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Inorganic arsenic in rice and rice-based diets: health risk assessment

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ABSTRACT

Total and inorganic arsenic (As) content in rice and rice-based diets (n=59) obtained from supermarkets in South Australia were studied to investigate the contamination levels and whether consumption of these products pose potential health risks to young children and adults. Results show that of the 59 rice-based products, 31 (53 %) exceeded the EU recommended value (100 µg/kg) of As for young children and 13 (22%) samples had higher than maximum level of 200 µg/kg recommended for adults. Arsenic content varies as rice crackers > baby rice > rice cakes > puffed rice > other rice-based snacks > ready-to-eat rice. Of the 6 categories of

rice-based products, except ready-to-eat rice, all others exceeded the EU recommended value for young children. Even manufacture recommended servings deliver significant amounts (0.56 to 6.87 μg) of inorganic As. These amounts are within the range of BMDL_{01} values indicated by the European Food Safety Authority (EFSA), which means the risk cannot be avoided for young children and adults considering the levels of total and inorganic As in rice-based products.

Keywords:

Rice-based products

Young children

Inorganic As

Health risk

BMDL

1. Introduction

Arsenic is a naturally occurring toxic element, which is ubiquitous in the environment and has been classified as a human carcinogen (group I), which with sustained exposure causes both carcinogenic and non-carcinogenic problems including nervous system disorder, developmental and reproductive issues, diabetes, heart disease and many more (IARC, 2004). Inorganic As [As(III) and As(V)] is more toxic compared to organic As [dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA)]. Both As(III) and As(V) are potentially harmful to humans and animals, although As(III) is more toxic (Hindmarsh, et al., 1986; Vega, et al., 2001). Humans' exposure to As mainly occurs through: firstly, drinking As-contaminated groundwater and consuming food crops grown in agricultural lands contaminated with As; and secondly, where contaminated irrigation water is used for cropping. Whenever, rice is the staple diet, As exposure from rice can be considerable and intake of inorganic As via this route is a significant risk factor, especially for populations who depend substantively on a rice diet

(Mondal & Polya, 2008). Elevated concentrations of As have been detected in rice in several South-East Asian countries, which poses an additional risk to consumers (Correll, et al., 2006; Mondal, et al., 2010; Pal, et al., 2009; Rahman, et al., 2009; Williams, et al., 2005). In rice grown in the Bengal Delta, the predominant As species present are usually inorganic and a small portion of organic As also exists (Williams, et al., 2005). It was reported from West Bengal, India, that cooked rice with elevated As ($>200 \mu\text{g/kg}$) caused genotoxicity and it was found that As from cooked rice alone was responsible for the observed genetic effects in the study population (Banerjee, et al., 2013). Due to the global food trade, millions of consumers are likely to be potentially exposed to As from the imported foods, especially rice and rice-based food products (Rahman, et al., 2014).

In most cases, whole grain and polished rice, and bran are used to produce a variety of rice-based foods. These rice-based products are very popular worldwide especially for young children who are assumed to be the most vulnerable consumer group to As toxicity; they have a higher As body burden than adults (Rahman, et al., 2001). A study in the US suggests that rice is a potential source of As exposure for children (Davis, et al., 2012). The impact of a mother's As consumption on fetal gene expression is evidenced by transcript levels in newborn cord blood (Fry, et al., 2007). Studies have also provided evidence that children are more susceptible to the toxic effects of inorganic As (Vahter, 2008, 2009).

Several studies have reported that rice and rice-based products used for infants contained high levels of both total and inorganic As (Ljung, et al., 2011; 2008; Signes-Pastor, et al., 2016; Sun, et al., 2009). Research has shown that at least 50% of rice-based food products in the UK have As levels which exceeded those being proposed by the European Union (EU); 179 different products were tested and 53% of these products had As higher than the maximum level of $100 \mu\text{g/kg}$ recommended for young children (Signes-Pastor, et al., 2016). The Commission Regulation (EU) 2015/1006 of 25 June 2015 has issued a limit value of $100 \mu\text{g/kg}$

for rice destined for the production of foods for infants and young children and 200 $\mu\text{g}/\text{kg}$ for adults. This regulation has been in force since January 1, 2016 (EFSA, 2014). In 2014, the European Food Safety Authority (EFSA) investigated the dietary exposure of people in 21 European countries to inorganic As, and the data show that grain-based processed products are the main contributors of inorganic As for all age groups except infants and toddlers (EFSA 2014). The mean dietary exposure to inorganic As among these groups ranged between 0.20 to 1.37 $\mu\text{g}/\text{kg}$ bw per day (EFSA 2014). The mean dietary exposure to inorganic As according to surveys in the adult population (including adults, elderly and very elderly) ranged from 0.09 to 0.38 $\mu\text{g}/\text{kg}$ bw per day (EFSA 2014).

A recent study on Australian rice, notably brown rice, found As content substantially higher than imported rice on sale in Australia which poses potential serious health risk to Asian adult immigrants (Rahman, et al., 2014). A few studies have been conducted on potential health risk of As to children from their rice-based food products in Europe and the US, but no information is available about the health risk of toxic inorganic As in products produced in Australia. This is especially so given that such products besides being consumed here are also exported to other countries, for example China and South Korea. For this reason, it is crucial to investigate the As levels in rice-based diets available in Australia and its associated health risk to both adults and young children. Considering that As is carcinogenic and highly toxic, reliable assessments of the health risks associated with the intake of As through rice-based products consumption are urgently needed, especially for children. In this study, we determine the levels of As (total and inorganic) in a variety of rice and rice-based products, and to assess inorganic As exposure and its associated health risks to both adults and young children.

