

# High levels of inorganic arsenic in rice in areas where arsenic-contaminated water is used for irrigation and cooking

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1 **High Levels of Inorganic Arsenic in Rice in Areas where Arsenic-**  
2 **Contaminated Water is Used for Irrigation and Cooking**

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25 **Abstract**

26 Rice is the staple food for the people of arsenic endemic South (S) and South-East (SE)  
27 Asian countries. In this region, arsenic contaminated groundwater has been used not only for  
28 drinking and cooking purposes but also for rice cultivation during dry season. Irrigation of  
29 arsenic-contaminated groundwater for rice cultivation has resulted high deposition of arsenic in  
30 topsoil and uptake in rice grain posing a serious threat to the sustainable agriculture in this region.  
31 In addition, cooking rice with arsenic-contaminated water also increases arsenic burden in  
32 cooked rice. Inorganic arsenic is the main species of S and SE Asian rice (80 to 91% of the total  
33 arsenic), and the concentration of this toxic species is increased in cooked rice from inorganic  
34 arsenic-rich cooking water. The people of Bangladesh and West Bengal (India), the arsenic hot  
35 spots in the world, eat an average of 450 g rice a day. Therefore, in addition to drinking water,  
36 dietary intake of arsenic from rice is supposed to be another potential source of exposure, and to  
37 be a new disaster for the population of S and SE Asian countries. Arsenic speciation in raw and  
38 cooked rice, its bioavailability and the possible health hazard of inorganic arsenic in rice for the  
39 population of S and SE Asia have been discussed in this review.

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42 **Keywords:** Arsenic, Rice, Dietary intake, Inorganic arsenic.

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## 48 **1. Introduction**

49 Arsenic is the 20<sup>th</sup> abundant element in earth crust, and is ubiquitous in the environment  
50 (soil, water, air and in living matters) (Tamaki and Frankenberger, 1992). It has been well  
51 recognized that consumption of arsenic-contaminated foods leads to carcinogenesis (Mandal and  
52 Suzuki, 2002). Chronic effects of arsenic toxicity on humans have been reported from most of  
53 the countries in South (S) and South-East (SE) Asia through its widespread water and crop  
54 contamination (Kohnhorst, 2005; Mukherjee et al., 2006; Smedley, 2005). Arsenic contaminated  
55 groundwater is used not only for drinking purpose but also for crop irrigation, particularly for the  
56 paddy rice (*Oryza sativa* L.), in S and SE Asian countries (Meharg and Rahman, 2003; Ninno  
57 and Dorosh, 2001). In Bangladesh, arsenic-contaminated groundwater has been used extensively  
58 to irrigate paddy rice, particularly during the dry season, with 75% of the total cropped area  
59 given to rice cultivation (Meharg and Rahman, 2003). Background levels of arsenic in rice paddy  
60 soils range from 4 to 8  $\mu\text{g g}^{-1}$  (Alam and Sattar, 2000; Williams et al., 2006), which can reach up  
61 to 83  $\mu\text{g g}^{-1}$  in areas where the crop land has been irrigated with arsenic-contaminated  
62 groundwater (Williams et al., 2006). The problem of arsenic contamination in groundwater is not  
63 just restricted to Bangladesh. Other countries in S and SE Asia such as West Bengal (India),  
64 Vietnam, Thailand, Nepal and Taiwan have also been reported to have high levels of arsenic in  
65 groundwater (Dahal et al., 2008; Nordstrom, 2002) (Fig. 1). Paddy rice is the staple food for the  
66 people of these regions. Increasing levels of arsenic in agricultural soils from contaminated  
67 underground irrigation water, and its uptake in rice, vegetables, and other food crops (Meharg  
68 and Rahman, 2003; Williams et al., 2006) has become a real health emergency in this region.  
69 The presence of high levels of arsenic in rice is supposed to be a health disaster in South Asia

70 (Meharg, 2004). Around 200 million people in S and SE Asia is supposed to be exposed to  
71 arsenic contamination from water and foods(Sun et al., 2006).

72 A large population in Asian arsenic endemic areas lives on subsistence diet of rice, a  
73 cereal which is grown mainly with groundwater contaminated by high level of arsenic. Therefore,  
74 rice contains relatively higher amount of arsenic, most of which is inorganic (Meharg et al.,  
75 2009; Sun et al., 2008; Torres-Escribano et al., 2008), compared to other agricultural products  
76 (Das et al., 2004; Schoof et al., 1999). The concentration of arsenic and its chemical forms in rice  
77 vary considerably depending on rice variety (Booth, 2008) and geographical variation (Booth,  
78 2007; Meharg et al., 2009). The inorganic arsenic species dominates over organoarsenic species  
79 in both raw and cooked rice (Williams et al., 2005), which is accumulated/absorbed from paddy  
80 soil, irrigation water, and cooking water. Therefore, arsenic speciation in rice grain is influenced  
81 by its speciation in soil and water. In addition, the amount of arsenic absorbed by the cooked rice  
82 from cooking water and, the dietary intake of arsenic in human body are depended on the type of  
83 rice and the way the rice is cooked (Musaiger and D'Souza, 2008; Ohno et al., 2009; Rahman et  
84 al., 2006; Signes et al., 2008a; Signes et al., 2008b). Considering the high concentration of  
85 arsenic (mainly inorganic arsenic) in rice grain, cooking method, and high consumption rate, rice  
86 is revealed to be a major threat to health of the people of arsenic endemic S and SE Asian  
87 countries. In this review, arsenic speciation in rice, dietary intake, and health risk of inorganic  
88 arsenic species to the arsenic endemic and rice subsistent population of S and SE Asian countries  
89 have been discussed.

90

## 91 **2. Arsenic in irrigation water: A threat to sustainable rice cultivation in S and** 92 **SE Asia**

93           The problem of arsenic contamination in groundwater is now well recognized in most of  
94 the S and SE Asian countries as discussed in the previous sections. Rice is the main cereal crop  
95 produced in this region, especially in Bangladesh and West Bengal (India), which is irrigated  
96 with groundwater during dry season. Recently, it has become apparent that arsenic-contaminated  
97 irrigation water is adding significant amount of arsenic in the topsoil and in rice, which pose  
98 serious threat to sustainable rice cultivation in these two countries (Brammer and Ravenscroft,  
99 2009; Dittmar et al., 2010; Khan et al., 2009; Khan et al., 2010a; Khan et al., 2010b; Meharg and  
100 Rahman, 2003). Since the agroecological and hydrogeological conditions of the S and SE Asian  
101 countries are broadly similar, irrigation of arsenic-contaminated groundwater is supposed to  
102 produce similar effects on paddy rice of this region. In addition, paddy rice is considered to be  
103 one of the major and potential exposure sources of arsenic for humans (Meharg and Rahman,  
104 2003; Mondal and Polya, 2008; Pillai et al., 2010; Rahman et al., 2008a; Singh et al., 2010; Tuli  
105 et al., 2010; Williams et al., 2006; Zavala and Duxbury, 2008) because of its increasing  
106 deposition in the topsoil from irrigation water and its subsequent uptake in rice grain (Dittmar et  
107 al., 2010).

108           Irrigation with arsenic-contaminated groundwater may particularly affect rice cultivation  
109 in terms of production and contamination. There may be two main reasons for this- i) a large  
110 amount of underground water containing high level of arsenic has been irrigated for rice  
111 cultivation in most parts of S and SE Asia during dry season and ii) rice is the crop that is most  
112 susceptible to arsenic toxicity (Brammer and Ravenscroft, 2009). Due to the decrease of rainfall  
113 in this region, even in monsoon season, the dependency on groundwater for rice cultivation is  
114 expected to be increased in the coming years in order to increase crop production to meet the  
115 demands of the increasing population. This practice will increase additional arsenic deposition in

116 topsoil. Roberts et al. (2007) reported that arsenic contents in topsoil in Bangladesh have  
117 increased significantly over the last 15 years because of irrigation with arsenic-rich groundwater.  
118 Other studies showed that arsenic concentrations remain unchanged at the start of two successive  
119 irrigation seasons suggesting that arsenic added during the first irrigation season had been  
120 leached by floodwater during the following monsoon season (Dittmar et al., 2007). Thus, the rate  
121 of arsenic deposition from contaminated irrigation water would be higher in flat terrain soil than  
122 that in floodland soil.

