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Inorganic arsenic in rice-based products for infants and young children

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ABSTRACT

Inorganic arsenic (As_i) is a chronic, non-threshold carcinogen. Rice and rice-based products can be the major source of As_i for many subpopulations. Baby rice, rice cereals and rice crackers are widely used to feed infants and young children. The As_i concentration in rice-based products may pose a health risk for infants and young children. As_i concentration was determined in rice-based products produced in the European Union and risk assessment associated with the consumption of these products by infants and young children, and compared to an identical US FDA survey. There are currently no European Union or United States of America regulations applicable to As_i in food. However, this study suggests that the samples evaluated may introduce significant concentration of As_i into infants' and young children's diets. Thus, there is an urgent need for regulatory limits on As_i in food, especially for baby rice-based products.

1. Introduction

Arsenic (As) is ubiquitous in the environment and occurs in different forms. As_i is a non-threshold human carcinogen (IARC, 2004). Other than cancer, human exposure to As has been associated to diverse health problems (WHO, 2011a), which may be exacerbated with early-life exposure (Smith et al., 2006; Vahter, 2009). The main sources of human exposure to As are water and food (WHO, 2010). As_i in water is tightly regulated (Council Directive, 1998; WHO, 2011b), however, there is no European Union (EU) or United States of America (USA) standard for As_i in food products despite the fact that food sources dominate exposure, especially rice and rice-based products (EFSA, 2009; US FDA, 2014). Indeed, it has been demonstrated that consumption of rice and/or rice-based products increases the occurrence of As species in human urine (Cascio, Raab, Jenkins, Felman, & Meharg, 2011; Gilbert-Diamond et al., 2011; Wei, Zhu, & Hguyen, 2014). Furthermore, a cohort study in West Bengal, India, has reported elevated genotoxic effects, as measured by micronuclei in urothelial cells, associated with the staple consumption of cooked rice with >200 μg As/kg (Banerjee et al., 2013). Recently, the JECFA proposed a maximum level of 0.2 mg/kg of As_i in polished rice (JECFA, 2014). The European Food Safety Authority (EFSA) has reviewed the diet of the European Union population and has recommend that dietary exposure to As_i should be reduced. Cereal and cereal-based products have been identified as contributors to daily As_i exposure in the general European population and young children (<3 years of age) have been categorised as the most exposed to As_i (EFSA, 2009). The review was mainly based on data reported as total As and a number of assumptions to estimate the As_i exposure were made. It was highlighted that more speciation data for different food commodities are required to support a comprehensive dietary exposure assessment and to redefine risk assessment of As_i, especially to high exposure risk subpopulations. The JECFA also reviewed and stated that dietary exposure to As_i should be reduced. In addition, the Provisional Tolerable Weekly Intake (PTWI) was withdrawn since cancer of the lung and urinary bladder in addition to skin and a range of adverse effects were reported at As_i exposure lower that those reviewed at the time the PTWI was established (JECFA, 2010).

Rice accumulates significantly higher levels of As_i from soil and water than other crops due to anaerobic paddy soil culture, which renders As_i highly available for plant uptake, leading to ~10-fold higher concentrations in grain compared to aerobically grown grains such as wheat or barley (Meharg & Zhao, 2012; William et al., 2007; Xu, McGrath, Meharg, & Zhao, 2008). Levels of As_i in rice are also of concern due to the fact that there is a high gut bioavailability of rice As_i (Juhasz et al., 2006; Signes-Pastor, Al-Rmalli, Jenkins, Carbonell-Barrachina, & Haris Parvez, 2012). Rice-based products also have high levels of As_i and show a positive correlation between rice content and their As concentration (Burlo, Ramirez-Gandolfo, Signes-Pastor, Haris, & Carbonell-Barrachina, 2012; Carbonell-Barrachina et al., 2012). Rice-based products are widely used during weaning and to feed young children due to its availability, bland taste, nutritional value and relatively low allergic potential (Da Sacco, Baldassarre, & Massotti, 2013; Meharg et al., 2008; Mennella, Ziegler, Briefel, & Novak, 2006).

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Consumption of rice and rice-based foods is particularly high for infants and young children affected by celiac disease, which is a common condition that affects 1% of children in the EU and USA, while their only viable treatment is a gluten-free diet (Da Sacco et al., 2013; Munera-Picazo, Burló, & Carbonell-Barrachina, 2014; Newton & Singer, 2012). Furthermore, the fact that infants and young children have higher food consumption rates on body weight basis than adults, *circa* 3-fold, increases their exposure to As_i with respect to adults for any given item of food, which exacerbates toxicological issues for this subpopulation (EFSA, 2009; Meharg & Zhao, 2012).

Information on As speciation data of rice-based products consumed by infants and young children is needed to define risk assessment of As_i for one of the most vulnerable subpopulations, and to set regulations for As_i content in food to protect them. In this study, therefore, As speciation was measured in 29 commercial baby rice, 53 commercial rice cereals and 97 commercial rice crackers from the EU market, and compared to 85 commercial baby rice, 105 rice cereals and 199 rice crackers included in the US FDA survey on As_i in rice and rice-based products (US FDA, 2014), and the findings put in context of exposure risks to infants and young children.

