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REGULAR ARTICLE

Accumulation of arsenic in soil and rice under wetland condition in Bangladesh

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Abstract Shallow tube well (STW) water, often contaminated with arsenic (As), is used extensively in Bangladesh for irrigating rice fields in the dry season, leading to potential As accumulation in soils. In the current study the consequences of arsenic from irrigation water and direct surface (0–15 cm) soil application were studied under field conditions with wetland rice culture over 2 years. Twenty PVC cylinders (30-cm length and 30-cm diameter) were installed in field plots to evaluate the mobility and vertical distribution of soil As, As mass balance, and the resulting influences on rice yield and plant-As concentration in *Boro* (dry season) and transplanted (T.) *Aman* (wet season) rice over the 2-year growth cycle. Treatments included irrigation-water As concentrations of 0, 1 and 2 mg L^{-1} (*Boro* season only) and soil-As concentrations of 10 and 20 mg kg^{-1}. Following the 2-year cropping sequence the major portion (39.3–47.6%) of the applied arsenic was retained within the rooting zone at 0–15 cm depth, with 14.7–19.5% of the total applied As at the 5–10 cm and 10–15 cm soil depths compared to 1.3–3.6% at the 35–40 cm soil depth. These results indicate the relatively low mobility of applied As and the likely continued detrimental accumulation of As within the rooting zone. Arsenic addition in either irrigation water or as soil-applied As resulted in yield reductions from 21 to 74 % in *Boro* rice and

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8 to 80 % in T. *Aman* rice, the latter indicating the strong residual effect of As on subsequent crops. The As concentrations in rice grain (0.22 to 0.81 μg g^{-1}), straw (2.64 to 12.52 μg g^{-1}) and husk (1.20 to 2.48 μg g^{-1}) increased with increasing addition of As. These results indicate the detrimental impacts of continued long-term irrigation with As-contaminated water on agricultural sustainability, food security and food quality in Bangladesh. A critical need exists for the development of crop and water management strategies to minimize potential As hazard in wetland rice production.

Keywords Irrigation · Arsenic · Arsenic retention · Soil arsenic · Arsenic uptake · Rice

Introduction

Widespread arsenic (As) pollution of shallow tube well (STW) irrigation water and increasing accumulation of As in soils have become a major threat to the production of rice, the staple food crop in Bangladesh (Hossain et al. 2008; Panaullah et al. 2009). The STWs, being the almost exclusive source of irrigation water, play a key role in the production of dry season winter rice (locally called *Boro* rice), which accounts for 50% of the total annual rice output in this country. Thus, *Boro* rice is an important determinant of food security or insecurity in Bangladesh, where due to a mounting population pressure, the balance between food demand and supply remains very delicate. Much of the groundwater aquifer of the major rice-producing regions of the country is contaminated with As (Smedley et al. 2002). Arsenic in irrigation water from contaminated shallow tube-wells is being transferred to soils, where it is potentially available for uptake by plants (Panaullah et al. 2009; Islam et al. 2007).

Rice is recognized as a major exposure route to As, representing about half of the total As intake in Bangladesh and India (Ohno et al. 2007; Mondal and Polya 2008). This crop is grown in wetland conditions (anaerobic), which greatly influences As bioavailability in soil (Xu et al. 2008), leading to rice being much more efficient at assimilating As into grain than the dry land cereal crops (Williams et al. 2007; Li et al. 2009). Use of high As irrigation water can lead to As build up in soil (Hossain et al. 2008; Khan et al. 2009), decreased rice yields (Jahiruddin et al. 2004; Heikens et al. 2007; Panaullah et al. 2009) and increased As concentrations in rice grain and straw (Duxbury et al. 2003; Huq et al. 2006; Williams et al. 2006, Islam et al. 2009).

Roberts et al. (2007) estimated that over 1000 tons of As can be transferred to arable land each year from irrigation with As-contaminated groundwater in Bangladesh. Meharg and Rahman (2003) have concluded that the As concentrations of Bangladesh soils can reach ~30 mg kg^{-1} in the areas where groundwater with elevated concentrations of As have been used for over a decade to irrigate crops. However, As accumulation in irrigated paddy soils and its transfer into rice can vary depending on the soil type, crop, background-As concentration, As concentration of irrigation water, distance from the pump source, and depth and duration of flooding (Meharg and Rahman 2003; Norra et al. 2005; Hossain et al. 2008).

In view of evidence for the adverse effect of As on the yield and quality of rice in Bangladesh, a clear understanding of the fate of As applied to soils through irrigation or direct addition is important to assess As accumulation in paddy fields and its potential impact on rice quality and yield and for developing As management strategies. Research on the problem of As contamination in agriculture has so far mostly centered around the effect of irrigation water or soil As on crop growth and accumulation of As in grain and other plant parts. Little attention has been paid to the movement or retention of As in soils, although these factors would ultimately determine the gravity of the As problem for agriculture in the long term implications of the As problem to agriculture in Bangladesh.

