Survey of arsenic and its speciation in rice products such as breakfast cereals, rice crackers and Japanese rice condiments

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Abstract

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Rice product
High inorganic As

Rice has been demonstrated to be one of the major contributors to arsenic (As) in human diets in addition to drinking water, but little is known about rice products as an additional source of As exposure. Rice products were analyzed for total As and a subset of samples were measured for arsenic speciation using high performance liquid chromatography interfaced with inductively coupled plasma-mass spectrometry (HPLC–ICP-MS). A wide range of rice products had total and inorganic arsenic levels that typified those found in rice grain including, crisped rice, puffed rice, rice crackers, rice noodles and a range of Japanese rice condiments as well as rice products targeted at the macrobiotic, vegan, lactose intolerant and gluten intolerance food market. Most As in rice products are inorganic As (75.2–90.1%). This study provides a wider appreciation of how inorganic arsenic derived from rice products enters the human diet.

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1. Introduction

A number of studies have indicated that in countries not suffering from high levels of As in drinking water, rice is the major contributor to inorganic As in the human diet (Meacher et al., 2002; Meliker et al., 2006; Williams et al., 2007a). This is in part due to rice being particularly efficient at taking up As from soil (Williams et al., 2007b) and exacerbated in major rice growing regions of the world with elevated As in paddy soil caused by anthropogenic contamination (Meharg 2004; Williams et al., 2005, 2006, 2007a,b).

A number of surveys have reported the contamination of As in rice (Schoof et al., 1998; Heitkemper et al., 2001; Alam et al., 2003; Kohlmeyer et al., 2003; Meharg and Rahman 2003; D’Amato et al., 2004; Meharg 2004; Williams et al., 2005). Recent studies have also shown that baby rice (precooked and milled rice) and rice milk (enzyme extracted rice product used as a dairy and soya milk alternative) have elevated inorganic arsenic contents (Meharg et al., 2008a,b).

Wholegrain and polished rice, and bran are utilized in a very wide range of foods such as: crisped rice, puffed rice, rice crackers, cereal bars, rice flour, rice noodles, fermented condiments (miso and mirin), rice malt, rice wine, rice bran oil. Some products are widely consumed by the general public, such as crisped and puffed rice, cereal bars, while others are highly popular in Japanese cooking, and have been subsequently been adopted by health conscious dietary regimes such as macrobiotic, vegan, gluten and dairy intolerance regimes. However, little research has focused on rice products as an additional source of exposure. The aim of the present study was to examine the total and inorganic As content of a range of rice products to quantify sources of inorganic As into the human diet from rice, and specifically to identify

<table>
<thead>
<tr>
<th>Product</th>
<th>N</th>
<th>Average concentration</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crisped rice</td>
<td>3</td>
<td>0.21 mg/kg</td>
<td>0.01</td>
</tr>
<tr>
<td>Puffed rice</td>
<td>2</td>
<td>0.24 mg/kg</td>
<td>0.02</td>
</tr>
<tr>
<td>Rice malt</td>
<td>3</td>
<td>0.21 mg/kg</td>
<td>0.08</td>
</tr>
<tr>
<td>Noodles</td>
<td>6</td>
<td>0.12 mg/kg</td>
<td>0.09</td>
</tr>
<tr>
<td>Sweats</td>
<td>5</td>
<td>0.14 mg/kg</td>
<td>0.02</td>
</tr>
<tr>
<td>Rice cracker</td>
<td>11</td>
<td>0.28 mg/kg</td>
<td>0.03</td>
</tr>
<tr>
<td>Amazake</td>
<td>1</td>
<td>0.16 mg/kg</td>
<td>0.01</td>
</tr>
<tr>
<td>Bran oil</td>
<td>3</td>
<td>0.03 mg/l</td>
<td>0.003</td>
</tr>
<tr>
<td>Vinegar</td>
<td>4</td>
<td>0.05 mg/l</td>
<td>0.023</td>
</tr>
<tr>
<td>Mirin</td>
<td>2</td>
<td>0.01 mg/l</td>
<td>0.0</td>
</tr>
</tbody>
</table>

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key dietary groups that are exposed from elevated inorganic As exposure from rice product consumption.

