Chemosphere 165 (2016) 478–486

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Effect of silicate on arsenic fractionation in soils and its accumulation in rice plants

Chuan Wu [a], Qi Zou [a], Sheng-Guo Xue [a, *], Wei-Song Pan [b, **], Xu Yue [b], William Hartley [c], Liu Huang [a], Jing-Yu Mo [a]

[a] School of Metallurgy and Environment, Central South University, Changsha, 410083, China
[b] College of Bioscience and Biotechnology, Hunan Agricultural University, Changsha, 410128, China
[c] Crop and Environment Sciences Department, Harper Adams University, Newport, Shropshire, TF10 8NB, United Kingdom

HIGHLIGHTS

- Si addition significantly increased root and grain biomass.
- Si reduced well-crystallized hydrous oxides of Fe and Al and residual phase As.
- Si addition decreased As concentrations in rice roots, straws and husks.
- Indica genotypes transported and accumulated less As than the hybrid genotypes.
- Si fertilization decreased DMA and iAs in rice straws, husks and grains.

ARTICLE INFO

Article history:
Received 15 January 2016
Received in revised form
6 September 2016
Accepted 15 September 2016
Available online 30 September 2016

Handling Editor: X. Cao

Keywords:
Arsenic
Arsenic fractionation
Radial oxygen loss
Rice
Silicate

ABSTRACT

Four rice genotypes, two hybrid and two indica, were selected to investigate the effects of silicate (Si) application on arsenic (As) accumulation and speciation in rice and As fractionation in soil. There were significant differences in root, straw and grain biomass among genotypes ($p < 0.05$), and Si application significantly increased root ($p < 0.05$) and grain biomass ($p < 0.001$). Silicate addition reduced the proportion of As associated with well-crystallized hydrous oxides of Fe and Al and residual phases, whilst increasing the proportions of specifically-sorbed As and As associated with amorphous and poorly-crystalline Fe and Al hydrous oxides. Furthermore, the results indicated that the fraction proportions of non-specifically sorbed, specifically-sorbed, and associated with amorphous and poorly-crystalline hydrous oxides of Fe and Al in rhizosphere soils, were greater than non-rhizosphere soils. Silicate application had a significant effect decreasing total As concentrations in root ($p < 0.005$), straw ($p < 0.05$) and husk ($p < 0.001$) of rice plants. The effect of Si on reducing As accumulation in rice leaves was revealed by SXRF. Indica genotypes transported and accumulated less As than hybrid genotypes. Both percentage and concentration of iAs were lower in indica genotype XFY-9 than in hybrid genotype XWX-12. Silicate reduced iAs and DMA by 21% and 58% in grain (polished) respectively. DMA may have a greater translocation capacity from straw to grain (polished) than inorganic As. The study provides the potential for understanding As uptake mechanisms in rice and mitigating the health risks posed by As contamination in paddy fields.

1. Introduction

Chronic and acute arsenic (As) exposure from either drinking water or the food chain has resulted in adverse health impacts such as cancers, neurological and cardiovascular diseases (Stone, 2008; Guo et al., 2009; Martinez et al., 2011). Irrigation of paddy fields with As-rich groundwater and mining activities have caused serious contamination of paddy soils (Huang et al., 2006; Wang et al., 2015; Xue et al., 2016). Liao et al. (2005) reported that As concentrations in rice grain grown in As-contaminated soils reached 7.5 mg/kg. Generally, rice is cultivated in flooded paddy soils (Meharg and Zhao, 2012; Pan et al., 2014). Under anaerobic

* Corresponding author.
** Corresponding author.
E-mail addresses: wuchuan@csu.edu.cn (C. Wu), sgxue@csu.edu.cn (S.-G. Xue), panweisong@hunau.edu.cn (W.-S. Pan).

http://dx.doi.org/10.1016/j.chemosphere.2016.09.061
0045-6535/

conditions, the mobilization and bioavailability of As is greatly elevated, as large concentrations of As are released into porewaters due to the reductive dissolution of Fe (hydr)oxides regulated by iron-reducing bacteria, and arsenate (As(V)) reduction to arsenite (As(III)), which is less sorbed (Roberts et al., 2011; Stroud et al., 2011; Peng et al., 2016). In addition, As(III) uptake and accumulation is more efficient in rice compared to other crops due to As(III) translocation occurring through a strong silicon uptake pathway (Su et al., 2009; Zhao et al., 2013a,b; Pan et al., 2014), thereby resulting in greater As concentrations in rice grain (Zhu et al., 2008). Studies have also shown that rice consumption is a major source of inorganic As (iAs) in the human diet (Meharg et al., 2009; Jia et al., 2012; Su et al., 2009).

Owing to the differences in toxicity and mobility of As species, total As concentrations are insufficient to indicate As bioavailability and toxicity in soils (Huang et al., 2015). Arsenic mobility, bioavailability, and toxicity largely depends on the chemical forms and types of binding (Novoa et al., 2007; Yang et al., 2016). In order to understand the bioavailability and toxicity of As to rice plants, As fractionation in soils must be understood (Li et al., 2007); this can be accomplished by using different extraction reagents, such as with sequential extraction procedures, to determine the chemical forms of As in soils (Wu et al., 2015). These procedures can also be used to predict changes in As mobility from various solid phases following amendment additions such as silicon (Si) (Wenzel et al., 2001).

