Geographical Variation in Total and Inorganic Arsenic Content of Polished (White) Rice

ANDREW A. MEHARG,^{*,†}
PAUL N. WILLIAMS,^{†,‡}
EUREKA ADOMAKO,[†]
YOUSSEF Y. LAWGALI,[†]
CLAIRE DEACON,[†] ANTIA VILLADA,[†]
ROBERT C. J. CAMBELL,[†] GUOXIN SUN,[‡]
YONG-GUAN ZHU,[‡] JOERG FELDMANN,[§]
ANDREA RAAB,[§] FANG-JIE ZHAO,^{||}
RAFIQUL ISLAM,[⊥] SHAHID HOSSAIN,[#]
AND JUNTA YANAI[∇]

Institute of Biological and Environmental Sciences, University of Aberdeen, Cruickshank Building, St. Machar Drive, Aberdeen, AB24 3UU, U.K., Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Haidian District, Beijing, 100085, China, Department of Chemistry, University of Aberdeen, Meston Building, Meston Walk, AB24 3TU, Aberdeen, U.K., Soil Science Department, Rothamsted Research, Harpenden, Hertfordshire AL5 2JQ, U.K., Bangladesh Agricultural University, Mymensingh - 2202, Bangladesh, Department of Soil, Water and Environment, Dhaka University, Dhaka-1000, Bangladesh, and Graduate School of Agriculture, Kyoto Prefectural University, Shimogamo Hangi-cho, Sakyo, Kyoto 606-8522, Japan

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An extensive data set of total arsenic analysis for 901 polished (white) grain samples, originating from 10 countries from 4 continents, was compiled. The samples represented the baseline (i.e., not specifically collected from arsenic contaminated areas), and all were for market sale in major conurbations. Median total arsenic contents of rice varied 7-fold, with Egypt (0.04 mg/kg) and India (0.07 mg/kg) having the lowest arsenic content while the U.S. (0.25 mg/kg) and France (0.28 mg/kg) had the highest content. Global distribution of total arsenic in rice was modeled by weighting each country's arsenic distribution by that country's contribution to global production. A subset of 63 samples from Bangladesh, China, India, Italy, and the U.S. was analyzed for arsenic species. The relationship between inorganic arsenic content versus total arsenic content significantly differed among countries, with Bangladesh and India having the steepest slope in linear regression, and the U.S. having the shallowest slope. Using country-specific rice consumption data, daily intake of inorganic arsenic was estimated and the associated internal cancer risk was calculated using the U.S.

Environmental Protection Agency (EPA) cancer slope. Median excess internal cancer risks posed by inorganic arsenic ranged 30-fold for the 5 countries examined, being 0.7 per 10,000 for Italians to 22 per 10,000 for Bangladeshis, when a 60 kg person was considered.

1. Introduction

Rice is the staple for around 50% of the world's population. It is grown widely in South and Southeast Asia with more discrete regional distribution in Southern Europe, Southern U.S., South America, Middle East, and Africa. All soils, including rice paddies, naturally contain the element arsenic (1). Rice is much more efficient at assimilating arsenic into its grain than other staple cereal crops (2). Inorganic arsenic and dimethylarsinic (DMA) dominate grain arsenic speciation (3–7). Exposure to inorganic arsenic, a nonthreshold class 1 carcinogen (8, 9), in populations not suffering from elevated arsenic in drinking water is dominated by the consumption of rice (4, 10–13).

Whether the baseline concentrations of arsenic vary in soils between rice growing regions, potentially resulting in rice grain with different arsenic burdens, has yet to be ascertained. However, paddy soils can become elevated in arsenic from a number of anthropogenic diffuse and point sources of contamination. Diffuse source pollution has, to date, not been actively studied for paddy soils, but there are scenarios in which paddy rice cultivation on deltas and floodplains downstream of industrial and urban centers become elevated in arsenic. Point source pollution of paddies and the resultant elevation in grain arsenic concentrations has been better characterized and include: application of arsenical pesticides (5, 13, 14), mining and processing of base and precious metals (15–17), irrigation with groundwater contaminated with arsenic (18, 19), and fertilization with municipal solid wastes (20).

Risk posed by inorganic arsenic from rice depends on both the concentration of inorganic present in the grain and the quantity of grain ingested, moderated by gut bioavailability. Previous studies have quantified inorganic exposure from rice and other sources in the U.S. (11, 12), but tended to use limited databases on inorganic arsenic concentrations for rice (14, 21). More focused, though geographically limited, studies have started to address arsenic ingested through rice in Bangladesh/West Bengal (22, 23).

This current study explores inorganic arsenic exposure from baseline consumption of white (polished) market rice for some of the world's major rice growing and consuming regions. Total arsenic content for 901 samples of white market rice was determined. A subset of these samples (63) was speciated for inorganic and organic arsenic contents. Data were then modeled to calculate daily inorganic arsenic intake from rice along with associated cancer risks.

