Cooking rice in a high water to rice ratio reduces inorganic arsenic content

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Total arsenic and arsenic speciation was performed on different rice types (basmati, long-grain, polished ([white] and wholegrain [brown]) that had undergone various forms of cooking. The effect of rinse washing, low volume (2.5 : 1 water : rice) and high volume (6 : 1 water : rice) cooking, as well as steaming, were investigated. Rinse washing was effective at removing circa. 10% of the total and inorganic arsenic from basmati rice, but was less effective for other rice types. While steaming reduced total and inorganic arsenic rice content, it did not do so consistently across all rice types investigated. Low volume water cooking did not remove arsenic. High volume water : rice cooking did effectively remove both total and inorganic arsenic for the long-grain and basmati rice (parboiled was not investigated in high volume cooking water experiment), by 35% and 45% for total and inorganic arsenic content, respectively, compared to uncooked (raw) rice. To reduce arsenic content of cooked rice, specifically the inorganic component, rinse washing and high volume of cooking water are effective.

Introduction

Rice is the only staple crop grown under flooded soil conditions. Under anaerobic conditions, arsenic in soil is converted readily to arsenite which is mobile, leading to arsenic in rice grain being around 10-fold higher than for other crops.[1] This occurs in soils which have no or limited anthropogenic contamination. Rice grain arsenic levels are elevated further when grown in soils subject to anthropogenic contamination such as: arsenical pesticide use, base and precious mining and smelting impacted soils, and contaminated water irrigated soils.[2–8]

Inorganic arsenic, a class 1 non-threshold carcinogen,[9,10] and dimethyl arsinic acid (DMA) constitute the dominant arsenic species present in rice while traces of monomethyl arsonic acid (MMA) are sometimes reported,[11] as well as a residual fraction that is either not extractable or does not elute from the chromatographic column. Inorganic arsenic can constitute up to 90% of total arsenic present in grain, but on average accounts for around 50% of total grain arsenic.[11]

A number of previous studies had suggested that rice cooking was important to the arsenic content of the cooked grain.[12–18] Some of these studies focus on how cooking techniques may reduce rice arsenic content,[12,13] while others focus on how arsenic in cooking water affects arsenic content of cooked rice.[14–18] Rinsing rice before washing and then cooking the rice in a high water : rice ratio (6 : 1) and not allowing the water to evaporate to dryness significantly reduced the arsenic burden of the rice,[12,13] with one study suggesting that the arsenic was primarily lost as inorganic arsenic, specifically arsenite.[12] Previous studies on rice cooking[12–18] had not systematically looked at: (a) differences between wholegrain (brown) or polished (white) rice or (b) commonly used cooking techniques such as low and high water : rice volume and steaming. Similarly, systematic speciation and/or mass balances are inconsistent or absent between previous studies.[13–8] Par-boiled rice also needs to be considered due to its widespread utilization. This current study sets out the systematic determination of the effect of cooking on the concentrations of arsenic species in rice.

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Experimental

Rice samples were purchased from major UK retailers. Two varieties of basmati, one wholegrain (packed in 1 kg portions, 4 portions were mixed before use) and one polished (packed in 2 kg portions, 2 portions, mixed before use) were of Indian origin. Wholegrain long-grain (4 times 1 kg portions, mixed before use) and polished long-grain (4 times 1 kg portions mixed before use) originated according to label from more than one country. The same origin was given for the long-grain easy cook (par-boiled) rice (2 times 2 kg portion, before use). The easy cook short-grain rice (4 times 1 kg portions mixed before use) was of Italian origin.

Raw rice was first rinse washed by placing 100 g portions of rice (packet weight) in an acid washed 800 mL beaker and then adding 600 mL of double distilled deionised (Milli-Q) water. The sample was allowed to sit for 3 min with routine agitation. The water was decanted and then the process repeated again with another 600 mL of water. The decanted water was then freeze dried. Dry weight determination was then made on both the raw and rinsed rice by oven drying at 80 °C until constant weight was reached. The quantity of freeze dried residue was recorded. Rinse washed rice was used in all subsequent cooking experiments.

In all boiling experiments the quantity of packet weight used was 100 g. Double distilled deionised water was used for the cooking water. All rice, including par-boiled, was subject to 2.5 : 1 (low volume) water to rice (packet weight) cooking, where the water was cooked to dryness. All rice with the exception of par-boiled, were also subject to 6 : 1 (high volume) water : rice cooking, where the rice was cooked to eating texture. The residual water was drained off and then freeze dried.

