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ARSENIC CONTAMINATION IN THE FOOD CHAIN AND ITS POSSIBLE MITIGATION APPROACHES[*]

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Abstract

Irrigating crops with arsenic contaminated ground water is slowly creeping into rice and other edible crops. Vegetables, particularly Arum (*Colocassia antiquorum*), Kalmi Shak (*Ipomea aquatic*) and Amaranths (*Amaranthus gangeticus*) are hyper accumulators of the element. Boro season rice receives the most irrigation water. Boro rice has been found to accumulate as high as 2. 81 mg/kg arsenic in grains. The accumulation of arsenic in rice grain depends on the rice variety and is directly related to the arsenic in the irrigation water. The accumulation of As in rice plant is in the order root > leaf > grain. Plant arsenic content was found to vary considerably with plant types, nature of soil types, and the irrigation water arsenic content. The soil As varies both spatially and vertically. The spatial variation is controlled by the soil formation and the aquifer characters, while the vertical distribution is controlled by the clay contents. In Bangladesh, the average is well below 10 mg kg^{-1}. But in areas where groundwater contamination is reported and where irrigation is practiced, the values have been found to be much higher ranging up to 80 mg kg^{-1}. Disposal of sludge produced from the arsenic removal water filters can pose another environmental threat *vis à vis* arsenic, iron and aluminum A number of approaches have been tried to mitigate the uptake of As in plants and subsequent entry into the food chain.

Introduction

Natural arsenic (As) pollution of drinking water supplies has been reported from over 70 countries, posing a serious health hazard to an estimated 150 million people world-wide (Ravenscroft *et al.*, 2009). Around 110 million of those people live in ten countries in South and South-east Asia: Bangladesh, Cambodia, China, India, Laos, Myanmar, Nepal, Pakistan, Taiwan and Vietnam. Arsenic (As) contamination of groundwater was reported in Bangladesh during the early 1990s. Extensive contamination was confirmed in 1995. Groundwater in the majority of wells in 60 of the 64 districts, covering approximately 118,000 sq km (nearly 80% of the country), has concentrations of arsenic exceeding the World Health Organization's limit of 10 µg/L, and only 30% of groundwater contains arsenic at levels below 50 µg/L, the Bangladesh drinking-water standard. Concentrations of arsenic exceeding 1,000 µg/L in shallow tube wells were reported from 17 districts in Bangladesh. High levels of arsenic in groundwater occur in the districts of Chandpur,

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Comilla, Noakhali, Munshiganj, Brahmanbaria, Faridpur, Madaripur, Gopalganj, Shariatpur, and Satkhira. High levels of arsenic have also been found in isolated 'hot-spots' in the southwestern, northwestern, northeastern, and north-central regions of the country (Imamul Huq *et al.*, 2006 a). More than 35 million people in Bangladesh are exposed to arsenic contamination in drinking water exceeding the national standard of 50 μg/l, and an estimated 57 million people are at the risk of exposure to arsenic contamination exceeding the World Health Organization (WHO) guideline of 10 μg/l (BGS/DPHE, 2001). However, widespread use of ground water for irrigation suggests that ingestion of irrigated crops could be another major exposure route for arsenic. Besides, phytotoxicity due to increased arsenic in soil/water and its long term impact on agricultural yield is another major concern. The arsenic contamination is not only a health hazard for the people; it also affects the environment and creates social problems. Long-term ingestion of inorganic arsenic in humans is associated with skin lesions and cancers of the urinary bladder, lung, and skin (WHO, 2001). Developmental toxicity, neurotoxicity, cardiovascular diseases, abnormal glucose metabolism, and diabetes are other adverse effects reported to be associated with long-term ingestion of inorganic arsenic in humans, and there is also emerging evidence of negative impacts on fetal and infant development (European Food Safety Authority, 2009).

Efforts have been made toward ensuring safe drinking water through either mitigation techniques or by finding alternative sources. Although As-safe drinking water supply has now been ensured, the same ground water however, is being used for irrigation purposes, leaving a risk of soil accumulation of this toxic element and eventual exposure to the food chain through plant uptake and animal consumption. The use of ground water for irrigation has increased considerably over the last couple of decades. About 86% of total ground water withdrawal is utilized in the agricultural sector. About 40% of the total arable land of Bangladesh is under irrigation and more than 60% of this irrigation need is met from ground water extracted from deep tube-well, shallow tube-well and hand tube-well. Most ground water used for irrigation in Bangladesh has been reported contaminated with arsenic, thus creating a cycle affecting crops, food, animals and humans (Imamul Huq and Naidu, 2005)

It has recently been recognized that As-contaminated groundwater used for irrigation may pose an equally serious health hazard to people eating food from the crops irrigated (Williams *et al.*, 2006), and that As accumulating in irrigated soils poses a serious threat to sustainable agriculture in affected areas (Heikens, 2006).

