Arsenic in Rice: I. Estimating Normal Levels of Total Arsenic in Rice Grain

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High levels of arsenic (As) in rice grain are a potential concern for human health. Variability in total As in rice was evaluated using 204 commercial rice samples purchased mostly in retail stores in upstate New York and supplemented with samples from Canada, France, Venezuela, and other countries. Total As concentration in rice varied from 0.005 to 0.710 mg kg^{-1}. We combined our data set with literature values to derive a global "normal" range of 0.08–0.20 mg kg^{-1} for As concentration in rice. The mean As concentrations for rice from the U.S. and Europe (both 0.198 mg kg^{-1}) were statistically similar and significantly higher than rice from Asia (0.07 mg kg^{-1}). Using two large data sets from Bangladesh, we showed that As contaminated irrigation water, but not soil, led to increased grain As concentration. Wide variability found in U.S. rice grain was primarily influenced by region of growth rather than commercial type, with rice grown in Texas and Arkansas having significantly higher mean As concentrations than that from California (0.258 and 0.190 versus 0.133 mg kg^{-1}). Rice from one Texas distributor was especially high, with 75% of the samples above the global "normal" range, suggesting production in an As contaminated environment.

Introduction

Arsenic (As) is considered one of the most important toxic elements found in the environment because of its potential risk to ecosystems and to human health (*1*). The International Agency for Research on Cancer (IARC) places inorganic As in drinking water in the highest health hazard category, i.e., a group 1 carcinogen, and there is substantial evidence that it increases risk of cancer of the bladder, lung, skin, and prostate (*1–3*), Food is also a potentially important source of dietary As intake (*4–6*). Rice (*Oryza sativa*) accumulates the highest amount of As of all grain crops, largely because of the high plant availability of As under reduced soil conditions (*7*). Rice is one of the major staple food crops in the world, with daily intake up to 0.5 kg (dry weight) per caput in Asian countries (*8*). Consequently, rice is a potentially major source of dietary As for much of the world's population, with the fraction that is inorganic varying from 10 to 90% (*9*). Reported levels of As in rice (*9–13*) are <0.01–2.05 mg kg^{-1} for Bangladesh, 0.31–0.70 mg kg^{-1} for China, 0.03–0.044 mg kg^{-1} for India, <0.10–0.76 mg kg^{-1} for Taiwan, 0.11–0.66 mg kg^{-1} for the U.S., 0.03–0.47 mg kg^{-1} for Vietnam, and 0.08–0.38 mg kg^{-1} for Italy and Spain. A recent market-basket survey in the U.S. (*14*) showed that rice grown in the South Central

U.S. contained higher As concentrations (0.15–0.66 mg kg^{-1}) compared to rice grown in California (0.10–0.30 mg kg^{-1}), with high levels attributed to the use of As containing agricultural chemicals on former cotton lands in the Southern U.S. Use of As containing irrigation water is an emerging problem for rice production in several parts of the world, especially in the Bengal basin (*15–18*), and can both supply As to a growing rice crop and lead to long-term soil contamination with As (*17, 19–21*).

The objectives of this study were (*1*) to evaluate the variability and trends in total As concentration in rice available to consumers in upstate New York, U.S. and around the world as a function of country of production, and rice characteristics (*2*) to estimate a global "normal" range for As concentration in rice based on our own and literature data (*3*) to evaluate the impact of arsenic contaminated environments on As concentration in rice, and (*4*) to evaluate effects of location of production on As concentration in U.S. rice.

Material and Methods

Rice Collection and Characterization. Rice was purchased in supermarkets and specialty stores in Ithaca and Syracuse (*n* = 158), New York and supplemented with samples from Ottawa, Canada (*n* = 23); San Cristóbal, Venezuela (*n* = 12); Paris, France (*n* = 5); and other countries (*n* = 6; Brazil, Madagascar, Dominican Republic, Sri Lanka (2), Uganda) during 2004, 2005, and 2006. Rice samples were classified based on country of production (Argentina, Bangladesh, Brazil, Bhutan, China, Greece, Egypt, France, India, Italy, Madagascar, Thailand, Pakistan, Lebanon, Dominican Republic, Spain, Sri Lanka, Surinam, Uganda, United States, Venezuela, and unknown); U.S. state of production (Arkansas, California, Texas, and unknown); grain size (short, medium, and long); color (white, brown, and other (red, black, green, pink)); cultural practice (organic and nonorganic); and U.S. distributor by state (California and Texas).