Previously we had conducted a soil column (30-cm diameter by 40-cm height) net-house experiment with 3 irrigation-water As concentrations (0, 1 and 2 ppm), with *Boro* and T. *Aman* rice grown in sequence for consecutive 2 years, to examine the fate of added As from irrigation water during flooded rice culture (Khan et al. 2009). About 70% of the As applied with irrigation water was found to be retained in the top 0–20 cm of soil, i.e., within the root zone, indicating a possibility of a rapid accumulation of As in topsoil which could adversely affect rice production and grain quality. As movement in soil and its accumulation in rice through root absorption and translocation in the plant body may be different in irrigation applied As and soil native As. Bangladesh has many locations and sites where soils have high As content (Hossain et al. 2008) and Boro rice is grown with As free irrigation water and on the other hand there are areas where soils have sufficiently low As status and *Boro* rice is cultivated with As contaminated irrigation water. Addition of As contaminated irrigation water to *Boro* rice but not *Aman* rice represents the pattern of addition of As from irrigation water but not from rainfall during the normal 2-crop sequence in Bangladesh.

The present study was designed to more fully evaluate the fate of irrigation-and soil-applied As under flooded rice culture in an actual field situation. The specific objectives were to evaluate: i) As accumulation at various soil depths resulting from irrigation with As-contaminated water or direct addition of As to soil, ii) the effects of added As on As accumulation in rice grain and straw, and iii) the nutrient concentrations in rice in relation to As concentration.

Materials and methods

Field characteristics

This study was conducted at the experimental farm of Bangladesh Agricultural University (BAU), Mymensingh, in central Bangladesh (24.75ºN latitude and 90.50ºE longitude) during February 2004 to January 2006. The study site has a subtropical monsoon climate, with a cool and dry winter (November–February), a hot and mostly dry pre-monsoon season (March–June) and a rainy monsoon season (June–October). The soil, classified as Aeric Haplaquept is a silt loam with 6.5 pH, 1.49% organic matter (Walkley and Black 1975), 10.3 μg g^{-1} available P (0.5 M $NaHCO_3$ extractable; Olsen and Sommers 1982) and 3.2 mg kg^{-1} total As. Mineral composition of the clay fraction of the 0–15 cm soil horizon is approximately 31% mica, 29% chlorite, 14% kaolinite, 8% vermiculite, 8% quartz, 5% interstratified mica-chlorite, 4% feldspar and 1% goethite (Moslehuddin et al. 2003).

Layout of micro-plots

Twenty micro-plots, each measuring 1 m x 1 m, surrounded by clayey levees on all sides, were laid out in a randomized complete block design with four replications. Inter-block and inter-plot spacings were 1 m and 0.5 m, respectively. A PVC cylinder (30 cm long x 30 cm diameter) was installed to a depth of 25 cm in the middle of each micro-plot to set up an experimental soil core (Supplemental Figure, SI Fig. 1). Initial soil samples were collected from the 0 to 40 cm depth at 5 cm intervals from 5 different spots. Samples from the separate cores were composited for determining the physical and chemical characteristics of the soil.

Arsenic treatments

There were five treatments: 2 concentrations of irrigation water As, i.e., 1 and 2 mg As L^{-1} (designated as I-As_1 and I-As_2); 2 levels of soil As addition, i.e., 10 and 20 mg As kg^{-1} (designated as S-As_{10} and S-As_{20}); and a control, i.e., no addition of As (As_0). Irrigation water from a deep tube well (DTW) installed in 1976 served as the irrigation source for the As_0 treatment. The concentration of As in the DTW water was below detection level (<5 μg L^{-1}). $Na_2HAsO_4 \cdot 7H_2O$ was added to the DTW water to obtain the desired irrigation water As concentrations for the I-As_1 and I-As_2 treatments. The same As source, i.e., $Na_2HAsO_4 \cdot 7H_2O$ was mixed with the topsoil (0–15 cm depth) of the designated soil cores before transplanting the seedlings to obtain the S-As_{10} and S-As_{20} soil treatments. The bulk density of the top 0–15 cm soil layer of the cores was used to calculate the soil weights and the required amounts of $Na_2HAsO_4 \cdot 7H_2O$ for the S-As_{10} and S-As_{20} soil treatments. Arsenic was added in solution and mixed thoroughly with the top soil prior to cropping.

Field experiment

Boro rice (dry season rice) and transplant (T.) *Aman* rice (wet-season rice) were grown in sequence in both years (2004 and 2005). Irrigation water and soil-As treatments were applied once a year in the *Boro* season of 2004 and 2005. Soil As was mixed uniformly with 0–15 cm soil before transplanting each *Boro* rice crop and irrigation As was applied during the growing season. Soil As was added in both years for increasing the level of soil As and the effects of residual As on rice were evaluated. The *Boro* and T. *Aman* rice varieties were BRRI dhan 29 and BRRI