The extent and severity of the threats to human health and livelihoods due to consumption of As contaminated food stuffs are yet to be directly assessed by any one. Several studies have been conducted to assess the presence of arsenic in food chain. However, more extensive and locality based studies are needed to develop a complete database on the presence of arsenic in irrigation water, irrigated soil and food samples to assess their interrelationships.

The distribution of arsenic pollution in the main aquifer in Bangladesh is shown in the figure 1. From 3198 evenly spaced sampling sites (wells less than 150m deep) from the surveys of DPHE (1999, 2000) the interpolated surfaces show the proportion of wells exceeding 10, 50, 200 and 400 µg/l of arsenic (Ravenscroft *et al.*, 2001).

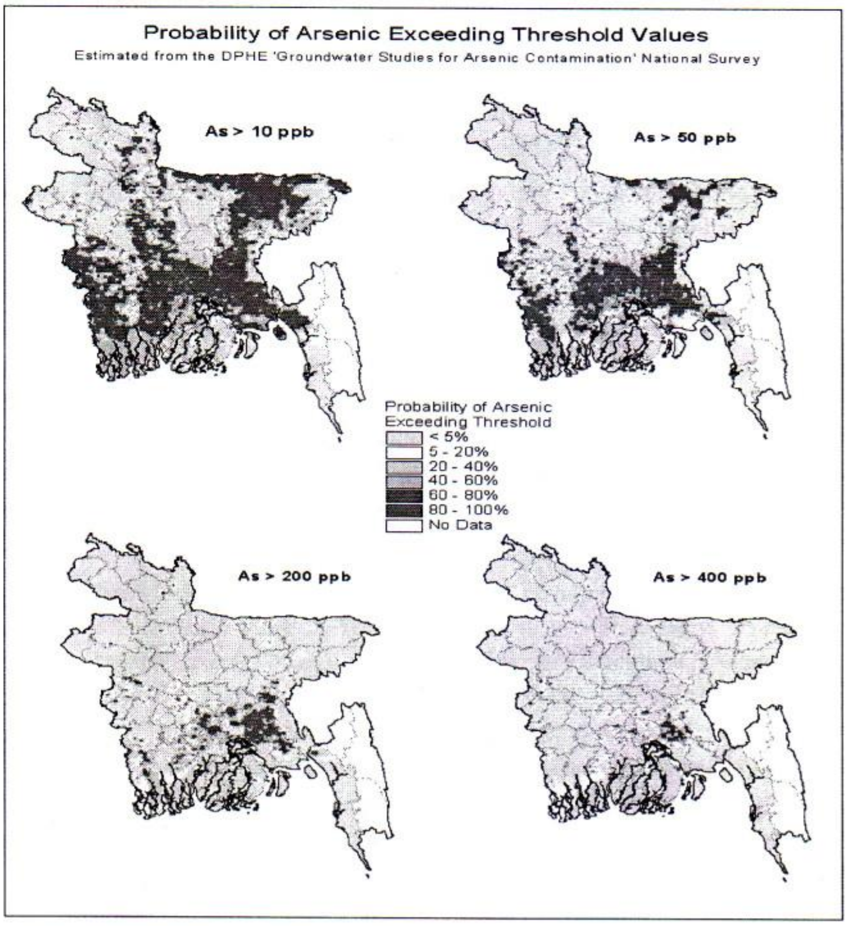

Fig. 1. Arsenic distribution in different aquifers of Bangladesh.

Arsenic in soil

It has been proved beyond doubt that the origin of arsenic in groundwater in Bangladesh is geogenic. Although several hypotheses regarding its release mechanism have been postulated, the iron oxyhydroxide hypothesis has more scientific support (Nickson *et al.*, 2000). Involvement of anaerobic bacteria in the dissolution of AS in groundwater has also been reported (Khan *et al.*, 2003).The dominant chemical speciation of As occurs in the form of arsenate [As(V)] in surficial water. However, other chemical forms of As such as arsenite [As (III)] are also prevalent in water more preferably in groundwater due to the influence of natural biogeochemical processes (Smedley and Kinniburgh, 2002; Bhattacharya et al., 2002; Naidu *et al.*, 2006). About 90% of the inorganic arsenic present in groundwater has been found to be in the arsenite form (Imamul Huq and Naidu 2003). Under aerobic soil conditions, arsenate dominates, whereas in submerged soil conditions the predominant species is arsenite (Masscheleyn *et al.*, 1991; Marin *et al.*, 1992). Groundwater is used for irrigating rice (Alam and Rahman, 2003) and vegetable crops throughout Bangladesh, especially during the dry season. It is probable that use of As-laden groundwater for irrigation has resulted in extensive diffuse loading of As in cultivated soils throughout West Bengal and Bangladesh.