2. Materials and methods

2.1 Selection of samples

Fifty-nine rice products in 6 categories commonly found in supermarkets were analyzed for total and speciated As. Samples of rice crackers [cracker is a baked food typically made from rice flour (n=10)], rice cakes [rice cake is a kind of food item made from puffed rice that has been shaped, condensed, or otherwise combined into a single object (n=11)], puffed rice [puffed rice is a type of puffed grain made from rice, commonly used in breakfast cereal or snack foods (n=6)], baby rice [ground rice cereals consumed by baby to young children (n=4)], ready-to-eat rice [cooked rice ready to eat, only need 2-3 minutes heat using microwave oven (22)] and other rice-based snacks [rice biscuits, rice hoops etc.(6)] of 25 different popular commercial brands were purchased from supermarkets in Adelaide, South Australia during February 2015. The samples' expiry date (best before use) was between April, 2015 and March, 2016.

2.2 Sample preparations

With the exception of ready-to-eat rice, all rice-based products were oven dried (60 °C) and ground with mortar and pestle before microwave digestion for analysis. Between each samples, mortar and pestle were washed in tap water, deionised water and dried in a fan forced oven. For total As examination, the powdered samples were weighed accurately to 0.5 g into microwave digestion tubes to which 2mL MQ water (ELGA Labpure), 3 mL trace analytical grade HNO₃ (70%), obtained from Fisher Chemicals and 2 mL H₂O₂ (30%, Ajax Finechem) were added and allowed to sit overnight (12 hours). A microwave digestion system with 40 rotors (MARS 6, CEM) served for the digestion of the samples. Batches of 30 samples were prepared including a blank and a standard reference material (SRM 1568b rice flour) obtained from the National Institute of Standard and Technology (NIST), USA. Firstly, the temperature was raised to 55 °C, and held for 10 minutes, and then 75 °C, and again held for 10 minutes. Finally, temperature was lifted to 90 °C and held for 30 minutes. The ready-to-eat rice was directly weighed and followed the same digestion procedure as described above. The digests

were diluted to 10 mL using 0.1% HNO₃ and then passed through a 0.45 µm syringe filter (MCE, Agilent Technologies). Finally, 10 mL aliquot of the digest from each tube was transferred to a plastic tube for instrumental analysis.

Arsenic speciation analysis (inorganic As, MMA and DMA) was carried out with the procedure utilized by Signes-Pastor, et al. (2016). Briefly, the powdered samples were weighed accurately to 0.25 g into microwave digestion tubes to which 10 mL of 1% conc. HNO₃ (trace analysis grade) was added and allowed to sit overnight (12 hours). Batches of 30 samples were prepared including a blank and a SRM (1568b rice flour), which has inorganic As [As(III) and As(V)], DMA and MMA concentrations certified. The samples were then digested in the microwave digestion system. The digests were diluted to 10 mL and filtered by a 0.45 µm syringe filter. Lastly, 1 mL aliquot of the digest from each tube was transferred to a 2 mL HPLC glass vial (amber) for chromatographic analysis. For both total As and its speciation we have run three replicates of each samples.

2.3 Instrumentation

An Agilent 7500ce (Agilent Technologies, Tokyo, Japan) inductively coupled plasma mass spectrometer (ICP-MS) coupled with auto-sampler (ASX-520, CETAC Technologies) and integrated samples introduction system (ISIS) was used to determine the amount of As in the digested samples. An Agilent 1100 liquid chromatography system (Agilent Technologies, Tokyo, Japan) equipped with a guard column and a Hamilton PRP-X100 separation column, coupled with ICP-MS served to determine As species. The detection limit (DL) of the total As was 0.01 µg/L. The detection limit for speciation in As standard solutions [As(III), As(V), DMA and MMA] by the IC-ICP-MS ranged between 0.1 and 0.3 µg/l (Chen, et al., 2008).

2.4 Quality control: analysis of Standard Reference Materials (SRM)

We found the concentration of total As in rice flour was SRM 270±13 (n=6) µg/kg, which indicates 95% recovery of the certified value of 285±14 µg/kg. Similar SRM was used to

validate the results of As speciation in rice-based samples included in this study. Our results revealed that inorganic As recovery was around 98%. The certified values for inorganic As, MMA and DMA of SRM 1568b were 92 ± 10 $\mu\text{g/kg}$, 11.6 ± 03 $\mu\text{g/kg}$ and 180 ± 12 $\mu\text{g/kg}$, respectively. The observed values ($n=6$) were 90 ± 20 and 176 ± 10 $\mu\text{g/kg}$ for inorganic As and DMA, respectively. We were unable to detect any MMA in rice SRM.

2.5 Statistical analysis

Data were analyzed by SAS Institute created statistical software JMP (the powerful statistical and analytic capabilities tool used for data explorers worldwide) version 11.1nk. Statistical analysis was also done employing Microsoft Excel 2013.

2.6 Calculation of health risk of inorganic As

According to the Food and Agricultural Organization (FAO)/World Health Organization (WHO), three basic approaches can be used to determine the dietary intake of chemical contaminants from foods: (i) total diet study, (ii) duplicate diet method, and (iii) diary study (WHO, 1985). These approaches combine the concentration of specific contaminants in foods with individual consumption rates. In this study, the total diet study approach was used to determine the dietary intake of inorganic As from rice-based products.

Inorganic As intake per serving (μg) from rice-based products:

$$\text{EIPS} = (C_{\text{iAs}} \times \text{RS}_{\text{rice-based products}}) \quad (1)$$

Where, EIPS represents estimated intake per serving (μg); C_{iAs} represents inorganic As concentration in rice-based products ($\mu\text{g/kg}$); RS: Average recommended serving (g/person/day) by the manufacturer.

Estimated Weekly Intake (EWI; $\mu\text{g/kg}$ body weight):

$$\text{EWI} = (\text{EIPS} \times 7) / W_{\text{AB}} \quad (2)$$

Where, EIPS is the estimated intake per serving (μg) and W_{AB} is average body weight, assuming 10 kg for young children (WHO, 2014) and 60 kg for adults (Li, et al., 2011) in this study to calculate the As intake.

