Chemosphere 183 (2017) 44–52

Contents lists available at ScienceDirect

Chemosphere

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

Accumulation, translocation and conversion of six arsenic species in rice plants grown near a mine impacted city

Li Ma [a], Lin Wang [a, b, *], Yuyu Jia [a], Zhaoguang Yang [a, b, c, **]

[a] College of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, China
[b] Hunan Provincial Key Laboratory of Efficient and Clean Utilization of Manganese Resources, Central South University, Changsha, 410083, China
[c] Center for Environment and Water Resources, Central South University, Changsha, 410083, China

HIGHLIGHTS

- AsB was detected in the rice roots and straws while AsC in the straws and grains.
- The straw iAs% increased with straw tAs concentration in a hyperbolic pattern.
- The grain iAs% was linearly and negatively dependent on grain tAs concentration.
- Demethylations of MMA and DMA were predicted when translocated from straw to grain.

ARTICLE INFO

Article history:
Received 5 March 2017
Received in revised form
4 May 2017
Accepted 15 May 2017
Available online 17 May 2017

Handling Editor: X. Cao

Keywords:
Arsenic speciation
Paddy rice
Methylation
Multiple linear regression

ABSTRACT

Paddy rice (*Oryza sativa* L.) as the staple food in China was found to be efficient in accumulating arsenic (As) due to cultivated in flooded paddy soil. Uptake and translocation of As in rice plant depended on the As species. In this work, rice plant samples including roots, straws and grains as well as rhizosphere soils were collected from paddy fields near Changsha, a mine impacted city in Southern China. The total As concentrations in the collected samples were observed in the descending order as root > soil > straw > grain. The predominant As species detected in rice plants were inorganic forms: arsenite [As(III)] and arsenate [As(V)]. Except monomethylarsonate (MMA) and dimethylarsinate (DMA), other two organoarsenicals, arsenobetaine (AsB) and arsenocholine (AsC), were also detected in rice plants. DMA and AsB were mainly formed in rice roots with the assistance of microorganisms. MMA and AsC detected in straws might be derived from methylation and oxidation of As(III). The results of multiple linear regressions indicated that the straw As species were remarkable predictors of the corresponding grain As species. Demethylation or degradation of MMA, DMA and AsC were predicted when translocated from straw to grain.

1. Introduction

Arsenic (As) as a ubiquitous trace metalloid is considered to be one of the most carcinogenic substances to human being. The As contamination in agricultural soil was primarily originated from anthropogenic sources including mining and smelting activities, fuel combustion, pesticide usage and wastewater irrigation (Zhao et al., 2015). In recent decades, elevated As levels in agricultural soil have been observed in China due to rapid industrialization and urbanization. Crops cultivated in As-contaminated soil would inevitably accumulate As in their edible and also inedible parts, increasing As exposure risk to the consumers (Zhu et al., 2008). The toxicity and bioavailability of As is mostly dependent on its species. Arsenite [As(III)] and arsenate [As(V)] categorized into inorganic As (iAs) are the most dangerous forms which were proved to be associated with various adverse effects on human health, for instance, skin, lung and bladder cancer (Rintala et al., 2014). Monomethylarsonate (MMA) and dimethylarsinate (DMA) are the predominant organic species (oAs) detected in soil and crop samples. Considered as metabolites of iAs, MMA and DMA are far less toxic than inorganic forms. Other organoarsenicals such as arsenobetaine (AsB) and arsenocholine (AsC) are non-toxic to organisms.

* Corresponding author. College of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, China.
** Corresponding author. College of Chemistry and Chemical Engineering, Central South University, Changsha, 410083. China.
E-mail addresses: linwang@csu.edu.cn (L. Wang), zgyang3@gmail.com (Z. Yang).

http://dx.doi.org/10.1016/j.chemosphere.2017.05.089

Paddy rice (*Oryza sativa* L.) is the staple food for two-thirds population of China, especially in southern area. Compared to other cereals, rice was found to be more efficient in accumulating As. This is due to the different planting pattern of rice. The bioavailability and mobility of As increased in flooded paddy soil, which led to more As transferred from soil to rice root and finally to shoots and grain (Carey et al., 2010; Su et al., 2010). Ingestion of rice grains is the major route for human exposure to As contamination. Moreover, the residual components of rice plant, such as rice husk, straw and root are partly utilized as the ingredient of food for livestock (Fu et al., 2008), which may transfer the As contamination through food chain and eventually to human body. Chronic exposure to relatively low dose of As could still pose considerable health risk to inhabitants. The allowable maximum level of iAs in rice grain regulated by China Food Standard Agency is 200 $\mu g\ kg^{-1}$ (China Food Standard Agency, 2012).

