

MOBILIZATION OF ARSENIC WITH IRON, MANGANESE AND COPPER IN BOREHOLE SEDIMENTS OF THE RIVER JAMUNA

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Abstract

Boreholes sediments (to a depth of 1-6 m) from the Jamuna River area in Bangladesh were collected for arsenic concentration and geochemical analysis. Chemical analysis reveals that Mn and Fe hydroxides and organic matter are the major leachable solids carrying As. High levels of arsenic concentration in aquifers are associated with fine grained sediments. Moreover, it is clearly shows that As is closely associated with Fe and Mn in sediments. Arsenic mobilized in sediments with Fe, Mn and organic matter from upper stream to lower stream of the river Jamuna. There was no significant relationship observed between arsenic and Cu in borehole sediments.

Introduction

Arsenic contamination of groundwater in sedimentary aquifers is a global health concern. High concentrations of naturally occurring As have been reported in groundwater from many regions, including Bangladesh, India, Nepal, Thailand, China, Taiwan, Vietnam, Chile, Hungary, and parts of the USA

¹⁻². Among these, arsenic contamination of groundwater in large areas of Bangladesh and West Bengal, India has received much attention and is considered as one of the worst environmental disasters in the world ³⁻⁴. A huge population is at health risk from exposure to As-contaminated groundwater in those areas⁵. Arsenic is widely distributed as a trace constituent in rocks and weathered soils. In Chapai-Nawabganj, Northwestern Bangladesh, arsenic may be derived from the weathering of rocks exposed along the Himalayan orogenic belt, or oxidation of metal sulfides ⁶. However, the poor correlation between dissolved sulfate and arsenic in Bangladesh groundwater argues against metal sulfides as the main source of As ⁷. Released arsenic is strongly adsorbed by stream sediments and Fe oxides under aerobic conditions when it is transported by surface water ⁸. As-sorbed sediments are then trapped in organic matter in alluvial settings. The process of As mobilization in alluvial sediments is complex. It may occur with Fe and Mn oxides and reduced by Fe(III)-reducing bacteria under moderately reducing conditions ⁹. Alternatively, arsenic may be mobilized by ionic competition with other ions (e.g., nitrate, carbonate, and silicate) on sorption sites of oxides ¹⁰. Thus the fate and mobility of arsenic is dependent on the biogeochemical transformations and desorption that occur in the sediments ¹¹. Over the last few decades, many geological and geochemical studies have been directed at sediments to determine the extent of contamination caused by As ⁸. Studies have shown that oxides and organic matter play an important role in elemental distributions in the sediments. Holocene sediments are significant due to their limited

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alteration during burial diagenesis and tectonic deformation, and their geochemical characteristics may provide a continuous record of environmental changes¹². Geochemical analyses of the Holocene alluvial sediments from several parts of Bangladesh have thus been carried out to elucidate the behavior of As in differing sedimentary environments¹³.

Previously we have reported the mobilization of arsenic with iron, manganese and copper in borehole sediments of the river Padma¹⁴. In this study, large amount of Fe has been obtained, which has endorsed the assumptions of the relations of As with Fe. The small correlation value in the case of As, Fe and Mn indicates that not all the minerals of arsenic and Mn but only hydroxides of Fe and Mn interfere with As. Therefore, it is required to find out the mobilization and the correlation of arsenic along with iron, manganese and copper in the river sediment of Jamuna which is connected with Padma River.

The objective of this work is to see the level of arsenic from upstream to downstream at different locations of the river Jamuna Bangladesh, from Sariakandi (Bogra) to the Jamuna Bridge flowing through Sirajganj. After finding arsenic level in the sediment, the specific objective of the work is to evaluate the influence of (Fe, Mn, and Cu) with arsenic mobilization on sediments.

Experimental

Sampling locations

Four locations were selected as sampling sites at the entry point (upstream) and end point (downstream) of the river Jamuna in Bangladesh. Sampling locations are: Sirajganj, Jamuna Bridge and Bogra of Jamuna River. All the sediment samples were collected at several depths ranging from 1 to 6 meters using 1.5 inches (diameter) pipe through normal digging procedure. These were taken in plastic bottles and sealed with tapes and then taken to the laboratory for further analysis.

Digestion procedure of sediments

The sediment samples were digested following the HNO₃ and HClO₄ Digestion method¹⁴. Both the acids were analytical reagent grade. Accurately weighed amount (0.10g) of the sample was taken in a Teflon acid bomb. 3.0 ml of nitric acid and 2.0ml of perchloric acid were added to the sample. Then the acid bomb was placed in an oven for heating at 200 °C for two hours. After digestion, the sample was cooled, filtered and transferred to a 25.0ml volumetric flask. The solution was then made up to the mark with the help of distilled deionized water. The sample solutions were then transferred in plastic bottles and preserved in freeze at 4 °C.