Arsenic in the aquifer seems to have a bearing on the distribution and loading of As in soils. For uncontaminated soil, the As content is usually less than 10 mg kg^{-1} with an average of 7.2 mg kg^{-1}. (Imamul Huq and Naidu, 2003). In Bangladesh, the data available suggest that the average is well below 10 mg kg^{-1} (Imamul Huq and Naidu, 2003; Ali *et al.*, 2003; Alam and Rahman, 2003). However, in areas where groundwater contamination is reported and where irrigation is practiced, the values have been found to be much higher ranging up to 80 mg kg^{-1}. The irrigation water that was being used on this soil was found to have 0.077 mg As L^{-1} (Imamul Huq and Naidu, 2003). As levels in unirrigated floodplain soils appear to be <10 mg/kg (Abedin *et al.*, 2002). Imamul Huq *et al.* (2006 b) reported that 21% of samples from a 24-upazila study had levels >20 mg/kg, with a highest level of 81 mg/kg.

The immediate and long-term impact of using As contaminated water for irrigating paddy soils is a burning concern as arsenic can be transferred from water to soil and several studies have revealed this phenomenon (Imamul Huq *et al.*, 2006 b). A Boro (dry season) rice requires approximately 1000 mm of irrigation water per season. With As concentration in irrigation water varying between 0.136 to 0.55 mg L^{-1}, Imamul Huq *et al.* (2006 a) calculated the As loading in irrigated soils for a Boro rice to be between 1.36 to 5.5 kg ha^{-1} yr^{-1}. Similarly, for winter wheat requiring 150 mm of irrigation water per season, As loading from irrigation water has been calculated to be in the range between 0.12 to 0.82 kg ha^{-1} yr^{-1}.

The soil As varies both spatially and vertically. The spatial variation is controlled by the soil formation and the aquifer characters, while the vertical distribution is controlled by the clay contents (Imamul Huq *et al.*, 2008a; Biswas *et. al.*, 2009). Actual soil loading rates will vary with the amount of irrigation water applied, As concentrations in the water and losses due to volatilization, leaching and crop removal. Moreover, the top 0-150 mm soils contain more As than the 150-300 mm soils. Most recent studies show that virtually all the As added in irrigation water remains in the top 10–15 cm of soils, implying that little is lost to the atmosphere by volatilization, leaching to deeper soil layers and removal by crops (Biswas *et. al.*, 2009). Some recent studies (Dittmar et al., 2007) show that input of As into rice field soils decreases significantly with increasing distance from the irrigation water inlet. However, Dittmar *et al.* (2007) reported similar topsoil As contents at the start of two successive irrigation seasons, and suggested that As added during the first irrigation season had been leached by floodwater during the following monsoon season. Imamul Huq *et al.* (2008 b) studied to observe the effect of alternate irrigation on the As loading in the soil and on its transfer to rice in four consecutive seasons, using As-contaminated water in the dry (boro) season and fresh water in the monsoon (aman). Soil arsenic content increased significantly after each boro season, whereas the soil As was found to have decreased significantly at the end of both of the aman seasons.

High As concentrations in soils have been reported to be positively correlated with high groundwater As, which is perhaps due to the irrigation with groundwater (Meharg and Rahman 2003). It has been observed, however, that arsenic in the topsoil of rice fields increases significantly after the dry-season irrigation with As contaminated water (Imamul Huq *et al.*, 2008 b). Arsenic thus accumulated in the topsoil would be bioavailable to the next crop of rice, even if the crop is cultivated with arsenic-free irrigation water or with rainwater (Imamul Huq *et al.*, 2007 a). A positive significant relationship between soil As and rain-fed rice-grain As observed in sites where As contaminated groundwater is used during the boro season, indicates the carry-over effect of irrigation-water As to rice cultivated under the alternate (As-free rainwater) irrigation system (Imamul Huq *et al.*, 2007 a).

Arsenic added in irrigation water is adsorbed to ferric oxyhydroxide in the topsoil (Roberts *et al.*, 2007) where it gradually accumulates over time (Meharg and Rahman, 2003). Arsenic accumulation is most serious in soils used for transplanted rice (paddy) cultivation, where the topsoil is puddled to hold water on the surface. That is partly because of the large amounts of water used to irrigate rice – of the order of 1000 mm per crop – and partly because, under the anaerobic conditions in flooded paddy fields, the As is mainly present as As (III), the form that is most readily available to plant roots.