Rice plant takes up As through different pathways depending on the As species. Uptake of As(V) by rice was shown through the phosphate pathway due to their chemical similarity. As(III) with analogous properties to silicic acid was described to be taken up via aquaporin channels (Ma et al., 2007). Same as As(III), MMA and DMA share the common silicic acid pathway from soil to rice plant (Li et al., 2009). The dominant As species in paddy soil are As(III) and As(V) while As(III) and DMA are dominant forms detected in rice grain (Ma et al., 2017a). Whether higher plants are capable to convert iAs into methylated forms is still unsolved (Zhao et al., 2010). However, microbial methylation was demonstrated to play a significant role in As interconversion and methylation (Zhao et al., 2013). None of methylated As was detected in rice plants grown under sterile conditions without addition of MMA or DMA (Lomax et al., 2012). The As distribution in the rice root, straw and grain was observed in the descending order as root » stem/leaf > grain (Smith et al., 2008). This might be due to the retention of As in rice root which restricted As translocation to other parts of rice plant (Amaral et al., 2013). Moreover, the methylated As with relatively low uptake efficiency were observed to possess higher translocation efficiency in rice grain than iAs (Raab et al., 2007). The percentage of DMA increased with the total As concentration increasing in rice grains (Ma et al., 2016a). On the contrary, iAs prefers to accumulate in roots, stems and leaves (Zhao et al., 2013).

Hunan Province located in Southern China is considered as the non-ferrous center for this country. The environment of Hunan Province suffers seriously from As and heavy metal contaminations due to long-term mining and smelting activities (Ma et al., 2015). Furthermore, Hunan Province is one of the largest rice-producing regions of China. Our previous survey on As contamination in rice grains from Hunan Province indicated elevated As levels near industrial and economic areas, especially in Changsha City, the capital of Hunan Province (Ma et al., 2016a). In this study, the rice plants consisting of grains, straws and roots, and also the paddy soils in the rhizosphere were collected from the mine impacted areas near Changsha City. Six As species including As(III), As(V), MMA, DMA, AsB and AsC were extracted and determined in rice plant samples. The accumulation and translocation of As in rice were investigated through statistical analysis.

2. Materials and methods

2.1. Sample collection and preparation

The rice plant and soil samples were collected from 27 paddy fields near Changsha City, Southern China during September to October 2015 (Fig. 1). In each field, three subsamples were harvested to combine as one representative sample. The combined sample was then separated into grain (with husk), straw and root (with soil in the rhizosphere) and sealed in respective polyethylene bags. After sent to the laboratory, soil samples were removed carefully from the roots. They were then air dried, ground and passed through a 0.15 mm nylon sieve. Grain (with husk), straw and root samples were washed thoroughly by tap water then were rinsed by ultrapure water several times to remove dust. All the samples were air dried and were further oven dried at 50 °C for 48 h. After the samples were totally dried, husk and raw grain were separated. The raw grain, straw and root samples were ground and passed through a 0.2 mm nylon sieve to obtain homogeneous powders severally.

2.2. Digestion and analysis of total As

The soil samples were digested following the USEPA Method 3051A with minor modification (USEPA, 2007). Briefly, 0.100 g of soil sample was dissolved by 12 mL mixed acid of HNO_3 and HCl (3:1, *v*/*v*) through microwave digestion at 210 °C for 30 min. The digestion procedure for grain, straw and root samples were described in our previous reports using microwave assisted methods (Ma et al., 2016a). The digested solution was diluted to 50 mL using ultrapure water. Prior to analysis, the sample was filtered through a 0.22 μm membrane. Total As (tAs) was determined by ICP-MS (Agilent 7700×). The polyatomic interference on *m*/*z* 75 from argon chloride (i.e. $^{40}Ar^{35}Cl^{+}$) was reduced by a collision/reaction cell (CRC) (Sun et al., 2015). A method blank was carried throughout the entire pretreatment for each analytical batch. Certified reference materials (CRMs) GBW-07443 (paddy soil), GBW-10045 (rice flour) and GBW-10049 (green onion) purchased from CRM/RM information center (Beijing, China) were employed to verify digestion efficiency in soil, grain and straw, respectively. The determined As concentrations were within 10% of the certified values.

2.3. Extraction and speciation of As in grain

The grain samples were extracted according to the procedure developed in our previous study (Ma et al., 2016b). After cooling down and centrifuged, the supernatant was filtered by a syringe filter. Six As species including As(III), As(V), MMA, DMA, AsB and AsC were simultaneously separated and determined by the HPLC-ICP-MS method (Ma et al., 2016c). Table S1 demonstrated the detailed operating parameters for this method. Figure S1(a) showed the typical chromatograph of As species extracted from the real rice grain sample in this study. The extraction efficiency and species stability were verified by standard reference materials SRM 1568b (NIST, Gaithersburg, MD, USA). The results were shown in Table S2. Satisfactory efficiencies were obtained for all the detected As species.

2.4. Extraction and speciation of As in straws and roots

The straw and root samples were extracted by the microwave assisted method reported before with minor modification (Ma et al., 2017b). Approximately 0.2 g of fine straw powders or 0.1 g of root powders were weighed for extraction. Six As species were determined by the HPLC-ICP-MS method. The typical chromatograph of As species extracted from the straw sample in this study was demonstrated in Figure S1(b). There is no certified reference material currently available for arsenic species in straw or root sample. In this study, the CRM GBW-10049 (green onion) was employed to examine the extraction efficiency, which was calculated based on the ratio between the extracted As species concentration and the certified tAs concentration. The results were in the range of 88–105%.