Chemical analysis

Arsenic was analyzed using the Hydride Vapor Generator (HVG-1, Shimadzu, Japan) attached to Atomic Absorption Spectrophotometer (AAS-680, Shimadzu, Japan.). The

total arsenic content was determined from the generated arsine gas (AsH₃). Fe, Mn and Cu were analyzed using flame Atomic Absorption spectrophotometer (AAS-680, Shimadzu, Japan.) using air-acetylene flame. All reagents and chemicals were of analytical grade. Preparation of reagents was made with de-ionized water. The analytical methods were checked analyzing SRM (Standard reference materials No 404F9229 KANTO CHEMICAL INC. Cho-ku, Tokyo Japan). The experimental values were varied between 2 to 5% of the certified value. The interferences of the matrix in the digested sediments were also checked by addition of standard addition method. 3-6% interferences were observed during the analysis.

Total organic carbon (TOC) contents of the sediment samples were measured by a dry combustion method using the Carbolite calibrated Muffle furnace (CWF 11/5, UK) furnace. The dried powdered sample (~0.5 g) were put into a screw-top glass vial (1.6 cm³), which was heated at 450 °C for 3 h to remove the organic contaminants and then weighed. About 1.0 mL of 1M HCl was added to decompose carbonate. The stoppered vial was put into an oven at 50 °C overnight, because some carbonate solids such as dolomite were not immediately dissolved in HCl. After cooling at room temperature, a few drops of 6M HCl were added to check when all the carbonates had been completely digested. The sample was put in a desiccators with NaOH pellets (as desiccant and to trap excess HCl) and dried for two weeks. After drying, TOC was determined in the sediments samples¹⁵.

Results and Discussion

Physical and chemical properties of the sediment samples

Considering texture and lithological variations, the sediments can be categorized into four distinct lithofacies, viz. (1) clay and silty clay, (2) silty (3) medium to coarse sand, and (4) clay and with gravel bed⁴. Grain size profiles were characteristically fine upward in all cases, indicating a fluvial environment of deposition. Arsenic affected areas in Bangladesh and West Bengal are mainly confined to the Holocene alluvial aquifers at shallow and intermediate depths⁵. In northwestern Bangladesh, sediments are rich in quartz, mica, feldspar, calcite, and dolomite¹⁶. Characteristics of the core sediments from surface to depths of 6 meter reveal that the stratigraphic sequence consist of silty clays with clay at top, passing downward into light gray to fine medium grained sands. The uppermost layers commonly consist of yellowish brown silty clays. Color typically consist of yellowish brown to dark gray and olive gray where arsenic was adsorbed by Fe(oxy)hydroxides. The aquifer sediments become gray when the reduction of Fe(oxy)hydroxides is complete and the majority load of sorbed arsenic is released to solution⁸. Sediments devoid of organic matter are generally oxidized to orange or yellow colored Fe- and Mn-oxyhydroxide minerals that strongly sorp arsenic, while gray sediments containing organic matter (such as peat) usually host arsenic rich groundwater under reducing conditions. The fine-grained sediments are relatively rich in organic

matter. The content of total organic carbon varied between 0.38 and 3.25 g Kg⁻¹ in sediments.

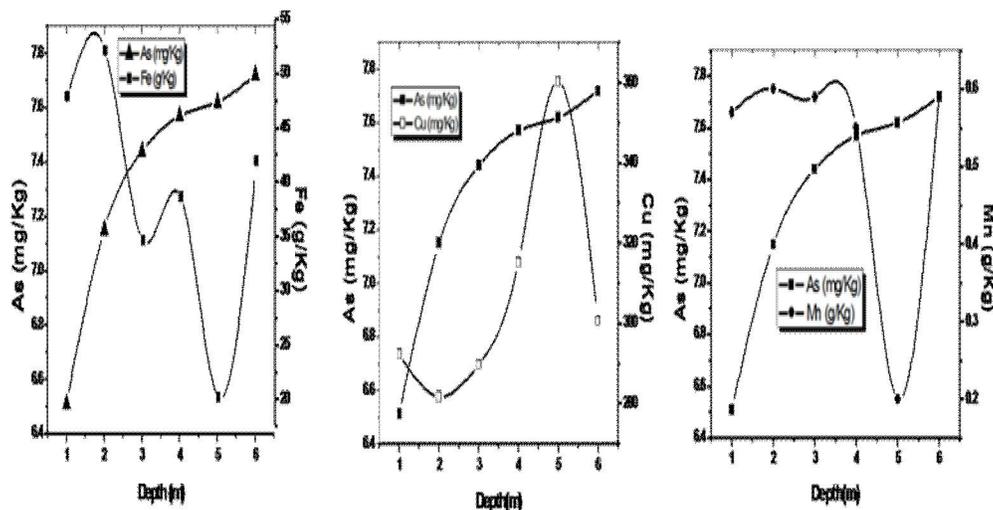


Fig. 1. As with Cu, Mn and Fe concentration in borehole sediments of the river Jamuna at upstream (Sirajganj).

