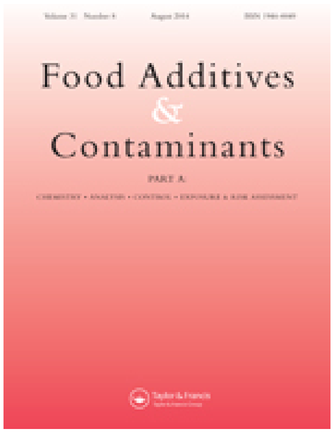

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Celiac disease (CD) may affect up to 1% of the Western population. It is a disease whose diagnosis has been made mainly in childhood, but now the profile has changed, with one out of five newly diagnosed individuals being over 65 years old. The only treatment for this population is a gluten-free diet. Therefore, the objective of this study was to analyse the occurrence of arsenic (As) in gluten-free products, basically those rice-based, intended for celiac adult consumers. The current study demonstrated that these rice-based products contained important contents of total arsenic (t-As) (up to 120 μg kg^{-1}) and inorganic arsenic (i-As) (up to 85.8 μg kg^{-1}). It was estimated that the contents of t-As and i-As in rice used as the main ingredient of these foods were as high as 235 and 198 μg kg^{-1}, respectively. The estimated daily intake of i-As was 0.46 and 0.45 μg kg^{-1} bw in women and men of 58 and 75 kg of body weight (bw), respectively. These values indicate that a health risk to these consumers cannot be excluded. Finally, legislation is needed to delimit the safety intake by health agencies and to improve the labelling of these special rice-based foods for celiac adult consumers. The label should include information about percentage, geographical origin and cultivar of the rice used; besides and if companies want to clearly prove the safety of their products, the exact content of i-As should also be included.

Keywords: dietary exposure; food safety; gluten-free food; *Oryza sativa*

Introduction

Celiac disease (CD) is a common condition that affects 0.5–1% of the Caucasian population. A high prevalence also occurs in North African and Middle Eastern populations, and it is rarely reported in oriental or black African people (Green & Cellier 2007; Woodward 2011; Evans & Sanders 2012). However, it is considered that the epidemiology of CD has the characteristics of an iceberg and that its prevalence is underestimated because often one silent intestinal involvement may go unnoticed and a large proportion of cases may remain undetected (Rodrigues & Jenkins 2006; Polanco 2008). Its diagnosis was traditionally made in childhood; however, the profile of the new CD patient has changed in the last years and now one out of five newly diagnosed individuals has an age above 65 years old. There is also a higher proportion of female patients and first- and second-degree familial aggregation is reported (De los Santos et al. 2012).

CD, also called gluten-sensitive enteropathy, consists of immunological gluten intolerance; gluten is found in processed foods from wheat, barley and rye. It produces a mucous inflammation and malabsorption syndrome, which is characterised by inappropriate absorption of nutrients in the bowel (proteins, fats, carbohydrates, vitamins and minerals) (De los Santos et al. 2012). Treatment of patients with CD is based mainly on the maintenance of a gluten-free diet as well as preventing the associated nutrient deficiency (NIDDK 2008).

Arsenic (As) has been a real problem for India's disadvantaged population, whose basic staple food was rice, along with drinking water contaminated with inorganic arsenic (i-As); as a result this situation has been considered as the largest poisoning event in history (Meharg 2005). In the last decade, it has been proved that this problem can also affect Western countries, such as those in the European Union. International authorities in charge of food safety issues are trying to establish recommended maximum residue limits for i-As but still there is big controversy on this issue. In 2009, the EFSA Panel on Contaminants in the Food Chain (EFSA 2009) indicated that the provisional tolerable weekly intake (PTWI) of 15 μg kg^{-1} established by JECFA was no longer appropriate. The panel concluded that the overall range of benchmark dose lower confidence 1% ($BMDL_{01}$) values between 0.3 and 8.0 μg kg^{-1} of body weight (bw) per day for an increased risk of cancer of lung, skin and bladder, as well as skin lesions, should be used instead of a single reference point in the risk characterisation of i-As. In 2010 JECFA determined the BMDL for a 0.5% increased incidence of lung cancer, from epidemiological data to be 3.0 μg kg^{-1} bw day^{-1}. The committee noted that the previously established PTWI of 15 μg kg^{-1} bw (equivalent

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to 2.1 μg kg^{-1} bw day^{-1}) for i-As was in the region of the $BMDL_{0.5}$ and therefore was no longer appropriate. This PTWI was therefore withdrawn by the committee, and no new tolerable intake level could be established (FAO/WHO 2010).