2. Materials and methods

2.1. Chemicals

Analytical grade nitric acid (HNO₃) (70%) was obtained from Fisher Scientific and Lancaster. Monosodium arsenate (Na₂HAsO₄) and sodium arsenite (NaAsO₂) of reagent grade were purchased from Merck. Methylenearsonic acid (MMA), was purchased from Chem Service MC, West Chester and dimethylarsinic acid (DMA) was purchased from Sigma Chemicals. Indium (In) prepared in-house from indium chloride was a plasma standard solution. The HPLC mobile phase was prepared using ammonium hydrophosphate (NH₄H₂PO₄) and ammonium dihydrogen orthophosphate (NH₄NO₃) AnalR from BHD chemicals Ltd. (Poole, England).

2.2. Sample preparation

Forty rice products (Table 1) were collected from markets in the UK. The products were bought predominantly from Internet stores, local supermarkets and health food shops. Some represented commonly available products that could be widely obtained in supermarkets (rice crackers, crispated/puffed rice cereal) whilst others represented commonly available products that could be widely obtained in supermarkets (rice crackers, crispated/puffed rice cereal) whilst others re

2.3. Total digestion procedures

For total arsenic measurements, duplicate subsamples were taken and the dried (0.2 g) or liquid samples (oil and vinegar, 0.5 ml) were digested in 2 ml of nitric acid using a standard published method (Williams et al., 2007a,b). NIST CRM 1568a rice flour, used as certified CRM, required no special preparation. Quality controls of CRM, spikes (0.200 g of 100 μg As/I) and blanks were run with each digest set.

2.4. Extraction procedures

Foster et al. (2007) showed that arsenic species in marine extracts were stable with microwave-assisted 2% nitric acid extraction. A similar method, using 1% nitric acid was utilized in rice, with good recoveries and minimal inter-conversion of As species (Zhu et al., 2008a,b). 1% nitric acid was utilized for extraction of As species as described below. Around 0.2 g of rice flour/powder was accurately weighed out into a 50 ml polypropylene digest tube and 10 ml of 1% nitric acid were added to steep overnight. Samples were extracted with a microwave oven (CEM Mars 5, CEM Corp, Matthews, NC). The temperature was raised first to 55 °C (and held for 10 min) then to 75 °C (and held for 10 min) and finally the digest was taken up to 95 °C and maintained for 30 min. Samples were cooled to room temperature and centrifuged at 3500 rpm for 1 h. The supernatant was filtered through 0.45 μm filter (Millipore) and kept into 4 °C until analysis. Quality controls of CRM and blanks were run with each extract batch.

2.5. Arsenic detection

ICP-MS 7500 (Agilent Technologies) was used to determine total arsenic concentration as reported (Williams et al., 2007a,b). Arsenic speciation was quantified by HPLC–ICP-MS as described elsewhere (Williams et al., 2007a). Chromatographic separation consisted of a precolumn (11.2 mm, 12–20 μm) (Hamilton) and a PRP-X100 10-μm anion-exchange column (150×4.1 mm) (Hamilton). The mobile phase consisted of 6.66 mM ammonium hydrophosphate (NH₄H₂PO₄) and 6.66 mM ammonium nitrate (NH₄NO₃), adjusted to pH 6.2 using ammonia. Retention time for the As species was determined using a species mix comprising standards of 50 μg/ml arsenite, arsenate, DMA and MMA (Fig. 1).

3. Results and discussion

Recovery of total As in NIST rice flour CRM was 0.29±0.01 mg/kg (Table 2), which is 100% recovery of its certified value of 0.29 mg/kg. The spike recovery was 95.4% (n=4) and limits of detection (LOD) were 0.00001 mg As/I. No rice CRM with certified speciation is available, so the NIST rice flour CRM speciation is quantified in a number of studies, summarized by Williams et al. (2005), and the characterization of this CRM for this study (Table 2) is in agreement with these previous investigations. The LOD for speciated As was 0.00007 mg As/l.

