# Increase in Rice Grain Arsenic for Regions of Bangladesh Irrigating Paddies with Elevated Arsenic in Groundwaters

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# Increase in Rice Grain Arsenic for Regions of Bangladesh Irrigating Paddies with Elevated Arsenic in Groundwaters

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Concern has been raised by Bangladeshi and international scientists about elevated levels of arsenic in Bengali food, particularly in rice grain. This is the first inclusive food market-basket survey from Bangladesh, which addresses the speciation and concentration of arsenic in rice, vegetables, pulses, and spices. Three hundred thirty aman and boro rice, 94 vegetables, and 50 pulse and spice samples were analyzed for total arsenic, using inductivity coupled plasma mass spectrometry (ICP-MS). The districts with the highest mean arsenic rice grain levels were all from southwestern Bangladesh: Faridpur (boro) 0.51 > Satkhira (boro) 0.38 > Satkhira (aman) 0.36 > Chuadanga (boro) 0.32 > Meherpur (boro) 0.29 $\mu$g As g$^{-1}$. The vast majority of food ingested arsenic in Bangladesh diets was found to be inorganic; with the predominant species detected in Bangladesh rice being arsenite ($As^{III}$) or arsenate ($As^{V}$) with dimethyl arsinic acid ($DMA^{V}$) being a minor component. Vegetables, pulses, and spices are less important to total arsenic intake than water and rice. Predicted inorganic arsenic intake from rice is modeled with the equivalent intake from drinking water for a typical Bangladesh diet. Daily consumption of rice with a total arsenic level of 0.08 $\mu$g As g$^{-1}$ would be equivalent to a drinking water arsenic level of 10 $\mu$g L$^{-1}$.

## Introduction

Bangladesh has extensive aquifers with elevated arsenic (As) (*1*). A large number of shallow tube wells have As concentrations above the Bangladesh standard of 50 $\mu$g L$^{-1}$, with an estimated 35 million people living in these affected regions (*2*). These tubewells are used both for drinking water (*1*) and for the widespread irrigation of rice and vegetables during the dry season (*3*–*5*).

There is compelling evidence of elevated rice grain As levels in regions of West Bengal and Bangladesh where paddy fields are irrigated with As rich waters (*3*, *6*–*9*). As contamination of vegetables grown on soils irrigated with As contaminated aquifer water has also been reported by a number of researchers (*10*–*13*). However, to assess the risk posed by As in the diet, As speciation must be ascertained, since inorganic As (arsenate and arsenite) is more toxic than methylated organic (monomethyl arsonic acid, $MMA^{V}$; dimethyl arsinic acid, $DMA^{V}$) forms found in plants (*14*, *15*). A previous study, although limited, suggests that the majority of As in Bangladesh rice is inorganic, with the rice variety influencing speciation (*8*). The forms of As in Bangladesh vegetables are presently unknown.

This is the first inclusive food market-basket survey from Bangladesh that addresses the speciation and concentration of As in rice, vegetables (leafy, fruit, and tuberous), pulses (commonly consumed annual leguminous beans, rich in protein), and spices. What is unique about this rice survey is that samples were obtained from both predominantly contaminated and uncontaminated aquifer regions of Bangladesh, with different groundwater irrigation practices, allowing regional differences in wet (aman) and dry (boro) season rice production to be observed.

Prior rice surveys such as by Meharg and Rahman (*3*) (number of samples = 13) have been limited in their scale or with Duxbury et al. (*7*) (number of samples = 150) focusing on specific geographic areas. This survey comprises 330 samples collected throughout Bangladesh, encompassing each of the main rice producing regions, with the rationale of estimating the human exposure of inorganic As in typical Bengali diets.

## Method

**Survey.** The extensive selection of rice collected included high yielding, locally improved, fine grained speciality, and deep-water varieties. Rice was obtained from both the aman and boro seasons. The survey encompassed regional areas with both high and low average arsenic tubewell waters. To reflect the way in which the Bangladeshi consumer obtains rice, grain was sourced from markets (local and wholesale) and directly from farmers. In each case details of variety and origin were recorded. Every sample collected was intended for direct human food use. Samples of market bought Chinese, Australian, Thai, Philippine, and Indian rice were obtained as a comparison to the Bangladesh samples (as grain levels are summarized in Table 2).

Vegetable samples were sourced from farmers' fields from the districts of Satkhira, Rajshahi, and Comilla. Pulses and spices were collected from farmers' homes in the Rangpur, Natore, Rajshahi, Pabna, and Mymensingh districts.

**Sample Preparation.** Only the edible portion of the samples was subject to analysis. Rice and pulses, if raw, were dehusked, by hand or in ceramic grinders. The epidermal layer of root vegetables was discarded. Garlic, ginger, and turmeric skins were removed. Samples were washed with distilled water and weighed prior to drying.