The Joint FAO/WHO Expert Committee on Food Additives (JECFA) withdrew the provisional tolerable weekly intake (PTWI) of 15 $\mu\text{g}/\text{kg}$ bw in 2010. Based on other epidemiological studies, JECFA identified a benchmark dose lower confidence limit for a 0.5% increased incidence of lung cancer ($\text{BMDL}_{0.5}$) of 3.0 $\mu\text{g}/\text{kg}$ bw per day (2-7 $\mu\text{g}/\text{kg}$ bw per day based on the estimated total dietary exposure range) (WHO, 2011). Prior to that, the EFSA Panel on Contaminants in the Food Chain concluded that the PTWI of 15 $\mu\text{g}/\text{kg}$ bw was no longer appropriate and the panel established a BMDL_{01} between 0.3 and 8 $\mu\text{g}/\text{kg}$ bw per day for an increased risk of cancer of the lung, skin and bladder, and skin lesions (EFSA, 2009). The US Environmental Protection Agency (EPA) has also declared that there is no "safe" level of exposure to inorganic As. Total dietary intake and health risk of inorganic As species were estimated for two major consumer groups: (i) young children and (ii) adults (only for ready-to-eat rice).

3 Results and discussion

Mean total and inorganic As content in 6 categories of rice-based foods is shown in Fig. 1. The average As content in rice-based products ranging between 30 to 273 $\mu\text{g}/\text{kg}$ (Table 1). Out of 59 rice-based products, 31 (53%) exceeded the EU recommended value (100 $\mu\text{g}/\text{kg}$) of As for young children, which is comparable with the previous study (Signes-Pastor, et al., 2016) conducted in Europe. It is also notable that As greater than 200 $\mu\text{g}/\text{kg}$ (EU recommended value for rice-based product for adults) was detected in 13 (22%) rice-based products. Out of 6 categories of rice products, except ready-to-eat rice, all others exceeded the EU recommended value of As for young children. Variations in total As in rice-based products appear to be linked to their source as well as type of product. About 93% of rice-based products including rice

crackers, rice cakes and baby rice produced from Australian-grown rice contained significant levels of total As (up to 456 $\mu\text{g/kg}$) and inorganic As (up to 270 $\mu\text{g/kg}$). For all rice products investigated in this study, inorganic As was the predominant species and ranged from 35% to 100%, with the remainder being DMA. The inorganic As percentage in different rice products differs and this may be due to the inherently found total As and their speciation (Williams, et al., 2005).

Arsenic content in rice varied widely due to the geographical variation, low in Indian Basmati and high in EU, US and Australian rice (Rahman, et al., 2014; Williams, et al., 2005; 2007; Zavala & Duxbury, 2008). The bioavailability of As species varied considerably and inorganic As is more toxic than organic As and usually present in rice diet (Petrick, et al., 2000), at around 90% which is high (Juhasz, et al., 2006). Processing of raw rice is likely to influence the speciation in rice-based products. The main As components in both white and brown rice are inorganic As and DMA (Laparra, et al., 2005; Williams, et al., 2006; Williams, et al., 2005; 2007), while brown rice has high levels of inorganic As. This is due to the presence of a brown layer. This study also confirms there is more As in brown rice-based products compared to white or Basmati rice.

3.1 Rice crackers

Rice crackers are popular rice-based diets and are eaten by people of all ages. Out of 10 samples analyzed, all exceeded the EU recommended value (100 $\mu\text{g/kg}$) of As for young children. Of much concern were 3 samples in which As exceeded 200 $\mu\text{g/kg}$. The average total As in rice crackers produced from Australian rice was 239 $\mu\text{g/kg}$, while the highest inorganic As content was 126 $\mu\text{g/kg}$, however, the Thai product contained 171 $\mu\text{g/kg}$ of total As and 61 $\mu\text{g/kg}$ of inorganic As (Table 1). Speciation of As in rice crackers (n=10) showed that inorganic As species comprised the major portion ranging from 42% to 83% compared to the organic species. These results are consistent with findings published in previous studies where

researchers found that inorganic As is the key species in rice crackers (average of 145 $\mu\text{g/kg}$ ranging from 75-90% of the total As (Sun, et al., 2009) and 102 $\mu\text{g/kg}$ ranging from 54-86% of the total As (Signes-Pastor, et al., 2016). The recommended serving is 30 g of rice crackers which was obtained from the product packet and one serving could deliver between 1.3 and 3.2 μg of inorganic As to consumers (Table 2). These values are within the current BMDL_{01} range. Since all rice crackers had As greater than the EU recommended value (100 $\mu\text{g/kg}$) for young children, the risk cannot be excluded for consuming rice crackers. This is also higher than the previous provisional tolerable daily intake (PTDI) value of 2.1 $\mu\text{g/day/kg}$ body weight, indicating that inorganic As species rice crackers may potentially pose considerable health risk to young children if this rice-based food is consumed on a daily basis.

3.2 Puffed rice

Rice constitutes the major ingredient for puffed rice, which is traditionally used as a snack food. Out of 6 puffed rice samples, half exceeded the EU recommended value (100 $\mu\text{g/kg}$) of As for young children and 2 samples had As greater than 200 $\mu\text{g/kg}$. The average total As content found in the puffed rice imported from New Zealand (213 $\mu\text{g/kg}$; $n=3$) was 3 times higher than that in Australian puffed rice (77 $\mu\text{g/kg}$; $n=3$). Speciation of As in puffed rice samples of this study showed inorganic As was the major species (32%-73%). Though the New Zealand rice contains total As 3 times higher than Australian rice, the average inorganic As content in puffed rice of Australian origin was 45 $\mu\text{g/kg}$, whereas it was 54 $\mu\text{g/kg}$ in New Zealand origin puffed rice. According to the manufacturers' recommendation, 20 to 30 g per day serving of puffed rice could deliver between 0.87 and 1.62 μg of inorganic As to consumers (Table 2). While these values are within the current BMDL_{01} range, it should be noted that 50% of puffed rice crackers had As exceeding 100 $\mu\text{g/kg}$, so the health risk from consuming puffed rice cannot be neglected. Based on the results presented here, it is apparent that inorganic As levels in puffed rice is of concern although this value is substantially less than the

previous PTDI limit (2.1 $\mu\text{g/day/kg}$ body weight). A previous study indicated that inorganic As species was the major component (77% of the total As) in puffed rice with an average total As content of 140 $\mu\text{g/kg}$ (Sun, et al., 2009), which is 3 times greater than that found in this study.