Total Arsenic Determination. Total As in rice grain was determined by digestion with HNO$_3$ (70% trace grade)/H$_2$O$_2$ (30%) followed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Spectro-CCD instrument. The transfer optics had been replaced with a short depth of field system to reduce matrix effects (*22*). Up to 9 g of whole rice grain was digested to obtain reliable As concentration data for samples with low As contents. Grain was weighed into a 60 mL quartz tube, 4 mL of HNO$_3$ was added and the tube left overnight at room temperature. Tubes were then heated in a digestion block using four temperature steps: (1) 80 °C with several 1 mL additions of HNO$_3$ until dryness and the digest color was light brown; (2) 100 °C with additions of 0.5 mL HNO$_3$, until the digest color was yellowish; (3) 130 °C, continuing additions of 0.5 mL HNO$_3$ until the digests were clear and, (4) 145 °C, with addition of 0.5 mL HNO$_3$ until the digest ashes were yellowish to white in color. Digestion tubes were cooled to room temperature, 1 mL of H$_2$O$_2$ was added and the tubes heated at 145 °C to dryness; this step was repeated until ashes were completely white. Ashes were dissolved in 6 mL of 5% HNO$_3$ and As analyses were performed using ICP-AES and the 189.042 nm line.

Quality control samples included in each digestion batch were: a blank, a replicate for every 10 samples, two secondary rice standards that contained the highest (0.714 mg kg^{-1}) and lowest (0.071 mg kg^{-1}) levels of As from the first rice batch analyzed and a primary reference sample (NIST-SRM 1568a rice flour). The mean and standard deviation for the quality control standards were 0.284 ± 0.02, 0.071 ± 0.005 and 0.714 ± 0.034 mg kg^{-1} for the NIST primary standard

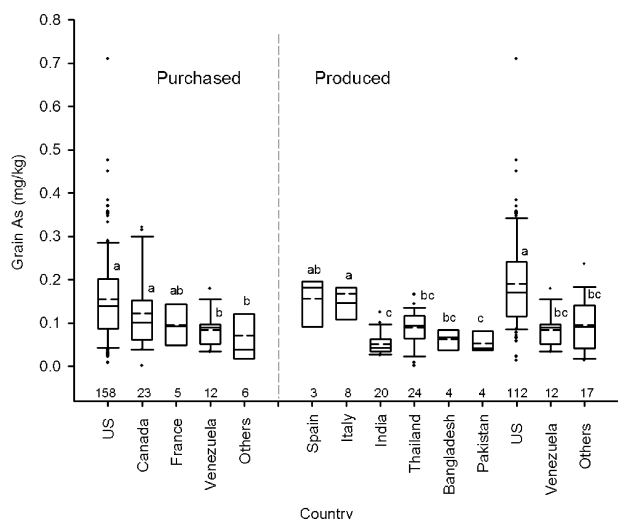* Corresponding author e-mail:yjz1@cornell.edu.

FIGURE 1. Total As concentration in rice grain by country of purchase and production. Numbers above the _x_-axis are numbers of samples. The box represents data between the 25th and 75th percentiles. The whiskers (error bars) above and below the box indicate the 95th and 5th percentiles and dots above and below them represent outliers. Lines inside the box represent the mean (--) and the median (-). Different letters above boxes indicate statistical differences at _p_ < 0.05 for country of purchase and production separately.
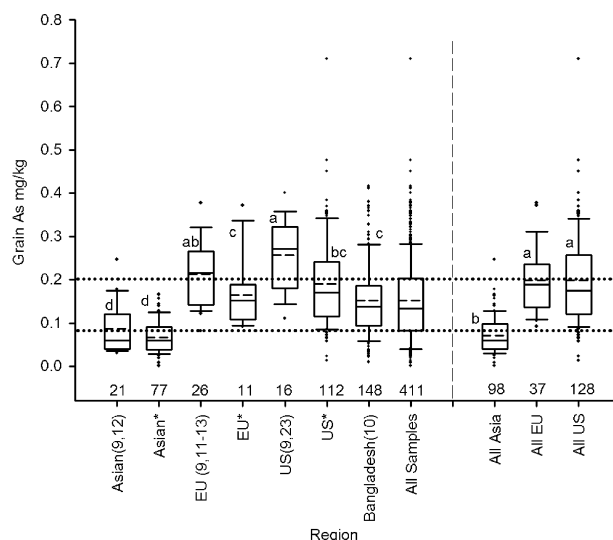

FIGURE 2. Total arsenic concentration in rice by region of the world. See Figure 1 for figure description. The numbers in parentheses represent the literature source and the asterisk data from this study. Asian rice is from Bangladesh (except that from ref _10_), China, India, Pakistan, Sri Lanka, and Thailand; EU is from Spain and Italy. The dotted lines show the distribution of the 25th to 75th percentiles for all data (global "normal" range).

and low and high secondary rice standards, respectively. Digestion of 0.6 or 7.5 g of the NIST 1568a standard did not affect As recovery. The mean coefficient of variation for replicate samples was $6.6 \pm 4.6\%$. Instrumental quality control was monitored using two As standards (0.5 and 1 mg L^{-1}) every 10 samples. The detection limit for As in rice grain was 0.005 mg kg^{-1} for a 7.5g sample. All As concentration data are expressed on a dry weight basis.