123 Another important concern regarding arsenic deposition in paddy soil is whether all  
124 arsenic delivered by the tube wells is reached and deposited throughout the fields equally. In  
125 addition, how arsenic in irrigation water and soil contributes to its uptake in rice plant and grain  
126 is also important concern. Brammer and Ravenscroft (2009) discussed these issues in a recent  
127 review on arsenic in S and SE Asia perspective. They urged that groundwater of most arsenic-  
128 affected areas in S and SE Asia is rich in iron (Gurung et al., 2005; Postma et al., 2007), which is  
129 oxidized upon exposure to the air, and is then precipitated as iron-hydroxides in the rhizosphere.  
130 Arsenate has high binding affinity to these precipitated iron-hydroxides. Therefore, arsenic  
131 concentration in soil is decreased with increasing distance of the location from the well-head  
132 (Dittmar et al., 2007; Roberts et al., 2007). But being an important nutrient, iron precipitation  
133 decreases its bioavailability and uptake resulting iron-chlorosis in rice plant. In such conditions,  
134 farmers use iron-fertilizers to increase iron bioavailability and uptake to correct iron-chlorosis  
135 (Alvarez-Fernandez et al., 2005; Hasegawa et al., 2010; Hasegawa et al., 2011). Since arsenic is  
136 adsorbed on precipitated iron-hydroxides in the rhizosphere soil, application of iron-fertilizer  
137 may increase both iron and arsenic bioavailability and uptake in rice plant (Hasegawa et al.,  
138 2011; Rahman et al., 2008b). In addition to iron fertilizer, rhizospheric microbes also solubilise

139 ferric iron in the rhizosphere by exuding siderophores to the root-plaque interface (Bar-Ness et  
140 al., 1992; Crowley et al., 1992; Crowley et al., 1991; Kraemer, 2004; Romheld, 1987), which  
141 may also render both iron and arsenic bioavailable and uptake in rice plant. Being the strategy II  
142 plant, rice roots also exude phytosiderophores in the rhizosphere soil under iron-deficient  
143 condition to increase iron bioavailability and uptake (Ishimaru et al., 2006; Romheld and  
144 Marschner, 1986). In this case, there is also a possibility of the increase of arsenic bioavailability  
145 to and uptake in rice plant. The rice cultivation conditions also favour arsenic uptake in rice plant.  
146 Rice is grown in flooded (anaerobic) conditions in which arsenic exists mainly as dissolve  
147 As(III) form and is readily taken up from the soil solution by rice plant (Xu et al., 2008).

148         The arsenic uptake mechanisms in rice is more complicated because of its ability to carry  
149 oxygen from the air down to its stem and discharge it in the rhizosphere through the roots  
150 (Brammer and Ravenscroft, 2009). This creates an oxidized zone around the roots in which iron  
151 is oxidized and precipitated to forms a coating (Liu et al., 2006). Hu et al. (2007) found that  
152 sulfur enhances the formation of iron plaque in the rhizosphere and reduces arsenic accumulation  
153 in rice. In another study, Hu et al. (2005) observed that the use of phosphate fertilizer decreased  
154 iron-plaque formation on rice roots. Although the formation of iron-coating on rice root surface  
155 should increase arsenic adsorption, and thus act as an arsenic filter, some studies showed that  
156 significant amount of arsenic is taken up by rice plants in this condition too (Meharg and  
157 Rahman, 2003).

158

### 159 **3. Arsenic concentration and speciation in raw rice**

#### 160 **3.1. Arsenic in raw rice**

161 Up to date, significant number of articles on arsenic concentrations in rice and in its  
162 fractions have been published (Bae et al., 2002; Meharg, 2004; Mondal et al., 2010; Mondal and  
163 Polya, 2008; Rahman et al., 2006; Rahman et al., 2007a; Rahman et al., 2008a; Williams et al.,  
164 2006; Williams et al., 2005; Williams et al., 2007b). This implies that the dietary intake of  
165 arsenic from rice has been received much attention to understand the fate of arsenic exposure.  
166 Rice is by far the largest dietary source (50-70% of the total meal) of arsenic for rural  
167 populations even where drinking water does not contain elevated levels of arsenic (Chatterjee et  
168 al., 2010). About ten-fold elevation of arsenic in Bangladeshi rice has been reported (Meharg and  
169 Rahman, 2003). Arsenic concentrations in rice grain from different countries are shown in Table  
170 1, which provide useful information to have an idea about the range of arsenic concentration in  
171 rice worldwide, and to predict the extent of possible dietary intake of arsenic from this food  
172 source.

173 Recently, high arsenic content in S and SE Asian rice is an important concern for the  
174 respective countries as well as for the countries which import rice from this region. Rice grain  
175 collected from arsenic-contaminated western part of Bangladesh had arsenic levels of 0.03-1.84  
176  $\mu\text{g g}^{-1}$  dry weight (d. wt.) (Meharg and Rahman, 2003). Williams et al. (2006) reported that  
177 arsenic level ranged between 0.04 and 0.92  $\mu\text{g g}^{-1}$  d. wt. (mean 0.08-0.36  $\mu\text{g g}^{-1}$  d. wt.) in *aman*  
178 (dry season) rice and between 0.04 and 0.91  $\mu\text{g g}^{-1}$  d. wt. (mean 0.14-0.51  $\mu\text{g g}^{-1}$  d. wt.) in *boro*  
179 (monsoon season) rice collected from southern part of the country (Table 1). In the same study,  
180 arsenic concentrations in *aman* and *boro* rice collected from markets across the country were  
181 found to be 0.18-0.31 and 0.21-0.27  $\mu\text{g g}^{-1}$  d. wt., respectively. These findings were in consistent  
182 with their previous study. Islam et al. (2004) found 0.05-2.05  $\mu\text{g g}^{-1}$  d. wt. of arsenic in *boro* rice  
183 collected from three districts of southern Bangladesh (Gopalganj, Rajbari, and Faridpur).

184 Rahman et al. (2006) also reported high level of arsenic in raw rice (0.57-0.69  $\mu\text{g g}^{-1}$  d. wt.)  
185 collected from Satkhira district, a highly arsenic-contaminated area in Bangladesh. All these  
186 studies reveal the subsistence of high arsenic in Bangladeshi raw rice.

187 Total arsenic concentrations in Indian rice, particularly from West Bengal, have been  
188 reported in a number of articles (Table 1). Williams et al. (2005) reported 0.05  $\mu\text{g g}^{-1}$  d. wt.  
189 arsenic (0.03-0.08  $\mu\text{g g}^{-1}$  d. wt.) in white basmati rice collected from Indian super markets. In a  
190 market basket survey, Meharg et al. (2009) found 0.07  $\mu\text{g g}^{-1}$  d. wt. arsenic (0.07-0.31  $\mu\text{g g}^{-1}$  d.  
191 wt.,  $n = 133$ ) in Indian white rice. Mondal and Polya (2008) investigated arsenic concentration in  
192 rice from some areas of Nadia district, West Bengal. They found that the mean concentration of  
193 arsenic in raw rice (the rice were either collected directly from farmers or purchased from local  
194 markets) ranged between 0.02 and 0.17  $\mu\text{g g}^{-1}$  d. wt. with a mean of 0.13  $\mu\text{g g}^{-1}$  d. wt. ( $n = 50$ ).  
195 This concentration was comparable to that in Bangladeshi rice (0.14  $\mu\text{g g}^{-1}$  d. wt.,  $n = 10$ )  
196 reported by Das et al. (2004), but was less than that reported by Williams et al. (2006) (0.08 to  
197 0.51  $\mu\text{g g}^{-1}$  d. wt.,  $n = 330$ ) and Ohno et al. (2007) (0.34  $\mu\text{g g}^{-1}$  d. wt.,  $n = 18$ ). Other studies also  
198 reported high level of arsenic in raw rice from West Bengal (0.11-0.44  $\mu\text{g g}^{-1}$  d. wt. by  
199 Roychowdhury et al. (2002) and 0.03-0.48  $\mu\text{g g}^{-1}$  d. wt. by Pal et al. (2009)).

200 Arsenic contamination in Taiwan has a long history, and a number of studies reveal high  
201 level of arsenic in Taiwanese rice. Schoof et al. (1998) reported 0.76  $\mu\text{g g}^{-1}$  d. wt. of arsenic in  
202 Taiwanese rice collected directly from farms. They also reported about 0.20  $\mu\text{g g}^{-1}$  d. wt. of  
203 arsenic (range 0.19-0.22  $\mu\text{g g}^{-1}$  d. wt.) in Taiwanese firm rice. A market basket survey,  
204 conducted by Lin et al. (2004) revealed <0.10-0.63  $\mu\text{g g}^{-1}$  d. wt. of arsenic in Taiwanese rice,  
205 which is comparable to that reported by Williams et al. (2005). The concentration of arsenic in

206 Vietnamese rice was found to be 0.03-0.47  $\mu\text{g g}^{-1}$  d. wt. (Phuong et al., 1999; Williams et al.,  
207 2005).

208 Thai rice has also been reported to contain high level of arsenic (Table 1). A recent  
209 market basket survey revealed that arsenic concentrations in Thai rice ranged between 0.01 and  
210 0.39  $\mu\text{g g}^{-1}$  d. wt. with a mean of 0.14  $\mu\text{g g}^{-1}$  d. wt. ( $n = 54$ ) (Meharg et al., 2009). Previously,  
211 Williams et al. (2005) reported  $0.11 \pm 0.01$   $\mu\text{g g}^{-1}$  d. wt. of arsenic in Thai rice. In another study of  
212 Williams et al. (2006) showed that the concentration of arsenic in Thai rice was 0.10  $\mu\text{g g}^{-1}$  d. wt.  
213 (range 0.06-0.14  $\mu\text{g g}^{-1}$  d. wt.). Compared to the previous reports of Williams et al. (2006; 2005),  
214 higher arsenic concentration in Thai rice was found in a recent study of Meharg et al. (2009)  
215 suggesting that arsenic levels in Thai rice have increased in recent years. Significant amount of  
216 arsenic was also found in rice from United States of America (USA). A market basket survey  
217 conducted by Schoof et al. (1999) reported that the total arsenic concentrations in USA rice was  
218 0.20-0.46  $\mu\text{g g}^{-1}$  d. wt., while Heitkemper et al. (2001) found 0.11-0.34  $\mu\text{g g}^{-1}$  d. wt. in rice of the  
219 country. A recent study of Meharg et al. (2009) reported 0.03-0.66  $\mu\text{g g}^{-1}$  d. wt. in USA rice,  
220 which is much higher than that reported by Williams et al. (2005) (0.11-0.40  $\mu\text{g g}^{-1}$  d. wt.) (Table  
221 1). All these studies reveal that arsenic concentration in Asian rice is higher than that of other  
222 countries. Thus, S and SE Asian rice would be a significant source of dietary arsenic for the  
223 population of this area, and also for the population of those countries that import rice from this  
224 region.