Vegetable, pulse, and spice samples for total analysis were oven dried at 65 °C for 48 h and then reweighed. Samples for speciation analysis were freeze-dried for 48 h. To assess the water content of the rice 0.5 g subsamples ($n = 34$) chosen to reflect origin and varietal variation were oven dried for 48 h. The average water content of the rice was 10 ± 0.1% ($n = 35$), in accord with previous studies (*8*, *7*). All samples were ground using a MM2 ball mill (Retsch, Germany).

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**TABLE 1. Summary of Arsenic Levels and Dietary Exposure of Bangladeshi Rice**[a]

| district (zilla) | total grain arsenic ($\mu$g As g$^{-1}$ d·wt) aman min-max | aman mean s.e. | aman *n* | boro min-max | boro mean s.e. | boro *n* | As contamination ($\mu$g As L$^{-1}$) | contribution to MTDI (%) aman | contribution to MTDI (%) boro |
|---|---|---|---|---|---|---|---|---|---|
| Barisal | 0.10−0.32 | 0.16 ± 0.01 | 14 | 0.17−0.44 | 0.25 ± 0.06 | 4 | 92 ++ | 45 | 72 |
| Bogra | 0.10−0.22 | 0.14 ± 0.02 | 5 | 0.13−0.17 | 0.15 ± 0.02 | 2 | 18 + | 40 | 43 |
| Brahmanbaria | 0.15−0.31 | 0.22 ± 0.04 | 3 | 0.21−0.31 | 0.26 ± 0.03 | 3 | 101 ++ | 64 | 73 |
| Chandpur | 0.13−0.40 | 0.22 ± 0.02 | 13 | 0.04−0.91 | 0.28 ± 0.09 | 8 | 366 ++ | 63 | 79 |
| Chuadanga | 0.10−0.48 | 0.24 ± 0.05 | 6 | 0.15−0.81 | 0.32 ± 0.03 | 27 | 79 ++ | 68 | 92 |
| Dhaka | 0.09−0.15 | 0.11 ± 0.02 | 3 | 0.12−0.23 | 0.18 ± 0.03 | 3 | 41 + | 32 | 51 |
| Dinajpur | 0.06−0.11 | 0.08 ± 0.01 | 5 | 0.13−0.17 | 0.15 ± 0.01 | 3 | 3 − | 23 | 42 |
| Faridpur | | | | 0.44−0.58 | 0.51 ± 0.07 | 2 | 140 ++ | | 146 |
| Gazipur | | | | 0.18−0.33 | 0.24 ± 0.02 | 7 | 4 − | | 68 |
| Jamalpur | 0.11−0.14 | 0.13 ± 0.01 | 2 | | | | 14 − | 36 | |
| Jessore | 0.06−0.25 | 0.13 ± 0.02 | 12 | | | | 70 ++ | 36 | |
| Khulna | <0.04−0.32 | 0.12 ± 0.01 | 24 | 0.14−0.20 | 0.17 ± 0.02 | 2 | 35 + | 34 | 49 |
| Kushtia | 0.07−0.28 | 0.19 ± 0.06 | 15 | 0.12−0.23 | 0.18 ± 0.01 | 8 | 104 ++ | 55 | 51 |
| Magura | 0.13−0.29 | 0.21 ± 0.03 | 5 | 0.21−0.31 | 0.18 ± 0.05 | 2 | 2 − | 60 | 52 |
| Meherpur | 0.06−0.42 | 0.18 ± 0.02 | 16 | 0.15−0.84 | 0.29 ± 0.04 | 18 | 116 ++ | 52 | 84 |
| Mymensingh | 0.04−0.18 | 0.11 ± 0.01 | 15 | 0.21−0.36 | 0.26 ± 0.05 | 3 | 16 − | 32 | 75 |
| Naogaon | | | | 0.12−0.17 | 0.14 ± 0.01 | 4 | 6 − | | 41 |
| Natore | 0.08−0.18 | 0.12 ± 0.01 | 6 | 0.11−0.20 | 0.17 ± 0.02 | 5 | 1 − | 34 | 48 |
| Nawabganj | <0.04−0.30 | 0.17 ± 0.03 | 8 | 0.08−0.13 | 0.09 ± 0.01 | 5 | 6 − | 48 | 26 |
| Rajshahi | 0.09−0.23 | 0.16 ± 0.03 | 4 | 0.14−0.15 | 0.14 ± 0.00 | 2 | 7 − | 46 | 41 |
| Rangpur | | | | 0.14−0.24 | 0.19 ± 0.02 | 5 | 8 − | | 55 |
| Satkhira | 0.08−0.92 | 0.36 ± 0.04 | 23 | 0.19−0.62 | 0.38 ± 0.03 | 14 | 133 ++ | 103 | 108 |
| Sherphur | 0.07−0.13 | 0.12 ± 0.01 | 8 | 0.13−0.23 | 0.17 ± 0.02 | 4 | 22 + | 34 | 49 |
| Tangail | | | | 0.18−0.33 | 0.25 ± 0.07 | 2 | 20 + | | 72 |
| Thakurga | 0.11−0.11 | 0.11 ± 0.00 | 2 | | | | 1 − | 32 | |