Statistical Analysis. The General Linear Models procedure of SAS 8.2 was used to test for As differences. When a significant _F_ value was detected ($P < 0.05$), mean comparisons were separated using Duncan's multiple range test. Sigma Plot (v 9.0) box and whisker plots were used to evaluate arsenic distribution in the rice grain.

Results and Discusion

A Global Comparison of Total Arsenic in Rice. Figure 1 shows box plots for arsenic in rice from different countries based on country of purchase and production. The As content of rice purchased in Canada, France, and the U.S. was not statistically different (Figure 1) and was mostly grown in the same countries. Rice bought in Venezuela and other countries contained less As than rice purchased in the U.S. and Canada, but was similar to that purchased in France. Rice grown in the U.S., Italy, and Spain contained the highest As levels, and mean values (0.156–0.19 mg kg^{-1}) were not statistically different. In contrast, rice from India and Pakistan contained significantly less As (mean 0.051–0.053 mg kg^{-1}) than rice from the three high countries. Rice from Bangladesh, Thailand, and Venezuela fell into an intermediate category with mean As concentrations (0.062–0.089 mg kg^{-1}) approximately half of those for rice from the U.S. and Europe. Rice grown in the U.S. showed the widest overall range (0.008–0.714 mg As kg^{-1}), widest range for the 5−95th percentile whiskers (0.071–0.357 mg As kg^{-1}) and the largest number of outliers. The higher mean than median value indicates the influence of a few samples with high As levels. Seventy five percent of the U.S. rice samples contained <0.240 mg As kg^{-1} and the highest concentration (0.714 mg As kg^{-1}) was similar to that reported by Williams et al. (0.66 mg As kg^{-1}) (_14_).

We combined data from the present study with published reports from the last six years in order to further evaluate differences in As content of rice from different regions and to determine what might be considered a normal range for As in rice (Figure 2). The additional data is from the U.S. (_9_, _23_), the EU (Italy (_11_, _12_) and Spain (_13_), and Asia (Bangladesh, China, India, Pakistan, Sri Lanka, and Thailand (_9_, _11_). A large data set (148 samples) for Bangladesh (_10_) was kept separate as this country is known to have As contaminated production areas (see later discussion). In all comparisons, rice from the U.S. and the EU contained significantly higher levels ($p < 0.05$) of As than rice from Asia (Figure 2). However, mean As concentrations for rice from the EU and U.S. in the present study were significantly lower than those determined from previous studies (0.152 versus 0.213 mg kg^{-1} for the EU; 0.19 versus 0.255 mg kg^{-1} for the U.S.) (_9_, _11–13_). The mean As concentration in the large data set from Bangladesh (_10_) was significantly higher by a factor of 1.5−2 times compared to the other data sets for Asian rice. When data was combined by region, the As levels in rice from the EU and the U.S. were not significantly different, and both were significantly higher than rice from Bangladesh and Asia. Mean values were 0.198 (both EU and the U.S) > 0.152 (Bangladesh) > 0.070 mg As kg^{-1} (Asia); with 75% of the values below 0.234, 0.268, 0.186, and 0.100 mg As kg^{-1}, respectively. The U.S. and EU rice samples show a wider variability in As concentration compared with Asian rice (Figure 2). Overall, the inclusion of additional data corroborates the conclusions from our market-basket survey that As concentrations in rice from the U.S., Spain, and Italy are not significantly different, and that they are significantly higher than rice from Asia.

To estimate what can be considered the "normal" range for As in rice grain, all data sets were used, giving the "All Samples" box plot in Figure 2. Fifty percent of the data, between the 25th and 75th percentiles, were in the range from 0.082 to 0.202 mg As kg^{-1} (represented by the dotted line in Figure 2), which we suggest can be considered the global "normal" range for As in rice. Values above and below the 75th and 25th percentiles then become unusually high and low, respectively. The majority of Asian rice has a grain

As content <0.098 mg kg^{-1} with several outliers within the "normal" range suggesting that the rice was grown in environments not contaminated with arsenic. In contrast, 40 and 20% of rice from the U.S. and EU, respectively, contained As concentrations above the "normal range", suggesting production in arsenic contaminated environments. Unusually high outliers (>95th percentile) were most frequent for Bangladesh and U.S. rice, suggesting the occurrence of some highly As-contaminated environments in these countries.