225

### 226 3.1.1. Variations in total arsenic concentration in raw rice

227 Arsenic concentrations in raw rice varied significantly with its origin, types and cultivars,  
228 and even with the growing seasons (Table 1 and 2). Geographical variations in total arsenic

229 concentration in rice have been found from market basket surveys in USA, European Union  
230 (EU), Japan, Philippines, Australia, China, Canada, and from S and SE Asian countries (Table 1).  
231 A recent study conducted by Meharg et al. (2009) showed the geographical variations in total  
232 and inorganic arsenic concentrations in rice. The EU rice had a mean arsenic level of  $0.18 \mu\text{g g}^{-1}$   
233 d. wt. ranging from  $0.13$  to  $0.22 \mu\text{g g}^{-1}$  d. wt. (Torres-Escribano et al., 2008). In another study,  
234 Williams et al. (2005) reported  $0.13$ - $0.20 \mu\text{g g}^{-1}$  d. wt. of total arsenic in EU rice. Arsenic  
235 concentration in rice from some districts of arsenic affected areas of West Bengal, India showed  
236 variations ranging between  $0.04$  and  $0.43 \mu\text{g g}^{-1}$  d. wt. Other studies also reported the variations  
237 of total arsenic concentration in rice for other geographical areas such as Australia ( $0.02$ - $0.03 \mu\text{g}$   
238  $\text{g}^{-1}$  d. wt. (Williams et al., 2006)), Canada ( $0.02$ - $0.11 \mu\text{g g}^{-1}$  d. wt. (Heitkemper et al., 2001;  
239 Williams et al., 2005)), China ( $0.02$ - $0.46 \mu\text{g g}^{-1}$  d. wt. (Meharg et al., 2009);  $0.07$ - $0.19 \mu\text{g g}^{-1}$  d.  
240 wt. (Williams et al., 2006);  $0.46$ - $1.18 \mu\text{g g}^{-1}$  d. wt. (Sun et al., 2008)), Egypt ( $0.01$ - $0.58 \mu\text{g g}^{-1}$  d.  
241 wt. (Meharg et al., 2009)), Europe ( $0.09$ - $0.56 \mu\text{g g}^{-1}$  d. wt. (Meharg et al., 2009)), Spain ( $0.05$ -  
242  $0.82 \mu\text{g g}^{-1}$  d. wt. (Meharg et al., 2009)), Japan ( $0.07$ - $0.42 \mu\text{g g}^{-1}$  d. wt. (Meharg et al., 2009)),  
243 and Philippines ( $0.00$ - $0.25 \mu\text{g g}^{-1}$  d. wt. (Williams et al., 2006)). These studies reveal that  
244 Australian, Philippines, and Canadian rice have the lowest total arsenic burden while  
245 Bangladeshi and Indian (West Bengal) rice have the highest burden. Taiwanese and Vietnamese  
246 rice also contain significant amount of arsenic. These variations were clearly correlated with the  
247 extent and type of pollution as well as with the rice cultivation methods. Soil chemistry, source  
248 of arsenic, arsenic concentrations in soil and geochemistry of the region also influence arsenic  
249 burden in rice.

250 Arsenic concentrations in rice also vary by region within a particular geographical area.  
251 The USA rice showed significant variations in total arsenic concentration by region (Booth,

252 2007). A market basket survey of arsenic in USA rice by Williams et al. (2007a) showed that  
253 rice from California contains, on average, about 40% less arsenic than that from the south central  
254 USA- Arkansas, Louisiana, Mississippi, Texas, and Missouri. This is supposed to be because the  
255 soils of south central USA contained higher arsenic from pesticides used to grow cotton (Booth,  
256 2008). Although arsenic concentrations in rice varied significantly for arsenic-contaminated and  
257 non-contaminated areas in Bangladesh and West Bengal, a uniform range of its concentration in  
258 rice was observed in contaminated areas of this region. Arsenic concentrations in raw rice were  
259 found to be significantly correlated ( $P < 0.001$ ) with its concentrations in irrigation water and  
260 soil (Pal et al., 2009). High arsenic concentrations in raw rice of arsenic endemic south Asian  
261 countries is the direct contribution of highly contaminated underground irrigation water and  
262 paddy soils rather than the other sources.

263 Meharg and Rahman (2003) also found variations in arsenic concentration in different  
264 rice varieties grown in Bangladesh Rice Research Institute's research station (between 0.043 and  
265  $0.206 \mu\text{g g}^{-1}$  d. wt.) and in those collected from different district of the country (between 0.058  
266 and  $1.835 \mu\text{g g}^{-1}$  d. wt.). Seasonal variations in arsenic concentrations in Bangladeshi rice have  
267 also been reported by Duxbury et al. (2003). Arsenic concentrations in *aman* and *boro* rice were  
268 found to be 0.11 ( $n = 72$ ) and 0.18 ( $n = 78$ )  $\mu\text{g g}^{-1}$  d. wt., respectively.

269

### 270 3.1.2. Distribution of arsenic in different fractions of raw rice

271 Significant variations in total arsenic concentrations in different fractions of raw rice (hull,  
272 endosperm, polished rice, whole rice, and bran) have been reported in literature. Rahman et al.  
273 (2007b) studied total arsenic concentrations in different fractions of parboiled and non-parboiled  
274 raw rice collected from arsenic-contaminated area (Satkhira district) of Bangladesh. Results

275 showed that arsenic concentrations in non-parboiled raw rice were significantly higher than those  
276 in parboiled rice. The highest arsenic concentrations were in husk (in the range of 0.7-1.6  $\mu\text{g g}^{-1}$   
277 d. wt.) followed by bran (0.6-1.2  $\mu\text{g g}^{-1}$  d. wt.), whole grain (0.5-0.8  $\mu\text{g g}^{-1}$  d. wt.), and polished  
278 rice (0.3-0.5  $\mu\text{g g}^{-1}$  d. wt.). Thus, the order of arsenic concentrations in rice fractions was husk >  
279 bran > whole rice > polish rice. Ren et al. (2007) also determined the total arsenic concentration  
280 in fractions of Chinese whole grain rice, and found that arsenic concentrations were highest in  
281 bran (in the range of 0.55-1.20  $\mu\text{g g}^{-1}$  d. wt.), followed by whole grain (0.14-0.80  $\mu\text{g g}^{-1}$  d. wt.)  
282 and polished rice (0.07-0.4  $\mu\text{g g}^{-1}$  d. wt.), showing the same trend reported by Rahman et al.  
283 (2007b). Sun et al. (2008) also determined total arsenic concentrations in different fractions  
284 (endosperm, whole grain, and bran) of freshly milled Chinese (two varieties) and Bangladeshi  
285 (four varieties) rice grains. Results showed that the mean ( $n = 6$ ) arsenic concentrations in  
286 endosperm, whole grain, and bran were  $0.56 \pm 0.08$ ,  $0.76 \pm 0.12$ , and  $3.3 \pm 0.6 \mu\text{g g}^{-1}$  d. wt.,  
287 respectively. The trend of total arsenic concentration in fractions of rice grain was endosperm <  
288 whole grain < bran, which is in consistent with the previous studies of Rahman et al. (2007b) and  
289 Ren et al. (2007).

290

### 291 **3.2. Arsenic speciation in raw rice**

292 Total arsenic concentrations in rice or in any other diets are not the only determinant of  
293 its toxicity. Arsenic toxicity mostly depends on its speciation, and inorganic arsenic species is  
294 more toxic than organoarsenicals (Meharg and Hartley Whitaker, 2002; Ng, 2005). More  
295 specifically, A(III) is more toxic than As(V), while dimethylarsinous acid (DMAA(III)) and  
296 monomethylarsonous acid (MMAA(III)) are more toxic than their parent compounds (Mass et al.,  
297 2001; Petrick et al., 2000). Rice is particularly susceptible to arsenic accumulation compared to

298 other cereals as it is generally grown under flooded (reduced) conditions where arsenic mobility  
299 is high (Zhu et al., 2008b). Baseline level of arsenic in rice is up to 10-fold higher than that in  
300 other cereal grains (Williams et al., 2007b). On average, around 50% of total arsenic in rice grain  
301 is inorganic arsenic, which can vary from 10 to 90%, and the remaining fractions are DMAA(V)  
302 with trace amounts of MMAA(V) in some samples (Zhu et al., 2008b). Therefore, arsenic  
303 speciation in rice is considered to be important for its possible impacts on human health.

