Market Basket Survey Shows Elevated Levels of As in South Central U.S. Processed Rice Compared to California: Consequences for Human Dietary Exposure

P. N. WILLIAMS, A. RAAB, J. FELDMANN, AND A. A. MEHARG*,†
School of Biological Sciences, University of Aberdeen, Aberdeen AB24 3UJ, U.K., and Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, U.K.

We report the largest market basket survey of arsenic (As) in U.S. rice to date. Our findings show differences in transitional-metal levels between polished and unpolished rice and geographical variation in As and selenium (Se) between rice processed in California and the South Central U.S. The mean and median As grain levels for the South Central U.S. were 0.30 and 0.27 μg g⁻¹, respectively, for 107 samples. Levels for California were 41% lower than the South Central U.S., with a mean of 0.17 μg g⁻¹ and a median of 0.16 μg g⁻¹ for 27 samples. The mean and median Se grain levels for the South Central U.S. were 0.19 μg Se g⁻¹. Californian rice levels were lower, averaging only 0.08 and 0.06 μg Se g⁻¹ for mean and median values, respectively. The difference between the two regions was found to be significant for As and Se (General Linear Model (GLM): As p < 0.001; Se p < 0.001). No statistically significant differences were observed in As or Se levels between polished and unpolished rice (GLM: As p = 0.213; Se p = 0.113). No significant differences in grain levels of manganese (Mn), cobalt (Co), copper (Cu), or zinc (Zn) were observed between California and the South Central U.S. Modeling arsenic intake for the U.S. population based on this survey shows that for certain groups (namely Hispanics, Asians, sufferers of Celiac disease, and infants) dietary exposure to inorganic As from elevated levels in rice potentially exceeds the maximum intake of As from drinking water (based on consumption of 1 L of 0.01 mg L⁻¹ In. As) and Californian state exposure limits. Further studies on the transformation of As in soil, grain As bioavailability in the human gastrointestinal tract, and grain elemental speciation trends are critical.

Introduction

Inorganic As is a group A human carcinogen (1), and it has also been shown to have an impact on fertility; to increase the risk of hypertension, diabetes mellitus, vascular disease, and birth defects; and to impair children’s development by reducing intellectual function (2, 3). Additionally, there is new evidence to suggest in utero and early childhood exposure can result in a marked increase in mortality from lung cancer and bronchiectasis (4).

Prior surveys have shown that rice is the primary source of As exposure in a nonseafood diet, typically possessing higher inorganic As levels than seafood (5, 6). Chinese safety standards (GB2762-2005) for inorganic As in imported rice have recently been set to 0.15 μg In. As g⁻¹ (7). Meachler et al. (8) conclude that food followed by drinking water is the greatest source of inorganic As intake for the U.S. population. In a recent study by Williams et al. (9) the levels of As found in U.S. market rice purchased in the U.K. were higher than those of market rice from Europe, India, and Bangladesh. Whether these elevated levels in U.S. rice are consistent throughout the rice growing regions of North America needs clarification. Although the average consumption of rice in the U.S. is moderate (~25 g dry weight per day), there are many ethnic groups whose daily rice consumption would be typically much higher (10). Despite the scale of production of U.S. rice and its overall importance as a major dietary constituent, little information is available on its role in defining exposure.

Williams et al. (9) suggested that high levels of As in U.S. rice may have been due to As pesticide usage. Old cotton soils are now being used to produce rice due to an expansion in rice acreage (11). Arsenical pesticide usage in the U.S. is high in traditional cotton (Gossypium spp.) growing states such as Mississippi and Arkansas, where it has been used to control outbreaks of the Boll weevil (Anthonomus grandis) and as a cotton desiccant (12, 13). Awareness of the problems of As on paddy soil fertility started in the early 20th century (14). Morris and Swingle warned of the hazards surrounding the incorporation of arsenical compounds in agricultural soils in 1927, calling it a “dangerous practice” (15). Yet despite this there is evidence of U.S. agricultural soils accumulating As, a direct result from the application of pesticides or desiccants, since the 1930s (16).