[a] Arsenic contamination status, based on BGS's data, for each district (+ + > 50; + > 10 < 50; − < 10 $\mu$g As L $^{-1}$). Contribution of inorganic arsenic to maximum tolerable daily intake (MTDI) is based on mean grain As levels, assumes a body weight of 60 kg, a consumption rate of 0.5 kg per day, a percentage of inorganic arsenic of 80% (*8*), and a bioavailability of 90% when cooked (*32*). Data for districts with only one sample not shown.

**TABLE 2. Summary of Arsenic Levels in Asian-Pacific Rice**

| origin | total grain arsenic ($\mu$g As g$^{-1}$ d·wt) min-max | mean ± s.e. | *n* |
|---|---|---|---|
| Thailand | 0.06−0.14 | 0.10 ± 0.01 | 15 |
| Philippines | 0.00−0.25 | 0.07 ± 0.02 | 22 |
| Australia | 0.02−0.04 | 0.03 ± 0.00 | 5 |
| Indian basmati | 0.03−0.07 | 0.05 ± 0.00 | 10 |
| China (Beijing) | 0.07−0.19 | 0.12 ± 0.01 | 32 |

**Chemical Analysis.** These were as for ref *8*. Full details are given in the Supporting Information

**Statistics.** All statistics were performed using general linear modeling (GLM) or *t*-tests and conducted using Minitab v.14 (State College, PA). Total As levels in rice data were ranked prior analysis to normalize distribution.

**Analytical Quality Control Data.** *Total Digest.* The ICP-MS detection limit for total As analysis was 0.36 $\mu$g As L$^{-1}$. Based on a sample weight of 0.1 g the detection limit equates to 0.036 $\mu$g As g$^{-1}$. The mean total recovery of As from NIST 1568a rice flour reference material was 98 ± 1.6% ($n = 11$).

*Extraction.* The ICP-MS detection limit for total As analysis precolumn was 0.009 $\mu$g As L$^{-1}$. Postcolumn limits ranged from 0.27 to 0.33 $\mu$g As L$^{-1}$. The mean recovery of As from NIST 1568a rice flour reference material precolumn was 83 ± 2.4% ($n = 3$), while postcolumn it was 82 ± 3.4% ($n = 6$), i.e., quantitative chromatographic recovery. Presently no certified rice reference exists for As speciation. The As speciation of NIST 1568a rice flour reference material has been repeatedly characterized and was used to validate our arsenic speciation technique. Our results are in agreement with previously published data (*8*, *16−18*).

## Results and Discussion

**Quantification of As in Bangladesh Foods.** *Rice.* Despite the scale and prevalence of arsenic poisoning in the Bengal Delta and the potentially significant contribution of rice on arsenic burdens (*3*, *7*, *8*), the scope of grain surveys found in the literature is limited. In a nonseafood diet, rice is the primary dietary source of As (*3*), particularly in Asia where consumption rates are high (*3*, *8*). Previous studies have reported the most contaminated Bangladesh rice to come from the southwest, with the highest mean grain levels being found in the districts of Nawabganj, Faridpur, Rajbari, and Gopalganj (*3*, *9*). A similar trend was observed in this survey. The geographical distribution of grain As levels are summarized in Figure S1 (see Supporting Information). The five highest mean grain arsenic levels were all from southwestern districts (Table 1): Faridpur (boro) 0.51 > Satkhira (boro) 0.38 > Satkhira (aman) 0.36 > Chuadanga (boro) 0.32 > Meherpur (boro) 0.29 $\mu$g As g$^{-1}$.

The districts of Satkhira, Chuadanga, Brahmanbaria, and Chandpur had the highest mean As grain levels for aman rice of 0.36, 0.24, and 0.22 $\mu$g As g$^{-1,}$, respectively. The districts of Faridpur, Satkhira, and Chuadanga had the maximum mean As grain levels for boro rice of 0.51, 0.38, and 0.32 $\mu$g As g$^{-1}$, respectively. The lowest district mean grain As level for aman rice of 0.08 $\mu$g As g $^{-1}$ was from Dinajpur. Mymensingh, Thakurga, and Dhaka all averaged 0.11 $\mu$g As g $^{-1}$. C'Nawabganj possessed the minimum mean grain As level for boro rice, of 0.09 $\mu$g As g$^{-1}$.