As with Cu, Mn and Fe concentration in borehole sediments

Arsenic concentration was found to vary from upper and downstream at different depths of every sampling location as presented in **Fig. 1**, **Fig. 2** and **Fig. 3** due to geochemical, biogeochemical transformation and geophysical aspect of sediments, rocks and different ores present in the soil. In most cases, As concentration was found to be higher in the downstream region than in the upper stream of the four sampling locations.

Distributions of major and trace elements in sediments are mainly controlled by a variety of factors including sediment texture, source-rock mineralogy, and geochemical processes¹⁷. Fine-grained clays are enriched in trace metals, as they possess higher surface areas than coarser grains do¹⁸. Factors controlling the spatial sediment composition can be broadly considered in terms of source effects, processes that occur during transport and deposition, and post-depositional processes¹⁹.

The distributions of As in the sediments are the same as that of Fe **Fig. 1**, **Fig. 2**, **Fig. 3** and **Fig. 4** in all the cases, suggesting that As is strongly sorbed by Fe-bearing minerals such as Fe oxyhydroxides. Arsenic may remain sorbed or coprecipitated with Mn species. Therefore, the concentration of Fe and Mn decreases sharply at depth of 6m.

It is to be noted that among these three metals, Cu content was the lowest in the sediments indicating no significant relationship were between the sources of arsenic and

Cu. Higher Fe/As ratio and relatively lower Mn/As ratio were found in the borehole sediments. This

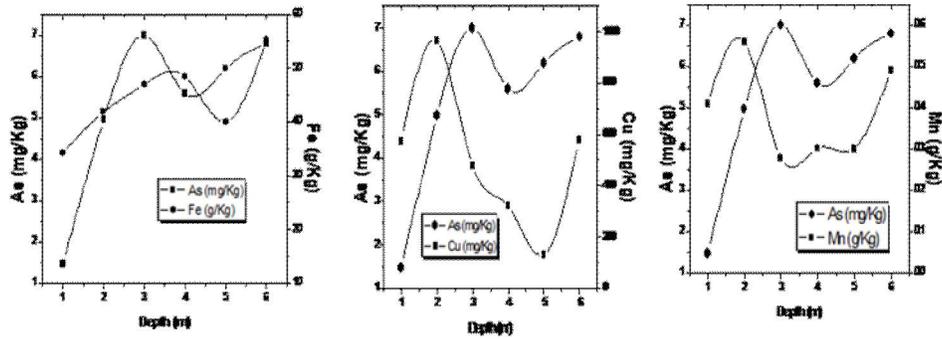


Fig. 2. Variation of As with Cu, Mn and Fe concentration in borehole sediments of the river Jamuna at downstream (Jamuna bridge).

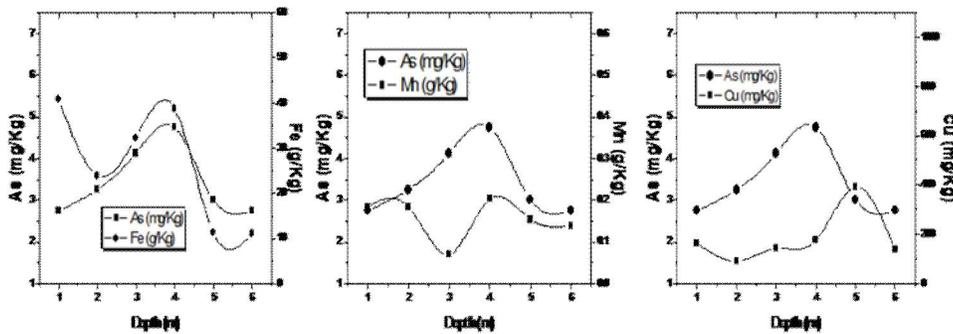


Fig. 3. Variation of As with Cu, Mn and Fe concentration in borehole sediments of the river Jamuna at upstream (Sariakandi, Bogra).

is because of the presence of more soluble Fe-oxides and hydroxides rather than insoluble Fe-silicate in the borehole sediments of the river

Padma. However, small value of Cu/As ratio is found in borehole sediments of different depths. This may be due to the transportation of Cu from the water stream to sediments, being rapidly remobilized from the solids and then transferred back to the water stream.

Very small amount of Cu in every sample are not suitable for drawing any conclusion about the relation between Cu and As.