For the steaming experiments, rinse washed rice (100 g packet weight) was soaked for 2 h in an acid washed 400 mL beaker with 200 mL of double distilled deionised (Milli-Q) water. On termination of soaking, the water was decanted and freeze dried. The steamer was filled with 200 mL of double distilled deionised (Milli-Q) water and the soaked rice placed on arsenic and lint-free cotton-cloth. Steaming time was 2 times 15 min with stirring in between. The residual water was drained off and then freeze dried.

All cooked rice was then dried at 80 °C until constant weight was reached and then milled using a coffee/spice grinder prior to analysis. All experiments were conducted with triplicate replication.

For total arsenic analysis 0.5 g dry weight of sample (rice or freeze dried residual washes or residual liquor) was placed into 50 mL polypropylene centrifuge tubes and 2.5 mL of Aristar nitric acid and 4 mL of hydrogen peroxide suprapur was added, followed by microwave digestion using a CEM Mars5 Microwave system. On digestion the sample was diluted to 25 mL using double distilled deionised water with rhodium (0.02 mL 10 mg Rh/L) as an internal standard. CRM NIST 1568a rice powder was used throughout for the totals determination. Arsenic content was measured using an Agilent 7500c ICP-MS with hydrogen as the collision/reaction gas. The ICP-MS operating conditions are given in Williams *et al.*[1]

Samples (rice or freeze dried residual washes or residual liquor) for speciation analysis were extracted in 1% Aristar nitric acid and 1% (vol/vol) hydrogen peroxide suprapur using a CEM Mars5 microwave system. The supernatant was used for determination of extractable arsenic and As-speciation. This oxidises arsenite to arsenate, improving chromatographic resolution as arsenate elutes at some distance to MMA and DMA, where arsenite elutes adjacent to MMA and DMA. Arsenic species were separated on a Hamilton PRP × 100 anion exchange column using phosphate buffer and the LC-system was an Agilent 1100 system directly coupled to the Agilent 7500c ICP-MS for arsenic determination. Indium (0.01 mg/kg) in 1% (v/v) nitric acid was added during the analysis *via* a T-piece as an internal standard. CRM NIST 1568a rice powder was used throughout for speciation determinations. There is no CRM available for inorganic and organic arsenic in rice, but NIST 1568a has been used routinely in previous studies as a reference (Table 1). Solutions (0.1 mL) containing known amounts of DMA (10 to 100 µg/kg) were subjected to LC-ICP-MS under the same conditions as the supernatants. Peak areas from these measurements were used to construct a calibration curve. Single species standards DMA, MMA and As(V) were used for identification of species by retention time. The supernatants (0.1 mL) were used as they were and injected onto the column. Peak areas were used for quantification of As-species.

Every 10th sample was digested in duplicate and measured. Each analytical batch contained procedural blanks, spiked samples (for recovery estimate purposes) and CRM.

Results

The reported mean value and standard error for total arsenic in the CRM was 0.280 mg/kg ± 0.007 mg/kg (n = 11) compared to its certified value of 0.29 mg/kg with a 95% confidence interval of ±0.03 mg/kg, so the CRM recovery reported here is well within the 95% confidence interval. Spike recovery was 103.8% ± 5.7% (n = 12). Limits of detection where 0.0004 mg/kg expressed on a sample weight basis.

Table 1 reports arsenic speciation of the rice flour CRM and compares the results of this study with those previously published in the literature as no cereal flour CRM has certified arsenic speciation reported for it. The results of this CRM analysis from the present study compare favourably with previously reported studies. Spike recoveries for arsenate and DMA are 110% ± 6.2% (n = 5) and 103% ± 4.3% (n = 5), respectively. Limits of detection for DMA are 0.004 mg/kg when expressed on a flour dry weight basis.

Total, inorganic and organic arsenic concentrations in raw, washed and cooked rice are presented in Table 2. Mass balances, *i.e.* summation of the individual measured components with respect to the initial arsenic in raw rice, are also presented. The average mass balance for all the data ± the standard error was 100.8 ± 1.3% (n = 20).

There was variation in the effectiveness of rinse washing in removing total/inorganic arsenic from raw rice (Table 2). Washing removed more total arsenic for both the polished (to 87% of raw rice content) and wholegrain (to 85% of raw rice content) basmati, while for all other rice percentage arsenic remaining ranged only from 96–99% of raw rice content, including parboiled. It appears that rinse washing is more effective for basmati rice than for other types of rice, though more samples would need to be analysed to confirm this. Virtually all the arsenic lost through washing was inorganic (91% on average of raw rice concentration), while negligible DMA was lost (99% on average of raw rice concentration).

