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Total and speciated arsenic levels in rice from China

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Although the need for policy development on arsenic (As) in rice has been recognized and a legally enforceable maximum contaminant level (MCL) for inorganic arsenic (Asi) in rice has been established in China, evidence reported in this article indicates that the risk of exposure to As for the Chinese population through rice is still underestimated. Polished rice from various production regions of China was analyzed for total As and arsenic species using HPLC–ICPMS. Total As concentration ranged 65.3–274.2 ng g\(^{-1}\), with an average value of 114.4 ng g\(^{-1}\). Four arsenic species, including arsenite (As(III)), arsenate (As(V)), dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA), were detected in most rice samples. The Asi (As(III) + As(V)) species was predominant, accounting for approximately 72% of the total As in rice, with a mean concentration of 82.0 ng g\(^{-1}\). In assessing the risk from As in rice, we found that As intake for the Chinese population through rice is higher than from drinking water, with a 37.6% contribution to the maximum tolerable daily intake (MTDI) of As recommended by World Health Organization (WHO), compared with 1.5% from drinking water. Compared to other countries, the risk for the Chinese from exposure to As through rice is more severe due to the large rice consumption in China. Therefore, not only the scientific community but also local authorities should take this risk seriously. Furthermore, more stringent legislation of the MCL for rice should be enacted to protect the Chinese consumer from a high intake of As.

Keywords: HPLC; ICP/MS; heavy metals; arsenic; rice

Introduction

Arsenic (As) is one of the most hazardous chemical elements, not only in the environment (mainly in soil and water) but also in some food (rice, seafood and milk). A high content of As in drinking water is recognized as a significant public health concern, and policies focusing on removing this chronic human carcinogen have been developed over the last two or three decades. However, recent evidence indicates that elevated As in rice may also contribute significantly to As intake (Heikens 2006). With China having the highest rice product consumption in the world and accounting for over one third of the global supply (Zhu et al. 2008a), an evaluation of the risk posed by dietary As intake through rice is essential.

Rice is generally grown under flooded conditions and accumulates As from the soil and water where As mobility is high. The transfer rate of As from soil to grain is an order of magnitude greater in rice than that in wheat or barley, leading to baseline levels of As in rice that are approximately 10-fold higher than those in other cereal grains (Williams et al. 2007). The As content in rice varies worldwide up to 60-fold, with rice from Canada having the lowest levels and levels from Taiwan being the highest (Williams et al. 2005). In many Asian regions, arsenic exposure from contaminated drinking water is considered to be a major source of As poisoning for local residents (Nguyen et al. 2009). In Europe and the United States, where only 140 g of grain product are consumed by an adult per day, rice is the primary source of As in a non-seafood diet (Schoof et al. 1999; Tao and Bolger 1999). In contrast, rice is the main diet for the 800 million people in China. The total and chemical forms of As in rice have been characterized in the Chinese market with the mean baseline concentration for Asi, which is more toxic than the methylated forms, estimated to be 96 ng g\(^{-1}\) (Zhu et al. 2008a). Little is known, however, about As exposure from rice for direct food use in Chinese consumers. Considering that 200–900 g per day rice is consumed by an adult in China, rice is potentially an important source of As exposure for the Chinese population.

In this study, the concentration of total arsenic and the four main chemical forms, including two inorganic forms (As(III), As(V)) as well as the main organic forms, were determined in polished rice from various production regions of China.
compounds (MMA, DMA), were determined in rice. The rice samples were collected from 13 provinces of China and were analyzed using HPLC coupled to ICP-MS. As levels and species in rice products in China and the safety levels for consumption are also discussed.

Materials and methods

Rice sampling and samples treatment
Twenty-one bleached white short grain rice samples were obtained from 13 provinces of China, including the three top producing provinces – Hunan, Jiangsu and Jiangxi (Rice Economy Database 2006) – as well as one brown rice sample from Fujian province. For sample preparation, as recommended by Zhu et al. (2008a), after drying at 50°C, the rice samples were individually milled and homogenized with an electric ultra-centrifugal mill, then placed into clean plastic bottles and stored at 4°C for total and speciated As analyses.

