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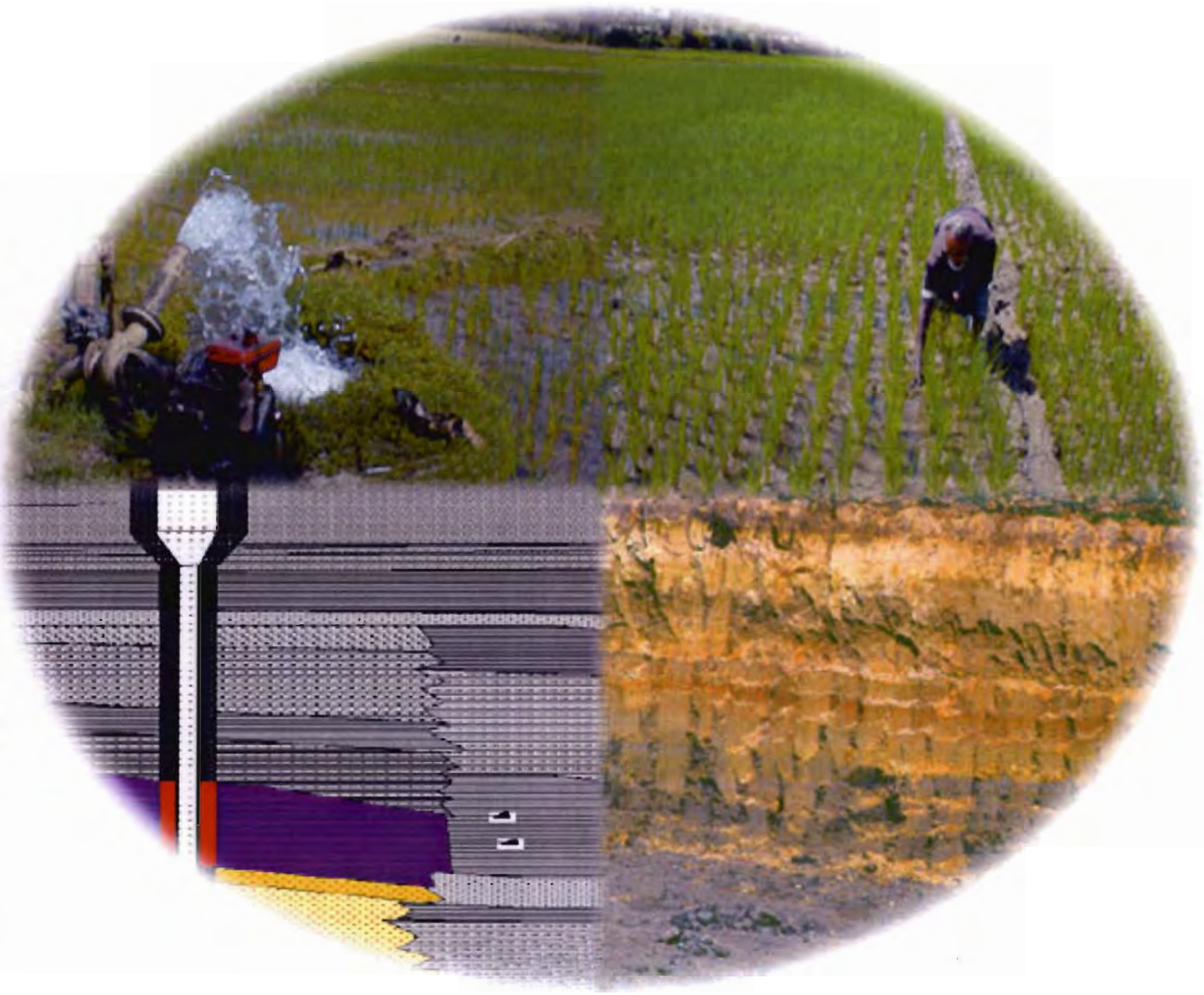
Symposium

Behavior of Arsenic in Aquifers, Soils and Plants: Implications for Management

Dhaka, January 16-18, 2005



Organized by: International Maize and Wheat Improvement Center (CIMMYT)
Cornell University (CU)
Texas A&M University (TAMU)
United States Geological Survey (USGS)
Geological Survey of Bangladesh (GSB)

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SYMPOSIUM

Behavior of Arsenic in Aquifers, Soils and Plants: Implications for Management

Dhaka, January 16-18, 2005

PROGRAM

Day 1 : January 16, Sunday, 2005

Inaugural Session: 1000 – 1115 hrs
Refreshments: 1115-1145 hrs

Technical Sessions

Theme I: Arsenic in Aquifers

Session 1: 1145-1300 hrs

Chair: Prof. Monirul Haque, Member, University Grants Commission
Rapporteur: Mr. AKM Khorshed Alam, Director, GSB

1. Introduction to aquifer studies : J. Whitney, 10 min

2. Potential disease burdens associated with different sources of groundwater in arsenic mitigation : Guy Howard, 20 min

3. Geological set-up and arsenic distribution of Kachua and Rajoir Upazila, Chandpur and Madaripur Districts, Bangladesh: M. Nehal Uddin, 25 min

4. Subsurface geology and geochronology studies of deep aquifers in the Bengal Delta: J.C. Yount, 20 min

Lunch: 1300-1400 hrs

Session 2: 1400-1700 hrs

Chair: Mr. M. Mizanur Rahman, Director General, GSB
Rapporteur: AKM Khorshed Alam, Director, GSB

1. Resistivity survey for mapping and characterization of deep aquifer in Kachua and Rajoir Upazilas of Chandpur and Madaripur Districts: Idris Miah, 15 min

2. Aquifer delineation in Kachua, Chandpur, SW Bangladesh by borehole logging: Razib Mostafa, 20 min

3. Investigation, characterization and mapping of the aquifer system in the Kachua Upazila Area, Southeastern Bangladesh: A. Zahid and D. Clark, 40 min

Tea: 1520-1540 hrs

5. Groundwater quality in two areas of Bangladesh: Implications for development of a safe water supply: A. Welch, 25 min

6. Geochemical characterization of sediment from deep aquifers in southern Bangladesh: G. N. Breit, 25 min

7. Arsenic in Bangladesh groundwater: From science to mitigation: Alexander van Geen, 30 min

Discussion: 1700-1715 hrs

Day 2: January 17, 2005

Session 3: 0930-1300 hrs
Chair: Mr. Abu Bakar, Former Director General, GSB
Rapporteur:

1. Not just red or green: An analysis of arsenic data from 15 Upazilas in Bangladesh: J. Rosenboom, 30 min

2. The temporal stability and spatial distribution of arsenic in Bangladesh: Mahfuzar Rahman, 20 min

Discussion: 10 min

Tea: 1030-1045 hrs

3. Oxidized aquifers as an arsenic free groundwater source, case study Matalab Upazila: Mattias von Bromsen, 25 min

4. Arsenic attenuation by oxidized aquifer sediment in Bangladesh: K. Stollenwerk, 30 min

5. Redistribution of arsenic and Iron in shallow sediment of Bangladesh: G.N. Breit, 30 min

6. Hydrogeologic analysis of the Bengal Delta: Numerical modeling of groundwater flow and seawater intrusion: M. Voss, 25 min

Discussion: 20 min

Lunch: 1305-1400 hrs

Theme II: Arsenic in irrigation waters, soils and crops
Session 1: 1400-1700 hrs

Chair: Prof. S.M. Imamul Huq, Dept. of Soil, Water and Environment, Dhaka University
Rapporteur: Dr. M.A. Saleque, BRRI

1. Arsenic in the irrigation water-soil environment and flows of arsenic in the food system: G. Panaullah, 15 min

2. Mineralogy and arsenic bonding in Bangladesh rice paddy soils: R. Loeppert, 25 min

3. Arsenic uptake and accumulation by rice: P. Williams, 25 min

4. Analysis of arsenic in water, soil, crop samples: B. Biswas, 15 min

Discussion: 15 min

Tea: 1535-1550 hrs

5. Arsenic in soils in 5 thanas of Bangladesh: Rafiqul Islam, 15 min

6. Arsenic in water, soil, rice in shallow tubewell command areas: A.T. M. Farid, 15 min

7. Nationwide survey of arsenic in soils, water and crops: M.A. Mazid Miah, 15 min

Discussion: 20 min

Day 3 : January 18, 2005

Session 2: 0930-1700 hrs
Chair: Dr. M. Shahidul Islam
Rapporteur: Prof. Rafiqul islam, BAU

1. Arsenic distribution in an irrigation command area: Baktear Hossain, 15 min
2. Arsenic mobility through the soil profile: Asaduzzaman Khan, 15 min
3. The water-soil-crop arsenic interrelationships: Zia Ahmed, 20 min
4. Effect of water management and arsenic-phosphorus interactions on arsenic uptake by rice: Hashim Talukder, 15 min

Discussion: 20 min

Tea: 1055-1115 hrs

5. Arsenic in irrigation water: Spatial variability: S. Kabir, 15 min
6. Spatial variability of arsenic in the environment and in rice – Debi Pau, 20 min
7. Arsenic in Bangladesh environment and its impact on food chain through crop transfer: I. Huq, 20 min
8. Arsenic in the Water-Soil-Crop Systems: PETRRA-BRRI-BAU-AAS Study: M. Jahiruddin, 15 min

Discussion: 20 min

Lunch: 1300-1400 hrs

9. Risk for contamination of Boro rice via groundwater: S. DeGloria, 20 min
10. Management strategies to reduce As uptake by rice: J. Lauren, 20 min
11. Safe levels of arsenic in food and the environment: How to assess? J. Duxbury, 30 min

Discussion: 20 min

Tea: 1530-1545 hrs

Symposium Concluding Session: 1545-1700 hrs

Chair: Prof. Feroze Ahmed, BUET
Rapporteur : Dr. Alex Heikens, Environmental Sciences, FAOR, Bangladesh

1. Aquifer summaries: D. Clark 10 min

2. Irrigation water-soil-crop summaries: 10 min

3. Recommendations presentations (deep aquifer use, drinking water, irrigation water-soil-crop research and risk assessment, education, training, national capacity building): J. Whitney, J. Duxbury, R. Loeppert, 25 min

4. General discussion: 25 min

5. Rapporteur's comments: Alex Heikens, 10 min

6. Concluding remarks by Session Chair.

Abstracts

Aquifer and Drinking Water Studies

USGS Arsenic Studies in South Asia : An Introduction

J. Whitney and David Clark
US Geological Survey

When significance of widespread arsenic contamination in West Bengal and then shortly thereafter in Bangladesh became international news, US Geological Survey scientists began to discuss appropriate ways to understand this new environmental health issue with their colleagues at the Geological Survey of Bangladesh. Having worked together on cooperative projects during the late 1980â€™s, USGS and GSB, supported by the U.S. State Department South Asia Regional Environmental Office, initially decided to characterize the shallow aquifers by examining the geochemistry and mineralogy of aquifer sediments in areas where both contaminated and uncontaminated wells were in close proximity. Initial studies were done on the active Meghna floodplain at two locations near Brahmanbaria, where soil bands with high concentrations of iron and arsenic were first observed.

A semi-permanent monitoring site was installed and sampled near Savar, west of Dhaka, in 2001-02. Eight piezometers were installed above, within, and below the arsenic-contaminated zone, and in the oxidized Madhapur sediments below the grey Holocene deposits. Geochemistry studies have been complemented by isotope studies in cooperation with BAEC and IAEA, by microbiology studies on water, and by luminescence dating of the aquifer sediments (University of Illinois at Chicago).

In 2003 a new project, funded by USAID, was undertaken to characterize the water quality of the deeper aquifers in the delta in order to determine whether deeper aquifers could be a medium- or long-term alternative drinking water source for areas where a high percentage of shallow wells are contaminated with arsenic. The Ministry of Local Governments and Rural Development agreed to support this effort through BAMWSP by covering costs of drilling, coring, well installation, sampling, and surface geophysics by BWDB and GSB. Dhaka University has supported this study with borehole geophysics in cooperation with USGS, and BAEC has conducted joint water sampling and analyses with the USGS. For the first time in Bangladesh, in situ samples were collected to depths over 450 m deep to examine the lithostratigraphy, geochemistry, and geohydrology of deeper aquifers in the delta.

Two study sites were selected and agreed upon by all participants. Both sites are located in areas where over 85 percent of the shallow wells are arsenic-contaminated. The first site is located in Srirampur village, Kachua upazila, Chandpur District. This site, drilled and sampled in 2003, appears to be representative of the southeastern delta north of the tidal zone belt. The second site is located in Rajoir headquarters, Rajoir upazila, Madaripur District. Drilled and sampled in 2004, the Rajoir site is believed to be representative of contaminated areas dominated by large active floodplains adjacent to large rivers. All data collected during the USGS cooperative studies of the shallow and deeper aquifers, and the interpretations and reports that result from those data will be made available to the public during this next year..

These studies would not have been possible without the outstanding cooperation between several scientific and government agencies within Bangladesh. The results of this work highlight the geologic and hydrologic complexity of the Bengal delta, and provide new insights into the arsenic contamination issue throughout the Ganges-Brahmaputra Basin.

Geochemical Characterization of Sediment from Deep Aquifers in Southern Bangladesh

G. N. Breit, H. A. Lowers, A. L. Foster, Ad. A. Muneem, Md. N. Uddin, J. Yount, J. W. Whitney, and C. J. Berry.

High concentrations of dissolved arsenic in shallow ground water in Holocene sediment of Bangladesh commonly are attributed to geochemical transformations within the sediment. Previous studies of relatively shallow sediment (<50 m) proposed that the arsenic is released by microbial reduction of ferric oxyhydroxides, oxidation of sulfide minerals or desorption from mineral surfaces (Nickson and others 1998; Chowdhury and others, 1999, Swartz and others, 2004). As part of our assessment of the residence and mobility of arsenic in the deeper aquifers, we analyzed sediment from depths to 450 m. Arsenic in deeper samples is primarily bound in pyrite that will remain immobile provided that oxidants are excluded from the deep aquifer.

Two deep bore-holes were cored at selected intervals by the Geological Survey of Bangladesh and Bangladesh Water Development Board in Rajoir upazilla, Madaripur district and Kachua upazilla, Chandpur district. Thirty-seven samples were collected from 10 to 450 meters depth at Rajoir and 58 samples were recovered from 7 to 390 meters depth at Kachua. The samples were consistently gray to green except for two yellow-brown samples collected at 378 meters at Rajoir and 46 meters at Kachua. Air-dried bulk samples were analyzed to determine chemical and mineral composition. Subsamples preserved in glass septa vials filled with argon and frozen were shipped to the United States for speciation analysis of iron, sulfur and arsenic.

Concentrations of selected components of the sediment are compared in table 1. Sulfur, organic carbon and arsenic have significantly greater concentrations in the Kachua samples than the Rajoir samples. This contrast is attributed tentatively to depositional conditions between the sites. Abundances of other elements are not significantly different. Vertical variations of element concentrations in each borehole are consistent with lithologic changes (sand, silt, and mud). Systematic variations in element concentrations with depth were not detected. Statistical analysis of the composition data identified five factors that explain much of the variance in sample composition (table 2). The factors for siderite and pyrite are the result of post-depositional redistribution of arsenic, sulfur, iron and manganese within the sediment in

response to changing chemical conditions, while the mica, rare earth element and plagioclase factors are attributed to the original composition of the detritus.

Figure 1 illustrates the vertical variation of arsenic and sulfur for each borehole. Arsenic and sulfur co vary for samples deeper than 80 meters. Assuming that the arsenic is contained in pyrite identified in these sediments by X-ray diffraction and the scanning electron microscopy, superposition of sulfur and arsenic points in Figure 1 corresponds to arsenic contents in the pyrite of 0.5 weight percent. This value is consistent with the range of arsenic concentration measured in pyrite from these sediments by electron probe microanalysis (<0.05 to 1.4 wt. %). X-ray absorption near edge structure spectroscopy analysis performed at the Stanford Synchrotron Research Laboratory verified that most arsenic in the deep aquifers is contained in pyrite. The low content of sulfur in the Rajoir sample at 378 meters depth is consistent with the presence of ferric oxyhydroxides indicating that this mud was not sufficiently reducing to preserve pyrite. The high content of arsenic in samples from approximately 326 meters depth in the Kachua borehole is similar to high arsenic concentrations in deep sediment reported by JICA (2002) at depths near 220 meters. The high content of arsenic in deep sediment supports the redistribution thousands of years prior to the arsenic problem in ground water, which supports the natural origin of the arsenic contamination. Arsenic and sulfur vary independently in the upper 80 meters of the boreholes relative to the deeper sediment, particularly for the Kachua borehole. The change at 80 meters is considered to be a product of changing depositional and diagenetic conditions.

Textures and the isotope data support diagenetic pyrite formation. Framboids with euhedral crystallites are the principal form of pyrite in the sediment. Massive and octahedral overgrowths on the framboids were detected; some overgrowths contain >0.9% As. Massive pyrite grains with abraded edges were interpreted as detrital and generally lack detectable arsenic. The $\delta^{34}S$ values of acid volatile sulfide and total reducible sulfur for 16 samples range from –9 to 40 per mil with a median near 0 per mil. Probable sources of sulfate are river water (4 per mil) and modern seawater (21 per mil), $\delta^{34}S$ values >21 per mil in 4 samples indicate reduction of sulfate along flow paths within the aquifers.

Subsidence and burial produces changing geochemical conditions that transform iron, arsenic, and sulfur species bound to the sediment. The form and solid phase residence of more than half of the arsenic in the sediment transported by the Ganges, Brahmaputra and Meghna

Rivers is affected by these changes, including the incorporation of arsenic within diagenetic pyrite. Recognition of the strong association of pyrite and arsenic in deep sediment within Bangladesh can account for the low concentration of dissolved arsenic in deep aquifers. Pyrite has a very low solubility; therefore arsenic is unlikely to leave the solid phase and enter the ground water. Pyrite is likely to remain stable in the deep aquifers as long as oxidants such as oxygen, nitrate and manganese oxides are excluded. Diagenetic partitioning of arsenic into pyrite may have occurred in older sediments shed during earlier stages of the Himalayan uplift. These sediments now eroding from the Indo-Burman range and Siwalik units may contribute to the arsenic flux of the modern Bengal delta by oxidation of contained pyrite.

References:

Chowdhury, U.K., Basu, G.K., Mandal, B.K., Biswas, B.K., Samanta, G., Chowdhury, U.K., Chanda, C.R., Lodh, D., Saha, K.C., Mukherjee, S.K., Roy, S., Kabir, S., Quamruzzaman, Q, and Chakraborti, D., 2000, Arsenic poisoning in the Ganges delta: Nature v. 401 p.545-546.

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Swartz, C.H., Blute, N.K., Badruzzman, B., Ali, A., Brabander, D., Jay, J., Besancon, J., Islam, S., Hemond, H.F., Harvey, C.F., 2004, Mobility of arsenic in a Bangladesh aquifer: Inferences from geochemical profiles, leaching data and mineralogical characterization: Geochimica et Cosmochimica Acta v. 68, p.4539-4557.

Table 1. Median and range of concentrations of selected elements in sediment samples from the Rajoir and Kachua boreholes. (range is in parentheses)

Bore-hole	Al (wt.%)	Fe (wt.%)	Ca (wt.%)	Mn (wt.%)	C_{org} (wt.%)	S (wt.%)	As (ppm)
Rajoir	4.9 (3.2-11)	2.1 (0.79-6.5)	0.83 (0.4-1.5)	0.047 (0.010 –0.28)	0.05 (<0.01 – 1.5)	0.01 <0.003 – 0.19	1.2 (0.6 – 22)
Kachua	4.8 (2.9-9.8)	2.3 (0.87-7.4)	0.69 (0.26-1.4)	0.057 (0.008-0.27)	0.17 (<0.01 – 0.7)	0.029 (0.002 –1.5)	2.9 (0.8 –190)

Table 2. Results of factor analysis on the total elemental composition of sediment samples from the Rajoir and Kachua boreholes.

Factors	Elements with high loadings
1: micas	Al, Fe, K, Mg, Ti, Cr, Cu, Ga, Li, Nb, Ni, Pb, Sc, V, Zn
2: REE	La, Ce, Nd, Y, P, Th, Yb,
3: siderite	Fe, Mn, C_{org}, C_{carb}
4: pyrite	As, S
5: plagioclase	Na, Ca, Sr

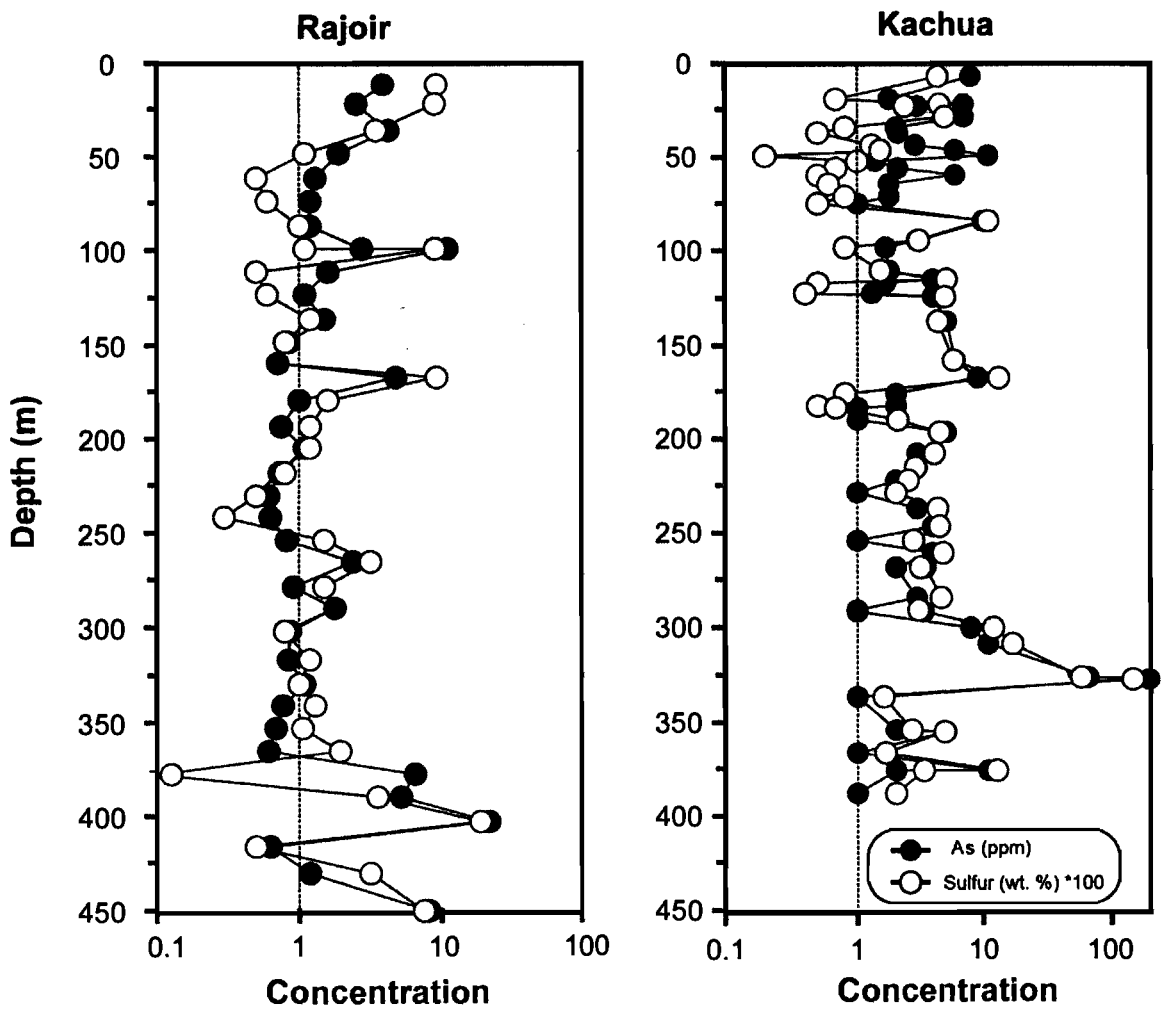


Figure 1. Concentrations of arsenic and sulfur in sediment samples from Rajoir and Kachua bore-holes.

Redistribution of Arsenic and Iron in Shallow Sediment of Bangladesh

G.N. Breit, H.A. Lowers, A.L. Foster, R.B. Perkins, J.C. Yount, J.W. Whitney, Md. N.l Uddin, and Ad. A. Muneem

Abstract

Shallow excavations (<5 meters) in eastern and southern Bangladesh typically expose sediment that changes color from yellow-brown to blue-gray across an abrupt boundary. This downward change marks the upper limit of water-saturated sediment. Mineralogical and chemical analyses of sediment samples determined that the oxidation state, and solid phase residence of iron, arsenic, manganese and sulfur are markedly different across the boundary. Given the proximity of these transformations to the ground surface, the role of land use should be considered in evaluating current and future impact on the release of arsenic to the environment.

Fifty-eight sediment samples from 25 excavations in the Brahmanbaria, Comilla, Chandpur, Dhaka, Faridpur, Manikganj, and Madaripur Divisions were collected. Thirty subsamples of 3 excavations were collected in glass septa vials that were purged with argon to preserve the oxidation state of iron and arsenic. Splits of these subsamples were treated sequentially with 0.5 N HCl (weak acid soluble species) and Ti^{3+}-EDTA (reducible species) to determine the amount and oxidations states of iron. Oxidation state and binding environment of arsenic were estimated further using X-ray absorption near-edge structure spectroscopy at the Stanford Synchrotron Research Laboratory.

Iron and arsenic are chemically reduced across the brown to gray boundary. The 0.5N HCl extracting solutions of the brown samples characteristically contain >98% of the extracted iron as ferric iron, while similar extractions of the gray sediment consistently yield <8% ferric iron. Results of the Ti^{3+} extraction recovered 76% of the total extracted iron from the brown sediment while only yielding 25% of extractable iron from the gray sediment. Goethite is the principal authigenic iron mineral in the brown sediment while gray sediment contains authigenic siderite, vivianite, pyrite and acid volatile sulfide minerals. Analysis of sediment by XANES determined that arsenic is

present as As^{5+} species associated with ferric oxides in brown sediment and As^{3+} of unknown residence in the gray. Reduction of oxidized species occurs as sediment is buried beneath the saturated zone because of microbial respiration of detrital and dissolved organic matter.

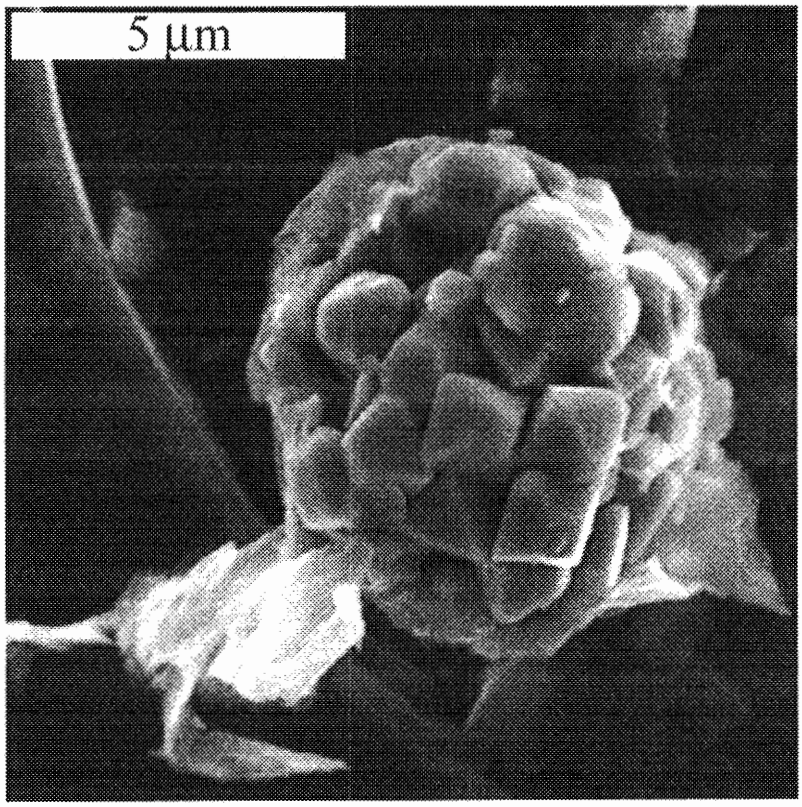
Walls of excavations in which the color transition is less than 3 meters below the ground surface typically expose an irregular subhorizontal layer enriched in ferric iron (up to 13 wt.%), arsenic (up to 760 ppm), and manganese (up to 1.7 wt.%). Layers in Brahmanbaria were traced laterally for approximately 1 km and a similar extent was indicated in Chandpur. Excavations with color transitions that are >3 m below the ground surface typically lack a distinct layer but contain similar element enrichments surrounding insect burrows and lining desiccation cracks. Within the ferric oxide enriched sediment, arsenic contents of goethite approach 2000 ppm while local grains of iron phosphate contain as much as 5 wt. % arsenic. Not all visible accumulations of iron oxides have similar element enrichments. Ferric oxyhydroxide accumulations developed in sediment beneath paddy fields and rimming shallow gray fine-grained sediment lack high arsenic contents and manganese enrichment is absent. Formation of the arsenic-rich ferric oxyhydroxide layers is attributed to oxidation of dissolved iron, arsenic and manganese near the top of the saturated zone. Arsenic is also oxidized and coprecipitated with forming ferric oxyhydroxides.

Gray sediment near the contact is typically enriched in sulfur (0.01 to 0.1 wt.%) compared to the brown sediment (<0.003 wt.%). Examination with the scanning electron microscope and sulfur speciation analysis determined that framboidal pyrite (Figure 1) and AVS phases are the dominant form of sulfur in this sediment. Electron probe microanalysis of the pyrite measured arsenic contents of <0.05 to 0.9 wt.% with a median value near 0.3 wt.%. Sulfur isotope compositions of 5 shallow gray sediment samples range from -0.4 to -10.5 per mil, which are consistent with microbial reduction of sulfate. A ferric oxide layer overlying gray sediment with high sulfur contents contains markedly lower contents of arsenic possibly as a result of trapping of reduced arsenic in pyrite.

The presence of high arsenic concentrations in goethite, iron phosphates and pyrite within 3 meters of the ground surface are a concern because of the sensitivity of these phases to changes in chemical conditions. Changes in depth of the saturated zone,

abundance of organic matter, and supplies of phosphate and sulfate as well as nitrate could modify the stability and abundance of phases containing arsenic. These factors are complexly interrelated, therefore further study of chemical changes in the shallow subsurface is encouraged to develop reliable evaluation of risk.

Figure 1. Scanning electron micrograph of pyrite framboid from gray sediment 2.5 meters below ground surface.



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Oxidised aquifers as an arsenic free groundwater source, case study Matlab Upazila, Bangladesh

Mattias von Brömssen[1], Prosun Bhattacharya[1], Kazi Matin Ahmed[2], Md. Jakariya[1,3], Linda Jonsson[1], Lisa Lundell[1] and Gunnar Jacks[1]

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[2]*Department of Geology, University of Dhaka, Dhaka 1000, BANGLADESH*
[3]*BRAC, BRAC Centre, 75 Mohakali, Dhaka 1212, BANGLADESH*

Extended abstract

INTRODUCTION

Naturally occurring (geogenic) arsenic in concentrations above the safe drinking water limit of World Health Organisation (WHO; 10 μg/L) is present in the groundwater of the Bengal Delta Plain (BDP), Bangladesh. As most of the population (98 %) are dependent on groundwater as their source of drinking water it has resulted in the exposure of nearly 35 million people.

Bangladesh is located at the head of the Bay of Bengal and is the largest sedimentary basin of the world. The basin is surrounded by the Tripura Hills in the east, an uplifted block of Precambrian Shield (Shillong Plateau) in the north, and a Precambrian basement complex (Indian Shield) in the west. The sediments are transported by the Ganges, Brahmaputra (Jamuna) and Meghna river systems that converge in this great delta complex - the Bengal Delta Plain (BDP). Three physiographic units characterize Bangladesh – the elevated Pleistocene terraces, the alluvial deposits of the Holocene lowlands and the Tertiary, hilly, areas of Chittagong in the southwest. The elevated concentrations of arsenic are associated with the Holocene aquifers and are mobilized through the reductive dissolution of iron oxy-hydroxides in reaction with organic matter after consumption of more favoured electron acceptors (BGS, 2001; Smedley and Kinniburgh, 2001; Bhattacharya *et al.*, 2002).

A number of safe-drinking water options such as household filters, pond sand filters etc. has been tested and implemented in high-risk areas. The results have not been very encouraging, as the different options have not been widely accepted by the people. In Matlab Upazila more than 82% of the tube wells have arsenic levels above the drinking water. During a recent field trip to Matlab Upazila in SE Bangladesh, it was found that local drillers prefer to install tube wells to a deeper depth than earlier (60 m instead of 30 m), primarily because of low iron in the groundwater. The sediments at this depth have been found to be reddish (described as red by the drillers) instead of the overlying greyish (described as black by the drillers). The reddish colour and the low concentrations of iron indicate that iron is present as oxy-hydroxide coatings on the sediments. As arsenic is adsorbed to the oxy-hydroxides of iron the groundwater can be used as a source of arsenic safe drinking water.

The objective of this study was to link the groundwater composition to the characteristics of the sediments in order to identify and target the presumed oxidised and safe aquifers for the installation of tube wells. As the use of tube wells,

as source for potable water is widely accepted, cheap and robust, this could be a viable option for safe drinking water.