The presence of high concentrations of As in soil is not only dependent on the concentration of As in soils but also on other factors. Many soil factors that influence the amount of As available for plant uptake include redox potential, pH, organic matter contents, iron, manganese, phosphorus and calcium-carbonate, and soil microbes. The influence of some of these soil properties and constituents also varies significantly within the year in soils that alternate between anaerobic and aerated conditions, As occurs in seasonally-flooded soils and irrigated upland soils used for paddy cultivation (Mahimairaja *et al.*, 2005). Sediments with finer texture usually contain more arsenic than sediments with coarser texture (Khan, 2003). For vegetable soils, the available fraction (ratio of available As to total As) of arsenic was found to have decreased with decreasing silt (particle size 0.02–0.002 mm) and free iron (DCB extractable) contents and with increasing soil pH and organic matter content. The available fraction of arsenic in the paddy rice soils increased with increasing free iron and organic matter contents and decreasing soil pH and silt content (Huang, 2006). Climate and geomorphic characteristics of an area, such as rainfall, surface runoff, rate of infiltration, and the groundwater level and its fluctuations, also affect the mobility and redistribution of arsenic (Bhattacharya *et al*., 2002).

Arsenic in the food chain through crop accumulation

Arsenic is not an essential element either for plants or for animals. Food crops such as vegetables and cereals can become a path by which As may enter into the food chain, because they can reflect the levels of As that exist in the environment in which they are grown (soil and irrigation water). As a result, the accumulation of As in soil and its introduction into the food chain through uptake by the plant is becoming a major concern, particularly in the arsenic hot spots.

Groundwater is the main source of drinking water in most of the countries. Now-days, 90% of Bangladeshi depends on ground water for drinking purpose because much of surface water of Bangladesh is microbially unsafe to drink (Ahsan and Del Valls, 2011)purchase. Although human exposure to arsenic is thought to be caused mainly through drinking of arsenic contaminated ground water, the use of this water for irrigation enhances the possibility of arsenic uptake into crop plants.

Arsenic (As) in groundwater and its fate and transport in the environment have become matters of great concern in Bangladesh. Tube-well water extracted in Bangladesh from shallow aquifers is the primary source of water for drinking and cooking for most of its population. Besides domestic use, huge quantities of water from shallow aquifer are also used for irrigation during the dry season. With an increased use of groundwater for irrigation, studies have shown that As accumulation by plants is a concern to be another major exposure pathway. As-contaminated groundwater used for irrigation leaves a risk of the accumulation of this toxic element in soil and the eventual exposure of the food chain through plant uptake and animal consumption (Imamul Huq and Naidu 2005).

Figure 2: A simplified version of rice & vegetables contamination with arsenic in Bangladesh and As exposure routes to humans and livestock (http://www.sydneybashi-bangla.com)

There are conflicting reports on the correlation between soil and plant As levels. In samples from 330 STW sites in two upazilas in western Bangladesh, Jahiruddin *et al*. (2005) found that As concentrations in grain were poorly correlated with soil and water As; so was the findings of Miah *et al*. (2005) who sampled 270 STWs in 67 upazilas across the whole of Bangladesh. On the other hand, Farid *et al*. (2005) considered that correlations were good at 96 sampling points within a single STW site studied at Brahmanbaria, Bangladesh. The concentration of arsenic in cereals, vegetables and fruits is directly related to the level of arsenic in the soil. Arsenic levels in soils and plants were positively correlated, while the ability of the plants to accumulate the element, expressed by their biological accumulation coefficients and arsenic transfer factors, was independent of the soil arsenic concentration (Zandsalimi *et al*., 2011). From a field survey conducted in arsenic impacted and non-impacted paddies of Bangladesh it has been found that both grain and shoot total arsenic concentrations were highly correlated ($P < 0.001$) with soil arsenic. When the Bangladesh data were compared to EU and US soil–shoot–grain transfers, the same generic pattern was found with the exception that arsenic was more efficiently transferred to grain from soil/shoot in the Bangladesh grown plants. This may reflect climatic or cultivar differences (Adomako, 2009).

Rice is one of the major food crops in many countries. Arsenic content in straw, grain and husk of rice is especially important since paddy fields are extensively irrigated with underground water having high level of arsenic concentration. As the cultivation of rice requires huge volume of water, long term use of arsenic contaminated groundwater for irrigation may result in the increase of arsenic concentration in the agricultural soil and eventually accumulation in rice plants.

