

SHORT COMMUNICATION

EVIDENCE OF BACTERIAL ACTIVITY IN THE RELEASE OF ARSENIC - A CASE STUDY FROM THE BENGAL DELTA OF BANGLADESH

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The Quaternary sediments and groundwater of the Bengal delta are contaminated by arsenic, a naturally occurring toxic element. The results presented here indicate that arsenic is released from sediments by the acid formation. The activity is indicated by the decrease in pH value from 7.2 to 7, due to the role played by bacteria that acted on the particulate material present in the sediments. The decrease in pH value in the preliminary experiment indicated the presence of the activity of thiosulphate oxidizers. In a preliminary *in vitro* study the presence of *thiobacillus* activity that was instrumental in lowering the pH by 0.2 unit was noted. However, a detail microbiological study is yet to be done. The aquifer sediments those contain arsenic, in turn by such release, can contaminate groundwater. It is observed that the values of the incubation study did not show any relationship with the total arsenic content of the sediments. Water extractable fraction of arsenic also did not show any trend with the total arsenic content of the sediments, probably due to solubility product constant of the arsenic compound in the sediments. However, the arsenic concentration in water treated samples and in thiobacillus treated samples show some correlation. All the samples, except one, show much greater concentration of arsenic in thiobacillus treated samples, thus indicating the release of arsenic from sediment by the acid formation.

Introduction

Arsenic poisoning in groundwater of the Bengal delta, Bangladesh has emerged as one of the most severe environmental health hazards. About 1.3 million tube wells have been marked contaminated above WHO's maximum permissible limit, 0.05mg/l. About 10,000 people have been identified as arsenicosis patients. Arsenic contaminated aquifers mostly occur in the Holocene depressions those undergone a major transgression during Holocene time (Fig.1, Khan et al., 2000). The presence of foraminifera (*Elphidium*) in the arsenic contaminated

aquifer sediments and the occurrence of thick (110m) aragonite mud (illite) immediate below the contaminated aquifer at 300 km inland from the present coast line lend support for wide spread marine transgression during Quaternary (Khan et al., 2000 and Khan et al., 2001). The sediment grains of the Holocene aquifers are dominantly coated with FeOOH and MnOOH with arsenic in adsorption (Khan and Alam, 2000). Arsenic alongwith Fe, Mn, Al, Mg, Ca, and Ti in the coatings has been determined by SEMEDX (Khan et al., 2001). Two hot spot regions of arsenic contamination have been identified for the study representing one from old Ganges delta region in the west-northwest (Nawabganj, 24.7°N 88.2°E) and the other from young Meghna delta region in the south-southeast (Laxmipur, 22.6°N 90.5°E) (Fig.1).

Methodology

An experiment has been conducted with fresh and sealed sediment samples of arsenic contaminated aquifers collected from drill-holes at Nawabganj (24.7°N 88.2°E) at a depth of 100-102ft to observe sulfur oxidation potential. Ten gram of sediment sample was taken in a conical flask and elemental sulfur (S⁰) was applied at a rate of 0 and 0.2gS/50gm soil. Treatment was replicated thrice. Water level was maintained at 40% of the sediment sample to ensure the activity of the organism, if any, responsible for the oxidation of S⁰. The sample was incubated at room temperature 30° ± 3°C for 21 days. The sample was extracted with 500µgPml⁻¹ from Ca (H₂PO₄).2H₂O solution for sulphate (sediment extractant ratio of 1 : 5). Sulphate was determined turbidimetrically (Hunt, 1980). Hydrogen ion concentration, pH, (sediment to water ratio of 1: 2.5), was determined by Jenway glass electrode pH meter. All the glassware used in this experiment was washed with freshly prepared distilled water. The same water was also used for preparing solutions and maintaining water level of the sediment. The conical flask was covered with parafilm to allow air passage and to prevent water loss through evaporation. Results obtained by this experiment indicated