In making the above judgments, we recognize that there are many factors contributing to the As uptake by rice plants and grain As content, including soil and irrigation water As levels, soil physical and chemical properties, irrigation water management practices, and genetic differences. We note, in particular, that rice purchased in our market-basket survey from India and Pakistan was mostly basmati and that from Thailand was mostly jasmine. We cannot distinguish whether the lower As levels in these rice types are due to genetic or other factors. Further, rice exported from these countries may not be representative of rice consumed within them and comprehensive studies are needed to fully characterize the levels of As in rice produced in individual countries.

Impact of Arsenic Contaminated Soil and Irrigation Water on Rice As Concentration. Williams et al. (*9, 14*) have suggested that there is a link between environmental contamination with As and As content in rice grain. To address this question, we used two large data sets from Bangladesh, where both As contaminated and noncontaminated groundwater aquifers are used extensively for irrigation of winter season (Boro) rice (*17*). One data set of 397 samples was a study at the upazilla level, where four of five selected upazilla were considered to have As contaminated irrigation water (*20*). An upazilla is an administrative unit about the size of a county in the U.S. The second study was a spatially structured national survey of As in irrigation water, soils and crops with 326 sampling points across the country encompassing contaminated and noncontaminated soil and water environments (*15, 24*). We chose values of 6 mg kg^{-1} and 50 μg L^{-1} to represent the division between noncontaminated and contaminated soils and irrigation waters, respectively. The 6 ppm level for soil is intermediate between the median values of 4.5 and 9.4 mg kg^{-1} found in the upazilla and national survey studies, respectively, which also ranged up to 49 and 67 mg kg^{-1} (*15, 20*), providing a good test of whether As in rice is low from "uncontaminated" soils and high from "contaminated" soils. It is also within the globally accepted average of 5–7 mg kg^{-1} for As in noncontaminated soil (*25, 26*). Similarly, the corresponding median irrigation water values were 0.074 and 0.026 mg L^{-1}, and the maximum levels were 0.73 and 0.51 mg L^{-1}. The Bangladesh standard for drinking water is currently 0.05 mg L^{-1}.

For the national survey, mean and median concentrations for As in rice grain were identical (0.194 ± 0.074 mg kg^{-1}), with ~75% of the samples within the global "normal" range when levels of As in the soil and irrigation water were low (Figure 3). Mean grain arsenic content increased to 0.242 ± 0.098 mg kg^{-1} (median 0.227 mg kg^{-1}) when high As irrigation water was combined with low soil As, and the 75th percentile value was shifted upward from 0.22 to 0.30 mg kg^{-1}. The same trend was observed at high soil and water As. In contrast, high soil As coupled with low irrigation water As gave only a small increase in mean grain As concentration but increased variability.

The same general effects of soil and water As levels on grain As content were also observed in the Upazilla data set but mean values were higher and data was much more variable than found for the national survey. At low As levels in irrigation water, regardless of soil As levels, mean and median grain As concentrations were 0.291 ± 0.212 and 0.242
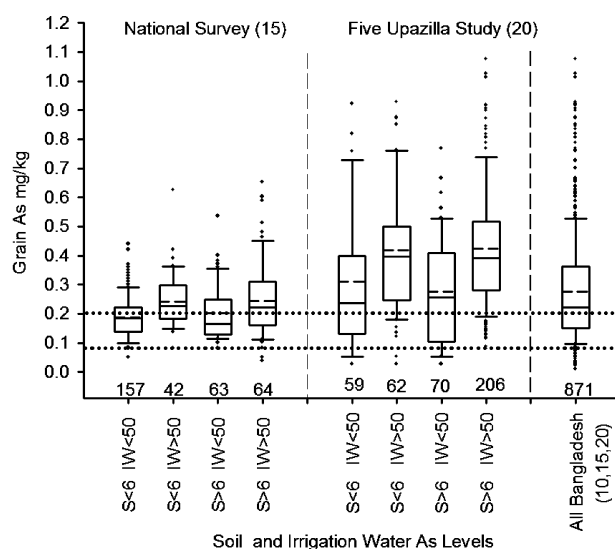

FIGURE 3. Effect of soil and irrigation water As levels on rice grain As concentration in Bangladesh. See Figures 1 and 2 for figure description. Soil (S in mg kg^{-1}) and irrigation water (IW in μg L^{-1}).

mg kg^{-1}, respectively, with 75% of the samples below 0.410 mg kg^{-1}. High irrigation water As increased the mean and median As concentrations to 0.422 ± 0.210 and 0.393 mg kg^{-1}, respectively; and shifted the 75th percentile value from 0.40 to 0.50 mg kg^{-1}. Overall, irrigation water As level was much more of a determining factor for As concentration in rice grain than was soil As level for the Bangladesh rice data. We do not know the reasons for the difference in absolute grain As values and variability between the national survey and upazilla studies; however, differences in the range of values in grain As between upazilla increase variability in that data set. It is also possible that differences in chemistry of soils and irrigation water between the upazilla influence arsenic availability and hence the relationship with As in rice grain.