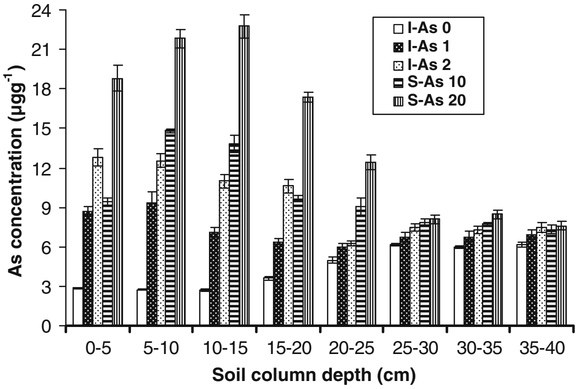

Fig. 1 Arsenic concentration in different soil depths with five As treatments. (SE represents error bar, *n*=4)

dhan 33 were planted in the 2nd week of February and mid July, respectively. Both are popular rice varieties widely used in Bangladesh. *Boro* and T. *Aman* rice seedlings were transplanted in the 2nd week of February and mid-July, respectively. Before transplanting the rice seedlings, the top 0–15 cm soil in the micro-plots, including that in the soil cores within the micro-plots, was thoroughly puddled and fertilizers were applied and mixed thoroughly with the topsoil. The applied N, P, K and S rates were 120, 25, 60 and 20 kg ha^{-1} as urea [$CO(NH_2)_2$], triple super phosphate [$Ca(H_2PO_4)_2$], muriate of potash (KCl) and gypsum ($CaSO_4$•$2H_2O$), respectively. In both years, 35-day old seedlings for *Boro* rice and 40-day old seedlings of T. *Aman* were transplanted in the micro-plots. The total number of hills/plot was 25 including two hills within the soil core, and two seedlings were transplanted in each hill. For the I-As_1 and I-As_2 treatments, measured quantities of As-spiked irrigation water were applied during each *Boro* season and As free DTW water was applied during the T. *Aman* seasons to maintain a 3–4 cm water depth for the duration of 4 cropping seasons.This As application pattern was chosen to mimic use of As-contaminated groundwater in the *Boro* season and As-free rainwater in the T. *Aman* season. During the fallow period between the *Boro* and T. *Aman* crops, the soil in the microplots, including the soil of cores was kept flooded to a depth of 1 cm with distilled water. In each micro-plot, the same irrigation water levels were maintained inside and outside the soil core during crop growth and fallow periods. The amount of total As load from irrigation water was calculated for each soil core.

The *Boro* and T. *Aman* rice crops were harvested at maturity in the 4th week of May and the 3rd week of November, respectively. The yield and yield components (i.e., plant height, tillers $core^{-1}$ and grains $panicle^{-1}$) were measured. Oven-dry samples of rice grain, straw and husk were ground separately and analyzed for N, P, K, Fe, and As concentrations. The husks were separated from the grain prior to grinding. After harvest of the 4th crop, each PVC cylinder containing the experimental soil core was carefully removed from the micro-plot by digging the surrounding soils to a depth of 40 cm and then cutting at the bottom of the soil core. Samples were collected from the inner area of the core up to 40-cm depth at 5-cm intervals, air dried and weighed, and sub-samples were analyzed for total-As concentration. The amount of As in each depth increment was calculated by using the soil weight and As concentrations, and the As in the individual layers was summed to give total column As quantities. Root samples from the 4th crop were collected from the soil fractions at the 0–5 cm and 5–10 cm soil depths and analyzed for As, Fe, Mn and P concentrations. For root-sample collection, the soil sub-samples were immersed in water in a plastic container to disperse the soil particles and the roots were separated by sieving with a 10-mesh sieve.

Soil and plant analyses

The organic-matter content of soil was determined by the wet oxidation method of Walkley and Black (1975), total-N content by the Kjeldahl method (Bremner and Mulvaney 1982) and the available-P content by the $NaHCO_3$-extraction method Olsen and Sommers (1982). For the determination of total Fe, Mn, P and As concentrations, soil and plant (root, straw and grain) samples were separately digested using a HNO_3 followed by H_2O_2 digestion mixture in open vessel. Total Fe and Mn concentrations were determined by flame atomic absorption spectrophotometry, and P concentration was determined colorimetrically by the phosphomolybdate ascorbic-acid method (Olsen and Sommers 1982). Total-As concentration was determined by flow-injection hydride-generation flame-atomic-absorption spectrophotometry (FI-HG-FAAS) (Samanta et al. 1999), using a UNICAM 969 FAAS. A certified rice flour reference material (NIST SRM 1568) was used in each analysis batch, and total As recovery was 88±5% (*n*=10).

Statistical analysis

Data were statistically analyzed and the mean values were compared using Duncan's Multiple Range Test (DMRT) (Gomez and Gomez, 1984) with the software package MSTAT-C, Dept. of Crop and Soil Science, Michigan State University. Correlation analysis was made between plant concentrations of As and nutrients (n=20).

Results

Arsenic accumulation in soil

The initial soil-As concentration was 2.9–3.0 μg g^{-1} at 0–15 cm depth and then gradually increased to 6.3 μg g^{-1} at 20–25 cm, below which the As concentration was relatively constant to 40 cm depth. Very little changes from the initial soil-As concentrations were observed in the control during the 2-year experiment.