Feeding of celiac people is inherently difficult because they must avoid even traces of gluten contaminating products which do not have gluten naturally, such as meat products. Furthermore, one of the few cereals they can consume, rice, can be highly contaminated with As. Relatively high contents of this metalloid have been found and reported in rice (Sun et al. 2008; Meharg et al. 2009; Burló et al. 2012), rice-based products (Sun et al. 2008, 2009), rice-based baby foods (Meharg, Sun, et al. 2008; Carbonell-Barrachina et al. 2012; Hernández-Martínez & Navarro-Blasco 2013; Juskelis et al. 2013; Llorente-Mirandes et al. 2014), and rice-based products intended for children with CD (Munera-Picazo, Ramírez-Gandolfo, Burló et al. 2014).

It is also important to mention that the other household members, living with a celiac person, could follow a gluten-free diet to avoid any cross-contamination of foods with this allergen. Consequently, families with a celiac member might have higher intake of i-As compared with families not affected by this health problem.

The main aim of this study was to evaluate the occurrence of both total arsenic (t-As) and i-As in foods intended for adults with the CD. After knowing the exact contents of t-As and i-As in celiac foods, two additional activities were conducted: (1) the contents of t-As and i-As in the rice used as raw material in the manufacture of these special items were estimated to check whether high quality and safe rice was used; and (2) the main health risks, as a result of the exposure to i-As from rice-based foods in this specific segment of consumers, were modelled and predicted. Finally, authors have provided practical recommendations about labelling and appropriate selection of rice cultivars and geographical sources for manufacturers, consumers and authorities.

Materials and methods

Sample preparation

In this study samples from seven groups of gluten-free food from different brands were analysed: baking flour, breadcrumbs, pasta, bread toast, pastries, beer and rice milk. All products were purchased (in triplicate) in national supermarket chains from the provinces of Alicante and Murcia (Spain) and were analysed in triplicate for t-As and i-As contents. All products contained rice at different concentration, except control samples (rice-free items); in each of the food groups there was a control sample. Finally, 32 products were analysed:

- Five baking flour samples intended for preparation of bread, cakes or waffles.
- Three breadcrumbs samples.
- Three pasta samples.
- Four bread toast samples.
- Nine pastries: biscuits, cereal bars, cupcakes and cakes.
- Three beer samples.
- Five rice and soya milks.

Solid products were first milled with a domestic grinder (Moulinex, Valencia, Spain) and later with a mortar grinder, Retsch, model RM200 (Haan, Germany); with this procedure the final fineness of the samples was below 10 μm. The grinders were cleaned after each sample to avoid cross-contamination of samples; no release of arsenic from the grinders has been detected at all. Samples were then dried at 70°C until constant weight in a hot-air oven (Selecta, Barcelona, Spain). Liquid products were analysed without any preparation.

Determination of t-As

All samples were analysed for t-As by hydride generation atomic absorption spectrometry (HG-AAS). In this analysis 10 ml of liquid samples or 1 g of dried, ground and homogenised solid samples were weighed and digested using the method first described by Muñoz et al. (2000) and later slightly modified by Burló et al. (2012). Calibration standards of $NaAsO_2$ (arsenite, As(III)) were prepared using the same HCl concentration of the samples and CRM. The instrumental conditions used for the hydride generation were: reducing agent: 1.4% (m/v) $NaBH_4$ in 0.4% (m/v) NaOH at a flow of 5 ml min^{-1}; HCl solution: 10% (v/v) at 10 ml min^{-1}; carrier gas: argon, at 250 ml min^{-1}; while the conditions for the atomic absorption spectrometer were: wavelength: 193.7 nm; spectral bandpass: 0.5 nm; intensity of the hollow cathode lamp 8 mA; air/acetylene flame.