Imamul Huq *et al.* (2006 c) studied field samples of vegetables, rice and wheat collected from both arsenic-affected and arsenic non-affected areas of the country. Plant arsenic content was found to vary considerably with plant types, nature of soil types, and the irrigation water arsenic content. The arsenic content of most plant samples from contaminated areas was found to be elevated, and often exceeded that of samples from uncontaminated areas, suggesting phytoaccumulation of soil arsenic in plants grown in contaminated areas. The more labile a soil As fraction (water extractable), the greater is plant accumulation of the element.

Arsenic content of rice grain samples collected from various districts varied from below detection limit to more than 1 mg/kg. The concentration ranged in root from less than 1 to as high as 267 mg/kg; in straw the range was between less than 1 to 30 mg/kg. In wheat grain the values ranged between 0.5 and 2 mg/kg; in straw, between 0.2 and 30 mg/kg; and in root, between 105 and 3 mg/kg (Imamul Huq, 2008 c).

A marked difference in the arsenic content of vegetables was found and was related to the arsenic content of the groundwater. Many crops receiving As contaminated water as irrigation have been found to accumulate As at levels that exceed the maximum allowable daily limit (MADL) of 0.2 mg per kg dry weight. Of the various crops and vegetables analyzed, green leafy vegetables were found to act as arsenic accumulators with arum (*Colocassia antiquorum*), gourd leaf, Kalmi (*Ipomoea aquatica*), Amaranthus (*Amaranthus* spp.) etc. topping the list. The transfer factor for arsenic has been found to exceed the value of 0.1 in a number of plants indicating their affinity towards this element. The arsenic content in these crops ranged from 8 in gourd to 158 mg/kg in arum (DW) or 6 to 125 mg/kg (FW). Arum seems to be unique in that the concentration of arsenic can be high in every part of the plant. Rice and wheat receiving As-contaminated irrigation water have been found to sequester the toxic metalloid preferably into roots and stems with a smaller fraction into the grains (Imamul Huq, 2006 a).

The toxic effect of arsenic in any foodstuff is highly dependent on its chemical speciation. Inorganic arsenic compounds are generally more toxic than organic forms. The toxicity of arsenic species follows the order AsH3 >As(III) >As(V) >MMAA (monomethylarsonic acid) >DMAA (dimethylarsinic acid). Unfortunately, Bangladesh rice contains more (Ca. 80% of the total As) inorganic arsenic with a small fraction of organic arsenic (Williams *et al.*, 2006).

Rice is the staple food for Bangladeshi people. There are two seasons for rice culture; aman and boro. Aman culture period is in the rainy season when no irrigation is required but the boro cultivation phase (in dry season) is completely dependent on irrigation. So, it can be predicted that As contaminated irrigation water could easily increase the As level in rice grain, straw and other part of rice plant. Arsenic contents in boro rice could be 1.3 times higher than for aman rice (Ahsan and Del Valls, 2011)purchase.

Imamul Huq *et al.* (2007 a) found much higher accumulation of arsenic in the rice grains grown in the boro season than that grown during the aman season. The average boro rice As content was 2.35 with minimum of 1.07 with a maximum of 4.42 mg/kg d.w. while the average aman rice As content was 0.91 with a minimum of 0.90 and a maximum of 1.763 mg/kg. Imamul Huq *et al.* (2011b) observed the carryover effect of As in rice from boro to aman. He found higher accumulation of As in boro than that of aman. No As-treated irrigation water was used in the aman season. The accumulation of As in aman season indicates that the As added through irrigation water during the boro season is accumulated in the soil and carried over to the next crop.

Arsenic was found to be concentrated primarily in the roots and straws of rice and other cereal crops. Ali (2003) has found that arsenic present in irrigation water and soil results in higher accumulation in rice plant root, leaf and stem. Similar observations have been made by others too (Abedin *et al.*, 2002, Imamul Huq and Naidu, 2003, Das et al., 2004). A distribution of As in different parts of rice plant is mentioned in Imamul Huq (2008). Some dry land crops also take up significant amounts of As, and accumulates it differentially in various plant parts. Williams *et al.* (2006), measured As contents of 37 vegetables, pulses and spices commonly grown in Bangladesh, and found that the levels were highest in radish leaves (0.79 mg/kg), arum stolons, spinach and cucumber, and lowest (<0.2 mg/kg) in most fruits, vegetables and spices. Liu *et al.* (2005) showed that the accumulation of As in rice plant was in the order root > leaf > grain and they detected the level of As up to 248±65 mg /kg in root tissue whereas only 1.25±0.23 mg /kg was detected in the grain. The root, shoot and leaf tissue of rice plant contain mainly inorganic As III and As V while the rice grain contain predominantly DMA (85 to 94%) and As III (Liu *et al.*, 2005). The information on rice grain is not particular to Bangladesh rice.