304

### 305 **3.2.1. Inorganic arsenic species**

306 Arsenic speciation in raw rice from different geographical areas is shown in Table 1.  
307 With exception for USA rice, inorganic arsenic have been reported to be the main species in raw  
308 rice from other geographical areas around the world (Booth, 2008; Meharg et al., 2009; Potera,  
309 2007; Schoof et al., 1999; Signes-Pastor et al., 2008; Sun et al., 2008; Sun et al., 2009; Williams  
310 et al., 2006; Williams et al., 2005; Zhu et al., 2008a; Zhu et al., 2008b). Although As(III)  
311 predominates over As(V) in rice in most cases (Williams et al., 2005; Zavala et al., 2008), the  
312 ratio of arsenic species in rice showed significant inconsistency with origin, types and varieties  
313 (Meharg et al., 2009; Williams et al., 2005). Williams et al. (2005) reported that about 42 ( $n =$   
314 12), 64 ( $n = 7$ ), 80 ( $n = 11$ ), and 81% ( $n = 15$ ) of the recovered arsenic was found to be inorganic  
315 for USA, EU, Bangladeshi, and Indian rice, respectively. A number of studies revealed that  
316 about 44-86% of the total arsenic concentration in Bangladeshi rice is inorganic (Meharg et al.,  
317 2009; Sun et al., 2008; Williams et al., 2006; Williams et al., 2005). In a field study, Ohno et al.  
318 (2007) found up to 100% inorganic arsenic in Bangladeshi rice. Schoof et al. (1998) reported 61,  
319 58, and 67% of the total arsenic to be inorganic in Taiwanese rice, while about 91% was  
320 inorganic in Thai rice (Williams et al., 2005). Chinese rice concentration about 60-87% inorganic

321 arsenic (Meharg et al., 2009; Sun et al., 2008), while the per cent concentration of inorganic  
322 arsenic species in France and Italian rice were about 44-62% and 57-73% (Meharg et al., 2009;  
323 Williams et al., 2005). Spanish rice also contains higher percentage of inorganic arsenic (about  
324 41-48% of the total arsenic) (Laparra et al., 2005; Williams et al., 2005), but was less than that in  
325 France and Italian rice. The fraction of inorganic arsenic in USA rice was about 40% of the total  
326 concentration, which is the lowest compared to that in rice from other countries. The results  
327 reveal that except for USA, the highly toxic inorganic arsenic species is the predominant species  
328 in rice. Other studies also showed that USA rice mostly contained less toxic methylated species  
329 where as EU and Asian rice contained more toxic inorganic arsenic (Zavala and Duxbury, 2008;  
330 Zavala et al., 2008).

331

### 332 **3.2.2. Organoarsenic species**

333 Methylated species of arsenic are the only organoarsenic species that were found in rice.  
334 Williams et al. (2005) conducted a market basket survey on arsenic speciation in USA rice and  
335 found methylated arsenicals (almost entirely as DMAA(V)) to be the major species (between 36-  
336 65% with a mean of 54% of the total arsenic). Previously, Heitkemper et al. (2001) also reported  
337 much higher percentage of methylated arsenicals (DMAA(V); between 70-80% with a mean of  
338 64% of the total arsenic) in USA rice. In contrast, methylated arsenicals were found to be the  
339 minor species in rice from Bangladesh (12-43%) (Sun et al., 2008; Williams et al., 2005),  
340 Canada (9-50%) (Heitkemper et al., 2001; Williams et al., 2005), China (10-15%) (Sun et al.,  
341 2008), EU (30%) (Williams et al., 2005), India (12%) (Williams et al., 2005), Italy (26-40%)  
342 (Williams et al., 2005), Spain (29%) (Williams et al., 2005), Thailand (27%) (Williams et al.,  
343 2005), and Taiwan (14-25%) (Schoof et al., 1998). The variations in organoarsenic concentration

344 in rice from different geographical areas have been suggested to be related to its sources and  
345 uptake efficiency of rice plant. In Asian arsenic endemic countries, inorganic arsenic-rich  
346 underground irrigation water is the main source of arsenic for rice plant. On the other hand,  
347 arsenical pesticides are the main source of arsenic for USA rice. In addition, microbial  
348 methylation of inorganic arsenic to organoarsenicals in the rice field (in water and rhizosphere  
349 soil) would also contribute to the organoarsenic content in raw rice.

350

### 351 **3.3. Variations in arsenic speciation in raw rice**

352 In addition to the geographical variations, arsenic speciation in raw rice also varied with  
353 the varieties, types, growing seasons and fractions of rice grain. These variations might be  
354 influenced by environmental factors as well as by internal factors such as morphological and  
355 physiological functions of the rice plants. But there are no clear evidences and specific  
356 information for which the speciation variations in rice grains of different rice varieties occurred.

357

#### 358 **3.3.1. Speciation variations in different varieties and types of rice**

359 Large variations in arsenic speciation in different Bangladeshi rice varieties have been  
360 reported by Williams et al. (2005). Organic and inorganic fractions of arsenic in chinigura, a  
361 local aromatic rice variety of Bangladesh, were about 49% and 48% of the total arsenic,  
362 respectively. However, inorganic species predominate in all other rice varieties with a range of  
363 42-86% of the total arsenic. Miniket had the highest content of inorganic arsenic (86% of the  
364 total arsenic) compared to other rice varieties. Arsenic speciation also varies with rice types of  
365 the same varieties. The DMAA(V) concentrations in USA white long rice grain were found to be  
366 between 0.05 and 0.26  $\mu\text{g g}^{-1}$  d. wt. (31-65% of the total arsenic), while its concentrations in

367 brown long rice were between 0.4 and 0.15  $\mu\text{g g}^{-1}$  d. wt. (32-45% of the total arsenic)  
368 (Heitkemper et al., 2001; Williams et al., 2005). In contrast, inorganic arsenic concentrations in  
369 white basmati rice from India ranged between 0.02 and 0.04  $\mu\text{g g}^{-1}$  d. wt. (36-67% of the total  
370 arsenic), while its concentrations in brown basmati and red long rice were about 0.04 and 0.05  
371  $\mu\text{g g}^{-1}$  d. wt. representing 61 and 65% of the total arsenic, respectively (Williams et al., 2005).  
372 Inorganic arsenic concentrations in white rice from Taiwan and Jasmine rice from Thailand were  
373 about 0.11-0.51 and 0.11  $\mu\text{g g}^{-1}$  d. wt. comprising 58-67% and 74% of the total arsenic content,  
374 respectively (Williams et al., 2005).

375

### 376 3.3.2. Speciation variations in rice of different growing seasons

377 Arsenic speciation in rice of different growing season has been reported from Bangladesh  
378 by Williams et al. (2006). They studied arsenic speciation in Bangladeshi rice grown in *amon*  
379 and *boro* seasons. Results showed that there were no statistical differences between *amon* and  
380 *boro* rice in terms of percentage inorganic arsenic content, although the relative amount of  
381 inorganic arsenic in *boro* rice (around 81-83% of the total arsenic) was higher than that in *amon*  
382 rice (around 60-71% of the total arsenic). These variations were possibly more related to the rice  
383 cultivars (varieties) than the growing seasons as significant differences in inorganic arsenic  
384 concentrations in different Bangladeshi rice varieties have been reported by other researchers  
385 (Williams et al., 2005).

386

### 387 3.3.3. Speciation variations in different fractions of raw rice

388 Arsenic speciation also varies with fractions of rice grain. Sun et al. (2008) analyzed the  
389 concentrations of arsenic species in different fractions of two Chinese and four Bangladeshi rice

390 varieties. They found that the concentrations of the organoarsenic species (DMAA + MMAA)  
391 were fairly uniform throughout the grain ( $0.18 \pm 0.05$ ,  $0.20 \pm 0.06$ , and  $0.18 \pm 0.03 \mu\text{g g}^{-1}$  d. wt.  
392 for polished grain, whole grain, and bran, respectively). The mean concentrations of inorganic  
393 arsenic species in different fractions of rice grain also varied greatly ( $0.21 \pm 0.03$ ,  $0.40 \pm 0.08$ ,  
394 and  $1.9 \pm 0.3 \mu\text{g g}^{-1}$  d. wt. for polished grain, whole grain, and bran, respectively). Percentage  
395 inorganic arsenic content ranged from 24 to 60%, 38 to 64%, and 51 to 67% in polished grain,  
396 whole grain, and bran, respectively. The results reveal greater variations in inorganic arsenic  
397 concentrations compared to that of organoarsenic species, and the trend of percentage inorganic  
398 arsenic content was polished grain < whole grain < bran. Meharg et al. (2008b) reported higher  
399 percentage of inorganic arsenic in brown rice (whole grain) compared to that in polished rice  
400 (white grain). Meharg et al. (2008b) also found that percentage inorganic arsenic decreased with  
401 the increase of total grain arsenic. Market-basket study in USA by Zavala et al. (2008) also  
402 reported that the DMAA concentration in rice increased with the increase of total arsenic  
403 concentration. But they did not consider the changes in grain arsenic speciation whether the rice  
404 was polished or not. It is not clear why the concentration of organoarsenic species increased with  
405 the increase of total arsenic concentration in rice grain. Whatever the reasons were, percentage  
406 increase of organoarsenic species in rice grain is considered to be better for humans since these  
407 species are less toxic.

