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Essential micronutrient and toxic trace element concentrations in gluten containing and gluten-free foods

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ABSTRACT

For individuals following a gluten-free (GF) diet, rice is commonly the major grain. People following a GF diet have a higher arsenic burden than the general population. We conducted a multielemental market basket study of GF and gluten containing ingredients and prepared foods (Mn, Fe, Ni, Cu, Zn, Cr, Co, Se, Cd, Sb, Pb, total As, As species, total Hg and methylmercury). Foods containing rice were significantly higher in As, Hg and Pb and lower in Se, Fe, Cu and Zn. Wheat-based foods were higher in Cd. Mercury concentrations were low (< 3.5 ng/g); speciation was predominantly methylmercury. Arsenic and mercury in rice were correlated. GF foods contained significantly more As and Hg. Eating a wide variety of GF grains may reduce contaminant exposure and increase micronutrient status compared to a rice-based GF diet.

1. Introduction

Grains have long been a staple of the human diet, being an excellent source of carbohydrate. The most widely consumed grains – rice, maize and wheat – provide 60% of the world's food energy intake (FAO., 1995). Like other plants, these staples can accumulate non-essential and potentially toxic trace elements from natural or human input to the soil. It is well-established that the concentration of arsenic in rice grain is higher than in the grains of other cereals such as wheat, oats and barley (Cubadda, Jackson, Cottingham, Van Horne, & Kurzius-Spencer, 2017). This is due in equal parts to the practice of rice paddy farming and the physiological requirement of rice for silicon, for which arsenite is a chemical analog. Flooding rice paddies promotes the dissolution of iron oxide minerals in the soil that otherwise sequester arsenic; the released arsenic is efficiently taken up by rice plants via silica transport systems and translocated to the rice grain (Punshon et al., 2017). Compared to environmental factors, it is the cultivar of rice that has the greatest influence on the amount of arsenic that accumulates in the rice grain (Norton et al., 2012). Grain arsenic concentration varies widely between different cultivars, which has given rise to breeding efforts to develop cultivars with low arsenic accumulation characteristics.

Inorganic arsenic, the most acutely toxic form (Le et al., 2000) and consequently the form regulated in food and water, tends to accumulate in the nutrient-rich outer layers of the rice grain (tegumen, pericarp and aleurone layers) known as the bran. Brown rice, therefore, usually contains higher concentrations of inorganic arsenic than white, in which the bran layers have been removed or 'polished' (Meng et al., 2014). Food products made primarily from rice bran can be particularly high in inorganic arsenic (Sun et al., 2008).

The EU has introduced regulations specifically for white rice of 0.2 µg/g for inorganic arsenic and rice products aimed at infants have a lower limit of 0.1 µg/g (EU, 2015). Because of their lower acute toxicity to humans, the organic forms of arsenic are not targeted for regulation. The US FDA has also set an action limit of 0.1 µg/g for inorganic arsenic in infant rice cereals (FDA, 2016). The regulatory focus on foods aimed at infants and young children reflects their heightened developmental vulnerability and higher exposure to arsenic (ingestion normalized to body weight) compared to adults (European Food Safety Authority, 2009). Concerns about arsenic exposure from rice-based diets have been raised for Asian populations and for individuals following a gluten-free (GF) diet where processed food products (such as bread and pasta) use rice as a staple grain instead of wheat (Meharg, Norton, Deacon, Williams, Adomako, Price, et al., 2013). A recent statistical analysis of the National Health and Nutritional Examination Study (NHANES) database (2009–2014) of urine and blood concentrations measured in the US population found that urinary arsenic was significantly higher in individuals that self-reported as being on a GF diet (n = 74) compared with the total individuals sampled (n = 7471) (Bulka, Davis, Karagas, Ahsan, & Argos, 2017).

Other potentially toxic elements have also been found in rice. Cadmium can reach levels of concern (Meharg et al., 2013) when rice is grown aerobically. In China, mercury contamination of rice grown on

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contaminated soils can contribute to human mercury exposure (Rothenberg, Windham-Myers, & Creswell, 2014). Arsenic and mercury are among the top three contaminants of concern on the Agency for Toxic Substances and Disease Registry's National Priority list; together with cadmium (at number 7) they are taken up by plants, and are developmental neurotoxins (Grandjean & Herz, 2015).

Food, in general, is the main source of cadmium exposure for non-smokers. In 2012 the European Food Safety Authority reviewed cadmium exposure in the European population and concluded that children and adults at the 95th percentile of exposure could be consuming cadmium levels in excess of health based guidelines (0.001 mg/kg/day) (European Food Safety Authority, 2009). Subsequently maximum allowable limits for cadmium in certain foods were adjusted down to reduce exposure to the general public. Wheat can be a major source of cadmium to diet and, like arsenic uptake in rice, cadmium uptake in wheat is dependent on the variety of wheat grown (Harris & Taylor, 2004).

There has been a recent focus on mercury uptake by rice and subsequent human exposure; this is primarily an issue with rice grown on mercury polluted soils, and again growing rice anaerobically exacerbates the problem, because sub-oxic conditions promote methylation of mercury to methylmercury, the most toxic form. Hence, when fish consumption is low, rice products can be the major source of methylmercury to the diet (Rothenberg et al., 2016). A recent market basket analysis of infant rice products found that rice cereals and rice teething biscuits were on average 61 and 92 times higher in methylmercury respectively than cereals made with wheat or oats (Rothenberg, Jackson, Carly McCalla, Donohue, & Emmons, 2017). Provisional tolerable weekly intake (PTWI) limits for methylmercury exposure from food were established in the EU by the Joint Expert Committee on Food Additives (JECFA) of 1.3 µg mercury/kg body weight (0.18 µg per day) (JECFA, 2007). The US EPA oral reference dose (RfD) for daily intake of methylmercury is 0.1 µg/kg body weight (USEPA, 2001). Analysis of data from NHANES, mentioned above, also found higher blood mercury (inorganic and methylmercury) concentrations in people following a GF diet (Bulka et al., 2017). Increased rice consumption is one possible explanation.