3.3 Rice cakes

The rice cake is a kind of food item made from rice that has been shaped, condensed, or otherwise combined into a single object. Like other rice-based products, rice cakes are used for light dinner or lunch, and in Australia they are made of 100% Australian-grown whole grain brown rice. The concentrations of total As in rice cake in this study ranged from 58 to 384 $\mu\text{g/kg}$ (Table 1), which is consistent with the results of total As concentrations in Australian-grown organic brown, medium grain brown, and organic white rice of 438 ± 23 , 287 ± 03 , and 283 ± 18 $\mu\text{g/kg}$, dry weight, respectively (Rahman, et al., 2014). Nine and 4 out of 11 rice cakes had As greater than 100 $\mu\text{g/kg}$ and 200 $\mu\text{g/kg}$, respectively. The highest levels of inorganic As was 105 $\mu\text{g/kg}$ in Australian rice cakes. The manufacturer's recommended serving is 15 to 20 g and therefore, one serving could deliver between 0.6 and 2.3 μg of inorganic As (Table 2) indicating that the rice cake itself can satisfy the previous PTDI of inorganic As (2.1 $\mu\text{g/day/kg}$ body weight) for a consumer. This value is also within the BMDL_{01} range. Since 82% and 36% of the samples had As greater than the EU recommended values of 100 $\mu\text{g/kg}$ (for children) and 200 $\mu\text{g/kg}$ (for adults), respectively, the risk cannot be avoided for children consuming rice cakes on a daily basis.

3.4 Baby rice

Total As concentration in baby rice samples ranged from 59 to 357 $\mu\text{g/kg}$ ($n=4$; Table 1). Although we investigated only 4 samples from this category, 3 samples had As greater than 100 $\mu\text{g/kg}$. The average concentration of total As in Australian baby rice was 268 $\mu\text{g/kg}$, whereas this value was 140 $\mu\text{g/kg}$ in baby rice imported from other countries. The inorganic

As concentration in 4 baby rice samples of 4 different commercial brands ranged from 46 to 108 $\mu\text{g/kg}$ (22% to 100%) (Table 1). This is consistent with the studies conducted in Spain by Carbonell-Barrachina, et al. (2012) and Signes-Pastor, et al. (2016). Baby rice of Australian origin contained less inorganic As (51%) than other countries (85%). The same trend regarding As speciation has been reported elsewhere (Meharg, et al., 2009; Torres-Escribano, et al., 2008). The manufacturer's recommended serving of baby rice is 30 to 90 g. Therefore, one serving of baby rice per day could deliver between 1.9 and 6.9 μg of inorganic As (Table 2). This value is also within the BMDL_{01} range. Considering the total As values detected in baby rice, the risk cannot be ignored for children consuming baby rice, thus indicating this rice-based food does pose a serious health risk to consumers.

3.5 Ready-to-eat rice

Total As concentration in ready-to-eat rice samples of 5 different commercial brands ranged from 14 to 90 $\mu\text{g/kg}$ (Table 1). Out of 21 samples, all had As less than the EU recommended value of 100 $\mu\text{g/kg}$ for young children. The average total As content in Australian ready-to-eat rice was 54 $\mu\text{g/kg}$ ($n=8$), while it was 30, 39 and 32 $\mu\text{g/kg}$ in Indian, Thai and UK ready-to-eat rice, respectively. While the inorganic As concentration ranged from not detectable (ND) to 94 $\mu\text{g/kg}$ (Table 1), the percentage of inorganic As in ready-to-eat rice ranged from ND to 100% of the total speciated As. The ready-to-eat rice of Australian origin contained more inorganic As (77%) than that imported from other countries (57 to 73%). The recommended serving of ready-to-eat rice is 125 g. Therefore, one serving of ready-to-eat rice per day could deliver between 1.6 and 5.6 μg of inorganic As (Table 2), which is substantially higher than that of previous PTDI of 2.1 $\mu\text{g/day/kg}$ bw set by the FAO/WHO Joint Expert Committee on Food Additives (JECFA). This value indicates consuming ready-to-eat rice does pose a serious health risk to the consumers.

3.6 Other rice-based snacks

We also analyzed 6 other rice-based snacks produced in Australia and imported from other countries. Four of these 6 samples had As greater than the EU recommended value of 100 $\mu\text{g/kg}$ for young children. On average, the snacks of Australian origin contained substantially higher amounts of total As (273 $\mu\text{g/kg}$) than that of other countries (93 $\mu\text{g/kg}$). Inorganic As content was also higher in Australian snacks (88 $\mu\text{g/kg}$) compared to snacks imported from other countries (28 to 44 $\mu\text{g/kg}$). Considering the recommended serving of 30 g snacks, inorganic As intake from Australian snacks was 7.7 μg , which is substantially higher than the previous PTDI (2.1 $\mu\text{g/day/kg}$ body weight). This indicates the rice-based food is a health risk to consumers. A comparison of the results of As content in rice-based products of this study and other published studies is presented in Table 3.

3.7 Inorganic As intake and health risk for young children

In this study, young children's health risk when exposed to inorganic As was determined with a consideration of the dietary intake of inorganic As from rice-based products by using equation numbers (1) and (2). The calculations of estimated weekly intake (EWI) and the percentage of PTWI of inorganic As were based on: firstly, the manufacturer's recommended serving of rice-based products; and secondly, the average body weight for young children (10 kg) and adults (60 kg). Estimations of inorganic As exposure for young children from baby rice, rice cakes, rice crackers, puffed rice and other snacks are presented in Fig. 2.