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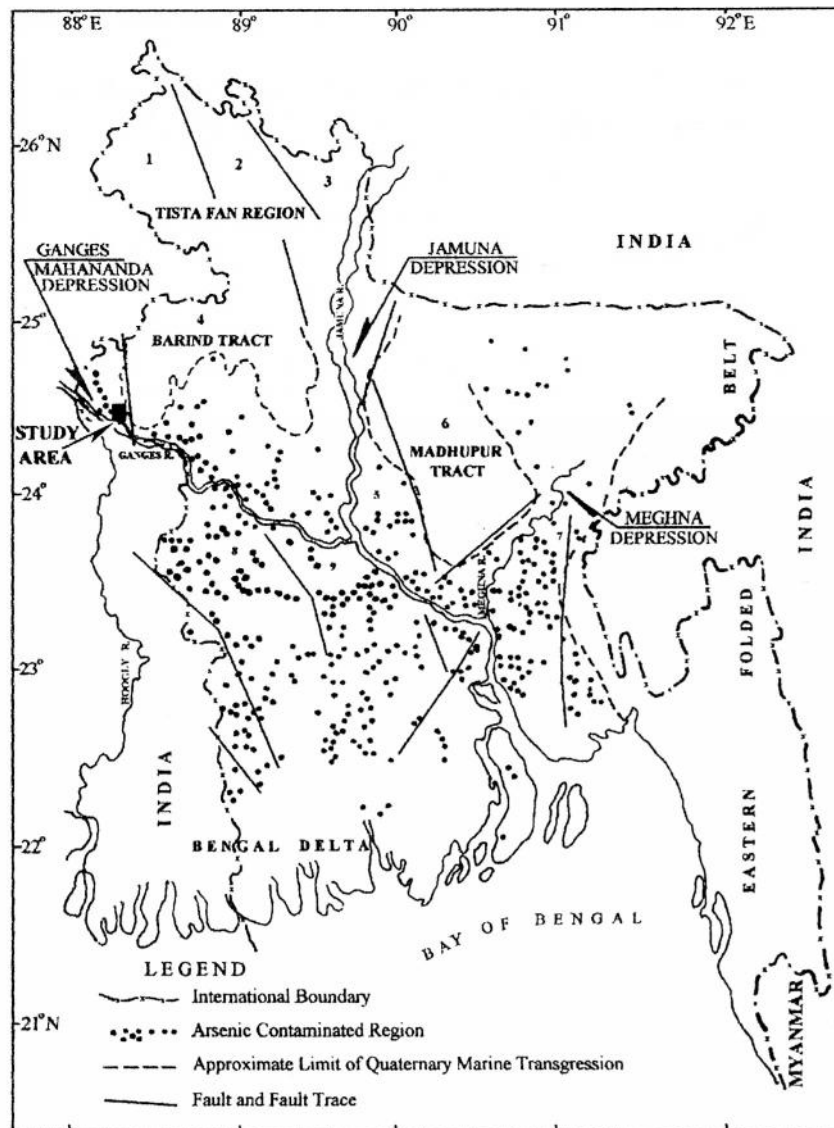


Fig. 1. Map showing the limit of Holocene transgression and distribution pattern of Arsenic contamination in the Bengal Delta (after Khan, et al., 2000).

that pH of the sediment was slightly decreased due to addition of elemental sulfur. It was noted that pH was decreased from 7.2 to 7. Sulphate concentration of $79.83\mu\text{gSg}^{-1}$ sediment was found in S-treated sediment compared to $17.3\mu\text{gSg}^{-1}$ in control treatment. The increase in S-concentration due to S-addition indicated the oxidation of elemental S to sulphate. However, the exact reaction can not be obtained, as the specific organism was not identified.

The above findings led to conduct further detailed investigation on the possible role of microorganism in arsenic release from sediments (Bhumbla and Keefer,

1994). An incubation experiment was conducted with arsenic contaminated aquifer sediments (fresh and sealed) collected from drill-hole at Laxmipur ($22.6^{\circ}\text{N } 90.5^{\circ}\text{E}$) by using a sterilized *Thiobacillus* media (Fig. 2). The nutrient broth was incubated at 35°C for 21 days and after filtration the samples were analyzed for arsenic content. A control, using only the nutrient broth was included in the experiment. A total of nine fresh and sealed sediment samples collected from different depths of arsenic contaminated aquifer (Table.1) with three replications were tested. For the determination of total arsenic content, sediment samples were wet digested with aqua regia.

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Table 1: Arsenic in sediments from Laxmipur, Meghna delta.

Sediment Sampling Depth(ft)	Arsenic in sediment samples (mg/kg)	Arsenic in water treated samples (ppb)	Arsenic in Thiobacillus treated samples (ppb)
20 - 22	2.40	0.26	0.65
46 - 48	1.23	0.10	0.55
88 - 90	1.78	0.77	2.37
160 - 162	0.03	below detection limit	0.25
190 - 192	0.75	0.05	0.54
220 - 222	0.35	0.56	2.86
280 - 282	2.47	below detection limit	0.99
320 - 322	0.96	4.06	below detection limit
430 - 432	0.86	0.80	1.21

Water-soluble arsenic was also determined by using sediment : water ratio of 1: 3. Arsenic concentration in the samples (both sediments and water) was determined by AAS.