Boro rice requires approximately 1000 mm of irrigation water per season. The immediate and long-term implication of using contaminated water for irrigating paddy soils is of pressing concern. Huq and Naidu (*12*) estimate that arsenic loading in rice paddies could be as high as 5.5 kg/ha/yr. Based on irrigation water concentrations of 100 $\mu$g L$^{-1}$,

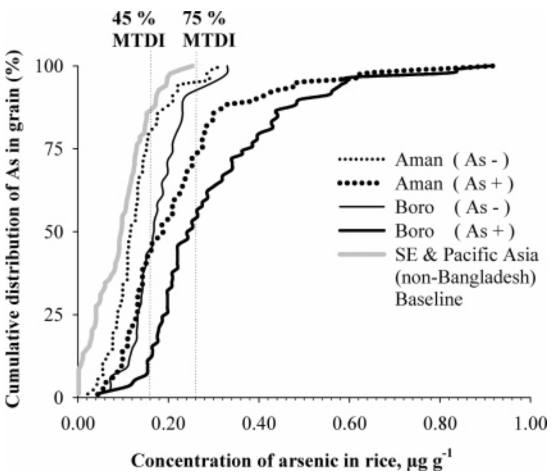


**FIGURE 1. Cumulative frequency distribution of As in the grain from aman and boro season Bangladesh rice, from districts with groundwater As levels above and below the Bangladesh safe limit. The cumulative frequency distribution of Chinese, Australian, Thai, Philippine, and Indian rice is shown as a comparison to the Bangladesh samples. Arsenic contamination status, based on district groundwater BGS's data (As + > 50; As − < 10 $\mu$g As L $^{-1}$). Contribution to maximum tolerable daily intake (MTDI) assumes a body weight of 60 kg, a consumption rate of 0.5 kg per day, a percentage of inorganic arsenic of 80% (*8*), and a bioavailability of 90% when cooked (*32*). Aman (As −), *n* = 91. Aman (As +), *n* = 103. Boro (As −), *n* = 46. Boro (As +), *n* = 90. Asian baseline, *n* = 84 (Beijing, *n* = 32, Australia, *n* = 5, Thailand, *n* = 15, Philippines, *n* = 22, Indian basmati, *n* = 10). A summary of the Asian baseline data is shown in Table 3.**

Meharg and Rahman (*3*) predicted soil arsenic levels to rise by 1 $\mu$g As g$^{-1}$ per annum. Paddy soil As surveys showed the highest levels to be in the southwest of Bangladesh (*3*).

There is increasing evidence that, at least for certain areas, soil arsenic levels have increased as a result of irrigating with arsenic contaminated water (*3*, *19*−*22*). A linear regression of shallow tube well As, using the British Geological Survey (*23*) data, against district mean As rice levels was significant (boro, $p = 0.002$; aman, $p = 0.022$) (Figure S3 and Table S5, see the Supporting Information). The cumulative frequency distribution of Bangladesh rice (aman + boro) (Figure 1) grown in districts with average shallow tube well waters equal or less than 50 $\mu$g L$^{-1}$ followed closely the cumulative frequency distribution from the Asia-Pacific baseline data (Figure 1).

Rice obtained from districts with contaminated waters (>50 $\mu$g As L$^{-1}$) were clearly more elevated than rice from uncontaminated districts (<50 $\mu$g As L$^{-1}$)—exhibiting a statistical difference (GLM, $p < 0.001$). Groundwater As concentrations are certainly important factors in predicting rice grain As levels.

The most severe groundwater contamination is confined mainly to southern Bangladesh (Figure S1 and Table 1). Districts in the southeast, such as Chandpur have a reported average shallow tube well As level in excess of 300 $\mu$g L$^{-1}$ (Table 1). This is more than 6 times over the Bangladesh safe drinking standard and more than 30 times over the WHO recommended limit (*24*). Presently, only a small proportion, between 5 and 40% in Chandpur and Comilla, and less than 5% of the net cultivated area in Lakshmipur, Noakhali, and Feni districts, is irrigated by shallow tube wells (*4*). The majority of the agricultural water supply is from surface waters. In contrast, in the southwestern districts shallow tube well irrigation is more prevalent. The percentage area under groundwater irrigation in the districts of Kushtia and Meherpur is ∼70%, with nearly all of the extraction (99%) being from shallow tube wells (*5*). Evidence suggests soil As levels are higher in areas with older shallow tube wells (*3*), because of the increased period of As loading. Shallow tube wells are predominantly younger in the north, followed by the southeast and finally the southwest (*23*). A combination of high average As water concentrations, extensive operation shallow tube wells for boro rice irrigation, and a longer history of usage could account for the consistently high levels found, by this survey and others, in the southwestern districts of Bangladesh. The majority of Bangladesh's rice is grown in the northwest. However in terms of productivity, the 4th, 5th, 12th, and 13th most productive districts are located in the South, with an estimated output of 5 305 000 mega tons (*25*).