Forty rice products belonging to 10 categories were analyzed. From Table 1 it can be seen that the total average As content in solid rice products ranged from 0.14 to 0.28 mg/kg. The arsenic content of these rice products reflects that of rice itself. There is wide geographic variation in arsenic content of rice, being low in Indian basmati and high in EU and US rice (Williams et al., 2005, 2007a,b; Zavala and Dubury, 2008). The levels found in rice products reported here reflect the higher end of arsenic reported in global market rice, suggesting that the grain used was sourced from high grain As regions of the globe. They also correspond to the range of total As content in baby rice reported by Meharg et al. (2008a), 0.12–0.47 mg/kg.

Liquid rice products, such as oil and vinegar, have As contents ranging from 0.01 to 0.03 mg/l, lower than solid rice products. This is probably due to the dilution of rice As by water added during processing. The levels of total As were low in the rice oil products, therefore As speciation was not determined. The findings from this study suggest grain As is not easily transferred to lipid fractions within the grain. US, EU and WHO water standards are set at 0.01 mg/l. While these liquid rice products although diluted, still exceed this level, because they are used only as condiments (vinegar and mini) or in cooking, dietary intakes from these sources would be expected to be small. The results for liquid products are similar to those for rice milk (0.01–0.03 mg/l), another liquid rice product. However, rice milk is used as a beverage, replacing cows milk in the diet, and thus routine use of rice milk product can lead to considerably elevated dietary intakes of As.

A subset of samples, representing products with the highest total As levels, was selected for As speciation with results presented in Table 2. For all of the rice products for speciation, the predominant As species are inorganic (75.2–90.1%), with the remainder being DMA. Inorganic As and DMA are known to be the main As components of both white and brown rice (Zaparre et al., 2005; Meharg et al., 2008a,b,c; Smith et al., 2006; Williams et al., 2005, 2006, 2007a,b), while Meharg et al. (2008c) has shown that inorganic arsenic is elevated in the bran layer of rice, resulting in brown rice having a higher inorganic content than corresponding white rice.

Determination of As speciation in rice products is important because the toxicity of organic and inorganic As species vary greatly (Petrick et al., 2000; Valher and Concha, 2001). Inorganic As species are more toxic than organic As (Petrick et al., 2000; Valher and Concha 2001). The percentage of inorganic As differs between different products, probably due to the variability of As concentration and speciation inherently found in

Table 2

<table>
<thead>
<tr>
<th>Rice product</th>
<th>Total As (mg/kg d wet)</th>
<th>Sum of speciation(mg/kg d wet)</th>
<th>Extr. effic. (%)</th>
<th>Organic As (mg/kg d wet)</th>
<th>Inorganic As (mg/kg d wet)</th>
<th>Inorg. As (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crisp rice</td>
<td>0.21±0.01</td>
<td>0.15±0.004</td>
<td>71.1</td>
<td>0.03±0.002</td>
<td>0.12±0.002</td>
<td>83.8</td>
</tr>
<tr>
<td>Crisp rice</td>
<td>0.19±0.02</td>
<td>0.11±0.001</td>
<td>58.9</td>
<td>0.01±0.001</td>
<td>0.10±0.002</td>
<td>90.1</td>
</tr>
<tr>
<td>Puffed rice</td>
<td>0.27±0.01</td>
<td>0.19±0.01</td>
<td>67.9</td>
<td>0.04±0.004</td>
<td>0.14±0.002</td>
<td>84.8</td>
</tr>
<tr>
<td>Rice noodles</td>
<td>0.19±0.01</td>
<td>0.14±0.00</td>
<td>70.1</td>
<td>0.02±0.00</td>
<td>0.12±0.001</td>
<td>86.3</td>
</tr>
<tr>
<td>Rice crackers</td>
<td>0.39±0.01</td>
<td>0.27±0.01</td>
<td>70.2</td>
<td>0.07±0.00</td>
<td>0.21±0.01</td>
<td>75.5</td>
</tr>
<tr>
<td>Rice crackers</td>
<td>0.37±0.003</td>
<td>0.27±0.01</td>
<td>72.0</td>
<td>0.07±0.002</td>
<td>0.20±0.01</td>
<td>75.2</td>
</tr>
<tr>
<td>NIST CRM 1568a</td>
<td>0.29±0.01</td>
<td>0.29±0.01</td>
<td>98.3</td>
<td>0.18±0.003</td>
<td>0.11±0.01</td>
<td>36.9</td>
</tr>
</tbody>
</table>

The standard errors are from duplicate analysis.
rice (Williams et al., 2005), and to potential alteration in speciation caused by processing raw rice into products.