METHOD

The local drillers of Matlab village were interviewed to see on how they identify good/safe water and if the presumed oxidised zone in the shallow aquifer could be identified. Next, 38 tube wells with known depth and sediment colour (at the depth where the groundwater is abstracted) were sampled. Thus, each groundwater sample could be linked to a certain type of sediment colour, and possible redox condition. In order to test the drillers knowledge of the subsurface geology, three new boreholes was drilled down to the depth of interest (60 m). Disturbed sediment samples were collected for ocular inspection. In two of the drillings new tube wells were installed and sampled. Parameters like pH, Eh and conductivity was measured in field. The samples (n = 40) were brought back to Sweden for analysis of major anions and cations, metals, DOC, etc.

RESULTS

The interviews and the work done together with the drillers showed that the presumed oxidised zone could be identified, both by the interviews and by the drillings that were done. In all drillings, a thick layer of black sediments overly a zone were the sediments are brownish, olive and yellowish in colour. The thickness of the black sediments varied between 40-50 m. Beside the texture of the sediment, four distinct colours were used by the drillers to describe the sediment in Matlab village, the colours were black, white, off-white and red (Figure 1). The lack of iron and the presence of red, white or off-white (i.e. not black) sediments were the most important parameter for the drillers when they defined good water.

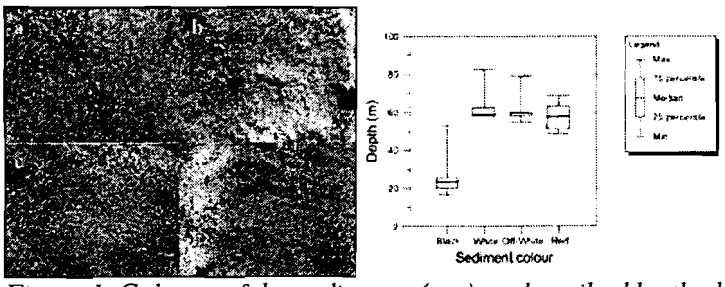

Figure 1. Colours of the sediments (wet) as described by the local drillers from the three drillings: a) black; b) white; c) red and d) off-white and their respective depth variation.

The groundwater was generally reducing with low concentrations of SO_4^{2-} and NO_3^- but with high concentrations of Fe_{tot} and Mn_{tot}. The groundwater had high HCO_3^- concentrations (60-500 mg/L), was of Na-Cl-HCO_3 or Ca-Mg-HCO_3 type (or a mix of them) and neutral or slightly acid (pH = 6-7). The arsenic (As_{tot}) concentrations varied between 0 and 355 µg/L.

The groundwater samples were classified in four groups with respect to the colour of the sediments from where they were abstracted (black, white, off-white and red). Basic statistics were done on each group and each group were presented in a box-diagram per analysed parameter. It was found that the four different groups represented a very distinct scale of groundwater composition with respect to the redox conditions. The water abstracted from black sediments was the most reduced, followed by white, off-white and red that was less reduced. However, all samples are considered to be reduced.

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The groundwater abstracted from the black sediment indicated a groundwater with relatively high concentrations of NH_4^+, DOC, Fe_{tot}, PO_4^{3-}, As_{tot} and relatively low Mn_{tot} and SO_4^{2-}. The concentrations of HCO_3^- were higher in the water extracted from the more reduced sediments compared to the less reduced ones while the opposite was found for Eh. The off-white and red sediments had higher Mn_{tot}- and lower Fe_{tot} concentrations which suggest Mn_{tot} reduction in these sediments. Consequently, neither iron nor arsenic is found in high concentrations in the groundwaters abstracted from the less reduced reddish/yellowish sediments as the reduction of iron oxy-hydroxides is buffered by Mn (Mn is reduced before Fe) in this zone (Figure 2). The groundwater had either high As or high Mn levels which is consistent with previous findings (BGS, 2001; Bhattacharya *et al.*, 2002).

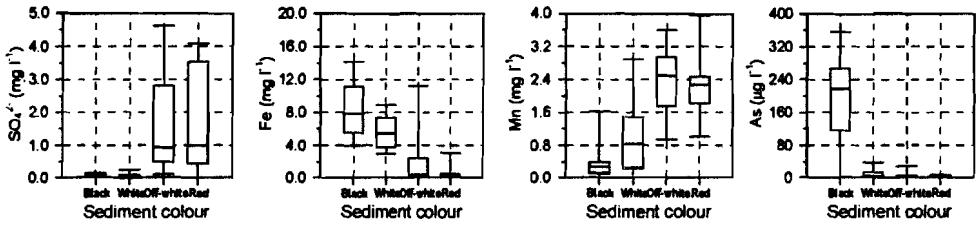

Figure 2. Box plots of selected redox parameters classified due to the colour of the sediment from where the water was extracted. From left, black, white, off-white and red.

CONCLUSION AND FURTHER STUDIES

On the basis of this study some conclusions can be drawn: *i)* arsenic is mobilised from grey (described as black by the drillers) sediments in reducing environments; *ii)* it is possible to estimate the relative risk of aquifers/sediments in terms of As mobilization if the characteristics of the sediments are known, and *iii)* it is possible to target safe aquifers by combining the indigenous knowledge and technique of the drillers along with modern geological and hydrogeochemical expertise.

A number of questions have not been answered by this study. Two of them are very important: *i)* Can the oxidised sediments be found elsewhere in Matlab thana and Bangladesh? And *ii)* are extractions of groundwater from these oxidised sediments a sustainable solution? What are the risks for cross contamination and depletion of the redox buffering minerals?

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Arsenic in Bangladesh Groundwater: from Science to Mitigation

Alexander van Geen, Kazi Matin Ahmed, Joseph H. Graziano

Abstract

Starting in January 2000, and in partnership with several Bangladeshi institutions, an interdisciplinary team of health, earth, and social scientists from Columbia University has focused its efforts to address this crisis on a 25 km2 region in Araihazar upazila, about 20 km northeast of Dhaka. The project started with the recording of the position and depth of ~6600 wells in the area, the collection of groundwater samples from these wells, and laboratory analyses for arsenic and a suite of other constituents. This was followed by the recruitment of 12,000 adult inhabitants of the area for a long-term cohort study of the effects of arsenic exposure, as well as cross-sectional studies of their children. This presentation will focus on (1) the extreme degree of spatial variability of arsenic concentrations in Bangladesh groundwater, (2) the notion that spatial variability hampers mitigation in the sense that it complicates predictions but also offers an opportunity for mitigation because many households live within walking or drilling distance of safe water, and (3) the implication of recent advances in our understanding of the mechanisms of arsenic mobilization for potential temporal changes in groundwater arsenic. In addition, (4) a unique data set documenting the response of 6500 households to 4 years of mitigation in Araihazar, supported by documented reductions in exposure to arsenic based on urine analyses, will be presented. The presentation will conclude with (5) a proposal for scaling up mitigation efforts to the rest of the country by targeting safe aquifers with information transmitted to the village level from a central data base using cellular phones. Additional information regarding some of these observations can be obtained from the following publications:

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Potential disease burdens associated with different sources of groundwater in arsenic mitigation

Guy Howard, Feroze Ahmed, Jafar Shamsuddin, SG Mahmud,
Daniel Deere and Annette Davison

Astract

Understanding the potential risks to health from different water sources is an area of increasing interest within the water and health sectors to support decision-making in water supply that will result in reduced risks to health. In Bangladesh, a risk assessment has been undertaken with support from the Arsenic Policy Support Unit (APSU) as a means to quantify potential health risks associated with different sources of water used in arsenic mitigation. This has included assessment of water quality at sites selected through cluster surveying, assessment of social acceptability of different sources and development of a quantitative health risk assessment model to estimate the potential disease burden from three reference pathogens and arsenic from different types of water source. This paper will present some of the findings from the risk assessment dealing with dug wells and deep hand tubewells under dry season and monsoon conditions.

The results show that overall water quality and potential disease burden associated with dug wells to be significantly greater than deep tubewells. However, the deep tubewells also show unacceptable levels of microbial contamination, primarily as a result of poor operation. Both technologies have a high degree of social acceptability, but there is a worrying lack of community involvement and management that suggests that there may be problems in long-term with operation and maintenance. The data shows the importance of addressing potential health risks associated with alternative water sources if public health risks are to be reduced. The data further indicate that whilst overall more robust in relation to microbial contamination, training of operators of deep tubewells in maintaining safe water is as important as for dug wells.

Resistivity Survey for Mapping and Characterization of Deep Aquifer in Kachua and Rajoir Upazilas of Chandpur and Madaripur Districts.

Idris Miah*, K. M. Shamsul Arefin**, M. Wahiduzzaman*** And K. K. Nag****

Abstract

Arsenic in groundwater is a new environmental health issue throughout the world. In Bangladesh the arsenic problem is becoming acute. Several older and newer techniques are being applied to understand and to solve this problem. Electrical resistivity is a well-established technique for groundwater investigations and aquifer mapping. This geophysical method can delineate water bearing layers and impervious clay layers. It can also detect zones of conductive saline water and iron-rich water. Considering these attributes, electrical resistivity surveys have been carried out in Kachua and Rajoir Upazilas of Chandpur and Madaripur Districts in 2003 and 2004 respectively. In both the areas the main objectives of the investigation were to delineate and map deep aquifers, and to determine their characteristics. Because impervious clay layers play a vital role in the formation of good aquifer, detection of the impervious layers was another main objective of the surveys. Schlumberger electrode configuration and Scintrex Resistivity Set were used for recording field data. In each of the areas data were recorded from fifteen deep Vertical Electrical Sounding (VES) probe locations. Maximum current electrode spacing of all the probes was kept at 1200m. However, in some cases this was not possible due to unusual field conditions. In those cases data were recorded from the largest possible spread. Two software programs were used to interpret the data. USGS software program ATO was used to obtain a preliminary idea about the subsurface. Based on this result, the final resistivity interpretation was done using the software program RESIXIP. Correlating the resistivity findings with known geology and available geoscientific information from the local people and DPHE, a number of geo-electric sections, panel diagrams, and resistivity and depth contour maps have been created.

Considering all the data and interpretations, we found that the resistivity of both the areas varies from few Ω -m to few hundred ?-m. Below topsoil and the near surface sediment, resistivity increases with depth. A significant variation of resistivity exists in the topsoil and near surface sediments. This may be due to different processes of sedimentation, artificial fill, wetness of the soil, and the presence of man-made materials. The subsurface consists of a number of discrete layers including aquifers. Known geology and other information provided by water authorities suggest that many shallow aquifers consist of medium to fine sand and are arsenic contaminated, which decreases with depth. Below a certain depth aquifers are generally found to be contamination free. Our study suggests that contamination decreases with the increase of resistivity. Resistivity interpretations of Kachua area suggest that there are two potable aquifers whose depths to the tops are 200m and 300m. Resistivity of the upper one is 75 Ω m to 100 Ω -m having thickness of around 100 m and resistivity of the deepest aquifer is few hundred Ω -m. These two aquifers are separated by a very low resistive (<10 Ω -m) thin layer that is interpreted as clay-shale layer. On the other hand, shallower aquifers of Rajoir are as arsenic contaminated as Kachua; however, their resistivity values are lower. Only one potable aquifer has been delineated in Rajoir area. The ranges of depth to the

top and resistivity are 150 m to 250 m and >50 Ω-m to <200 Ω -m respectively. A very low resistive (resistivity range 2 Ω -m to 6 Ω -m) layer lies just above this potable aquifer representing clay, silty clay, silty sand and perhaps even saline water. Thin clay beds of this layer probably prevent arsenic percolation downward from the contaminated aquifer to the deep potable aquifer.

Comparison between Kachua and Rajoir surveys highlight some striking features. Resitivity of arsenic-free aquifers are much higher and their resistivity values depend on the amount of conductive materials present such as iron, chloride, manganese, arsenic etc. So higher resistivity values may be considered as one of the important characteristics of arsenic-free aquifers. Very low resistive layers generally represent thin impervious clays and/or shale, which play a vital role for the preservation of arsenic-free aquifers. These important impervious layers, which protect deeper aquifers from percolation downward from contaminated aquifers, can easily be detected by the resistivity technique. Thus, the resistivity technique is an effective tool for the delineation of potable aquifers in arsenic contaminated areas.

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Hydrogeologic Analysis of the Bengal Delta:

Numerical Modeling of Groundwater Flow and Seawater Intrusion

Holly A. Michael and Clifford I. Voss

Abstract

A study of groundwater flow in the Bengal Delta of Bangladesh and India has been initiated at the U.S. Geological Survey as a means to better understand the processes controlling contamination problems in the region and to help manage use of groundwater resources. The research will result in a model that may provide a large-scale framework for understanding smaller-scale hydrologic and geochemical processes that are currently under investigation throughout the region. Initial work may focus on topics that include evaluation of the relative importance of regional vs. local flow as well as the sensitivity of the simulated groundwater systems to aquifer structure and properties. The effect of groundwater extraction on the spatial and temporal distribution of recharge, discharge, and flow pattern may be considered, with particular emphasis on recharge to deeper aquifers that do not currently produce water high in dissolved arsenic. Further exploration may include the evaluation of seawater intrusion, its progression in shallow and deep aquifers, and the vulnerability of near-coastal parts of the delta to heightened seawater intrusion due to changes in the magnitude and configuration of groundwater extraction.

Initial modeling of the delta is being carried out with the USGS-SUTRA groundwater flow and solute transport code, which has the capacity to evaluate the variable-density dynamics introduced by saltwater intrusion. The model structure will remain relatively simple in order to focus the evaluation on the major hydrogeologic controls on groundwater flow in the delta. This basic modeling framework will support the exploration of local flow regimes by providing a context for their regional interaction. Thus, current flow systems and the implications of future changes can be assessed on several scales.

Aquifer delineation in Kachua, Chandpur, SW Bangladesh by borehole logging

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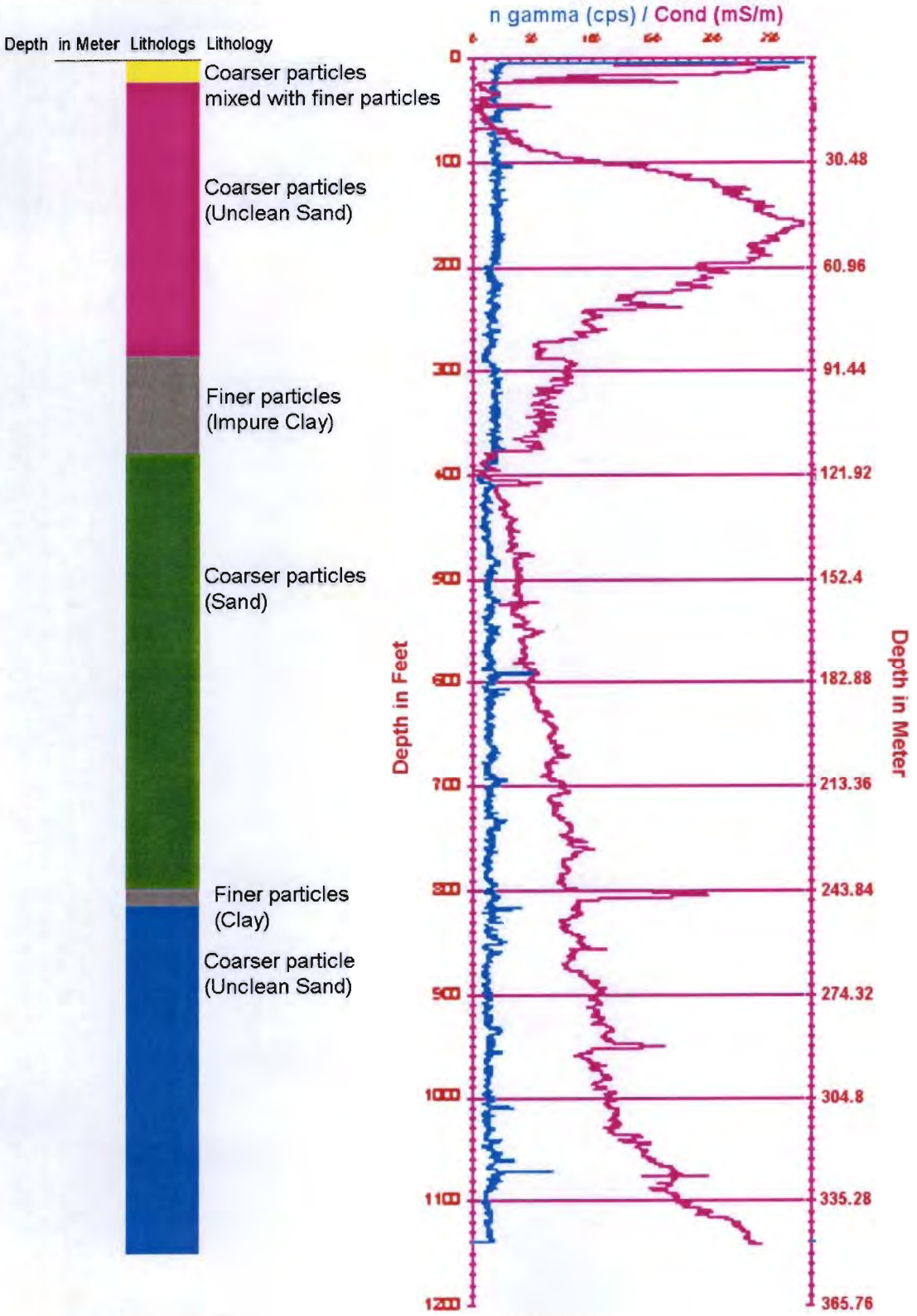
Abstract

Deep aquifer of the southern Bangladesh is the prime source of safe water which needs to be fully assessed before development. Though there are thousands of deep hand tube wells in the area, there exist very little information about the subsurface lithology and this is a major constraint in mapping of the deep aquifer. As drilling is an expensive venture, a specially designed slim-hole composite logger (Electro-Magnetic Conductivity and Natural Gamma) has been used to investigate the lithology and water quality of the deep aquifers in existing holes cased with PVC liners. 16 existing deep hand tube wells have been logged in Kachua Upazila of Chandpur district for the delineation of hydrostratigraphy and to decipher water quality in the different depths.

For calibration of geophysical logs, it is important to have good lithological logs. The wells drilled by Geological Survey and Bangladesh Water Developmemnt Board in the area have been used for this purpose. As depicted from the lithologs, stratigraphy of Kachua is characterised by the Holocene and Pre-Holocene deltaic sequences that can be divided as the upper Chandina Alluvium of Holocene age and lower Dupi Tila Formation of pre Holocene age.

Three distinct aquifers can be identified from the geophysical logs which are separated from each other by the two impermeable to semi-permeable layers (aquitards). The first aquifer or the shallow aquifer extends below a thin surface clay to a depth of about 15-52 m and the thickness of this layer varies from place to place. This aquifer consists of unclean sand, i.e. very fine to fine sand. This aquifer separated from the second aquifer by the prominent impermeable clay layer in some places and in some areas this clay become unclean with fine sandy particles indicated by the spiky gamma signal. The thickness of this clay layer is low in the north and high in the south. The second aquifer [intermediate] is mainly composed of unclean sand indicated by the spiky gamma and conductivity signatures. The depth of the second aquifer varies from 45-120 m below the ground surface. There is another sandy sequence below the second aquifer separated by a discontinuous clay unit in some places. This could be termed as third aquifer which is hydraulically connected with the second aquifer. Depth of this aquifer ranges between 152-310 m. The third aquifer consists of the series of the fine to very fine sand and fine to medium sand.

The synergistic interpretation of conductivity and gamma logs (Fig 1) reveals that the first aquifer contains brackish water in the north-western portion of the area. The second or the intermediate aquifer contains more or less fresh water. The third or the deep aquifer has fresh water in the upper portion while the lower portion contains saline water. The geometry of the deep aquifer and hydrostargraphic succession will be presented. Applications and limitations of the logging techniques for deep aquifer mapping will be discussed.


Depth in Meter
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Lithology
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Finer particles (Impure Clay)
Coarser particles (Sand)
Finer particles (Clay)
Coarser particle (Unclean Sand)
n gamma (cps) / Cond (mS/m)
Depth in Feet
Depth in Meter
0
100
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400
500
600
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1000
1100
1200
30.48
60.96
91.44
121.92
152.4
182.88
213.36
243.84
274.32
304.8
335.28
365.76

The temporal stability and spatial distribution of arsenic in Bangladesh

Mahfuzar Rahman, N. Sohel

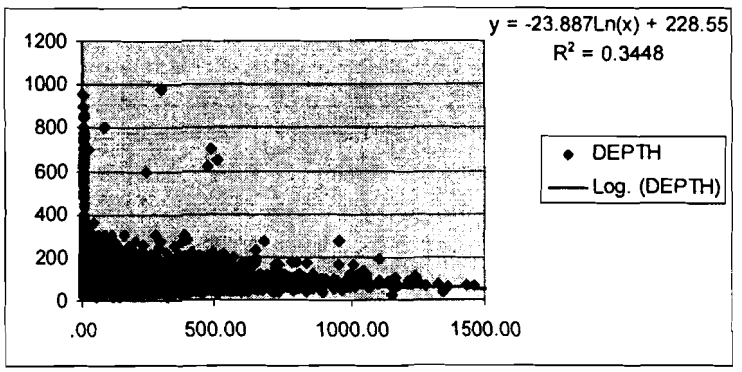
Abstract

Millions of people worldwide are exposed to drinking water containing arsenic, and epidemiologic studies have identified associations between the ingestion of arsenic-contaminated water and increased risks of cancer. In many of these studies, the assessment of arsenic exposure is based on a limited number of drinking water measurements. The assessment of long-term or past exposure relies on the assumption that arsenic concentrations in sources of drinking water remain stable over time.

In this investigation arsenic concentration was assessed in 16,521 tubewells. Arsenic concentrations in these wells ranged from no detectable to 3644 μg/L (median=176.2, SD=213.5). Location of all 16,521 tubewell in the area were collected and plotted into the maps. Most of the functioning and non-functioning tubewell were tested for arsenic concentration in the water. Initially, field-kit was used for measuring the level of arsenic. Subsequently all tubewells water was analyzed by AAS. Depth of the tubewells was self reported and ask for the number of pipes used in that tubewells. In this analysis tubewells (n=13,358) were considered and after excluding the missing depth, finally 11,965 tubewells were considered for analysis.

One-third of the tubewells at rural Bangladesh found arsenic concentration < 10 μg/L and six percentages of the tubewells found 10-49 μg/L. The two-third of the tubewells found arsenic concentration 50 μg/L or more which is harmful for human. It might have some clustering effect and depth of tubewells may differ in different locations. The mean depth of tubewells was 134 ft with mean arsenic concentration 206.5 μg/L. Mean depth of tubewells varies with the mean arsenic concentration. Average depth of tubewells increased with the decrease of arsenic concentration ($F=3423$, $\rho < .001$). Average depth of tubewells were 218, 169, 91 ft respectively when considering arsenic concentration levels of < 10, 10-50 and >50 μg/L respectively. The average concentrations of those levels of arsenic were 2.7, 28.6 and 323.8 μg/L. The correlation coefficient showed that arsenic concentration varied depending upon the depth of the tubewells ($r^2 = 0.35$)

AAS	Depth
1	228.55
5	190.1054
10	173.5481
20	156.9909
30	147.3056
50	135.1035



Two-third of the populations in rural Bangladesh are exposed with arsenic contaminated water and urgent replacement is needed with arsenic free water to avoid health consequences. People consider using at least 135 ft deep pipes to avoid arsenic exposure. Other source of water can be used to avoid arsenic contamination like pipe water, deep tubewells water. Surface water can also be used after some filtration process to avoid water born diseases.

Not Just Red or Green: An Analysis of Arsenic Data from 15 Upazilas in Bangladesh

Jan Willem Rosenboom

Abstract

Introduction

This presentation provides a summary of a data analysis report based on the UNICEF/DPHE 15 upazila arsenic mitigation programme. In particular, the following data were analysed:

- Well screening data;
- Patient data;
- Survey data on arsenic Knowledge, Attitudes and Practices (KAP);
- Spatial data on wells and patients in three of the 15 upazilas; and
- Comparative arsenic Field Test Kit (FTK) and laboratory data.

The full report including the data sets are available from UNICEF and APSU in Dhaka.

Study Area

All 15 upazilas are located in the southern half of Bangladesh. They cover 10 administrative districts. More than 4.5 million people live in the project area, representing 3.6% of Bangladesh's population.

The geomorphology and the near-surface geology of these areas are quite diverse. The surface areas of Damurhuda, Manirampur, Kalia, Bhanga, Rajoir, and Shib Char, which are located within the Ganges delta generally comprise of sand and silt at the top. Located within the Meghna floodplains and Padma floodplains, the surface deposits of Serajdikhan, Nabinagar, Bancharampur, Muradnagar, and Homna are predominantly silty with occasional clay deposits. Barura and Shahrasti are located in the lower Meghna floodplains, and marsh clay and peat units. Estuarine deposits are present in the Haim Char area. The Babuganj area, characterized by tidal deltaic deposits, is located within the fluvio-tidal transitional Ganges deltaic region.

Like many other parts of the country, the Holocene fluvio-deltaic and coastal sediments form prolific aquifers in the studied upazilas. The aquifer systems can be broadly divided into three units: (i) an upper shallow aquifer occurring mostly within 50-60m of the surface, and which is extensively arsenic affected; (ii) a lower shallow aquifer extending up to 200m in depth which is substantially arsenic free, but which is in hydraulic contact with the upper shallow unit and so may become contaminated over time (through vertical "leakage"), and (iii) a deep aquifer of Pleistocene fine to medium sands which yields arsenic safe water, and is expected to remain safe because in most places it is separated from the lower shallow aquifer by a clay aquitard.

Well Data

Arsenic contamination

Of the 316,951 wells tested, 65.5% (207,582 wells) exceed the 50 ppb national arsenic standard. In 29% of the arsenic-safe wells, no arsenic could be detected at all. A full 29% of wells shows 500 ppb of arsenic in their water. Because 500 ppb (0.5 mg/L) is the highest point of the test kit scale, the *actual* concentration of arsenic in those wells may be higher still. So not only is the proportion of contaminated wells much higher than the national average of about 27%, the arsenic concentrations in the affected wells also are very high.

Arsenic and well age

Well construction slowly started in the 1970s, and strongly accelerated in the 1980s. Worrying is that half of all wells were constructed since 1995, while arsenic was first discovered in 1993. The ever-accelerating rate of new tubewell construction seems to indicate that people either do not worry about arsenic, or believe that new wells are free of danger.

Although new tubewells are not by definition arsenic safe, tubewells older than 25 years have a significantly higher arsenic concentration than younger wells. Related to this is the finding that older wells have a higher chance of exceeding the permissible arsenic level (75% for wells older than 25 years, against 65% for all wells).

Arsenic and well depth

The vast majority of wells (75%) is completed in the range of 50-150 ft (15-45 m). In more than half the upazilas the interquartile range of well depths is around 10 meters The largest number of wells exceeding 50 μg/L of arsenic is also found in the 50-150 ft depth range, and looking at the proportion of wells beyond the arsenic standard in this interval confirms that it is generally a poor choice for locating arsenic safe water.

There is very little variation in depths to which wells are completed over time. This means that the higher arsenic concentrations in older wells cannot be explained by assuming that older wells are shallower; they are not.

Generally speaking, wells deeper than 500 ft (152 m) offer a good chance of finding arsenic safe water. Exceptions are Bancharampur, Homna and Muradnagar, where 46% to 80% of reportedly deep wells exceed the arsenic standard. Because well depths were not measured at the time of testing, these results should be investigated further before they are accepted.

At an arsenic contamination rate of 11%, dug wells offer a lower risk alternative to shallow tubewells, although they are not completely risk free. They have clearly lost in popularity though, seeing that their average age is almost 42 years. Risk substitution because of microbial contamination is also a real danger with the use of dug wells.

There are large variations in the proportions of arsenic affected wells in different areas. Practically, this variation means that there is no "one size fits all" solution to the arsenic problem. Every (new) well still needs to be tested, and approaches to alternative water supplies and (for example) decisions about the continued use of shallow wells will need to be made based on a review of local data, and a judgment by responsible authorities or individuals.

Patterns of contamination: the use of maps

In three upazilas, arsenic contamination maps were prepared on the basis of GPS surveys carried out after well screening. These showed distinct clustering of arsenic affected wells in some areas. In three heavily affected unions, access to arsenic safe water for users of "red" wells varied significantly; 23% to 94% were within 100 meters of a "green" well. Maps are thus useful in mitigation planning. In addition, their use as a tool in awareness raising should be encouraged.

Field test kit performance

A total of 6,341 laboratory test results from 14 upazilas were examined and compared with FTK results. All in all, this showed a test kit sensitivity[1] of 88%, and specificity[2] of 84%. Overall, 86% of all test kit results identify the correct category for the well (either "green" below 50 ppb, or "red" above that). With these numbers, the continued use of test kits should not be at issue. The Merck "sensitiv" arsenic test kit is no longer widely used in Bangladesh, and it would be helpful to obtain comparative results for kits currently in use. Continued development could mean that better results can be obtained using newer kits.

Patient Data

Arsenicosis prevalence

A total of 2,682 patients were identified in the 15 upazilas. In every upazila for which a breakdown by sex is available, the number of male patients exceeds the number of female patients. This apparent discrepancy is likely a reflection of the fact that access to health care is more restricted for women than for men, so fewer women end up being diagnosed. A real difference in prevalence rates could be caused by behavioural influences which are known to increase susceptibility to arsenicosis, such as smoking.

For each 1,000 people exposed to arsenic in drinking water above 0.05 mg/L, there are 0.78 arsenicosis patients in the 15 upazilas. The highest prevalence figures occur in the upazilas with the lowest percentage of wells contaminated above the standard (Damurhuda and Shib Char). Not considering these two upazilas, there is a significant positive correlation between arsenic exposure level (measured as mean arsenic concentration in wells) and arsenicosis prevalence.

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[1] Sensitivity: when the well is truly unsafe, how likely is the kit to say red?
[2] Specificity: when the well is truly safe, how likely is the kit to say green?

Patient characteristics

Mean age for patients is 36 years, and 68% have either no education, or primary education only. Among the patients, 78% of wells exceed the arsenic standard (vs. 66% for the 15 upazilas as a whole). There is no correlation between the duration of water use and the duration of arsenicosis symptoms. There is no discernable pattern in the severity of symptoms vs. their duration; if anything, severity seems to diminish over time. However, only 2% of patients (32 in total) have had symptoms for more than ten years and this is a small number to base any conclusions on. Changes in water use practices over time, as well as mortality should be investigated as possible explanations for the small number of long-term patients and their diminishing symptoms.

The majority of patients (71%) have used well water for longer than they have owned a well themselves. This points to a need to consider a complete history of water use when interviewing patients; actual exposure to arsenic may predate current water use.

An investigation of arsenic levels in nails and urine shows 55% of patients have elevated urinary arsenic levels (>40 μg/L), and 95% of all patients have elevated nail arsenic levels (>1 ppm), ranging from 0.5 mg/kg (normal) to 13 mg/kg.

A large proportion of patients (35%) is underweight. There is no data on a control group, and it is not clear whether this finding is in any way unusual. A recent prevalence comparison study concluded that poor nutritional status may increase an individual's susceptibility to chronic arsenic toxicity, or alternatively, that arsenicosis may contribute to poor nutritional status. It was not able to resolve causality (Milton, Hasan *et al.* 2004).

KAP Survey Data

Survey set-up and data analysis

Prior to well and patient screening, a baseline arsenic Knowledge, Attitudes and Practices (KAP) survey was carried out in the 15 upazilas. After the completion of all field work, a follow-up survey was carried out. A total of 4,453 observations (2,909 baseline and 1,544 follow-up) were analyzed. Specifically, the analysis considered seven arsenic-related knowledge questions, four attitude questions, two practice and action questions, and four willingness to pay questions.

Knowledge, attitudes and practices

Results suggest that the follow-up group is more knowledgeable about problems related to arsenic contamination than is the baseline group. The education campaign carried out in the 15 upazilas is a possible reason for this change. Also, we see that the increase is more pronounced among the low income, low education group.

Dissemination seems to have influenced attitudes in all four questions about attitudes. Changes in practice are hard to evaluate, given a very low response rate to the practice and action questions during the baseline survey.

The response rates for knowledge, attitudes and practice questions rose significantly between baseline and follow-up surveys. The increase in the response rates can itself be

considered an effect of the dissemination program. Those who did not respond during the baseline survey probably did not know the correct answers and hence opted not to respond.

Regression analysis

In the regression analysis, the variable indicating the baseline or follow-up survey is significant in all questions that were considered, indicating significant changes in "before" and "after" which could be explained by the communication campaign. Education, income and marital status are significant in a number of the knowledge related questions, while in the attitude questions education alone is the most relevant predictor. Income and to a lesser extent TV watching habits are important predictors for willingness to pay for testing, well maintenance and new water supply installation. Gender is a significant explanatory variable for willingness to pay, as well as the "amount to pay" for maintenance of a new well. Women are less likely to respond positively to "willingness to pay" questions. This is not surprising, seeing that women would generally not be in control of household finances, and thus may be reluctant to commit to more expenditure.

Summary Remarks and Recommendations

Organization of large scale surveys

The observable quality of available data is mostly very good; almost 97% of all well data was without problem. However, the experience of setting up a mass screening programme in 15 upazilas offers some lessons for other organizations or countries facing a similar need. In summary these are:

- Training and supervision of testers is important;
- Minimize perverse incentives;
- Establish a standard (national) database based on the use of standard data collection forms;
- Establish a working system for uniquely identifying wells;
- Incorporate lists of location names into the database prior to beginning field work;
- Ensure a link between patient data and data on wells; and
- Establish clear procedures for quality assurance and quality control.