Agricultural applications of As (predominately inorganic) peaked in the 1940s. They proved popular due to their low cost and effectiveness (17) accounting for more than 90% of total U.S. As use (12). In the mid 1970s inorganic As compounds increasingly lost favor with farmers—who now sought the less toxic methylated arsenicals. In 1987 the U.S. EPA took preliminary steps effectively banning inorganic As applications on cotton (12). This might, however, have been too late because large tracts of agricultural lands would have already been contaminated (18). In 1974, methanearsonate use in cotton production accounted for in excess of 90% of all the As used by U.S. agriculture, adding around 3 million kg of As to the environment (19). The 1990s saw usage of monosodium methanearsonate (MSMA) and disodium methanearsonate (DSMA) decrease, but application still resulted in environmental inputs of more than 1 million kg of As (20). In 1997 nearly 4 million acres of U.S. cotton were treated with MSMA, while ~650 000 and 200 000 acres were sprayed with DSMA and cacodylic acid, respectively (21).

The As-rice situation in the South Central U.S. is quite unusual in that rice varieties were specifically selected to grow on arsenical-pesticide-treated soils (22), where rice yields were known to be affected by As, causing the physiological disorder “straighthead.” Symptoms of straighthead range from an increase in blank florets to complete grain failure (23). In field experiments by the University of Arkansas, MSMA was found to induce straighthead, with significant correlation coefficients for straighthead rating (r = 0.50) and grain yield (r = −0.55) (24).
soil texture, low soil pH, low free iron, and rich soil organic matter (22) all contribute to the diseases onset, although their precise importance is hard to determine as they all increase As bioavailability.

Here we present a trace element survey of U.S. grown rice, purchased in U.S. supermarkets, comparing and contrasting grain from California and the South Central U.S., to investigate variation in As contamination between these 2 regions.

Method

**Market Basket Design.** The principal aim of the study was to assess the geographical variation in As rice levels between the U.S.’s major rice production areas and to consider the consequences for human exposure. Other elements such as Se, Mn, Cu, Zn, and Co were analyzed to help clarify grain origin. The South Central States of the U.S. form the largest production unit for rice (~80%), followed by California (~20%). Rice production is greatest in Arkansas which commands nearly 50% of total U.S. rice production. The other states that rank in importance are thus the following: California (CA) > Louisiana (LA) > Mississippi (MS) > Texas (TX) > Missouri (MO) (28). The sampling strategy was adjusted similarly, with ~20% of the samples being obtained from California and ~80% from the South Central.

One hundred and thirty-four samples of rice were collected from numerous large supermarkets in the towns and cities of Little Rock (AR), Pine Bluff (AR), Stuttgart (AR), Sacramento (CA), and San Francisco (CA) during the month of September, 2005. In each case the rice sourced was commercially available and intended for direct food use, reflecting the choice on offer to the average/local consumer. A range of different grains (including medium, extra long, long, and aromatic varieties) processed in various ways (such as polished, unpolished, parboiled, instant, and iron enriched) were obtained. Processing mills tend to use locally produced rice to limit transport costs. At a national scale it is assumed that South Central processed rice was grown in this region and similarly for California. This hypothesis is tested later using PCA analysis of trace element profiles. Processing classification was first by California (n = 27) or by South Central U.S. (TX, LA, AR, MS, and MO) (n = 107). Further division of the South Central was by the Gulf Coast of Texas (n = 14) or by the Mississippi Delta (LA, AR, MS, and MO) (n = 51). For 42 South Central U.S. samples it was not possible to identify from which region they were processed. Five samples of Bangladeshi imported rice on sale in the U.S. were analyzed.

**Total Element Detection.** An Agilent 7500c (Agilent Technologies, Toyo, Japan) octopole reaction system (ORS)-ICP–MS, with a Meinhard nebulizer, was used to measure the elements. Further details are provided in the Supporting Information. The limits of detection for As and Se were 77 ng As L\(^{-1}\) and 79 ng Se L\(^{-1}\). This is equivalent to a level in rice of 0.019 μg As g\(^{-1}\) and 0.020 μg Se g\(^{-1}\), assuming sample weights of 0.2 g are maintained. Limits of detection for the other elements are reported in Table S15, in the Supporting Information. NIST Certified Reference Material (CRM) 1568a Arkansas long grain rice flour was used to validate the analysis. The average CRM recovery for all the elements was 94 ± 5%. As CRM recovery was 112 ± 1.2%. Se CRM recovery was 96 ± 1.2%. Spike recoveries for As and Se were 90 ± 0.0% and 76 ± 1.8%, respectively. CRM and spike recoveries for the other elements are reported in Table S15, in the Supporting Information. The presented data have not been corrected for these recoveries.