2. Materials and Methods

The analytical methodologies used in this paper are identical to those previously published for total arsenic determination (ICP-MS) and arsenic speciation (HPLC-ICP-MS) by Williams et al. (3, 19). As in those papers, powdered rice NIST CRM 1568a was used with each batch to monitor analytical performance, and the results from this certified material were within the ranges reported by Williams et al. (3, 19).

The market basket survey for this study was conducted across 4 continents, collected from markets or supermarkets, and all designated for human consumption. White market rice was selected as opposed to field-collected rice, data on

* Corresponding author tel: +44 (0)1224 272264; fax: +44 (0) 1224 272703; e-mail: a.meharg@abdn.ac.uk.

[†] Institute of Biological and Environmental Sciences, University of Aberdeen.

[‡] Chinese Academy of Sciences.

[§] Department of Chemistry, University of Aberdeen.

^{||} Rothamsted Research.

[⊥] Bangladesh Agricultural University.

[#] Dhaka University.

[∇] Kyoto Prefectural University.

TABLE 1. Descriptive Statistics of Total Arsenic and Inorganic Arsenic Contents in White Rice Produced in Different Countries

	total As					inorganic As				
	<i>N</i>	mean (mg/kg)	median (mg/kg)	min. (mg/kg)	max. (mg/kg)	<i>N</i>	mean (mg/kg)	median (mg/kg)	min. (mg/kg)	max. (mg/kg)
Bangladesh	144	0.13	0.13	0.02	0.33	15	0.08	0.07	0.01	0.21
China	124	0.14	0.14	0.02	0.46	21	0.16	0.12	0.07	0.38
Egypt	110	0.05	0.04	0.01	0.58	-	-	-	-	-
France	33	0.28	0.23	0.09	0.56	-	-	-	-	-
India	133	0.07	0.07	0.31	0.18	12	0.03	0.03	0.02	0.07
Italy	38	0.15	0.13	0.07	0.33	5	0.11	0.12	0.07	0.16
Japan	26	0.19	0.18	0.07	0.42	-	-	-	-	-
Spain	76	0.20	0.14	0.05	0.82	-	-	-	-	-
Thailand	54	0.14	0.13	0.01	0.39	-	-	-	-	-
U.S.	163	0.25	0.25	0.03	0.66	10	0.10	0.10	0.05	0.15
all rice analyzed	901	0.15	0.13	0.01	0.82	-	-	-	-	-

which have been published elsewhere (13, 19), as market rice should integrate inherent field-to-field variation, and has been prepared and milled according to local custom. Brown rice was also excluded as its speciation and arsenic localization differs from white rice due to elevated arsenic, as arsenite, in the bran (24, 25). White rice is by far the most popularly consumed, especially in traditional rice-growing regions.

Data for the bulk of the samples reported here have not been previously reported. Specifically, here is their provenance. The Egyptian data are all new. All the French data are new and the samples were specifically collected from food markets in the rice-growing region of France, the Camargue. The bulk of the Indian data are new, collected in the markets in the UK, Ghana, and Middle East; a very limited subset (9 samples for both totals and speciation) was published in Williams et al. (3). Italian rice was purchased in the UK where it is widely imported; a small subset (3 samples for total and speciation) was published in Williams et al. (3). Japanese rice was obtained from supermarkets in Kyoto and Okayama, with samples originating from various areas along the length of the main Honshu Island; none of the data have been previously published. Spanish rice was sampled from the Northern Spanish markets obtaining their rice from the Valencia and Ebro rice-growing regions, also specifically collected for this study; a very limited subsample (1 sample for totals and speciation) was published by Williams et al. (19). Thai rice was obtained from markets in the UK, Ghana, and Middle East and is all unpublished data.

Part of the U.S. survey was collected in the U.S. ($n = 134$) and the data for total arsenic were published by Williams et al. (13), with a subset of the speciation data ($n = 7$) for UK imported rice published in Williams et al. (3). The rest of the U.S. data are new and were collected in the UK, Ghana, and Middle East (Morocco, Libya, Algeria, Tunisia, Egypt, and Syria), with rice packaging carrying no specific information with respect to where in the U.S. the rice had originated ($n = 11$). For the U.S., around 80% of rice is produced in the South Central region which has higher arsenic concentrations than the California region that makes up the rest of the production. U.S. rice was sampled from U.S. supermarkets in these two regions at a frequency proportional to their rice production (13).

The total arsenic and speciation data for Chinese rice samples were, in the main, published in Zhu et al. (26), with samples coming from markets in 8 major urban conurbations.

Sampling from Bangladesh reported here was entirely focused on market rice from major town and city markets throughout Bangladesh, including Dhaka, the capital, that were previously published in Williams et al. (3). Rice for major population centers is supplied, in the main, from the

nonarsenic-impacted northwestern region as reported in Williams et al. (3). Thus, this survey reflects urban population exposure, not that of subsistence farmers who are dependent on very locally produced rice, and therefore have the potential to be exposed to high arsenic concentrations when local irrigation sources are arsenic contaminated (18, 19).