408

#### 409 **4. Arsenic concentrations and speciation in cooked rice**

410 The residents of arsenic contaminated areas of Bangladesh and West Bengal (India)  
411 depend mostly on rice for their daily caloric intake, and high arsenic concentration in rice  
412 indicates that rice is the major dietary source of arsenic for the population of this area (Mondal

413 and Polya, 2008; Rahman et al., 2011). In South Asian countries, rice is usually cooked with a  
414 substantial amount of water. A number of studies reveal the influence of cooking methods on the  
415 retention of total and organic arsenic in cooked rice (Bae et al., 2002; Pal et al., 2009; Raab et al.,  
416 2009; Rahman et al., 2006; Sengupta et al., 2006; Signes et al., 2008b), which is summarized in  
417 Table 2. In arsenic-contaminated areas of Bangladesh, approximately 10-35% higher arsenic was  
418 found in cooked rice compared to that in raw rice (Misbahuddin, 2003). The additional arsenic is  
419 supposed to come from arsenic-contaminated cooking water. The increase of total arsenic  
420 concentration in cooked rice was resulted either from chelation by rice grains or due to  
421 evaporation during the cooking process (Rahman et al., 2011).

422 The effect of arsenic concentration in cooking water on the retention of arsenic in cooked  
423 rice is of great relevance to the South Asian countries where arsenic concentration in  
424 groundwater used for cooking has been reported to be much higher than the maximum allowable  
425 limit by World Health Organization (WHO) ( $10 \mu\text{g l}^{-1}$ ). The total arsenic concentration in cooked  
426 rice is claimed to be less than that in raw rice if the cooking water contain low level of arsenic  
427 (Bae et al., 2002). Pal et al. (2009) also reported that the concentration of total arsenic in rice  
428 cooked with water containing low level of arsenic ( $<0.003 \mu\text{g l}^{-1}$ ) was lower ( $0.07\text{-}0.02 \mu\text{g g}^{-1}$  d.  
429 wt.) than that in raw rice ( $0.25\text{-}0.08 \mu\text{g g}^{-1}$  d. wt.) (Table 2). Not only the concentrations of  
430 arsenic in cooking water but also the cooking methods (the ways the rice is cooked for  
431 consumption) have significant influence on arsenic retention in cooked rice (Rahman et al.,  
432 2006; Sengupta et al., 2006). Most of the populations of South Asian countries consume  
433 parboiled rice (boiling and drying raw rice before dehusking/milling). But the populations of E  
434 and SE Asian countries and Japan solely use non-parboiled rice for cooking. Moreover, the rice  
435 cooking method also differs even within the locality of a county. In some countries, people cook

436 rice with excess water and discard the gruel (concentrated cooking water) after cooking. This  
437 cooking procedure is popular in South Asian countries. On the other hand, cooking rice with  
438 limited water (therefore, no gruel remain after cooking) is a popular method worldwide. It has  
439 been reported that these different rice cooking methods affect the retention and the subsequent  
440 intake of arsenic from rice (Rahman et al., 2006; Sengupta et al., 2006; Signes et al., 2008b).

441 Arsenic concentration in non-parboiled rice cooked with limited water was  $0.75 \pm 0.04$ -  
442  $1.09 \pm 0.06 \mu\text{g g}^{-1}$  d. wt. ( $n = 3$ ), which was about 13-37% higher than that in raw rice, and 27-  
443 60% higher than that in rice cooked with excess water (Rahman et al., 2006). In the same study,  
444 Rahman et al. (2006) also found that total arsenic concentration in parboiled rice cooked with  
445 limited water was about 45% higher than that in rice cooked with excess water. On the other  
446 hand, arsenic concentration in parboiled rice cooked with excess water was about 6.59% less  
447 than that in raw rice, while its concentration in gruel was about 57.18% higher than that in raw  
448 rice. These results elucidate that arsenic concentration in cooked rice is influenced by cooking  
449 method, arsenic concentration in raw rice and cooking water. Cooking rice with excess water  
450 results in the decrease of arsenic concentration in cooked rice when gruel is discarded, while its  
451 concentration increased significantly when rice is cooked with limited water and the gruel is not  
452 discarded. Raab et al. (2009) also found that cooking rice with high volume (excess) water  
453 (water : rice = 6 : 1) reduced total and inorganic arsenic burden in cooked rice by 35% and 45%,  
454 while cooking with low volume (limited) water did not remove arsenic substantially. Sengupta et  
455 al. (2006) reported that cooking rice with low-arsenic water by the traditional cooking method in  
456 India (wash until clear, rice : water = 1: 6, and discard excess water (gruel) after cooking)  
457 removed up to 57% of the arsenic burden from cooked rice. This removal of arsenic was  
458 irrespective to the concentration of arsenic in raw rice and cooking water, which might be

459 because the water soluble arsenic was released from soft cooked rice into the cooking water  
460 (gruel) during cooking process, and was discarded with gruel after cooking. But arsenic  
461 concentration in cooked rice was found to be increased by 35-40% when arsenic concentration in  
462 cooking water was  $50 \mu\text{g l}^{-1}$  (standard for many developing countries) (Sengupta et al., 2006).  
463 Rahman et al. (2006) also found the increase of arsenic concentration in cooked rice when the  
464 cooking water was arsenic contaminated. This was because arsenic is absorbed by rice (through  
465 osmotic process) from cooking water during the cooking process.

466 Arsenic speciation in cooked rice depends on its speciation in raw rice and in cooking  
467 water since arsenic speciation changes have not been found to occur during cooking process.  
468 Laparra et al. (2005) investigated the effect of inorganic arsenic in cooking water on total and  
469 inorganic arsenic retention in cooked rice of different types collected from Spanish super  
470 markets. They observed that there were no important modifications in the total and inorganic  
471 arsenic concentrations in cooked rice when cooked with uncontaminated water. In contrast,  
472 addition of As(V) in cooking water produced significant increase in inorganic arsenic content in  
473 cooked rice (Table 2). The increase of total and inorganic arsenic concentrations in cooked rice  
474 was depended on As(V) concentration in cooking water as well as on rice types. For example,  
475 arsenic concentrations in raw basmati and round white rice were  $0.05 \pm 0.001$  and  $0.13 \pm 0.008 \mu\text{g}$   
476  $\text{g}^{-1}$  d. wt., respectively. When these rice were cooked with water containing  $0.6 \mu\text{g l}^{-1}$  of As(V),  
477 total arsenic concentrations in cooked basmati and round white rice were found to be  $2.36 \pm 0.080$   
478 and  $2.29 \pm 0.050 \mu\text{g g}^{-1}$  d. wt. of which inorganic arsenic were 96 and 81% of the total arsenic,  
479 respectively. In addition, total and inorganic arsenic concentrations were low ( $1.96 \pm 0.01$  and  
480  $1.66 \pm 0.002 \mu\text{g g}^{-1}$  d. wt., respectively) when the rice was cooked with water containing  $0.4 \mu\text{g l}^{-1}$   
481 As(V) (), and there concentrations were increased ( $4.21 \pm 0.09$  and  $3.73 \pm 0.04 \mu\text{g g}^{-1}$  d. wt.,

482 respectively) when the rice was cooked with water containing  $1.0 \mu\text{g l}^{-1}$  As(V) (). These results  
483 imply that, in addition to the concentration and speciation in raw rice, arsenic concentration and  
484 speciation in cooked rice are also varied for rice type as well as for the speciation and  
485 concentration of arsenic in cooking water.

486

#### 487 **4.1. Contribution of rice to dietary intake of arsenic**

#### 488 **4.2. Dietary intake of arsenic from rice**

489 It has been proved that arsenic pollution poses a serious threat to human health. To  
490 minimize the health risks of arsenic toxicity, the main concern is to identify the sources of  
491 exposure to avoid the intake of this toxic element. Although there are many possible routes of  
492 arsenic exposure (([Rahman et al., 2008a](#)), the majors are inhalation ([Pal et al., 2007](#)), ingestion,  
493 and dermal contact ([Mondal and Polya, 2008](#)), of which ingestion is the largest contributor.  
494 Among the many possible pathways of arsenic ingestion ([Mondal and Polya, 2008](#)),  
495 epidemiological data, that has been published during last couple of years, revealed that  
496 contaminated drinking groundwater is the major source of dietary arsenic in many countries,  
497 especially in S and SE Asia. A number of recent studies showed that, in addition to the  
498 contaminated drinking water, foods such as rice, vegetables and fishes would also be potential  
499 sources of dietary arsenic exposure ([Bhattacharya et al., 2010](#); [Lin et al., 2004](#); [Ohno et al., 2007](#);  
500 [Roychowdhury et al., 2003](#); [Schoof et al., 1999](#); [Signes-Pastor et al., 2009](#); [Signes-Pastor et al.,](#)  
501 [2008](#)). High levels of arsenic ( $0.03\text{-}1.83 \mu\text{g g}^{-1}$  d. wt.) have been found in rice grain from some S  
502 and SE Asian countries (discussed in the previous sections), which was the contribution of  
503 extensive use of arsenic-contaminated groundwater for rice cultivation ([Carey et al., 2010](#); [Khan](#)  
504 [et al., 2009](#); [Khan et al., 2010b](#); [Rahman et al., 2008a](#); [Rahman et al., 2009](#); [Singh et al., 2010](#)).