*Rice Season.* It has been shown here that As levels in boro season rice are more elevated than aman season rice. It is probable that this is a direct result of increased irrigation with As tainted groundwaters in the boro season (*7*). However, variation in grain As level could also be accounted for by differences in accumulation of As by rice; which is influenced by redox potential, in planta and soil phosphate concentration, rhizosphere iron plaque formation, microbial activity, and rice variety (*26*, *27*). The precise mechanisms controlling the translocation of As to grain is yet to be determined. However clear varietal differences are observed from pot experiments (*8*, *28*).

This survey found a significant (GLM, $p < 0.001$) difference in As grain level between aman and boro rice. Comparison of aman and boro rice collected from the same districts showed a mean As content for boro rice to be 1.3 times higher than for aman rice, concurring with Duxbury et al. (*7*). In 13 of the 17 districts jointly surveyed, boro mean grain As concentrations were more elevated than in aman.

Comparison of the cumulative frequency distribution of aman and boro rice from districts with mean shallow tube well As levels of less than 50 $\mu$g L$^{-1}$ (Figure 1) showed elevated As grain levels in boro rice. Approximately 90% of the aman samples were equal to or below 0.2 $\mu$g As g$^{-1}$, while ∼70% were below the same value. A similar, yet more pronounced trend was observed in rice obtained from districts with shallow tube well As levels in excess of 50 $\mu$g L$^{-1}$. A linear regression of groundwater As level against district grain level (boro, $p = 0.002$, $r^2 = 0.38$; aman, $p = 0.022$, $r^2 = 0.26$), shallow tube well showed As concentration was a more important factor in determining grain As levels in boro than aman rice (Figure S3 and Table S5). This concurs with evidence from Meharg and Rahman (*3*), Alam and Sattar (*19*), and Ullah (*20*) that irrigation with As contaminated groundwater is contributing to increases in paddy soil arsenic.

*Speciation of As in Rice.* The predominant species detected in Bangladesh rice were inorganic ($As^{III}$ or $As^{V}$), with $DMA^{V}$ being a minor component (Table 3). Trace amounts of $MA^{V}$ were found in a selected number of samples. Apart from a limited survey in ref *8*, this is the first time that speciation trends between aman and boro rice have been documented. In this survey each rice variety was composed of three replicates, grown in different areas. The criterion for grain selection for speciation was that As levels in each sample were similar. Each sample was digested and analyzed in duplicate.

Recovery of As based on sum of species from TFA extracts varied from 90% in BRRI dhan 29 rice to 69% in Kalizira rice (Table 3). The lower recovery could be due to the glutinous qualities of Kalizira rice. The mean recovery for all the rice was 81%. No statistical differences between aman and boro rice were found in terms of percentage recovery (*t*-test, $p = 0.111$) or percentage inorganic arsenic (*t*-test, $p = 0.094$), although the relative amount of inorganic As in boro rice (mean = 82%) was higher than in aman rice (mean = 66%). Analysis of deep-water rice shows that the As present is mainly