All data presented in this study are expressed on a dry weight basis.

Results and Discussion

Total Arsenic Concentrations. Mean and median total arsenic concentrations in baseline market white rice differed by 5–6-fold for rice sourced from different countries of origin (Table 1), with one-way analysis-of-variance (ANOVA) revealing a highly significant ($P < 0.001$) difference between these means. Egyptian rice had the lowest mean at 0.05 mg/kg, followed by countries from the Indian subcontinent (Bangladesh, India) and China. The highest concentrations were found in French rice from the Camargue region (0.28 mg/kg) and U.S. produced rice (0.25 mg/kg). The overall range found for the individual samples was from 0.01 mg/kg (found in Egyptian, Indian, and Thai rice) to 0.82 mg/kg for a Spanish rice sample, representing an 82-fold difference.

Zavala et al. (14) published a survey of U.S. rice ($n = 112$) and found a mean total arsenic concentration of 0.20 mg/kg. This compared to 0.25 mg/kg ($n = 163$) reported here (Table 1). Mean total arsenic concentrations from 3 other more limited U.S. surveys (total n of the 3 studies = 15), ranged from 0.20 to 0.30 mg/kg total arsenic (4, 27, 28). All 5 surveys had mean total arsenic concentrations ranging from 0.2 to 0.3 mg/kg for U.S. rice. A survey of Spanish rice ($n = 24$) found a mean total arsenic concentration of 0.21 mg/kg (7), which compares well to the value reported here of 0.20 mg/kg ($n = 76$) (Table 2). A baseline rice survey for Taiwan found average concentrations of 0.08 mg/kg total arsenic ($n = 407$) (29), comparable to the baseline for SE Asian rice reported here.

The distribution of the total arsenic in the whole data set is compared with that of individual countries (Table 1). Also the global distribution is modeled from the whole database (Figure 1). For this modeling, the distribution for each individual country was weighted by that country's percentage contribution to rice production of all the countries in the database (Table 2), with the weighted individual distributions from each country summed to give an overall global distribution. The countries surveyed comprise 66% of total global rice production. The samples themselves were not collected to reflect geographic distribution of rice production within each country, or subsampled to reflect cultivars/types available at market. For example, Indian rice reported here was dominated by Basmati, and Thai rice was dominated by

TABLE 2. Rice Consumption and Mean Excess Internal Cancer Risk by Country^a

	contrib. to global product (%)	husked rice prod. (1000 t)	husked rice cons. (1000 t)	husked rice import (1000 t)	husked rice export (1000 t)	country populat. (1000)	husked rice cons. (g/d)	polished rice cons. (g/d)	median inorg. content of rice (mg/kg)	As intake (μg/d)	country-specific rice cons. median inorg. As intake (μg/d)	100 g per day rice cons. median inorg. As intake (μg/d)	country-specific rice cons. median excess cancer rate per 10,000	100 g per day rice cons. median excess cancer rate per 10,000
Bangladesh	6.3	39,796	34,929	1,189	2	141,822	675	445	0.081	36.2	22.1	8.1	22.1	5.0
China	29.0	182,042	156,959	1,543	1,379	1,304,500	330	218	0.109	23.7	15.2	10.9	15.2	7.0
Egypt	1.0	6,125	4,313	24	773	74,033	160	105	-	-	-	-	-	-
France	0.02	102	509	672	138	60,873	23	15	-	-	-	-	-	-
India	21.7	136,574	116,138	395	5875	1,094,583	291	192	0.059	11.3	6.9	5.9	6.9	3.6
Italy	0.2	1,413	535	208	1077	58,607	25	17	0.071	1.2	0.7	7.1	0.7	4.3
Japan	1.8	11,342	11,840	1,483	119	127,774	254	168	-	-	-	-	-	-
Spain	0.1	839	497	201	504	43,398	31	21	-	-	-	-	-	-
Thailand	4.6	29,201	8,522	83	11,772	64,233	363	240	-	-	-	-	-	-
U.S.	1.6	10,125	3,864	972	5695	296,410	36	24	0.088	2.1	1.3	8.8	1.3	5.4

^a Rice production data are for 2004, obtained from the UN FAO (38); country population statistics are from World Bank (39). Polished rice is 66.7% of husked rice by weight. Inorganic rice consumption rates were calculated using median total arsenic concentrations reported in Table 1 and converting these to inorganic arsenic contents using the regression equations in Figure 2, and then multiplying the inorganic arsenic concentration by polished rice consumption rate, also presented in this table. Inorganic arsenic intake assuming 100 g/d rice consumption is also presented. Median excess internal cancer risks per 10,000 for consumption of white rice for country-specific rice consumption rate or at 100 g d.wt. per day where then calculated. A body weight of 60 kg for the consuming human was used. The EPA excess internal cancer slope of 3.67 (mg/kg-d)⁻¹ (12) was than applied to convert inorganic arsenic consumption rates into a cancer slope. Abbreviations: prod, production; cons, consumption; populat, population.