When all of the As data for Bangladesh rice are combined, it can be seen (Figure 3) that approximately half of the samples contained more As than the upper limit that we established for the global "normal" range and that there is wide variability with the range from 0.009 to 1.076 mg kg^{-1} reflecting, inter alia, As contamination in the environment.

Impact of Rice Characteristics on Grain As Levels. The effect of rice characteristics on grain arsenic concentration was studied using the set of 204 commercial source samples collected in the present study. Significant differences were found for rice color with brown rice having a mean As concentration of 0.196 ± 0.111 > white rice 0.127 ± 0.087 > other colors 0.070 ± 0.050 mg kg^{-1} (Figure 4). The higher concentration of As in brown rice is attributed to the fact it still retains its outer layers (pericarp and bran) which are removed in the whitening (milling) process. The three highest grain As concentration values were found for brown rice (also nonorganic and long grain) and the mean values for both brown and white rice were shifted upward by a number of high outliers. Arsenic concentration increased significantly as the size of grain increased with mean and standard deviation values of 0.105 ± 0.067, 0.133 ± 0.070, and 0.160 ± 0.160 mg As kg^{-1} for short, medium, and long grain sizes, respectively. This result may be influenced by the origin of the rice since only 22% of the long grain samples, but 67 and 77% of the short and medium grain samples, were from California. Ninety five percent of the short and medium grain rice samples were in the estimated "normal" range for rice while 62% of the long grain rice samples were in this range.
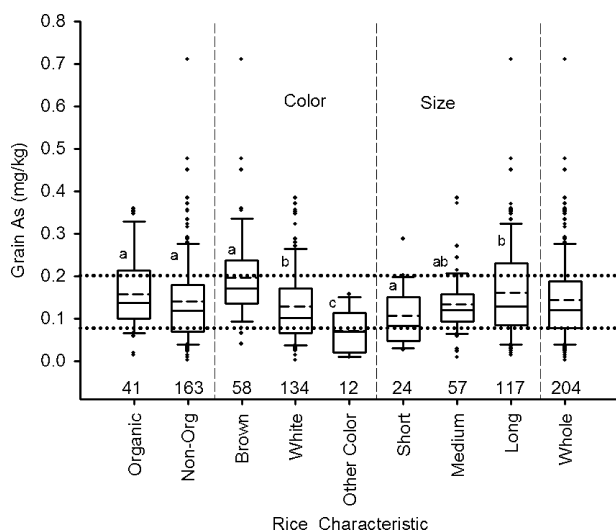
FIGURE 4. Effect of rice characteristics on grain total As concentration. See Figures 1 and 2 for description of figure.
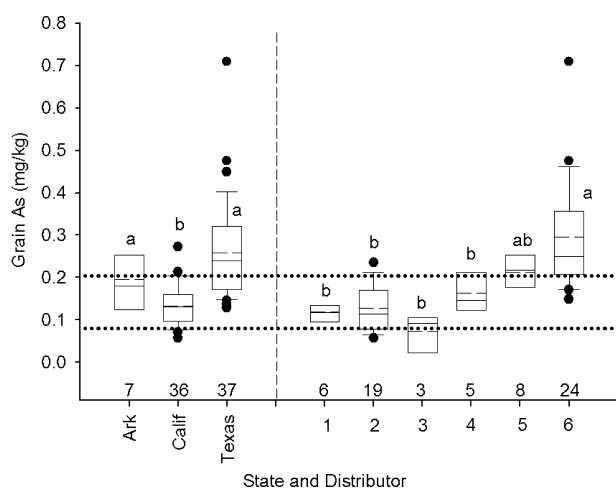

FIGURE 5. Rice grain total As content by U.S. state and distributor. Double dotted line represents the global "normal range" (Figure 2). U.S. distributors: California (one to three) and Texas (four to six). See Figure 1 for figure description.

The method of production (organic versus conventional) was not a significant determinant of grain As concentration (Figure 4).