In each analytical batch, at least one reagent blank, one spike and one internationally CRM were included to assess precision and accuracy of chemical analysis. The CRM (rice flour, NIST SRM 1568a) used for testing this analytical method was obtained from CYMIT Química S. L. (Barcelona, Spain) and produced by the US National Institute of Standards and Technology.

As speciation

The methodology used for the extraction of the As species was that first described by Heitkemper et al. (2001) and later by Signes et al. (2008). A total of 1 g of dried solid samples or 5 ml of liquid samples were treated with 3 ml of 2 M trifluoracetic acid (TFA). The mixture was allowed to stand for 6 h at 100°C in 60 ml capped high-density polyethylene (HDPE) centrifuge tubes. The mixture was then centrifuged and the supernatant collected and diluted to proper volume with deionised water. The TFA extracts were filtered through a 0.45 mm nylon syringe filter before analysis by high performance liquid chromatography-hydride generation-atomic fluorescence spectrometry (HPLC-HG-AFS). Separation of the As compounds – arsenite, arsenate, mono-methyl arsonate (MMA) and di-methyl arsinate (DMA) – was carried out in about 12 min in the anion-exchange column using 25 mM phosphate buffer (pH 6.0) as the mobile phase at a 1.1 ml min^{-1} flow rate. The elution order was arsenite, DMA, MMA and arsenate. A total of 50 µl of the sample was injected in the HPLC-HG-AFS system. The retention times were 3.15, 4.24, 5.07 and 8.75 min for arsenite, DMA, MMA and arsenate, respectively. External calibration was accomplished using standards of 1, 10, 20, 30, 40, and 50 µg l^{-1} of each of the four As species studied [arsenite: $NaAsO_2$, DMA: $(CH_3)_2AsO(ONa) \cdot 3H_2O$, MMA: $CH_4AsNaO_3 \cdot 1.5\ H_2O$ and arsenate: $Na_2HAsO_4 \cdot 7H_2O$].

Statistical analyses

All data were first subjected to analysis of variance (ANOVA) and later to Tukey's least-significant difference multi-comparison test to determine significant differences among samples (food type). The statistical analyses were performed using IBM SPSS Statistics 21.0 (IBM Corporation, Armonk, NY, USA).

Results and discussion

The analytical characteristics of the t-As methodology were as follows: LOQ, 4 µg kg^{-1}, and LOD, 1.2 µg kg^{-1} (calculated according to the European Standard prEN 13804, which establishes that the LOQ and LOD are numerically equal to 10 and three times the SD of the mean of blank determination, respectively); precision 2% (calculated as mean RSD obtained from six independent analyses of certified material NIST SRM 1568a); accuracy for rice flour (NIST SRM 1568a), the found value was 275 ± 9 µg kg^{-1}, while the certified value was 290 ± 30 µg kg^{-1}. Additionally, no rice CRM certified speciation is available; however experimental results: i-As 95 ± 3 µg kg^{-1} and o-As 187 ± 5 µg kg^{-1} were in good agreement with those previously reported by Raab et al. (2009) (i-As 99 µg kg^{-1} and organic arsenic (o-As) 185 µg kg^{-1}) and Carbonell-Barrachina et al. (2012) (i-As 95 µg kg^{-1} and o-As 182 µg kg^{-1}). These data confirmed the goodness of the extraction and quantification protocols.

t-As and i-As in control and rice-based samples

To establish whether a significant dependence of the t-As and i-As contents on the rice percentage included in the formulation of rice-based foods for celiac adults, a product prepared using no rice was included in each one of the food groups, and it was considered as the control sample. The content of t-As in these control samples was below the LOQ and therefore was considered to be zero (Table 1). Similar results were obtained by Matos-Reyes et al. (2010) who reported unmeasurable contents of t-As in cornmeal, oatmeal and wheat; their LOD and LOQ were 0.5 and 1.7 µg kg^{-1}, respectively. However, very recently Llorente-Mirandes et al. (2014) analysed cereal-based products and found t-As concentrations lower than 9 µg kg^{-1}, but measurable, in corn snacks. Summarising, the foods for celiac adults based on cereals other than rice (basically corn-based) under analysis in this study were As-free.