The average concentration of arsenic and total organic carbon in sediments on the river

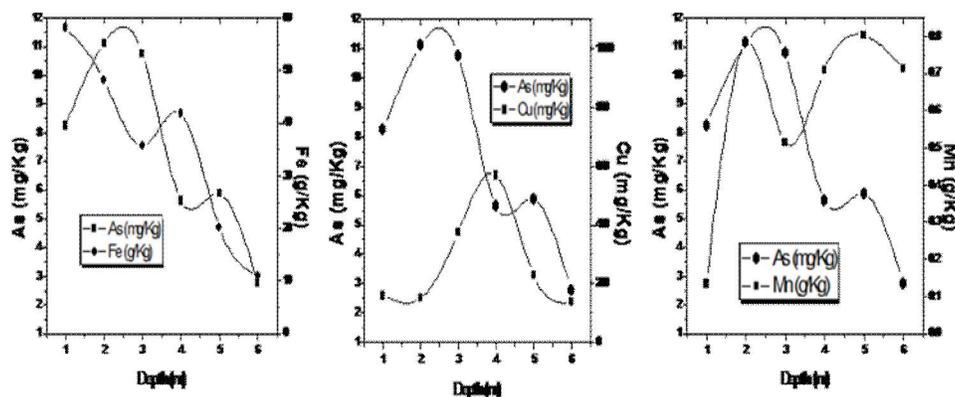


Fig. 4. As with Cu, Mn and Fe concentration in borehole sediments of the river Jamuna at downstream (Sariakandi, Bogra).

Jamuna is presented in Fig. 5. It is found that there is a correlation between arsenic and total carbon in sediment samples. A significant correlation between organic carbon content and arsenic distribution suggests that organic matter plays a significant role in controlling arsenic transport. The fine grained sediment has higher content of organic carbon ($0.82\text{--}3.25\text{ g Kg}^{-1}$, mean = 2.5 g Kg^{-1}). Fine grained sediments contained a higher arsenic concentration ($8\text{--}15\text{ mg Kg}^{-1}$, mean = 13.3 mg Kg^{-1}) as compared to the large grained sediments ($7\text{--}11\text{ mg Kg}^{-1}$, mean = 10.75 mg Kg^{-1}). The grain sizes of sediments have a pronounced role in controlling the distribution and mobility of arsenic in sediments, because, fine-grained sediments possess greater surface areas and thereby adsorb the bulk of arsenic onto their surface¹⁵.

Factors controlling arsenic mobilization

The distribution of As in the subsurface sediments is not solely controlled by a single mineral phase¹⁶. Fine-grained sediments, As-sorbed Fe oxyhydroxides, and natural organic matter were deposited together in low lying areas in the alluvial plain, leading to the local As enrichment in sediments.

It is also likely that the co-existence of Fe (oxy) hydroxides, As, and organic matter is caused by the strong adsorption affinity of metal hydroxides for both As and organic matter in the finer sediments¹⁶. Positive correlation of As and Fe observed in the sediments of Jamuna river is consistent with the previous reports by Alam et. al¹⁴ for the padma river sediments, Bangladesh. There are strong correlations among As, Fe and Mn in sediments which are consistent with the mobilization of arsenic from upperstream to downstream in the Jamuna river sediments.

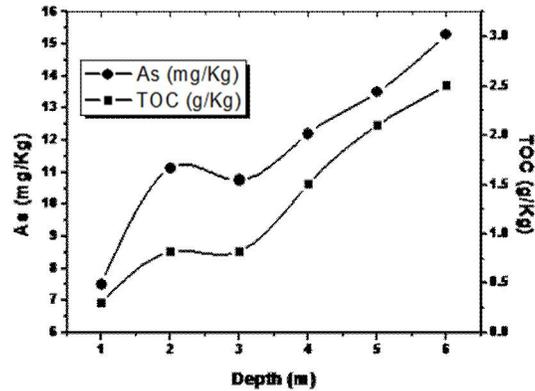


Fig. 5. Relationship of As with TOC in sediment on the river Jamuna at upstream and downstream.

Conclusion

Arsenic was found to be mobilized from one location to another and as a result the variation in arsenic content was found in different locations. Ultimately, it may be deposited to the lower sediments. The study also suggests that the distribution of arsenic in the sediments is not only controlled by single mineral phase, but it may remain partitioned into three phases: metal (Fe and Mn) hydroxides, Fe sulfides, and also organic matter. Arsenic is correlated to Fe and slightly with Mn and hardly correlated to Cu. It has also been observed that the river Jamuna changes its course in every rainy season or during the flood; as a result, deposited arsenic from the fresh land of the Jamuna River is likely to be leached to the shallow aquifers, which in turn shows higher content of arsenic in water of the new tube wells installed at neighboring locations of the river Jamuna.

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Depth(m)	Depth(m)	Depth(m)	Depth(m)	Depth(m)
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Fig. 5. Relationship of As with TOC in sediment on the river Jamuna at upsream and downstream.