FIGURE 1. Histograms of total arsenic distribution in rice from different countries. The modeled global distribution is explained in the text.

fragrant rice. Also, total numbers (*n*) sampled per country (Table 1) were not scaled with respect to the individual country's contribution to global rice production, i.e., the U.S. has the greatest *n* sampled, but only contributes 1.6% of global production (Table 2). However, weighting total arsenic concentrations by the country's contribution to global production does give a better model of global distribution than simply combining all the individual country databases without regard to contribution to global production, as conducted by Zavala et al. (14). The contrast in these two approaches is illustrated by comparing the modeled global distribution with the distribution of the unmodeled database, termed "whole database" in Figure 1. The modeled global distribution approximates to a normal distribution, while the whole database distribution is highly skewed to higher arsenic concentrations. It is notable that developing countries (Bangladesh, China, Egypt, India, Thailand) have normally distributed total grain arsenic concentrations, while those of developed countries (France, Italy, Japan, Spain, and the U.S.) have distributions highly skewed to high arsenic concentrations. Box plots presented in Supporting Information Figure 1 show percentile data for individual countries presented with

FIGURE 2. Regression of inorganic arsenic and DMA against total arsenic concentrations in rice for countries from different regions. Regression slopes and fits for inorganic arsenic given in Table 3. Graph A is for inorganic arsenic, graph B is for DMA.

respect to the modeled global percentiles. The median value for total arsenic in Egyptian rice is below the modeled global fifth percentile, while the median concentrations for France and the U.S. are above the 95th percentile of the modeled global data. Total arsenic distributions for Bangladesh and China best follow the modeled global distribution. The high percentage of samples from the U.S. and Europe in the present database and in that of Zavala et al. (14) account for the skewing of the unweighted "global" distribution data. Any analysis of what constitutes "global" arsenic concentrations must take into account the quantities of rice produced in individual countries.

Arsenic Speciation. Arsenic speciation in rice grain is dominated by inorganic arsenic and DMA (3–5, 19, 21, 27, 28). The relationships between total grain arsenic and inorganic and DMA content on a region-specific basis (Bangladesh, Chinese, Indian, Italian and U.S.) are shown in Figure 2. Two-way-ANOVA of these data, using general linear modeling, with total grain arsenic content as a covariate, showed that there was a significant ($P = 0.008$) and highly significant ($P < 0.001$) interaction between country of origin and total grain arsenic for inorganic arsenic and DMA content, respectively. Therefore, grain speciation differs between countries. Regression analysis of inorganic arsenic against total arsenic content showed that the slopes for Indian and Bangladesh (0.796 and 0.719) were similar, while Chinese and Italian rice were similar (0.599 and 0.506), and that from the U.S. rice was much lower (0.275) (Table 3). For the slopes of DMA against total arsenic, all other countries were low (ranging from 0.137–0.199) compared to the U.S. (0.774). It should be noted however that the r^2 for U.S. for the inorganic

TABLE 3. Linear Regression Analysis of Total Grain Arsenic versus Inorganic Content (the intercept is "a" and the slope is "b")

		inorganic As			DMA		
	<i>N</i>	a	b	<i>r</i> ²	a	b	<i>r</i> ²
this study							
Bangladesh	15	−0.012	0.719	0.912	0.000	0.145	0.526
China	21	0.025	0.599	0.951	0.013	0.199	0.512
India	12	0.003	0.796	0.796	0.002	0.178	0.118
Italy	5	0.005	0.506	0.819	0.030	0.137	0.119
U.S.	10	0.021	0.275	0.370	−0.099	0.774	0.830
literature studies							
Spain (7)	11	0.054	0.193	0.677	−	−	−
U.S. (5)	15	0.154	−0.204	0.266	−0.073	0.861	0.815

