s in the grain of rice grown in soils polluted with both As and Cd.

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## Introduction

Arsenic (As) and cadmium (Cd) are two common pollutants found in soil and water. As, especially inorganic As, is classified as a non-threshold carcinogen with a linear dose–response for chronic low level exposure. Cd is a highly toxic heavy metal which can readily accumulate in crops and thus lead to chronic toxicity diseases in livestock and humans. Contamination of agricultural

soils by Cd and As has become an important issue as a result of industrial activities in the proximity of agricultural areas, excessive application of contaminated fertilizers, manures and sewage sludges, and irrigation with water contaminated with metal(loid)s (Roberts et al., 2007; Chen et al., 2008; Williams et al., 2009; Arao et al., 2010). Rice, the most important staple food in Asia, is considered to be a major source of Cd and As in the human diet in some parts of Japan, India and China (Tsukahara et al., 2003;

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Mondal and Polya, 2008; Liang et al., 2010). There is therefore an urgent need to develop mitigation measures to reduce As and Cd concentrations in rice.

Several methods have been developed during the past few decades. Selection and breeding of rice cultivars with low As and Cd accumulation have been practiced to reduce As and Cd in the rice grains (Zhang and Duan, 2008; Li et al., 2012; Ye et al., 2012). Water management is another promising method that affects Cd and As bioavailability in soils and their subsequent uptake by rice (Arao et al., 2009; Rahaman et al., 2011; Hu et al., 2013b). When a paddy field is flooded and the soil has a low redox potential, any Cd present in the soil combines with sulfur (S) to form CdS which has low solubility in water (Bingham et al., 1976). Thus, flooding during the growing season, especially during later stages of plant growth, can effectively reduce Cd concentrations in rice grains (Arao et al., 2009; Hu et al., 2013a). In contrast, anaerobic conditions in paddy soils usually lead to the reduction of arsenate (As(V)) to arsenite (As(III)) which enhances the bioavailability of As to the rice plants (Masscheleyn et al., 1991; Marin et al., 1993; Takahashi et al., 2004). Thus, growing rice aerobically results in a marked decline in As accumulation in the rice (Xu et al., 2008; Li et al., 2009b; Hua et al., 2011; Somenahally et al., 2011; Spanu et al., 2012). However, Cd and As often occur together as contaminants in agricultural soils (Liu et al., 2005) and it is therefore necessary to investigate the feasibility of simultaneously mitigating both As and Cd accumulation in rice grains through appropriate water management.

The chemical speciation of As influences its biotoxicity. Inorganic As is generally considered to be more toxic than methylated As compounds (Cheng et al., 2004). A large variation in the proportions of inorganic As (As(III) and As(V)) and organic As (dimethylarsinic acid, DMA) in rice grain has been found but the factors involved are poorly known although both genetic and environmental factors are implicated (Williams et al., 2005; Zavala et al., 2008; Meharg et al., 2009). Water management has been reported to affect As species in rice grains. Compared with flooding, aerobic treatments markedly decreased organic As (mainly DMA) and thus increased the percentage of inorganic As in grain, although the concentrations of inorganic As remained lower than those in flooded rice (Xu et al., 2008; Li et al., 2009b).

Water shortage threatens the sustainability of agricultural systems and food security in many parts of Asia. Rice cultivation consumes more than half of the irrigation water used (Dawe, 2005). Unfortunately, the efficiency of water usage in this sector is very poor and never exceeds 45% (Hamdy et al., 2003). To meet this challenge many upland rice cultivars have been developed. Brazilian upland rice (*Oryza sativa* cv. IAPAQ-9), an important upland rice cultivar, was introduced to China during the 1990s and currently thousands of hectares of this variety are cultivated in the central and northern regions to combine water saving with high grain yields (Cheng et al., 2000). To the best of our knowledge all previous reports on the effects of water management practices or experiments on Cd and/or As accumulation have involved lowland rice cultivars (Arao et al., 2009; Li et al., 2009b; Hua et al., 2011; Somenahally et al., 2011) with few studies on upland rice cultivars. In the present study pot and field experiments were therefore conducted to investigate the effects of water management regimes on both As and Cd speciation and bioavailability in the soil and their accumulation in the grains of Brazilian upland rice.