Bhattacharya (2009) found the highest accumulation of arsenic in the root (7.19±0.166 to 18.63±0.155 mg kg^{-1}) and the lowest in the grain (0.25±0.014 to 0.73±0.009 mg kg^{-1}). Regardless of the sampling locations the arsenic accumulation follows the order of root >

straw > husk > grain. This author concludes that consumption of rice straw containing considerable amount of arsenic (1.17±0.014 to 4.15±0.033) by cattle could potentially lead to increased arsenic levels in meat or milk.

Excessive accumulation of As, particularly inorganic arsenic (As_i), in rice (*Oryza sativa*) poses a potential health risk to populations with high rice consumption. Rice is efficient at As accumulation owing to flooded paddy cultivation that leads to arsenite mobilization, and the inadvertent yet efficient uptake of arsenite through the silicon transport pathway (Zhao *et al.*, 2010).

Plant uptake of As from soils is complicated by a number of factors. Arsenic accumulation in plants grown under experimental conditions has been found to depend on the type of plant, plant part (root vs. shoot), concentration, the nature of arsenic in solution, the amount of iron oxide in the soil, the amount of phosphorus added to the soil (Carbonell-Barrachina *et al.*, 1999). In aerated soils used for crops such as wheat, maize and most vegetables, As is present mainly as As(V) and, as such, is likely to be in the solid phase. Therefore, in such soils, As in groundwater used for irrigation is quickly adsorbed by iron hydroxides and becomes largely unavailable to plants. In anaerobic soil conditions that occur in flooded paddy fields, As is mainly present as As(III) and is dissolved in the soil-pore water (the soil solution) (Xu *et al.*, 2008). It is thus more readily available to plant roots. Considerable differences in As uptake exist between rice varieties and between the kinds of rice grown in different countries.

Plants vary considerably in their tolerance to arsenic and in the amount of arsenic that they can take up from soils and water (Feng *et al.*, 2009). The magnitude of As concentration in rice grain is related to the magnitude of As concentration in soil and variety of rice species. Rice is especially susceptible to arsenic toxicity compared to upland crops, because of an increase in both the bioavailability and toxicity of As under the reducing conditions of submerged soil in paddy fields (Horswell and Speir, 2006).

Transfer of As from soil to grain has been reported an order of magnitude greater in rice than for wheat and barley, despite lower rates of shoot-to-grain transfer. The differences in these transfer ratios are probably due to differences in As speciation and dynamics in anaerobic rice soils compared to aerobic soils for barley and wheat (Williams *et al.*, 2007).

In pot experiments with arsenic-spiked soil, Imamul Huq *et al.* (2006 b) observed that arsenic accumulation in rice is dependent on variety and soil. Not all varieties accumulate arsenic to the same extent. For example, under similar experimental conditions, BRRI dhan 28 was found to accumulate more arsenic than BRRI dhan 29. As usal, in either variety, arsenic accumulation was more from As (III) than from As (V), and root accumulated the maximum. While working with a salt-tolerant local variety, Sraboni, and and a nontolerant HYV, BRRI dhan 26, in spiked soil with 10 mg/L As irrigation, Rabbi *et al.* (2007) observed that the HYV accumulated more arsenic than the local variety. Yet in another experiment, while working with three varieties *viz.*, BRRI dhan-29, BRRI dhan-35 and BRRI dha-36, Imamul Huq *et al.*, (2011 b) observed that BRRI dhan-36 was found to be most sensitive to As treatment. In a recent work by the author, it has been further observed that of the three varieties BRRI dhan 28, BRRI dhan 29 and HIRA, BRRI dhan showed the most susceptibility to As treatment, the accumulation of As in grain by the three varieties were in the order 0.096, 0.533 and o.221 mg per kg.

Williams *et al.* (2006) reported As levels ranging between <0.04 and 0.92 mg/kg in rice samples obtained from 299 markets in 25 (of 64) districts across Bangladesh; (the samples included several different rice varieties from irrigated and rain fed land and from areas with high and low-As tube well water). Meharg and Rahman (2003) found rice grain contents ranging between 0.058 and 1.835 mg/kg As in 13 different rice varieties tested in Bangladesh.