Implications for policy development and mitigation

The 15 upazila data have confirmed the enormous variation that exists in arsenic levels from place to place. Overall well contamination rate may be close to 66%, but that average hides variations from a low of 20.2% to a high of 98.4%. In each of the upazilas there are communities where 100% of the tubewells exceed the arsenic limit, as well as communities where none of the tubewells do. The obvious initial conclusion is that there is no "one size fits all" solution to the problem. Based on the data presented here, mitigation approaches and national policy development should at a minimum pay attention to the following:

- Invest time and effort in collecting and analyzing locally available data. Use local data in deciding whether shallow tubewells or deep wells should be offered as mitigation options. Blanket rules applied nationally would needlessly constrain feasible options;

- Where emergency mitigation measures are to be used, use not only the percentage of wells exceeding the standard as selection criterion. It appears that absolute level of exposure plays a role in the prevalence of arsenicosis, and it should be part of the decision making;
- Ensure the inclusion of schools in mitigation plans. Children form a vulnerable group, and reducing exposure for them means taking into account all places where they potentially use water;
- Improved guidelines for patient data collection and –management (including a link to well data and the collection of case control data) would increase the usefulness of future health data.

Report follow-up

1. This report presents a first comprehensive look at the data from the 15 upazilas, and more work could be done on it. This is especially true for data at the local level. More of the data can be considered at union level, especially with a view to formulating locally appropriate advice for mitigation options.

2. The well data show rather high contamination rates for deep well in three upazilas. The total number of deep wells in those upazilas with arsenic above 50 ppb is small, only 65. It would be advisable to visit those wells, to measure their depth, and to re-test the arsenic level. Results would usefully to inform the debate on the continued use of deep wells.

3. On the health side, it would be useful to pursue the existence of a data set on a control group of non-patients. If such data exist and can be obtained, a comparative analysis of the two datasets should be completed, rather than a description of patient data only, as done in chapter three.

4. Lastly, it would be useful to look across Bangladesh's borders for a moment. Arsenic contamination in groundwater affects at least nine countries in South- and Southeast Asia. Bangladesh is the country with most experience in addressing this problem, certainly from a perspective of mass screening of wells and identifying patients. Based on this experience, and given the probable need to implement similar surveys in other countries, it would be helpful if a field guide for setting up screening programmes could be developed.

Arsenic Attenuation by Oxidized Aquifer Sediment, Bangladesh

Kenneth G. Stollenwerk

Abstract

Introduction

Shallow aquifers in many regions of Bangladesh and neighboring West Bengal, India contain arsenic (As) concentrations >50 μg/L. These aquifer sediments are typically reducing and gray in color. Arsenic in ground water is present primarily as arsenite [As(III)]; however, arsenate [As(V)] can also be present. Beneath these high-As aquifers, in some areas, are aquifers with <10 μg/L As. These aquifer sediments are typically oxidized and brownish in color. Efforts are underway to utilize the deeper aquifers for domestic water supply and irrigation. However, there are concerns that ground-water extraction from the deeper aquifers could lead to increased amounts of recharge from the overlying aquifers and higher concentrations of As. This research was conducted to evaluate the potential for deeper aquifer sediments to mitigate As contamination from shallow aquifers.

Methods

Column experiments were used to evaluate the capacity of oxidized sediments to attenuate dissolved arsenic. Sediment was collected from an oxidized aquifer at a site located about 10 km west of Dhaka. Arsenic concentrations in ground water associated with these sediments were <5 μg/L. The sediment was packed into columns and eluted with ground water having a chemical composition similar to the overlying high-As aquifer. Dissolved constituents of primary interest in the eluent included 700 μg/L As(III), 250 μg/L As(V), and 5 mg/L Fe(II). Eluent pH was 6.8, bicarbonate was 380 mg/L, and dissolved oxygen was 0.2 mg/L. The average flow rate through the column was 0.6 m/d. Results from one column experiment are presented here.

Batch reactor experiments were used to quantify adsorption of As by oxidized sediments. A solution/solid ratio of 18 ml/gram was used in the batch experiments. Initial As(III) and As(V) concentrations were varied from 0 to 2,000 μg/L.

Results and Discussion

Concentrations of As(III) and As(V) in leachate from one of the column experiments are shown in Figure 1. Ground water entering the column contained 650 μg/L As(III) and 250 μg/L As(V). All As(III) and As(V) were removed from the first 50 pore volumes of ground water eluted through the column. Adsorption is the primary mechanism responsible for removing As from solution. After pore volume 50 the concentration of As(V) slowly increased, reaching 400 μg/L by pore volume 100. Of significance is the observation that As(V) concentrations became greater than the initial concentration of 250 μg/L, while As(III) concentrations remained below detection for 110 pore volumes. Independent evidence from batch reactor experiments has shown that manganese oxide minerals present in the sediment oxidize some As(III) to As(V). Eventually, the available

manganese oxide concentration in the column decreases and leachate concentrations of As(III) and As(V) become similar to those in the eluent (data not shown).

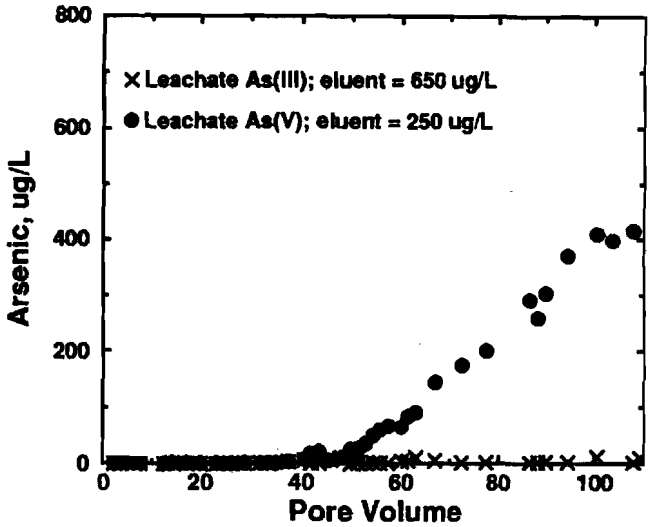

Figure 1. Arsenic concentration in column leachate.

Oxidation of As(III) to As(V) has important consequences regarding potential transport of high-As ground water into the oxidized sediments. In batch experiments, four times more As(V) was adsorbed than As(III) (Figure 2). Therefore, the oxidized aquifer sediments have a greater capacity for As removal than if As(III) adsorption were the only attenuation mechanism.

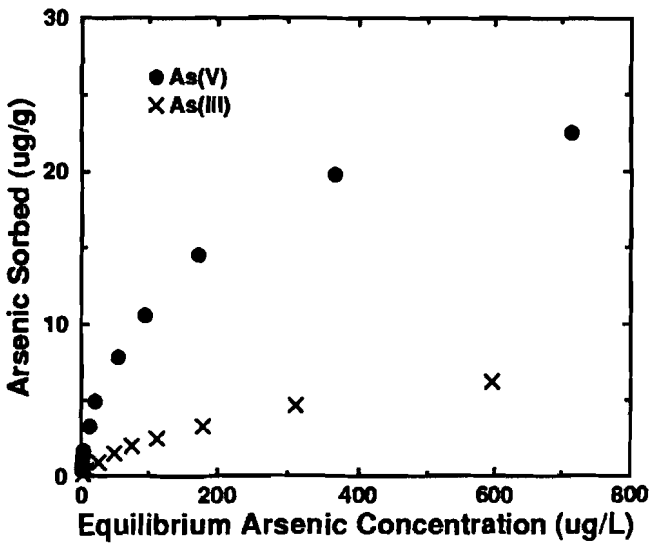

Figure 2. Adsorption isotherms for As(III) and As(V) at pH 6.8.

Conclusions

The potential for contamination of deeper, low-As aquifers by pumping-induced infiltration of high-As shallow ground water is significantly mitigated by adsorption onto oxidized aquifer sediments. Aquifer sediments have a significantly greater capacity for adsorption of As(V) than As(III). Therefore, oxidation of As(III) to As(V) by manganese oxide minerals facilitates removal of As from ground water. However, the capacity of sediments to remove As from solution if finite.

Geologic setting and arsenic distribution in Kachua and Rajoir Upazilas, Chandpur and Madaripur Districts, Bangladesh

Md. Nehal Uddin, Reshad Md. Ekram Ali, Md. Ehsanul Bari, Md. Nuruddin Sarker, Ahmed Ataul Munim, Md. Monirul Islam, John W. Whitney, James C. Yount and George N. Breit

Abstract

Arsenic in the shallow aquifers of Bangladesh has become a major health hazard in the country. To characterize the geology of arsenic-contaminated and arsenic-free aquifers, two severely affected areas, Kachua and Rajoir Upazilas of Chandpur and Madaripur Districts, in the Meghna and Ganges floodplains were selected for detailed lithologic and geochemical studies. The research included geomorphic and geologic surface mapping, detailed characterization of subsurface sediments, and testing for arsenic in a vertical sequence of aquifers. Near surface sediments were studied by augering and subsurface sediments by borehole logging to depths of 408 meters at Kachua and 450 at Rajoir.

Bangladesh is primarily a riverine land covered by alluvial and deltaic deposits of the Ganges-Brahmaputra-Meghna river systems. The study areas occupy part of the Chandina alluvium (Bakr, 1977) and Ganges flood plain deposits of the south-central Bengal Basin. Tectonically this area is a part of Faridpur trough (Alam et al, 1990), which is bounded by Barisal gravity high to the southeast. The hinge zone (shelf break) lies to the west and north west of the area. Faridpur trough is characterized by a general gravity low in the NE-SW direction.

The elevation of Kachua upazila from the mean sea level (AMSL) indicates that the southwestern and northeastern areas are relatively lower (4.61m AMSL) and southeastern part is situated at a relatively higher (7.99 m AMSL) elevation. The area has very low drainage density and part of this area is tidally influenced, especially during spring tides. The Kachua upazila is divided into 3 geomorpholological units: i) Chandina Alluvium High (southeasttern part), ii) Chandina Alluvium - Medium (northwestern and southwestern part) iii) Chandina Alluvium Low (northeastern and miiddle western part). Chandina Alluvium-High always remains above normal flood levels. There are some depressions in the Chandina alluvium-Low unit. The near surface sediments in the Kachua study area are clayey silt, silty clay, silty sand and sand. There are deep brown oxidized bands above the water table that contain high arsenic.

The borehole stratigraphic sequences of Kachua upazila at Srirampur (SH-1) suggest two formations- Chandina Alluvium (Holocene) and Dupi Tila Formation (Pre-Holocene). Chandina Alluvium is composed of sand and clay. The sand is grey to yellowish grey, mottled, oxidized at the top part, mostly fine grained, and is unconsolidated. The clay is grey, sticky, plastic and soft. In places the clay is sandy and/or silty. The thickness of the Chandina Alluvium is interpreted to be 45 m. The Dupi Tila Formation is composed of sandstone, pebbly sandstone with thin clay interbeds, and shale bands. The upper units are

grey to yellowish grey and lower units are grey. The thickness of the Dupi Tila Formation is over 335 m.

The highest elevation of land in Rajoir upazila, at Rajoir sadar, is 4.30 meters. The land gradually slopes lower in elevation from the middle to the southern part of Rajoir upazila. Some of the places, like Kadambari and Amgram, are lower in elevation than mean sea level (0.5 meter). The area is drained by the Ganges and several of its tributaries: Arial Khan, Madhumati, Kumar (Bhubaneswar) and Gorai. The Madhumati-Kumar link canal plays an important role for siltation in the area.

Geomorphologically Rajoir upazila is divided into two parts: high Ganges floodplain (northern part) and low Ganges floodplain (southern part). The high Ganges floodplain is formed by comparatively new alluvium with a network of channels formed as the Ganges River migrated from west to eastwards. This unit is characterized by a number of abandoned as well as active channels. This unit mainly consists of silt and sand with minor clay. South of the abandoned Kumer River land is mapped as low Ganges floodplain. This area consists of chains of large depressions separated by strips of high land. This area normally remains under water about nine months of year. Deposits in these depressions consist of alternating layers of clayey silt and silty clay, and peat and fine sand.

The borehole stratigraphic sequences at Rajoir upazila also suggest two formations: Holocene Alluvium and Dupi Tila Formation. The Holocene alluvium at bore hole SH-2 is interpreted to continue to 65.5 m below the surface. The contact between the alluvium and Dupi Tila is drawn arbitrarily on the basis of lithologic data and needs further confirmation. Holocene Alluvium consists of unconsolidated silty clay, clay, peat and fine sand. Silty clay is light grey to yellowish brown, grey to bluish grey, soft, and contains partly decomposed organic debris. Clay is grey to brownish black, bluish grey near the top of peat layers, and is sticky and plastic when wet. Partly decomposed organic materials are also present. Peat is dark grey to brownish grey, fibrous, soft, partly decomposed, and becomes fragmentary on drying. Sand is medium grey, fine grained, subangular to subrounded, and composed of quartz (~80%), mica, and dark minerals. In places micaceous bands are present. Thin beds of peat are interbedded with alluvial silt in the depressions that suggest continual subsidence.

At Rajoir the Dupi Tila Formation is found at 65.5 m depth and continues up to the bottom of the borehole at a depth of 450 m. The Dupi Tila Formation is composed of sandstone, pebbly sandstone and clay. There is no remarkably thick clay bed in between Dupi Tila and Alluvium Formations at Rajoir. Thin clay bands are often interlayered with the sandstones. There are brownish grey clay bands between 205 and 230 m depth that suggest prior aerial exposure of the sediments during times of Pleistocene low sea levels.

One hundred sixty-six hand tubewells, shallow tube wells, and deep tubewells (tara pumps) at Kachua, and one hundred twenty two at Rajoir were sampled using a 21/2 sq. km grid to map the distribution of arsenic concentrations in groundwater. At Kachua tube wells greater than 152.40 m depth consistently produced water with arsenic contents <50 ug/L while

tube-wells with depths of 21.33 to 60.95 m produced water with high concentrations of arsenic. At Rajoir, tube wells within depths of 67 m produced high arsenic water. Most deep tubewells within depths of 200-260 m produced arsenic safe water; however, there are iron, manganese, and salinity water quality problems.

The litho-stratigraphy of the area indicates there are two types of aquifers: shallow Holocene aquifers and deeper Pleistocene aquifers. In the Kachua borehole a thick clay layer separates the Holocene and Pleistocene aquifers; however, there is no such clay layer in the Rajoir borehole. Holocene aquifers are found at 10-45 m depth at Kachua and at 10-67 m depth at Rajoir. Pleistocene aquifers are divided into three zones: upper (73-299 m at Kachua and 70-135 m at Rajoir), middle (314-374 m at Kachua and 228-373 m at Rajoir), and lower (381-409 m-plus at Kachua and 410-350 m-plus at Rajoir). At Kachua, aquifers are separated by clay layers. At Rajoir interlayered clay and sand/sandy clay separates each of these aquifers. At both localities the upper Pleistocene aquifers are arsenic safe but rich in iron and the middle aquifer is commonly saline. The lower aquifer contains potable water at Kachua, but the quality of water in lower Pleistocene aquifer at Rajoir is not yet known, because water from this depth has not been tested. Borehole data indicate that there is a 59.45 m-thick impervious clay layer between the Holocene and Pleistocene (Dupi Tila) sediments at Kachua; however, no such impervious layer was found at Rajoir.

Groundwater Quality in Two Areas of Bangladesh: Implications for Development of a Safe Water Supply

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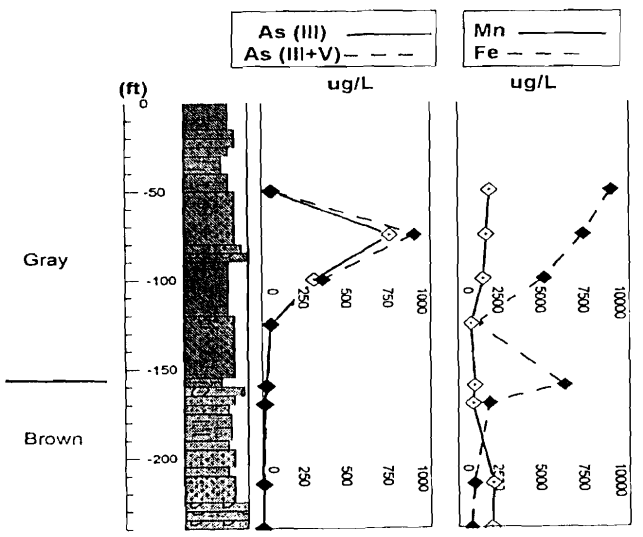
Abstract

The USGS, in collaboration with the Geological Survey of Bangladesh, the Bangladesh Atomic Energy Commission, and the Ground Water Development Board, have been conducting geologic, hydrologic, and geochemical investigations Kachua Thana in eastern Bangladesh and Shib Char, Bhanga, and Rajoir thanas in central Bangladesh. Wells completed to depths greater than 500 feet in the last few years have provided greater access to deep ground water than has been previously possible. Because deep aquifers are a potential source of low arsenic water, water from these deeper wells was analyzed for arsenic and other constituents.

Coring and sampling of the shallow aquifer at several locations suggest that high arsenic concentrations are often restricted to a relatively restricted depth range. At one location near Dhaka, arsenic concentrations are associated with grey sediments that overlie more oxidized orange sediments as shown in the following figure depicting the lithology and arsenic concentrations in shallow sediments near Dhaka.

Fig 1

IDE Drill Hole WW6-1 Shampur Bazar, Savar



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Analysis of water from nearby wells suggests that arsenic concentrations are restricted to depths above the oxidized sediments. At a second location, near Brahmanbaria, high arsenic concentrations are at, and above, the depth of the contact between grey and underlying orange sediments. Arsenic concentrations in ground water below the grey-orange contact are low at this location. Movement of the high-arsenic shallow ground water may affect the viability of a deeper aquifer as a long-term source of safe drinking water.

The observation that orange sediments yield water with low arsenic concentrations has been previously recognized and has led to the suggestion that ground water beneath the top of these sediments may be a source of safe drinking water. Where present, laterally extensive, low-permeability sediments may retard downward movement of high-arsenic ground water. Additionally, downward movement of arsenic may be attenuated by reaction with sediments may limit arsenic concentrations in deeper, pumped aquifers. Movement of arsenic into deep wells can result from improper well construction. Anecdotal evidence in Kachua Thana suggests that high-arsenic ground water is entering deep aquifers because of improper well construction. In several cases, water withdrawn from wells that were idle for periods of days to months produced high arsenic water for a short period of time. In one case, specific conductance values also suggest that shallow water had invaded the deep aquifer because of improper well construction. Because the shallow aquifer has a greater hydraulic head than the deeper aquifer, water can flow from the shallow to the deep aquifer. Unless the issue of adequate well construction is addressed the deep aquifer may be contaminated by arsenic and potentially other harmful substances, including pathogenic bacteria.

Arsenic concentrations in Kachua Thana wells with depth greater than 300 feet deep are low (Figure 2), with the exception of three samples that are from wells that appear to be affected by downward flow of water as discussed above. Although these deep wells may be acceptable from the standpoint of arsenic, the salinity is not acceptable in some wells. The specific conductance, which provides a broad measure of the dissolved solids content of water, more commonly exceeds 2,000 uS/cm in wells with depths of 500 feet compared with shallower wells. Some residents of Kachua find the salinity objectionable and do not use the deep wells for drinking. The specific conductance appears to be broadly predictable, with lower concentrations present in the north and east (Figure 4). Salinity is a more severe problem in the three thanas investigated in central Bangladesh (Shib Char, Rajoir, and Bhanga), where most deep wells produce slightly saline water.

The presence of deep ground water with an unacceptably high salt content demonstrates a need for a better understanding of the hydrology and chemistry of the hydrologic system. Also, the long-term use of ground water may be compromised by inflow of saline water in response to large scale ground water withdrawals.

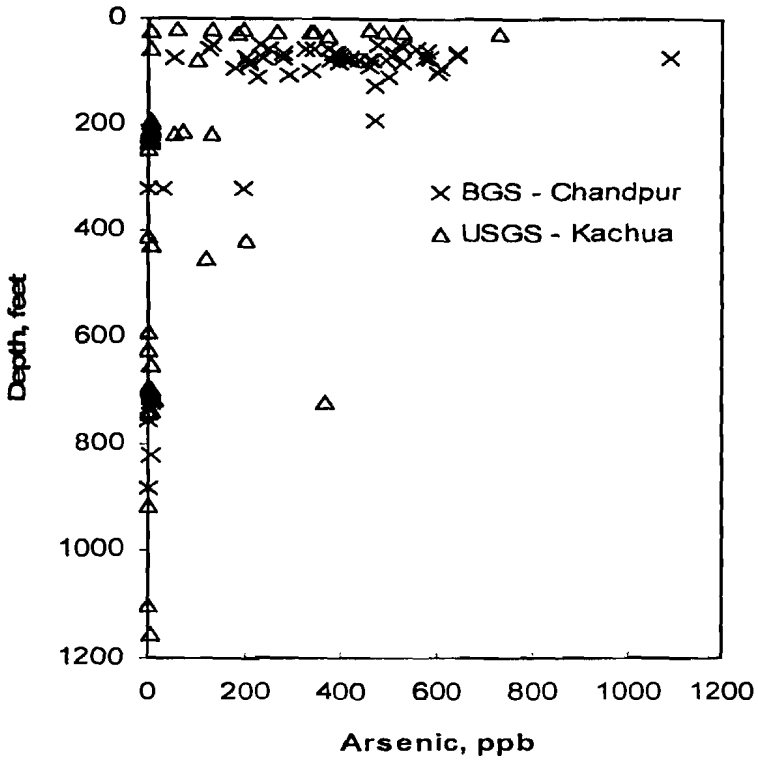

Figure 2. Arsenic concentrations in ground water of Chandpur. BGS data are from the British Geological Survey Technical Report WC/00/19, Data Compilation.

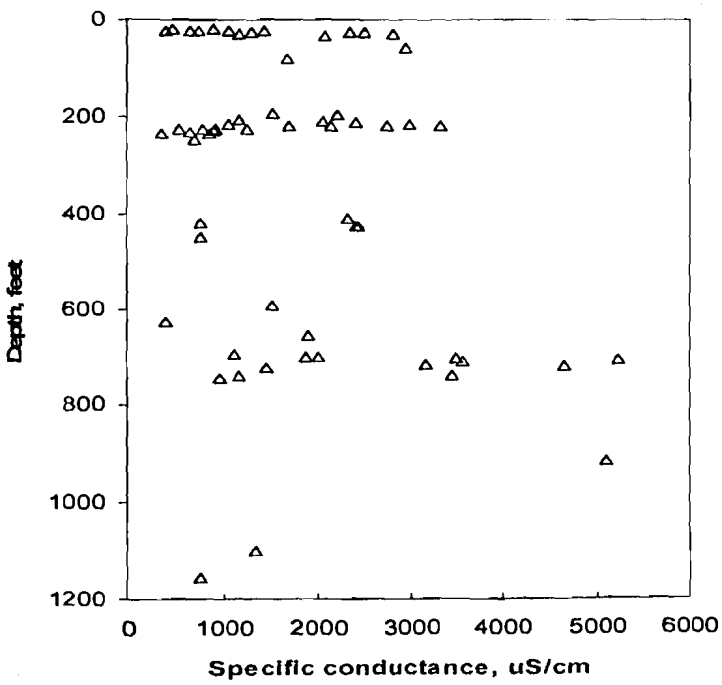

Figure 3. Relation between specific conductance and depth in ground water of Kachua Thana.

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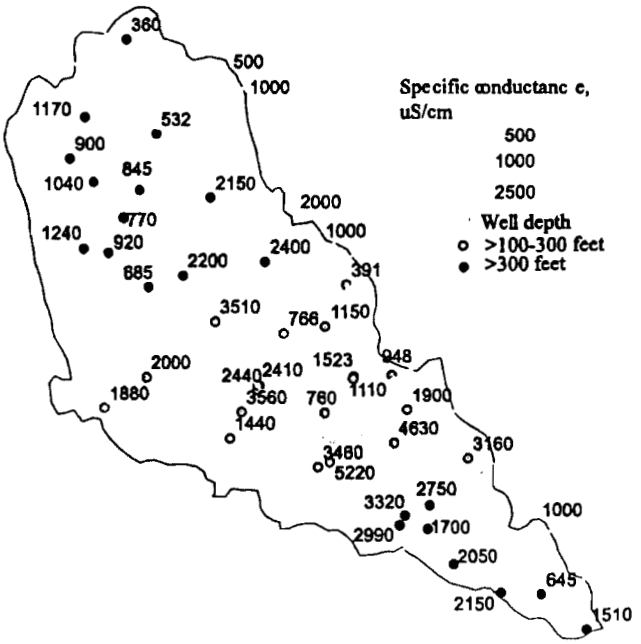

Figure 4. Specific conductance of ground water in Kachua Thana.

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Subsurface Geology and Geochronology Studies of

Deeper Aquifers in the Bengal Delta

J.C. Yount, Md. Nehal Uddin, S.L. Forman, J.W. Whitney

Abstract

Subsurface geologic studies were carried out at two sites in southeast and central Bangladesh as part of the USGS-GSB-BWDB deep aquifer characterization project. The first site at Srirampur Village, Kachua Thana Chandpur Distrtict was investigated during spring and early summer in 2003. One deep bore hole, drilled and sampled to a depth of 408 meters by GSB, obtained subsurface lithologic and stratigraphic data that provides a geologic framework for nearby water monitoring and hydrologic testing performed by USGS and BWDB at 7 pieziometer and pump test holes. The second site, located at Rajoir Thana headquarters, Madaripur District, was investigated in similar fashion during the spring and summer of 2004. The deep bore hole was drilled and sampled by GSB to a depth of 450 meters and supplemented an array of water monitoring wells installed by BWDB within the headquarters compound.

The two sites represent different depositional environments on one of the world's largest subaerial deltas. The Srirampur site is located on the lower portion of the Chandina Deltaic Plain, a region presently dominated by south and east flowing rivers and streams that drain the nearby Lal Mai Hills south of Comilla and the more distant Tripura Hills to the east. The bedrock units underlying these source areas consist dominantly of Tertiary sandstone and shale of fluvial and fluvio-deltaic affinities. The Srirampur site lies near the limit of active flooding of the lower Meghna Estuary which flows south to the Bay of Bengal approximately 30 kilometers west of the site.

The Rajoir site is situated roughly 30 kilometers south of the Padma River in a region of dry-season low-flow rivers, such as the Kumar and Aril Khan, that become channels of major overflow during flood season. Numerous abandoned channels and oxbows surround the site and a large peat accumulation area, east of Madaripur, lies a few kilometers to the southwest. Sediment presently deposited in the Rajoir area is a mixture of Ganges and Brahmaputra sources, ultimately derived from the Himalayas.

Both sites are dominated by gray fine- to coarse-grained quartzo-feldspathic sand throughout their sections. Within each site area (roughly 0.05 square kilometers at both sites), lithologic units lack detailed lateral continuity. In spite of somewhat different drilling and logging methods employed at some drill holes, the poor correlation of lithologic units appears to be real. At Srirampur, coarse sand and pebbly gravel units exist between 70 and 100 meter depths in some, but not all drill holes. Another coarse pebbly interval, between 320 and 360 meter depth, grades eastward into sand over the 500 meter length of the site area. Thin silt and clay intervals above and below the upper gravel may thicken to the east into a 20-meter thick clay at 40 to 60 meter depth at the main Srirampur bore hole. A 20-meter thick silty clay unit at 300 meter depth in the west part of the site area persists through the three drill holes; however, it appears to thin eastward. This unit is the most likely low-permeability unit in the lower part of the section. Brown oxidized sand and pebble gravel are rarely encountered in the deep bore hole and do not persist laterally. The bulk of the sediment underlying the Kachua area is gray (reduced).

The Rajoir site is underlain by organic-rich clay and silt in the upper 40 meters. Thick, pebbly sand and gravel extend from 60 to 120 meters and from 340 meters to the bottom of the GSB hole at 450 meters. A pattern of crude, extremely thick, fining upward sequences exists in the vertical succession of strata that suggests large channel migration through the area. Thin (<5 meters) clay and silt units separate bodies of coarse sand and pebble gravel in the lower 340 to 440 meters of the section; however, their lateral extent is unknown. As at Srirampur, oxidized brown intervals of sediment are thin and do not persist laterally, nor do the thicker gravel units located in the upper 120 meters. Although the predominant sediment color is gray throughout the Rajoir section, brown oxidized units are inter-bedded with gray sands between 70 and 90 meters, and between 300 meters and the bottom of the hole in the Rajoir bore hole. These oxidized units may represent buried soils and former surfaces of the delta during times of low sea level in the past. But, unlike areas north of the Padma River where significant brown and red Madhupur sediment is encountered at depth, the sections studied here are dominantly

gray (reduced) throughout, with only sporadic and discontinuous zones of oxidation that lack lateral continuity.

A common property of both sites is the significant accumulation of gravel and coarse sand between 60 and 120 meters. Worldwide sea level lowering during glacial times would have caused Bangladesh rivers to incise into the delta to nearly 120 meters. Downcutting and increase in river grade dramatically increase the amount of coarse debris deposited in the entrenched deltaic river valleys. These low sea level gravel and sand bodies may provide valuable marker beds for mapping subsurface stratigraphy throughout the Ganges/Brahmaputra delta.

Quartz sand from undisturbed bore hole samples were analyzed by the Green Light Stimulated Luminescence (GSL) method in order to determine the amount of time that the sediment sample has been buried. Modern sand samples from the Meghna and Ganges Rivers were tested and found to be 0-250 years old. Thus, the age of the sediment burial is a close approximation of the age of the sediment.

Sediment dating has been completed for shallow bore holes at Brahmanbaria, Savar, and Meherpur, as well as for some of the deep bore holes at Srirampur. The thickness of Holocene (<10,000 years old) sediment across the delta ranges from 24 meters at Brahmanbaria to 42-44 meters at Savar and Meherpur. At Srirampur, basal Holocene sediment is found at a depth between 30 and 44 meters in the GSB hole; however basal Holocene sediment is recorded in a nearby BWDB bore hole at over 60 meters. The latter sample probably represents infilling of an incised valley. Average Holocene aggradation rates range from 2.4 mm/yr to 4.5 mm/yr across the middle and lower delta. More rapid short-term aggradation rates occurred at the beginning of the Holocene when sea level was rapidly rising and again during the middle Holocene when sea level approached its present position.

An age unconformity of several tens of thousands of years often is found below the Holocene deposits and is sometimes marked by oxidation and rare paleosols indicating

subaerial exposure of the delta surface. In GSB's Srirampur bore hole, mainly gray deltaic sediment at a depth of 104 meters is approximately 115,000 years old and at a depth of 158 meters, the lowest sample to yield a finite age, the sediment is 140,000 to 160,000 years old. The long-term aggradation rate at Srirampur for the entire late Pleistocene is about 1 mm/yr.

Investigation, Characterization and Mapping of the Aquifer System under Kachua Upazila Area, Southeastern Bangladesh

Anwar Zahid, D. Clark, Alamgir Hossain, J.Earle, M.A. Karim, Satish Chandra Das

Abstract

Groundwater is a vital resource that is withdrawn for municipal and rural supplies, agricultural, industrial and other uses. With the increasing demand and quality hazard of groundwater usage in the country understanding the long term sustainability and distribution of this resource is very important. Sustainable long term yield from aquifers, effective use of the water stored in aquifers, preservation of water quality and integration of groundwater and surface water in to a comprehensive management system has to be considered for exploration and development of groundwater resources.

A detailed investigation and study has been completed to provide the methodologies to describe the subsurface geologic and hydrogeologic conditions for aquifer mapping and characterization of the properties of the aquifers in Kachua Upazila area, southeastern Bangladesh. The hydrogeologic components in the study have been emphasized to assess the following aquifer parameters in the investigated area;

- Subsurface lithology, location and extent of the aquifers;
- Aquifer characteristics and properties of aquifer materials;
- Groundwater quality and any possibility of degradation with it's development;
- Arsenic distribution patterns in the aquifers on a broad scale;
- Fluctuations of groundwater table and movement of groundwater.

The study area of Kachua under Chandpur District was selected because of the severity of arsenic contamination in groundwater at shallow depth of the Upazila area. Kachua Upazila area can be divided into three units based on elevation and morphological features. Southeastern part has been defined as Chandina Alluvium High, which remains above normal flood level. Northwestern and southwestern parts have been defined as Chandina alluvium Medium and generally are under water for about 3 to 4 months. Maximum and minimum elevation of this unit is 6.0 and 4.6m from AMSL respectively. The water table ranges from 1.5 to 2.0 m below the surface. Northeastern and middle western depressed part of the area is defined as Chandina Alluvium Low.

The detailed study site is located at Sreerampur town in Kachua Upazila. The aquifer system at the study site can basically be divided into three fairly distinct systems. The upper aquifer system or 1st aquifer is essentially the shallow aquifer, the middle or 2nd aquifer system has generally been called the "deep aquifer" and the deeper system or the 3rd aquifer system is newly discovered at this site. The shallow aquifer extends down to has a thickness that varies between 35 and 70m. The aquifer sediments are composed of sand with lenses of clay. Water within this shallow aquifer is severely contaminated by arsenic.