Results & Discussion

Results indicated (Table. 1) that the highest total arsenic content was obtained in the samples collected from

20-22ft and 280-282ft depths and the lowest value was found at 160-162ft depth. Water extracts contain variable amounts of arsenic, the highest being 4.06ppb at a depth of 320-322ft and the content of arsenic was non-detectable at 160-162ft where the total arsenic content was lowest and also at a depth of 280-282ft. The percentage of water-soluble arsenic content varied from 0.011 to 0.42 percent of the total arsenic.

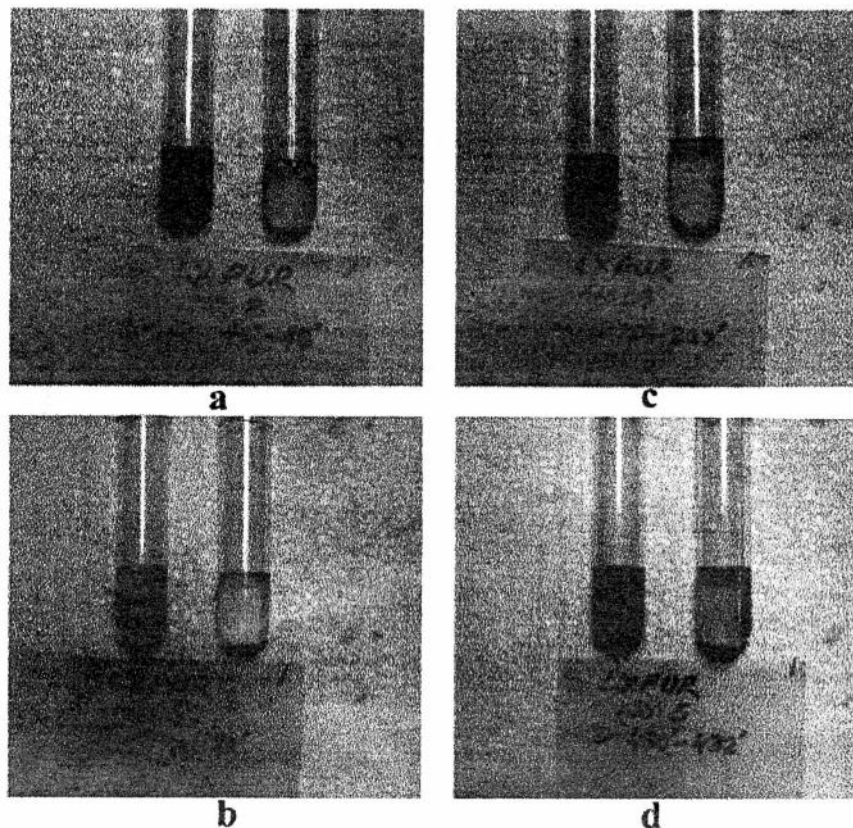


Fig. 2. *Thiobacillus* activities at various depths. Blue color is the media and brown color is the reaction after adding arsenic contaminated sediments. The intensity of the brown color is the indicative of the level of activity.