Table 1 Performance of CRM speciation compared to previous studies. As_i refers to inorganic arsenic (arsenate and arsenite). As_o refers to organic arsenic (DMA and MMA). Numbers in italics are the standard error of the mean from the current study. Column recovery is the sum of species expressed as a percentage of total arsenic determined in that solution

Extraction	As_o (µg/kg)	As_i (µg/kg)	$\sum$ of species (µg/kg)	Extraction efficiency (%)	Column recovery (%)	Reference
2M TFA	180	87	267	95	96	14
Enzymatic digest, pepsin and pancreatin	159	101	260	*	*	14
2M TFA	182	92	274	112	84	19
2M TFA	162	80	240	*	*	11
Methanol : water with sonication	180	109	288	99	*	20
Enzymatic hydrolysis, α-amylase	171	106	277	*	*	21
Ultrasonic & enzy. hydrol., protease & α-amylase	143	88	231	99	81	22
1 M H_3PO_4 with sonication	164	102	267	*	*	23
1% HNO_3	**185**	**99**	**284**	**104**	**98**	**This study**
	3	***2***	***4***	***1***	***1***	

Table 2 Summary of As_T (total), As_i (arsenate and arsenite) and As_o (DMA and MMA) concentrations, in rice cooked in various ways. Percentage of As_T, As_i and As_o concentrations in the processed rice compared to raw rice are shown in parenthesis. Mass balances were obtained by summing the rice with rinse wash and cooking liquor. Note all rice was rinse washed with the exception of raw rice. Data are the averages of 3 replicates. Numbers in italics are the standard deviation (s.e.) of the mean

Rice type	Cooking technique	As_T (μg/kg)	s.e.	As_i (μg/kg)	s.e.	As_o (μg/kg)	s.e.	Mass balance (%)	s.e.
Polished basmati	**Raw**	162	*3*	93	*1*	18	*1*		
	Raw washed	141 (87)	*5*	86 (92)	*2*	19 (106)	*1*	*(96)*	*(6)*
	2.5 : 1 water to rice	141 (87)	*1*	90 (92)	*3*	18 (106)	*1*	*(93)*	*(2)*
	6 : 1 water to rice	103 (64)	*5*	56 (60)	*5*	18 (100)	*1*	*(98)*	*(6)*
	Steamed	122 (75)	*8*	61 (66)	*2*	15 (83)	*2*	*(103)*	*(3)*
Wholegrain basmati	**Raw**	131	*8*	89	*3*	18	*1*		
	Raw washed	111 (85)	*3*	80 (90)	*1*	16 (89)	*3*	*(88)*	*(5)*
	2.5 : 1 water to rice	119 (85)	*3*	82 (90)	*1*	21 (89)	*2*	*(97)*	*(5)*
	6 : 1 water to rice	72 (55)	*3*	48 (54)	*2*	19 (106)	*1*	*(96)*	*(3)*
	Steamed	119 (91)	*12*	76 (85)	*3*	22 (122)	*2*	*(100)*	*(19)*
Polished long-grain	**Raw**	229	*2*	138	*1*	58	*2*		
	Raw washed	222 (97)	*13*	131 (95)	*5*	59 (102)	*3*	*(103)*	*(13)*
	2.5 : 1 water to rice	238 (97)	*6*	144 (95)	*20*	50 (102)	*6*	*(110)*	*(5)*
	6 : 1 water to rice	165 (72)	*2*	70 (51)	*3*	53 (91)	*2*	*(113)*	*(1)*
	Steamed	177 (77)	*4*	107 (78)	*2*	52 (90)	*1*	*(99)*	*(4)*
Wholegrain long-grain	**Raw**	314	*9*	183	*14*	87	*2*		
	Raw washed	311 (99)	*18*	157 (86)	*3*	86 (99)	*2*	*(104)*	*(11)*
	2.5 : 1 water to rice	324 (99)	*7*	165 (86)	*3*	109 (99)	*2*	*(108)*	*(5)*
	6 : 1 water to rice	219 (70)	*5*	102 (56)	*9*	87 (100)	*5*	*(104)*	*(3)*
	Steamed	280 (89)	*5*	156 (85)	*24*	76 (87)	*6*	*(102)*	*(4)*
Italian parboiled	**Raw**	211	*5*	157	*2*	54	*3*		
	Raw washed	203 (96)	*7*	149 (95)	*3*	54 (100)	*4*	*(100)*	*(5)*
	2.5 : 1 water to rice	211 (96)	*7*	157 (95)	*4*	54 (100)	*2*	*(97)*	*(9)*
Long-grain parboiled	**Raw**	186	*2*	115	*2*	56	*3*		
	Raw washed	180 (97)	*1*	99 (86)	*2*	57 (102)	*1*	*(104)*	*(1)*
	2.5 : 1 water to rice	163 (97)	*10*	86 (86)	*13*	39 (102)	*6*	*(95)*	*(12)*
AVERAGE of ALL RICE TYPES	**Raw washed**	(93)	*(2)*	(91)	*(2)*	(99)	*(2)*	*(99.2)*	*(2.6)*
	2.5 : 1 water to rice	(93)	*(2)*	(91)	*(2)*	(99)	*(2)*	*(100.0)*	*(2.9)*
	6 : 1 water to rice	(65)	*(4)*	(55)	*(2)*	(99)	*(3)*	*(102.8)*	*(3.8)*
	Steamed	(83)	*(4)*	(78)	*(5)*	(96)	*(9)*	*(101.0)*	*(0.9)*