The gluten-free products under analysis contained rice contents ranging from as low as 5% to 100% (Table 1). The highest values of t-As (quantified by HG-AAS) and i-As (quantified by HPLC-HG-AFS) were found in the samples from the pasta group; values were 109 and 120 µg kg^{-1} for t-As and 73.0 and 84.2 µg kg^{-1} i-As. Other samples with high contents of t-As and i-As were: (1) sample 1B (baking flour) with 107 and 85.8 µg kg^{-1}, respectively; (2) sample 4B (bread toast) with 80.2 and 60.6 µg kg^{-1}, respectively; and (3) sample 2B (bread-crumbs) with 78.4 and 61.7 µg kg^{-1}, respectively. The rice percentages in these samples were the highest: 93% in sample 3B, 99% in 3A and 100% in 1B; however, the bread samples (4B and 2B) contained only 50% of rice.

These results are comparable with those previously found in rice-based products intended for celiac children (Munera-Picazo, Ramírez-Gandolfo, Burló et al. 2014); these authors concluded that the products with the highest As contents were pasta and bread.

As shown in Figure 1, there are significant relationships ($R^2 > 0.80$) among t-As and i-As and rice percentage; these relationships took R^2 values of 0.839 and 0.781, when only rice-based samples were considered. However, this trend was not always so evident. For instance in the pastries group, samples containing 20% of rice had values of t-As as different as 0, 37.9 and 46.9 µg kg^{-1}; in the same way, sample 5E, which contains 30% rice, only presented 6.20 and 5.60 µg kg^{-1} of t-As and i-As, respectively. These differences in the As contents of samples with the same rice percentage indicated that there are rice samples, raw material, with low initial content of As, perhaps due to genetics (cultivar) or farming practices (cultivation using more aerobic soil conditions). Therefore, it is essential that rice batches with as low as technologically and economically possible contents of both t-As and especially i-As, are selected for foods intended for people potentially exposed to high levels of toxic elements.

Regarding As speciation, inorganic species predominate in all rice-based foods (Table 1). Arsenite and DMA

Table 1. t-As and i-As contents in foods for celiac adult consumers.

Group	Sample code	Rice (%)	t-As (μg kg^{-1})	As speciation (μg kg^{-1})					
				Arsenite	Arsenate	MMA	DMA	∑t-As Species	∑i-As Species
Control samples									
Baking flour	1	0	n.d.	–	–	–	–	–	–
Breadcrumbs	2	0	n.d.	–	–	–	–	–	–
Pasta	3	0	n.d.	–	–	–	–	–	–
Bread toast	4	0	n.d.	–	–	–	–	–	–
Pastries	5	0	n.d.	–	–	–	–	–	–
Beer	6	0	n.d.	–	–	–	–	–	–
Milk (soya)	7	0	n.d.	–	–	–	–	–	–
Rice-based samples									
Baking flour	1A	40.0	30.5 e[a]	16.8 gh	4.3 c	n.d.	7.0 g	28.1 i	21.1 g
	1B	100	107 a	66.6 b	19.2 a	12.1 a	18.0 c	116 a	85.8 a
	1C	20.0	14.0 hi	11.0 i	n.d.	n.d.	5.3 h	16.3 j	11.0 i
	1D	28.0	58.0 c	50.1 c	n.d.	n.d.	11.8 ef	61.9 e	50.1 d
Breadcrumbs	2A	50.0	49.8 cd	38.5 d	n.d.	n.d.	14.7 d	53.2 f	38.5 e
	2B	50.0	78.4 b	53.3 c	8.4 b	n.d.	13.3 de	75.0 d	61.7 c
Pasta	3A	99.0	109 a	73.0 a	n.d.	n.d.	26.0 b	99.0 b	73.0 b
	3B	93.0	120 a	75.8 a	8.4 b	n.d.	30.6 a	115 a	84.2 a
Bread toast	4A	30.0	33.9 e	17.5 gh	4.3 c	n.d.	13.2 de	35.0 h	21.8 g
	4B	50.0	80.2 b	52.2 c	8.4 b	6.2 b	18.0 c	84.8 c	60.6 c
	4C	30.0	38.9 de	24.6 f	6.6 b	n.d.	4.4 h	35.6 h	31.2 f
Pastries	5A	7.0	13.1 hi	12.6 hi	n.d.	n.d.	n.d.	12.6 k	12.6 i
	5B	9.0	16.4 h	15.1 gh	n.d.	n.d.	n.d.	15.1 k	15.1 h
	5C	5.0	7.0 kl	7.7 j	n.d.	n.d.	n.d.	7.7 l	7.7 j
	5D	20.0	46.9 cd	32.4 e	4.5 c	n.d.	9.1 f	45.9 g	36.9 ef
	5E	30.0	6.2 l	5.6 k	n.d.	n.d.	n.d.	5.6 l	5.6 k
	5F	20.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	5G	10.0	22.8 f	19.8 fg	n.d.	n.d.	n.d.	19.8 j	19.8 g
	5H	20.0	37.9 de	34.7 de	n.d.	n.d.	n.d.	34.7 hi	34.7 ef
Beer	6A	10.0	15.7 hi	16.5 gh	n.d.	n.d.	n.d.	16.5 j	16.5 h
	6B	10.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Rice milk	7A	17.0	11.3 i	7.3 jk	n.d.	n.d.	n.d.	7.3 l	7.3 j
	7B	14.5	18.5 g	13.7 hi	n.d.	n.d.	6.2 g	19.9 j	13.7 i
	7C	20.0	18.9 g	17.2 gh	n.d.	n.d.	n.d.	17.2 j	17.2 gh
	7D	15.0	8.4 jk	7.97 j	n.d.	n.d.	n.d.	8.0 l	8.0 j