As addition in irrigation water during crop growth or directly to soil before transplanting of rice (February–May, 2004, 2005) significantly increased soil-As concentrations (Fig. 1). For soil applied As, the As concentrations were greatest in the 5–10 cm and 10–15 cm soil layers, before decreasing to levels close to that of control treatment below 25 cm depth. For the two irrigation-water As treatments, the concentrations of soil As were highest in the top two layers, i.e. to 10-cm depth, then decreased to levels close to that of the control below 20-cm depth. Although As-concentration differences between the As-treated and control soils below 20 cm (irrigation-As treatments) or 25 cm (soil-As treatments) were relatively small, they were still significant, indicating some downward movement of As through the soil column. The maximum soil-As concentrations for the As-treated soils ranged from 10–23 μg g^{-1} and generally reflected the relative amounts of As added, i.e. 150, 300, 310 and 620 mg $core^{-1}$, or a ratio of 1:2:2:4, for the I-As_1, I-As_2, S-As_{10} and S-As_{20} treatments, respectively.

Mass balance calculations indicated that 69.8% and 62.3% of the total irrigation-water As was retained within the 0–40 cm soil column for the I-As_1 and I-As_2 treatments, respectively (Fig. 2). For the soil-As additions, the As retention was 67.8% and

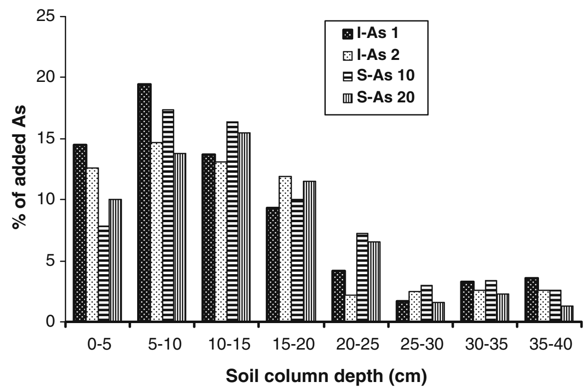

Fig. 2 Per cent retention of added As in different soil depths

62.5% for the S-As_{10} and S-As_{20} treatments, respectively. In both cases, the bulk of the As (51–57%) was retained in the 0–20 cm soil depth. Comparatively, 10–16 % of the total applied As was found at the 20–40 cm soil depth, which is below the plow layer. Retention of As in the soil layers below 25 cm varied somewhat between treatments but was about 2% of the total applied As in each of the three soil layers collected.

Effects of As treatment on rice growth and grain yield

In the first year (2004), the I-As_1 irrigation-water treatment had no effect on rice growth in either season. The I-As_2 treatment significantly reduced grain and straw yields of BRRI dhan 29 in the *Boro* season, but had no effect on BRRI dhan 33 in the T. *Aman* season (Table 1). The reduction in the yield of BRRI dhan 29 was associated with fewer tillers. The lower level (S-As_{10}) of addition of As to soil resulted in reduced grain and straw yields and tiller numbers of BRRI dhan 29 substantially more than the I-As_2 treatment although these treatments represented similar amounts of total applied As. The effect of the S-As_{10} treatment on BRRI dhan 33 was similar to that of the I-As_2 treatment and yields were significantly lower than that of the control treatment. The higher level of soil As addition (S-As_{20}) reduced the productivity of BRRI dhan 29 even further and also caused a further significant reduction in the yield of BRRI dhan 33. With subsequent additions of As in the second year (2005) of the study, all As treatments resulted in significant reductions in crop yield, in both seasons, and the impact increased with greater As additions with both the irrigation-water and soil As treatments.

Table 1 Effects of irrigation water and soil added As on grain yield, straw yield and tillers of rice during 2004 and 2005

Arsenic treatment	Grain yield (g core^{-1})				Straw yield (g core^{-1})				Tillers core^{-1}			
	Boro 2004	T. *Aman* 2004	*Boro* 2005	T. *Aman* 2005	*Boro* 2004	T. *Aman* 2004	*Boro* 2005	T. *Aman* 2005	*Boro* 2004	T. *Aman* 2004	*Boro* 2005	T. *Aman* 2005
I-As_0	57.2a	48.6a	68.7a	43.0a	60.5a	49.5a	69.4a	47.9a	22.0b	22.3	23.8a	17.0a
I-As_1	60.8a	44.6ab	52.7b	36.2b	63.6a	46.1a	54.0b	43.4a	24.5a	22.0	21.3ab	17.0a
I-As_2	45.5b	43.6ab	47.8c	24.1c	51.0b	44.4a	52.6b	30.1b	20.0b	20.0	20.0b	14.8a
S-As_{10}	24.9c	42.2b	48.8bc	14.5d	28.5c	45.1a	55.0b	20.8c	13.0c	20.5	18.8b	8.3b
S-As_{20}	14.8d	29.8c	31.6d	8.6e	16.8d	31.2b	32.9c	17.1c	10.5d	17.5	13.8c	7.0b
CV (%)	7.06	7.76	5.79	8.53	9.35	7.46	7.49	10.43	7.99	15.60	10.07	15.01
SE (±)	1.44	1.62	1.45	1.08	2.07	1.61	1.96	1.66	0.79	NS	0.99	0.96

