



Geographical variations of cadmium and arsenic concentrations and arsenic speciation in Chinese rice[☆]

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ABSTRACT

Rapid industrialization in China in recent decades has resulted in soil contamination in some areas, raising the concern about food safety. Consumption of rice represents a major exposure route for the toxic elements cadmium (Cd) and arsenic (As). We collected 160 polished rice from local markets in 20 provinces in China and determined total Cd and As concentrations and As speciation. Total Cd concentration ranged from below the detection limit to 0.77 mg kg⁻¹, with 10% of the samples exceeding the Chinese limit (0.2 mg kg⁻¹). Rice Cd concentration showed a distinct geographical pattern, increasing from low levels in the north to high levels in the south of China. Median daily Cd intake from rice varied from 0.01 μg kg⁻¹ body weight in the north to 0.61 μg kg⁻¹ body weight in the south of China, representing between 1% and 73% of the tolerable daily intake (TDI) recommended by FAO/WHO. The highest median Cd intake from rice was in Hunan province with 2 times TDI. Total As concentration ranged from 0.011 to 0.186 mg kg⁻¹, with inorganic As (iAs) and dimethylarsinic acid (DMAs) on average accounting for 69% and 31%, respectively. All samples were below the Chinese limit for iAs in rice (0.2 mg kg⁻¹). There was no clear geographical pattern in rice total As concentration, but rice produced in northeastern China contained higher percentages of DMAs and lower percentages of iAs. This study highlights a high risk of Cd exposure from rice consumption for the population of southern China and suggested strategies for reducing Cd accumulation in rice crop.

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1. Introduction

Rice is a staple food for about 50% of the global population. However, consumption of rice also contributes substantially to the intakes of the toxic elements cadmium (Cd) and arsenic (As) (Clemens et al., 2013; Zhao et al., 2010). For example, a recent total diet study showed that rice contributes 56% of the total dietary Cd intake for the general population in China and up to 65% for the population in southern China (Song et al., 2017). Cadmium intakes from rice in Bangladesh and Sri Lanka were found to be high in a subset of their populations (Meharg et al., 2013), approaching or even exceeding the tolerable daily intake (TDI, 0.83 μg kg⁻¹ body weight) recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) (Joint FAO/WHO Expert Committee on Food Additives, 2010). The average dietary intakes of Cd in Asian

countries are higher than those in Europe or the USA, likely reflecting the amounts of rice consumption (Wang et al., 2017). Similarly, rice is the dominant source of inorganic As (iAs) for populations in south Asian countries where As concentration in drinking water is not elevated (Kile et al., 2007; Meharg et al., 2009). In China, rice contributes approximately 60% of the dietary intake iAs for the general population (Li et al., 2011). Chemical speciation is important when considering the health risk of As in food. Rice grain contains both iAs, mainly arsenite [As(III)], and organic As, mainly dimethylarsinic acid (DMAs) (Meharg et al., 2009; Tenni et al., 2017; Zavala et al., 2008; Zhao et al., 2013; Zhu et al., 2008). Inorganic As is considered to be much more toxic to humans than DMAs (Meharg et al., 2009; Zhao et al., 2013). Therefore, the newly introduced As limits in rice in China and European Union are based on the concentration of iAs (Ministry of Health of the People's Republic of China, 2012; The European Commission, 2015).

The reasons why rice accumulates As more efficiently than other cereal crops are now well understood. Rice is typically grown under flooded conditions. Anaerobic conditions in paddy soil are conducive to arsenate [As(V)] reduction and As(III) mobilization (Arao

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et al., 2009; Takahashi et al., 2004; Xu et al., 2008). Arsenite is then absorbed inadvertently by the membrane transporters for silicon, OsLsi1 and OsLsi2 (Ma et al., 2008). These transporters are highly expressed in rice roots. Rice roots take up Cd primarily via the manganese (Mn) transporter OsNRAMP5 (Ishikawa et al., 2012; Sasaki et al., 2012; Yang et al., 2014), which may explain why rice apparently accumulates Cd more efficiently than other cereals. However, the biogeochemical behaviors of As and Cd in paddy soils are markedly different, with the soil redox potential having the opposite effect on their mobilization (Arao et al., 2009; de Livera et al., 2011; Xu et al., 2008; Zhao et al., 2015). Management options of paddy water that decrease Cd availability in paddy soil often lead to increased As availability and vice versa (Arao et al., 2009; Hu et al., 2013). In field trials, the abilities of Cd and As accumulation in rice cultivars were found to correlate with each other negatively (Duan et al., 2017). Thus, reducing the accumulation of both Cd and As in rice grain presents a difficult challenge.

Rapid industrialization in China during the recent decades has resulted in contamination of paddy soils with heavy metals and metalloids in some regions (Zhao et al., 2015). Some areas in southern China have long histories of base metal mining and smelting, discharging substantial amounts of toxic metals and metalloids into the environment. Rice grain collected from paddy fields contaminated by mining or industrial activities often exceeds the maximum permissible limits of As and Cd (Du et al., 2013; Williams et al., 2009; Zhu et al., 2008). Local scale surveys of rice in some areas of Hunan province reported large percentages (>60%) of samples exceeding the Chinese limit of Cd (0.2 mg kg^{-1}) (Du et al., 2013; Zhu et al., 2016). The Chinese limit for Cd in rice (Ministry of Health of the People's Republic of China, 2012) is stricter than that of JECFA (0.4 mg kg^{-1}) (Codex Alimentarius Commission, 2006). This stricter limit is considered to be necessary because the amount of rice consumption by Chinese population is high, especially for the population in southern China (Zhao et al., 2015). Rather worryingly, the average dietary intake of Cd for the Chinese general population has doubled during the past 25 years from 1990 to 2015 (Song et al., 2017). The current average dietary Cd intake for the 4–11 year age group in China has already approached the level of TDI recommended by JECFA (Song et al., 2017). These reports raise a serious concern about the potential risk of dietary exposure of Cd and As, especially from the consumption of rice.