Numerous market basket studies have measured the concentration and speciation of arsenic in whole grain rice, food containing rice, and ingredients processed from rice. This has provided the basis for the food-arsenic regulation mentioned above. Databases of arsenic concentrations and speciation in many rice-containing food products are available (FDA, 2016) and it is clear that some iterations of a GF diet could potentially provide a higher arsenic exposure (Munera-Picazo, Ramirez-Gandolfo, Burlo, & Carbonell-Barrachina, 2014) than is considered safe in terms of increases in life-time cancer risk. Elevated cadmium, lead and nickel concentrations were also found (Orecchio et al., 2014). However, side-by-side comparisons of the concentration of arsenic and other relevant elements in GF and non-GF products – needed to inform a dietary arsenic exposure risk assessment – have not been extensively carried out. In addition to the 1% of the US population who have celiac disease based on seroprevalence, GF diets are also necessary for those with non-celiac gluten sensitivity and wheat allergies. Despite concerns about the nutritional adequacy of the GF diet (Theethira & Dennis, 2015), it has gained a reputation as being more beneficial for health and weight maintenance than diets containing gluten. Surveys conducted in 2013 indicated that almost 25% of the US population had adopted a GF diet (DiGiacomo, Tennyson, Green, & Demmer, 2013). In line with this, the GF food retail market more than doubled in value between 2011 and 2016 (Group, 2013), a trend which is expected to continue.

In this study, we measured the concentration of arsenic, mercury, lead, cadmium and other elements including micronutrients manganese, iron, zinc, copper and selenium, in locally-available rice grains and rice-containing products and compared them to metal concentrations measured in equivalent wheat-based products. Arsenic and mercury speciation was determined in rice grains and rice-containing products, because total concentrations of these elements were high enough in these products to allow reliable speciation analysis and/or exceed proposed regulatory limits. We examined the elemental content of other readily available GF flours and grains such as amaranth, oat, sorghum, almond and coconut. We show that, consistent with observations of mercury in blood of GF diet followers (Raehsler, Choung, Marietta, & Murray, 2017; Vici, Belli, Biondi, & Polzonetti, 2016), rice-containing products appear to be a source of methylmercury at very low concentrations (up to 3.5 ng/g) in comparison with products made from wheat or other grains.

2. Methods and materials

2.1. Sample procurement and preparation

Sixty-seven food products were purchased from local food stores in Hanover and West Lebanon (New Hampshire, USA) and from on-line suppliers from late 2016 through mid 2017. The choice of food products was intended to compare readily available GF cooking ingredients and staple prepared food products and their gluten-containing counterparts. Products were grouped into flours, whole grain rice, and prepared foods. Designation of the products as GF, organic or enriched were made on the basis of information on the packaging. We purchased 19 different rice grains, three rice flours, and 19 non-rice flours (including corn, corn masa, whole wheat, all-purpose wheat, sprouted wheat, spelt, millet, oat, buckwheat, chickpea, coconut, and almond, amaranth) as well as other popular grains (black chia seed and tricolor quinoa). The GF and non-GF prepared food products consisted of gluten free pastas, breads, cakes (Table 1). Most GF products contained rice as one of top 3 listed ingredients.

Whole grains were not rinsed or cooked prior to being prepared for analysis, and were ground in a clean, dry coffee grinder. Flour and powder samples were acid digested without further preparation. Moist prepared food samples were freeze-dried and homogenized prior to analysis. The final results were corrected so they reflected the wet weight concentration. Foods were analyzed for Mn, Fe, Ni, Cu, Zn, Cr, Co, As, Se, Cd, Sb, Hg, and Pb (Table 1). Whole grain rice and rice flour were subject to speciation analysis for arsenic (inorganic As, dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA)) and mercury (methylmercury and total mercury).

2.2. Sample digestion for total metals analysis

Samples were acid digested by closed vessel microwave assisted digestion; 5 ml of 9:1 Optima HNO_3:HCl was added to 0.25 g of sample and the digestion temperature was ramped to 220 °C over 15 min and held for a further 20 min. Following digestion, the sample was diluted to 50 ml with deionized water.

For arsenic speciation, 0.25 g of sample was heated to 100 °C in 2% HNO_3 following our previous methods (Jackson, 2015). Methylmercury analysis was performed by species specific isotope dilution, acid extraction, ethylation, purge and trap concentration, gas chromatographic separation and ICP-MS analysis following our previous methods (Taylor, Jackson, & Chen, 2008).

2.3. Elemental analysis

Samples digested for total elemental analysis were analyzed by collision cell inductively coupled plasma mass spectrometry (ICP-MS) (Agilent, 7900x) operated in helium gas mode for all elements and no gas mode for lead and mercury. For digestions and extractions, one sample per batch (where a batch is denoted as ≤20 samples) was digested/extracted in duplicate and spiked with analyte and taken through the digestion/extraction process. Additionally, one spiked blank (fortified blank), reagent blank and standard reference material