I-As_0=no addition of As; I-As_1, I-As_2 =1, 2 mg As L^{-1} irrigation water, respectively; S-As_{10}, S-As_{20} =10, 20 mg As kg^{-1} soil, respectively

As added in two *Boro* crops only (2004 and 2005)

Means followed by same letter are not significantly different at 5% level by DMRT

The application of As exclusively to *Boro* rice over the soil-As and irrigation-As treatments resulted in yield reductions from 0 to 74 % in *Boro* rice (cv. BRRI dhan 29) and 8 (not significant) to 80 % in T. *Aman* rice (BRRI dhan 33), indicating a strong residual effect of added As on the next crop. Similarly straw yield was reduced by 16–72 % in the *Boro* season and 7–64 % in the T. *Aman* season. Corresponding reductions in tiller numbers were 0–52 % and 0–22 %. Plant height and grains panicle^{-1} (Supplemental SI Table 1) were also significantly affected by the As treatments. Grain yield across season and treatment was positively correlated with tillers pot^{-1} (r=0.95, P<0.01, n=20) and grains panicle^{-1} (r=0.87, P<0.01, n=20), indicating that the addition of As reduced grain yield through reduced tillering and fewer grains panicle^{-1}. These results indicate substantial adverse effects of added As on the two rice varieties utilized in this study.

Concentrations of As in rice grain, husk and straw

The As concentrations in rice grain, straw and husk followed the order grain<husk<straw and consistently increased with the level of As addition in each cropping season. Grain-As concentration increased from values of 0.22–0.32 µg g^{-1} with the As_0 treatment to 0.59–0.81 µg g^{-1} with the S-As_{20} treatment, but varied inconsistently between the varieties over the 2 years. The As concentrations in rice straw varied over season and treatment varied from 2.6 to 12.5 µg g^{-1} and, apart from the As_0 treatment, were higher in BRRI dhan 29 than BRRI dhan 33 (Table 2). The ratio of As concentrations in straw:grain was 12 for both varieties in the As_0 treatment and increased with As additions to ~20–24 with BRRI dhan 29 and to ~12–16 with BRRI dhan 33. The As concentrations in rice husk ranged from 1.2 to 2.5 µg g^{-1}, or 3–6 times that in grain, with no clear difference between the varieties.

Plant root concentrations of arsenic, iron, manganese and phosphate

The measurements of root concentrations of As, Fe and P included the Fe-oxide plaque and adsorbed inorganic As species and phosphate that are on the surface of the root as well as the amounts of these elements that are within the root. The root-As concentration varied with soil depth and treatment, with As concentrations generally lower in the roots at the 0–5 cm soil depth compared to the 5–10 cm depth. In the roots from 0–5 cm soil depth, the mean As concentration with the As_0 treatment was 88.5 µg g^{-1}, which increased 3.9, 4.0, 4.4 and 6.1 fold with the I-As_1, I-As_2, S-As_{10} and S-As_{20} treatments, respectively (Table 4). Similarly at the 5–10 cm soil depth, the lowest root As concentration of 149 µg g^{-1} was observed with the As_0 treatment and 2.9 to 5.0 fold higher root-As concentrations were observed with the various As treatments. The Fe concentrations for the irrigation-As treatments

Table 2 Effects of irrigation water and soil added As on As concentrations in rice grain, straw and husk during 2004 and 2005

Arsenic treatment	Grain As (μg g^{-1})				Straw As (μg g^{-1})				Husk As (μg g^{-1})			
	Boro 2004	T. *Aman* 2004	*Boro* 2005	T. *Aman* 2005	*Boro* 2004	T. *Aman* 2004	*Boro* 2005	T. *Aman* 2005	*Boro* 2004	T. *Aman* 2004	*Boro* 2005	T. *Aman* 2005
I-As_0	0.22d	0.32d	0.32c	0.22d	2.66d	2.67e	2.64d	2.65d	1.30d	1.32c	1.20c	1.32c
I-As_1	0.37c	0.45c	0.48b	0.37c	8.87c	4.79d	9.59c	5.54c	1.67c	1.90b	2.09b	1.81ab
I-As_2	0.42bc	0.58b	0.56ab	0.49b	10.19b	6.06c	10.34 bc	6.00c	1.79c	2.07ab	2.35ab	1.89a
S-As_{10}	0.44b	0.56b	0.57a	0.51b	10.35b	7.49b	11.25b	8.10b	2.02b	2.07ab	2.17b	1.70b
S-As_{20}	0.59a	0.81a	0.65a	0.65a	12.14a	9.98a	12.52a	10.32a	2.17a	2.24a	2.48a	1.98a
CV (%)	10.03	9.19	9.91	4.11	8.08	8.85	8.43	7.63	4.85	6.06	8.47	6.72
SE (±)	0.02	0.025	0.025	0.009	0.357	0.274	0.391	0.249	0.043	0.06	0.087	0.059

I-As_0=no addition of As; I-As_1, I-As_2 =1, 2 mg As L^{-1} irrigation water, respectively; S-As_{10}, S-As_{20} =10, 20 mg As kg^{-1} soil, respectively

As added in two *Boro* crops only (2004 and 2005)

Means followed by same letter are not significantly different at 5% level by DMRT

remained approximately the same as that of the control, but for the soil-As treatments the root Fe concentrations decreased by 17–40% compared to the control. Unlike root-Fe concentrations, the root-Mn concentrations were relatively unaffected across As treatment. The root-P concentrations with the four As treatments increased by 12–13 % relative to that of the control.