Notes: n.d., Below the LOQ, 4 μg kg^{-1} (10 times the SD of the mean of blank determination).
[a]Values followed by different letters in the same column were significantly different ($p < 0.05$) according to Tukey's test.

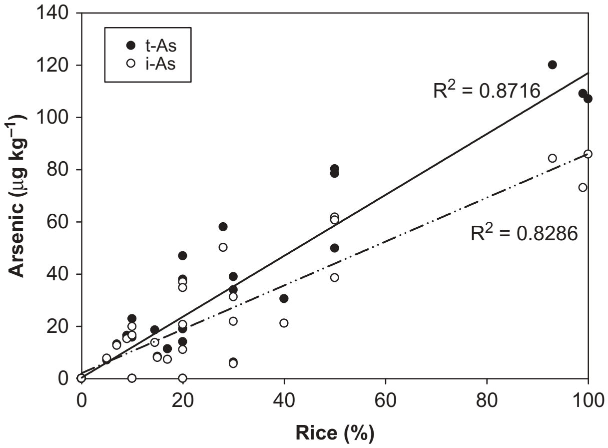

Figure 1. Relationship between t-As and i-As and rice percentage in samples of rice-based foods for celiac adult consumers.

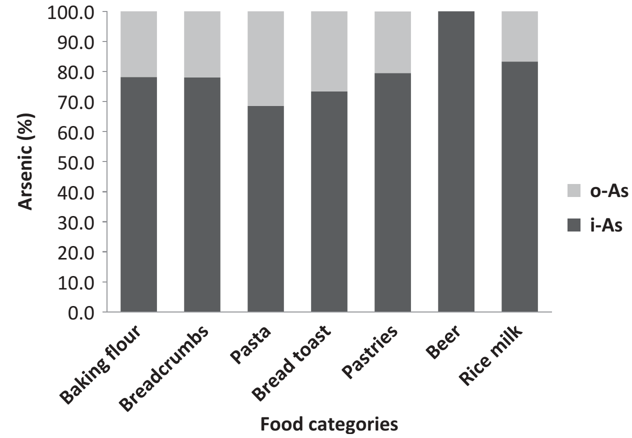

Figure 2. Percentage of o-As and i-As contents in the seven categories of rice-based foods for celiac adult consumers under study.

were the most abundant inorganic and organic species, respectively. The same trend (predominance of inorganic species) was previously described by Meharg et al. (2009) and previously Torres-Escribano et al. (2008).