Rice is grown in China from the most southern to the most northern provinces, encompassing huge variations in soil and climatic conditions. Although some surveys of Cd or As in Chinese rice have been reported (Williams et al., 2009; Zhu et al., 2008, 2016), they are often limited in the geographical scope or lack the geographical information. The objectives of the present study were to investigate the geographical patterns of Cd and As concentrations and As speciation in rice from different regions of China and to estimate dietary intakes of Cd and inorganic As (iAs) from the consumption of rice.

2. Materials and methods

2.1. Collection of samples

We collected 160 polished (white) rice samples from local markets in 20 provinces across China where rice is grown. Only samples with known region of production were collected. Sample collection was carried out during February and March 2017, meaning that most of the rice samples were produced in 2016.

2.2. Sample preparation and analysis

Rice samples were dried at 65°C for 48 h, and ground to fine

powders used a stainless steel grinder. A preliminary test showed that grinding did not introduce contamination of Cd or As. Ground samples (0.25 g each) were digested with 5 mL of high-purity concentrated HNO_3 in a microwave digester (Ma et al., 2014). After digestion, excess HNO_3 was evaporated. The digest was diluted in 10 mL 2% HNO_3 . Within each batch of 40 samples, two duplicate samples, a reagent blank and a certified reference material (NIST 1568b rice flour) were included for quality assurance. Cd and As concentrations of the solutions were quantified by inductively coupled plasma mass spectrometry (ICP-MS, NexION 300X, Perkin Elmer, USA). Indium ($20 \mu\text{g L}^{-1}$) was added on-line to the digest solutions as an internal standard. Repeated analysis of NIST 1568b yielded Cd and As concentrations of $0.0212 \pm 0.0011 \text{ mg kg}^{-1}$ and $0.281 \pm 0.014 \text{ mg kg}^{-1}$, respectively. These values agree well with their certified values of $0.0224 \pm 0.0013 \text{ mg kg}^{-1}$ and $0.285 \pm 0.014 \text{ mg kg}^{-1}$, respectively. The detection limits for Cd and As were 0.004 mg kg^{-1} and 0.006 mg kg^{-1} , respectively.

To determine As speciation, a portion (0.5 g) of each powdered rice sample was weighed and extracted with 0.15 M high-purity HNO_3 in a microwave digester according to Zhu et al. (2008). After cooling, the extract was centrifuged at 4000 g for 15 min and filtered through a $0.22 \mu\text{m}$ membrane (mixed cellulose ester). The filtrate was divided into two portions, one without further treatment and the other subject to oxidation with H_2O_2 (filtrate/ H_2O_2 , 4/1, v/v) in order to convert As(III) to arsenate [As(V)]. Arsenic species in the solutions were analyzed using HPLC-ICP-MS (PerkinElmer Series 200 HPLC and NexION 300X). HPLC separations were performed using both anion exchange and cation exchange columns. For anion-exchange separation, a Hamilton PRP-X100 column (250 mm by 4.6 mm) was used with a mobile phase of 6.5 mM $\text{NH}_4\text{H}_2\text{PO}_4$ and 6.5 mM NH_4NO_3 (pH 6.0, flow rate 1.0 ml min^{-1}) (Xu et al., 2008). For cation exchange separation, an IonoSpher 5C (100 mm by 3.0 mm) was used with a mobile phase of 10 mM pyridine buffer (pH 2.8, flow rate 1.0 ml min^{-1}) (Zaccone et al., 2017). Germanium ($20 \mu\text{g L}^{-1}$) was added on-line after HPLC separation as an internal standard. Arsenic species were identified by retention time matching with the standard As compounds As(III), As(V), DMAs, monomethylarsonic acid (MMAs), and trimethylarsenic oxide (TMAO). The concentrations of As species were quantified using external calibration curves. Samples were also spiked with standard As compounds to verify the identity of As species. Repeated analysis of NIST 1568b yielded iAs, DMAs and MMAs concentrations of $0.086 \pm 0.002 \text{ mg kg}^{-1}$, $0.180 \pm 0.004 \text{ mg kg}^{-1}$ and $0.0120 \pm 0.0003 \text{ mg kg}^{-1}$. These values agree well with their certified values of $0.092 \pm 0.010 \text{ mg kg}^{-1}$, $0.180 \pm 0.012 \text{ mg kg}^{-1}$ and $0.0116 \pm 0.0035 \text{ mg kg}^{-1}$, respectively. The concentrations of Cd and As species were calculated on a dry weight (DW) basis.

2.3. Statistical analysis

Descriptive statistics for Cd and As concentrations in samples from different provinces are presented. Analysis of variance (ANOVA) was used to test the difference between provincial means using the SPSS software (version 20, IBM).

3. Results

3.1. Geographical variation in total Cd concentration

The concentration of Cd in Chinese polished rice samples ranged from below the limit of detection (LOD, i.e. 0.004 mg kg^{-1}) to 0.774 mg kg^{-1} , with a mean of 0.093 mg kg^{-1} and a median of 0.045 mg kg^{-1} (Table 1). For the samples containing <LOD Cd, half of the LOD was used in the calculation of the mean. Among the 160 Chinese polished rice samples, 10% had a Cd concentration

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