505 Therefore, rice is supposed to be another major source of arsenic exposure followed by drinking  
506 groundwater (Mondal and Polya, 2008; Stone, 2008). Williams et al. (2006) modeled the  
507 possible intake of inorganic arsenic from rice with the equivalent intake from drinking water for  
508 a typical Bangladeshi diet. It was predicted that the daily consumption of rice with a total arsenic  
509 level of  $0.08 \mu\text{g g}^{-1}$  d. wt. would be equivalent to a drinking water arsenic level of  $10 \mu\text{g l}^{-1}$ .

510 Arsenic in rice is a threat to human health not only for its high concentration but also for  
511 its speciation. Although previous studies have revealed drinking water as the largest source of  
512 inorganic arsenic for humans, rice is also considered to be another significant source of this  
513 arsenic species. A number of arsenic speciation studies showed that about 42 to 91% of the total  
514 arsenic in S and SE Asian rice is toxic inorganic species (Heitkemper et al., 2001; Meharg et al.,  
515 2008b; Meharg et al., 2009; Schoof et al., 1998; Schoof et al., 1999; Williams et al., 2005; Zhu et  
516 al., 2008b), while the major species in USA rice is organic DMAA (Williams et al., 2005). A  
517 more recent study showed that rice products such as breakfast cereals, rice crackers, rice milk,  
518 baby rice and other rice condiments also contain high percentage of inorganic arsenic (75-90%)  
519 (Meharg et al., 2008a; Meharg et al., 2008c; Sun et al., 2009). Some other studies also revealed  
520 that the total (Bae et al., 2002; Laparra et al., 2005; Pal et al., 2009; Rahman et al., 2006;  
521 Rahman et al., 2011; Sengupta et al., 2006) and inorganic arsenic (Laparra et al., 2005; Smith et  
522 al., 2006) concentrations in cooked rice increased due to cooking with arsenic-rich water  
523 (Laparra et al., 2005; Raab et al., 2009). Cooking rice with water containing  $0.05 \text{ mg l}^{-1}$  of As(V)  
524 produced 5-17-fold higher inorganic arsenic content in cooked rice than that in raw rice (Laparra  
525 et al., 2005).

526 Second to fish and seaweed, rice is the major dietary source of total arsenic (around 34%)  
527 for the people of North America and EU (Meharg and Rahman, 2003; Schoof et al., 1999). The

528 contribution of rice to the dietary intake of arsenic in Bangladesh, where rice is the subsistence  
529 food, was modeled by Meharg and Rahman (2003). They showed that with drinking water intake  
530 of  $0.1 \text{ mg l}^{-1}$ , dietary intake of arsenic from rice containing  $0.1$  and  $0.2 \mu\text{g g}^{-1}$  d. wt. of total  
531 arsenic would be around 17.3 and 29.6%, respectively. If the grain arsenic concentration was  $2$   
532  $\mu\text{g g}^{-1}$  d. wt. (the level found in rice from some areas of the country), the contributions would be  
533 98, 80, and 30% at drinking water arsenic concentrations of  $0.01$ ,  $0.1$  and  $1 \text{ mg l}^{-1}$ , respectively.  
534 Rahman et al. (2008a) reported that with average rice consumption of  $400$  to  $650 \text{ g d}^{-1}$  (the  
535 typical range of rice consumption by adults in Bangladesh (Duxbury et al., 2003)), arsenic intake  
536 would be  $0.16$  to  $0.27 \text{ mg d}^{-1}$  if the concentration of arsenic in rice was  $0.4 \mu\text{g g}^{-1}$  d. wt. In  
537 contrast, dietary intake of arsenic from drinking water would be  $0.2$  to  $0.3 \text{ mg d}^{-1}$  for adult  
538 consuming  $4$  to  $6 \text{ L}$  water (the typical range of water consumption by adult of the country. The  
539 rate would be much higher for the rural people since they involved mostly in agrarian manual  
540 labor (Farmer and Johnson, 1990)) containing  $0.05 \text{ mg l}^{-1}$  arsenic, respectively. Thus, it is  
541 evident that rice would be a major source for dietary arsenic intake for the population of S and  
542 SE Asian countries where rice is the subsistence diet.

543

#### 544 **4.3. Bioavailability of arsenic from rice**

545 The toxic inorganic arsenic species is readily assimilated into blood stream (Meharg and  
546 Rahman, 2003). Therefore, bioavailability and bioaccumulation of arsenic species from cooked  
547 rice are important for its intake in humans from this food source. Laparra et al. (2005)  
548 investigated the bioaccessibility and bioavailability of inorganic arsenic in cooked rice to assess  
549 the potential toxicological risk of this species. Results showed that the total arsenic  
550 concentrations in bioaccessible fractions were  $1.06$ - $3.39 \mu\text{g g}^{-1}$  d. wt. when its concentrations in

551 cooked rice were 0.88-4.21  $\mu\text{g g}^{-1}$  d. wt. The results reveal high bioavailability of inorganic  
552 arsenic from cooked rice (> 90%). In addition, the concentrations of inorganic arsenic in  
553 bioaccessible fractions of cooked rice varied from 0.8 to 3.1  $\mu\text{g g}^{-1}$  d. wt. This indicates that a  
554 significant fraction of the inorganic arsenic can be available for intestinal absorption. To further  
555 estimate the bioavailability (retention, transport, and uptake) inorganic arsenic, however, the  
556 bioaccessible fractions were added to Caco-2 cells. Results showed that arsenic retention,  
557 transport, and uptake by the cells from cooked rice were 0.6-6.4, 3.3-11.4, and 3.9-17.8%,  
558 respectively. Considering the lowest (3.9%) and the highest (17.8%) total arsenic uptake values  
559 of the study, Laparra et al. (2005) estimated that the daily consumption of 5.7 and 1.2 kg cooked  
560 rice containing  $4.21\pm 0.09$  and  $2.29\pm 0.05$   $\mu\text{g g}^{-1}$  d. wt., respectively, would be required to reach  
561 the tolerable daily intake (TDI) of inorganic arsenic recommended by the WHO ( $2.1 \mu\text{g d}^{-1} \text{kg}$   
562  $\text{body wt.}^{-1}$  (Williams et al., 2006)). In arsenic endemic SE Asia, an average adult male consumes  
563 1.5 kg cooked rice a day indicating that the people of this region might reach the TDI of arsenic  
564 only from rice diet.

565 Williams et al. (2006) also determined the total and inorganic arsenic concentrations in  
566 Bangladeshi rice to estimate the contribution of inorganic arsenic to the maximum tolerable daily  
567 intake (MTDI) for a Bangladeshi adult of 60 kg weight (Table 3). Results showed that the  
568 contribution of inorganic arsenic in rice to MTDI of arsenic for a Bangladeshi adult would be 55-  
569 79% depending on inorganic arsenic concentration and rice type. When the concentrations of  
570 inorganic arsenic in rice were high, the MTDI exceeded the 100% level (Ohno et al., 2007;  
571 Schoof et al., 1998; Sun et al., 2008). The contribution of inorganic arsenic to the MTDI for a 60  
572 kg person is about 4-36% since the concentrations of this arsenic species in American, European  
573 and Canadian rice are low (Table 3).

574

## 575 **Conclusion**

576 Rice comprises the major part of daily diet of the population of S and SE Asian countries.  
577 Irrigation of arsenic-contaminated groundwater for rice cultivation has resulted high deposition  
578 of this toxic element in the top soil posing a serious threat to the sustainable rice farming in this  
579 region. Compared to other cereal crops, rice contains higher amount of arsenic most of which is  
580 toxic inorganic species. A number of studies reveal that, in addition to the drinking water, rice is  
581 another major and potential source of dietary arsenic intake. Inorganic arsenic is classified as a  
582 human carcinogen by the international agency for research on cancer because of its high toxicity  
583 (Laparra et al., 2005). Exposure to inorganic arsenic may cause various internal cancers- liver,  
584 bladder, kidney, and lungs as well as other health problems, including skin cancer and diabetes  
585 (Booth, 2009). High concentration of inorganic arsenic in S and SE Asian rice is, therefore, a  
586 health emergency for the population of this region.

587 In a recent study, Meharg et al. (2009) modeled cancer risks of arsenic from rice in  
588 Bangladesh, China, India, Italy, and USA by multiplying projected daily intake of inorganic  
589 arsenic in rice and a risk factor proposed by the United States Environmental Protection Agency  
590 ( $3.67 \text{ mg kg}^{-1} \text{ d}^{-1}$  (Tsuji et al., 2007)). For a fixed consumption of  $100 \text{ g rice d}^{-1}$  by a man  
591 weighting 60 kg, the median excess internal cancer rate was highest in Bangladesh (22 per  
592 10,000 people) followed by China (15 per 10,000), India (7 per 10,000), and Italy and USA (~1  
593 per 10,000). It was speculated from this estimation that the median cancer risk from arsenic-rich  
594 rice was about 200, 150, and 70 times higher than the WHO standard (1 per 100,000 people) for  
595 Bangladesh, China, and India, respectively. Using a probabilistic risk assessment, Mondal and  
596 Polya (2008) projected that the contributions of drinking water and cooked rice to median total

597 risk for the population of Chakdaha block, Nadia district, India would 48 and 8%, respectively.  
598 Thus, arsenic-rich rice would be a potential health risk for the population of arsenic-affected S  
599 and SE Asia, particularly in Bangladesh and West Bengal.