The products from the pastries and beers had very low or even not detected amounts of DMA. This experimental result could be due to different reasons: (1) the rice used for their manufacturing might come from India, Bangladesh or countries in which arsenic is mainly present as inorganic forms and its main source is irrigation water; in countries such the USA, rice has high contents of organic species, including DMA, because of the wide use of organic pesticides, herbicides and defoliants in the past (WHO 1981; Ramírez-Gandolfo et al. 2013); and/or (2) DMA is lost during the heating treatment or baking (pastries) or the fermentation step (beers) (Ramírez-Gandolfo et al. 2013).

It is important also to comment that the results from t-As (HG-AAS) and those from the sum of the species obtained after HPLC-HG-AFS were equivalent; with differences presenting a mean value below 1.5%. These small differences could result from some complex compounds, such as arsenosugars and arsenolipids, being present at very low levels, and certainly below the detection limit of the analytical techniques used in this study.

Figure 2 shows the percentages of i-As and o-As present in each of the seven food categories under study. i-As predominated in all groups, with the highest value being found in beer (100%) and rice milks (83%), with the pasta samples in the lowest end (68%); the mean value for i-As in all samples under study was 83.5%.

Estimation of t-As and i-As contents in rice

As in the case of the study of As contamination in rice-based food for celiac children (Munera-Picazo, Ramírez-Gandolfo, Burló et al. 2014), in foods intended for grown up consumers, only few values of the rice percentage were directly included in the product labelling. Most of the percentages shown in Table 2 were directly provided by

Table 2. Estimation of total (t-As) and inorganic (i-As) arsenic contents in rice used as ingredient for foods for celiac adult consumers.

Group	Sample	Rice (%)	t-As (µg kg^{-1})	i-As (µg kg^{-1})
Baking flour	1A	40.0	76.3 h[a]	52.8 k
	1B	100	107 f	85.8 gh
	1C	20.0	70.0 h	55.0 j
	1D	28.0	207 a	179 bc
Breadcrumbs	2A	50.0	99.6 fg	77.0 h
	2B	50.0	157 c	123 e
Pasta	3A	99.0	110 f	73.7 i
	3B	93.0	129 d	90.5 g
Bread toast	4A	30.0	113 f	72.7 i
	4B	50.0	160 c	121 e
	4C	30.0	130 d	104 f
Pastries	5A	7.0	187 b	180 bc
	5B	9.0	182 bc	168 c
	5C	5.0	140 d	140 d
	5D	20.0	235 a	184 b
	5E	30.0	20.7 j	18.7 l
	5F	20.0	n.d.	n.d.
	5G	10.0	228 a	198 a
	5H	20.0	190 b	173 c
Beer	6A	15.0	105 h	103 f
	6B	10.0	n.d.	n.d.
Rice milk	7A	17.0	66.5 h	42.9 k
	7B	14.5	128 e	94.5 fg
	7C	20.0	94.5 g	86.0 gh
	7D	15.0	56.0 i	53.1 j

Notes: n.d., Below the LOQ, 4 µg kg^{-1} (10 times the SD of the mean of blank determination).
[a]Values followed by different letters in the same column were significantly different ($p < 0.05$) according to Tukey's test.

the manufacturing companies after direct inquiries done by telephone or email; the rest of the data were directly taken from the labelling of the products.

As an example, sample 1D was the only one including in its labelling that brown rice flour was used in its preparation. These results are similar to rice were determined in Europe (Torres-Escribano et al. 2008; Sommella et al. 2013). Several studies (Sun et al. 2008; Burló et al. 2012) have proved that the levels of t-As and i-As in brown rice are higher than those in white rice.

In this study, t-As and i-As contents in the 'rice' used for manufacturing these products were in the range of 0–235 and 0–198 μg kg^{-1}, respectively, with means being 120 and 100 μg kg^{-1}, respectively. There were up to eight samples out of the 25 studied samples with t-As content being above 150 μg kg^{-1}; in the same way five samples had values of i-As above this value.

On the other hand, there were two samples (5F and 6B) with rice percentages being 20% and 10%, which t-As and i-As contents were below the LOQ of the analytical techniques used in this study. This is a clear proof that rice with low levels of As are available in the market and it is essential that this type of rice is used for special foods intended for groups of consumers with high potential health risks, and also high price.