The 2nd aquifer system extends beneath an aquiclude underlying the shallow aquifer down to 290 to 300m depth. This "deep aquifer" is hydraulically connected through out the depth and is separated from the deeper or 3rd aquifer system by a confining layer of considerable thickness. The aquifer is composed mainly of fine to medium sand, grey to

light brown in color, occasionally inter-bedded with clay bends. The thickness of this formation varies between 145 and 180m. The lower part of the upper aquifer consists mainly of grey medium to fine sand and extends down to 285 to 295m underlain by silty clay bed. The thickness of this part ranges between 40 and 85m. Although the "deep aquifer" appears to be free of arsenic, in some areas and depths high concentrations of salt, iron, or manganese makes it unsuitable for drinking purposes.

Below 10 to 12m thick silty clay/shale bed the deeper (lower) or 3rd aquifer was encountered, composed mainly of grey to dark grey fine to medium sand in places alternated with thin sandy shale/clay lenses. This deeper aquifer below 285 to 295m from surface is assumed to be sustainable safe and potential for good quality groundwater. Geophysical bore hole lithologic logs conducted at existing wells in upper aquifers throughout the Upazila area also reveal nearly similarity of grain size distribution up to investigated depth.

The groundwater chemistry in the area is very complex. Spatial and lateral variation of different chemical parameters of groundwater has been observed. The pH value ranges between 5.9 and 7.6, higher in the deeper samples. The most important physico-chemical parameter is wide variation of electrical conductivity (EC) values (360-5220μS/cm). With few exceptions, brackish groundwater tendency has been detected in deepest sections of the "deep aquifer" in almost entire Upazila area. But, the deeper aquifer shows good quality water with EC value of 525μS/cm. In many of the water samples collected from different depth levels concentration of chloride exceeds the WHO and DoE maximum allowable limit. Maximum chloride concentration in the "deep aquifer" was 1550mg/l in a sample collected from 280m depth at Sreerampur. However, in the deeper aquifer at the same location, chloride values are 90-94mg/l. Many of the wells finished in the "deep aquifer" contain iron far higher than the accepted level. Large concentrations in other dissolved ion concentrations such as iron, manganese, and sodium in the "deep aquifer' also make the water from some depths undrinkable.

Concentration of arsenic in all water samples from the shallow aquifer exceed maximum allowable limit of WHO and DoE for drinking water. Most samples collected from the "deep aquifer" have concentrations less than the limits. Where arsenic concentrations in wells finished in the "deep aquifer' exceed the limit it is likely the result of contamination from the shallow aquifer. The groundwater of deeper aquifer that is hydraulically separated by impervious clay layer from upper aquifer is safe from arsenic contamination.

Results of long duration (98.5 hours) aquifer pumping test on the deeper aquifer shows that the deep aquifer is hydrogeologically distinct from the shallow and 'deep aquifer' aquifer, and can yield significant amounts of potable water. Water-level data measured in two deep observation wells during the aquifer test was analyzed to determine deeper aquifer hydraulic properties. The aquifer properties estimated using the Hantush-Jacob solution are an aquifer storage of 0.0017, aquifer transmissivity of 2386 m^2/day, vertical to lateral aquifer hydraulic conductivity ratio of 0.0044, and a confining unit vertical hydraulic conductivity of 0.35 m/day. Drawdown in both deep observation wells becomes nearly constant in the interval from about 200 minutes to about 500 minutes.

Five observation wells were installed at the Sreerampu study site for use in the aquifer pumping test, one well in the shallow aquifer 2 wells (591 and 918 feet deep) in the 'deep

aquifer' and 2 wells (1100 and 1155 feet deep) in the deeper aqufier. Static water levels have been measured in the wells on a weekly basis since May 2003. Under natural conditions, there is a downward gradient from the water table to the 'deep aquifer', and water levels in the deeper aquifer are higher than water levels 'deep aquifer'. Therefore, natural ground-water flow is into the 'deep aquifer' from above and below and laterally away from the area towards coastal discharge areas.

Water levels in the shallow aquifer range from about 2 meters above sea level in the dry season to about 6 meters above sea level during the monsoon season. Water levels in the 'deep aquifer' are generally about 4 meters above land surface during the monsoon season, and drop dramatically with the onset of ground water pumping for irrigation starting in February. Water levels decline as much as 6 meters below sea level. Water levels in the deeper aquifer also decline during the irrigation season but only to about 2 meters below sea level. Monthly water levels have been measured in a series of 17 wells throughout the Kachua Upazila since February 2004. All of these wells are completed in the 'deep aquifer.' Water levels in all of these wells fell considerably below sea level during the pumping irrigation season and recovered at the end of large scale groundwater irrigation prior to the onset of the monsoon. Water levels dropping below sea level may cause concern for saline water intrusion.

Large-scale exploration of groundwater in the region has not been encouraged due to possibility of saline water intrusion or leakage from upper aquifer. Continued installation of large diameter production wells in the 'deep aquifer' can only be initiated for community drinking water supply conducting appropriate investigation. Proper sealing has to be considered in the confining clay layer during tube well installation to protect any leakage of arsenic contaminated water from shallow aquifer. Because of problems of sand boiling in dug wells and lack of preserved ponds due to use of chemicals for fisheries, dug wells and pond sand filters are not working properly in the region. Therefore installation of small diameter hand tube well in the 'deep' and deeper aquifers may be a necessity in many areas even with poor water quality.

Regional modeling of groundwater system has to be developed for effective water resource management plan to agricultural, rural and urban water supplies and to forecast the groundwater situation in advance for dry season usage. Maintaining water budget is vital for understanding human impact on water and ecological resources. Because of increasing demand and inadequate fresh water resources in the area, more effective and sustainable use of groundwater and surface water has to be formulated.

Deep Aquifer Recommendations -- Symposium Discussion

J. Whitney, D. Clark, G. Breit, A. Welch, J. Yount, C. Hoard, J. Earle, J. Imes

United States Geological Survey (USGS)

The USGS-GSB-BWDB cooperative studies on deeper aquifers in Chandpur and Madaripur Districts illustrate the geologic, geochemical, and hydrologic c complexity of the aquifers down to 450 m depth. The vertical and lateral complexity of the aquifer systems prevents the creation of simple and straightforward guidelines for the exploration and development of
deeper aquifers. Instead, these studies indicate that great care must be exercised in the development of deeper aquifers for human exploitation. The relative scarcity of thick aquitards in the Kachua and Rajoir study areas indicates that the depths chosen by government agencies, NGOs, and private drillers for new deep tube well must be based on knowledge of the local hydrogeological conditions.

In both Rajoir and Chandpur districts, many deep tube wells contained water of unacceptable quality for human consumption. However, arsenic was not the contaminant. Iron, manganese, and saline water were the common culprits. Water quality testing must become an integral part of subsurface water exploration and well installation. We recommend that prudent water quality standards be established for new wells installed at depths greater than 200 feet.

Potentially mobile arsenic is still a component of the deep sediment. Aggressive chemical treatments in deep tube wells should be avoided.

Recommended methods to characterize the water quality in the deep aquifer system in the Bengal delta before recommending installation of deep tube wells:

1. Create water quality aquifer maps for upazilas and districts by testing water quality in existing deep wells.

2. Conduct geophysical logging in existing deep tube wells to define local aquifers and aquitards.

3. Conduct surface resistivity surveys to map presence and/or absence of aquitards.

4. Install test wells in target aquifers and conduct water quality tests in the field and/or laboratory. Arsenic, iron, chloride, manganese, boron, and TDS (total dissolved solids) are the minimum concerns that should be tested for.

5. Standards for well installation, including well sealing, need to be established in order to prevent contamination of deeper aquifers by shallow aquifers.

6. Teach appropriate methods to government and private drillers.

7. Create a national database of tested deep tube wells that is easily accessible to public agencies and private individuals who wish to install new deep tube wells on the delta. The agency or institute that oversees the database can produce district and upazila maps upon demand and update their database on a regular basis with newly acquired water quality data. permits for new deep tube wells should include water quality testing. The results of those tests would then be added to the national or district database.

In order to determine the long-term effects of increasing the number of deep tube wells in an upazila or district, it would be useful to model the effects of ground water extraction Groundwater models are especially important near the coast, where the danger of aquifer contamination by sea water is very real.

Government agencies should consider implementation of criteria or regulations that govern the minimum subsurface conditions necessary to install multiple deep tube wells in an area. These conditions should address minimum water quality standards and reasonable aquifer protection (thickness and continuity of aquitards). Use of deep tube wells should be limited to providing domestic drinking water.

In areas where aquitards are thin, discontinuous, or absent, deep tube wells should be monitored on a regular basis to determine if shallow-aquifer arsenic is being drawn down to the deeper aquifers. Water levels should also be monitored.

Caution is the watchword for the development of the deeper aquifers. Pollution of clean drinking water, a precious natural resource, by human activities is not only a waste of economic resources, but may create another environmental health catastrophe. Deep aquifer water should be viewed as part of the solution to providing safe drinking water -- not the sole or preferred alternative.

Abstracts

Irrigation Water-Soils-Crops

Water-Soil-Crop Arsenic Interrelationships

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Introduction

The chemical properties of irrigation water coupled with soil properties may have an influence on the variation of arsenic accumulation in paddy rice soils. Soil properties such as clay content, pH and redox conditions (Marin et al., 1993), ionic composition (Khattak et al., 1991), type and amount of organic matter (Mitchell and Barr, 1995) are considered to be the important variables for availability and phytotoxicity of plants to arsenic. However, our understanding of the factors that regulate arsenic accumulation in paddy soils and rice is quite limited. The objective of this paper is to develop multiple regression (MLR) models to predict arsenic content in paddy soils and rice grain and to assess which soil and water chemical characteristics are most highly related to arsenic contents.

Methods

Data from survey work by the USAID-funded project in the dry boro rice of 2002 were used to develop multiple regression models. Three hundred thirty samples each of water, soil and rice from Senbag, Faridpur, Paba, Brahmanbaria and Tala thanas were collected. Soil and grain arsenic were used as response variables in MLR models using soil and ground water properties (Table 1) as predictor variables. For adding or dropping predictors from the MLR models we calculated C_p statistics, which provides a convenient criterion for determining the most appropriate variables. We used S-plus (version 6.2 for windows) (Insightful Corp., 2003) for all statistical analyses.

Table 1. Description of variables used

Codes	*Variables Description*	*Unit*
WP	Irrigation water Phosphorous	ppm
WFe	Irrigation water Iron	ppm
WS	Irrigation water Sulphur	ppm
WAs	Irrigation water Arsenic	ppm
SpH	Soil pH	unit less
SOM	Soil Organic Matter	%
Clay	Soil Clay	%
SP	Soil Available Phosphorous	ppm
FeO	Soil Fe-oxide	ppm
SAs	Soil Total Arsenic	ppm
GAs	Rice Grain Arsenic	ppm

For developing the MLR model for soil and grain arsenic prediction, we hypothesized that at least one predictor variable among WP, WFe, WAs, SpH, SOM, SP and FeO was a significant explaining power on soil or grain arsenic. The initial MLR models are:

$$SAs = \beta_0 + \beta_1 WP + \beta_2 WFe + \beta_3 WS + \beta_4 WAs + \beta_5 SpH + \beta_6 SOM + \beta_7 Clay + \beta_8 SP + \beta_9 FeO + \epsilon_{(error)}$$

$$GAs = \beta_0 + \beta_1 WP + \beta_2 WFe + \beta_3 WAs + \beta_4 SAs + \beta_5 SpH + \beta_6 SOM + \beta_7 Clay + \beta_8 SP + \beta_9 FeO + \epsilon\ (error).$$

Results

The Analysis of Variance on the initial model for soil arsenic showed that there is strong evidence that at least one of the predictor variables has a statistically significant influence on soil arsenic (p-value < 0.0001). The R^2 value indicates that all predictors (WAs, WP, WS, WFe, pH, OM, Clay, SP, FeO) explain 63.1% of the variation in arsenic concentration in paddy rice soils

Table 2. Coefficient Table of soil arsenic prediction model.

	Value	*SE*	*t value*	*Pr(>|t|)*
Intercept	-14.1	5.15	-2.73	0.0068
WAs	32.7	5.01	6.52	0.0000
WP	-2.34	0.686	-3.41	0.0007
WS	0.025	0.089	0.28	0.7762
WFe	0.397	0.106	3.73	0.0002
SpH	1.34	0.671	1.99	0.0473
SOM	-0.381	0.362	-1.05	0.2923
Clay	0.260	0.026	9.88	0.0000
SP	0.214	0.023	9.29	0.0000
FeO	0.0012	0.0003	3.90	0.0001

The relationships between soil arsenic and WAs, WP, WFe, SpH, Clay, SP and FeO were significant (Table 2). The relationship between soil arsenic and WS and SOM were not significant. We refitted the model without WS and OM, and examined the *Cp*-statistics values to determine whether they should be included. The *Cp*- statistics of WS and SOM were lower than that of the current model. Therefore, we dropped these two predictors from the initial MLR model.

The final MLR model for soil arsenic prediction was:

$$SAs = -14.8 - 2.3\ WP + 0.4\ WFe + 32.1\ WAs + 1.4\ SpH + 0.25\ Clay + 0.26\ SP + 0.001\ FeO$$

The Analysis of Variance on the initial model for grain arsenic showed that at least one of the predictor variables is statistically significant in explaining the response variable grain arsenic (p-value < 0.0001). The R^2 value indicated that all predictors (WAs, WP, WFe, SAs, pH, OM, Clay, SP, FeO) explained 42.4 % of the variation in arsenic concentration of the rice grain.

Table 6. Coefficient Table of grain arsenic prediction model

	Value	**SE**	**t value**	**Pr(>|t|)**
Intercept	1.3022	0.1768	7.3668	0.0000
WAs	0.3159	0.1784	1.7703	0.0776
WP	0.0735	0.0237	3.0968	0.0021
WFe	0.0028	0.0037	0.7748	0.4390
SAs	0.0101	0.0019	5.3412	0.0000
SpH	-0.1533	0.0228	-6.7299	0.0000
SOM	-0.0162	0.0123	-1.3221	0.1871
Clay	-0.0006	0.0010	-0.6118	0.5411
SP	-0.0002	0.0009	-0.2161	0.8290
FeO	0.0000	0.0000	0.6793	0.4974

The relationships between grain arsenic and predictors SAs, WP, and SpH were significant, whereas, the predictors WAs, WFe, SOM, Clay, SP and FeO were not significant. The *Cp*- statistics of WFe,

OM, Clay, SP and FeO were lower than those of the current model, and were dropped from the initial MLR model.

The final MLR model for grain arsenic prediction was:

$$GsAs = 1.3 + 0.4\ WAs + 0.08\ WP + 0.01\ SAs - 0.16\ SpH$$

Conclusions:

- WAs, WP, WFe, SpH, SOM, SP and FeO explained 63% of the total variation in arsenic accumulation in paddy rice soil.
- WAs, SAs,WP and SpH explained 42.4% of the total variation in rice-grain arsenic.

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Building and Improving Arsenic Analytical Capacity in Bangladesh

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Abstract

The Bangladesh agricultural agencies are facing big challenges to understand the potential impacts of arsenic from soil and water on the food chain, including the possibility of increased arsenic in soil, plant uptake of arsenic, reduced crop yields, degradation of food quality, loss of agricultural sustainability, and adverse impacts of arsenic on livestock. To address these issues, one of the highest priorities is the ability to accurately and precisely analyze arsenic in soil, plant and water. Until 2001, the Bangladesh agricultural sector had a very limited capacity for arsenic analysis. To address the situation, our collaborative research project, including national and international partners, established goals of improving analytical capacity, improving advanced education and training for scientists and students involved with arsenic, and developing research capacity to address arsenic issues in Bangladesh agriculture. This approach involves not only the enhancement of human resources through training but also the establishment of uniform methodologies and analytical quality control/quality assurance procedures. A major objective is the development of appropriate analytical and quality control procedures for the study of arsenic in irrigation water, soils and crops. Emphases are with (i) pore water sampling and extraction, (ii) assessment of soil-water arsenic, and soil properties that are useful to understand soil-water arsenic dynamics, and (iii) arsenic analysis including speciation. The national agricultural research and education institutions will eventually strengthen their own ways and means for generating capacity when and where it is needed to meet the goals they formulate and implement.

Capacity building is a comprehensive process, which includes the identification of constraints and the development and implementation of plans to overcome these constraints. It involves both the development of analytical capacity and human resources. Capacity development through graduate fellows program, distance education, training initiatives, and communication enhancement within the international community (scientist's participation program in international conferences and national workshops in which international scientists will participate), and provide current scientific literatures. It also involves effectively mobilizing and using existing and newly created capacities, establishing ways to bridge the gap between existing and required capacity, and sustaining the capacity over time.

At present each of our project partner institutions has established capacity to analyze arsenic (Figure 1), and also the partners are conducting collaborative research, training and human resources development utilizing their own analytical capacity.

To ensure quality of analytical work, our project is developing an analytical reference laboratory for arsenic analysis (BARI-CIMMYT Arsenic Laboratory) in the Bangladesh Agricultural Research Institute.

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Figure 1: Instrumental Set up and human resources development

This laboratory will play a lead role in the development of analytical quality control protocols, standardizing analytical methods, identifying internal reference materials, and assisting in routine internal quality control. The analytical reference laboratory will take the leadership in creating a quality assured arsenic data base which will be useful in understanding the nature and extent of the arsenic problem in Bangladesh and facilitating research for the development of arsenic management strategies.

What are Safe Levels of Arsenic in Food and Soils?

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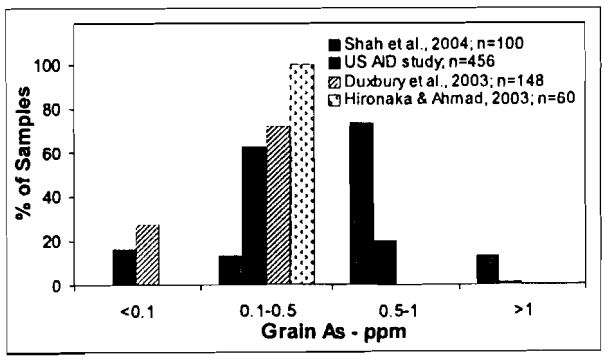
Abstract

A perspective on arsenic "safety" in food and soils in Bangladesh is provided by using current limits or standards for arsenic (As) that have been established by various countries and organizations. Approaches to setting standards for Bangladesh using some of these values are discussed.

One approach to determining safe levels of As in food is by comparison to safety standards for drinking water. This comparison is made on the basis of inorganic As species as these are considerably more toxic than organic As species. Rice is considered by itself because of the large intake of rice in the Bangladesh diet (~ 450g/adult/day or 80% of caloric intake). With an adult daily intake of 450 g rice and 4L of water, equivalent intakes of inorganic As from these two sources occur at As levels of 550 and 110 ppb As in rice for water standards of 50 ppb (Bangladesh) and 10 ppb (WHO and many western countries), respectively. This calculation assumes that 80% of the As in rice is inorganic (Williams et al., this symposium) and that the bioavailability of As in rice is similar to that in water (demonstrated in a pig feeding study; Naidu [personal communication]). Several countries, including the UK and Australia, currently use a 1 ppm limit for arsenic in food and this is often cited as a "safe"level for rice. This value is clearly too high for the Bangladesh level of rice consumption.

An alternative strategy in establishing As standards for both drinking water and rice is to consider the combined dietary intake of inorganic arsenic from these sources, rather than evaluating each individually. In 1989, the FAO and WHO jointly established a provisional tolerable dietary intake of 0.015 mg inorganic As/kg body weight/week, or 130 µg/day for a 60 kg adult. This level is already exceeded by the intake of 200 µg/day from drinking 4 L of water containing 50 ppb As. A tolerable limit for intake of inorganic As has not been established for Bangladesh, but how this could be used to evaluate dietary As intake from rice and water at daily intakes of 450 g and 4 L, respectively, is illustrated in the table for a 200 µg/day inorganic As intake limit.

Scenario	Max. Acceptable As (ppb)	
	Rice	Water
Sources equal	277	25
Water 10 ppb	444	10



The distribution of arsenic in raw rice grain from various studies with fairly large numbers of samples is shown in the figure. Overall 22% of the samples exceeded 0.5 ppm (500 ppb), indicating that inorganic arsenic intake from rice will exceed that from water at the 50 ppb level in a significant number of instances. It is noted, however, that this conclusion is strongly influenced by the data from Shah et al., which is all from Chapai Nawabganj Sadar. Other studies are from a variety of areas across Bangladesh that represent varying levels of environmental As contamination.

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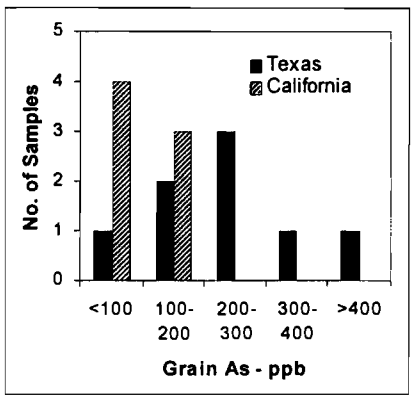
A survey of total As in rice purchased in the USA (Ithaca and Syracuse, NY) found that the average As concentration of rice consumed in this part of the USA was 107 ppb, or one-third of that consumed in Bangladesh. Rice produced in the USA contained an average of 181 ppb, with substantial differences between California and Texas. One sample from Texas contained 753 ppb As. Rice samples from Bangladesh, India and Pakistan had unusually low As contents and were all aromatic types. The per capita exposure to inorganic As in rice is estimated to be 32x higher in Bangladesh than in the USA (using more representative data for As in Bangladesh rice [340 ppb], differences in per capita intake and differences in inorganic As percentages between rice grown in Bangladesh and the USA [Williams et al., this symposium]).

Country	No. of Samples	Mean As ppb	Country	No. of Samples	Mean As ppb
Argentina	1	136	Korea	2	45
B'gladesh	3	46	Lebanon	1	169
Bhutan	1	32	Pakistan	3	33
China	2	146	Spain	2	186
Egypt	2	32	Thailand	9	93
Greece	1	114	USA	22	181
India	16	37	V'nzuela	12	84
Italy	7	158	**TOTAL**	**84**	**107**
				Median	**84**



Arsenic intake in Bangladesh from food sources other than rice is minimal, with the possible exception of vegetable and root crops. Unfortunately, reports of consumption data for these foods as well as their As content vary widely, making it impossible to derive arsenic intake data with any degree of confidence. A systematic approach is needed to evaluate the importance of dietary intake of arsenic from vegetable and root crops.

The question of what is a safe level of arsenic in soil is considered from the following perspectives:
- Phytotoxicity to rice (agricultural sustainability and food security)
- Ingestion (human health)
- Leaching to groundwater (environmental and human health)
- Variability in soil characteristics (a safe level in one soil may be unsafe in a different soil)

Pot studies (Jahiruddin et al, 2004; Khan, this symposium) have shown that levels of As (arsenate) in irrigation water above 1 ppm, and raising soil As content by more than 5 ppm, reduce the yield of Br 29 rice, the most productive boro season variety. These treatments also showed residual effects on BR 33 rice in the following Aman season. An interaction between arsenic and phosphate additions to soil was observed with P inputs increasing As toxicity and grain As content.

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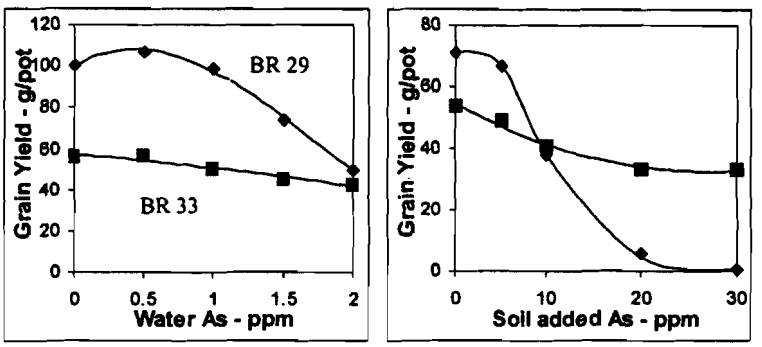
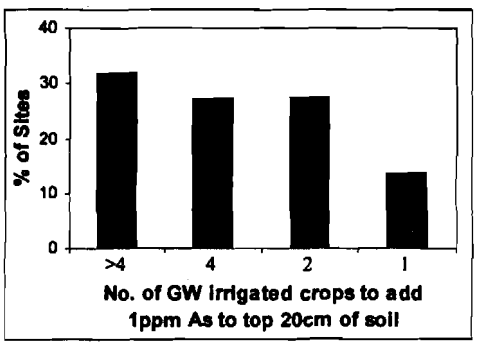


Constructed from data in Jahiruddin et al., 2004.



It is uncertain that adding As to soil immediately before doing an experiment duplicates the behavior of contaminated As soils, which have gone through many redox cycles. Nevertheless, addition of As at levels that reduce rice yields in pot experiments will occur quite quickly given the quality of irrigation water in Bangladesh. Without losses, As in the top 20 cm of soil will be increased by 5-10 ppm in 10 crops (years) at 41% of the 456 irrigation well sites in the US-AID study.

There are no federal regulations limiting soil As levels in the USA. However, the US Environmental Protection Agencies (EPA) superfund risk model gives a value of 0.43 ppm total soil As for a cancer risk of 1 in 10^6 for exposure by *soil ingestion*. This has created an interesting situation for regulation of soil As by individual States as the average background As level in USA soils is ~ 5 ppm. State standards for remedial action vary tremendously, but many require this when soil As is above the natural background, which is often less than 10 ppm. Background soil As levels have been shown to vary with soil type (Chen et al, 2002), which is sometimes considered in evaluations of soil contamination. Soil As standards in other countries (Canada, UK, Netherlands, Australia) are generally in the 10-20 ppm range for agricultural use of soils.

Total soil As in the top 15 cm of Bangladesh soils was above 10 ppm for 48% and 65% of the 456 sites in the 2002 US-AID study and 161 sites in Shah et al. (2004), respectively.

Similarly, 21% and 4% were above 20 ppm. Lower soil As levels were reported by Huq et al. (2003) for a 24 upazila study; average values > 10 ppm were found in only 3 upazila while 18 upazila were <5 ppm. A nationwide map of soil As (M. Miah, this workshop) will provide

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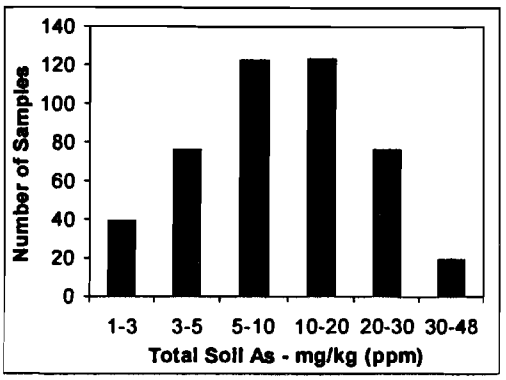
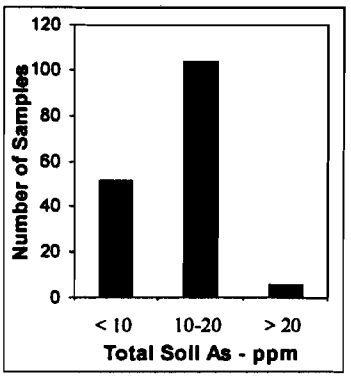
a better perspective on soil As levels, but it is clear that there is cause for concern from both agricultural sustainability and human health perspectives.



US-AID, 2002 study



Shah et al. 2004

Establishment of soil As limits based on the potential for leaching to groundwater is not very developed. Wenzel et al., (2002) derived upper limits of ~200 and 1000 ppm total soil As for protection of groundwater at the 10 and 50 ppb As levels, respectively, in Austria. The USA EPA uses a "toxicity characteristic leaching procedure" (TCLP) to determine the As leaching potential of potential hazardous wastes, including contaminated soils. This procedure uses a dilute acid extraction with a 1:20 soil to solution ratio and concentrations of As > 5 ppm in the extracting solution indicate that the soil requires remediation. A soil can only fail this test when its total As level greater than 100 ppm. These studies suggest that leaching of As from soils to groundwater is unlikely to be a problem in Bangladesh. However, leaching of As from flooded and reduced paddy soils has been little studied (A. Khan, this symposium).

It is important to consider whether the safety standards used by developed countries are appropriate for the Bangladesh context where there are multiple severe health and environmental issues. Therefore there is a need for Bangladesh to establish it's own safety standards for arsenic in food and soils. These standards will depend on acceptable risk levels, tempered by what is achievable. In considering standard development, it is clear that potential impacts of As on food security and direct human exposure to arsenic are both important for human health outcomes.

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Arsenic status of water, soil, rice grain and straw of individual shallow tube well command area of Brahmanbaria

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Introduction

Through a general survey, it has been reported that two third of Bangladesh is affected by groundwater-arsenic (As) contamination (BGS, 1999). Use of ground water for irrigation in Bangladesh is increasing to achieve increased agricultural production. Presently, about 47 % of the net cultivated area is under irrigation, of which about 71 % utilizes groundwater (NMIDP, 1998). Most of the groundwater in irrigated areas of Bangladesh is contaminated with arsenic (Khan *et al.*, 1998). Survey work conducted by project partners (BARI, BRRI, BINA and BAU) also revealed the same results and identified many hot spots of As-contaminated areas. Brahmanbaria is one of the worse As-contaminated areas. To understand the distribution and transport of As in water and soil and its uptake by rice crops, an investigation was conducted in Brahmanbaria. The present paper reports the results of the command area study at Brahmanbaria of Bangladesh.

Methods and Materials

A few studies on the arsenic status of water, soil, rice grain and straw of a shallow tube well command area of Brahmanbaria (Old Meghna Estuarine Floodplain Soil, AEZ-19) were conducted during the boro season of 2003. Arsenic content of experimental STW water is 200 ppb, and the command area size is 2.1 hectare. Temporal and seasonal variation of As content of STW was studied **(Study 1)**. Water and soil of the irrigation channel were collected at 10 m intervals from the STW, to study the distribution pattern of arsenic in the drain **(Study 2)**. Four rice varieties (BR 28, BR 29, BR 36 and BINA 6) replicated four times were grown in the study field of the STW using the arsenic contaminated water to study the As contents of grain and straw **(Study 3)**. Ninety-six sampling spots in a 20 m grid arrangement were selected and geo-referenced by a GPS. Soil, grain and straw samples were collected from these sampling spots. In 86 sampling spots, BRRI Dhan 29 was grown. The other varieties grown were BRRI Dhan-28, BRRI Dhan-36 and BINA-6 in 1 spot each and the local variety in 7 spots. The crop was harvested from a 1m x 1m area for determination of grain and straw yields and arsenic contents **(Study 4)**. Soil, rice grain and straw samples were analyzed, following tri-acid digestion, by HG-AAS (for arsenic) and FAAS. Descriptive statistics and correlations were obtained for arsenic contents of water, soil, rice grain and straw samples.

Results and Discussion

Study 1 : Seasonal and temporal variation of arsenic content in irrigation water from the shallow tube well (STW).

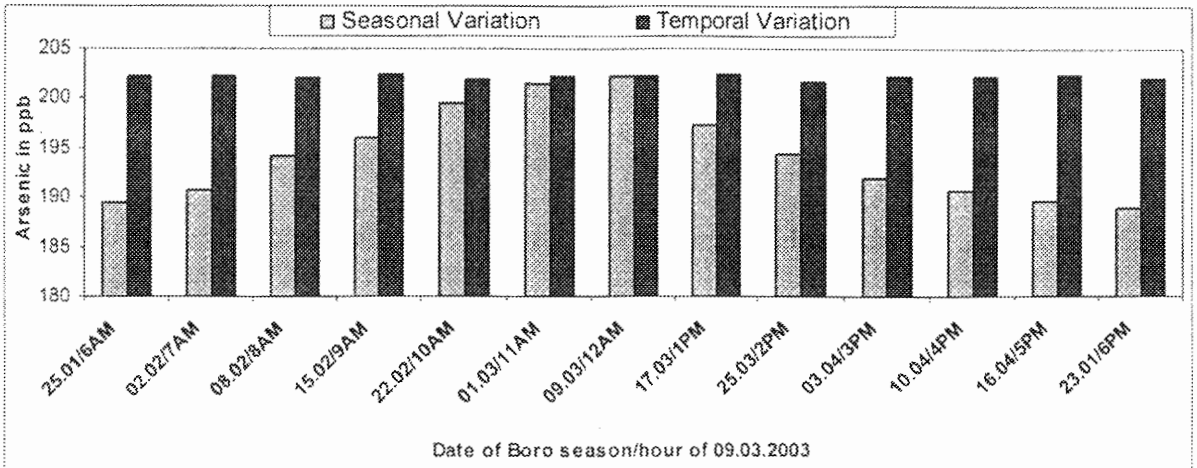

Fig. 1. Seasonal (Boro, 2003) and temporal (09.03.2003) variation of As content in STW water

higher in early march and declined thereafter (Fig. 1).

Study 2 : Study of Arsenic content in irrigation water and corresponding soil samples from the irrigation channel.