Dietary Intake of Arsenic

A Bangladeshi consumes, on an average, about 500 g of rice per day. The maximum allowable daily limit (MADL) of arsenic ingestion without injury is 0.22 mg/kg. Assuming that 3 L/day of drinking water with an arsenic content of 0.05 mg/kg and nothing but rice is to have been consumed with an average arsenic content of 0.437 mg/kg, it has been simulated that the mean load becomes 304 µg/day, and effectively, all cases will exceed the 0.22 mg/day limit. Rice here is found to contribute to 144 µg/day, approximately 65% of the 220 µg/day limit (Correll *et al.*, 2006). It has been observed that even if a rice sample does not contain any detectable amount of arsenic, the cooked rice contains a substantial amount of the element when it is cooked with arsenic contaminated water. The amount of arsenic in cooked rice, plus an average consumption of 4 L of the same source of water as drinking water that has the Bangladesh standard of 50 µg/L arsenic along with arsenic-rich vegetables, is sufficient to bring the value of daily ingestion of arsenic above the maximum allowable daily limit (MADL) of 0.22 mg/day (Imamul Huq *et al.*, 2008 c).

Table: Maximum arsenic (mg/day DW) of various plant materials, amount of material (a-c) that will exceed an MADL of 02 mg/day when ingested (Imamul Huq *et al.*, 2008 c)

Plant Type	District									
	Dha	Din	Jes	Kur	Meh	Mun	Nar	Pab	Ran	Overall
Amaranthus	-	0.0	1.0^{a}	-	-	1.7	1.1^{a}	18.7^{b}	0.3	18.7^{b}
Arum	1.0^{a}	0.2	11.4^{b}	0.9	0.5	0.6	19.8^{b}	9.0^{b}	5.5^{b}	19.8^{b}
Arum root	0.4	-	-	-	1.5^{a}	2.6^{a}	-	115.3^{c}	-	115.3^{c}
Bean	0.4	-	0.4	-	0.2	0.3	-	5.1^{b}	-	5.1^{b}
Gourd leaf	-	-	1.0^{a}	-	-	0.3	2.4^{a}	20.1^{c}	-	20.1^{c}

a>200 g/day
b>40 g/day
c>10 g/day
d(Dha, Dhaka; Din, Dinajpur; Jes, Jessore; Kur, Kurigram; Meh, Meherpur; Mun, Munshiganj; Nar, Narayanganj; Pab, Pabna; Ran, Rangpur.

A person consuming daily 100 g Dw of arum with an average arsenic content of 2.2 mg/kg, 600 g DW of rice with an average arsenic content of 0.1 mg/kg, and 3 L of water with an average arsenic content of 0.1 mg/kg would ingest 0.56 mg/kg, which exceeds the threshold value calculated using the Environmental Protection Agency model (Imamul Huq *et al.*, 2008 c)

With the average rice consumption between 400 and 650 g/day by typical adults in the arsenic-affected areas of Bangladesh, the intake of arsenic through rice stood at 0.20–0.35 mg/day. With a daily consumption of 4 L drinking water, arsenic intake through drinking water stands at 0.2 mg/day. Alike human beings, arsenic gets deposited into cattle body through rice straw and husk as well as from drinking water which in turn finds a route into the human body. Arsenic intake in human body from rice and cattle could be potentially important and it exists in addition to that from drinking water (Rahman, 2008).

Imamul Huq and Naidu (2003) estimated the dietary load on the basis of arsenic content in Bangladesh rice grain, and according to them, about 19% of the total population are at risk of exceeding the maximum allowable daily limit (MADL) value, which is 0.2 mg/day.

Arsenic, a non-essential nutrient, interferes with plant metabolisms and inhibits plant growth, because arsenate decouples phosphorylation in mitochondria and arsenite inactivates many enzymes by reacting with sulfhydryl groups of proteins (Dixon, 1997). Arsenic may also influence nutrient uptake and distribution in plants through competing directly with nutrients and/or altering metabolic processes. Iron, phosphorus, sulfur, and silicon interact strongly with As during its route from soil to plants. Plants take up arsenate through the phosphate transporters, and arsenite and undissociated methylated As species through the nodulin 26-like intrinsic (NIP) aquaporin channels (Zhao *et al.*, 2010). Arsenite (As^{III}) reacts with dithiol groups on proteins, and thus inhibits enzyme reactions requiring free sulfhydryl groups, leading to membrane degradation and cell death (Jiang and Singh, 1994). As (V) competes with phosphate due to its chemical similarity and acts as an uncoupler of oxidative phosphorylation, resulting in an adequate supply of energy at the cellular level (Scott-Fordsmand and Pederson 1995). These events ultimately affect the nutritional quality of the food crops that accumulates arsenic. In a recent study with two varieties of *Amaranthus* the author has observed that As reduces the accumulation of P, K, S while that of crude protein, Ca, Mg increases in green *Amaranthus*. Vitamin E has been found to be significantly reduced in As treated plants. With rice, vitamin B1 contents of three rice varieties have been found to be negatively affected due to As treatment. This is an indication that As has a negative effect on the nutritional quality of food crops. Wallace *et al.* (1980) showed that depression of K concentration in roots of bush bean plants was due to arsenic in the nutrient solution. Merry *et al.* (1986) reported the interaction between sulphur and arsenic and pointed out that sulphur and arsenic exists in soil solution in similar ionic forms (e.g. sulphate and arsenate) and there should be competition between these two ions.