## 1. Materials and methods

### 1.1. Pot experiment

Soil in the pot experiment was collected from the plow layer (0–20 cm) of arable land in the suburbs of Hangzhou City, Zhejiang Province, east China. The soil was heavily polluted

by decades of deposition of smelter dust. The soil had a pH of 6.95 and contained 35.7 g/kg of organic carbon, 3.00 g/kg of total N, 0.23 g/kg of total P and 22.8 g/kg of total K. Soil total As and Cd were 7.31 and 2.07 mg/kg, respectively. The soil was air-dried and passed through 2-mm nylon sieve. To simulate combined contamination with As, 15 mg/kg of As(V) (as  $\text{Na}_2\text{HAsO}_4$ ) in aqueous solution was mixed into the soil. Then the soil was adjusted by weight to 40% water holding capacity (WHC). After a preincubation conditioning for two weeks the soil was mixed again and placed in plastic pots each containing 1.5 kg soil. Urea, monopotassium phosphate and potassium chloride were added as basal fertilizers giving N, P and K application rates of 0.36, 0.18 and 0.27 g/kg. Additional urea was applied as topdressing at a rate of 0.12 g/kg N to all treatments at the tillering stage. Watering tubes and soil moisture samplers (Rhizon SMS, Rhizosphere Research Products, Wageningen, the Netherlands) were installed in the soil in each pot. Brazilian upland rice (*Oryza sativa* cv. IAPAQ-9) seedlings were transplanted on 15 June 2009 and the water treatments started two days later. There were four water treatments: (1) aerobic, in which the soil was maintained at 70% WHC throughout the growth period; (2) flooding, in which a 2 cm layer of water was maintained on the soil surface throughout the growth period; (3) intermittent irrigation, in which the soil was flooded with a 2 cm layer of water and then the water layer was allowed to decrease gradually through evaporation and plant uptake; when the soil was dry and similar to the 'aerobic' treatment it was flooded again; and (4) intermittent-aerobic, in which the intermittent irrigation was used until the heading stage (26 August) and then changed to aerobic treatment. There were four replicate pots for each treatment. About 10 mL of soil solution was extracted from each pot through a moisture sampler using a disposable plastic syringe on day 11 (early growth stage), day 49 (tillering stage) and day 101 (maturity stage) after the water treatments. To obtain enough solution in the aerobic treatment the water content of the soil was increased to 75% of WHC one night in advance of sampling. Plants were harvested on 22 September. The soil in all water treatments was drained off two days before harvest. Soil acetate-extractable metal concentrations were determined after harvest.

### 1.2. Field experiment

The field experiment was conducted in 2010 in the suburbs of Hangzhou City, Zhejiang Province, east China. The soil had a pH of 5.30 and contained 16.9 g/kg organic carbon, 1.46 g/kg of total N, 0.68 g/kg of total P and 10.2 g/kg of total K. Soil total As and Cd were 6.49 and 0.48 mg/kg, respectively. The soil was slightly polluted by Cd according to the Chinese Soil Environmental Standard (GB 1995-15618). Brazilian upland rice (IAPAQ-9) seeds were sown on 28 May and the seedlings were transplanted (25 cm × 25 cm) on 21 June. The basal nutrients were applied one day before transplanting at a dosage of 375 kg/ha of mixed fertilizer (N:P<sub>2</sub>O<sub>5</sub>:K<sub>2</sub>O weight ratio of 15%:15%:15%). The first topdressing was applied on 1 July (10 days after transplanting) at a dosage of 120 kg/ha of urea. The second topdressing was applied on 7 July at a dosage of 150 kg/ha of urea, 150 kg/ha of mixed fertilizer and

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