Total arsenic determination
For each determination, approximately 0.2 g of each rice sample was loaded into a PFA-lined digestion vessel with 3 ml of 35% HNO₃ and 1 ml of high-purity H₂O₂, and then samples were placed in a high-pressure microwave (Ethos 320; Milestone, Italy). As recommended, a four-stage temperature program with a maximum temperature of 180°C and a total digestion time of 31 min was used.

As measurements were carried out on an X series 7 ICP-MS instrument (Thermo Scientific USA) equipped with a concentric nebulizer and hexapole collision cell technique (CCT). ICP-MS operation conditions were as follows: radiation frequency (RF) power was set to 1350 W, carrier gas flow rate and peristaltic pump rate were 1 ml min⁻¹ and 25 rpm, respectively. The sampler and skimmer cones were made of Ni. The dwell time was set to 10 ms for total As determination.

Arsenic speciation analysis
Approximately 0.5 g of milled sample was treated with 3 ml of extraction solution. The mixture was left to incubate for 10 h at 80°C in a 10-ml capped centrifuge tube. The mixture was centrifuged; the supernatant was filtered with a 0.22-µm syringe filter and then directly injected to the HPLC–ICPMS system for speciation analysis.

As speciation analysis was done on a chromatographic system consisting of a Finnigan Spectra SYSTEM pump, SCM1000 solvent degasser and Spectra SYSTEM autosampler with 20 µl injection valve (Thermo Scientific USA). As species were separated using a PRP-X100 anion exchange column (250 × 4.1 mm, 10 µm; Hamilton, USA). A buffer solution of 10 mmol l⁻¹ NH₄H₂PO₄ and 10 mmol l⁻¹ NH₄Ac at pH 6.3 was employed as mobile phase. Carrier flow of 0.8 ml min⁻¹ was used in the isocratic mode.

An ICP-MS Thermo X Series II (Thermo Scientific, USA) equipped with a Xs cone was used as chromatographic detector. The column was directly linked to a concentric nebulizer and cooled conical spray chamber with a length of PEEK tubing ~60 cm long and 0.25-mm I.D. through a T-type interface. The operation conditions were as follows: RF power was set to 1400 W, carrier gas flow rate and peristaltic pump rate were 1 ml min⁻¹ and 15 rpm, respectively, while m/z 75 and 72 was monitored for As and Ge, respectively.

Quality assurance

Total As determination
To validate the measurement of As in rice, GBW CRM 10010 (Chinese Academy of Geological Sciences, Beijing, China) rice flour was used as certified standard reference material (SRM) for quality assurance. The certified and measured As concentrations were 102.0 ± 8.0 and 109.9 ± 7.2 ng g⁻¹, respectively. The GBW CRM 10010 was dried at 50°C for 6 h prior to microwave digestion. Thus, mild heat treatment did not affect As content.

Arsenic speciation analysis
Speciation analysis required extraction of the species of interest into the solvent prior to identification and quantification. For validation of the speciation analysis, GBW CRM 10010 rice flour was also used as a certified SRM. Many publications have focused on the extraction efficiency of different solvents for As species from different matrices (Pizarro et al. 2003; Narukawa et al. 2008). Acids, such as trifluoroacetic acid (TFA), acetic acid and nitric acid, and solvent mixtures, including water, have been used to extract As species (Mihucz et al. 2007; Mir et al. 2007). The most popular solvent for the efficient extraction of As is TFA, in spite of the partial reduction of As(V) to As(III) during the procedure (Heitkemper et al. 2001). Table 1 indicates that the extraction efficiencies of different extraction solvents varied from 75.7 to 95.6%. When 2 mol l⁻¹ TFA, 50% methanol and a solvent mixture including 50% methanol and 0.2 mol l⁻¹ TFA were used as extraction solvent, the relative standard deviation was larger than that of other solvents due to the high volatility of these solvents. Therefore, these three solvents failed to extract As efficiently. Even though...
2% HNO₃ has been used successfully to extract As from terrestrial and marine plant matrices with high extraction efficiencies (Foster et al. 2007), our results revealed that As(V) content after extraction with 1% HNO₃ was 7.9/5.1 ng g⁻¹, lower than that measured after extraction with 0.2 mol l⁻¹ TFA (11.0/0.3 ng g⁻¹). The 0.2 mol l⁻¹ TFA solution successfully extracted As from rice powder, therefore, it was used as the extraction solvent.