Nutrient concentrations in rice grain

Application of As either through irrigation water or directly to soil resulted in decreased P concentration in rice grain, irrespective of variety (Table 3). The concentrations of P in rice grain over season and treatment ranged from 0.13 % with S-As_{20} to 0.20% with As_0 treatment. Likewise, the rice-grain K concentration decreased significantly with increasing irrigation-water or soil As concentration (Table 3).

Relationships between As in plant parts and with other elements

There was a significant, positive correlation between grain-As and straw-As concentrations with each variety over the 2 years (BRRI dhan 29, $r=0.83$, $p<0.01$; BRRI dhan 33, $r=0.86$, $p<0.01$). Grain-As concentration was positively correlated with root-As concentration for BRRI dhan 33 in 2005 ($r=0.83$, $p<0.01$). Grain-As concentration was significantly and negatively correlated with grain-P concentration (BRRI dhan 29, $r=-0.91$, $p<0.01$; BRRI dhan 33, $r=-0.54$, $p<0.05$) and grain-K concentration (BRRI dhan 29, $r=-0.86$, $p<0.01$; BRRI dhan 33, $r=-0.39$, $p<0.05$). There was no significant correlation between grain-As concentration and grain-N or grain-Mn concentration.

Discussion

Comparative As accumulation in soil at different depths

After 4 cropping seasons and 2 years, most of the As added via soil amendment or irrigation water was retained in the 0–20 cm soil depth with only 10–16% found in the 20–40 cm depth. The soil-As concentration at 0–20 cm depth with the 20 mg kg^{-1} soil-As treatment was 7.6 times higher compared to that with the As_0 treatment, while at the 35–40 cm soil depth it was only 1.2 times higher. This result indicates a relatively low mobility of As in this paddy soil. The surface horizons provided a good sink for As that largely prevented its transport to deeper soil horizons, although the high levels of applied As and the continuous flooding throughout the 2-year period would have maximized the potential for As solubility and As leaching. This trend has significant implications to plant growth, since the applied As is predominantly retained within the plant root zone where As is more accessible for uptake by the rice

Table 3 Effects of irrigation water and soil added arsenic on P and K concentrations in rice grain during 2004 and 2005

Arsenic treatment	Grain P (%)				Grain K (%)			
	Boro 2004	T. *Aman* 2004	*Boro* 2005	T. *Aman* 2005	*Boro* 2004	T. *Aman* 2004	*Boro* 2005	T. *Aman* 2005
I-As_0	0.20a	0.19a	0.20a	0.15a	0.27a	0.24a	0.26a	0.22a
I-As_1	0.20a	0.16b	0.14b	0.14ab	0.22b	0.22b	0.20b	0.19b
I-As_2	0.18b	0.14c	0.14b	0.14ab	0.22b	0.16c	0.19b	0.18c
S-As_{10}	0.17b	0.13c	0.15b	0.13bc	0.21b	0.17c	0.19b	0.18c
S-As_{20}	0.15c	0.13c	0.11c	0.12c	0.22b	0.22b	0.14c	0.18c
CV (%)	7.66	9.20	13.56	9.25	7.31	10.05	10.64	4.93
SE (±)	0.007	0.006	0.01	0.005	0.008	0.01	0.01	0.005

I-As_0=no addition of As; I-As_1, I-As_2 =1, 2 mg As L^{-1} irrigation water, respectively; S-As_{10}, S-As_{20} =10, 20 mg As kg^{-1} soil, respectively

As added in two *Boro* crops only (2004 and 2005)

Means followed by same letter are not significantly different at 5% level by DMRT

plant and would have the greatest potential impact on plant metabolic processes. Similar As-retention patterns were observed in the previous net-house study with undisturbed soil columns, where greater than 70% of irrigation-water As was retained in the surface soil horizons (Khan et al. 2009).

Higher As concentrations were observed in the roots in the 5–10 cm than in the 0–5 cm depth which imply either mobility of applied As or more oxic conditions and less arsenic solubility in the top layer. The extent of As retention is impacted by many soil, environmental and crop management factors; however, a predominant factor under flooded rice culture is the availability of As-adsorption sites to prevent the downward mobility of dissolved As. The proportion of As retained was only slightly greater at the lower concentration of applied As, e.g., 57 and 52 % of irrigation-water As was retained in the 0–20 cm zone with the I-As_1 and I-As_2 treatments, respectively. This result suggests significant movement or loss of As from top soil (0–20 cm).