**TABLE 3. Arsenic Speciation of Asian Rice**

| country | rice season | rice variety | total arsenic ($\mu$g As g$^{-1}$ d·wt) | n | inorganic As ($\mu$g As g$^{-1}$ d·wt) | species sum ($\mu$g As g$^{-1}$ d·wt) | recovery (%) | inorganic arsenic[b] (%) | inorganic arsenic[c] (%) | contribution to MTDI (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| Bangaldesh | aman | BRRI dhan 10 | 0.31 ± 0.02 | 3 | 0.22 ± 0.02 | 0.25 ± 0.03 | 81 ± 7 | 71 ± 5 | 88 ± 4 | 79 |
| | | BRRI dhan 11 | 0.21 ± 0.00 | 3 | 0.14 ± 0.02 | 0.16 ± 0.01 | 78 ± 5 | 66 ± 10 | 85 ± 8 | 48 |
| | | Kalizaira | 0.18 ± 0.03 | 3 | 0.11 ± 0.03 | 0.12 ± 0.03 | 69 ± 8 | 60 ± 7 | 88 ± 1 | 38 |
| Bangladesh | boro | BRRI dhan 28 | 0.25 ± 0.00 | 3 | 0.21 ± 0.02 | 0.21 ± 0.03 | 84 ± 11 | 83 ± 11 | 99 ± 1 | 74 |
| | | BRRI dhan 29 | 0.21 ± 0.01 | 3 | 0.17 ± 0.02 | 0.19 ± 0.02 | 90 ± 2 | 82 ± 6 | 91 ± 4 | 62 |
| | | Nayanmoni | 0.27 ± 0.02 | 3 | 0.22 ± 0.03 | 0.24 ± 0.01 | 87 ± 3 | 81 ± 3 | 94 ± 1 | 79 |
| Bangladesh | aman | Digha (DWR) | 0.21 ± 0.04 | 3 | 0.15 ± 0.04 | 0.16 ± 0.04 | 77 ± 7 | 72 ± 8 | 94 ± 2 | 55 |
| Chinese | unknown | long grain | 0.22 ± 0.03 | 3 | 0.07 ± 0.01 | 0.19 ± 0.02 | 85 ± 10 | 32 ± 7 | 37 ± 4 | 25 |
| NIST CRM 1568a | | long grain | 0.29 ± 0.03 | 6 | 0.10 ± 0.01 | 0.24 ± 0.01 | 84 ± 3 | 33 ± 2 | 40 ± 2 | |

[a] Contribution to maximum tolerable daily intake (MTDI) assumes a body weight of 60 kg, a consumption rate of 0.5 kg per day, and a bioavailibilty of 90% when cooked (*32*). [b] Inorganic arsenic= ([inorganic As]/[total As]) × 100. [c] Inorganic arsenic = ([inorganic As]/[species sum]) × 10.

inorganic (72%), with recoveries similar to both aman and boro rice.

In the Chinese rice samples the predominant As species detected was organic (DMA$^{V}$). Similarly high proportions of organic As compared to inorganic As were observed in a pot experiment using Chinese rice cultivars (*28*). The only other country reported, that has a low percentage of inorganic arsenic in comparison to total As, is the United States (*8*, *16*).

*Vegetables.* There was wide variation in As levels between and within vegetable types. Based on maximum recorded As levels the 10 vegetables with the highest As values were arum stolon (1.93 $\mu$g g$^{-1}$ d·wt) > brinjal (1.59 $\mu$g g$^{-1}$ d·wt) > cucumber (1.17 $\mu$g g$^{-1}$ d·wt) > lady's finger (1.06 $\mu$g g$^{-1}$ d·wt) > coriander (0.98 $\mu$g g$^{-1}$ d·wt) > potato (0.89 $\mu$g g$^{-1}$ d·wt) > long yard bean (0.87 $\mu$g g$^{-1}$ d·wt) > radish leaf (0.79 $\mu$g g$^{-1}$ d·wt) > giant taro (0.69 $\mu$g g$^{-1}$ d·wt) > vegetable papaya (0.69 $\mu$g g$^{-1}$ d·wt). The mean maximum recorded As level for root and tuberous vegetables (0.74 $\mu$g g$^{-1}$ d·wt) was higher than for fruit vegetables (0.56 $\mu$g g$^{-1}$ d·wt) and leafy vegetables (0.39 $\mu$g g$^{-1}$ d·wt) (Table S1, see the Supporting Information).

High levels of As have been repeatedly found in arum (*Colocassia antiquorum*). The soil/plant transfer factor for this widely consumed vegetable, popular with pregnant woman in South Asia (because it is a good source of vitamins A and C and iron), is very high at 2.64 (*12*). Huq and Naidu (*12*) reported levels in arum of up to 153 $\mu$g g$^{-1}$ d·wt. Das et al. (*29*) recorded maximum As arum leaf concentrations of 4 $\mu$g g$^{-1}$. Similarly, potato has been shown to accumulate high levels of As: Das et al. (*29*) reported maximum levels of 1.4 $\mu$g g$^{-1}$ d·wt, while Huq and Naidu (*12*) found levels as elevated as 2.4 $\mu$g g$^{-1}$ d·wt (*12*). There is a clear imperative for continued investigation into variation in As levels and dietary exposure associated with the consumption of arum and potatoes.

*Speciation of As in Vegetables.* Speciation of As in freeze-dried samples was conducted on arum stolon and tuber, potato, bitter gourd, ribbed gourd, pointed gourd, teasel gourd, plantain banana, and long yard bean (Table S2, see the Supporting Information). In all the samples, only the inorganic forms of As were present. There are only limited reports available on the forms of As in Bengal delta vegetables samples. Rahman et al. (*6*) and Chowdhury et al. (*30*) found that As in rice and vegetables from Kolsur village, in the As affected area of West Bengal, India, were 95−96% inorganic and 4−5% organic As, respectively. Meharg and Hartley-Whitaker (*14*) summarized what was then known about As speciation in plants. Data on vegetables were limited to carrots, pea, mung bean, Indian mustard (the only inorganic species present), and tomatoes (inorganic and organic species present), while a range of inorganic and organic As species was detected in fruits.

