

# PRELIMINARY EVALUATION OF ARSENIC CYCLING IN THE SEDIMENTS OF BANGLADESH

G. N. Breit, J. Whitney, A. Foster, A.H. Welch, J. Yount, R. Sanzolone, U.S. Geological Survey

Md. K. Islam, Md. S. Islam, Md. M. Islam, Geological Survey of Bangladesh, Dhaka, Bangladesh

S. Sutton and M. Newville, University of Chicago, Advanced Photon Source, Argonne National Laboratory

## INTRODUCTION

Members of the Geological Survey of Bangladesh (GSB) and the U. S. Geological Survey (USGS) are investigating the processes responsible for the high concentrations of arsenic in ground water underlying much of Bangladesh. The dissolved arsenic concentrations have been attributed to reductive dissolution of iron oxides (Nickson and others, 2000), oxidation of sulfides (Roy Chowdhury, 1999), and anion exchange (Acharyya and others, 2000). Preliminary analysis of our results indicate iron oxide dissolution is important but adsorption of As(III) to phyllosilicates is also a component of arsenic cycling in the sediments.

Bangladesh is underlain by the Bengal delta, which formed by deposition of sediments from the Ganges, Brahmaputra and Meghna Rivers. The sediment is mainly sand and silt from the Himalayan highlands. The delta has a monsoonal climate, with alternating wet and dry seasons. The sedimentation rate is rapid, approximately  $0.2 \text{ cm yr}^{-1}$ .

## APPROACH

Samples were collected in Brahmabaria thana on the flood plain of the Meghna River in eastern Bangladesh. Seventeen sediment samples were collected from a bore-hole drilled to a depth of 48 m and shallow sediments were collected from an excavation in a flooded rice field. Water was collected from nine wells installed at varying depths near the bore-hole. Sediment samples were analyzed chemically and mineralogically. Speciation of arsenic in the sediments was determined using chemical extractions (Table 1) at USGS Denver Laboratories and x-ray absorption near edge structure spectroscopy (XANES) at the Stanford Synchrotron Radiation Laboratory and the Advanced Photon Source at Argonne National Lab. XANES spectra of arsenic were evaluated to determine oxidation state and general characteristics of the bonding environment using least-square optimization curve fitting with model compounds. Water samples were collected using standard protocols and analyzed for major and trace chemical constituents.

## RESULTS

Sampled sediment ranges in grain size from coarse sand to clay. Shallow sediment from the surface of the rice fields down to the water table (2 m depth) are light brown-gray, clayey silt. An irregular but distinct dark orange-brown layer about 5 cm thick characterizes the sediment at 1.3 m depth. Below the water table to a depth of approximately 21 m, the sediment is gray-to-black, micaceous, clayey silt and sand. Below 21 meters to a depth of about 42 m the sediment is dominantly brown sand with minor brown-to-gray clay and silt. From 42 to 48 m recovered sediment suggests an alternation of gray and brown sand and silt. The change in color at approximately 26 m is believed to be the unconformity between the

Holocene and Pleistocene sediments. Brown-gray sediments are considered to be oxidized sediments, whereas gray-black samples are considered reduced.

The arsenic concentration of the bore-hole sediments fall in the range expected in sand and mud (Fig. 1). Most of the excavated shallow sediment samples are also within the range expected, except for the orange-brown sediment, which contains 300 ppm As.

Table 1. Chemical extraction treatments applied to sediments from Bangladesh

Sequential extractions (0.25-0.5 g sample). Solutions analyzed by ICP-MS

1. *Exchangeable*: 25 mL of 0.1 M  $\text{KH}_2\text{PO}_4$ ; 30 minutes with shaking at room temperature.
2. *Manganese Oxides*: 25 mL of 0.1 M hydroxylamine hydrochloride in 0.01 N  $\text{HNO}_3$ ; 30 minutes with shaking at room temperature.
3. *Amorphous Iron and Aluminum Oxides*: 25 mL of 0.25 M hydroxylamine hydrochloride in 0.25 M HCl; place in hot water bath at 50° C for 30 minutes with occasional shaking.
4. *Crystalline Iron and Aluminum Oxides*: 25 mL of 4 N HCl; place in hot water bath at about 90° C for 45 minutes with occasional shaking.
5. *Organic Matter and Sulfides*. 0.5 g  $\text{KClO}_4$  and 10 mL of concentrated HCl; 45 minutes with occasional shaking.
6. *Residual*. Add  $\text{HNO}_3$ , HCl,  $\text{HClO}_4$ , and HF; heat to dryness and redissolve in HCl.

Single Extraction (2 grams of sample). Solutions analyzed by GFAAS and ICP-AES

*Total reducible iron oxides*: Separate sample aliquot is combined with 30 mL of 0.008 M  $\text{TiCl}_3$ , 0.05 M EDTA, pH 6.5 for 24 hours in sealed serum vial purged with nitrogen gas

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Extraction results indicate that most of the arsenic is tightly bound to the sediment. Less than 10% of the total arsenic in the sediment was extracted from the exchangeable phases, manganese oxide, or amorphous iron oxides. Ninety percent of the arsenic was extracted in the crystalline iron-aluminum oxide extraction (4N HCl). Arsenic was below detection in the subsequent organic matter-sulfide extraction. Ferric oxides were selectively dissolved from a second aliquot of sample using  $\text{TiCl}_3$ -EDTA (Heron and Christensen, 1995). More than 70% of the arsenic was extracted from the oxidized sediments using this extraction, while less than 30% was extracted from the reduced sediments.