**Results and Discussion**

**Quantifying Elemental Composition. Total Arsenic Level.** In October 1997 (6), 4 rice samples (3 of which originated from Texas) were collected from large supermarkets in the towns of Bryan and Tyler (Texas, U.S.). The mean As level was the highest published in the literature for U.S. markets rice at 0.30 μg As g\(^{-1}\) (6). In our survey we found this level to be representative of the average As level of rice grown in South Central U.S., although not representative of the levels for California (Figure 1). The mean and median As grain levels for the South Central U.S. were 0.30 and 0.27 μg As g\(^{-1}\), respectively, for 107 samples. Levels for California were 41% lower than the South Central U.S., with a mean of 0.17 μg As g\(^{-1}\) and a median of 0.16 μg As g\(^{-1}\) for 27 samples. The difference between the 2 regions was found to be significant (GLM, p < 0.001). No statistically significant differences in As levels between polished and unpolished rice were observed (GLM: p = 0.213).

The sample with the lowest As grain level (0.10 μg As g\(^{-1}\)) was found to be organically grown long grain brown basmati variety from California; the highest (0.66 μg As g\(^{-1}\)) was a white long grain aromatic speciality rice from Louisiana mills. Grain levels in excess of 0.30 μg As g\(^{-1}\) are indicative of serious agricultural As contamination, commonly observed globally in paddy rice grown: near to industrial districts or mining areas, in paddies irrigated by high As waters, or on soils amended with municipal waste (9, 25). As levels in rice for countries/regions with no history of extensive arsenic paddy soil contamination (Thailand, Australia, Philippines, and Taiwan) typically have mean As grain levels <0.10 μg As g\(^{-1}\) (26, 27)—lower than averages for Californian grain.

**Comparison of South Central and California As Grain Trends. California.** Approximately half of the Californian rice was found to possess grain As levels equal to or below 0.15 μg As g\(^{-1}\), while 70% of the samples were below 0.18 μg As g\(^{-1}\). The grain levels ranged from 0.10 to 0.30 μg As g\(^{-1}\) (Figure 1; Table 1). Based on an inorganic As content of 42%, derived from the average of 2 separate studies on U.S. rice grain As speciation trends (9, 28), 100% of the Californian rice would meet food safety standards for export to China (GB2762-2005) (7) of 0.15 μg In. As g\(^{-1}\).

**South Central U.S.** None of the South Central samples were below 0.14 μg As g\(^{-1}\). Only 2% were equal to or below 0.15 μg As g\(^{-1}\). The difference in As rice grain level between the lowest and the highest sample was considerable at 0.51 μg As g\(^{-1}\), with the maximum level found being at 0.66 μg As g\(^{-1}\). Of the samples 66% were between 0.20 and 0.30 μg As g\(^{-1}\), while 29% of the samples were in excess of 0.30 μg As g\(^{-1}\) (Figure 1; Table 1). No difference between Texan and Mississippi Delta rice was detected (Mann–Whitney, p = 0.5701). Assuming an inorganic As content of 42% (9, 28), 21% of the South Central rice would exceed food safety standards for export to China (GB2762-2005) (7).

The lowest recorded grain levels in the entire survey were from five samples of white Baby Basmati (Kalijari) rice bought in Sacramento (CA), but which originated from Bangladesh. They ranged from 0.06 to 0.10 μg As g\(^{-1}\), with mean and median values of 0.08 and 0.07 μg As g\(^{-1}\), respectively (Table S1, see the Supporting Information).