600 Another important concern relevant human health is the increase of total and inorganic  
601 arsenic concentrations in cooked rice. The increased arsenic in cooked rice comes mainly from  
602 arsenic-contaminated cooking water. Therefore, it is important to investigate and justify the  
603 bioavailability and bioaccumulation of arsenic species from rice. Unfortunately, information on  
604 this issue is very limited. Researchers should focus their efforts in this issue to estimate the real  
605 health hazard of arsenic from rice diet.

606

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612

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858 **Table 1:** The concentration ( $\mu\text{g g}^{-1}$  d. wt.) of total, inorganic and organoarsenic fractions in raw rice from different countries

Country	Total As mean (range)	Inorganic As mean (range)	Organic As mean (range)	% of inorganic As mean (range)	Survey range	References
Australia	0.03 (0.02-0.04)	-	-	-	-	(Williams et al., 2006)
Bangladesh	0.13 (0.02-0.33)	0.08 (0.01-0.21)	-	61	market basket	(Meharg et al., 2009)
	0.50 (0.03-1.84)	-	-	-	field	(Meharg and Rahman, 2003)
	0.34 (0.15-0.59)	-	-	-	field	(Ohno et al., 2007)
	0.39 (0.26-0.58)	0.39 (0.26-0.58)	0.005 (0.001-0.010)	100	field	(Ohno et al., 2007)
	0.08-0.36 (0.04-0.92)- <i>aman</i>	-	-	-	field	(Williams et al., 2006)
	0.14-0.51 (0.04-0.91)- <i>boro</i>	-	-	-	-	-
	0.23 (0.18-0.31)- <i>aman</i>	0.16 (0.11-0.22)	-	65 (60-71)	market basket	(Williams et al., 2006)
	0.24 (0.21-0.27)- <i>boro</i>	0.20 (0.17-0.22)	-	82 (81-83)	market basket	(Williams et al., 2006)
	0.13 (0.03-0.30)	0.08 (0.01-0.21)	0.02 (<LOD*-0.05)	60 (44-86)	market basket	(Williams et al., 2005)
	0.69 (0.41-0.98)	0.31 (0.23-0.39)	0.23 (0.05-0.43)	44 (45-59)	-	(Sun et al., 2008)
0.57-0.95 (0.05-2.05)	-	-	-	field	(Islam et al., 2004)	
	0.57-0.69	-	-	-	field	(Rahman et al., 2006)
Canada	0.11	0.08	0.01	76	market basket	(Heitkemper et al., 2001)
	0.02	< LOD	0.01	71	-	(Williams et al., 2005)
China	0.14 (0.02-0.46)	0.16 (0.07-0.38)	-	87	market basket	(Meharg et al., 2009)
	0.12 (0.07-0.19)	-	-	-	-	(Williams et al., 2006)
	0.82 (0.46-1.18)	0.50 (0.25-0.76)	0.10 (0.07-0.12)	60 (55-64)	-	(Sun et al., 2008)
	0.49 (0.31-0.70)	-	-	-	Contam. field	(Xie and Huang, 1998)
	0.93	-	-	-	Contam. field	(Liu et al., 2005)
Egypt	0.05 (0.01-0.58)	-	-	-	-	(Meharg et al., 2009)
Europe	0.15 (0.13-0.20)	0.08 (0.06-0.10)	0.04 (0.04-0.06)	52 (44-62)	-	(Williams et al., 2005)
France	0.28 (0.09-0.56)	-	-	-	market basket	(Meharg et al., 2009)
India	0.07 (0.07-0.31)	0.03 (0.02-0.07)	-	43	market basket	(Meharg et al., 2009)
	0.05 (0.03-0.08)	0.04 (0.02-0.05)	< LOD*-0.01	56 (36-67)	-	(Williams et al., 2005)

Italy	0.15 (0.07-0.33)	0.11 (0.07-0.16)	-	73	market basket	(Meharg et al., 2009)
	0.21 (0.19-0.22)	0.12 (0.10-0.14)	0.07 (0.05-0.09)	57 (53-65)	-	(Williams et al., 2005)
Japan	0.19 (0.07-0.42)	-	-	-	market basket	(Meharg et al., 2009)
Philippines	0.07 (0.00-0.25)	-	-	-	-	(Williams et al., 2006)
Spain	0.20 (0.05-0.82)	-	-	-	market basket	(Meharg et al., 2009)
	0.34 (0.29-0.41)	0.14 (0.10-0.20)	-	41 (34-48)	market basket	(Laparra et al., 2005)
	0.17±0.01	0.08	0.05	48	-	(Williams et al., 2005)
Thailand	0.14 (0.01-0.39)	-	-	-	market basket	(Meharg et al., 2009)
	0.10 (0.06-0.14)	-	-	-	-	(Williams et al., 2006)
	0.11±0.01	0.08	0.03	74	-	(Williams et al., 2005)
Taiwan	0.76	0.51	0.11	67	-	(Schoof et al., 1998)
	0.05 (<0.10-0.14)	-	-	-	shed	(Lin et al., 2004)
	0.10 (<0.10-0.63)	-	-	-	market basket	(Lin et al., 2004)
	0.19 (0.06-0.17)	0.12	0.04	61	open	(Schoof et al., 1998)
	0.20 (0.19-0.22)	0.11	0.05	58	farm	
U.S.A.	0.25 (0.03-0.66)	0.10 (0.05-0.15)	-	40	market basket	(Meharg et al., 2009)
	0.30 (0.2-0.46)	-	-	-	market basket	(Schoof et al., 1999)
	0.28 (0.21-0.34)	0.10 (0.02-0.11)	0.18 (0.17-0.24)	35 (9-32)	-	(Heitkemper et al., 2001)
	0.26 (0.11-0.40)	0.08 (0.02-0.14)	0.14 (0.04-0.26)	35 (10-61)	market basket	(Williams et al., 2005)
Vietnam	0.21 (0.03-0.47)	-	-	-	open	(Phuong et al., 1999)
West Bengal (India)	0.14 (0.02-0.40)	-	-	-	household	(Pal et al., 2009)
	0.25 (0.14-0.48)- <i>boro</i>	-	-	-	household	(Pal et al., 2009)
	0.08 (0.03-0.16)- <i>aman</i>	-	-	-	(contam. area)	
	0.13 (0.02-0.17)	-	-	-	field, market	(Mondal and Polya, 2008)
	0.21 (0.11-0.44)	-	-	-	household	(Roychowdhury et al., 2002)
0.33 (0.18-0.43)	-	-	-	(contam. area)		

859 \* LOD = Level of detection

860 **Table 2:** Arsenic concentrations ( $\mu\text{g g}^{-1}$  d. wt.) in raw and cooked rice from different countries, and the contribution of arsenic concentration in  
 861 cooking water on total and inorganic arsenic content in cooked rice

Country	Rice type		As in cooking water ( $\mu\text{g ml}^{-1}$ )	Total As	Inorganic As (total)	Inorganic As (%)	References
Bangladesh	raw	mixed	-	0.26-0.58	0.26-0.58	100	(Ohno et al., 2007)
	cooked		0.05	0.40-2.37	0.39-2.42	97-102	(Rahman et al., 2006)
	raw	BIRRI dhan28	-	0.57±0.040	-	-	
	parboiled		0.13	0.40-0.89	-	-	
	cooked		0.13	0.39-0.75	-	-	
	raw	BIRRI hybrid dhan1	-	0.69±0.210	-	-	(Rahman et al., 2006)
	parboiled		0.13	0.58-1.08	-	-	
	cooked		0.13	0.44-1.09	-	-	
	raw	-	-	0.173	-	-	(Bae et al., 2002)
	cooked		0.223-0.372	0.28-0.38	-	-	
Spain	raw	red whole grain	-	0.53±0.003	-	-	(Laparra et al., 2005)
	cooked		0.4 (As <sup>V</sup> )	1.96±0.010	1.66±0.002	84	
	raw	basmati white	-	0.05±0.001	-	-	(Laparra et al., 2005)
	cooked		0.6 (As <sup>V</sup> )	2.36±0.080	2.28±0.110	96	
	raw	round white	-	0.13±0.008	-	-	(Laparra et al., 2005)
	cooked		0.6 (As <sup>V</sup> )	2.29±0.050	1.87±0.100	81	
	raw	large white	-	0.25±0.008	-	-	(Laparra et al., 2005)
	cooked		0.7 (As <sup>V</sup> )	3.05±0.030	3.13±0.170	109	
raw	round white	-	0.13±0.001	-	-	(Laparra et al., 2005)	
cooked		0.9 (As <sup>V</sup> )	3.66±0.770	3.34±0.080	91		

	raw	bomba white	-	0.09±0.002	-	-	(Laparra et al., 2005)
	cooked		1.0 (As <sup>V</sup> )	4.21±0.090	3.73±0.040	88	
	raw	round white	-	0.25±0.020	-	-	(Laparra et al., 2005)
	cooked		0.2 (As <sup>V</sup> )	0.88±0.030	0.81±0.007	92	
	raw	large Thai	-	0.17±0.004	-	-	(Laparra et al., 2005)
	cooked		0.4 (As <sup>V</sup> )	1.51±0.150	1.49±0.020	98	
West Bengal (India)	raw	mixed	-	0.09-0.17	-	-	(Mondal and Polya, 2008)
	cooked		0.001-0.044	0.07-0.34	-	-	
	raw	<i>boro</i>	-	0.25 (0.14-0.48)	-	-	(Pal et al., 2009)
	cooked		< 0.003	0.07 (0.03-0.14)	-	-	
	raw	<i>aman</i>	-	0.08 (0.03-0.17)	-	-	
	cooked		< 0.003	0.02 (0.008- 0.06)	-	-	
	raw	-	-	0.14 (0.02-0.39)	-	-	
	cooked		< 0.003	0.03 (0.006- 0.10)	-	-	