Total Arsenic in U.S. Rice. Rice in the U.S. is grown in California and the southern states of Arkansas, Texas, Louisiana, and Mississippi, with approximately 50 and 20% of total production coming from Arkansas and California, respectively. Most of the rice samples that could be identified by the state of production were from California and Texas, with relatively few from Arkansas (7 versus 36 and 37 for California and Texas). Mean As concentrations in rice from Texas ($0.258 \pm 0.0.117$ mg kg^{-1}) and Arkansas (0.196 ± 0.095 mg kg^{-1}) were statistically equal and significantly higher ($p < 0.0001$) than that for rice from California (0.133 ± 0.047 mg kg^{-1}) (Figure 5), similar to the market basket survey results of Williams et al. (*14*). Arsenic in rice from California was also less variable than that from the Southern States.

California rice, with only two high outliers, was almost entirely within the global "normal" range, but rice from Texas was mostly above this range. The difference in rice As concentration between California and the southern states increases variability of As in rice from the U.S. as a whole (Figure 2). When rice grain As concentration was evaluated by distributor, no difference was found between the three sources in California and two of the Texas sources. Arsenic

TABLE 1. Arsenic Concentration in Different Batches of Basmati Rice from Texas Distributor 6

year	arsenic concentration (mg kg^{-1})	
	brown	white
2004	0.218	0.240
	0.290	0.352
	0.714	
2005	0.247	0.203
	0.358	0.351
	0.450	
	0.476	
2006	0.170	0.173
	0.238	0.222
	0.332	
mean	0.35 ± 0.16	0.26 ± 0.08

concentration in rice from Texas distributor no. 6 was significantly higher than that from all of the California and one of the other two Texas distributors. More than 75% of the samples from distributor 6 were above the "normal" range (>0.202 mg kg^{-1}).

The rice grain with the highest As concentration of 0.714 mg kg^{-1} was a nonorganic, brown, long grain basmati type from distributor 6 in the first rice batch that we purchased in 2004. Subsequently, 15 other samples of this rice, both brown and white, representing different batches were purchased in 2004, 2005, and 2006. The concentration of As in individual batches ranged from 0.17 to 0.714 mg kg^{-1} for brown rice and from 0.17 to 0.35 mg kg^{-1} for white rice (Table 1). Differences in mean values were not significant. This high variability is likely associated with differing levels of As contamination in production fields and distributor handling of rice from different farms. Contrary to Bangladesh, where As contaminated irrigation water appears to be the driving force for increasing As concentration in rice grain (Figure 3), elevated As concentrations in U.S. rice have been linked to use of arsenic-containing compounds on former cotton fields (*14, 27*) and, therefore, soil contamination. Soil arsenic levels ranging up to 73 mg kg^{-1} (mean of 450 samples = 23 mg kg^{-1}) (*28*) have been measured in Louisiana but, to our knowledge, there are no published data from Texas or Arkansas. Even though the commercial applications of most As containing chemicals were banned in the 1980s and 1990s, more than 30 000 tones of As compounds (arsenic acid, Ca arsenate, and organo-arsenicals) were applied to more than 3 million ha of cotton land in the southern cotton states (*29–31*), so it is understandable that arsenic residues still remain in the environment. Indeed, rice breeding for resistance to arsenic toxicity, manifested as panicle sterility or "straighthead" disorder, has been ongoing in the southern U.S. for at least 30 years.

Variability in Rice Grain As Concentration. We found that the As concentration in rice grain grown under flooded soil or paddy conditions varied widely from ~0.05 to 0.71 mg kg^{-1} and others have reported values above 1 mg kg^{-1} (*19*). The causes for this wide variability are generally considered to arise from a combination of environment, management and genetic factors that control As availability, uptake and translocation by rice. The interactions among all of these factors are complex and incompletely understood, although low redox potential and reduction of Fe and Mn oxides are considered to be critical factors governing As availability (*5, 32*) in flooded rice paddies. Polishing to generate white rice lowers As concentration and can also contribute to variability (*8, 33*). For dehusked (unpolished) Bangladesh

rice, we found that the As concentration in rice grain was increased by elevated levels of As in irrigation water but not soil. In contrast, high As concentrations in rice from the southern U.S. are consistent with the use of As containing chemicals in agriculture and therefore soil As content. The reasons for these apparently differing effects of soil As remain to be established and possibly include differences in soil As speciation and/or behavior, water management practices, and plant genes.