arsenic relationship was much lower than for all other countries, while the converse was true for DMA (Table 3). Zavala et al. (5) analyzed 15 U.S. white rice samples for arsenic speciation, and these data are also illustrated in Supporting Information Figure 2, giving a lower r^2 (0.266) and a negative slope (-0.204) with a large positive intercept (0.154). However, as their data set, and indeed our data set, did not contain any grain samples in the lower grain arsenic range, interpreting the total versus inorganic arsenic relationships in U.S. rice is difficult. There are 3 possible reasons for the shape of the relationship shown by the data set of Zavala et al. (5): (a) the curve is parabolic, (b) inorganic arsenic concentrations plateau at higher concentrations, or (c) the data show wide variance. The later two explanations seem more likely when comparing the current study and this previous study together (Supporting Information Figure 2). It may be that U.S. rice types cover the 3 origin classes characterized in Figure 2: Indian subcontinent, Italian/Chinese, and a lower inorganic arsenic type as yet only identified in the U.S. Zavala et al. (5) data have 3 samples on the Indian subcontinent regression line, 3 on the Italian/Chinese line, 5 on the U.S. line of this current study, and 4 outliers, which are forcing the negative regression, with high grain arsenic and low inorganic arsenic. When the data of Torres-Escribano et al. (7) for Spanish white rice are considered with the other data sets presented here (Supporting Information Figure 2), Spanish rice had a relationship similar to that of U.S. rice with an even lower slope of 0.193 and a higher r^2 0.677, differing from Italian rice which had a 3 times higher slope. However, as pointed out for U.S. rice, these slopes must be considered with caution as it is only for Indian and Bangladeshi rice that samples have been obtained that are close to the origin, and only for Bangladeshi and Chinese rice that a wide spectrum of data from low to high concentrations are available. It is notable in Figure 2 and Supporting Information Figure 2 that data from all geographical regions converge at concentrations around 0.1 mg/kg total arsenic. For example, the low slope of the Spanish rice is derived from 3 outliers with high total arsenic that have relatively low inorganic arsenic contents. More study is required to establish the relationships between total grain arsenic and its speciation, especially at lower total grain arsenic concentrations.

The lower inorganic arsenic found in U.S. rice may be because (a) percentage inorganic arsenic content decreases at high concentrations of total grain arsenic (24); (b) inherent genetic differences, differences in water management regime, or differences in climate and soils may affect grain unloading from shoots (30); or (c) methylated arsenical pesticides were used extensively on soils cultivated for rice in the south central region of the U.S. (5, 13, 14), potentially resulting in direct uptake of MMA/DMA from soils. These hypotheses need testing before any conclusions can be made.

Modeling Cancer Risks from Intake of Inorganic Arsenic in Rice. Zavala et al. (5) suggested that there was “Inorganic As type” and “DMA type” rice and that “the DMA type is likely to be less of a health risk”. However, it is inorganic arsenic that is the nonthreshold class 1 carcinogen, not DMA (8, 9), so it is inorganic arsenic content that drives potential cancer risks. In this respect DMA content is irrelevant unless DMA is also proven to have notable health impacts. While U.S. rice had a lower slope in the relationship between inorganic and total arsenic concentration than that from Bangladesh, China, India, and Italy (Table 3), the higher total content of U.S. rice meant that absolute inorganic arsenic contents of the 5 countries tested ranged only 2-fold from a median of 0.059 mg/kg for Indian to 0.109 mg/kg for Chinese rice, with U.S. rice being 0.088 mg/kg (Table 2). Note that Egyptian rice has not been speciated but its total arsenic content had a median of 0.04 mg/kg, thus its inorganic arsenic content must be at or lower than this.

The risk posed by inorganic arsenic in rice is dependent on the concentration in rice, the quantity of rice ingested, and gut bioavailability. For this study, daily consumption rates of rice per capita were calculated from FAO country-specific rice production, export, and import data, and World Bank population data for 2004, detailed in Figure 2. For the countries studied in this investigation the per capita rice consumption rate ranged from 15 g/d for France to 445 g/d for Bangladesh, while Chinese consumption was 218 g/d and U.S. consumption was 24 g/d. These data are in agreement with other reports. A traditional Bangladeshi diet has a rice consumption rate ranging from 400–650 g/d (31), while a traditional Chinese diet typically contains around 180–300 g/d (17, 29). Tsuji et al. (12) report consumption rates for the U.S. population based on the U.S. Department of Agriculture Continuing Survey of Food Intake by Individuals (CSFII) database. The mean rice consumption rates showed 40 g/d for 20–29 year olds, falling to below 20 g/d for the 70+ age group. At the 90th percentile in the 20–29 age group, rice consumption was over 150 g/d, falling below 100 g/d for age 70+. Batres-Marquez and Jensen (32) found that the “others” grouping in the CSFII survey, consisting of Asians, Pacific Islanders, and Native Americans, ate more than 115 g d.wt. of rice per day compared to the average U.S. intake of 11.4 g/d.wt.

Modeled inorganic U.S. arsenic intakes using the CSFII database and the mean concentrations for children and adults from rice were 1 and 1.67 $\mu\text{g/d}$ inorganic arsenic, respectively (Tsuji et al. (12)). From the present study the median inorganic arsenic consumption in the U.S. from rice was calculated at 2.1 $\mu\text{g/d}$ (Table 2), showing the two approaches to be in good agreement.