The results from Table 2 clearly indicate that young children are at risk of inorganic As exposure from most rice-based products. Even manufacturers' recommended servings deliver significant amounts (0.56 to 6.87 μg) of inorganic As to consumers. These values were within the range of BMDL_{01} identified by the EFSA, meaning the risk cannot be avoided for young children and even adults when accounting for the levels of total and inorganic As in rice-based products. On average, young children under 5 years of age eat three times more food than adults on a body weight basis. Also, this sub-population is much more vulnerable than adults.

These facts may suggest young children face three times greater risk of exposure to inorganic As from the same food item. Children being exposed to As also associated with increased risk of respiratory infections (Gardner, et al., 2013). Early life chronic exposure to high levels of As is associated with poor growth and other long-term consequences such as increased blood pressure and compromised kidney function (Flanagan, et al., 2012; Gardner, et al., 2013; Hawkesworth, et al., 2012). One study found that an increase of 1/4-cup cooked rice consumption results in 14% increase of urinary As concentration in American children (Davis, et al., 2012). Vahter, et al. (2014) noted that the impact of early-life As exposure may constitute a major human health problem.

4 Conclusions

Rice-based food products are popular and half of the world's population relies on rice-based diets. Some particular brands are favored by young children and eaten almost every day. This study shows that more than 53% of rice products had As greater than the EU recommended value of 100 µg/kg for young children and even 22% of samples had As greater than 200 µg/kg. Almost all rice-based products have been found to contain a good percentage of inorganic As, therefore the health risk posed by consuming rice-based products cannot be ignored for young children. It is crucial to minimize the inorganic As exposure from rice-based diets for young children. To reduce the risk of As, we recommend that young children eat no more than 1 serving of rice-based products per day on average and their diets should include cereals that contain significantly lower levels of As. When manufacturing rice-based products, rice varieties with much less inorganic As should be used to abate exposure to inorganic As.

As this preliminary study focuses on inorganic As exposure in rice-based products on sale in Adelaide supermarkets, the main limitation of this study is the sample size of each rice-based product. Future studies should investigate the other major rice-based products from all supermarkets of Australia. The main strength of this paper is that it provides useful data on

inorganic As concentration in food products sale in Australia and their associated health risks for young children who consume these products. The results will be of great interest to researchers, stakeholders, policy-makers, and agriculture managers. They will be able to develop management strategies to minimize young children's exposure to inorganic As and curtail the risks associated with these rice-based products. Since Australia is recognized as an exporter of quality food products and China is the largest consumer market for them, we need to ensure that Australia's international market access and trade interests are secure, and enhance its reputation as a reliable supplier of 'clean and green' foodstuffs.

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References

- Banerjee, M., Banerjee, N., Bhattacharjee, P., Mondal, D., Lythgoe, P. R., Martínez, M., Pan, J., Polya, D. A., & Giri, A. K. (2013). High arsenic in rice is associated with elevated genotoxic effects in humans. *Scientific Reports*, 3, 2195.
- Carbonell-Barrachina, Á. A., Wu, X., Ramírez-Gandolfo, A., Norton, G. J., Burló, F., Deacon, C., & Meharg, A. A. (2012). Inorganic arsenic contents in rice-based infant foods from Spain, UK, China and USA. *Environmental Pollution*, 163(0), 77-83.
- Chen, Z., Akter, K. F., Rahman, M. M., & Naidu, R. (2008). The separation of arsenic species in soils and plant tissues by anion-exchange chromatography with inductively coupled mass spectrometry using various mobile phases. *Microchemical Journal*, 89(1), 20-28.
- Correll, R., Huq, S. I., Smith, E., Owens, G., & Naidu, R. (2006). Dietary intake of arsenic from crops. In *Managing Arsenic In the Environment* (pp. 251-257): CSIRO Publishing.

- Davis, M. A., Mackenzie, T. A., Cottingham, K. L., Gilbert-Diamond, D., Punshon, T., & Karagas, M. R. (2012). Rice Consumption and Urinary Arsenic Concentrations in U. S. Children. *Environmental Health Perspectives*, 120(10), 1418-1424.
- EFSA. (2009). Panel on Contaminants in the Food Chain. *EFSA Journal*, 7(10), 1351.
- EFSA. (2014). (European Food Safety Authority) Panel on Contaminants in the Food Chain. Scientific opinion on arsenic in food. *EFSA Journal*.
- Flanagan, S. V., Johnston, R. B., & Zheng, Y. (2012). Arsenic in tube well water in Bangladesh: health and economic impacts and implications for arsenic mitigation. *Bulletin of the World Health Organization*, 90(11), 839-846.
- Fry, R. C., Navasumrit, P., Valiathan, C., Svensson, J. P., Hogan, B. J., Luo, M., Bhattacharya, S., Kandjanapa, K., Soontararuks, S., Nookabkaew, S., Mahidol, C., Ruchirawat, M., & Samson, L. D. (2007). Activation of Inflammation/NF- κ B Signaling in Infants Born to Arsenic-Exposed Mothers. *PLoS Genet*, 3(11), e207.
- Gardner, R. M., Kippler, M., Tofail, F., Bottai, M., Hamadani, J., Grandér, M., Nermell, B., Palm, B., Rasmussen, K. M., & Vahter, M. (2013). Environmental exposure to metals and children's growth to age 5 years: A prospective cohort study. *American journal of epidemiology*, 177(12), 1356-1367.
- Hawkesworth, S., Wagatsuma, Y., Kippler, M., Fulford, A. J., Arifeen, S. E., Persson, L.-A., Moore, S. E., & Vahter, M. (2012). Early exposure to toxic metals has a limited effect on blood pressure or kidney function in later childhood, rural Bangladesh. *International Journal of Epidemiology*, dys215.
- Hindmarsh, J. T., McCurdy, R. F., & Savory, J. (1986). Clinical and environmental aspects of arsenic toxicity. *CRC Critical Reviews in Clinical Laboratory Sciences*, 23(4), 315-347.
- IARC. (2004). IARC monograph 84: Some drinking water disinfectants and contaminants including arsenic. Lyon: World Health Organization. 84.
- JECFA. (2010). (Food and Agriculture Organization/ World Health Organization), Joint FAO/WHO food standards committee of the Codex Alimentarius.
- Juhasz, A. L., Smith, E., Weber, J., Rees, M., Rofe, A., Kuchel, T., Sansom, L., & Naidu, R. (2006). In vivo assessment of arsenic bioavailability in rice and its significance for human health risk assessment. *Environmental Health Perspectives*, 114(12), 1826-1831.