Munera-Picazo, Ramírez-Gandolfo, Cascio et al. (2014) made some recommendations about how processing may be used to reduce As contents from the initial rice used as ingredient or raw material of food items for celiac adult consumers; however at this time the effects are still minimal and uncontrolled. Some of the foods included in this study (breadcrumbs, bread toast and pastries) include some heating steps in their manufacturing. This heat could be used, if properly applied, to reduce the contents of As; however, this process is still not industrially used. Consequently, the effects of rice processing during the manufacture of foods for celiac adult consumers are insignificant and the t-As and i-As contents initially present in the rice will reach the final consumers, according to the rice percentage included in the formulation of the products.

Therefore, it is essential that rice with very low contents of this metalloid are selected to prepare foods for celiac consumers. This final statement makes clear that at this time, the use of brown rice for this type of products is not recommended unless it is clearly proven that it contains low i-As content. Meharg, Lombi, et al. (2008) studied the contents of t-As and i-As in white (*n* (number of samples) = 39) and brown (*n* = 45) rice grains and concluded that brown rice had a higher proportion of i-As than white rice.

Estimation of t-As and i-As intake in celiac adult consumers

In previous studies, it has been demonstrated that consumption of rice and/or rice-based products leads to an increased exposure to As, as evidenced by the occurrence of high amounts of As species in human urine (Cascio et al. 2011). Bioavailability of i-As has been proved high, reaching values of about 90% (Juhasz et al. 2006; Signes-Pastor et al. 2012). Therefore, it will be considered that i-As from rice-based foodstuffs will be as toxic to celiac adult consumers as that coming from other sources, such as drinking water.

In addition to analysing the content of t-As and i-As in gluten-free foods, it was necessary to estimate the intake of this contaminant in adult men and women (Table 3). The mean weights used for this study were inside of the normal body mass index (WHO 2014): women: 58 kg bw, and men: 75 kg bw. The menu designed in this particular study consisted of foods with the highest t-As from each group; this is, the situation represented here is the worst possible scenario. The portions of each food used in the design of the menu were those considered appropriate for this population according to AESAN (2003) and SENC (2004); however, it is necessary to indicate that the variability in the food intake of each person is so wide that the values discussed here are those for the mean consumers but there would be people with higher and lower intakes.

The final results of the weekly intake of t-As and i-As through the consumption of the products studied are summarised in Table 3. According to WHO, the tolerable intake level of i-As is the same for both children and adults, male or female, and it should be below 2.1 μg kg^{-1} bw day^{-1} or 15 μg kg^{-1} bw $week^{-1}$ (FAO/WHO 2010). The weekly i-As dietary intake estimated for a woman of 58 kg was 3.31 μg kg^{-1} bw and for a man of 75 kg was 3.21 μg kg^{-1} bw, which are equivalent to 0.47 and 0.46 μg kg^{-1} bw day^{-1}. These values are within the range of the $BMDL_{01}$ values identified by EFSA (2009), and therefore there is little margin of exposure and the possibility of a risk to these consumers cannot be excluded. However, these values are lower than those reported in celiac children by Munera-Picazo, Ramírez-Gandolfo, Burló et al. (2014); these authors reported weekly values of approximately 4.3–5.9 μg kg^{-1} bw (0.60–0.87 μg kg^{-1} bw day^{-1}).

However, it must be highlighted that other sources of As may exit in the diet of celiac consumers and that if other products and larger, but not impossible, portions are considered, some celiac adult patients may have even higher values.

There are recent indications that biotransformation among As species occur in the colon and may induce additional risk to health (Sun et al. 2012; Alava et al. 2013). On the other hand, it is relevant to consider that patients with untreated CD have villous atrophy, and this can cause a decrease in the absorption of nutrients and trace elements, including As. But studies on the absorption of minerals, such as iron, have revealed that when these people keep a proper gluten-free lifestyle, consuming

Table 3. Weekly intake estimation of t-As and i-As in celiac adult consumers.