This rice is a speciality grain grown just in the wet season where irrigation is predominately by precipitation. Despite high As grain levels being reported in Bangladesh, the rice used from there for export appears much lower in As than much of the rice used for domestic consumption (26).

**Total Selenium Level of American Rice Grain.** The Se levels in grain ranged from 0.02 to 0.10 μg Se g\(^{-1}\), from an ecofarmed grown brown basmati variety from California, to 0.41 μg Se g\(^{-1}\) in a white long grain precooked enriched (coated with nutrients, such as iron, niacin, thiamin, and folic acid) rice from the South Central. The mean and median Se grain levels for the South Central were 0.19 μg Se g\(^{-1}\). Californian rice levels were lower, averaging only 0.08 and 0.06 μg Se g\(^{-1}\) for mean and median values, respectively. The difference
between the two regions was found to be significant (GLM, \( p < 0.001 \)). Mean levels of Se followed the order Mississippi Delta (0.21 \( \mu g \) Se g\(^{-1}\)) > Gulf of Texas (0.10 \( \mu g \) Se g\(^{-1}\)) > Californian Central Valley (0.08 \( \mu g \) Se g\(^{-1}\)) > Bangladesh (0.05 \( \mu g \) Se g\(^{-1}\)). All samples were within a normally reported range for U.S. grain and cereal products of between 0.01 and 0.42 \( \mu g \) Se g\(^{-1}\) d wt (based on grain moisture contents of 10% (29)). No statistically significant differences in Se levels between polished and unpolished rice were observed (GLM: \( p = 0.113 \)).

Se diseases have been commonplace in the Sacramento River Valley (California). Low levels of Se in the soil parent material is the primary reason for the low levels reported in crops (30). The mean soil background Se levels for rice production areas, derived from the Shacklette data set (31), are as follows: Mississippi Delta (0.7 \( \mu g \) Se g\(^{-1}\), \( n = 17 \)) > Gulf Coast of Texas (0.4 \( \mu g \) Se g\(^{-1}\), \( n = 6 \)) > Californian Central Valley (0.2 \( \mu g \) Se g\(^{-1}\), \( n = 7 \)) (Table S11, see the Supporting Information); concurring with the levels reported in rice. This is further supported by a regional study of Se levels in soybeans. Soybeans from the Mississippi Delta floodplain had levels exceeding those in areas considered as having adequate background Se levels, suggesting agricultural soils in the delta were exceptionally high in available Se (32).
TABLE 1. Summary of Grain Trace Element Levels

<table>
<thead>
<tr>
<th>Trace Element</th>
<th>California mean ± SE</th>
<th>South Central mean ± SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>0.022 ± 0.00</td>
<td>0.017 ± 0.00</td>
</tr>
<tr>
<td>Se</td>
<td>0.080 ± 0.01</td>
<td>0.20 ± 0.01</td>
</tr>
<tr>
<td>As</td>
<td>0.17 ± 0.001</td>
<td>0.30 ± 0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>3.1 ± 0.16</td>
<td>2.5 ± 0.05</td>
</tr>
<tr>
<td>Zn</td>
<td>17 ± 1</td>
<td>18 ± 1</td>
</tr>
<tr>
<td>Mn</td>
<td>27 ± 3</td>
<td>17 ± 1</td>
</tr>
</tbody>
</table>

Principal Component Analysis (PCA). Multivariate methods, such as PCA, have been used to explore the relationships between grain element levels and rice characteristics (33). In the current analysis, 97 rice samples (those that could be accurately sourced to a state level via mills) were compared with 6 elements. Biplots of PCA 1 vs PCA 2 (Figure 2) explain approximately 65% of total variance, with PCA 1 and PCA 2 accounting for 40% and 25% of the variance, respectively. Separation on PCA 1 was primarily by Mn, Co, and Cu, all with positive loading values. PCA 2 separation was influenced mainly by As then Se (positive loading values). A highly significant relationship was found between grain As level and PCA 2 ($R^2 = 0.84, P < 0.0001$) (Figure S2, see the Supporting Information).