2. Materials and methods

Samples of baby rice ($n = 29$), rice cereals ($n = 53$) and rice crackers ($n = 97$) belonging to 21 different and most popular commercial brands or manufacturers were purchased from 36 food shops (15 local shops and 21 big supermarkets) in the United Kingdom (UK). Duplicate samples of the same product and brand were always purchased from different stores. The rice-based products sampled showed use by date between February 2014 and March 2016.

2.1. Sample preparation for As speciation

All samples of rice-based products were freeze-dried, and then powdered using a Retch PM100 rotary ball-mill using a zirconium oxide lined vessel and zirconium oxide grinding balls. The powdered samples were weighed accurately to a weight of 0.1 g into 50 ml polypropylene centrifuge tubes to which 10 ml of 1% conc. Aristar nitric acid was added and allowed to sit overnight. Batches of 30 samples approximately were prepared which also include a blank and rice CRM (NIST 1568b Rice flour) which has the As species As_i, dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA) concentrations certified, then microwave digested in an CEM MARS 6 instrument for 30 min. at 95 °C using a 3 stage slow heating program: to 55 °C in 5 min. held for 10 min., to 75 °C in 5 min., held for 10 min. to 95 °C in 5 min., held for 30 min. A 1 ml aliquot was transferred to a 2 ml polypropylene vial and 10 μl of analytical grade hydrogen peroxide was added to convert any arsenite to arsenate to facilitate subsequent chromatographic detection.

2.2. Chemical analysis

To speciate As in rice-based products the diluted 1% nitric acid digested sample solutions were run on a Thermo Scientific IC5000 Ion Chromatography (IC) system, with an Thermo AS7, 2 × 250 mm column (and a Thermo AG7, 2 × 50 mm guard column) and a gradient mobile phase (A: 20 mM Ammonium Carbonate, B 200 mM Ammonium Carbonate – Starting at 100% A, changing to 100% B, in a linear gradient over 15 min.) interfaced with a Thermo ICAP Q ICP-MS that monitored m/z^+ 75, using He gas in collision cell mode. The resulting chromatogram was compared with that for authentic standards; DMA, As_i, MMA, tetratmethyl arsonium (TETRA) and arsenobetaine (AB). As present under each chromatographic peak was calibrated using a DMA concentration series.

2.3. Statistical analyses

Data were subjected to general lineal model (GLM) and the Duncan multiple range test to determine significant differences among samples. The statistical analyses were performed using IBM SPSS Statistic version 21.0.

3. Results and discussion

The analysis of the As speciated CRM gave excellent recovery results (mean ± SE), based on $n = 15$, with 105 ± 3% recovery for DMA, 93.4 ± 5% for MMA and 94.5 ± 2% recovery for As_i. The CRM had a certified concentration of 0.182, 0.012 and 0.092 mg/kg As for DMA, MMA and As_i, respectively. The limits of detection (LOD) for both DMA and As_i (calculated from a DMA calibration) was 0.003 mg/kg rice d.wt., $n = 6$. All samples presented were above LOD for As_i and only a few samples were below LOD for DMA and MMA, and in this case 1/2 LOD was used in statistical analysis of the data.

3.1. Baby rice

The summation of As species concentration (ΣAs) in 29 baby rice samples belonging to 5 different commercial brands ranged from 0.063 to 0.334 mg/kg (Table 1). The As_i percentage ranged from 51.4% to 84.6% of the ΣAs species concentration. The baby rice brands M001, M003 and M005 had a significantly higher percentage of As_i (71.6%, 73.4% and 79.3%, respectively) than M002 and M004 (66.3% and 53.5%, respectively; $p < 0.001$). The As_i concentration ranged from 0.056 to 0.268 mg/kg. This shows that 14% of the baby rice samples evaluated would be above the JECFA proposed As_i maximum level for rice (0.200 mg/kg). The baby rice brand M005 had the highest As_i concentration (median of 0.190 mg/kg; $p < 0.001$). DMA ranged from 0.030 to 0.123 mg/kg (Table 1). The same trend of As speciation has been previously described in rice (Meharg et al., 2009; Torres-Escribano, Leal, Vélez, & Montoro, 2008). Baby rice samples labelled as produced under organic standard showed higher levels of As_i than non-organic samples (Fig. 1), which was associated with the inclusion of whole grain rice. In fact, organic baby rice samples including whole grain contain a higher concentration and percentage of As_i (median of 0.190 mg/kg and 79.3%) than those manufactured with milled rice (median of 0.121 mg/kg and 55.1%; $p < 0.001$) (Table 2). This is in agreement with previous studies that show that brown rice contains higher proportion of As_i than white rice, which is mainly concentrated at the surface of the whole grain, in the region corresponding to the pericarp and aleurone layer (Choi et al., 2014; Meharg et al., 2008). This is of particular concern as organic products are usually associated with a healthier and more nutritious option that is increasing production of organic baby food and may exacerbate As_i exposure and health risk for infants and young children (Da Sacco et al., 2013).

In September 2013 the US Food and Drug Administration (US FDA) released analytical results of As_i in approximately 1100 samples of rice and rice products from the US market, which were in addition to approximately 200 samples of rice and rice products initially tested, the results of which were released in September 2012 (USFDA, 2013). These results include 85 samples of baby rice (product subcategory: infant cereals and toddler cereals). The median and range of As_i in baby rice from the USA market is 0.114