Cooking rice to dryness in a 2.5 : 1 water : rice ratio, for all rice types, resulted in no loss of arsenic from the cooked grain throughout for all four rice types. All rice types tested for high volume cooking (6 : 1 water to rice ratio), that is all the non-parboiled types tested, considerably reduced both total and inorganic arsenic content. There was no reduction in organic arsenic content on high volume cooking.

Total arsenic content was reduced to a mean of 65% of raw rice content following rinsing and high volume cooking (Table 2), ranging from 55% in whole grain basmati to 72% in polished long-grain. This reduction was on average 55% for inorganic arsenic content, ranging from 51% for polished long-grain to 60% for polished basmati. Even though the rinse washing was ineffective for both types of the long-grain rice, high volume cooking water reduced inorganic arsenic content to those of basmati rice, where rinsing was more effective. This suggests that high volume cooking by itself is enough to reduce total and inorganic arsenic content, though rinse washing is normally recommended as part of the preparation of rice *per se*.

Steaming did reduce mean total and inorganic arsenic content to 83% and 78% of the raw rice values, respectively. However, the effects were variable, ranging from 91% for wholegrain basmati to 75% for polished basmati for total arsenic. Percentage inorganic arsenic was reduced lower compared to total arsenic content, with inorganic concentrations ranging from 85% in polished long-grain to 60% in polished basmati. While steaming did reduce total and inorganic arsenic content it did not do so as effectively or as consistently as high volume cooking.

Discussion

The most comparable to the present study, though more limited in cooking treatments and rice types, was a high water rice (6 : 1) investigation conducted by Mihucz *et al.*[12] Two Hungarian and one Chinese rice types, for none of which was it recorded if the rice was wholegrain or polished, were used in that study. They found a 42–63% reduction in total arsenic in cooked rice, with the cooking liquor containing most of the removed arsenic from the rice (26–49%), while the quantity removed by rinse washing was less (8–17%). It was found that raw rice contained both arsenate and arsenite, and it was primarily arsenite that was removed from the rice on rinsing and boiling. Arsenite is uncharged at physiological pHs and hence more mobile than arsenate or DMA, both of which are anionic. The DMA findings in that study[12] confirm our results. As the present report only records total inorganic arsenic, because the extraction process oxidises arsenite to arsenate, the observation that primarily arsenite was removed from the rice could not be confirmed.

In another comparable study, three West Bengali samples where rinse washed and then cooked in a large water volume.[13] Total arsenic, not speciation, was determined. The rinse washing step was more exhaustive, involving 5–6 rinses until the rinse water discarded was clear, the traditional Indian preparation, rather than the double rinse wash step used in the experiments reported here. The rinse wash step removed 28% of the arsenic compared to raw rice. Combined rinse washing and large volume (6 : 1 water : rice) reduced arsenic up to 58% of the raw rice content. This is compared to an average of 35% removal (maximum of 45%) or total arsenic reported in the current study (Table 1). The increased efficiency of removal for the Indian rice of that study[13] may be due to more exhaustive rinse washing, or due to the intrinsic nature of the rice used in that study.

Other studies have been conducted on the effects of cooking rice on arsenic content, but have focused on the impact of arsenic contaminated cooking water on rice arsenic burdens.[14–18] While relevant to S.E. Asian and US scenarios where cooking and drinking water is arsenic contaminated, they are not relevant to many parts of the globe.

It was found here that cooking rice in a large volume of water (6 : 1, water : rice) had the greatest effect with regards to lowering arsenic levels in cooked rice. Specifically, it preferentially reduced the inorganic arsenic content by 45% of that in the raw rice, when combined with rinse washing. It is recommended that to reduce total and inorganic arsenic content of rice, that rice is rinse washed and cooked in a 6 : 1 water to rice ratio. Exhaustive rinse washing, as practised in India, may reduce arsenic content even further when combined with large cooking water volume.

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