- Laparra, J. M., Velez, D., Barbera, R., Farre, R., & Montoro, R. (2005). Bioavailability of inorganic arsenic in cooked rice: Practical aspects for human health risk assessments. *Journal of Agricultural and Food Chemistry*, 53(22), 8829-8833.
- Li, G., Sun, G. X., Williams, P. N., Nunes, L., & Zhu, Y. G. (2011). Inorganic arsenic in Chinese food and its cancer risk. *Environment International*, 37(7), 1219-1225.
- Ljung, K., Palm, B., Grandér, M., & Vahter, M. (2011). High concentrations of essential and toxic elements in infant formula and infant foods – A matter of concern. *Food Chemistry*, 127(3), 943-951.
- Meharg, A. A., Sun, G., Williams, P. N., Adomako, E., Deacon, C., Zhu, Y.-G., Feldmann, J., & Raab, A. (2008). Inorganic arsenic levels in baby rice are of concern. *Environmental Pollution*, 152(3), 746-749.
- Meharg, A. A., Williams, P. N., Adomako, E., Lawgali, Y. Y., Deacon, C., Villada, A., Cambell, R. C. J., Sun, G., Zhu, Y.-G., Feldmann, J., Raab, A., Zhao, F.-J., Islam, R., Hossain, S., & Yanai, J. (2009). Geographical variation in total and inorganic arsenic content of polished (white) rice. *Environmental science & technology*, 43(5), 1612-1617.
- Mondal, D., Banerjee, M., Kundu, M., Banerjee, N., Bhattacharya, U., Giri, A., Ganguli, B., Sen Roy, S., & Polya, D. (2010). Comparison of drinking water, raw rice and cooking of rice as arsenic exposure routes in three contrasting areas of West Bengal, India. *Environmental geochemistry and health*, 32(6), 463-477.
- Mondal, D., & Polya, D. A. (2008). Rice is a major exposure route for arsenic in Chakdaha block, Nadia district, West Bengal, India: A probabilistic risk assessment. *Applied Geochemistry*, 23(11), 2987-2998.
- Pal, A., Chowdhury, U. K., Mondal, D., Das, B., Nayak, B., Ghosh, A., Maity, S., & Chakraborti, D. (2009). Arsenic burden from cooked rice in the populations of arsenic affected and nonaffected areas and Kolkata City in West-Bengal, India. *Environmental science & technology*, 43(9), 3349-3355.
- Petrick, J. S., Ayala-Fierro, F., Cullen, W. R., Carter, D. E., & Vasken Aposhian, H. (2000). Monomethylarsonous acid (MMAIII) is more toxic than arsenite in Chang human hepatocytes. *Toxicology and applied pharmacology*, 163(2), 203-207.
- Rahman, M., Ng, J., & Naidu, R. (2009). Chronic exposure of arsenic via drinking water and its adverse health impacts on humans. *Environmental geochemistry and health*, 31(1), 189-200.

- Rahman, M. A., Rahman, M. M., Reichman, S. M., Lim, R. P., & Naidu, R. (2014). Arsenic Speciation in Australian-Grown and Imported Rice on Sale in Australia: Implications for Human Health Risk. *Journal of Agricultural and Food Chemistry*, 62(25), 6016-6024.
- Rahman, M. M., Chowdhury, U. K., Mukherjee, S. C., Mondal, B. K., Paul, K., Lodh, D., Biswas, B. K., Chanda, C. R., Basu, G. K., & Saha, K. C. (2001). Chronic arsenic toxicity in Bangladesh and West Bengal, India-a review and commentary. *Clinical Toxicology*, 39(7), 683-700.
- Signes-Pastor, A. J., Carey, M., & Meharg, A. A. (2016). Inorganic arsenic in rice-based products for infants and young children. *Food Chemistry*, 191, 128-134.
- Sun, G.-X., Williams, P. N., Zhu, Y.-G., Deacon, C., Carey, A.-M., Raab, A., Feldmann, J., & Meharg, A. A. (2009). Survey of arsenic and its speciation in rice products such as breakfast cereals, rice crackers and Japanese rice condiments. *Environment International*, 35(3), 473-475.
- Torres-Escribano, S., Leal, M., Vélez, D., & Montoro, R. (2008). Total and Inorganic Arsenic Concentrations in Rice Sold in Spain, Effect of Cooking, and Risk Assessments. *Environmental science & technology*, 42(10), 3867-3872.
- Vahter, M. (2008). Health effects of early life exposure to arsenic. *Basic & clinical pharmacology & toxicology*, 102(2), 204-211.
- Vahter, M. (2009). Effects of Arsenic on Maternal and Fetal Health. *Annual Review of Nutrition*, 29(1), 381-399.
- Vahter, M., Ahmed, S., Kippler, M., Raqib, R., & Broberg, K. (2014). Prospective evaluation of arsenic-related health effects in children. In *One Century of the Discovery of Arsenicosis in Latin America (1914-2014) As2014: Proceedings of the 5th International Congress on Arsenic in the Environment, May 11-16, 2014, Buenos Aires, Argentina* (pp. 8): CRC Press.
- Vega, L., Styblo, M., Patterson, R., Cullen, W., Wang, C., & Germolec, D. (2001). Differential effects of trivalent and pentavalent arsenicals on cell proliferation and cytokine secretion in normal human epidermal keratinocytes. *Toxicology and applied pharmacology*, 172(3), 225-232.
- WHO. (1985). Guidelines for the study of dietary intakes of chemical contaminants. *World Health Organization: Geneva, Switzerland*, 104.