To monitor the stability of the ICP-MS analytical system, a 5 ng ml⁻¹ Ge solution was added to the column as an internal standard for As speciation determinant, as the initial ion potential energy of Ge (7.899 eV) is similar to that of As (9.81 eV).

### Results and discussion

#### Total arsenic concentrations in rice

The concentrations of total arsenic in rice from different producing areas are shown in Figure 1. The mean concentration of total As was 114.4 ng g⁻¹, which is very close to the average level in China (Zhu et al. 2008a), but much lower than levels from other countries, such as 140 ng g⁻¹ in Thailand, 120 ng g⁻¹

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**Table 1. Summary of arsenic species characterization and extraction recoveries for GBW10010 rice certified reference material.**

<table>
<thead>
<tr>
<th></th>
<th>Certified total as (ng g⁻¹)</th>
<th>As(III) (ng g⁻¹)</th>
<th>As(V) (ng g⁻¹)</th>
<th>DMA (ng g⁻¹)</th>
<th>MMA (ng g⁻¹)</th>
<th>Sum of as species (ng g⁻¹)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultra-pure water</td>
<td>109.9</td>
<td>46.1±2.4</td>
<td>15.6±1.6</td>
<td>19.4±0.8</td>
<td>2.0±0.3</td>
<td>83.2±4.4</td>
<td>75.7±4.0</td>
</tr>
<tr>
<td>Acetic acid (1%)</td>
<td>109.9</td>
<td>47.7±0.9</td>
<td>15.2±0.4</td>
<td>21.9±0.6</td>
<td>1.3±0.2</td>
<td>86.2±0.1</td>
<td>78.4±0.1</td>
</tr>
<tr>
<td>Nitric acid (1%)</td>
<td>109.9</td>
<td>61.6±4.5</td>
<td>7.9±5.1</td>
<td>22.2±0.9</td>
<td>1.4±0.6</td>
<td>93.0±4.4</td>
<td>84.6±4.0</td>
</tr>
<tr>
<td>TFA (0.2 mol l⁻¹)</td>
<td>109.9</td>
<td>64.5±0.9</td>
<td>11.0±0.3</td>
<td>24.4±0.6</td>
<td>1.4±0.0</td>
<td>101.2±1.5</td>
<td>92.1±1.4</td>
</tr>
<tr>
<td>TFA (2 mol l⁻¹)</td>
<td>109.9</td>
<td>61.9±4.0</td>
<td>17.4±3.0</td>
<td>24.0±1.8</td>
<td>1.8±0.4</td>
<td>105.1±8.1</td>
<td>95.6±7.3</td>
</tr>
<tr>
<td>Methanol (50%)</td>
<td>109.9</td>
<td>53.6±7.7</td>
<td>12.8±2.0</td>
<td>26.3±1.9</td>
<td>2.0±0.5</td>
<td>94.8±8.9</td>
<td>86.3±8.1</td>
</tr>
<tr>
<td>Methanol (50%)/TFA (0.2 mol l⁻¹)</td>
<td>109.9</td>
<td>62.6±5.6</td>
<td>11.8±2.9</td>
<td>27.7±3.0</td>
<td>1.7±0.4</td>
<td>103.8±11.9</td>
<td>94.5±10.8</td>
</tr>
</tbody>
</table>