Numerous studies have shown that silicate (Si) application not only increases rice yield, but also suppresses uptake and accumulation of As in rice grains, though Si was not considered as an essential element of rice (Li et al., 2009a; Seyfferth and Fendorf, 2012; Fleck et al., 2013). In flooded soils, rice is inherently efficient at taking up and transferring As(III) (Su et al., 2009) due to the translocation of As(III) into rice via silicon transport systems (transporters Lis1 and Lsi 2) as a silicon acid analogue (Ma et al., 2006, 2008; Chen et al., 2012). Transporter Lis1 acts as a major uptake channel for As(III) in rice plants and Lsi 2 plays an essential role in mediating As(III) translocation to shoots and subsequent accumulation in the grains (Ma et al., 2006, 2008). Consequently competition for uptake and translocation between Si and As(III) occurs, and hydroponic experiments have demonstrated that addition of Si reduced As uptake and accumulation in rice (Guo et al., 2005, 2007; Tripathi et al., 2013). Fleck et al. (2013) reported that Si application reduced As concentrations by 22% in brown and polished rice grains by suppressing As(III) transport. Li et al. (2009a) revealed that Si addition reduced iAs concentrations by 59% and increased DMA concentrations by 39% in rice grains. However, due to similar physicochemical properties, Si may also compete against As(III) for retention sites on soil minerals. It was found that silicate reduced arsenite adsorption rates and competed for adsorption sites, thus increasing As concentrations in soil solutions (Luxton et al., 2008; Lee et al., 2014).

The present study aimed to investigate the effect of Si on As mobility and bioavailability to rice with different radial oxygen loss (ROL) rates in rhizosphere and non-rhizosphere soils and to determine the effect of Si on As fractionation in soil, As uptake, translocation and speciation in rice plants.

2. Materials and methods

2.1. Materials

Pot experiments were conducted with four rice genotypes, comprising of hybrid genotypes Xiangfengyou 9 ('XFY-9') and T-you207 ('TY-207') and indica subspecies Xiangwanxian 17 ('XWX-17') and Xiangwanxian 12 ('XWX-12') which were obtained from Hunan Agricultural University. The four rice genotypes ROL values are as follows, 9.55, 15.41, 19.76 and 27.00 μmol O_2 g^{-1} root dry weight h^{-1} respectively (Wu et al., 2015). Rice seeds were sterilized (30% H_2O_2) for 15 min, and then thoroughly washed with deionized water. They were then germinated in petri dishes containing moist filter paper for three days. Subsequently the seedlings were cultivated in Kimura B nutrient solution for two weeks.

The soils used in this investigation were obtained from a paddy field (1–20 cm depth) located at the Central South University, China. The soils had a sandy texture, a pH of 6.6 and contained 9.4 mg/kg pseudo-total As. After being air-dried at room temperature, the soils were ground and sieved (<2 mm). Basal fertilizers were added to soils and mixed thoroughly (P as $CaH_2PO_4 \cdot H_2O$ at 0.15 g/kg P_2O_5, K as KCl at 0.2 g/kg K_2O, and N as CO $(NH_2)_2$ at 0.2 g/kg N) (Wu et al., 2011).

2.2. Pot trail under waterlogged conditions

Soils were supplied with arsenate solution ($Na_2HAsO_4 \cdot 12H_2O$) at 60 mg As/kg. Silicon was added as a silica gel which provided a sparingly soluble source of Si for rice growth (Seyfferth and Fendorf, 2012). Treatments were conducted as follows:

Control: no As or Si
Treatment A: 60 mg/kg As only, no Si (Si0)
Treatment B: 60 mg/kg As and 10 mg/kg Si (Si10)
Treatment C: 60 mg/kg As and 20 mg/kg Si (Si20)
Treatment D: 60 mg/kg As and 40 mg/kg Si (Si40).

Soils were mixed and allowed to equilibrate for two weeks, and the seedlings were subsequently transplanted into polyethylene pots (20 cm diameter, 20 cm high) filled with 3.5 kg of the treated soils. All treatments were carried out in triplicate.

Following planting, soils were saturated with water and the water level was maintained 2–3 cm above the soil surface until harvest. Pot experiments were performed in the greenhouse with controlled temperature (20/25 °C, night/day) and relative humidity (70%). Natural sunlight was supplemented with sodium light (1200 Lux), providing a light period of 12 h per day. After maturity the rice plants were harvested and subsequently separated into grain (polished), husks, straw and roots. The straw harvested from below the water level was discarded due to contamination by the irrigation water. Plant tissues were washed with tap water and then with deionized water. From the plant tissues subsamples were collected and freeze-dried at −20 °C in order to preserve the As species prior to determination and the remaining samples were oven-dried at 70 °C for total analysis. Biomass (dry weight) was also determined for root, straw and grain.

2.3. Sequential extraction of As

After harvest, rhizosphere and non-rhizosphere soils were collected to determine As fractionation using the sequential extraction procedure described by Wenzel et al. (2011). Soil samples (1.0 g) were weighted into 50 ml centrifuge tubes and 25 ml of each extracting reagent was added sequentially. The sequential extraction processes involved five stages as follows:

1) 0.05 mol/L $(NH_4)_2SO_4$ at 20 °C for 4 h;
2) 0.05 mol/L $NH_4H_2PO_4$ at 20 °C for 16 h;
3) 0.2 mol/L NH_4+-oxalate buffer in the dark at pH 3.25 and 20 °C for 4 h;
4) 0.2 mol/L NH_4^+-oxalate buffer + ascorbic acid at pH 3.25 and 96 °C for 0.5 h;
5) HNO_3/H_2O_2 with microwave digestion.