- WHO. (2011). Safety evaluation of certain contaminants in food. WHO Food Additives Series No. 63.
Available: http://apps.who.int/iris/bitstream/10665/44520/1/9789241660631_eng.pdf.
- WHO. (2014). Child growth standard. Weight-for-age. *World Health Organization: Geneva, Switzerland*.
- Williams, P. N., Islam, M. R., Adomako, E. E., Raab, A., Hossain, S. A., Zhu, Y. G., Feldmann, J., & Meharg, A. A. (2006). Increase in rice grain arsenic for regions of Bangladesh irrigating paddies with elevated arsenic in groundwaters. *Environmental science & technology*, 40(16), 4903-4908.
- Williams, P. N., Price, A. H., Raab, A., Hossain, S. A., Feldmann, J., & Meharg, A. A. (2005). Variation in arsenic speciation and concentration in paddy rice related to dietary exposure. *Environmental science & technology*, 39(15), 5531-5540.
- Williams, P. N., Villada, A., Deacon, C., Raab, A., Figuerola, J., Green, A. J., Feldmann, J., & Meharg, A. A. (2007). Greatly Enhanced Arsenic Shoot Assimilation in Rice Leads to Elevated Grain Levels Compared to Wheat and Barley. *Environmental science & technology*, 41(19), 6854-6859.
- Zavala, Y. J., & Duxbury, J. M. (2008). Arsenic in Rice: I. Estimating Normal Levels of Total Arsenic in Rice Grain. *Environmental science & technology*, 42(10), 3856-3860.

Figure Captions

Fig. 1. Mean of total and inorganic As content in 6 categories of Australian rice-based food products.

Fig. 2. Estimation of inorganic As exposure for young children from rice-based food products.

Inorganic As intake ($\mu\text{g}/\text{kg bw}$)

Number of servings per day

Table 1

Mean total and inorganic As concentration ($\mu\text{g/kg}$) in Australian produced and imported rice-based products (ranges are also given in the brackets).

Product category	Origin*	n	Inorganic As ($\mu\text{g/kg}$)	DMA ($\mu\text{g/kg}$)	Σ Speciated As ($\mu\text{g/kg}$)	Inorganic As (%)	Total As ($\mu\text{g/kg}$)
Rice crackers	Australia	5	126 $\pm$ 11 (59-270)	56 $\pm$ 2 (40-66)	182 $\pm$ 9 (125-326)	66 $\pm$ 13 (47-83)	239 $\pm$ 13 (167-456)
	Thailand	3	61 $\pm$ 8 (58-63)	35 $\pm$ 3 (13-57)	96 $\pm$ 6 (76-120)	66 $\pm$ 15 (53-83)	171 $\pm$ 11 (140-231)
	Others	2	77 $\pm$ 4 (56-99)	64 $\pm$ 2 (49-79)	141 $\pm$ 11 (135-148)	54 $\pm$ 18 (42-67)	219 $\pm$ 9 (172-266)
p-value			0.39	0.16	0.25	0.61	0.66
Puffed rice	Australia	3	45 $\pm$ 4 (37-61)	20 $\pm$ 1 ^b (16-22)	65 $\pm$ 7 ^b (55-83)	69 $\pm$ 4 ^a (65-73)	77 $\pm$ 12 ^b (62-98)
	New Zealand	3	54 $\pm$ 6 (43-61)	101 $\pm$ 6 ^a (91-107)	155 $\pm$ 11 ^a (134-166)	35 $\pm$ 3 ^b (32-37)	213 $\pm$ 8 ^a (200-228)
p-value			0.41	<0.001	<0.003	<0.0003	<0.0005
Rice cakes	Australia	7	105 $\pm$ 8 (27-158)	55 $\pm$ 11 (10-107)	161 $\pm$ 13 (42-284)	68 $\pm$ 12 ^b (52-91)	204 $\pm$ 19 (58-384)
	Belgium	1	94 $\pm$ 0	18 $\pm$ 0	112 $\pm$ 0	84 $\pm$ 0 ^{ab}	170 $\pm$ 0
	Netherlands	3	96 $\pm$ 3 (45-141)	12 $\pm$ 2 (0-19)	108 $\pm$ 6 (45-159)	92 $\pm$ 7 ^a (87-100)	152 $\pm$ 11 (94-221)
p-value			0.94	0.20	0.53	<0.04	0.74
Baby rice	Australia	2	73 $\pm$ 6 (50-73)	99 $\pm$ 1 (23-175)	173 $\pm$ 9 (120-225)	51 $\pm$ 41 (22-81)	268 $\pm$ 6 (180-357)

p-value	Others	2	77±3 (46-108)	24±3 (0-48)	101±7 (46-156)	85±22 (69-100)	140±7 (59-222)
			0.94	0.45	0.45	0.42	0.40
Ready-to-eat rice	Australia	8	45±5 (10-94)	11±2 (0-34)	55±5 (29-94)	77±29 (22-100)	54±5 (14-62)
	India	7	13±2 (0-57)	4±1 (0-26)	17±2 (0-57)	57±42 (0-100)	30±2 (15-44)
	Thailand	6	36±5 (0-87)	8±1 (0-36)	44±1 (0-123)	73±39 (0-100)	39±1 (16-90)
	UK	1	41±0	0	41±0	100±0	32±0
			0.16	0.65	0.11	0.69	0.07
Other rice- based snacks	Australia	2	88±2 ^a (71-105)	128±4 (36-219)	215±2 (107-324)	49±24 (32-66)	273±6 (122-424)
	Others	4	33±6 ^b (28-44)	23±9 (0-60)	56±3 (32-100)	68±28 (60-133)	93±5 (60-133)
p-value			<0.01	0.15	0.08	0.48	0.13

*Origin of the samples based on label of the particular product. Values with the same letters were not significantly different at p-value < 0.05 for the variable studied

Table 2

Estimated weekly intake of inorganic As and its potential health risk via consumption of Australian produced and imported rice-based products (ranges are also given in the brackets).