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Figure 1. Total arsenic in rice from different provinces (HN, Hunan; GZ, Guizhou; CQ, Chongqing; YN, Yunnan; XJ, Xiangjiang; GS, Gansu; GX, Guangxi; FJ, Fujian; AH, Anhui; JX, Jiangxi; JS, Jiangsu; JL, Jilin; HLJ, Heilongjiang).
in Bangladesh, 190 ng g\(^{-1}\) in Japan, 180 ng g\(^{-1}\) in Spain, 270 ng g\(^{-1}\) in USA, 280 ng g\(^{-1}\) in France, and 160 ng g\(^{-1}\) in Italy (Figure 2). According to Zavala and Duxbury (2008), the typical range should be 80–200 ng g\(^{-1}\) for As concentration in rice; 17 of 22 rice samples in this survey fell within this range. However, four (~18% of all samples) were below this range and one was above this range. Therefore, most rice from China is not as contaminated as in many other countries.

The lowest As levels were found in the rice samples from Jiangsu and Jilin, while the highest levels were in rice from Hunan, Anhui and Guangxi. Because Hunan is the main rice-producing province, accounting for 12.7% of total rice production in China in 2006 (Rice Economy Database 2006), it is important to investigate the As level in rice grown in this province. The mean concentration of total As in rice from Hunan was 199.1 ± 106.3 ng g\(^{-1}\), which is higher than that from other provinces and the allowable MCL of 150.0 ng g\(^{-1}\) for As in rice in China. Moreover, the sample with highest As content of 274.2 ± 1.0 ng g\(^{-1}\) in this survey, which is outside the reported typical range of 80–200 ng g\(^{-1}\) (Zavala and Duxbury 2008), was also found from Hunan province. The high As levels in this sample might be a result of As-contaminated soil in the proximity of a heavy metal mine. Therefore, a detailed As speciation analysis was conducted.

**Figure 2.** Arsenic content in rice from eight countries (data of China are our results and others are from Zhu et al. (2008a)).

**Figure 3.** Arsenic speciation of Chinese rice.

### Arsenic speciation in rice

Speciation analysis of arsenic in rice utilized a hyphenated HPLC–ICP–MS technique, the results are summarized in Figure 3. One species of As\(_i\) (As(III)) was detected in all rice samples and represented the most abundant arsenic species extracted. Since the ability of plants, especially rice, to methylate As\(_i\) has not been conclusively demonstrated (Meharg and Hartley-Whitaker 2002), DMA in rice mainly comes from uptake of DMA through the soil, although the methylation of inorganic As within the plant as a detoxification pathway cannot be disregarded. In our result, DMA was found in all of rice samples. When TFA is used as the extraction solvent, As(V) can be transformed into As(III) during the extraction process (Heitkemper et al. 2001). Thus, we investigated the As\(_i\) species, instead of just As(III) and As(V).
The concentrations of $\text{As}_i$ in all rice samples were in a range 48.5–216.6 ng g$^{-1}$, with an average value of 82.0 ng g$^{-1}$.

Depending on As speciation (DMA and $\text{As}_i$ type), there are two rice production groups: one with an increased total As level, mainly associated with a higher level of DMA, and one related to increasing $\text{As}_i$ (Zavala et al. 2008). The main species in this survey was $\text{As}_i$, which was linearly correlated with the total As ($r^2 = 0.94$), as shown in Figure 4. This finding is consistent with previously reported results that the $\text{As}_i$ is the major type found in Asian rice products, while the DMA is the main type in rice from the USA (Zavala et al. 2008). Because the $\text{As}_i$ type of rice represents potentially a greater health risk than the DMA type, we assessed the health risk of As exposure of rice for the Chinese population.