The impact of As contamination on grain As concentrations for the Bangladesh studies was moderate, with mean concentrations increasing by $0.05-0.13$ mg kg^{-1}, or $25-45\%$, above levels found in rice grain grown in noncontaminated environments. Similar absolute ($0.06-0.12$ mg kg^{-1}) but higher relative increases (47–94%) were found for comparisons of U.S. rice from Arkansas and Texas with rice from California. For the Bangladesh data sets, there were low outliers in As contaminated environments and high outliers in noncontaminated environments. Overall, it is clear that environmental contamination with As is not necessarily the overriding factor controlling the As concentration in rice grain. In this regard, we found 0.36 mg As kg^{-1} in dehusked rice grain of *cv.* BRRI dhan 28 grown in a soil from New York containing 6 mg As kg^{-1}, which is considered to be a typical background level for New York soils, and irrigated with water containing <0.010 mg As L^{-1}.

Acknowledgments

Literature Cited

(1) *Managing Arsenic in the Environment-from Soil to Human*; Naidu, R.; Smith, E.; Owens, G.; Bhattacharya, P.; Nadebaum,P., Eds.; CSIRO Publishing: Melbourne, Australia, 2006.

(2) ISome Drinking-Water Disinfectants and Contaminants, Including Arsenic. In *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*; ARC (International Agency for Research on Cancer): Lyon, France, 2004; Vol. 84.

(3) National Research Council. *Arsenic in Drinking Water Update*; National Academies Press: Washington, DC. 2001.

(4) Vahter, M.; Concha, G.; Nermell, B.; Nilsson, R.; Dulout, F.; Natarajan, A. T. A unique metabolism of inorganic arsenic in Native Andean women. *Eur. J. Pharmacol.* **1995**, *293*, 455–462.

(5) Schoof, R. A.; Yost, L. J.; Eickhoff, J.; Crecelius, E. A.; Meacher, D. M.; Menzel, D. B. A Market basket survey of inorganic arsenic in food. *Food Chem. Toxicol.* **1999**, *37*, 839–846.

(6) Das, H. K.; Mitra, A. K.; Sengupta, P. K.; Hossain, A.; Islam, F.; Rabbani, G. H. Arsenic concentration in rice, vegetables and fish in Bangladesh: A preliminary study. *Environ. Int.* **2004**, *30*, 383–387.

(7) Marin, A. R.; Masscheleyn, P. H.; Patrick Jr, W. H. Soil redox-pH stability of arsenic species and its influence on arsenic uptake by rice. *Plant Soil.* **1993**, *152*, 245–253.

(8) FAO. *Rice Information*; FAO: Rome, Italy, 2002; Vol. 3.

(9) Williams, P. N.; Prince, 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.

(10) Duxbury, J. M.; Mayer, A. B.; Lauren, J. G.; Hassan, N. Food chain aspects of arsenic contamination in Bangladesh: Effects on quality and productivity of rice. *J. Env. Sci. Health.* **2003**, *38*, 61–69.

(11) Caroli, S.; Frazzoli, C.; D'Amato, M.; Záray, Gy. Arsenic and Other Potentially Toxic Trace Elements in Rice. In *The Determination of Chemical Elements in Food: Applications for Atomic and Mass Spectrometry*; Caroli, S., Ed.; John Wiley: Rome, Italy, 2007.

(12) Caroli, S.; D'Ilio, S.; Alessandrelli, M.; Cresti, R. Arsenic content of various types of rice as determined by plasma-based techniques. *Microchem. J.* **2002**, *73*, 195–201.

(13) Pizarro, I.; Gómez, M. Evaluation of stability of arsenic species in rice. *Anal. Bioanal. Chem.* **2003**, *376*, 102–109.

(14) Williams, P. N.; Raab, A.; Feldmann, J.; Meharg, A. A. Market basket survey shows elevated levels of As in south central U.S. processed rice compared to California: Consequences for human dietary exposure. *Environ. Sci. Technol.* **2007**, *41*, 2178–2183.

(15) Miah, M. A M .; Rahman, M. S.; Islam, A.; Paul, D. N. R.; Farid, A. T. M.;Jahiruddin,M.; Sattar, M. A.; Panaullah, G. M.; Meisner C. A.; Loeppert, R. H.; Duxbury, J. M. Nationwide Survey of Arsenic in Soils, Water and Crops. *CIMMYT Proceedings of the International Symposium "Behavior of Arsenic in Aquifers, Soils and Plants. Implications for management"*, Dhaka, Bangladesh, Jan 16–18, 2005.

(16) Rahman, G. K. M. M.; Hossain, M. B.; Jahiruddin,M.; Islam, M. R., Panaullah; G. M., Miah, M. A. M.; Farid, A. T. M.; Biswas, B. K.; Loeppert, R. H.; Duxbury, J. M.; Meisner, C. A. Arsenic in Irrigation Water in Five Thanas in Bangladesh. *CIMMYT Proceedings of the International Symposium "Behavior of Arsenic in Aquifers, Soils and Plants. Implications for Management"*, Dhaka, Bangladesh, Jan 16–18,2005.