High accumulation in the soil surface layers of As applied in irrigation water has been reported by other researchers. It was our previous observation from soil-column net-house experiment (Khan et al. 2009) that the increases in soil As concentration at the 0–15 cm depth was 1.7–3.0 mg kg^{-1} year⁻when 1 mg As L^{-1} was added in irrigation water during the *Boro* season. Islam et al. (2005) had previously concluded that the concentration of As in the rice field would increase by 0.50 mg kg^{-1} $year^{-1}$ when 0.10 mg As L^{-1} is added in irrigation water to *Boro* rice. Similarly, Meharg and Rahman (2003) estimated that if the field is irrigated with 0.1 mg As L^{-1} irrigation water, soil As would increase by 1 mg kg^{-1} per year.

Norra et al. (2005) reported that the As concentration in the upper most soil layers of the rice paddy field (38 mg As kg^{-1}) was roughly twice as high as that in the soil of the less intensively watered wheat field (18 mg kg^{-1}) and more than 5 times higher than that of a soil (7 mg As kg^{-1}) of a rice paddy irrigated with uncontaminated water. Peryea et al. (1994) examined the vertical distribution of As in contaminated field soils and found that most of the As was restricted to the upper 40 cm of soil. Saha and Ali (2007) observed an enrichment of As in the top soil of rice fields irrigated with As contaminated ground water. In contrast, Dittmar et al. (2007) observed that As accumulated in the top soil during the *Boro* season was largely lost during the monsoon season and suggested leaching as a possible mechanism. Later, Roberts et al. (2009) observed that monsoon floodwater removed 13–62% of the As added to paddy soils through irrigation at this site, which was under deepwater and connected to a river in the summer season. These authors suggested that soils not subject to monsoon flooding are particularly risk of As accumulation. The current study and other studies as summarized above support this conclusion, in that solubilization and columnar leaching of dissolved soil As is not a major factor where soils are also cropped to rice in the monsoon season. In our case continuous flooding of soil maximized the opportunity for leaching.

Reduction in rice yield

Both grain and straw yields decreased significantly with As addition in irrespective of season, year, and method and level of As application. Generally higher levels of As addition of As resulted in greater reduction in yield. Similar amounts of total As were added with the I-As_2 and S-As_{10} treatments, but higher yield reduction was observed with the S-As_{10} treatment. The As_{10} treatment likely resulted in greater toxicity to rice because the total amount of soil As was added at the very beginning (just prior to transplanting) while the irrigation-As was distributed gradually over the growing period. The yield *of T. Aman* in 2005 was more detrimentally affected than that of *Boro* rice, indicating a strong residual effect of As addition during the *Boro* season.

Studies of As accumulation in soils (Heikens et al. 2007) have suggested that the long-term use of As-contaminated water for irrigation would result in an increase soil-As concentration, which has long-term implications to crop productivity and food quality. Yield reduction in rice as a result of long term use of As contaminated irrigation water has recently been demonstrated by Panaullah et al. (2009). Our finding that rice grain yields were negatively correlated with the quantity of As addition to soil, either directly or via irrigation water is in good agreement with the previous observation. In addition, the high retention of applied As in the upper soil layers is important, since most of the As remained in the rice rooting zone, where it would have the greatest impact on plant growth.

Arsenic accumulation in rice

Arsenic concentration in rice straw, husk and grain increased with increasing As addition whether via irrigation water or direct addition to soil. For the same reason, the grain-As concentrations of both *Boro* and T. *Aman* rice were consistently higher in 2005 than in 2004, attributable to the effect of residual As and the renewed application of As. The grain-As concentrations resulting from the irrigation-water As treatments were lower than those with the soil-As treatments, indicating that the quantity of As addition was a dominant factor impacting grain-As concentration. Duxbury et al. (2003) observed 1.5 times higher As concentrations in rice grown in the winter or dry season (*Boro* rice) than in the summer (monsoon) season (T. *Aman* rice), consistent with the use of groundwater for irrigation in the *Boro* season but not the T. *Aman* season.

Relatively high As concentrations in Bangladeshi rice grain, attributable to high irrigation water or soil As concentrations have been reported by some other researchers. For example, Hossain et al. (2008) reported that the concentration of As in rice grain of *Boro* rice increased significantly with increasing As concentrations in soil induced by use of As contaminated irrigation water. Williams et al. (2006) reported higher As concentrations in rice grain in southwestern Bangladesh where As contaminated irrigation water was used for irrigation, compared to areas without As contamination of irrigation water.

Relationship of grain As concentration with nutrient concentrations and grain yield

The significant negative correlations of grain As concentration with grain-P and grain-K concentrations suggest that As toxicity can affect nutrient uptake. Williams et al. (2009) concluded from pot culture and field survey studies in Bangladesh that arsenic contamination can limit trace-mineral nutrition (Se, Zn, and Ni) in *Boro* rice grain and result in marked yield reduction. The reduced uptake of P in As-treated plots might also be attributed to phosphate-arsenate competition during adsorption by roots. Plant roots absorb arsenate by means of the phosphate transporters, resulting in competition of these two ions for absorption by the rice plant (Abedin et al. 2002). Hence, soil As concentration can be an important factor that can impact P uptake by plants and vice-versa. A significant negative correlation was observed between grain yield and grain-As concentration, which indicates a detrimental impact of As on rice-grain yield. The results taken together indicate that there is a loss of grain yield and a deterioration of grain quality (i.e., higher grain-As concentration) from As contaminated irrigation water or soil. These factors directly and indirectly impact both food security and human health.