*Pulses and Spices.* The concentrations of As in pulses and spices were lower compared to those found in vegetable samples (Table S1). The average As levels in pulses did not exceed 0.10 $\mu$g As g$^{-1}$ d·wt. Roychowdhury et al. (*10*) reported the As concentrations in lentil of Jalangi block and Domkol block of Murshidabad, India were 0.0044 and 0.041 $\mu$g g$^{-1}$, respectively. Average total As concentrations in different types of spices varied widely ranging between 0.04 $\mu$g g$^{-1}$ in garlic to 0.49 $\mu$g g$^{-1}$ in coriander. Information on As concentration in spices is limited. Roychowdhury et al. (*10*) reported the mean As concentrations in turmeric of Jalangi block and Domkol block of Murshidabad, India were 0.43 and 0.27 $\mu$g g$^{-1}$, respectively. In our study there were no organic forms of As detected in any of the pulses or spices.

**Dietary Exposure.** Bangladesh has a subsistence rice diet, with vegetables supplementing high rice grain intake (*3*). Bangladeshi grain has a high inorganic As content, averaging around 80%, with the rest of the TFA extractable species being DMA$^{V}$ (*8*). Considering the Williams et al. study q (*8*) and this current study, the vast majority of food ingested As in Bangladesh diets is inorganic.

The WHO's provisional maximum tolerable daily intake (MTDI) for As is 2.1 $\mu$g d$^{-1}$ kg body wt$^{-1}$ (*31*). When As ingestion is modeled based on a 0.5 kg d wt d$^{-1}$ rice consumption rate for a 60 kg adult, assuming 80% of the As is inorganic (*8*) with a bioavailability of 90% when cooked (*32*), then a grain As level of 0.16 $\mu$g As g$^{-1}$ and 0.26 $\mu$g As g$^{-1}$ would equate to 45% and 75% of the MTDI, respectively. Ten of the 20 districts surveyed for aman rice had average As levels that contributed 45% or more to the MTDI, while aman rice from Satkhira contributed to nearly 110% of the MTDI (Table 1.). In the boro survey only five out of 22 districts had average grain levels that contributed less than 45% to the MTDI, while nine of the districts averaged levels exceeding 70% of the MTDI. The districts of Satkhira and Faridpur both had mean boro rice levels that when modeled contributed to As intakes in excess of the MTDI (Table 1).

In aman rice from districts with groundwaters below the Bangladeshi National Drinking Water As Standard of 50 $\mu$g As L$^{-1}$ approximately 80% of the samples contributed 45% or less to the MTDI. In striking contrast, only 10% of boro rice obtained from contaminated districts (>50 $\mu$g As L$^{-1}$) when modeled accounted for the same (Figure 1). This prediction of dietary As intake does not take into account the possible increase in grain As level caused by cooking with As contaminated water, which is estimated to increase inorganic As grain levels by up to 35% (*33*).

In Bangladesh, vegetables make up approximately 16% of the total diet (*34*). Average As ingestion from vegetables (from this study), based on the daily intake of 130 g f wt (*34*), would be from 0.9 to 16.9 $\mu$g day$^{-1}$ which is about 0.7−13.4% of the MTDI. Alam et al. (*11*) estimated the average intake of 5.6 $\mu$g As person$^{-1}$ d$^{-1}$ from the consumption of 130 g of vegetables in the Bangladesh village of Samta, Jessore district of Bangladesh. In comparison, Roychowdhury et al. (*10*)

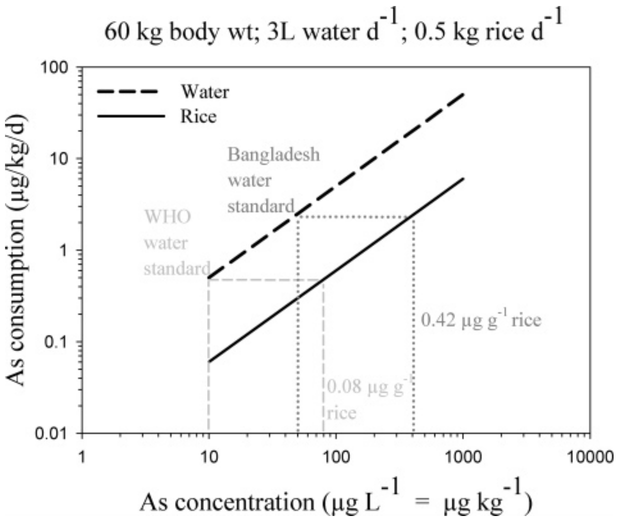


**FIGURE 2. Modeling water/rice As injestion equivalents. Assumes the percentage of inorganic As in rice to be 80% (*8*) and in water 100%. Bioavailability of rice when cooked is calculated at 90% (*32*), and bioavailability of water is taken to be 100%. Long dash = WHO safe level of As in drinking water (10 $\mu$g As $L^{-1}$). Short dash = Bangladesh Nation Standard for As in drinking water (50 $\mu$g As $L^{-1}$). Light/dark gray lines show the modeled rice equivalence for the WHO and the Bangladesh water standards, respectively.**