		Woman			Man		
Rice-based sample	Times per week	Amount (g or ml)	t-As (μg)	i-As (μg)	Amount (g or ml)	t-As (μg)	i-As (μg)
Breakfast							
Milk (7C)	7	200 × 7 = 1400	28.8	28.8	200 × 7 = 1400	28.8	28.8
Toast (4B)	4	60 × 4 = 240	19.3	14.6	80 × 4 = 320	25.7	19.4
Cake (5H)	2	50 × 2 = 100	3.79	3.47	60 × 2 = 120	4.55	4.16
Biscuits (5D)	1	40	1.88	1.48	60	2.81	2.21
Mean As intake (μg)			53.8	48.4		61.9	54.6
Snack							
Cereal bar (5B)	3	25 × 3 = 75	1.23	1.13	25 × 3 = 75	1.23	1.13
Bread (with 1B)	2	37 × 2 = 74	7.92	6.35	49 × 2 = 98	10.5	8.41
Muffin (5G)	2	50 × 2 = 100	2.28	1.98	60 × 2 = 120	2.74	2.38
Mean As intake (μg)			11.4	9.46		19.2	15.6
Lunch							
Pasta (3B)	3	80 × 3 = 240	28.8	20.2	100 × 3 = 300	36.0	25.3
Rice (5G rice)	2	80 × 2 = 160	36.5	31.7	100 × 2 = 200	45.6	39.6
Beer (6A)	2	200 × 2 = 400	6.60	6.60	330 × 2 = 660	10.9	10.9
Bread (1B)	7	31 × 7 = 217	23.2	18.6	37 × 7 = 259	27.7	22.2
Breadcrumbs (2B)	2	20 × 2 = 40	3.14	2.47	30 × 2 = 60	4.71	3.70
Mean As intake (μg)			98.2	79.6		125	102
Snack							
Cereal bar (5B)	3	25 × 3 = 75	1.23	1.13	25 × 3 = 75	1.23	1.13
Biscuits (5H)	2	40 × 2 = 80	3.03	2.78	60 × 2 = 120	4.55	4.16
Waffle (1D)	1	100	5.80	5.01	100	5.80	5.01
Milk (7C)	4	200 × 4 = 800	13.2	13.2	200 × 4 = 800	13.2	13.2
Mean As intake (μg)			23.3	22.1		24.8	23.5
Dinner							
Pasta (3B)	1	60	7.20	5.05	80	9.60	6.74
Rice (5G rice)	1	60	13.7	11.9	80	18.2	15.8
Bread (1B)	7	18 × 7 = 126	13.5	10.8	25 × 7 = 175	18.7	15.0
Breadcrumbs (2B)	1	20	1.57	1.23	30	2.35	1.85
Beer (6A)	1	200	3.30	3.30	330	5.45	5.45
Mean As intake (μg)			39.3	32.3		53.3	44.8
Weekly As intake (μg)			226	192		284	241
Weekly As intake (μg kg^{-1} bw)			3.90	3.31		3.79	3.21

products such as the ones studied here, the absorption of these nutrients, and therefore that of As, can be virtually the same as those of healthy persons (Annibale et al. 2001).

Conclusions

The gluten-free products studied in this experiment, which did not contain rice in their formulations, did not contain measurable amounts of As. In rice-based foods intended for celiac adult consumers, t-As and i-As reached contents as high as 120 and 85.8 μg kg^{-1}, respectively. The highest contents of t-As and i-As were found in products from the pasta, baking flour and breadcrumbs groups. The daily i-As intake from the studied rice-based products (those containing the highest contents of As) was estimated at 0.47 and 0.46 μg kg^{-1} bw in adult women and men with the CD. These levels are within the $BMDL_{01}$ values identified by EFSA, and consequently a risk to this segment of consumers cannot be excluded. It is also important to consider that these values can increase with the intake of other contaminated products and more unsafe levels can be achieved. Besides, the effects of a chronic intake of i-As by patients with health problems, such as those suffering the CD, are not clear because clinic studies are still not available. Finally a key conclusion from this study is that there are rice-based products (sample 5F: pastry and 6B: beer) for celiac adults which are completely As-free; this means that if a proper selection of rice with low i-As content is made, final commercial products also with low i-As can be achieved. This should be a must for food companies manufacturing this type of products and willing to provide their clients/consumers with the safest products.

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