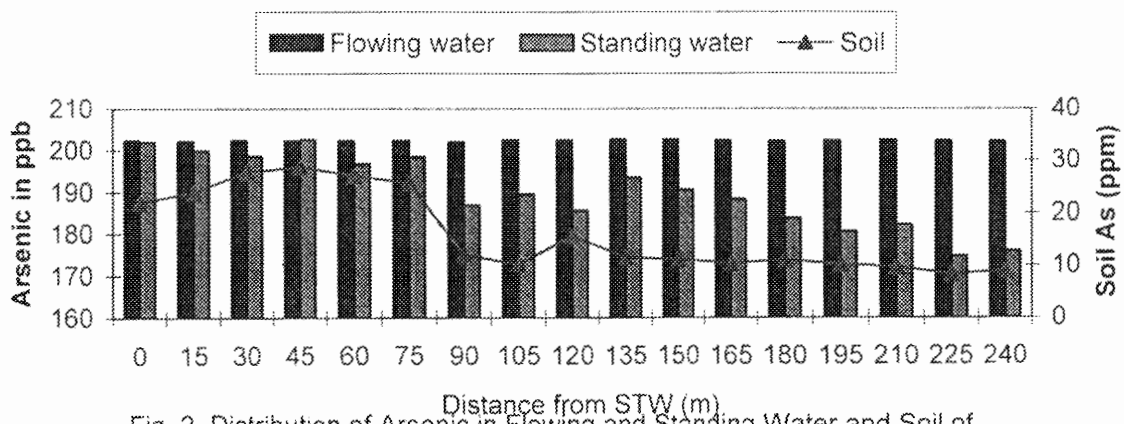

Fig. 2. Distribution of Arsenic in Flowing and Standing Water and Soil of Irrigation Channel

It was found that As contents of irrigation water (standing water) were slightly higher and those of drainage-canal soil were considerably higher at the starting point than at the far point of the irrigation channel, while that of the flowing water of the irrigation channel remained the same at all points (Fig. 2).

Study 3: Study on the influence of arsenic-contaminated irrigation water on yield and uptake of four Boro rice varieties.

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Table 1: Yield, yield attribute and As content of Boro varieties grown with As contaminated irrigation water.

Treat ment	Life duratio n	Plant height (cm)	No. of filled grains/ panicle	1000 grain weight (gm)	Grain yield (t/ha)	Straw yield (t/ha)	Arsenic content in ppm	
							Grain	Straw
BR 28	137	85.3c	89.3b	21.82	4.00b	4.82c	0.550 ab	3.79ab
BR 29	154	93.8b	103.2a	21.33	4.92a	6.19b	0.576 ab	3.81ab
BR 36	140	87.9bc	86.5b	21.48	3.84b	4.65c	0.507 b	3.57b
BINA6	159	115.8a	106.5a	21.51	5.02a	6.56a	0.612 a	4.06a
SE (±)	-	3.2	5.6	NS	0.12	0.14	0.03	0.17
CV (%)	-	4.8	8.3	2.5	3.9	3.5	7.6	9.3

It was found that As content was higher in long duration varieties and lower in short duration varieties (Table 1).

Study 4 : Study of macro level variation of arsenic content in boro rice grain, straw and soil from the STW command area.

Arsenic contents of soil, rice grain and straw of the Brahmanbaria STW command area are described in Table 4 (a).

Table 4 (a). Arsenic contents of soil, rice grain and straw of Brahmanbaria command area.

Parameter	Arsenic concentration		
	Min.	Max.	Mean
Soil (ppm)	3.21	24.4	9.42
Rice grain (ppm)	0.16	1.20	0.43
Rice straw (ppm)	0.33	4.02	2.00

Table 4 (b). Correlation between arsenic content of soil, grain and straw of Brahmanbaria command area.

Arsenic content	Soil-As	Grain –As
Grain-As	0.62**	
Straw-As	0.84**	0.61**

Significant correlations between arsenic contents of soil, grain and straw were observed in samples of Brahmanbaria (Table 4b). Arsenic content was higher in near and depressed points of the command area while it was lower in far and elevated points of the command area.

Conclusion

Study 1 : 1. There is no variation of Arsenic content in irrigation water of a specific Shallow Tube Well within a day.

2. Arsenic content of irrigation water was higher in early march and declined there after.

Study 2: 1. There is no variation of Arsenic content of irrigation water (flowing water) in a irrigation channel.

2. Arsenic content of irrigation water (standing water) was higher at starting point and lower at end point of an irrigation channel

3. Arsenic content of adjacent soil sample was higher at starting point and lower at end point of a irrigation channel

Study 3: 1. Arsenic content in rice grain and straw is higher in long duration BINA-6 and BR 29 and lower in short duration BR 28 and BR 36.

Study 4: 1. Arsenic content of rice grain, straw and soil sample is comparatively higher at nearest point of STW and lower at far point of STW

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Arsenic in Bangladesh Environment and its Impact on Food Chain through Crop Transfer

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Abstract

Arsenic contamination of ground water in Bangladesh and the incidence of Arsenicosis patients do not go hand in hand. People living in the same household and drinking from the same source of As-affected water are not equally affected. Moreover, the manifestation of Arsenicosis also varies from region to region in the country. This has raised the question about the sole contribution of As-contaminated drinking water as to the cause of Arsenicosis. Many efforts have been directed towards ensuring supply of As-free drinking water with varying successes. Even if As-safe drinking water is assured, the question of irrigating soils with As-laden ground water will continue for years to come. The possibility of As accumulation in soils through irrigation water and its subsequent entry into the food chain through various food materials cannot be overlooked. The average background concentration of arsenic in Bangladesh is much below 10 mg kg^{-1} soil. However, in some areas where soils receive As-contaminated ground water irrigation, the concentration has been found to be as high as 80 mg kg^{-1} soil. 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. The surface 0-150 mm soil contain more As than the sub-surface 150-300 mm soil. The maximum As concentration in irrigation water was found to be 0.55 mg L^{-1}; irrigating a rice field with this water when the requirement is 1000 mm of water, it has been calculated that the As load will come to 5kg As ha^{-1} yr^{-1}. Many crops receiving As contaminated water as irrigation have been found to accumulate As at levels that exceed the minimum allowable daily limit (MADL) of 0.2 mg per kg dry weight. Some vegetables crops like Arum (*Colocassia antiquorum*), Kalmi (*Ipomea aquatica*), Amaranthus (*Amaranthus* spp.) etc. were found to be As accumulators. In arum, the concentration of As have been found to be as high as more

than 150 mg kg^{-1} dry weight. Rice and wheat receiving As-contaminated irrigation water have been found to sequester the toxic metalloid into roots and stems. However, the quantity of rice consumed per person per day with the content of As in the grain may in many instances, surpass the MADL. Study with animals has shown that the As in rice is more bio-available than that in vegetables. Irrigated rice fields, on the other hand, allow the growth of green and blue-green algae that has been considered as helpful in auto-renewal of nutrient status of paddy soils, more particularly with nitrogen, phosphorus and other minerals. It has been observed that these algae accumulate high amount of As along with other heavy metals. The algae, besides being consumed by the fish, release the As for the subsequent crop on mineralization, thus intensifying the vicious cycle of As contamination of the food chain. However, the growth of green and blue-green algae in the irrigated rice fields could be used as a measure for phytoremediation of As contamination.

Arsenic in paddy soils of Bangladesh: levels, distribution and contribution of irrigation and sediments

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Introduction

Arsenic is widely distributed in nature. It is associated with igneous and sedimentary rocks, particularly with sulphide ores. Natural phenomena such as weathering, biological activity, and volcanic activity, together with anthropogenic inputs, are responsible for the release of arsenic into the atmosphere, soil and water. Bangladesh is currently facing the challenge of high arsenic concentration in shallow aquifers (Nickson *et al.*, 1998). A large number of hand and shallow tube wells (STW) in some of the localities of 59 districts out of 64 districts have been identified to have arsenic (As) concentration above the Bangladesh standard of 0.05 mg As L^{-1} (Alam *et al.*, 2002). To meet the growing demand for food, the farmers had to cultivate high yielding varieties of Boro rice, which require a large volume of irrigation water. Irrigation with arsenic contaminated groundwater increases its concentration in soil (Jahiruddin *et al.*, 2000; Meharg and Rahman, 2003; Ali *et al.*, 2003), and eventually arsenic enters the food chain through crop uptake and poses long term risk to human health ((Duxbury *et al.*, 2003; Islam *et al.* 2004a). But detailed study on the levels and distribution of arsenic in irrigated paddy soils, and the contribution of different sources of arsenic on build up of soil arsenic levels are still lacking in Bangladesh. This paper presents the levels and distribution and also quantifies the contribution of different sources of As on the build up of As in paddy soils of five upazilas of Bangladesh.

Materials and Methods

Four hundred fifty six geo-referenced samples for each of irrigation water, soil (0-15 cm depth), rice grain and rice straw were collected from 456 STW command areas of five upazila of Bangladesh during the boro season of 2002. The upazilas were B.Baria, Faridpur, Paba, Senbagh and Tala. The soils of B. Baria and Senbagh were developed from the sediments deposited by the Old Meghna river, while the soils of the remaining three upazilas from the Ganges river borne sediments. The soils were analyzed for clay, organic matter, pH, available P and free Fe oxide along with total As, phosphate extractable and oxalate extractable As. Soil, rice grain and straw samples were digested with concentrated HNO_3 and H_2O_2. Total As in the digest and water samples was determined by flow-injection hydride generation atomic absorption spectroscopy (HG-AAS).

Results

There was a wide variation in total As concentration in the soil samples from different STW command areas of five upazilas (Table 1). The levels of total As in soils over the locations of the upazilas ranged from 0.3 –48.8 μg g^{-1} with a mean of 12.3 μg g^{-1}. The soils of the Ganges river floodplain (Paba, Tala and Faridpur) had higher soil As levels compared to those of Meghna river floodplain (B. Baria and Senbagh). Mean total As levels of 4.6, 6.5, 7.2, 19.4 and 19.6 μg g^{-1} were found in Senbagh, B.Baria, Paba, Tala and Faridpur upazila, respectively . Of the 456 samples, 53% of the soils had total As from 0-10.0 μg g^{-1}, 26% of the soils had 10.1 – 20.0 μg g^{-1}, 17% had 30.1-40.0 μg g^{-1}, and the remaining 1% of the soils had >40.0μg g^{-1} (Fig 1).

Table 1. Arsenic concentration in soil, water and grain samples of different upazilas of Bangladesh

Parameter	Statistical analysis	Upazila					All Upazila (n=456)
		B. Baria (n=110)	Faridpur (n=100)	Paba (n=100)	Senbagh (n=41)	Tala (n=105)	
Soil total As ($\mu g\ g^{-1}$)	Range	6.7-38.6	9.9-48.3	0.3-23.6	0.3-7.7	5.2-48.8	0.3-48.8
	Mean±SD	6.5±6.9	19.6±6.7	7.2±2.9	4.6±1.5	19.4±7.3	12.3±8.8
Phosphate extractable As ($\mu g\ g^{-1}$	Range	0.12-10.6	1.0-20.8	0.4-4.5	0.3-2.1	0.8-14.8	0.1-20.8
	Mean±SD	1.9±2.1	4.7±3.5	1.2±0.6	0.8±0.4	4.3±2.3	2.8±2.7
Oxalate extractable As As ($\mu g\ g^{-1}$)	Range	0.5-32.5	3.4-28.9	0.9-9.5	0.8-5.2	2.7-24.8	0.6-28.9
	Mean±SD	4.8±5.1	9.4±4.5	2.6±1.6	2.5±0.9	11.5±5.3	6.6±5.4
Water-As ($\mu g\ ml^{-1}$)	Range	0.00-0.51	0-0.28	0-0.13	0.02-0.36	0.002-0.46	0-0.51
	Mean±SD	0.11±0.11	0.10±0.07	0.02±0.01	0.14±0.07	0.15±0.09	0.10±0.09
Grain-As As ($\mu g\ g^{-1}$)	Range	0.08-0.93	010-1.08	0-0.53	0.13-0.92	0.09-1.01	0-1.08
	Mean±SD	0.42±0.22	0.48±0.22	0.07±0.10	0.44±0.20	0.33±0.15	0.34±0.24

Total As content in soils was positively correlated with clay content (r=0.52**) , soil pH (r=0.45**) and Fe oxide (r=0.62**) (Figs. 2-4). The results indicated that fine textured, high-pH soils might have higher As content compared with coarse textured soils. The soil As status was very weakly correlated with organic matter (r=0.10 ns) indicating that organic matter did not contribute to the As in soils (Fig. 5). A highly significant relationship between phosphate extractable As and oxalate extractable As (r=0.88**) indicated that these extractants extracted As from the same pool in the soil (Fig. 6).

Cultivation of boro rice in Bangladesh requires about 1000 mm of irrigation water. Irrigating the fields with water of 0.10 μg As mL^{-1} would add 1000 g As ha^{-1}. Sediment deposition is important for medium low to very lowland only. Our data showed that deposition of 2.53 t sediment $year^{-1}$ in Meghna river floodplain added 16.0 g As $ha^{-1}year^{-1}$. But sedimentation is very low in medium high and high lands where two rice crops are grown annually. The average yields of Boro and T.Aman rice are 3.2 and 2.5 t ha^{-1}, respectively. The mean As concentrations in Boro rice grain and straw in this study were 0.34 and 3.44 $\mu g\ g^{-1}$, respectively. The As concentrations of T. Aman rice grain and straw were about 0.25 and 2.0 $\mu g\ g^{-1}$, respectively (Islam *et al.*, 2004 b; Jahiruddin *et al.*, 2004). The total As uptake by Boro and T. Aman crops was 23 g ha^{-1}. With the remaining 981 g ha^{-1} As, if it stays in the rice field, level of soil As would increase by 0.50 $\mu g\ g^{-1}$ per year.

The vertical distribution of As in irrigated Boro fields and adjacent non-irrigated fields showed that the level of soil As was higher in the top soil compared to sub-soils of irrigated Boro fields while the reverse was found for non-irrigated fields indicating the contribution of irrigation water As in building up the level of soil As in paddy soils. During the monsoon season, a good amount of As may be lost from the soil with runoff water and also through volatilisation as gaseous arsines under anaerobic condition. The percolation of irrigation water in paddy field is low, generally 1-2 cm a day. Besides, the upper 1-2 cm of a flooded paddy field is aerobic where As will be adsorbed by the soil particles. Therefore, the leaching loss of As through the rice soil will be minimal. The As accumulated in the top layers may also be subject to losses by water erosion due to heavy monsoon rains.

Conclusion

At present 42% of the soils of the five upazilas have more than 10 $\mu g\ g^{-1}$ As but irrigating Boro rice with high-As water will likely increase the level of As in soils as well as uptake by the crops. It may not be cost effective to remediate As-contaminated paddy soils. There may be a number of options for reduced inflow of As in the rice fields. The concentration of As in STW water decreases with increasing well depth. Therefore, pumping irrigation water from greater depths might lead to a decrease in the As load on the rice fields. Another option is the economic use of irrigation water by reducing the depth of ponded water and by alternate wetting/drying practice for Boro rice cultivation.

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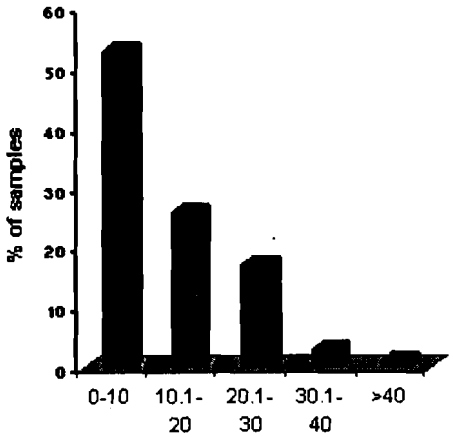

Fig. 1 Distribution of soil As

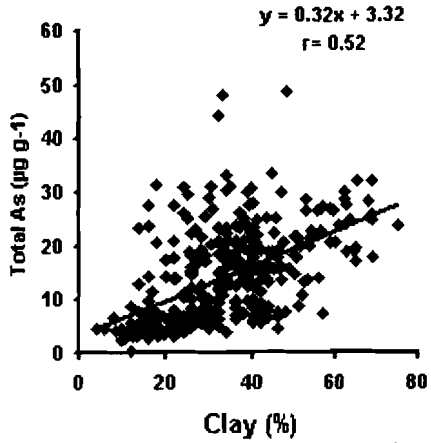

Fig 2. Relationship bet. clay and total As

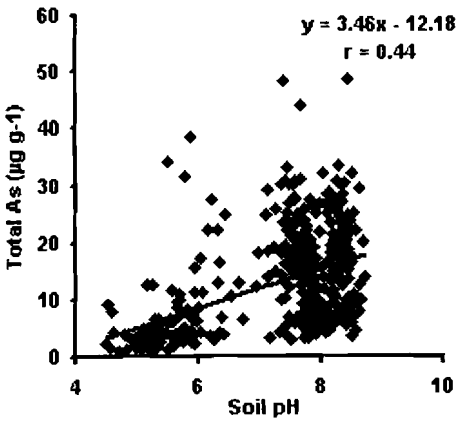

Fig 3 Relationship bet. soil pH and total As

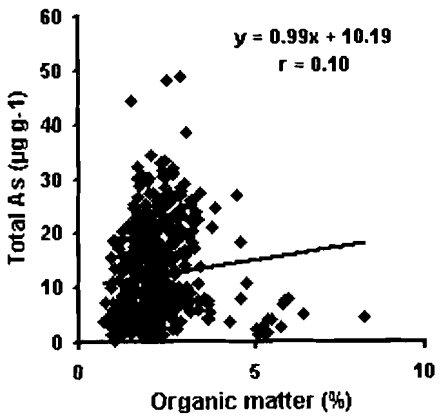

Fig 4 Relationship bet. OM and total As

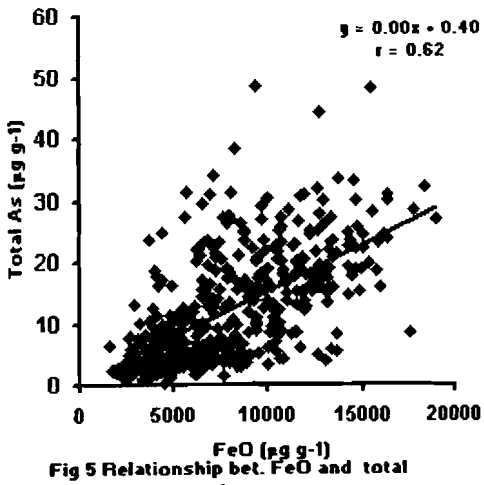

Fig 5 Relationship bet. FeO and total As

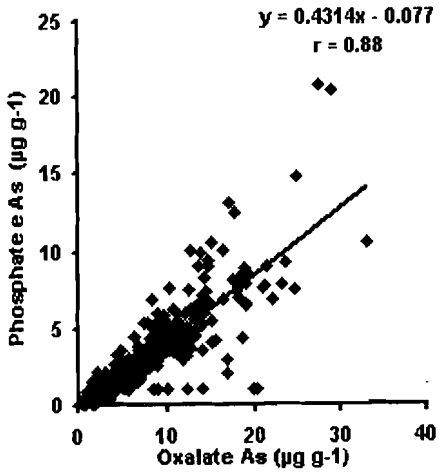

Fig. 6 Relationship bet. oxalate As and phosphate As

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Arsenic in the Water-Soil-Crop Systems: PETRRA-BRRI-BAU-AAS Study

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Introduction

Groundwater contamination by arsenic (As) is a severe problem in Bangladesh. About 20 million people are at risk of As contamination (WHO, 2001). Most attention has been given to the arsenic contamination of drinking water. Besides domestic use (drinking, cooking, washing, etc.), significant quantities of water from shallow aquifers are being used in the dry season especially for irrigating Boro rice. In Bangladesh, both shallow tube-wells (STW) and deep tube-wells (DTW) are used in large numbers (approximately 2.6 million) to irrigate about 2.5 million ha of land, which contributes significantly to the country's food grain production. About 86% of the total groundwater withdrawn is utilized in the agricultural sector (WRI, 2000). Long-term use of As-contaminated water for irrigation may result in elevated As concentration in soils and plants (Ullah, 1998; Jahiruddin *et al.*, 2000; Huq *et al.*, 2003; Panaullah *et al.*, 2003; Islam *et al.*, 2004). Arsenate and phosphate are analogues, and addition of one of the elements to soil may affect the uptake and availability of the other. The objective of this study was to assess the arsenic status in the irrigation water-soil-rice plant system.

Methodology

Levels of As in the irrigation waters, soils, and boro rice (grain and straw) from 100 shallow tubewell (STW) areas of Chapai Nawabganj sadar upazila were measured. Similarly, the As concentration in 230 STW water samples from Charghat upazila were determined. Again, water As concentrations of 171 DTWs and STWs in the PETRRA sub-project areas were analyzed. Besides these, fluctuation of water-As concentration in the observation wells in Charghat and Chapai Nawabganj was monitored over the year. Further investigation was undertaken during the 2002 & 2003 boro seasons to examine the variation of water As concentration, if any, due to well depth, well age, and distance of wells from rivers.

The effects of As contamination on yield and As accumulation in rice were investigated. Two sets of pot experiments, one with soil-added As and the other with irrigation-water As, were conducted in the net-house at BAU, Mymensingh. The levels of soil added arsenic were 0, 5,

10, 15, 20, 30, 40 and 50 ppm, and those of irrigation-water As were 0, 0.1, 0.25, 0.5, 0.75, 1.0, 1.5 and 2 ppm. The effect of added As (plus 2.6 ppm initial soil As) was tested directly on Boro rice (cv. BRRI dhan 29) and its residual effect on T. Aman rice (cv. BRRI dhan 33). Further pot experiments were carried out to evaluate the effect of As in the presence of P on Boro rice. The effects of added As on rice, Indian spinach and red amaranth were also investigated in the green-house at BRRI (3.0 ppm background-soil As).

Results and Discussion

The As concentrations varied widely between locations. The STW-water As concentrations ranged from 0.015 to 0.352 $\mu g\ mL^{-1}$ (Fig. 1), and the soil As contents ranged from 5.8 to 17.7 $\mu g\ g^{-1}$ over the locations. There was a good correlation between water As and soil As (Fig. 3), indicating a possibility of As build up in soil with time. The rice-grain As concentration was in the range of 0.24 to 1.30 $\mu g\ g^{-1}$; 11% of the samples had As levels < 0.5 $\mu g\ g^{-1}$, and the remaining 89 % were in the range of 0.50 to 1.0 $\mu g\ g^{-1}$ (Fig. 2). The grain-As concentration was poorly correlated with soil-As concentration as well as irrigation-water As concentration. Thus, the availability of soil As for plant uptake indicates a complex system. The rice straw-As concentrations ranged from 1.48 to 17.6 $\mu g\ g^{-1}$ and were strongly associated with grain As concentration (Fig. 4). High concentration of As in rice straw fed to cattle may be a threat to cattle health. About 89% of the rice grain grown in Chapai Nawabganj irrigated with As-contaminated water may lead to an intake of more than 100% of the potential maximum tolerable daily intake (PMTDI) for an adult of 70 kg body weight.

From another study it appeared that 8% of the STWs in Charghat (n=230), 56% in Chapai Nawabganj (n = 100) and 29% in the other districts (n = 171) had As concentrations above 0.05 mg L^{-1} (the maximum permissible limit). Further it was observed that As concentration tended to increase in the beginning of the dry months, peaked in May, and then declined with the start of the monsoon. Comparing types of wells, water-As concentration was found to be the highest with HTWs (27%), followed by STWs (21%) and DTWs (7%). Well depth between 40 and 160 ft had the highest level of water As. There was no correlation between water As and well age. The water As level in wells decreased with increasing distance from the rivers.

The results of pot experiments demonstrate that there was a significant yield reduction above 10 ppm soil-applied As or above 1 ppm irrigation-water added As (Figs. 5 & 6). The As concentration in rice grain increased with increasing application of As added either through

irrigation water or direct addition to the soil; however, all concentrations were below 1 ppm. The maximum permissible limit of As is 1 ppm for seafoods where organic As comprises above 90 % of the total As. This limit could be less for rice since about 80 % of As in rice grain is inorganic. Again, the straw-As concentrations in all cases were much greater than 1 ppm. There was a residual effect of both soil- and water-added As on the second crop (T. Aman rice). The As-P interaction study indicated that the adverse effect of As was further aggravated by P addition to soil. The leaf size of Indian spinach was reduced and the leaves turned yellowish green color when As was applied at 20 mg kg^{-1} soil. Such negative effect of added As was not observed in case of red amaranth. The highest As content was recorded in roots followed by leaves and stems.

Acknowledgement

The authors are grateful to IRRI-PETRRA, Bangladesh for providing financial support to carry out this work.

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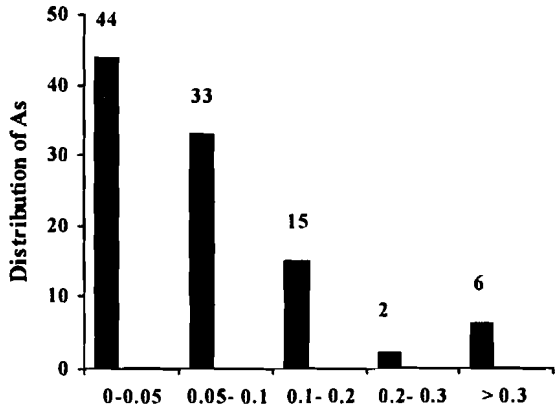

Fig. 1 Frequency distribution of water As (n = 100)

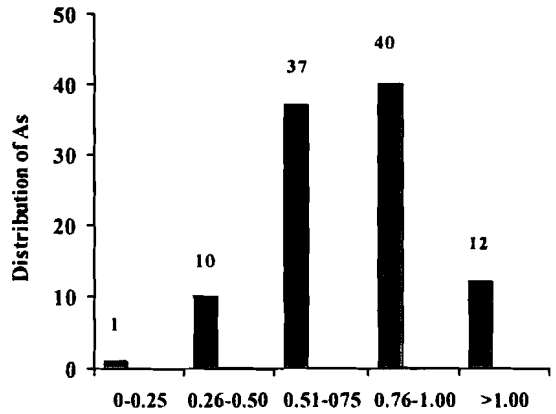

Fig. 2 Frequency distribution of grain As (n = 100)

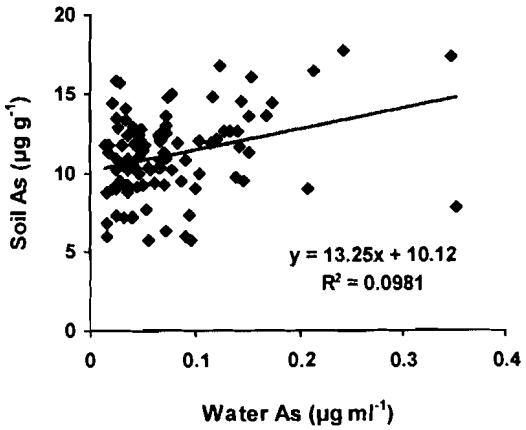

Fig. 3 Relationship between soil As and water As (n = 100)

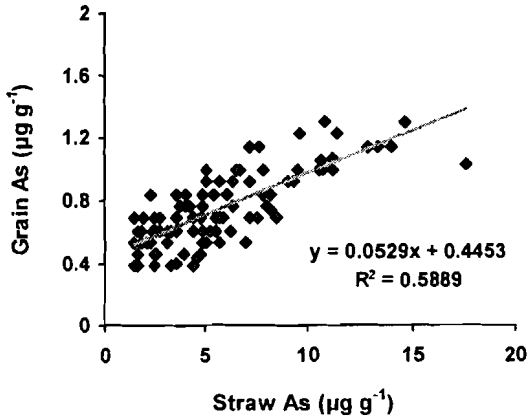

Fig. 4 Relationship between grain As and straw As (n = 100)

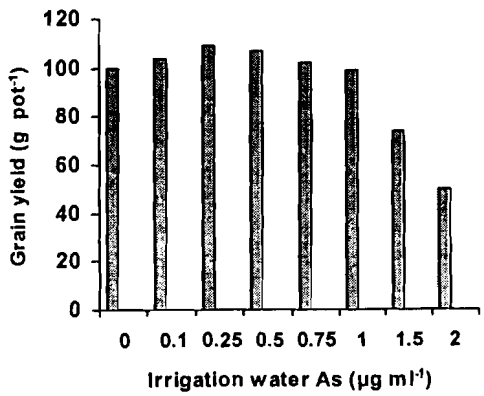

Fig. 5 Effect of irrigation water As on grain yield of rice (Pot expt.)

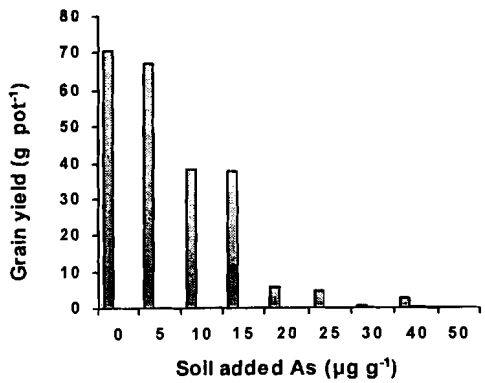

Fig. 6 Effect of soil added As on grain yield of rice (Pot expt.)

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Arsenic in Irrigation Water: Spatial Variability of As Content and Selected Chemical Parameters - Comparison with BGS Data

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Introduction

In Bangladesh, groundwater from shallow depth is contaminated by naturally occurring As in 59 out of 64 districts (BGS/DPHE, 2001). Groundwater is used extensively in irrigation of rice, the staple food of Bangladesh, with 83% of the total irrigated area under rice cultivation (Dey et al., 1996). Large areas of Bangladesh have to rely on groundwater for irrigation of staple crops such as rice (Panaullah et al., 2003; Nickson et al., 1998). Irrigation with arsenic contaminated groundwater is leading to elevated levels of arsenic in paddy soils (Alam and Satter, 2000) which may lead to increased concentration of arsenic in rice (Meharg and Rahman, 2003; Duxbury at el., 2003), vegetables (Alam et al., 2003) and other agricultural products (Abedin, 2002a). The exact cause of arsenic release that is poisoning the ground water and soil is still poorly understood, and variability of arsenic in soil and water across the space is not clear. Moreover, there are diverse opinions about the exact cause of arsenic release and the variability in soil and water and strong disagreements on the source of arsenic in the ground water (Islam, 2003). Relatively little is known about the spatial variability of arsenic in soil. Arsenic in groundwater has been extensively studied by BGS (BGS, 2001) in relation to its implications on the health ecosystem and has established a huge database on arsenic and other chemical constituents of groundwater. On the other hand, the USAID funded Arsenic Project is assessing arsenic concentration in irrigation water and its impact on the food chain, particularly through rice. These studies have some common aspects such as arsenic concentration and chemistry of groundwater. This current study aims (i) to determine the spatial variability of As and some selected parameters in shallow tube well (STW) water and (ii) to compare the results of data generated through Arsenic project funded by USAID with those using BGS data.

Methodology

The study used ground water data generated by Arsenic project and BGS in Faridpur Sadar Thana and south-west hydraulic zone of Bangladesh where sizeable geo-referenced database on As, Fe, Mn and P concentration in ground water are available. Faridpur is located in the alluvial and deltaic plain of Bangladesh which has been recognized as the most arsenic contaminated area, and detailed chemical analysis of ground water has been provided by both Arsenic Project and BGS. In south-west hydraulic zone, wide range of data has been collected by both the projects at the national scale. Data were analyzed by "Test kit" method in BGS and "Tri Acid method" in Arsenic Project.

Semivariograms were calculated to determine the spatial dependency of water As, Fe, Mn and P both for the surveys in Faridpur and south-west region by GS+ 5.3.2. Maximum lag distance and lag interval for the semivariance were determined iteratively to best fit the model having highest R^2, the lowest residual sum of squares (RSS) and spatial dependence close to unity. Kriging interpolation was performed to spatially describe the distribution of As, Fe, Mn and P concentration in irrigation water. Comparisons are made both in surface and tabular forms.

Results and Discussions

There is significant difference ($P<0.01$) in the average As level of the two data sets both in Faridpur and south-west hydraulic zone (Table 1). Average level of Mn of BGS data does not differ significantly from that of Arsenic project in both the locations (Table 1) but Fe and P concentrations were higher for BGS data in Faridpur. All the water parameters were highly variable with CV as high as 143% for As data generated by BGS and lowest 56% for Mn concentration determined by the Arsenic project both in Faridpur. The variability in data generated by BGS was, in general, higher than that generated by Arsenic project irrespective of locations. The higher variability in BGS data could bepartially attributable to the use different agencies involved in analysis of the sample water. Arsenic concentration correlated positively with Fe and P but in general, have little to negative relationship with Mn.

The distribution of As was strongly positive skewed except for Arsenic Project data from Faridpur. This result suggests that the data are randomly distributed, that is, not normally distributed for the BGS data in Faridpur and in the south-west hydraulic zone; hence, the changes in value seemed to be independent of the respective sampling location. All other parameters were strongly positive skewed in south-west hydraulic zone and BGS in Faridpur. The coefficient of skewness of As, Fe, Mn and P in Arsenic project in Faridpur was very low. The frequency distribution can be regarded as being normally distributed, and this result indicates that dependence exists between change in value and increasing sampling distance. Semivariance is, therefore, developed with increasing distance between sampling points. Semivariance for As, BGS data in Faridpur and Arsenic project data in south-west hydraulic zone suggest spherical model while, BGS data in south-west hydraulic zone and Arsenic project data in Faridpur suggest exponential model with high R^2, the lowest residual sum of squares (RSS) and spatial dependence close to unity (Table 3). Semivariance of Arsenic project in Faridpur reaching the sill within the sampled scale, whereas in the other cases semivariance displayed a different trend. This suggests that for Arsenic project in Faridpur, the changes in value will be independent when their separation distance exceeds effective range 4890 meters and all other cases the samples will not be stochastically independent from each other within their scale value. The random distribution of the data points indicates a nugget effect, i.e. the variance is not spatially structured at the effective range (95160m for BGS Faridpur, 287700m for BGS SW and 27560m for Arsenic SW). However, spatial dependence could be exist below these ranges. Similarly, Fe, Mn and P in Arsenic project in Faridpur the semivariance models are Spherical, Exponential and Spherical respectively and hence the changes in value will be independent when their separation distance exceeds effective range 3110, 17490 and 3108 meters. Other cases spatial dependence could be exist below the ranges (For Fe, 36240m in Faridpur BGS, 633000m in sw BGS, 240468m in sw Arsenic. For Mn, 9630m in Faridpur BGS, 82300m in sw BGS, 125100m in sw Arsenic. For P, 40410m in Faridpur BGS, 591900m in sw BGS.