estimated the intake of 10.4 $\mu$g As $day^{-1}$ by an adult in the Jalangi block of Murshidabad, India which is about 1.3% of the total dietary intake of As $d^{-1}$.

Drinking water ingestion of As has also to be considered alongside food intake. The Bangladesh National Standard of As for drinking water is 50 $\mu$g $L^{-1}$. The NRC's Theoretical Maximum-Likelihood Estimates, for arsenic-derived cancer above the U.S. baseline cancer rate over a lifetime exposure, given as incidence per 10 000 people, for drinking water containing 50 $\mu$g As $L^{-1}$ is as follows: for male bladder cancer, 112.5, and for male lung cancer, 67.5 (*35*). High As burdens also increase the risk of developing kidney and skin cancers as well as other health problems such as hypertension, diabetes mellitus vascular disease, and reproductive disorders (*36*).

Predicted inorganic As intake from rice is modeled with the equivalent intake from drinking water for a typical Bangladesh diet (Figure 2). What is shown is that the daily consumption of rice with a total As level of 0.08 $\mu$g As $g^{-1}$ would be equivalent to a drinking water As level of 10 $\mu$g $L^{-1}$ (the WHO safe limit in drinking water, which is the internationally agreed limit in many countries) (Figure 2). Only one district (Dinajpur) in the aman survey possessed an average grain level below 0.08 $\mu$g As $g^{-1}$, while all of the districts surveyed had average boro grain levels in excess of this level.

The Bangladesh national As standard for drinking waters, 50 $\mu$g $L^{-1}$, is equivalent to the predicted intake of rice at a grain level of 0.42 $\mu$g As $g^{-1}$ (Figure 2). Only boro rice from the district of Faridpur was found to have an average As grain level exceeding 0.42 $\mu$g As $g^{-1}$. However the sample size surveyed from this district was limited. The average grain levels of aman ($n = 23$) and boro ($n = 14$) surveys from the district of Satkhira were within 15% of 0.42 $\mu$g As $g^{-1}$ (Table 1). Reliable estimates of dietary exposure from food are paramount. Without considering dietary exposure from food, As ingestion rates are being considerably underestimated in epidemiological studies. Additionally methylated arsenicals cannot be assumed to be benign. There is a lot of concern regarding the reduction of pentavalent methylated As to highly toxic trivalent species (*37*, *38*), prompting a new major area of research with obvious consequences for food derived risk assessments.

Our findings support previous studies that suggest that alternatives to groundwater irrigation must be considered if the As levels in rice are not to increase year on year. Also, it has been speculated that the extraction process used to irrigate paddy soil with tube well water could raise bioavailable pools of As in aquifer sediments, by drawing down arsenic from surface horizons to depth (*39*). Development of surface waters for the purpose of boro rice irrigation and implementation of modern water saving techniques such as reducing ponded water depths or alternating wetting and drying (*40*) as well as substituting rice for cereal crops that require less irrigation could alleviate some of the reliance of shallow tube wells in area suffering from high As groundwater.

Evidence suggests that genetic variation accounts for differences in As uptake (*8*, *27*, *41*−*43*), speciation (*8*, *29*, *43*), and reaction to As stress (*41*, *43*−*46*), giving impetus to focus on rice breeding programs that result in reductions in grain As levels, that improve *in planta* As methylation systems, while still retaining high yields.

In conclusion, the As detected in vegetables, pulses, and spices was found to be inorganic, contributing to As body burdens, but to a lesser extent than rice due to lower rates of consumption. There is clear evidence that in certain districts in Bangladesh rice is highly elevated in inorganic As, posing a real health risk. The low levels of inorganic As detected in Chinese rice could be important in breeding rice to reduce the dietary exposure associated with rice subsistence diets.

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## Supporting Information Available

Details of chemical analysis, graphical summary of As grain levels, district map, further summary of As levels and speciation in Bangladesh vegetables, pulses, and spices, further quality control, and As grain level/groundwater regression. This material is available free of charge via the Internet at http://pubs.acs.org.

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