Risk assessment for inorganic arsenic in water by the WHO (33) and U.S. EPA (34) are based on consumption of 1 L per day, with both organizations having a standard of 0.01 mg/L, which equates to 10 $\mu\text{g/d}$ intake. The calculated intakes of inorganic arsenic from rice for India, China, and Bangladesh exceed this figure, by 3.5 and 3.6 fold for China and Bangladesh, respectively (Table 2). A number of arsenic dietary exposure studies are available for Bangladesh that compare drinking water and food exposure pathways (22, 23, 35). Kile et al. (22) considered only composite food intake and found that median total arsenic intake in food by women was 48 $\mu\text{g/d}$, a figure 10-fold higher than drinking water intake of 4 $\mu\text{g/d}$. Their median inorganic arsenic intake from food was higher than our estimated mean intake for Bangladesh (not sex denoted) of 36.2 $\mu\text{g/d}$ (Table 2) from rice alone. Kile et al. (22) did not separate rice from other foods. The study of Ohno et al. (23) did look at the relative contribution to dietary intake of different foods but did not appreciate the arsenic so only total concentrations were reported. They calculated mean total arsenic intakes of 150 $\mu\text{g/d}$, with men consuming 180 $\mu\text{g/d}$ and women 96 $\mu\text{g/d}$, with 56% of this

intake coming from cooked rice, i.e., for the overall mean consumption rice contributes 84 $\mu\text{g/d}$. Arsenic from drinking water only contributes 13% of total arsenic intake in this study. The study of Mondal and Polta et al. (35), for an arsenic drinking water affected area of West Bengal, India, found that drinking water contributed 48% of arsenic intake while for rice this figure was 44%, with the remaining 8% coming from the cooking water. Other studies that have looked at inorganic arsenic in specific food items such as common vegetables, spices, and pulses have shown that rice is by far the dominant food source of dietary inorganic arsenic (19). In a U.S. market basket survey, Schoof et al. (4) found “that rice has higher inorganic arsenic concentrations than most other foods, and consequently, diets that rely heavily on rice may contain the most inorganic arsenic”. Therefore, when assessing the risk from inorganic arsenic in the diet, it is essential to consider intakes from rice as well as water.

With respect to gut bioavailability of inorganic arsenic in white rice, Juhasz et al. (6) used large female white swine to compare orally gavaged or intravenously (IV) delivered pure arsenic salt solutions (arsenate, arsenite, MMA, and DMA) with white rice ingested as feed. They found that inorganic arsenic in rice had a high bioavailability at $\sim 90\%$. In vitro studies (27) have also found a similarly high solubilization of arsenic in rice using gastric conditions. For the modeling presented in this current study 100% bioavailability was assumed, though the model may be adjusted in a linear manner to consider other degrees of bioavailability.

Internal cancer rates can be modeled by multiplying daily arsenic intakes by the slope of internal lifetime excess cancer risk of 3.67 (mg/kg/d) $^{-1}$ proposed by U.S. EPA (12). The risk calculated here can be altered linearly to compare the outcome for other cancer slopes. For this calculation a human body weight of 60 kg was considered. Cancer rates were modeled for 100 g/d rice consumption, as this reflects 90–95th percentile rates in developed countries (12, 32). They were also modeled using country-specific rice consumption rates given in Table 2. For a fixed consumption of 100 g/d rice, median internal cancer risks ranged from 3.6 per 10,000 for India to 7.0 per 10,000 for China. When country-specific rice consumption rates are considered, Italy and the U.S. have a median excess internal cancer risk of ~ 1 in 10,000, India has a risk of 7 in 10,000, China has 15 in 10,000 and Bangladesh has 22 in 10,000. The U.S. EPA upper risk goal target for carcinogens is that the risk from any given source should not exceed 1 in 10,000 (12). The WHO cancer risk standards state that this value should be 1 in 100,000 with respect to arsenic (33). Modeled median cancer risk from rice for Bangladesh is over 200 times greater than this WHO value.

The deterministic lifetime excess cancer risk calculated in Table 2 here for Bangladesh was 22.1 in 10,000. Rice agronomics, tubewell arsenic concentrations, and rice consumption rates are similar in West Bengal, India and Bangladesh, with both populations being Bengali. A probabilistic calculation of this risk calculated for West Bengal, using an older U.S. EPA cancer slope of 1.5 (mg/kg/d) $^{-1}$ (36), calculated the excess cancer risk from arsenic due to rice consumption at 7.6 in 10,000 (35). If this slope of 1.5 (mg/kg/d) $^{-1}$ had been used in the deterministic calculation reported in Table 2, the calculated value for Bangladesh would be 9.0 in 10,000. Cooking rice can have little effect on total arsenic concentrations in cooked grain if the cooking water contains little arsenic and rice is boiled to dryness (37), but if cooking water is elevated in arsenic (35), or a high volume of (low-arsenic) water to rice is used and cooking water is discarded (37), inorganic arsenic content of cooked rice can be increased or decreased respectively. These factors also have to be born in mind in assessing risk.

The modeling outlined here indicates that eating rice at typical Southeast Asian consumption rates, or at higher

percentile consumption rates in developed countries, constitutes a significant excess cancer risk to these populations, well above the targets set by U.S. EPA (12) and WHO (33) for carcinogenic sources. As cancers caused by chronic exposure to arsenic have a latency of ~20 years (8, 9), the data presented here suggest that long-term epidemiological studies need to be undertaken to characterize this risk.