Separation of rice by origin was clearly evident in relation to grain element composition. In general, the Mississippi Delta rice clustered tightly in the top right quadrant of the biplot (Figure 2), concurrent with higher As and Se and lower Mn, Co, and Cu grain levels. Gulf of Texas rice was located adjacent to the Mississippi Delta samples, indicating a common feature among all South Central rice. However, due to the lower levels of Se, the samples were placed in closer proximity to the origin. The 5 South Central samples with the highest As grain levels were separated from the clusters by their transition elements, especially Mn and Co. The Mn levels in these samples were 1.5 times greater than the overall mean for South Central rice, while the Co levels were 3 times greater. The element composition for the highly As elevated grains was unusual when compared with the rest of the subset. The Californian samples showed no similarity with South Central U.S. rice along PC2. Both regions exhibited variation on PCA 1 indicating differences within transition elements. PCA 1 separation was more evident for California.

This is most probably due to there being a higher proportion of unpolished rice in the Californian samples (Figure 2). The clear separation between California and South Central processed rice is clearly supportive of processing mills using locally and regionally grown rice. Bangladesh rice was lowest in all elements, except Mn, grouping the samples tightly in the bottom right biplot quadrant.

As in U.S. Soil. Ori et al. (13) analyzed over 450 samples of Louisiana rice, revealing a mean As level of 23.2 µg g⁻¹ with minimum and maximum values of <2.8 and 73 µg g⁻¹, respectively. This is higher than the mean baseline levels reported from the USGS Shacklette data set for nonagricultural soils in Louisiana, at 8 µg As g⁻¹ (Table S11). Pettry and Switzer (34) concur, finding a significant difference in soluble As between undisturbed and cultivated land in Mississippi (Table S12, see the Supporting Information).

As from past agricultural applications may be potentially lost from fields through various mechanisms—volatization, leaching, crop removal, water runoff, and soil erosion (35). In field experiments with both organic and inorganic As applications, average losses were in the order of 0.03%. However, losses in other experiments are greater (16). The soils ability to retain As is governed by its composition and characteristics, both of which are highly heterogeneous. Additionally soils influence the As speciation (18), facilitating both oxidative metabolism and reductive methylation (35). Organic As pesticides have been shown to undergo partial transformation into inorganic As (20, 36), affecting toxicity and bioavailability. Speciation may be of importance as volatization rates are higher with increased methylation of As compounds (35). Robust estimates of As volatization and cycling in paddy rice agricultural systems are lacking. Soil, however, still remains the primary sink for As in agroecosystems (35), and it is clear that applications of As pesticides lead to As build up in North American soils (18).

If the increase in rice grain As was a direct consequence of natural geochemical profiles of the region, then the Californian rice should be higher in As than South Central rice as stream sediments are over twice that of the South Central averages (Table S13). A similar trend is observed for groundwater with levels in California being much higher than the equivalent levels in the South Central (Table S14, see the Supporting Information). Further studies of the As level in California rice are still recommended. The majority of California rice is produced in the Northern Central Valley. However, the rice producing Southern Central Valley counties of Merced and Fresno also grow extensive amounts of cotton; together they planted over 300,000 acres of cotton in 2004 (37). Even if rice is not grown directly on old cotton soils, grain can still potentially become contaminated by pesticide spray drift if the crops are grown in close proximity with cotton (38).

Rice Consumption. U.S. rice consumption during the latter half of the 20th century has steadily increased until the present. Daily per capita consumption in 2003 was 25 g dry weight per day (10). Therefore, an average adult American weighing 70 kg would ingest 0.36 g dry weight/kg/d. This value underestimates the rice consumption of the very young (39), those in or close to poverty, certain ethnic groups whose cultural preference is for a high rice diet (10), and sufferers of Celiac disease. Approximately 880,000 U.S. citizens (1 in 333 Americans) are affected by Celiac disease (40). Suffers must adhere to a gluten-free diet. This involves not eating foods such as wheat, rye, and barley. Rice therefore becomes an obvious substitute to these prohibited grains.

Although the average age of rice consumed by infants and children is low, their body weights are also proportionally low. Clear cultural differences have been observed in the foods fed to Hispanic and non-Hispanic infants and toddlers, with a significantly higher prevalence of rice in the Hispanic...
children’s diets (41). Yost et al. (42) estimated that for those U.S. children (1–6 year olds) with the highest dietary intakes of inorganic As (85th percentile) rice and rice products accounted for 49.9% of total inorganic As intake.