Arsenic mass balance

The As balance at the end of the experiment accounted for 63 to 70% of the arsenic added (Tables 4 and 5).

Table 4 Effects of irrigation As additions on root As, Fe, Mn and P concentrations for T. *Aman* rice 2005

Arsenic treatment	Soil depth (cm)	As conc. (μg g^{-1})	Fe conc. (%)	Mn conc. (μg g^{-1})	P conc.(%)
I-As_0	0–5	88.5 ± 23.2	6.20±0.73	449.9±87.8	0.10±0.01
	5–10	148.8 ± 27.5	7.20 ± 1.32	415.7±45.0	0.10±0.02
I-As_1	0–5	349.2 ±112.6	6.30±0.63	446.1 ± 107.2	0.12±0.03
	5–10	566.8 ±164.1	7.69 ± 1.25	447.2 ± 100.0	0.14±0.04
I-As_2	0–5	356.2 ± 86.7	6.35 ± 1.46	419.7 ±75.9	0.13±0.02
	5–10	682.8 ± 179.1	7.88 ± 2.65	440.7±57.3	0.13±0.03
S-As_{10}	0–5	389.0±38.5	5.35 ±1.06	510.4±99.0	0.12±0.01
	5–10	429.2 ± 105.6	4.36 ± 1.45	426.1 ± 55.5	0.12±0.02
S-As_{20}	0–5	539.6 ± 164.6	5.15 ± 1.34	420.3 ± 107.0	0.13±0.02
	5–10	741.9±336.6	4.82 ± 2.04	401.6 ± 118.0	0.13±0.03

I-As_0=no addition of As; I-As_1, I-As_2 =1, 2 mg As L^{-1} irrigation water, respectively; S-As_{10}, S-As_{20} =10, 20 mg As kg^{-1} soil, respectively

As added in two *Boro* crops only (2004 and 2005)

Most of the added arsenic was retained in the 0–25 cm layer. A small, and consistent, amount of added As was found in the 5 cm depth increments between 25–40 cm, suggesting that some As could have moved deeper in the profile. Leaching losses measured in an earlier confined column experiment with essentially the same soil were a maximum of only 3% of the applied As (Khan et al. 2009) and it is unlikely that this would be very different in the current experiment. However, there is also the possibility of bypass flow along root channels and column walls or some horizontal loss of As from the soil column by gravity induced mass flow when water heights inside and outside the column were not identical. Volatilization losses are another possibility but were not measured.

Implications to rice cultivation in south Asia

In the current study, the As from irrigation of *Boro* rice over 2 years accumulated predominantly in the plow layer (0–15 cm depth), with a relatively small proportion of the total applied As leached to deeper horizons. These results corroborate results of a previous nethouse study (Khan et al. 2009). The predominant accumulation of As was in the active

Table 5 Arsenic budget for irrigation water-soil-rice plant system

Arsenic treatment	Total added As mg $core^{-1}$	Total As in grain	Total As in straw	Total As in husk	Total As retained in soil	Total As recovered	Recovery of added As (%)
As_0	0	0.04	0.60	0.08	187.10	187.82	–
As_1	150	0.06	1.54	0.10	291.74	293.44	70.41
As_2	300	0.06	1.52	0.09	373.75	375.42	62.53
As_{10}	310	0.05	1.42	0.08	397.23	398.78	68.05
As_{20}	620	0.04	1.10	0.05	574.70	575.89	62.59

As_0=no addition of As; As_1, As_2 =1, 2 mg As L^{-1} irrigation water, respectively; As_{10}, As_{20} =10, 20 mg As kg^{-1} soil, respectively

As added in two *Boro* crops only (2004 and 2005)

% recovery of added As={As accumulation by soil & plant in the treated core(mg)}—{ As in soil & plant in the As control core(mg)} / Total As added to the core (mg)×100 rooting zone of the rice plant, where it has the greatest potential impact on As uptake and plant metabolic processes. The arsenic treatments did indeed lead to both decreased grain yields and increased grain-As concentration. Continued long-term irrigation with As-contaminated water represents a potential risk to food security and sustainable rice production in Bangladesh as well as to grain quality (as expressed in grain-As concentration). The findings of the present study have implications to other countries in central south and south-east Asia. Household studies in Bangladesh and West Bengal, India have shown that for the people who suffer from poisoning due to elevated As in drinking water, a substantial proportion of the total ingested As can come from rice (Kile et al. 2007; Ohno et al. 2007; Mondal and Polya 2008). Recently, rice has been identified as an important route of exposure to inorganic-As in the Red River Delta, Vietnam where groundwater has high As concentrations (Agusa et al. 2009). Arsenic contamination of groundwater and/or soils and its potential implications to food security and food quality is also a big concern in the Nepal terai, Myanmar (Irrawady), and Cambodia (Mekong) (Heikens et al. 2007). Soil, crop and irrigation-water management strategies are urgently needed to minimize the potential detrimental consequences of As contamination.

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