Spatial variability maps of As, Fe, Mn and P in ground water pumped through shallow tube well has been created for BGS and Arsenic project both for Faridpur and south-west hydraulic zone of Bangladesh and are presented in Fig. 1. Both BGS and Arsenic project data show that arsenic concentration is relatively higher in the south and south- eastern part of south-west hydraulic zone although the pattern of concentration varied between the two data sets. The situations were very different in Faridpur Thana, where Arsenic project data indicated that most of the area have high As concentrations, while for the BGS data As concentration were low (<50ppb) in most of the area. One of the reasons for the difference between the spatial variations exhibited by two data sets is that the sampling points of the two data sets were not the same. Other explanations are the difference in the analytical method and the involvement of several agencies in the analysis of samples in the case of the BGS data. The spatial relationship between As and the parameters are also supported to the relationship earlier mentioned.

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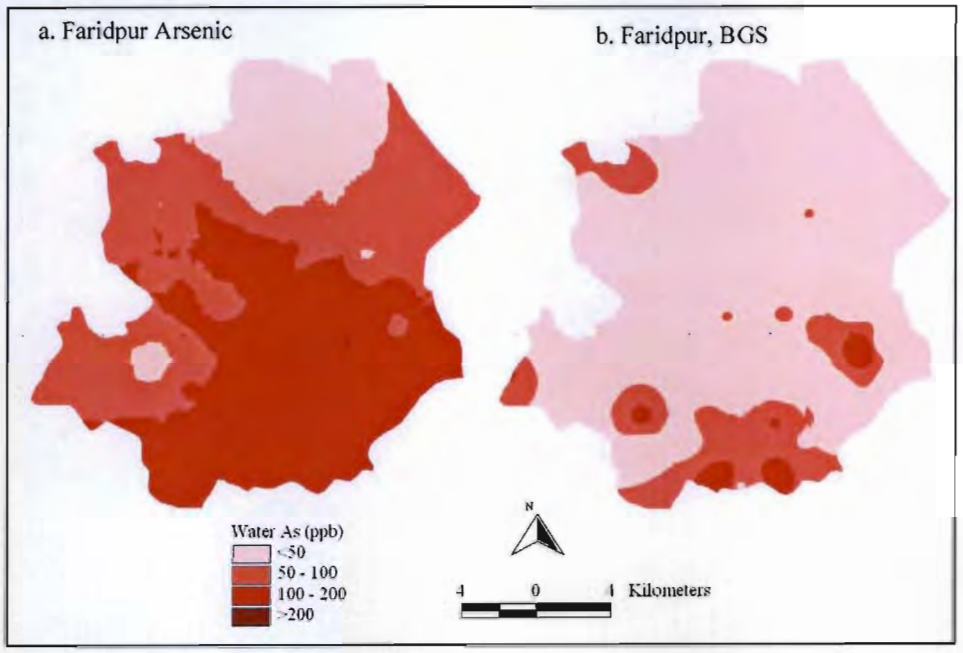
1. Descriptive statistics and mean comparison of Arsenic Project and BGS data

Items	Arsenic Project				BGS			
	Faridpur							
	As	Fe	Mn	P	As	Fe	Mn	P
Mean	112.63	4.08	0.64	91.00	31.94	5.64	0.66	127.00
SD	67.36	2.57	0.36	56.90	45.72	4.92	0.72	106.00
Max	247.04	10.75	1.56	222.9	200.00	19.60	4.23	500.00
Min	13.24	0.15	0.01	3.40	1.00	0.05	0.04	20.00
Skewness	0.36	0.46	0.16	0.34	2.16	0.90	2.17	0.78
CV (%)	59.81	62.99	56.25	59.81	143.14	87.23	109.09	83.46

Items	Arsenic Project				BGS			
	Faridpur							
	As	Fe	Mn	P	As	Fe	Mn	P
t- value	9.13**	2.34*	0.21	2.50*				
SW Region								
Mean	87.30	4.56	0.45	-	121.70	3.85	0.52	1.26
SD	86.94	3.69	0.47	-	164.20	3.65	0.62	1.59
Max	530.31	18.41	2.35	-	1660.00	30.40	3.87	11.70
Min	0.30	0.02	0.02	-	0.00	0.00	0.00	0.00
Skewness	1.76	1.29	1.63		2.02	1.73	1.73	2.84
CV (%)	99.59	80.92	104.44		134.92	94.81	119.23	126.19
t-value	3.18**	1.79	1.32					



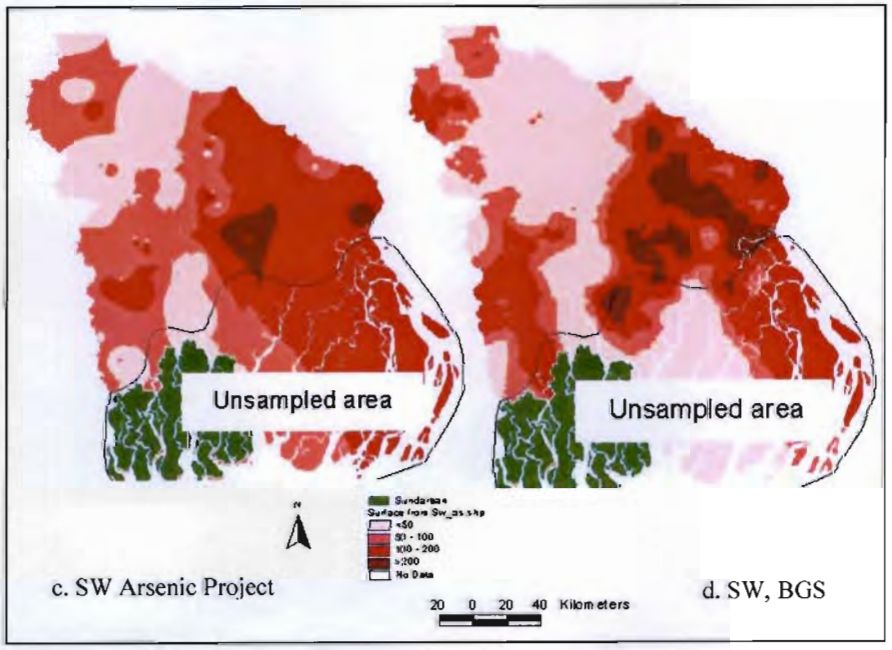


Figure 1 (a, b, c, d). Spatial variability maps of As in ground water pumped through shallow tube well.

Management Strategies to Reduce Arsenic Uptake by Rice

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Abstract

Arsenic contaminated irrigation water in Bangladesh is most likely responsible for high arsenic levels in soils used for growing rice. Elevated arsenic concentrations in rice grain produced in such high arsenic water-soil environments have been demonstrated. Because Bangladeshi diets are dominated by rice, arsenic contaminated rice could be aggravating existing human health risks from arsenic contaminated drinking water in southern and central Bangladesh.

Recently several surveys of arsenic in rice grain (788 samples total) have been undertaken (Shah et al., 2004; USAID, 2003; Duxbury et al., 2003; Hironaka & Ahmad, 2003, Meharg & Rahman, 2003). Utilizing the distribution of these grain arsenic concentrations and per capita daily consumption of rice (450 g), we estimate that daily arsenic intakes from 24% of the rice samples would be in excess of daily water intakes at the current Bangladeshi standard of 50 ppb. Alternatively, daily arsenic intakes from 84% of the Bangladeshi rice samples would exceed daily arsenic intakes from water at the US and European drinking water standard of 10 ppb. These simplified estimates of arsenic consumption from only rice and water indicate that arsenic from rice is an important source of exposure in the Bangladeshi food system. Thus management strategies need to be developed to reduce arsenic uptake by rice.

Reduction of arsenic uptake by rice can be addressed by avoidance or minimization strategies. One avoidance approach can be derived from the spatial analysis work of Ross et al. (2005). Their study identified that 24% of total irrigated boro rice in Bangladesh is grown in areas where groundwater arsenic is greater than the 50 $\mu g\ L^{-1}$ Bangladesh standard. Many of the areas with high groundwater arsenic (100-200 $\mu g\ L^{-1}$; > 200 $\mu g\ L^{-1}$) are found in the central part of the country near the Padma and Meghna rivers with ample surface water. Development of more irrigation schemes with these surface water sources could provide a clean substitute for contaminated groundwater and avoid further degradation of soils in these areas.

Reduction of iron oxides under flooded, anaerobic conditions releases inorganic arsenic from soils/sediments which is then more available for uptake by rice. Under aerobic soil conditions, most arsenic remains bound to iron oxides and unavailable to plants. So for irrigated boro rice areas with high arsenic groundwater and no uncontaminated surface water substitute, avoidance options might include shifting to upland (nonflooded) cereal crops such as wheat or maize. Upcoming data from the USAID Arsenic Project nation-wide survey will be used to make comparisons of arsenic contents in maize or wheat relative to boro rice in Bangladesh.

Minimization management strategies to reduce arsenic accumulation in rice include varietal selection and more aerobic cultivation practices. Limited studies comparing arsenic uptake in Bangladeshi rice varieties points to significant genetic and site variation (Table 1), but more comparative studies of genotype x environment (G x E) interactions with existing varieties are

needed. Also plant breeding programs need to seek traits that both increase tolerance to arsenic and reduce arsenic uptake. The recent work of Liu and colleagues (2004, 2005) is an important contribution to this area. They demonstrated that differences in arsenic uptake between rice varieties are influenced by iron plaque formation and regulated by plant phosphorus status.

Table 1

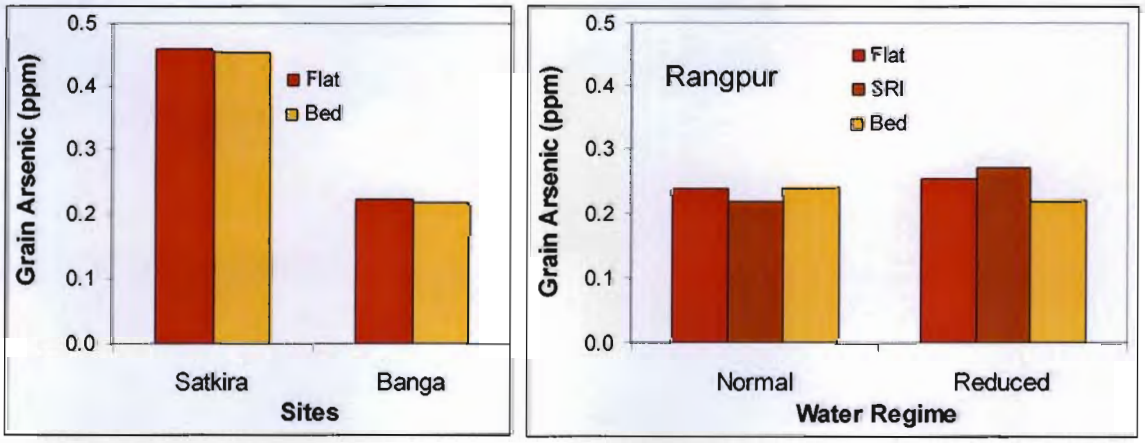
Bangladesh Varieties	Dinajpur[1]	Gazipur[2]	Brahmanbaria[3]
	Grain arsenic ((µg/g)		
BR11	0.104	0.043	-
BR28	-	0.067	0.550
BR29	-	0.180	0.576
BR32	0.173	0.044	-
BR33	0.378	0.206	-
BR 36	-	-	0.527
BR39	0.196	-	-
BINA 6	-	-	0.591

[1] Soil Management CRSP, unpublished
[2] Meharg and Rahman, 2003
[3] USAID, 2004

For the reasons stated above, uptake of arsenic by rice is reduced when the growing environment is more aerobic. Permanent raised beds, SRI (System of Rice Intensification) and aerobic rice are emerging cultivation practices that produce rice in a more aerobic soil environment by avoiding flooding and using less irrigation water. So far experiment station and farmer participatory trials with permanent raised beds and SRI show promise, while aerobic rice is still a new, developing technology.

Despite our expectations that aerobic cultivation practices would reduce arsenic uptake by rice, results from experiments with permanent raised beds and SRI have not shown differences in arsenic concentration to date (Fig 1). Nevertheless, on a highly contaminated soil (68 mg/kg) Xie and Huang (1998) observed a 22% increase in yield and a 24 % decrease in rice grain arsenic after furrow drainage and maintenance of moist soil.

Fig 1.



Opportunities for remediation of arsenic contaminated flooded soils by amendments are limited because most proposed additions such as ferrous sulfate would have negative secondary effects in flooded soils (iron toxicity). Xie and Huang (1998) found that MnO_2 addition effectively reduced As (III) in the soil solution, but only slightly changed the arsenic concentration in rice grain. Under aerobic soil conditions and with a very contaminated soil, Lombi et al. (2004) reported that gypsum additions reduced extractable arsenic and arsenic in the soil pore water. Arsenic uptake by lettuce was decreased with the gypsum treatment but not in ryegrass. The use of gypsum and MnO_2 as amendments for flooded rice in Bangladesh should be investigated further.

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Mineralogy and Arsenic Bonding in Bangladesh Rice Paddy Soils

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The objective of this paper is to review the mineralogical factors that impact the reactions of arsenic in the rice-paddy soils of Bangladesh, with emphases on mineralogical composition, mineralogical controls of soil-arsenic retention and release, and the implications of mineralogy to arsenic in rice culture.

METHODS OF MINERALOGICAL ANALYSIS

Soil samples for this study were collected from the 0-15 cm depth of *boro* (dry season) rice paddies in five *thanas* of Bangladesh, including Paba (High Ganges River Floodplain), Tala (Ganges Tidal Floodplain), Faridpur (Low Ganges River Floodplain), Brahmanbaria (Old Meghna Estuarine Floodplain), and Senbag (Old Meghna Estuarine Alluvium). Individual samples were air dried, separated into sand, silt, and clay particle-size separates. Individual samples were analyzed for total arsenic and total iron following total dissolution by closed vessel microwave digestion by HF/HNO_3. Additionally soil Fe was assessed by selective extraction with (i) citrate dithionite to determine total free Fe-oxide content, and (ii) pH 3.0, 0.2 M ammonium oxalate (in the dark) to determine poorly crystalline Fe-oxide content; soil arsenic was assessed by selective extraction with (i) pH 3.0, 0.2 M ammonium oxalate (in the dark) to determine arsenic associated with poorly crystalline Fe oxide, and (ii) pH 4.0, 0.1 M Na phosphate to determine readily exchangeable arsenic (1). Particle mineralogy was investigated by x-ray diffraction, synchrotron x-ray microprobe, XANES, SEM, and TEM procedures.

RESULTS AND DISCUSSION

Spatial Variability and Soil Mineralogy

Soil mineralogy, though relatively similar with respect to the principal minerals present, was highly variable with respect to soil texture and mineral concentrations. The major factors influencing soil-surface mineralogy are alluvial source material, position in landscape, soil weathering, and soil management.

The principal reactive minerals were di- and tri-octahedral micas (especially biotite), high-Fe vermiculites, smectites, Fe-chlorite, and the Fe oxides, goethite, lepidocrocite, and ferrihydrite (Fig. 1A, B). All samples also contained quartz and feldspar. In the current study, gibbsite was not identified in any of the rice-paddy soils. Relatively low concentrations of calcite were observed in almost all Faridpur samples. Fe sulfides (pyrite, mackinawite) were detected in only a few samples. There was a positive correlation (r^2 = 0.45) between free Fe-oxide content and layer-silicate Fe content, indicating that the Fe oxides likely originated from the weathered high Fe layer silicates. Layer silicate weathering follows the following sequence: micas → chlorite → vermiculite → smectite. Fe-oxide content of the soil would be expected to increase with

this weathering sequence for biotite mica, due to the release and reprecipitation of layer silicate structural Fe during weathering.

Arsenic Retention and Release by Soil Minerals

The arsenic contents of the 472 surface soils in this study varied from 0.7 to 66.0 mg As kg^{-1}. Arsenic concentration decreased in the following approximate order by *thana* (Tala > Faridpur > Paba > Brahmanbaria > Senbag). Soil-As concentration was moderately correlated ($r^2 = 0.33$) with soil Fe-oxide content, indicating the probable association with soil Fe-oxide minerals. Ammonium-oxalate extractable As averaged approximately 70 % of total arsenic. This result indicates that As was highly associated with the poorly crystalline Fe-oxide component. An average of 23 % of total As was extracted to pH 4.0, 0.1 M Na phosphate, indicating that most of the As was strongly bound and was not readily ligand exchanged by phosphate.

In an assessment of 15 high As soils, with soil As concentrations averaging 22.0 mg As kg^{-1}, As was associated with sand (29.9 mg As kg^{-1}), silt (17.5 mg As kg^{-1}), and clay (34.1 mg As kg^{-1}) particle-size fractions. A synchrotron x-ray microprobe study indicated that As bonding to layer silicate (mica, chlorite, vermiculite) edge sites was negligible. In the sand fraction, As was largely associated with Fe oxide weathering rinds within schist and weathered mica aggregates (Fig. 1C, D, E)

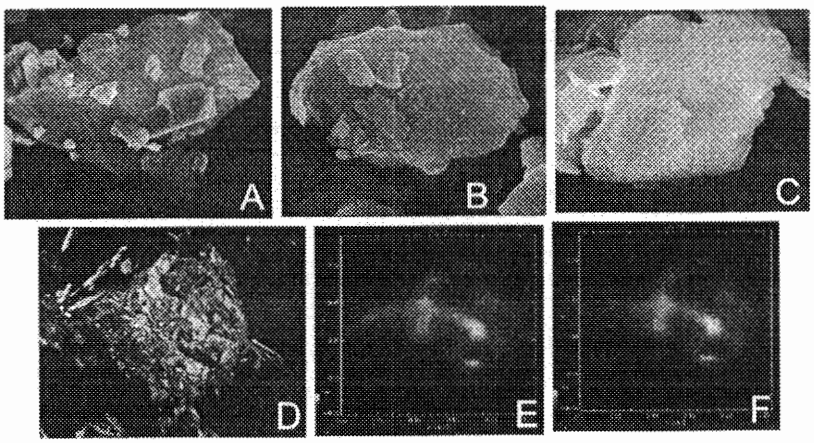

Fig. 1. (A) SEM of vermiculite from a Bangladesh rice-paddy soil; (B) SEM of biotite; (C) SEM of chlorite; (D) SEM of a weathered biotite aggregate (white ring in center is an Fe oxide weathering product); (E) map of Fe in aggregate D; (F) map of As in aggregate D (The close correspondence of the maps of Fe and As indicate that As in the weathered sand aggregate is largely associated with the Fe oxide weathering product.).

Both As^{3+} and As^{5+} species are largely retained by ligand exchange to soil Fe oxides, predominantly as inner sphere adsorption complexes at the oxide surface (Fig. 2).

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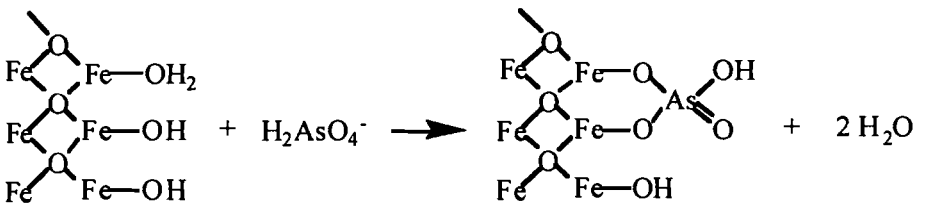

Fig. 2. Both As^{3+} and As^{5+} are largely adsorbed in the rice-paddy soils of Bangladesh by the formation of inner sphere surface adsorption complexes with soil Fe oxides.

Bonding to layer silicate edge sites was negligible compared to bonding to Fe oxides. Fe sulfide phases (pyrite and mackinawite) were identified in only a few of the rice-paddy soils of Bangladesh, but if present, these minerals would also expect to contribute to As bonding.

The dissolution and solubility of soil Fe-oxide minerals are highly redox dependent. Under reducing conditions, soil Fe-oxide minerals are solubilized, especially the highly reactive poorly crystalline Fe oxides, such as ferrihydrite. Upon dissolution, surface-adsorbed As is also released, resulting in the increased solubility of soil As.

Influence of Soil Minerals on Arsenic Dynamics in Rice Paddy Soils

The solubility of arsenic in rice-paddy soils is strongly impacted by redox potential and the dissolution and solubility of soil Fe oxide (Fig. 3). Arsenic toxicity is more problematic under flooded rice culture than under dryland conditions, because of the enhanced solubility of arsenic with the former.

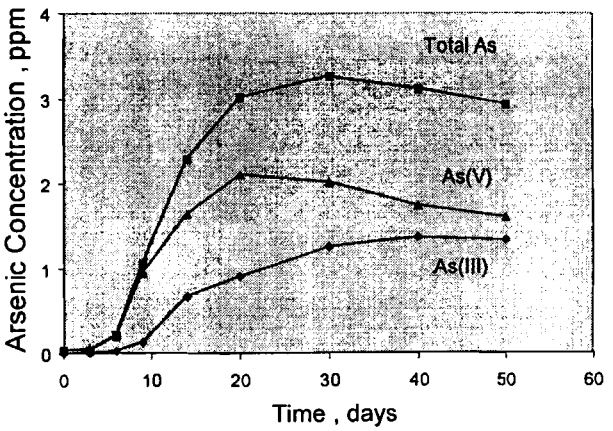

Fig. 3. The time-dependent solubilization of soil As resulting from the dissolution of soil Fe oxide during flooding and reduction of a soil.

Under the conditions of flooded rice culture, the rice plant pumps oxygen to the roots. The oxygen diffusing from the plant roots results in an increase in redox potential at the

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root/soil-solution interface and the precipitation of Fe oxide (lepidocrocite, goethite, ferrihydrite) at the root surface (Fig. 4). The mineralogy and morphology of this Fe-oxide plaque is influenced by soil environmental conditions, including dissolved Fe^{2+} concentration, soil texture, and mineralogy, and soil solution pH and dissolved ionic composition. This plaque is also a site for adsorption of dissolved As^{3+} and As^{5+}, and is likely to strongly impact As adsorption by plants.

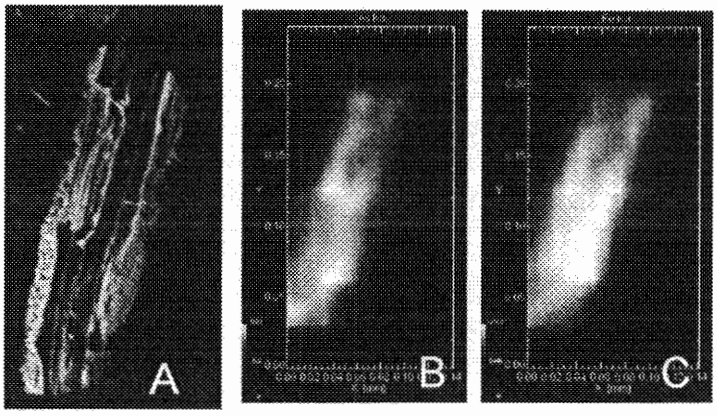

Fig. 4. (A) SEM of the Fe-oxide plaques of a rice root; (B) map of As associated with the plaque (the light colored region indicates a region of higher As concentration); (C) map of Fe associated with the plaque. In these images there is a high correlation between regions of high As and Fe concentrations, indicating that the As is associated with Fe oxide.

CONCLUSIONS

Fe-oxide minerals strongly impact arsenic dynamics in flooded rice culture, primarily because of their impact on arsenic solubility, retention, and release. Rice plants are able to modify their environment by the formation of an Fe-oxide plaque at the rice root surface, even in a highly reduced soil. This reaction likely strongly impacts arsenic retention by rice, though specifics of this reaction are still not fully understood.

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Nationwide Survey of Arsenic in Soils, Water and Crops in Bangladesh

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INTRODUCTION

Arsenic (As) poisoning has become a major public health problem and environmental issue in Bangladesh. It is well-reported that most of the ground water from shallow tube well, which is widely used for both drinking and irrigation is highly contaminated with As (BGS/DPHE, 2001). Consumption of As contaminated water and foods in the As affected areas of Bangladesh is a significant risk to public health. Contamination of ground water by As has been reported from many countries including Argentina, Australia, Chile, China, Hungary, Mexico, Peru, Thailand, Vietnam and USA (Smedley and Kinniburgh, 2002; WHO, 2004). But the most serious occurrences identified globally are clearly in Bangladesh and West Bengal (India). Shallow tube wells (STW) (<150 m) in 60 out of 64 districts are contaminated by As (BGS/DPHE, 2001). It is estimated that the number of people exposed to arsenic concentrations above 0.05 mg/L (the Bangladesh standard for acceptable limit of As) is 28-35 million and the number of those exposed to more than 0.01 mg/L (WHO guideline value) is 46-57 million (BGS/DPHE, 2001). More than 10,000 patients of As poisoning have so far been identified in the country (Hussain, 2001). Ground water is extensively used for irrigation of crops resulting in elevated levels of As in soils and As uptake to rice and other crops (Meharg and Rahman, 2003, Huq and Naidu, 2003). In order to implement As mitigation programs, detailed studies should be carried out to be aware of the real As hazard in the affected areas. A good number of studies have been made for assessing the status of As in ground water, soil and crops but most of them have been done in sporadic way and were concentrated in particular areas of the country. This paper discusses the findings of a concerted and widespread survey throughout Bangladesh for assessing As status in irrigation water and corresponding soils and crops.

MATERIALS AND METHODS

Prior to the sampling Bangladesh was divided into seven hydrological sub-regions (HSR) on the basis of river network (WARPO, 2002). The composition of the sub-regions were northwest (NW), north centre (NC), north east (NE), south west (SW), south centre (SC), south east (SE) and eastern hill (EH) areas of the country (Fig. 1). From each of the HSR, every alternate thanas having ground water irrigation system were selected for sample collection. All thanas in the eastern hill areas and in the Sundarbans were excluded. From each of the selected thanas of the HSR, two unions were selected randomly using GIS sampling tool of Bangladesh Country Almanac. From each of the selected unions three shallow tube wells (STW) used for irrigating rice fields were selected for sampling. For convenience of the survey work, the seven HSR were again grouped into four regions. Region 1 consisted of the SW and SC sub-regions having 41 unions under 21 thanas. Region 2 comprised of the NC sub-regions having 38 unions of 19 thanas. Region 3 consisted of the

NW sub-regions having 26 unions under 13 thanas and Region 4 was composed of the NE and SE sub-regions having 30 unions under 14 thanas. A total of 270 STW from 135 unions under 67 thanas were selected for sampling. Water samples from each of the STW and nearby hand tube wells (HTW), ponds, canals and rivers were also collected. Soils and plant samples (rice straw and grains) were collected from within the command area of each of the STW. Soils were collected from 0-15 cm, 15-30 cm and 15-45 cm depths. Soil samples were also collected from nearby non-irrigated field. Acidified water samples were analyzed immediately after reaching the laboratory. Soils and plant samples were digested with tri-acid mixture (HNO_3 + $HClO_4$ + H_2SO_4) and As was determined using atomic absorption spectrophotometer equipped with hydride generation system (HG-AAS) (Alam et al., 2001).

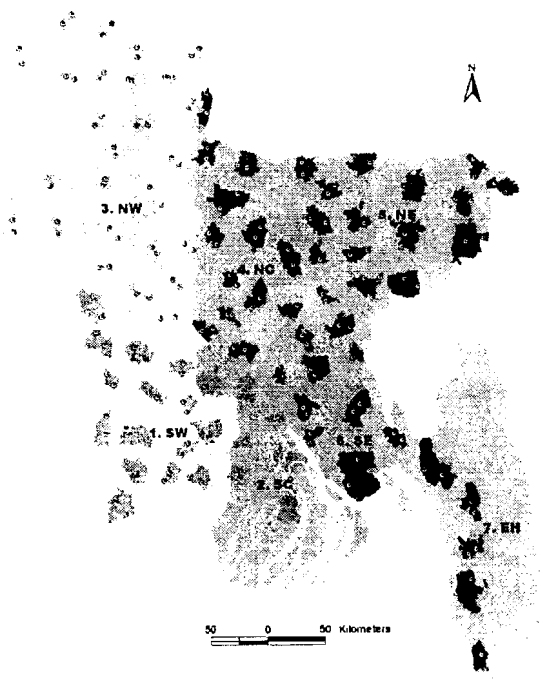

Fig. 1. Sampling sites located at different regions of Bangladesh.

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RESULTS AND DISCUSSION

Arsenic in water sources:

The concentration of As in STW water ranged from < 1 μg/l to > 650 μg/l. The highest mean As concentration of STW was observed in the SE/NE region while the lowest was recorded in the NW region (Fig. 2).

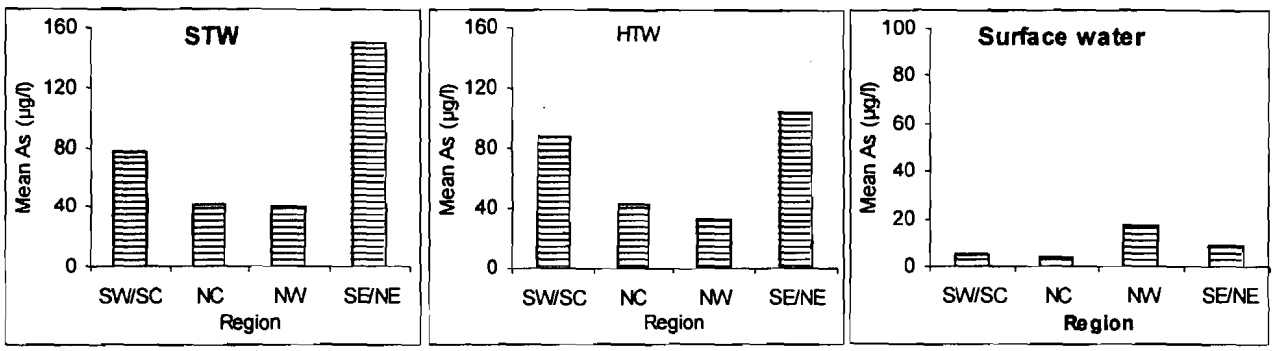

Fig. 2. Arsenic concentration in water of STW, HTW and surface water bodies collected from different regions.

The distribution pattern of As concentration in HTW was similar to that of STW, i.e., the highest in SE/NE regions and the lowest in NW region (Fig. 2). The range of As concentration in HTW water varied from <1 μg/l to >530 μg/l. The similarity in the distribution of As concentration in STW and HTW implies that both of this wells may withdraw water from the same aquifer. The level of As contamination in STW and HTW in the SW/SC and SE/NE regions of the country was much higher than those of the NC and NW regions (Figs. 1 & 2). This is in accordance with the findings of others (BGS/DPHE, 2001).

Among the three water sources the highest As concentration was observed in STW and the As concentration followed the trend: STW>HTW>surface water. The concentration of As in the surface water bodies (pond, river, canal etc.) ranged from 2 μg/l to as high as 63 μg/l. It is interesting to note that the surface water bodies, which were assumed to contain As-free water, exhibited high As values (>50 μg/l) particularly in the NW region (Fig.2). It was noticed during the survey period that the source of high As containing water in the ponds was the As-contaminated water from STW.

As in soils:

The range of As concentration in surface soil varied from 0.2 mg/kg in the NC region to 67.5 mg/kg in the SW/SC regions. Most of the surveyed soils contained below 20 mg/kg As, the maximum tolerable soil limit for the crops. The highest mean soil As was recorded in SW/SC region which is located in the Gangetic and Meghna floodplain and the lowest was observed in the NC region located mainly in the Pliestocene terraces (Figs.1 & 3). Similar findings have been reported by others (BGS/DPHE 2001).

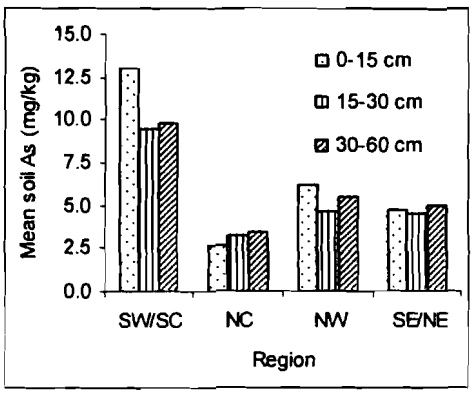

Fig. 3. Vertical distribution of As in irrigated soil of different regions of Bangladesh

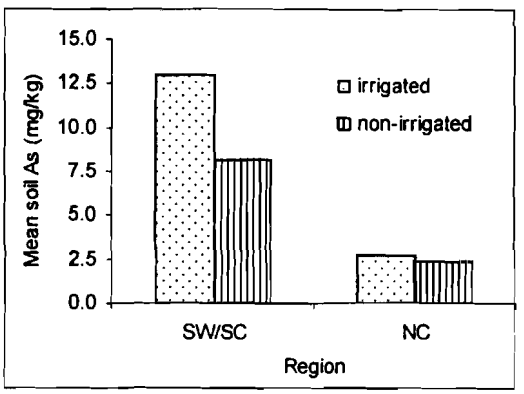

Fig 4. Arsenic concentration in irrigated and non-irrigated soils of two regions

The As concentration in the surface soil (0-15 cm) was higher than that of the subsurface soil (15-30 cm) in SW/SC, NW and SE/NE regions (Fig. 3). In these regions As concentration in the 30-60 cm soil layer was found higher than that of the immediate upper soil layer (15-30 cm) while reverse trend of the vertical distribution of As was observed in the NC region (Fig. 3), i.e., lowest in the surface soil and highest in the 30-60 cm soil. The average As concentration of non-irrigated soil was lower than that of the irrigated soil (Fig.4) although the difference was negligible in NC region.