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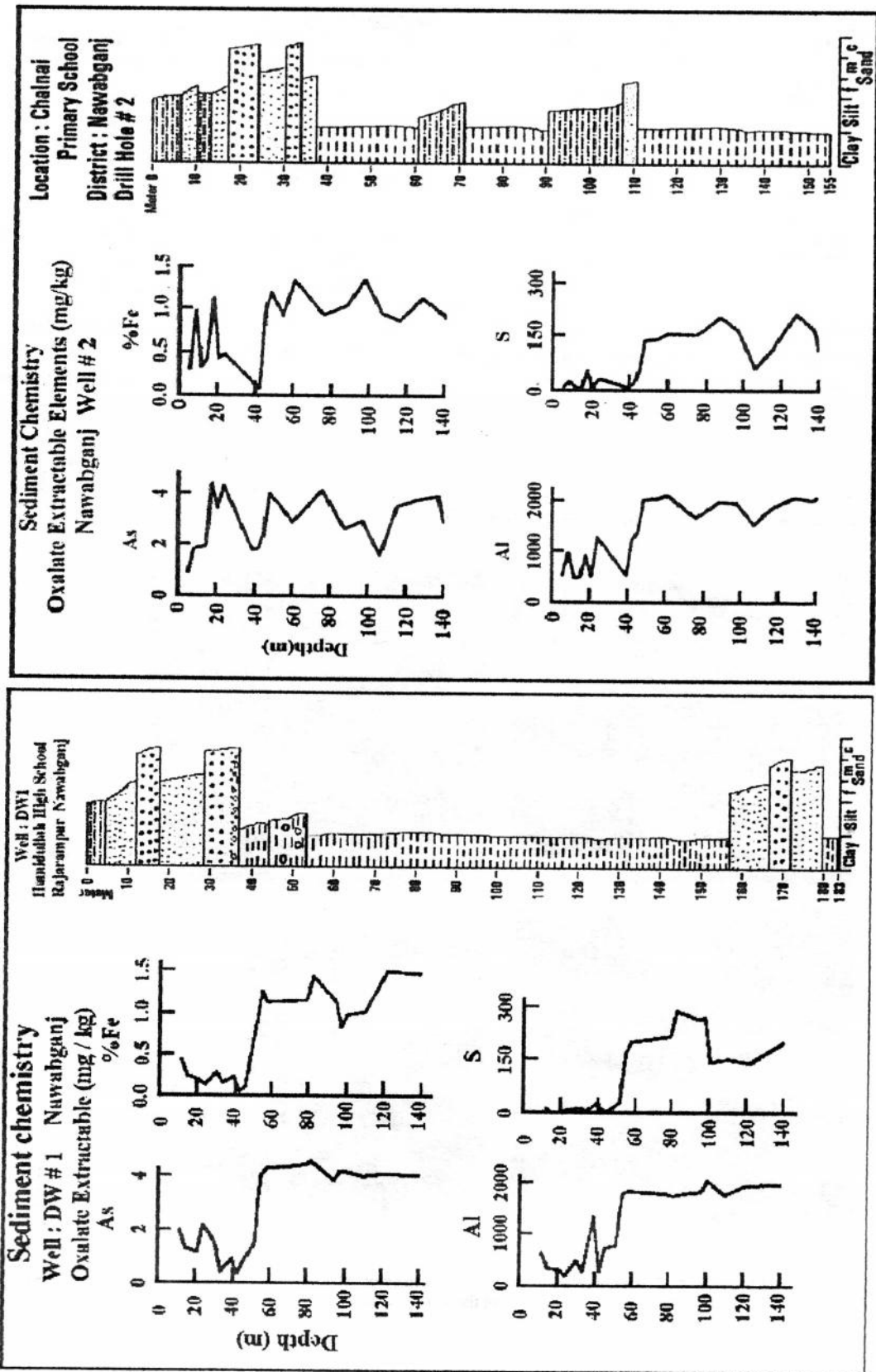


Fig. 3. Presence of Fe, Al, S and As in clay layer rich in organic matter. Sediment chemistry from Nawabganj sediments, Ganges delta.

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Results of the incubation study indicated that with the exception of the sediment collected from the depth of 320-322ft, the arsenic content in all other samples was higher than that of the water-soluble fraction.

Arsenic content in Thiosulphate treated samples from 88-90ft, 220-222ft and 430-432ft depths was found to be higher in spite of the relatively low total-arsenic content in sediments at these depths (Table 1). While, arsenic content in Thiosulphate treated samples from 20-22ft, 46-48ft and 280-282ft depths is low in spite of the relatively high total-arsenic content in the sediments at these depths. The pH of the original medium was adjusted at 7.2 and after incubated it was lowered down below 7.0 which was tested with the help of bromothymol blue indicator. The results indicate that arsenic is released from the sediments by the role principally played by bacteria. The most possible mechanism for arsenic release is attributed to the acid formation by oxidizing bacteria, which acted on the particulate material present in the sediments.

However, it is found that most of the groundwater of arsenic contaminated areas of Bangladesh contain very low concentration of dissolved oxygen (less than 0.1 mg / L) (BGS/DFID/DPHE, 2001) and the aquifer sediments contain quite high concentration of organic carbon (maximum upto 1.9 %) (Khan et al., 2000). The pertinent question on the activity of the oxidizing bacteria requires the availability of oxygen. On the otherhand, when oxygen is depleted, as in the case of waterlogging and/or compaction of sediments under overburden, microorganisms with anaerobic respiration predominate and susceptible elements like Mn, Cr, Hg, Fe, Cu and Mo are reduced (Rowell, 1981; Sposito and Page, 1985). In addition, redox reactions in soils are frequently slow but are catalyzed by soil microorganisms which are able to live over the full range of pH and pE conditions normally found

in soils (pH 3-10 and pE +12.7 to -6.0) (Sposito and Page, 1985). Table 2 provides the quantitative estimate of Fe, Mn, Mg, S, Eh, pE and pH in support of the above statement.