(17) Heikens, A.; Panaullah, G. M.; Meharg, A. A. Review of arsenic behavior from groundwater and soil to crops and potential impacts on agriculture and food safety. *Rev. Environ. Contam. Toxicol* **2007**, *189*, 43–87.

(18) Roberts, L. C.; Hug, S. J.; Dittmar, J.; Voegelin, A.; Saha, G. C.; Ali, M. A.; Badruzzaman, B. M.; Kretzschmar, R. Spatial distribution and temporal variability of arsenic in irrigated rice fields in Bangladsesh. 1. Irrigation Water. *Environ. Sci. Technol.* **2007**, *41*, 5960–5966.

(19) Meharg, A. A.; Rahman, M. M. Arsenic contamination of Bangladesh paddy field soils: Implications for rice contribution to arsenic consumption. *Environ. Sci. Technol.* **2003**, *37*, 229–234.

(20) Islam, M. R.; Jahiruddin, M.; Rahman, G. K. M. M.; Miah, M. A. M.; Farid, A. T. M.; Panaullah, G. M.; Loeppert, R. H.; Duxbury, J. M.; Meisner C. A. Arsenic in Paddy Soils of Bangladesh: Levels, Distribution and Contribution of Irrigation and Sediments. *CIMMYT Proceedings of the International Symposium "Behavior of Arsenic in Aquifers, Soils and Plants. Implications for management"*, Bangladesh, Dhaka, Jan 16–18, 2005.

(21) Dittmar, J.; Voegelin, A.; Roberts, L. C.; Hug, S. J.; Saha, G. C.; Ali, M. A.; Badruzzaman, B. M.; Kretzschmar, R. Spatial distribution and temporal variability of arsenic in irrigated rice fields in Bangladesh. 2. Paddy soil. *Environ. Sci. Technol.* **2007**, *41*, 5967–5972.

(22) Rutzke, M. A. an Optical Transfer Interface System for an Axially Viewed Plasma Improves Analysis of Biological Samples. Ph.D. Dissertation. Cornell University Libraries. January 2002.

(23) Heitkemper, D. T.; Vela, N. P.; Stewart, K. R. Determination of total and speciated arsenic in rice by ion chromatography and inductively coupled plasma mass spectrometry. *J. Anal. At. Specrom.* **2001**, *16*, 299–306.

(24) Duxbury, J. M.; Panaullah, G. M. Remediation of Arsenic for Agriculture Sustainability, Food Security and Health in Bangladesh. FAO Water Working Paper, 2007. www.fao.org/nr/water/docs/FAOWATER_ARSENIC.pdf.

(25) Smith, E.; Naidu, R.; Alston, A. M. Arsenic in the soil environment: a review. *Adv. Agron.* **1998**, *64*, 149–195.

(26) Kabata-Pendias, A.; Pendias, H. *Trace Elements in Soils and Plants*, 3rd ed.; CRC Press: Boca Raton, Florida, 2001.

(27) Reed, J. F.; Sturgis, M. B. Toxicity from arsenic compounds to rice on flooded soils. *J. Am. Soc. Agron.* **1936**, *28*, 432–436.

(28) Ori, L.; Amacher, M. C.; Sedberry, J.E. Jr. Survey of the total arsenic content in soil in Lousiana. Commun. *Soil Sci. Plant Anal* **1993**, *24*, 2321–2332.

(29) *Arsenic*; National Academy of Science:Washington, DC, 1977.

(30) Manners, I. The Persistent problem of the boll weevil: Pest control in principle and in practice. *Geogr. Rev.* **1979**, *69*, 25–42.

(31) Peters, J. A.; Blackwood, T. R. *Source Assessment: Defoliation of Cotton-State of the Art*, Technology Series.EPA-600/2–77–107g; U.S. Environmental Protection Agency: Washington, DC, 1977.

(32) Masscheleyn, P. H.; Delaune, R. D.; Patrick, W. H. Jr. Effect of redox potential and pH on As speciation and solubility in a contaminated soil. *Environ. Sci. Technol.* **1991**, *25*, 1414–1418.

(33) Rahman, M. A.; Hasegawa, H.; Rahman, M. M.; Rahman, M. A.; Miah, M. A. M. Accumulation of arsenic in tissues of rice plant (*Oryza sativa* L) and its distribution in fractions of rice grain. *Chemosphere.* **2007**, *69*, 942–948.

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