As in rice:

The concentration of As in rice grain ranged from 0.04 to 1.1 mg/kg. Except very few samples in the NW region, the rice grain As concentrations was much less than 1 mg As/kg. The mean As concentration of rice grain was found highest in the NW region (Fig. 5).

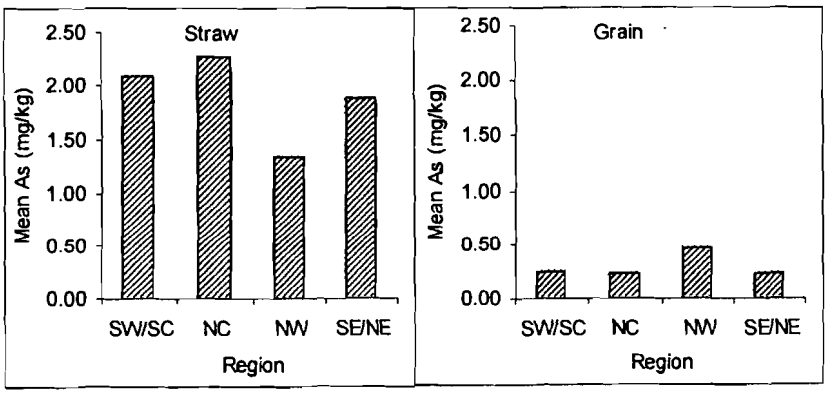

Fig. 5. Average As concentration in rice straw and rice grain of different regions.

On an average, the As content in rice straw was 7 times higher than that in grain. It is interesting to note that the distribution pattern of neither irrigation water As nor soil As was alike the grain or straw As (Figs. 2, 3 and 5). From the observed data it may not be assumed that the grain/straw As is directly influenced by the As concentration of irrigation water or soil.

CONCLUSION

The high concentration of As in irrigation and drinking water particularly in the southern areas of the country indicates an alarming situation. In these areas in terms of As-associated health risks, surface water may be a viable alternative source of drinking and irrigation water. The As concentration in most of the studied soils was less than 20 mg/kg, the maximum tolerable limit for crops. With very few exceptions, the As content in most of the rice grain samples was <1 mg/kg. No consistent relationship among the As concentration of irrigation water, soil and rice grain was observed. Further research is needed giving particular emphasis on these issues to alleviate the As problem successfully.

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Arsenic in the Irrigation Water-Soil Environment and Flows of Arsenic in the Food System

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Groundwater from shallow aquifers is extensively used for drinking and irrigation in Bangladesh. The installation of hundreds of thousands of shallow tube wells (STW) in Bangladesh over the last three decades may, very justifiably, be considered a "groundwater revolution" because it supplied "safe" drinking water for hundreds of millions of people and, on the other hand, uniquely contributed to the tripling of the annual production of rice, the staple food crop. This paved the way for the long cherished goal of achieving self-sufficiency in food production for the teeming millions of Bangladesh citizens. However, two decades since the first STWs were commissioned it began to be known that the water which was once thought to be safe for drinking had, in many places, been slowly contaminated with As, a dreaded poison. Alarming levels of As in shallow groundwater in about 35% of the STWs in Bangladesh have been reported. Agricultural soils in many areas of the country also have been found to contain high As levels. Also, evidence of elevated As accumulation in rice is mounting. There is a growing national concern about arsenic contamination of groundwater in Bangladesh, because many millions of people in Bangladesh is facing a two-way risk of exposure, directly through drinking water and indirectly through food crops grown on soils contaminated by arsenic through groundwater irrigation. The grave consequences of arsenic pollution of water, soils and crops to the environment and human and animal health notwithstanding, the behavior of As, especially in agricultural-production systems and the food chain is not yet well understood. There is an urgent need, especially in Bangladesh, which is probably the worst affected country, for an understanding of the nature and extent of arsenic pollution of the irrigation waters, soils and crops and developing water-soil-crop management practices to mitigate the arsenic problem in agriculture and food.

Irrigation-water As interacts with the soil in a very complicated manner. The interactions are influenced by both water and soil properties, like pH, texture, mineralogy, organic C, redox potential, reactions with free iron oxide, P, etc. These water-soil interactions largely regulate the bioavailability of As, e.g., its uptake and accumulation in edible plant parts. Of special interest is the behavior of As in rice soils that remain flooded and anaerobic throughout the rice-growing season. In the reduced condition, As (III) predominates, and this species of As is believed to be responsible for an elevated level of

As in rice. High As accumulation in rice grain and straw in Bangladesh has been reported.

Little is known about the real or potential As exposure of the rice-eating people of Bangladesh. Estimates showed about 50% of daily As intake could come from rice grain when the intake of both water As and rice As was considered. Arsenic may also affect animals through feeding with high-As straw, which can be an additional indirect health hazard for humans. However, very little is known about this potential hazard in Bangladesh.

There are critical knowledge gaps in the understanding of As in crop-production systems. Continued research/education is needed for the development of As-management technology to ensure food security and safe food. Some important issues that need attention are summarized below.

- Develop a nationwide database on current As levels in soils
- Assess impact of As in irrigation water on soil As levels
- Understand which arsenic species predominate in plants; understand the bioavailability of As in food and feed
- What should be the safe levels of arsenic be in irrigation water, soils and crops under the prevailing cropping systems of Bangladesh in terms of yield and crop quality?
- How do crops and cultivars vary in their tolerance and uptake of arsenic? If there is significant variation, can this be used as a management tool?
- Fill the void in the education sector. Help develop undergraduate and graduate level courses for Bangladeshi students on the behavior of arsenic in agricultural systems and options for management

Spatial Variability of Arsenic in the Environment and in Rice - Implications and Uses of Information at Different Scales

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Introduction

Soils are prone to contamination from atmospheric and hydrological sources (Ana and Javier, 2002). Contamination of this natural resource is posing serious environmental concerns. Spatial variability of soil input data can strongly influence the reliability of results of logical, empirical and physical models of soil (Burrough, 1993, Wilding et al, 1994). Information on the soil macro- and micro-nutrient levels and trace elements could be of great interest for agricultural use (Wilcke et al., 1998). Studies to establish the environmental levels of various heavy metals are of increasing interest in order to delineate areas of potential toxicity. Around the world, several studies have evaluated the heavy metal concentrations in soils (Kabata-Pendias and Pendias, 1984; Brummner et al., 1986; Wopereis et al., 1988; Vaselli et al., 1997). However, in Bangladesh, such studies are non-existent to date, and therefore, very little are known about the distribution of such elements in general and arsenic (As) in particular. With the growing concern of As in ground water used for drinking and irrigation in Bangladesh, an adequate understanding of its spatial variability in soils and plants becomes essential. A spatial database on soil and ground water arsenic would be a basis for a wide variety of economic and environmental applications and to assess the relationship between geochemistry and health.

Scale is one of many factors influencing soil variability. The spatial characteristics of the sampling units – their size, shape, spacing (lag distance) and extent – are important scale concepts (Dungan, 2002). Scale is defined as the resolution within the range of a measured quantity (Schneider, 1994). The characteristics of a variable's distribution depend on the area or volume, i.e., on the scale over which it is measured or calculated. Inference about mean and variance, strength and nature of spatial autocorrelation, spatial anisotropy, patch and gap sizes, as well as multivariate relationship are all dependent on the scale of measurement, i.e., on size and shape of the sampling units and lags and extent of sampling (Dungan et al, 2002). Quantification of soil spatial variability across multiple scales is important in ecological modeling, environmental prediction, precision agriculture and natural resources management (Hangsheng, et al, 2004). Knowledge of soil As across multiple scales and its impact on rice plants will enhance the use of soil information for designing appropriate management techniques for rice production. This study, therefore, is aimed at providing analysis of As concentration in ground water, soils and rice grains and its implications across multiple scales of measurement.

Methodology

The scales in this study were the combination of extent and lag of the sampling units. Three different scales were used for soil sampling: (1) national scale - sampling points were located in every alternate Upazilla at a lag distance of approximately 20-40 km; (2) *Upazilla* scale - sampling points were selected at random but approximately at the lag distance of **1-2** km apart; and (3) field (STW command area) level - the sampling points were approximately along a 20x20 m grid. In each case, soil samples (top soils: 0-15 cm depth) and plant samples

(for measuring As concentration in rice grain) were collected within the command area of the selected shallow tube well (STW) used for irrigation, using standard soil sampling procedures. Flow-injection hydride-generation flame-atomic-absorption spectrocopy was used to determine As concentration in irrigation water, soil and in rice grain.

Results and Discussion

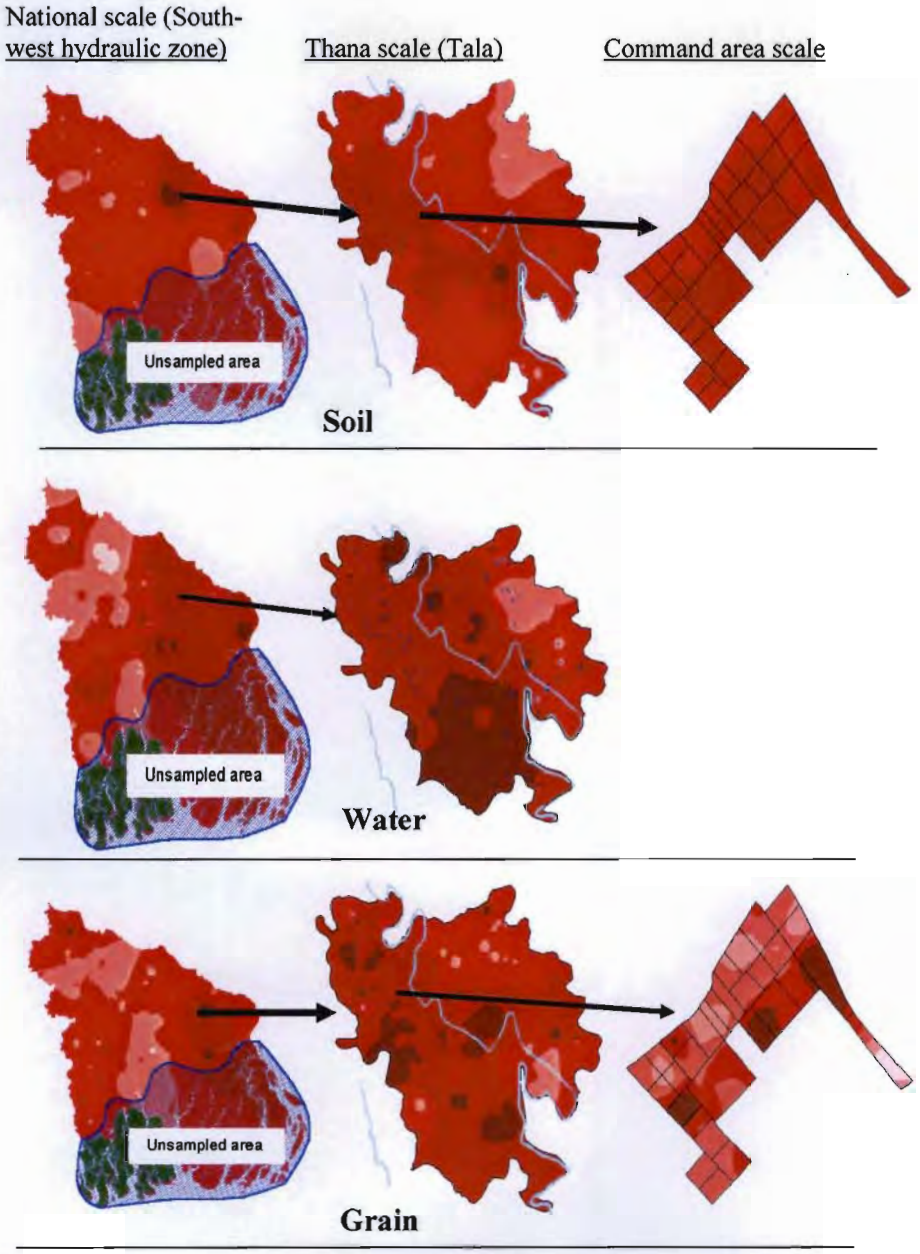
The descriptive statistics presented in Table 1 showed that As concentration in any measure (mean, maximum, quartile, etc) was the highest for ground water and lowest for rice grain. Average water As was approximately 200 times higher than soil As, and soil As was 55-65 times higher than As concentration in rice grain. Scale of sampling greatly affects almost all measures of As. Spatial variability of As was, in general, greater for command area scale than for *thana* scale. In contrast, variability of As concentration, as measured by CV, was lowest for command area scale and highest for national scale (Fig. 1). The very high value of CV indicated spatial variability of As level for all of ground water, soil and rice grain, irrespective of scale of sampling. The extent of variability appeared to be similar for soil and rice grain, but comparatively smaller for water. Results give clear indication that sampling in smaller extent provides a better understanding of the extent or intensity of As contamination in ground water, soil and rice grain.

Table 1. Some descriptive statistics of arsenic concentration in ground water, soil and rice grain under different scales of measurement.

Statistics	Ground water		Soil			Grain		
	Thana	National	Command area	Thana	National	Command area	Thana	National
	As level (ppb)		As level (ppm)			As level (ppb)		
Minimum	7.46	0.30	12.28	4.30	4.48	0.11	0.09	0.04
Maximum	441.17	291.05	25.19	51.79	39.00	0.59	1.01	0.67
Mean	134.57	82.78	20.16	18.13	13.22	0.29	0.32	0.24
Stdev.	86.76	74.78	2.66	7.83	6.90	0.11	0.14	0.14
1st quartile	70.17	14.70	18.49	12.11	8.78	0.21	0.23	0.15
2nd quartile	121.18	65.37	20.33	17.65	11.29	0.26	0.30	0.20
3rd quartile	179.17	136.01	21.83	23.54	15.30	0.35	0.38	0.31
CV(%)	64.47	90.34	13.21	43.17	52.21	36.35	44.43	56.17
Sample size	105	98	63	104	98	59	103	88

The frequency distribution of As concentration (not shown) was positively skewed in almost all cases and deviated from normal distribution in terms of either skewness or kurtosis or both. Square root transformation made the distribution of data approximately normal indicating dependency of the change in As concentration on the distance of sampling points (Stark et al, 2004). Semivariance was computed on a square root scale to determine the spatial dependency of As concentration. The semivariance (not shown) exhibited spatial dependence in all cases.. Both nugget and sill values were highest for the national scale and lowest for the command area, meaning that both non-structured (random) and structured variance were highest for the national scale and lowest for the command area. In general, the relative spatial range of dependence was longer in case of smaller sampling extent, implying that spatial variation in As concentration can be assessed more precisely in the smaller geographical area than the larger ones.

Surface maps of As in Figure 2 shows the distribution of As contamination in ground water, soil and rice grain over the extent of three different scales. At the national scale, the figures provided a generalized pattern ofa large area with similar concentration level but also definitely gives an indication of the location where more intensive investigation of As contamination needs to be undertaken. At the thana scale, the surface gives a clearer picture of As status within the thana. The information provided is important for local level planning for designing appropriate management techniques, research strategy or action plan to combat the As problem. The spatial distribution of As in the command area provides the actual As status at the field level and provides a basis for management options for crop production to avoid the toxic effects of As.



Conclusions

The semivariance exhibited spatial dependence of As. The As concentrations in water, soils and rice grain can be assessed more precisely in smaller geographical areas than at the regional/national scales.

The spatial distribution at the national scale gives an indication of the locations where more intensive investigation of As contamination needs to be undertaken, and the *thana* scale is important for local-level planning for the design of appropriate management techniques, research strategy or action plan to combat the As problem. In the command areas, the spatial distribution provides the actual As status at the field level, which might assist in developing management options for crop production to minimize the toxic effects of As.

Arsenic in Irrigation Water in Five Thanas of Bangladesh

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Background

Contamination of shallow groundwater in Bangladesh has been well documented by the BGS/DPHE survey of drinking water tubewells (Mc Arthur et al., 2001). The shallow groundwater aquifer is also widely used for irrigation of boro rice, with large volumes of water removal. The objective of the present study was to characterize As in STW's used for irrigation of boro season rice in five selected thanas of Bangladesh.

Methodology

Figure 1 shows the five thanas studied, viz., Brahmanbaria sadar, Faridpur Sadar, Paba, Senbag and Tala. Selection criteria were widespread use of groundwater for irrigation

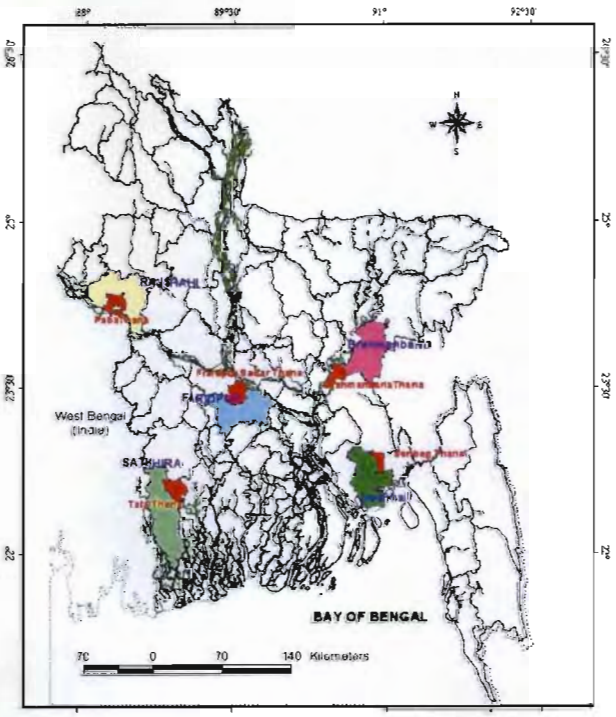

Figure 1. Location of Thanas for STW sampling

and moderate to high levels of aquifer contamination with As based on the BGS/DPHE survey. They represent diverse physiographic and hydrological situations in the central, eastern, southern and western districts of Bangladesh, where arsenic bearing sediments of three majors rivers (Ganges, Brahmaputra and Megna) are deposited. One hundred to

110 STWs (except in Senbag where the number was 42) were selected in each thana to cover as much of the thana area as possible. The locations of all STWs were geo-referenced. Before collection of water samples, the selected STWs were allowed to run for 15 minutes, then duplicate 90 mL water samples were filtered through 0.45 μm membrane filter fitted to a 50mL syringe into 100-mL plastic bottles containing 10 mL 2M HCl. The bottles were pre-washed with 1 M HCl. A total of 456 water samples were collected. Arsenic was determined by FI-HG-AAS in laboratories at BRRI, BARI, and BINA. Samples were also analyzed by ICP-AES at Cornell University.

Results and Discussion

Analytical results from the Bangladesh laboratories and Cornell University were highly correlated and close to 1:1 relationships.

Arsenic concentration in the STW waters varied widely within the five thanas. Mean As concentrations in the thanas followed the order Tala > Senbag > Brahmanbaria > Faridpur > Paba (Fig.2). More than one half of the STW's had a water As content > 0.1 mg L^{-1} and sixty two were > 0.2 mg L^{-1}, indicating quite a high risk of soil and plant contamination from irrigation water (Fig. 3). The highest As concentration found was ~ 0.6 mg L^{-1}. Overall, 60 % of the 456 water samples tested were above the Bangladesh drinking quality level of 0.05 mg L^{-1} (Karim, 2000).

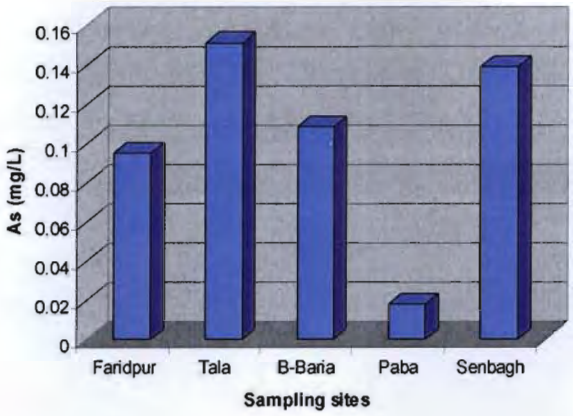

Fig.2 Mean As values of five thanas

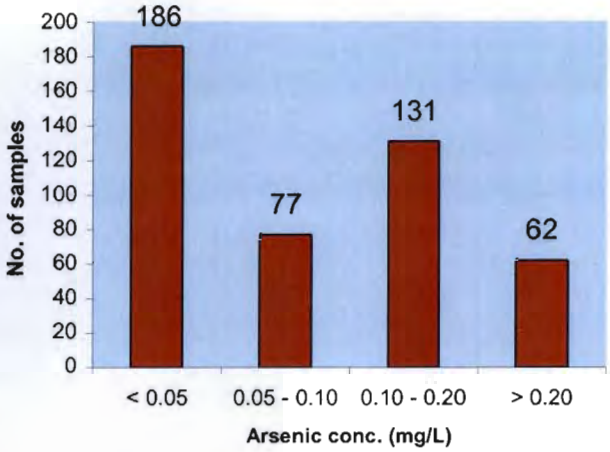

Fig. 3 Distibution of As in STWs water

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Potential for Arsenic Contamination of Rice in Bangladesh: Spatial Analysis and Mapping of High Risk Areas

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Abstract

Knowledge of the location and severity of arsenic contamination in Bangladesh is required to develop land and resource management strategies to reduce both human exposure to arsenic and arsenic contamination of food and water supplies. While the threat posed by directly drinking arsenic contaminated water has been well documented, the potential for exposure through secondary sources is not as well-understood. Given that rice accounts for 70% of an average adult's caloric intake in Bangladesh, the potential for exposure to arsenic through rice consumption must be considered in environmental health investigations.

The present study provides a spatial assessment of the risk of arsenic contamination of rice based on the use of arsenic contaminated groundwater for irrigation in Bangladesh. Specifically, we evaluate the potential risk of arsenic contamination of *boro* rice based on the average arsenic concentration of groundwater and the proportion of *boro* rice irrigated with groundwater by *upazila*. The potential consequences of exposure to high arsenic groundwater are elevated levels of arsenic in rice grain and straw and, possibly, over time, accumulation of arsenic in soil to levels that are toxic to rice. These outcomes raise the possibility of increased human exposure to arsenic as well as food security concerns if rice yields are reduced.

Potential high risk areas for arsenic contamination of rice were identified using spatial analysis and modeling. Existing country-wide data on groundwater arsenic contamination, winter (*boro)* rice production and irrigation methods were used to identify areas where high production of groundwater irrigated *boro* rice corresponds to areas with high arsenic contamination of groundwater. Our general approach was to combine data on groundwater arsenic concentrations, *boro* rice production and use of groundwater for irrigation to identify areas of the country with both high arsenic in groundwater and high production of groundwater irrigated rice. The resolution of the analysis was limited to the *upazila*-level by the production and irrigation databases.

The *boro* rice production data were multiplied by the percent irrigated by groundwater to obtain the total production of groundwater irrigated *boro* rice (in 1000s of tonnes) in each *upazila*. The arsenic point database was aggregated "up" from the point data to the *upazila* level using block kriging methods rather than simply taking the average of the data points in each *upazila*. This approach has the advantage that it makes use of both the values at nearby locations in addition to the overall spatial pattern in the measured data.

Unlike many other kriging methods, block kriging does not explicitly require data to be normally distributed. The arsenic data exhibits a long right tail, however, a comparison with predictions based on log-transformed data as well as a comparison with predictions based on a model computed by removing extreme values (greater than 500 $\mu g\ L^{-1}$) suggests that kriging the untransformed data is appropriate and not unduly influenced by large values. Rather than impose a transformation and risk the "exaggerated" error in the back-transformation, we kriged the *untransformed* arsenic data. To evaluate the uncertainty in the kriged point predictions we also computed a map of prediction standard errors and used these to identify and eliminate from the analysis *upazila* with particularly unreliable estimates. In order to achieve area wide estimates by *upazila* we used block kriging in which point kriged estimates within *upazila* were arithmetically averaged.

Results show that seventy-six percent of the total irrigated *boro* rice is grown in *upazila* where mean groundwater arsenic concentrations are below 50 $\mu g\ L^{-1}$, the Bangladesh health standard. Seven percent, however, is grown in areas with mean concentrations greater than 100 $\mu g\ L^{-1}$, primarily in south-central and western-central Bangladesh. Mitigation strategies are suggested for the areas considered to be at risk for arsenic contamination of *boro* rice.

This spatial analysis and mapping of arsenic contamination risk for *boro* season rice is, to our knowledge, the first attempt to identify and map high risk areas for potential arsenic contamination of rice consumed by a large population. It is a first step in the assessment of risk of human exposure to arsenic through the food system. Fortunately for Bangladesh, much of the *boro* rice production using groundwater for irrigation is in the northern part of the county where arsenic concentrations are generally below the WHO drinking water standard of 10 $\mu g\ L^{-1}$. Additionally, greater use of surface water for irrigation and lower levels of *boro* rice production moderate the risk for contamination in the central area where groundwater arsenic levels are high.

The inability to include soil arsenic concentrations in the analysis and the level of spatial resolution are important limitations to the current study. A systematic determination of soil arsenic content across Bangladesh, similar to that done for groundwater, should be undertaken. The combination of soil and groundwater arsenic data layers would provide a more accurate representation of risk for arsenic contamination of *boro* rice, and could extend the analysis to the *aman* season rice.

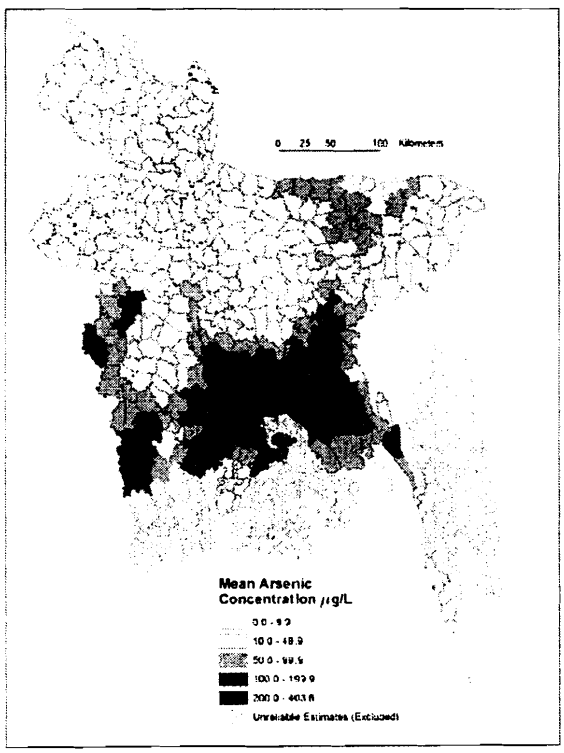
We emphasize that the risk analysis presented here assumes that the arsenic content of groundwater leads to a buildup of arsenic in soils and that these parameters are important drivers of the arsenic content of rice. On this basis, our analysis suggests several strategies to avoid contamination of both rice and soils with arsenic. These are:

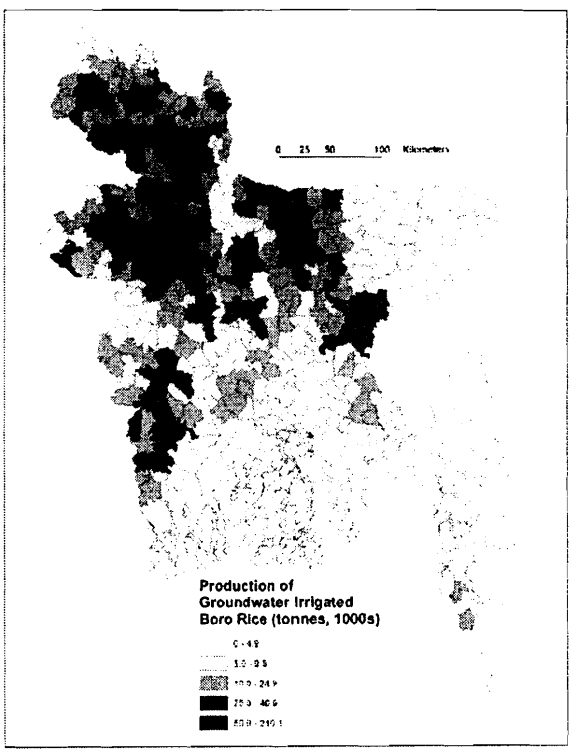
1. Further develop surface water resources for those *upazila* in the central part of the country that have high levels of arsenic in groundwater.
2. Avoid production of *boro* rice where groundwater arsenic levels are high and this is the only source of irrigation water. Other cereal crops such as maize and wheat, which require far less water, could be substituted for rice in the winter season.

Modern water conserving technologies, such as using raised beds and furrow irrigation in place flood irrigation, would further reduce arsenic loading to soil.

3. Expand *boro* rice production in the northern part of the country where groundwater arsenic levels are low.

Such changes would require substantial investment in infrastructure for use of surface water and policies that control where *boro* rice is grown. However, the long-term pay-off from avoiding soil contamination with arsenic cannot be overstated and reaches to the core of agricultural sustainability in Bangladesh.





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Effect of Water Management and Phosphorus rates on the Growth of Rice in a High-Arsenic Soil-Water System

ASM HM Talukder

Introduction

Water and phosphorus management of soil can potentially be used to mitigate arsenic phytoxicity and uptake of arsenic in rice. Under high soil arsenic conditions, addition of phosphate to aerobic soils may displace arsenate from the soil adsorption sites and enhance downward movement of arsenic, leading to increased leaching from the topsoil (Davenport *et al., 1991* and Peryea *et al., 1997*). On the other hand, arsenic may also compete with phosphate for uptake by plants, increasing the availability of arsenic in the soil solution resulting in higher uptake of As by the plants (Creger *et al., 1994)*. Under anaerobic soil conditions, phosphate addition will more likely displace arsenite from adsorption sites making it more readily available for plant uptake since it is not competitive with phosphate.
Rice is the staple food for the population, and rice straw (leaves and stalk) is used as cattle feed. Therefore, it is necessary to evaluate the impact of using irrigation water contaminated with arsenic with the application of phosphorus on the arsenic uptake and accumulation in rice grain and straw. So, this study has been undertaken to evaluate (i) the impact on crop productivity (yield) and (ii) impact on crop quality.

Material and Methods

Aman and boro rice were grown in pots at the Wheat Research Centre, Nashipur, Dinajpur, Bangladesh, during 2003-04 season. Soil used in the pots was extracted from a typical field in Dinajpur and had very low amount of organic matter (0.23%), phosphorus (7.31 μ of P g soil^{-1}), iron (23.24 μ of P g soil^{-1}) and arsenic (1 mg of As kg soil^{-1}).

Two 30-45 day old seedlings per pot were transplanted into plastic pots and grown to maturity in a polyethylene tent house. Treatments consisted of three levels, each of arsenic (0, 20 and 40 mg of As kg soil^{-1}) and phosphorus (0, 12.5 and 25 mg of P kg soil^{-1}) and two water management (flooded and saturated conditions) regimes. The design was completely randomized and each treatment was replicated three times. Yield and yield component data were collected at plant maturity and rice plant parts (grain, straw and roots) were sampled for determination of arsenic content. Data were subjected to analysis of variance MSTAT-C. Treatment means were compared using Duncan's Multiple Range Test (DMRT) at $p \leq 0.05$.

Results and Discussion

Main effects of As, P and water management on yield and rice plant parts

The concentration of arsenic in soil has a marked effect on plant growth and yield (Figures 1 & 2). With increasing of arsenic doses grain yield significantly decreased from 30 to 20 g/pot in t-aman and from 49 to 25 g/pot in boro rice. Phosphorus rate and water management also had significant effects on grain yield. The treatment without arsenic yielded the most straw (32 g/pot in t-aman and 106 g pot^{-1} in boro rice) while the lowest straw production (22 and 69 g pot^{-1} in t-aman and boro rice, respectively) was found in the highest arsenic treatment (40 mg of As kg $soil^{-1}$). The lowest root bio-mass (10 g in t-aman and 31 g pot^{-1} in boro) were obtained in the highest arsenic treatment (40 mg of As kg $soil^{-1}$) followed by the use of medium dose of arsenic (20 mg of As kg $soil^{-1}$). The highest root biomass (16 and 49 g pot^{-1} in t-aman and boro rice, respectively) was recorded from zero arsenic. No significant differences ($p>0.05$) were observed in root biomass production from the use of P, but there were significant effects of saturated water management on straw and root biomass. These results are also consistent with the findings of Abedin *et al* (2002). They reported that increasing the concentration of arsenic in irrigation water significantly decreased plant height, grain yield, the number of filled grains, grain weight, and root biomass.

Interaction effects of As, P and water management on yield and rice plant parts

The interaction effects of arsenic, phosphorus and water management had a significant role on straw and root biomass production (Table 1). The highest grain yield (35 and 63 g in t-aman and boro rice, respectively) was obtained in plants grown without arsenic and with a moderate dose of phosphorus (12.5 mg of P kg $soil^{-1}$) under saturated conditions (Table 1). A similar trend was also observed with rice straw and root biomass. Rice straw and root biomass varied significantly with arsenic concentration. The highest straw yields (36.10 and 120.5 g pot^{-1} in t-aman and boro rice, respectively) and root biomass (16.20 in t-aman and 57.0 g pot^{-1} in boro rice) were recorded in plants grown without arsenic, with a medium rate of phosphorus (12.5 mg P kg $soil^{-1}$) under saturated conditions. Plants grown under saturated conditions treated with arsenic and phosphorus (except T_{13} and T_{16}) produced superior plant height, number of tillers, filled grain, grain and straw yield and root biomass compared to plants grown under flooded condition. Under saturated conditions, P is less available in the soil solution and may be in a from (As V) assimilated competively with phosphate which ultimately reduces the phytotoxicity of arsenic.