Low-income (<185% of the poverty threshold; as defined by the U.S. National Health and Nutrition Examination Survey 2001–2002) families ate rice more frequently and in greater quantities than more affluent households, with rice intake estimated at 0.96 g dry weight of rice/kg/d (10), for a 70 kg adult. The average daily intake of rice for Asian, Pacific, and Native Americans is high: over 115 g per day (10) or 1.64 g dry weight of rice/kg/d, for a 70 kg adult. A study of U.S. Chinese women’s dietary habits observed rice intake a total of 38 times a month (43). A similar survey of Korean-American adolescents found rice to be the most commonly consumed dish, for both males and females (44). U.S. rice consumption, classified by ethnicity increases from White, non-Hispanic < Black, non-Hispanic < Mexican-Hispanic < Hispanic, non-Mexican < Other (including Asian, Pacific, and Native American) (10).

**Risk Assessment.** Most terrestrial food contains low to moderate levels of As, typically less than 0.25 μg As g⁻¹ (45). We have shown that for certain U.S. rice the levels are atypical in regards to As concentration. When drinking water As levels are low food becomes the dominant inorganic As exposure route for the U.S. population (45). In California the Office of Environmental Health Hazard Assessment has derived a public health goal of 4 ng As L⁻¹ for drinking water (45), based on cancer epidemiological studies of As affected populations in Taiwan and South America (46). If this is achieved, then daily As intake from water would be 4 ng As L⁻¹, based on NRIs daily water consumption rates of 1 L.

For Asian Americans dietary As exposure from rice even at an inorganic arsenic level of 0.10 μg In. As g⁻¹ could be higher than for water, with respect to the U.S. EPA MCL of 10 μg As L⁻¹ and average drinking water consumption rates of 1 L per day (46) (Figure 3). Rice could be the principal dietary source of inorganic As in a Hispanic diet if grain arsenic exceeds 0.20 μg In. As g⁻¹. Even for the average American, rice would still contribute significantly to total dietary exposure. If inorganic As exposure from rice and water are considered together, then daily exposure to more than 10 μg In. As d⁻¹ is easily breached.

Any development of rice safety standards based on total As is compounded by the apparent large ranging variation in speciation of arsenic in U.S. rice. The percentage of inorganic As from market rice has been shown to vary from 10 to 61% (28) and 27 to 59% (9). A pot experiment with American cultivars grown in As spiked soil, the percentage of inorganic As differed from 44 to 69% (9). In a study of U.S. market rice by Lamont (47) over 40% (n = 40) of the samples exceeded levels of 0.15 μg In. As g⁻¹ d wt, the Chinese standard (7), and approximately 15% exceeded 0.20 μg In. As g⁻¹ d wt. The same study also recorded a value of 0.30 μg In. As g⁻¹ d wt (assuming a grain moisture content of 10%) (9). Additionally organic arsenicals, although not as toxic as inorganic arsenic, cannot be assumed to be completely benign. Reduction of pentavalent methylated As to the highly toxic trivalent species can occur in vivo (48, 49).

Regardless of whether South Central U.S. rice is elevated due to As pesticide usage or due to geographical reasons, the consequences for human health are identical.

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**Supporting Information Available**

Tables of arsenic, selenium, copper, manganese, cobalt, and zinc levels in U.S. rice (Tables S1–S6); U.S. rice brands (Table S7); element levels in polished/unpolished U.S. rice (Table S8); analysis of variance for transition metals (Table S9) and for arsenic and selenium (Table S10); background levels of Se, As, and Mn in soils (Table S11); summary of total and water soluble As in soils (Table S12), of As and Se levels in stream sediments (Table S13), and of As levels in potable groundwaters (Table S14); quality control (Table S15); duplicate analysis of samples (Table S16); and composition and concentration of multielement standard (Table S17) and figures of interaction plots for polished and unpolished rice (Figure S1) and regression of As grain level vs PCA (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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