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Supporting Information Available

Additional figures and references. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- Smedley, P. L.; Kinniburgh, D. G. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **2002**, *17*, 517–568.
- Williams, P. N.; Villada, A.; Deacon, C.; Raab, A.; Figuerola, J.; Green, A. J.; Meharg, A. A. Greatly enhanced arsenic shoot assimilation in rice leads to elevated grain concentrations compared to wheat and barley. *Environ. Sci. Technol.* **2007**, *41*, 6854–6859.
- Williams, P. N.; Price, A. H.; Raab, A.; Hossain, S. A.; Feldmann, J.; Meharg, A. A. Variation in arsenic speciation and concentration in paddy rice related to dietary exposure. *Environ. Sci. Technol.* **2005**, *39*, 5531–5540.
- Schoof, R. A.; Yost, L. J.; Eickhoff, J.; Crecelius, E. A.; Cragin, D. W.; Meacher, D. M. A market basket survey of inorganic arsenic in food. *Food Chem. Toxicol.* **1999**, *37*, 839–846.
- Zavala, J. J.; Gerads, R.; Gurleyuk, H.; Duxbury, J. M. Arsenic in rice: II. Arsenic speciation in USA grain and implications for human health. *Environ. Sci. Technol.* **2008**, *42*, 3861–3866.
- Juhasz, A. L.; Smith, E.; Weber, J.; Rees, M.; Rofe, A.; Kuchel, T.; Sansom, L.; Naidu, R. In vivo assessment of arsenic bioavailability in rice and its significance for human health risk assessment. *Environ. Health Perspect.* **2006**, *114*, 1826–1831.
- Torres-Escribano, S.; Leal, M.; Velez, D.; Montoro, R. Total and inorganic arsenic concentrations in rice sold in Spain, effect of cooking and risk assessments. *Environ. Sci. Technol.* **2008**, *42*, 3867–3872.
- NRC (National Research Council). *Arsenic in drinking water 2001 Update*; National Academy Press: Washington, DC, 2001.
- IARC. *84 Some Drinking-Water Disinfectants and Contaminants, Including Arsenic*; Geneva, 2004.
- Meacher, D. M.; Menzel, D. B.; Dillencourt, M. D.; Bic, L. F.; Schoof, R. A.; Yost, L. J. Estimation of multimedia inorganic arsenic intake in the US population. *Hum. Ecol. Risk Assess.* **2002**, *8*, 1697–1721.
- Meliker, J. R.; Franzblau, A.; Slotnick, M. J.; Nriagu, J. O. Major contributors to inorganic arsenic intake in southeastern Michigan. *Int. J. Hyg. Environ. Health* **2006**, *209*, 399–411.
- Tsuji, J. S.; Yost, L. J.; Barraj, L. M.; Scrafford, C. G.; Mink, P. J. Use of background inorganic arsenic exposures to provide perspective on risk assessment results. *Reg. Toxicol. Pharmacol.* **2007**, *48*, 59–68.
- Williams, P. N.; Raab, A.; Feldmann, J.; Meharg, A. A. High levels of arsenic in South Central US rice grain: consequences for human dietary exposure. *Environ. Sci. Technol.* **2007**, *41*, 2178–2183.
- Zavala, Y. J.; Duxbury, J. M. Arsenic in rice: I. Estimating normal levels of total arsenic in rice grain. *Environ. Sci. Technol.* **2008**, *42*, 3856–3860.
- Lee, S. Geochemistry and partitioning of trace metals in paddy soils affected by metal mine tailings in Korea. *Geoderma* **2006**, *135*, 26–37.
- Liao, X.-Y.; Chen, T.-B.; Liu, Y.-R. Soil arsenic contamination and its risk assessment in areas near the industrial districts of Chenzhou City, Southern China. *Environ. Int.* **2005**, *31*, 791–798.
- Liu, H.; Probst, A.; Liao, B. Metal contamination of soils and crops affected by the Chenzhou lead/zinc mine spill (Hunan, China). *Sci. Total Environ.* **2005**, *339*, 153–166.
- Meharg, A. A.; Rahman, M. Arsenic contamination of Bangladesh paddy field soils: Implications for rice contribution to arsenic consumption. *Environ. Sci. Technol.* **2003**, *37*, 229–234.
- Williams, P. N.; Islam, M. R.; Adomako, E. E.; Raab, A.; Hossain, S. A.; Zhu, Y.-G.; Meharg, A. A. Increase in rice grain arsenic for regions of Bangladesh irrigating paddies with elevated arsenic in groundwaters. *Environ. Sci. Technol.* **2006**, *40*, 4903–4908.
- Bhattacharyya, P.; Ghosh, A. K.; Chakraborty, A.; Chakrabarti, K.; Tripathy, S.; Powell, M. A. Arsenic uptake by rice and accumulation in soil amended with municipal solid waste compost. *Commun. Soil Sci. Plant Anal.* **2003**, *34*, 2779–2790.