In conclusion, arsenic depressed rice yields, indicating phytotoxicity. Adding phosphorus to the soil reduced arsenic toxicity. Saturated soil conditions reduced arsenic toxicity compared to flooded soil conditions for all phosphorus levels. Both water and phosphorus management are thus tools to manage potential arsenic toxicity in rice.

Acknowledgement
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Fig 1: Effects of Phosporus, Arsenic and Water Management on transplanted aman rice in a pot culture

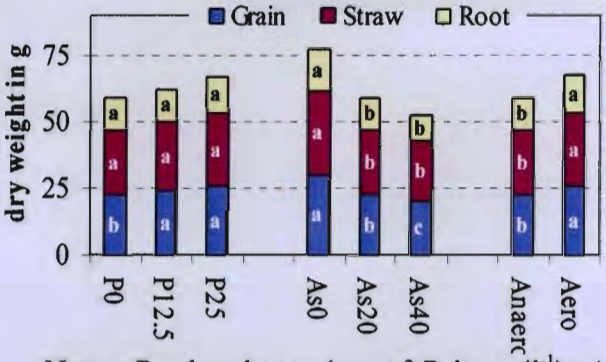
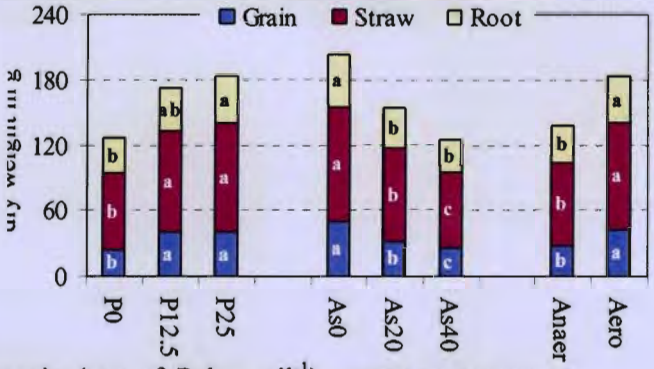


Fig 2: Effects of Phosphorus, Arsenic and Water Management on transplanted boro rice in a pot culture



Notes: P, phosphorus (mg of P kg soil^{-1}); As, arsenic (mg of P kg soil^{-1}); water management (saturated and flooded) within the bar graph figures having the same letters are not significantly difference at 5% level by DMRT

Table 1: Interactions effects of Phosphorus, arsenic and Water management on plant growth, yields and plant parts in transplanted aman and boro rice in a pot culture

Treatment code	Treatment combination			Grain yield (g pot^{-1})		Straw yield (g pot^{-1})		Root biomass (g)	
	P (mg/kg soil)	As (mg/ kg soil)	W M	t-aman	boro	t-aman	Boro	t-aman	boro
T_1	0	0	An	27.8 bc	30.1 d	28.4 cd	88.1 fg	13.1 c-f	43.1 bc
T_2	0	20	An	18.2 ij	17.2 g	19.5 g	58.1 j	9.2 ghi	29.1 de
T_3	0	40	An	16.5 j	7.7 h	20.8 fg	35.8 k	7.1 i	19.9 f
T_4	12.5	0	An	30.1 b	50.4 b	33.2 ab	115.8 ab	17.1 a	40.3 bc
T_5	12.5	20	An	18.5 hij	24.2 ef	21.0 fg	78.3 gh	10.5 fg	34.7 cd
T_6	12.5	40	An	17.7 j	16.2 g	18.2 g	58.0 j	8.0 hi	27.1 def
T_7	25	0	An	28.7 bc	46.4 bc	27.3 cd	101.9 cd	15.5 abc	47.4 b
T_8	25	20	An	25.6 cde	29.5 de	25.0 def	85.0 fgh	13.1 c-f	34.4 cd
T_9	25	40	An	21.0 f-i	20.6 fg	24.1 def	66.2 ij	11.5 fg	35.6 cd
T_{10}	0	0	A	29.7 b	43.1 c	28.4 cd	90.5 ef	17.2 a	48.1 b
T_{11}	0	20	A	23.5 def	27.9 de	25.7 cde	76.2 hi	14.2 b-e	35.2 cd
T_{12}	0	40	A	21.5 fgh	20.5 fg	21.1 fg	63.7 j	11.6 efg	25.0 ef
T_{13}	12.5	0	A	35.0 a	63.0 a	36.1 a	120.5 a	16.2 ab	57.0 a
T_{14}	12.5	20	A	22.6 efg	44.1 c	24.6 def	98.8 de	11.7 efg	45.0 b
T_{15}	12.5	40	A	19.5 g-j	41.1 c	22.1 efg	80.0 fgh	9.9 gh	35.1 cd
T_{16}	25	0	A	18.1 bc	58.7 a	33.7 a	117.0 ab	15.2 abc	60.0 a
T_{17}	25	20	A	26.1 cd	45.8 bc	29.6 bc	110.0 abc	14.3 bcd	48.2 b
T_{18}	25	40	A	23.5 def	43.2 c	27.1 cd	108.3 bcd	12.6 def	42.0 bc
CV (%)				4.20	5.38	5.11	4.06	6.33	6.82

An, anaerobic water management; A, aerobic water management

±Within the treatment interactions the figures having the same letters are not significantly difference at 5% level by DMRT

Arsenic Absorption by Rice

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Introduction

There is considerable concern globally about arsenic (As) in potable/drinking waters extracted from contaminated aquifers. The regions affected from contaminated ground water include the USA, Argentina, China, Myamar, Taiwan, Nepal, India and Bangladesh. The situation is at its worst in the Bengal Delta, with over 80 million people living in zones with arsenic above 50 µg/L arsenic in their groundwaters **(Smedley & Kinniburgh 2002)**

It is becoming apparent that ingestion of drinking water is not the only elevated source of arsenic to the diet in the Bengal Delta, irrigation of paddy rice fields with arsenic contaminated groundwaters has led to arsenic build-up in paddy soil, with subsequent elevation in rice grain arsenic **(Meharg and Rahman 2003)**. Meharg and Rahman **(2003)** calculated that even at "background" levels of arsenic in rice5 that rice contributed considerably to arsenic ingestion in affected areas of Bangladesh.

The forms of arsenic present in rice for direct food use need to be better characterised, as inorganic species are believed to be more toxic than methylated species **(Cullen & Reimer, 1989)**. The studies to date are relatively limited **(Heitkemper et al, 2001; Scoof et al, 1999; Kohlmeyer et al 2003; D'Amato et al, 2004)**. It appears that arsenite (As^{III}), arsenate (As^{V}) and dimethylarsinic acid (DMA^{V}) are the predominant species present.

We set out to provide a wide survey of As speciation in different rice varieties from different parts of the globe to understand the contribution of rice to arsenic exposure. Pot experiments were utilised to ascertain whether growing rice on As contaminated soil affected speciation and whether there was genetic variation in uptake and speciation.

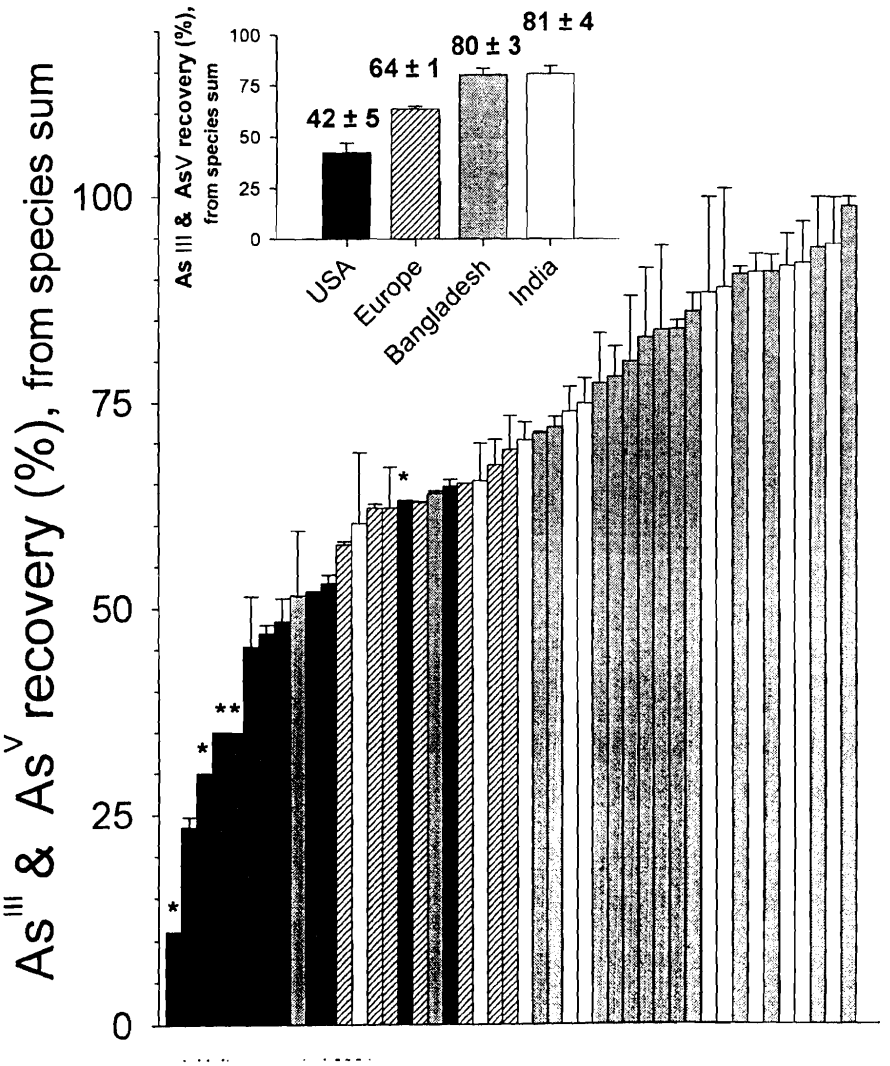
Method

For total concentrations of arsenic, milled sub-samples (0.1 – 0.2 g) were digested with nitric acid. Trifluoro-acetic acid (TFA) extractions were used to speciated arsenic in rice.

Speciation analysis was performed on a HP1100 HPLC system (Agilent Technologies, Stockport, Cheshire, UK). Optimal separation of arsenic species was achieved with a PRP-X100 anion-exchange column and a mobile phase of 6.66 mM ammonium hydrophosphate ($NH_4H_2PO_4$) and 6.66 mM ammonium nitrate (NH_4NO_3), pH 6.2. Post-column, element specific detection of arsenic was performed using an ICP-MS 7500 (Agilent Technologies). Nitrogen and carbon content was determined using a NCS analyser. Phosphorus was determined using flow injection colourimetric analysis.

Results

Percentage of inorganic arsenic in rice. The legend shows the mean, plus or minus s.e,



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of the percentage inorganic arsenic levels in rice for the USA, Europe, Bangladesh and India

This study found highly significant differences ($p = < 0.001$) in total arsenic concentration between Bangladeshi, USA, Indian and European rice. No differences were observed between white and brown rice. USA long grain rice had the highest mean arsenic level in the grain at 0.26 µg As g^{-1} ($n = 7$), and the highest grain arsenic value of the survey at 0.40 µg As g^{-1}. This fits well with other USA rice surveys, which range from mean values of 0.24 to 0.30 µg/g^{-1} ($n = 11$ samples).

Bangladeshi wet season rice's mean arsenic level was 0.13 µg As g^{-1} ($n = 15$), ranging from 0.03 to 0.30 µg As g^{-1}. This is similar to a previous Aman rice survey (**Duxbury et al, 2003**), with a mean arsenic grain level of 0.12 µg As g^{-1} (0.07 to 0.17 µg As g^{-1}). However, there is large variability in the mean arsenic values of other Bangladeshi rice surveys, 0.10 – 0.95 µg As g^{-1} ($n= 151$ samples). This is mirrored by the large variability in soil arsenic level of individual paddy fields in Bangladesh (3.1- 42.5) µg As g^{-1} (**Meharg & Rahman, 2003**).

The main species detected were $As^{(III)}$, $DMA^{(V)}$ and $As^{(V)}$; quantifiable amounts of MMA were observed in one Indian sample and also in the CRM. In European, Bangladeshi and Indian rice 64 ± 1 % ($n=7$), 80 ± 3 % ($n = 11$) and 81 ± 4 % ($n = 15$) of the recovered arsenic was found to be inorganic, with $As^{(III)}$ predominating. Scoof *et al* (**1998**) report similar values of 61%, 58% and 67% for Taiwanese rice. In contrast $DMA^{(V)}$ was the predominant species in rice from the USA, with only 42 ± 5 % ($n = 12$) of the arsenic being inorganic. This data concurs with Scoof *et al* (**1999**) who report that DMA contributes 54% ($n = 4$) to the arsenic in the grain of US rice. This study found highly significant differences ($p = < 0.001$) in the percentage of recovered inorganic arsenic between Bangladeshi, USA, Indian and European market rice. No differences were observed between white and brown rice.

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Arsenic Distribution in Soil and Water of a STW Command Area

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Introduction

In Bangladesh, arsenic contamination in soil probably mainly occurs from the shallow tubewell (STW) irrigation water, particularly in the rice field. Arsenic distribution in the soil can vary depending on soil composition, depth and distance from the water source. It is also assumed that the concentration of arsenic in the irrigation channel will not be equal at every point of distribution. It may vary depending on the distance from the pump source due to arsenic immobilization and co-precipitation. The current study presents the spatial variability of As in soil and the water distribution channel of a particular STW command area in Faridpur.

Methodology

Water and soil samples were collected from a STW command area in Faridpur Sadar Upazila. The STW command area is a medium highland covering 10 acres of land, and Boro rice is being cultivated with irrigation water having 136 ppb As for the last 15 years. The soils were silt loam, silty clay loam, silty clay and clay loam. Fifty mL water samples were collected from the irrigation channel 30 minutes after starting the pump. Water samples were filtered (0.45μm) and acidified with 5 mL of 2 M HCl. Water samples were analyzed for pH and As, Fe and Mn concentrations. Two hundred and twelve soil samples were collected from 56 geo-referenced points at 4 depths (15 cm intervals up to 60 cm). Micro-land elevation of each geo-referenced point was determined using a theodolite. Soils were air-dried, and soil pH, texture, organic carbon, available P and clay content were determined. Three arsenic parameter were utilized (i) total by HNO_3/H_2O_2 digestion, (ii) extractable by pH 4.0, 0.1 M Na phosphate, and (iii) extractable by pH 3.0, 0.2 M ammonium oxalate (in the dark). Total free Fe oxide and poorly crystalline Fe oxide were determined by citrate dithionite and pH 3.0, 0.2 M NH_4 - oxalate (in the dark) extraction, respectively. Arsenic, Fe and Mn concentration of soil extracts were determined by FI-HG-AAS and FAAS. Data were evaluated by linear regression statistical procedure. Semivariograms were calculated to determine the spatial dependency of As by GS+5.3.2.

Results and Discussion

The As concentration of channel water showed a wide variation from 68 to 136 ppb. Higher As concentration was recorded with the nearest point of STW channel and decreased gradually with distance (Fig.1). The Fe and Mn concentrations ranged from 0.3 to 2.3 and 1.0 to 1.1 mg L^{-1}, respectively. The total soil As in the surface soil varied widely from 11 to 61 mg kg^{-1} with an average of 24. mg kg^{-1} in the command area. Some 30 soil samples (geo-referenced points) out of 56 had an As content more than 20 mg kg^{-1} and the remaining 16 samples had values above 30 mg As kg^{-1} (Fig 2). The As concentration of surface soil in the command area decreased with distance from the STW,

with a few exception (Fig.3). Micro-elevation data showed a downwards gradient from the the pump source and was significantly correlated with As concentration (Fig. 4). Vertical distribution of arsenic level in the command area decreased with soil depth. This result indicates a build-up of As in the command area due to long-term irrigation water use for Boro rice culture. The amount of arsenic extracted by the various arsenic assays decreased in the following order: total arsenic > oxalate-extractable arsenic >> phosphate- extractable arsenic. The oxalate-extractable arsenic represents an average of approximately 36 % of the total arsenic, which indicates the relative importance of poorly crystalline Fe oxides in the retention of arsenic in the soil. Arsenic extracted by three assays showed a positive correlation with. pH, available P, and citrate-dithionite and NH_4-oxalate extractable Fe and Mn, but negative correlation with soil clay and organic-carbon contents. The results indicate that the arsenic distribution in the command area depends on the distance from the pump source and soil mineralogical properties

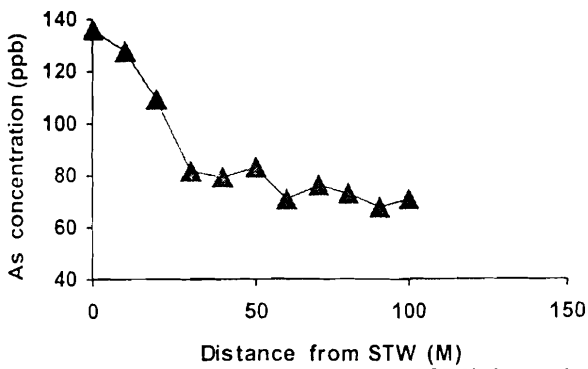

Fig.1 Arsenic concentration of STW channel water over

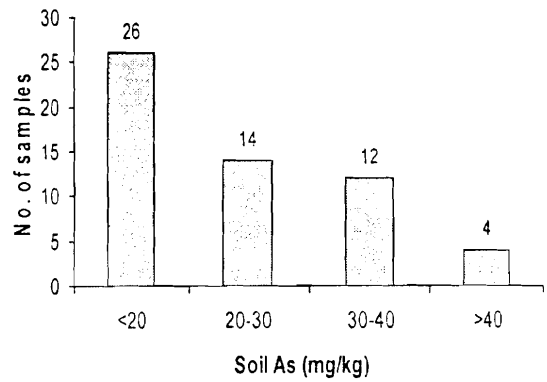

Fig. 2 Frequency distribution of arsenic in the STW command area (n=56)

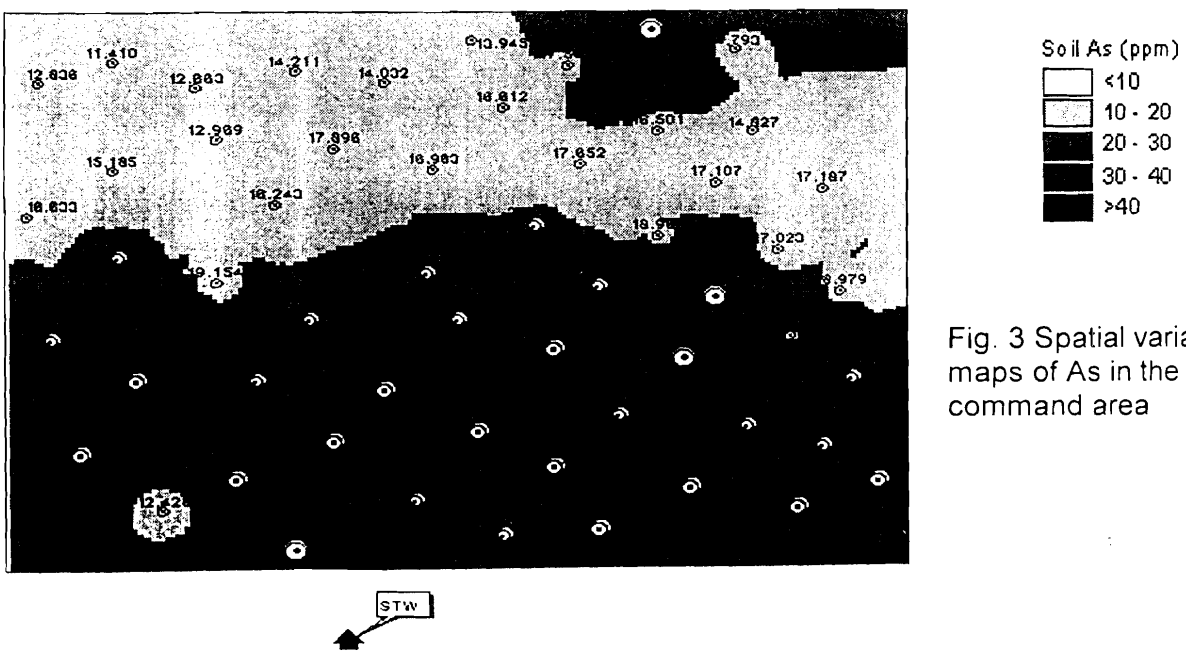

Fig. 3 Spatial variability maps of As in the STW command area

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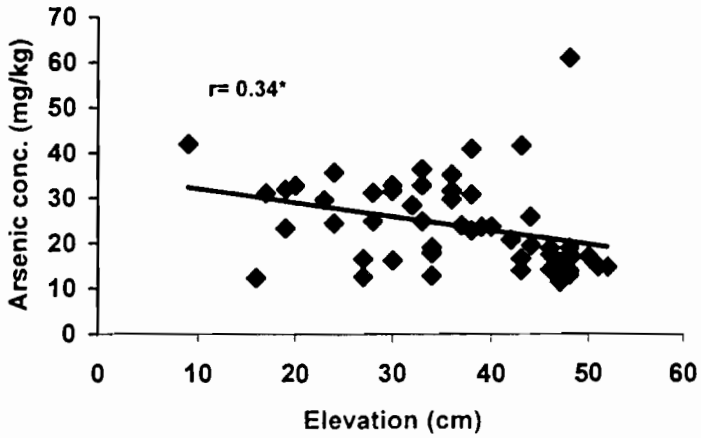

Fig. 4 Relationship between micro-land elevation with arsenic concentration

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Movement of Arsenic in undisturbed Soil Columns with Irrigated Rice Culture

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Introduction

Arsenic from irrigation water is accumulating in soils (Ullah, 1998; Panaullah *et al.*, 2003). The presence of high As in Bangladeshi soils and continuing use of As contaminated irrigation water may affect the movement of As in soil and accumulation of As in rice (Abedin *et al.*, 2002). Transport of As in soil, as well as uptake by plants is governed by mobility, yet mobility of As in soil is imperfectly understood. The objective of this study was to determine the mobility of As in soil columns, irrigated with As contaminated water, with and without rice cultivation.

Methodology

The experiment was conducted in a net house of Bangladesh Agricultural University (BAU) Mymensingh during January to November 2004. High arsenic containing soils were collected from Faridpur district (35, 10 ppm) and low As soils from BAU farm, Mymensingh (1.7, 1.6 ppm). Undisturbed soil cores were collected in PVC pipe. Three As treatments (irrigation water having 0, 1 and 2 ppm As as $NaHAsO_4.7H_2O$) were imposed during the Boro season. Boro rice (cv. BR 29) and T. Aman rice (cv. BR 33) were grown in the soil core units and As contaminated irrigation water treatments were applied to the soils during boro cropping only. Arsenic free irrigation water was used during T. Aman season. Continuous flooded conditon was maintained in the soil to avoiding soil cracking.

Leachate samples were collected periodically from soil cores and analyzed for pH, Eh, arsenate, arsenite, available P, Fe and Mn contents. Arsenic was determined by AAS-HG method (Unicam model 969 and MHS-10 hydride generator assembly using matrix-matching standard). After harvest of Boro and T.Aman rice, the yield and yield components were recorded. Rice grain, straw and husk were analysed for N, P, K, Fe, Mn, Zn and As levels.

Results and Discussion

The average As concentration of the leachate was very low in all soils irrespective of the level of As applied through irrigation water. However, the soils irrigated with higher As had higher As concentrations in the leachate. Although As free irrigation water was provided to the T. Aman rice, higher As levels were observed in the leachate from the aman season compared to Boro season, which can be attributed to the effects of residual As and maximum soil reduction. Concentration of As in the leachate increased with time continuously from the day after transplanting (DAT) of boro (Fig. 1). In T.Aman, the leachate As concentration increased from 10 DAT up to 55 days (Fig. 1) followed by a gradual decrease. As (III) was the dominant As species, which was an average of 76% and 63% of the total As in the leachate from the Boro and T. Aman season. In the paddy-soil environment, the applied arsenate was readily converted to arsenite. Agett and Kriegman (1988) observed that mobilized As is almost entirely As(III) in the soil column.

Variation in As concentration was observed in the leachate from the T. aman season. With the Faridpur-1 soil, the mean concentrations of As in the leachate were 76, 105 and 146 μg/L and the total As leached were 0.73, 0.97 and 1.4 mg, respectively (Fig.2 &Table 1). Similarly, with the BAU-1, BAU-2 and Faridpur-2 soils higher leachate-As concentrations was observed in the T.Aman season compared to the Boro season.

Table.1 Arsenic budget

Soil& Treatments	As added (mg)	As leached in Boro season (mg)	As leached in T. Aman season (mg)	Total As leached	% of As added
BAU-1(As-0 ppm)	-	0.17	0.33	0.50	-
BAU-1 (As-1 ppm)	43.5	0.28	0.76	1.04	2.4
BAU-1 (As-2 ppm)	86.0	0.33	1.18	1.51	1.8
BAU-2(As-0 ppm)	-	0.14	0.25	0.39	-
BAU-2 (As-1 ppm)	40.5	0.19	0.40	0.59	1.5
BAU-2 (As-2 ppm)	82	0.26	0.55	0.81	1.0
Faridpur-1 (As-0 ppm)	-	0.16	0.73	0.89	-
Faridpur-1(As-1 ppm)	40.5	0.23	0.97	1.20	2.9
Faridpur-1 (As-2 ppm)	82.0	0.33	1.40	1.73	2.1
Faridpur-2 (As-0 ppm)	-	0.08	0.37	0.45	0
Faridpur-2(As-1 ppm)	37.0	0.12	0.56	0.68	1.8
Faridpur-2 (As-2 ppm)	75.0	0.18	0.80	0.98	1.3

A significant positive correlation was observed between As and Fe and P concentrations, and a significant negative correlation were found between Mn and As concentrations in the leachate (Fig. 3). The leachate As concentration was lower at the higher redox value and increased with decreasing Eh value of the leachate. At lower soil redox levels, arsenic solubility was high and the major part of the arsenic in leachate was present as As (III) (Fig.4). Leachate pH was lower in the Boro season ranging from 5.5- 6.5 and higher in the T. Aman season with range from 6.0- 7.5 . The As(III)/As(V) ratio was found to be highly associated with the redox potential (Eh) and pH. Arsenic leaching in soil was positively correlated with the rate of As application and to the volume of water that percolated through the soil column.

Rice yield decreased with increasing As concentration in irrigation water. The As concentrations in rice straw, husk and grain increased with increasing As levels in irrigation water.

Acknowledgement

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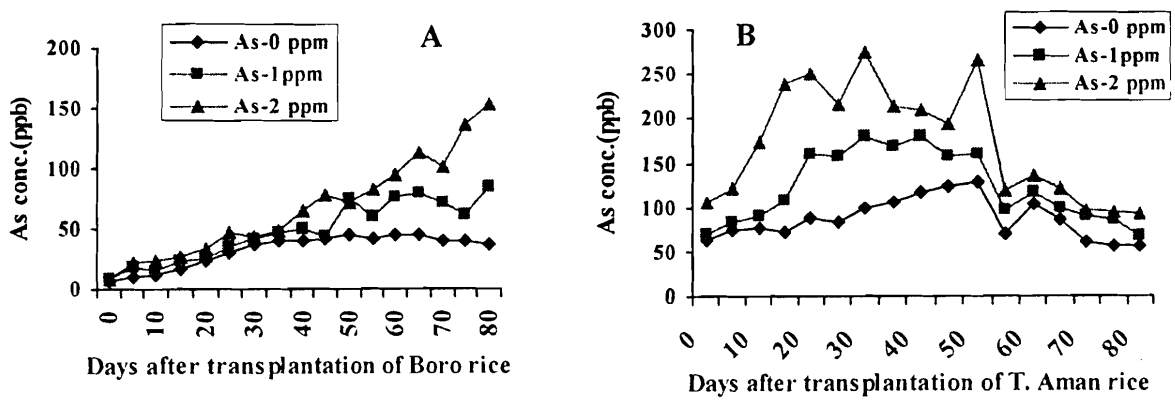

Fig. 1 Arsenic concentration in the leachate of Boro (A) and T. Aman (B) seasons with time in Faridpur-1 soil

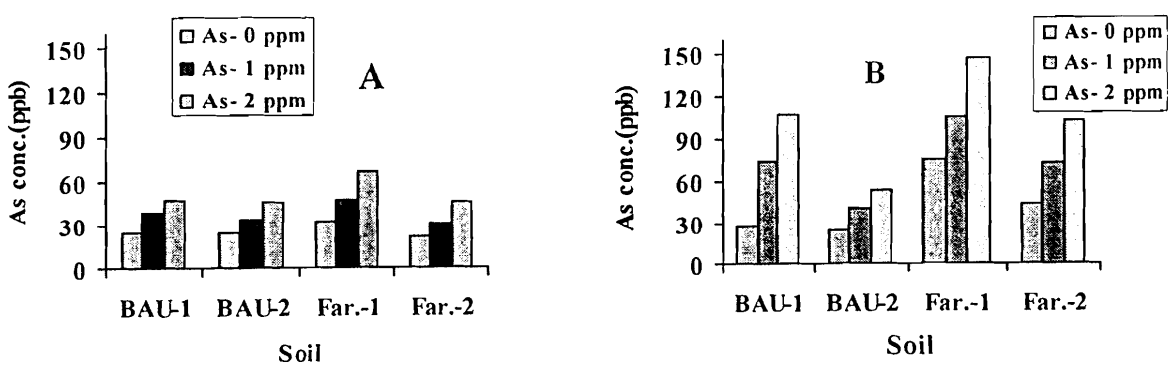

Fig. 2 Mean As conc. in the leachate of 4 soils x 3 irrigation As treatments during Boro (A) and T. Aman (B) seasons-2004

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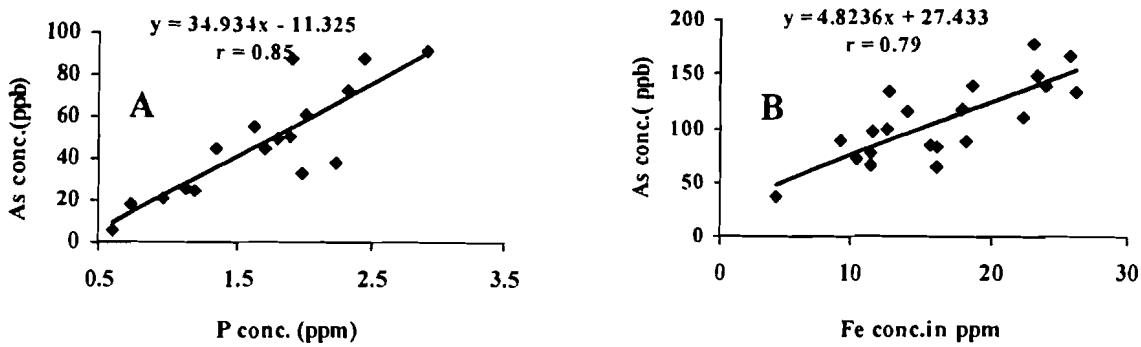

Fig. 3 Relationship of As with P and Fe in the leachate of BAU-1 soil during Boro (A) and T. Aman (B) seasons (Irrigation As 2 ppm applied in Boro season)

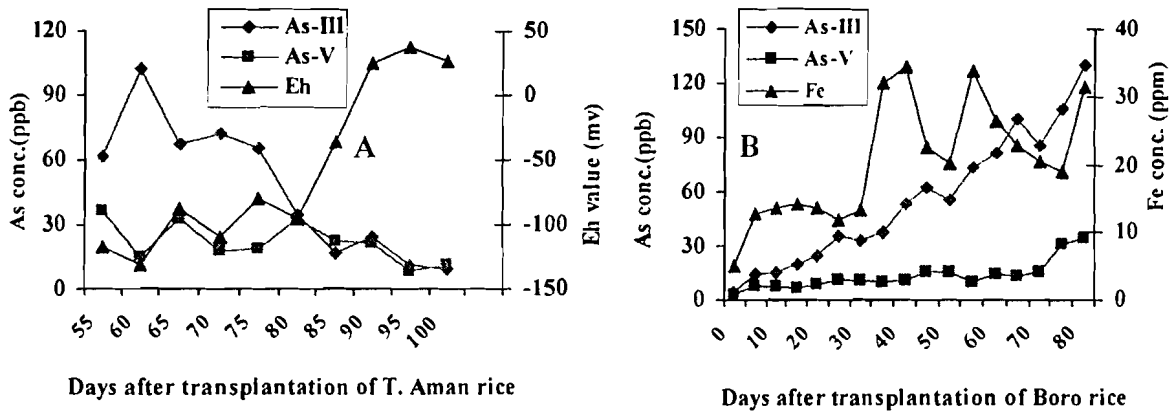

Fig. 4 A) Relationship between As (As-III & As-V) and Eh values of the leachate of T. Aman season in Faridpur-1 soil (Irrigation As-1 ppm applied in Boro season). B) As-III, As-V and Fe conc. in the leachate of Faridpur-1 soil during Boro season (Irrigation As 2 ppm)

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