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868 **Table 3:** Total and inorganic arsenic concentrations ( $\mu\text{g g}^{-1}$  d. wt.) in rice grain, and the contribution of inorganic arsenic to the WHO's provisional  
869 maximum tolerable daily intake (MTDI) of arsenic for humans ( $2.1 \mu\text{g d}^{-1} \text{ kg body wt}^{-1}$ , (Williams et al., 2006)). The MTDI is based on total  
870 grain arsenic concentration, a body weight of 60 kg, a consumption rate of 0.5 kg rice  $\text{d}^{-1}$ , inorganic arsenic content (%), and bioavailability  
871 of inorganic arsenic in cooked rice (90% (Laparra et al., 2005)).

Country	Rice type/variety	Total As	Inorganic As	Inorganic As (%)	Contribution of inorganic As to MTDI (%)	
Bangladesh	BRR1 dhan10	0.31±0.02	0.22±0.02	71	79	(Williams et al., 2006)
	BRR1 dhan11	0.21±0.00	0.14±0.02	66	48	(Williams et al., 2006)
	Kalizira (local variety)	0.18±0.03	0.11±0.03	60	38	(Williams et al., 2006)
	BRR1 dhan28	0.25±0.00	0.21±0.02	83	74	(Williams et al., 2006)
	BRR1 dhan29	0.21±0.01	0.17±0.02	82	62	(Williams et al., 2006)
	Nayanmoni (local variety)	0.27±0.02	0.22±0.03	81	79	(Williams et al., 2006)
	Digha	0.21±0.04	0.15±0.04	72	55	(Williams et al., 2006)
	Mixed	0.39	0.39	100	139	(Ohno et al., 2007)
	Mixed	0.13	0.08	61	29	(Meharg et al., 2009)
	Mixed	0.13	0.08	60	29	(Williams et al., 2006)
	Mixed	0.69	0.31	44	111	(Sun et al., 2008)
Canada	-	0.11	0.08	76	26	(Heitkemper et al., 2001)
	-	0.02	0.01	71	4	(Williams et al., 2005)
China	Long grain	0.22±0.03	0.07±0.01	32	25	(Williams et al., 2006)
Europe	-	0.15	0.08	52	29	(Williams et al., 2005)
India	-	0.07	0.03	43	11	(Meharg et al., 2009)
	-	0.05	0.04	56	14	(Williams et al., 2005)
Italy	-	0.15	0.11	73	39	(Meharg et al., 2009)
	-	0.21	0.12	57	43	(Williams et al., 2005)

Spain	Red whole	1.96	1.66	84	85	(Laparra et al., 2005)
	Basmati white	2.36	2.28	96	97	(Laparra et al., 2005)
	Round white	2.29	1.87	81	82	(Laparra et al., 2005)
	Large white	3.05	3.13	109	103	(Laparra et al., 2005)
	Round white	3.66	3.34	91	91	(Laparra et al., 2005)
	Bomba white	4.21	3.73	88	89	(Laparra et al., 2005)
	Round white	0.88	0.81	92	92	(Laparra et al., 2005)
	Large Thai	1.51	1.49	98	99	(Laparra et al., 2005)
Thailand	-	0.11	0.08	74	29	(Williams et al., 2005)
Taiwan	-	0.76	0.51	67	182	(Schoof et al., 1998)
	-	0.19	0.12	61	43	(Schoof et al., 1998)
	-	0.20	0.11	58	39	(Schoof et al., 1998)
USA	-	0.25	0.10	40	36	(Meharg et al., 2009)
	-	0.28	0.10	35	36	(Heitkemper et al., 2001)
	-	0.26	0.08	35	29	(Williams et al., 2005)

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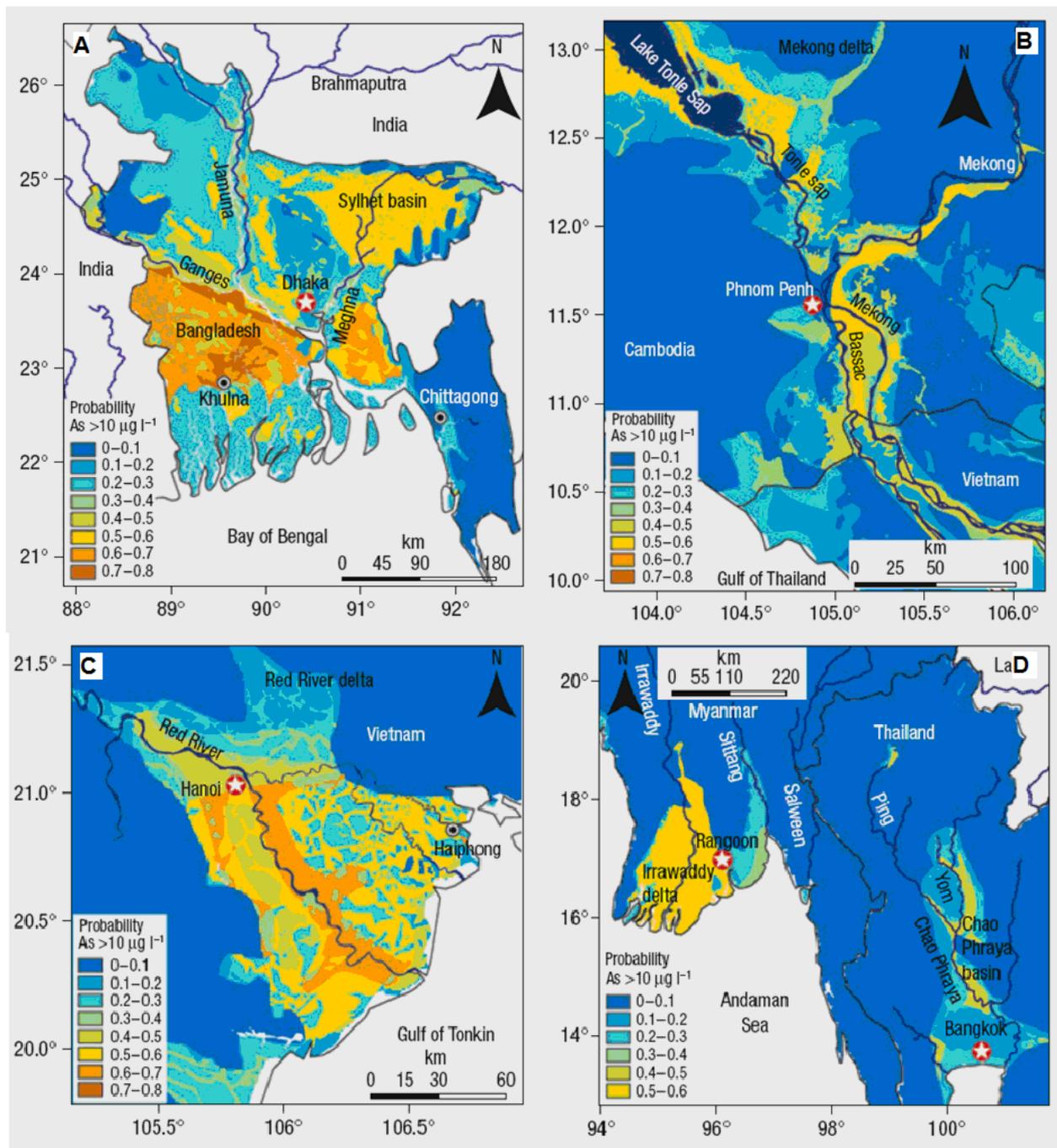
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879 **Fig. 1:** Arsenic concentrations in groundwater of South-East Asian regions under reducing  
 880 conditions. **A**, Ganges delta (Bangladesh); **B**, the Mekong delta (Cambodia and Vietnam);  
 881 **C**, Red River delta (Vietnam); **D**, Irrawaddy River delta (Myanmar) and Chao Phraya basin  
 882 (Thailand) (Winkel et al., 2008).