In recent times, a variety of arsenic-rich solids and semisolids, such as arsenic-saturated hydrous ferric or aluminium oxides and other filter media are being generated from arsenic removal filters. The disposal of the sludge from these filters has become a great concern for the environmental, as well as plant and soil scientists. Soils are regarded as a natural sink for all unwanted materials. Once the unwanted materials are disposed of into the soil, it would decompose in soil at a certain time and there is a possibility of soil contamination with the toxic elements and it is likely that the element will end up in the growing plants (Imamul Huq *et al.*, 2011 a). Hussain (2008) also reported that the indiscriminate disposal of the arsenic waste from filters is potentially hazardous for air, water, and soil media. People will have nasal intakes (inhalation) of the wastes from breathing polluted air. Also, they will have oral intakes (ingestion) from eating the bottom-feeder fish species, cattle and poultry products, and crops, vegetable and fruits produced on contaminated soil.

A gradual release of arsenic from sludges (Granular ferrichydroxide and Activated alumuna) was found in the soils treated with the sludge under both upland and wetland conditions. Rice (*Oryza sativa*) and Kalmi (*Ipomoea aquatica*) were grown in soils treated with sludges from both sources at the rates of 0.5 and 1 T/ha and analyzed for the uptake of arsenic from these sludges. It was found that both the plants showed an increased uptake of arsenic. The maximum uptake of arsenic by roots and the edible parts of Kalmi was observed for the Granular ferrichydroxide sludge at 1 T/ha, which was 62% and 38% of total plant uptake respectively for the two plant parts. The roots of rice plants were also found to take up the highest amount of arsenic (72.27 to 87.66%of total uptake) followed by stem+leaves (6 to 14%) and rice grain (4 to 14%) (Imamul Huq *et al.*, 2011a). The disposal of As-rich wastes thus needs serious attention.

Mitigation Approaches to Reduce Arsenic Toxicity in Food Crops

A number of approaches have been evolved to mitigate the uptake of As in plants and subsequent entry into the food chain. Mixing of surface water with irrigation water (groundwater) could reduce about 50% of As accumulation in arum (*Colocassia antiquorum*) and kangkong (*Ipomea aquatica*) (Imamul Huq *et al.* 2008 c). Marigold (*Tagetes patula*), ornamental arum (*Syngonia* sp.) and ferns (*P. vittata* and *N. molle)* have been found to be good phytoremediators for soil clean-up (Imamul Huq *et al.* 2007 b, Hossain *et al.*, 2006). Bioremediation by efficient algal strains in rice culture could be a good strategy. The presence of algae in rice culture was found to have decreased As accumulation in rice plants by about 72% (Imamul Huq et al., 2007b). Organic matter application to soil prior to rice culture has been found to reduce As accumulation in plants. The ability of various types of organic matter to reduce soil As toxicity in *Ipomoea aquatic* was found be as much as 75% in the vegetative part of the plant

(Imamul Huq *et al.*, 2008 c). In another study, by manipulating the water regime in the rice rhizosphere, Imamul Huq *et al.* (2006 b) attempted to devise mitigational measures to minimize As toxicity by oxidizing arsenite as well to reduce the entry of As into the growing rice. Reducing the water requirment by 25% of the field capacity was found to have alleviated As accumulation significantly in two varieties of rice (BR 28 and BR 29) without any significant decrease in their yield. In a recent study, Imamul Huq *et al.* (2011 b) observed the response of rice to balanced fertilization in reducing arsenic accumulation. When balanced fertilizers were applied to the medium, the accumulation of As was found to have decreased by 227, 229 and 397% repectively for BR 29, BR 35 and BR 36. There are several means to mitigate the arsenic accumulation in crops, particularly rice. The best way would be to screen the variety/varieties that avoid As accumulation. This ultimately will need research in genomics.

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