With respect to legislation, As in food is out of step with As in water. US water regulations have a limit of 0.01 mg/l inorganic arsenic in water (US EPA, 2001). The World Health Organization (WHO) has a provisional 0.01 mg/l inorganic arsenic standard (WHO, 1993) while in the EU it is 0.01 mg/l for total As (Council of the European Union, 1998). For food, the level of 1 mg/kg total As is often cited with respect to rice (The Stationary Office, 1959), which equates to the 1959 UK standard (The Stationary Office, 1959). If As in rice is bioavailable, which all evidence points towards (Laparra et al., 2005; Smith et al., 2006), the toxicity of arsenic mobilized across the gut wall will be the same whether it is derived from water or food. On an equivalence basis, 100 g of 0.1 mg/kg As in food equates to 1 l of 0.01 mg/l water, remembering that water limits are set in the US and EU based on the assumption that 1 l of water is consumed per day.

Breakfast cereals are popular within EU countries, especially in the UK and Ireland. In particular they are favored by children and taken almost everyday, with average daily consumption being ~30 g (Henderson et al., 2002; Gregory et al., 2000), this is nearly twice the amount reported for the US (Miller et al., 2000). The daily exposure to inorganic As from eating rice cereal could be at least 0.0042 mg, modeled for a typical UK diet and based on inorganic As levels found in this survey. Meacher et al. (2002) estimate that the 50th percentile intake of inorganic As from soil, air, drinking water and food for US men is 0.0040 mg, whilst for women it is 0.0031 mg. For US children, average exposure from dietary sources alone is estimated at 0.0032 mg (Yost et al., 2004). When exposure is considered on a body mass basis, though, children are more vulnerable than adults (Meharg et al., 2008a,b,c). The daily consumption of rice based cereals therefore constitutes an important exposure pathway for inorganic As for some European children.

The highest levels of inorganic As in this study were found in the rice crackers (Table 2). Similar to the breakfast cereals, these rice snacks are often eaten by children, especially those with a preference for oriental food. The manufacturer’s recommended servings are usually ~30 g – the same as British breakfast cereal consumption. Therefore, one portion of rice crackers could deliver a dose of between 0.006 and 0.0063 mg of inorganic As, calculated from our findings. Increasingly rice has been used as the primary ingredient in a number of oriental snack foods, like crisps and tortilla chips, that traditionally are based on other cereals. In India also, savors snacks called Chaat (Hindi) often use Muri (puffed rice). Muri is common throughout southeast Asia as it is less perishable than normal rice. The As levels found in the puffed rice from UK were 5 times higher than the average level for rice in India, found to be 0.05 mg/kg (n = 100). (Meharg, personal communication). Therefore those in the UK following a southeast Asian diet may be inadvertently exposed to more inorganic As by taking puffed rice than they would if they were actually in southeast Asia.

It is the diets that comprise of numerous sources of rice or rice based products, such as in macrobiotic, vegan, gluten and dairy intolerance regimens (Lightowler et al., 1998; Schoof RA, Yost LJ, et al. 2003;) that water limits are set in the US and EU based on the assumption that 1 l of water is consumed per day. The Stationary Office, 1959). If As in rice is bioavailable, which all evidence points towards.

4. Conclusions

The results obtained from this study demonstrated that content of As in some rice products reflected elevated levels in rice grain. Arsenic speciation analysis of rice products demonstrated that predominantly As speciation was dominated by inorganic forms (75.2–90.1%). The study provides useful information for better understanding of the distribution of arsenic species in rice products. These are important considerations in the formulation of new rice based foods.

References