Further, the presence of clay minerals, Fe and Al oxides and organic matter in the sediments those are abundant in the sediments of the Bengal delta, can influence solubility and rate of oxidation (figure 3). *Quote: A further complicating factor may be the presence of clay minerals, Fe and Al-oxides and organic matter that can influence solubility and rate of oxidation* (Alloway, 1995; page 110). The source of sulfur (S) in the sediments has been inferred as the results of bacterial oxidation of hydrogen sulfide (H₂S) formed due to methanogenesis process / SO₄ reduction and the source of magnesium (Mg) is attributed to environment of hypersaline water that occasionally flooded the lagoon (Khan et al., 2000).

This clearly signifies the prevalence of a geological environment of arsenic contaminated subsurface zone for the enrichment of organic matter and microorganism. Organic matter can influence the solubility and the oxidation rates. Pore water chemistry of the sediments collected from the arsenic contaminated aquifers has revealed that Fe and Mn both are below detection limit (BGS/DFID/DPHE, 2001). This finding lends support for faster oxidation rate than reduction. Hence it is inferred that the oxidation is faster than the reduction due to high organic content of arsenic contaminated sediments and this enhances the reducing condition in the aquifer. Since arsenic in the sediments occurs mainly by adsorption on grain coatings of FeOOH and MnOOH, the release of arsenic from FeOOH may be visualized by the following reactions:

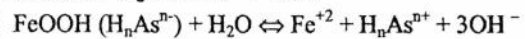
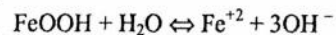


Table 2: Sediment Chemistry of the sediments from Laxmipur, Meghna delta.

Depth (ft)	pH	Eh (mV)	pE	S (ppm)	Na (ppm)	Fe (ppm)	Mn (ppm)	Ca (ppm)	Mg (ppm)
2-4	7.42	309	5.2	1012	144	19.14	6.22	72	2162
36-38	8.13	134	2.3	891	304	18.15	8.08	124	752
48-50	8.11	226	3.8	682	224	14.19	5.74	122	3008
88-90	7.68	18	0.3	1111	560	13.2	10	167	2726
122-124	7.36	80	1.4	5467	816	47.19	8.54	8	2068
146-148	8.2	-39	-0.7	1056	784	21.12	7.24	79	564
160-162	7.66	295	5.0	605	448	14.85	4.28	6	376
190-192	7.21	306	5.2	396	96	6.93	4.78	42	188
230-232	7.36	-280	-4.7	231	96	4.62	2.04	77	376
270-272	8.49	-104	-1.8	1936	656	14.85	498.56	200	846
310-312	7.76	305	5.2	341	160	6.336	2.96	47	282
370-372	7.86	-44	-0.7	1210	624	21.78	157.44	42	188
420-422	8.81	184	3.1	352	368	6.006	2.96	51	188
490-492	7.96	3	0.1	2673	656	25.41	498.56	65	470

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Very low concentration (less than 0.1 mg / L) of dissolved oxygen in groundwater and the relative abundance of organic carbon in the arsenic contaminated aquifer led to infer that both oxidation and reduction processes are in prevalence. Both oxidizing and reducing bacteria are in operation for the release of arsenic in groundwater. Akai et al., (2001) have also proposed a hypothetical mechanism of microbial reductive acceleration of arsenic release into groundwater by enrichment cultural experiments using Bangladesh sediments and from the sediments of Lake Sagata and Lake Mitarase, Japan.

The preliminary experiment indicated the presence of Thiobacillus activity. However, a detailed microbial characterization of bacteria has not been carried out in the present study and warrants for future study. It is also observed in the present study that the values of the incubation test did not show any relationship with the total arsenic content of the sediments. The environmental conditions of the sediments possibly have a greater influence on arsenic speciation and mobility than does the total concentration of arsenic in the sediment. It was also observed (Bhumbla and Keefer, 1994) that in six months of leaching of arsenic containing sediments, no relationship was found between total arsenic concentrations in sediments and release of arsenic

to solution following leaching. Water-soluble arsenic also did not show any trend with change of total arsenic content.

Conclusion

Arsenic in the aquifer sediments in the Bengal delta mostly occurs by adsorption on grain coatings of FeOOH and MnOOH. The release of arsenic and its mobility in the groundwater from these sediments is due to the acid formation principally role played by chemolithotrophic bacteria. The presence of higher percentage of organic matter, Fe and Al oxides enhances the oxidation rate that in turn reduces the aquifers environment for arsenic release and solubility. However, the study shows no relationship of the release of arsenic with the total arsenic content of the sediments. The preliminary experiment indicated the presence of Thiobacillus activity in the sediments. The study warrants for further detailed study on the characterization of bacteria in the release of arsenic.

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