- Lamont, W. H. Concentration of inorganic arsenic in samples of white rice from the United States. *J. Food Compos. Anal.* **2003**, *16*, 689–695.
- Kile, M. L.; Houseman, E. A.; Breton, C. V.; Smith, T.; Quamruzzaman, Q.; Rahman, M. Dietary arsenic exposure in Bangladesh. *Environ. Health Perspect.* **2007**, *115*, 889–893.
- Ohno, K.; Yanase, T.; Matsuo, Y.; Kimura, T.; Rahman, M. H.; Magara, Y. Arsenic intake via water and food by a population living in an arsenic-affected area of Bangladesh. *Sci. Total Environ.* **2007**, *381*, 68–76.
- Meharg, A. A.; Williams, P. N.; Schekel, K.; Lombi, E.; Feldmann, J.; Raab, A.; Zhu, Y. G.; Islam, R. Speciation of arsenic differs between white and brown rice grain. *Environ. Sci. Technol.* **2008**, *42*, 1051–1057.
- Sun, Y.-G.; Williams, P. N.; Carey, A.-M.; Zhu, Y.-G.; Deacon, C.; Raab, A.; Feldmann, J.; Islam, A. A.; Meharg, A. A. Inorganic arsenic in rice bran and its products are an order of magnitude higher than in bulk grain. *Environ. Sci. Technol.* **2008**, *42* (19), 7542–7546.
- Zhu, Y.-G.; Sun, G.-X.; Lei, M.; Teng, M.; Liu, Y.-X.; Chen, N.-C.; Wang, L.-H.; Carey, A. M.; Deacon, C.; Raab, A.; Meharg, A. A.; Williams, P. N. High percentage inorganic arsenic content of mining impacted and nonimpacted Chinese rice. *Environ. Sci. Technol.* **2008**, 5008–5013.
- Ackerman, A. H.; Creed, P. A.; Parks, A. N.; Fricke, M. W.; Schwegel, C. A.; Creed, J. T.; Heitkemper, D. T.; Vela, N. P. Comparison of a chemical and enzymatic extraction of arsenic from rice and an assessment of the arsenic absorption from contaminated water by cooked rice. *Environ. Sci. Technol.* **2005**, *39*, 5241–5246.
- Heitkemper, D. T.; Vela, N. P.; Stewart, K. R.; Westphal, C. S. Determination of total and speciated arsenic in rice by ion chromatography and inductively coupled plasma mass spectrometry. *J. Anal. Atom. Spectrom.* **2001**, *16*, 299–306.
- Lin, H. T.; Wong, S. S.; Li, G. C. Heavy metal content of rice and shellfish in Taiwan. *J. Food Drug Anal.* **2004**, *12*, 167–174.
- Adomako, E. E.; Solaiman, A. R. M.; Williams, P. N.; Deacon, C.; Rahman, G. K. M. M.; Meharg, A. A. Enhanced transfer of arsenic to grain for Bangladesh grown rice compared to US and EU. *Environ. Int.*, advanced online.
- Rahman, M. A.; Hasegawa, H.; Rahman, M. A.; Rahman, M. M.; Miah, M. A. M. Influence of cooking method on arsenic retention in cooked rice related to dietary exposure. *Sci. Total Environ.* **2006**, *370*, 51–60.
- Batres-Marquez, S. P.; Jensen, H. H. *Rice Consumption in the United States: New Evidence from Food Consumption Surveys*; Staff Report 05-SR 100; Food and Nutrition Policy Division, Centre for Agricultural and Rural Development, Iowa State University, 2005.
- World Health Organization. *Drinking Water Guidelines and Standards*; http://66.102.1.104/scholar?hl=en&lr=&q=cache:UPV-kpFMWHWj:www.who.int/entity/water_sanitation_health/dwq/arsenicun5.pdf+ [accessed 05/07/08].
- National Research Council. *Arsenic in Drinking Water*; National Academy of Sciences: Washington, DC, 2001.
- Mondal, S. P.; Polya, D. A. Rice is a major exposure route for arsenic in Chakdaha block, Nadia district, West Bengal, India: A probabilistic risk assessment. *Appl. Geochem.* **2008**, advanced online.
- USEPA. *Arsenic, inorganic, CASRN 7440-38-2*; (04/10/1998); Integrated Risk Information System; www.epa.gov/iris/subst/0278.htm.
- Raab, A.; Baskaran, C.; Feldmann, J.; Meharg, A. A. Cooking rice in a high water to rice ratio reduces inorganic arsenic content. *J. Environ. Monit.* in press.
- FAO (Food and Agriculture Organization of the United Nations). <http://faostat.fao.org/site/336/DesktopDefault.aspx?PageID=336; 2004>; [accessed 04/12/07].
- World Bank. <http://web.worldbank.org/WBSITE/EXTERNAL/DATASTATISTICS/0,,contentMDK:20535285~menuPK:1390200~pagePK:64133150~piPK:64133175~theSitePK:239419,00.html>; [accessed 04/12/07].

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