Product category	Origin	n	Inorganic As ($\mu\text{g/kg}$)	Recommended serving (g)	Estimated inorganic As intake per serving (μg)	Estimated weekly intake ($\mu\text{g/kg}$ body weight)	%PTWI
Rice crackers	Australia	5	126 $\pm$ 11 (59-270)	25	3.16 $\pm$ 2.09 (1.47-6.75)	2.21 $\pm$ 1.46 (1.03-4.72)	14.74 $\pm$ 9.70 (6.84-31.49)
	Thailand	3	61 $\pm$ 8 (58-63)	22 (20-25)	1.32 $\pm$ 0.06 (1.28-1.38)	0.93 $\pm$ 0.04 (0.90-0.97)	6.17 $\pm$ 0.30 (5.97-6.46)
	Others	2	77 $\pm$ 4 (56-99)	25	1.94 $\pm$ 0.75 (1.40-2.47)	1.35 $\pm$ 0.53 (0.98-1.73)	9.03 $\pm$ 3.53 (6.53-11.53)
Puffed rice	Australia	3	45 $\pm$ 4 (37-61)	19 (5-30)	0.87 $\pm$ 0.26 (0.69-1.16)	0.61 $\pm$ 0.18 (0.49-0.81)	4.07 $\pm$ 1.21 (3.24-5.39)
	New Zealand	3	54 $\pm$ 6 (43-61)	30	1.62 $\pm$ 0.30 (1.28-1.83)	1.14 $\pm$ 0.21 (0.90-1.28)	7.57 $\pm$ 1.40 (5.97-8.55)
Rice cakes	Australia	7	105 $\pm$ 8 (27-158)	22 (11-25)	2.32 $\pm$ 0.94 (0.59-3.48)	1.62 $\pm$ 0.66 (0.41-2.44)	10.81 $\pm$ 4.40 (2.75-16.24)
	Belgium	1	94 $\pm$ 0	6	0.56 $\pm$ 0.00	0.39 $\pm$ 0.00	2.63 $\pm$ 0.00
	Netherlands	3	96 $\pm$ 3 (45-141)	9 (8-12)	0.88 $\pm$ 0.43 (0.40-1.27)	0.62 $\pm$ 0.30 (0.28-0.89)	4.11 $\pm$ 2.02 (1.89-5.90)

Baby rice	Australia	2	73±6 (50-73)	26 (7-45)	1.90±0.86 (1.30-2.51)	1.33±0.60 (0.91-1.76)	8.84±3.99 (6.07-11.72)
	Others	2	77±3 (46-108)	90 (74-105)	6.87±3.99 (4.10-9.73)	4.81±2.79 (2.87-6.81)	32.08±18.61 19.11-45.42)
Ready-to-eat rice (only for adult)	Australia	8	45±5 (10-94)	125	5.56±3.36 (1.20-11.76)	0.65±0.39 (0.14-1.37)	4.32±2.62 (0.94-9.15)
	India	7	13±2 (0-57)	125	1.60±2.57 (0-7.07)	0.19±0.30 (0-0.82)	1.24±1.99 (0-5.50)
	Thailand	6	36±5 (0-87)	125	4.50±3.92 (0-10.83)	0.52±0.45 (0.18-1.26)	3.50±3.05 (1.23-8.42)
	UK	1	41±0	125	5.10±0.00	0.60±0.00	3.97±0.00
Other rice-based snacks	Australia	2	88±2 (71-105)	30 (5-55)	2.64±0.71 (2.1-3.1)	1.84±0.50 (1.5-2.2)	12.28±3.31 (9.94-14.62)
	Others	4	33±6 (28-44)	14 (4-28)	0.46±0.10 (0.39-0.61)	0.32±0.07 (0.27-0.43)	2.13±0.47 (1.83-2.84)

Provisional tolerable weekly intake (PTWI) of total As (15 µg/kg bw) (JECFA 2010)

Table 3

Comparison of the results (As content in rice-based products) of this work and other published works (ranges are also given in the brackets).

Rice Products	n	tAs ($\mu\text{g/kg}$)	iAs ($\mu\text{g/kg}$)	iAs (%)	References
Baby rice	4	204 $\pm$ 13 (59-357)	75 $\pm$ 4 (46-108)	68 (22-100)	This study
	29	-	121 (56-268)	70 (51-85)	Signes-Pastor, et al. (2016)
Infant rice (without gluten)	13	126 $\pm$ 26 (46-315)	69 $\pm$ 8 (29-121)	64 (36-89)	Carbonell-Barrachina, et al. (2012)
Infant rice (with gluten)	9	33 $\pm$ 6 (15-65)	26 $\pm$ 5 (10-49)	98 (90-100)	
Puffed rice	6	145 $\pm$ 21 (62-228)	50 $\pm$ 6 (37-61)	52 (32-73)	This study
	2	270 $\pm$ 10	140 $\pm$ 2	77	Sun, et al. (2009)
Rice crackers	10	215 $\pm$ 23 (140-456)	97 $\pm$ 8 (56-270)	64 (42-83)	This study
	11	390 $\pm$ 10	210 $\pm$ 10	76	Sun, et al. (2009)
	97	-	111 (18-211)	81 (45-100)	Signes-Pastor, et al. (2016)
Ready-to-eat rice	22	41 $\pm$ 17 (15-90)	32 $\pm$ 2 (0-94)	71 (0-100)	This study
Rice cakes	11	187 $\pm$ 18 (58-384)	102 $\pm$ 9 (27-158)	76 (52-100)	This study
Other rice-based snacks	6	153 $\pm$ 8 (60-424)	51 $\pm$ 5 (28-104)	62 (32-100)	This study

Highlights

- Significant level of arsenic (As) in all rice-based products.
- Arsenic content varies as crackers>baby rice>cakes>puffed rice>ready-to-eat rice.
- 75% of rice-based products had inorganic As greater than the EU recommended value.
- Manufacturer recommendation may lead to 0.56 to 6.87 μg inorganic As/serving.
- Young children are most at risk from ingestion of rice-based products.