**Risk assessment of exposure to arsenic through rice**

Even though As levels in most of the rice did not exceed the MCL, the health risk for the Chinese population needs to be investigated. Although As can enter the human body via many routes, oral intake is the most significant. Critical sources of As intake for the general Chinese population are the drinking water and diet. The contribution to the MTDI of As is one of the most important parameters for assessing the health risk of the various sources. In China, Xu et al. (2006) estimated that the average daily intake of $\text{As}_i$ through drinking water is 1.83 µg per day, only 1.5% of the MTDI of $\text{As}_i$ recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) in 1983. Assuming a consumption rate of 550 g per day of dry weight of rice for Chinese people, the average daily intake of $\text{As}_i$, though rice is 45.1 µg per day based on the average value of $\text{As}_i$ in rice in our result, which is 37.6 % of the MTDI and about 25 times higher than the value for drinking water. This study shows that rice is the primary source of As in China and may even be underestimated, since only a few areas with a predominant seafood diet were considered.

The contributions to MTDI of rice from different countries or regions are listed in Figure 5, showing that $\text{As}_i$ in Chinese rice is a high contributor to MTDI, even more so than in Bangladesh, which has heavily As-contaminated rice. Even though rice from France and the US had the highest total As levels (Figure 2), the contribution of $\text{As}_i$ to the MTDIs ranged 21–36% for Europe, only 8–50% for the USA, but 22.3–99.3% for China, as shown in Figure 5. Therefore, the health effects resulting from dietary exposure of $\text{As}_i$ from rice are more severe in China than in other countries.

Considering that rice is the main food for Chinese people and rice consumption is high throughout an entire Chinese lifetime, the cumulative As exposure was estimated to evaluate the health risk from $\text{As}_i$ in rice. Total levels of $\text{As}_i$ from rice for a person’s entire life was estimated using the following equation (Agusa et al. 2006):

$$\text{Cumulative } \text{As}_i \text{ intake (ng)} = [\text{As}_i \text{ level in rice (ng g}^{-1})] \times [\text{average lifetime (69.98 year)}] \times [\text{Ingestion rate of rice (365 days year}^{-1})] \times [\text{rice consumption (550 g day}^{-1})].$$

The cumulative $\text{As}_i$ ingestion from rice for the lifetime of a Chinese consumer is 1152.0 mg, which is very close to the threshold levels for internal cancer from As exposure for Fowler’s solution patients, as summarized by Bates et al. (1992). Due to high rice consumption by Chinese people, exposure to As from...
rice is much more serious, even though the total and inorganic As levels in rice were not as high as other counties. A similar situation may occur in other Asian countries where rice is one of the main foods.

With respect to As$_i$, the legally enforced MCLs of 150 ng g$^{-1}$ for rice (CFSA 2005) and 10 µg L$^{-1}$ for drinking water (CSDWQ 2006) have been adopted in China. Approximately 130 million metric tons of milled rice are consumed each year in China, accounting for nearly one third of the total global rice consumption (Zhu et al. 2008a). For rice subsistence diets with an average daily consumption ranging 200–900 g per day of dry rice weight (Zhu et al. 2008b), As$_i$ exposure would equate to a daily exposure of 16.4–73.8 µg, which is below the tolerable daily intake of 150 µg recommended by Torres-Escribano et al. (2008), but exceeding the daily exposure of 10 µg based on the MCL of drinking water. While As$_i$ in drinking water is highly regulated internationally, more stringent regulations for As$_i$ in rice than the current MCL of 150 ng g$^{-1}$ should be established in China to protect consumers from high As exposure through their diet.

**Conclusions**

The total level of As in rice samples ranged 65.3–274.2 ng g$^{-1}$, with an average of 114.0 ng g$^{-1}$. Our analysis showed that there are only four arsenic species (As(III), DMA, MMA, As(V)) in the majority of the Chinese rice samples, with the As$_i$ species being the most abundant extractable species with concentrations of 48.5–216.6 ng g$^{-1}$. Based on our analysis, combined with the risk assessment, we conclude that the Chinese population have a high As exposure from rice. Therefore, it is highly recommended that the legally permitted MCL for As$_i$ in rice be more stringently enforced in China to protect consumers’ health.

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**References**