XANES analysis of the sediments detected variations in the oxidation state of the arsenic as well as its mineral association (Fig. 1). Spectral characteristics of the oxidized sediments are consistent with As(V) species mostly bound to ferric oxides. Reduced sediments contain mostly As(III) species associated with Al-Si-oxides, possibly as clay minerals. The transformation of oxidation state and binding environment is abrupt, occurring immediately below the water table in both the bore-hole (Fig. 1) and excavated shallow sediments. Results of the XANES and  $\text{TiCl}_3$ -EDTA extraction are consistent.

Detailed analysis of selected grains of mica using microbeam x-ray fluorescence at the Advanced Photon Source verified the association of arsenic with ferric oxides in oxidized sediments. In addition, analysis of randomly selected mica grains from the reduced sediment determined that at least some of the As(III) is bound to grains of weathered mica. X-ray diffraction analysis determined that vermiculite is a component of the micas, presumably formed by alteration of biotite.

The dissolved arsenic concentrations in the nine water samples are presented in figure 2. In general the pore water from Holocene sediments contains significant concentrations of arsenic, but the maximum concentration was detected in the Pleistocene sediments beneath the

Holocene contact. Overall the concentrations of bicarbonate, sulfate, iron, phosphate, or any other measured parameters do not vary systematically with arsenic concentration.

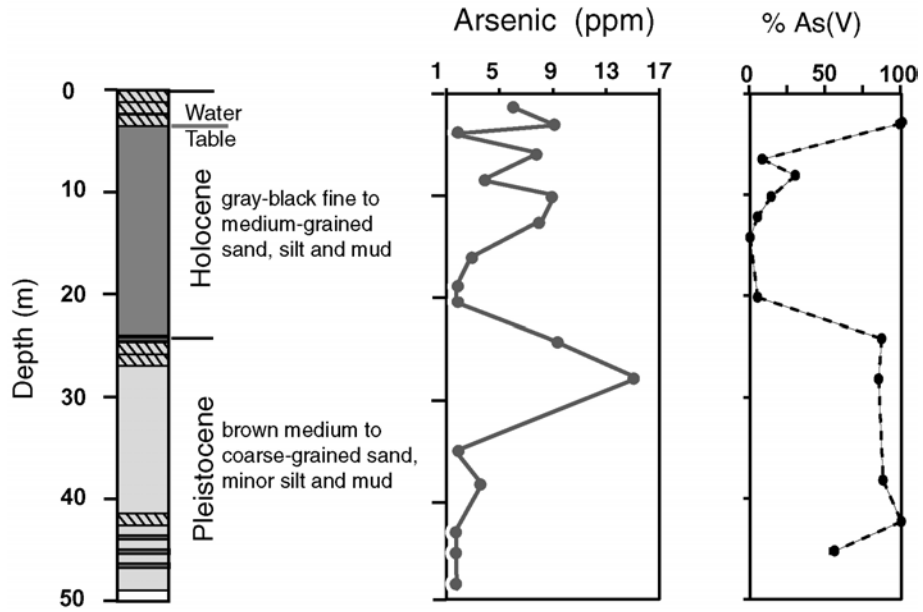


Figure 1. Total arsenic concentration and percent of arsenic present as As(V) in the bore-hole sediment. Relative amounts of As(V) are estimated from XANES spectra. Note that not all bore-hole samples were analyzed by XANES.

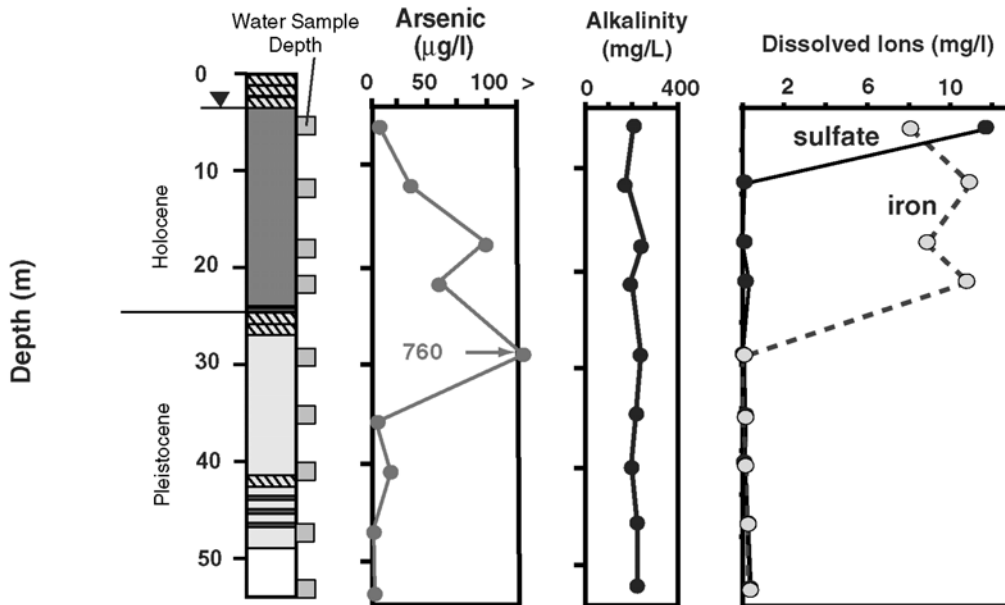


Figure 2. Variation of alkalinity, dissolved arsenic, sulfate and iron with depth from water wells installed at Ramrail study site.

## INTERPRETATION

The residence and oxidation state of arsenic varies with changing redox conditions in the sediment. Sediments collected above the water table contain mainly As(V) bound to iron oxides. The sediments are likely subject to multiple episodes of iron oxide dissolution and precipitation during transport downstream. An annual cycle has been proposed for changing the redox state of iron in many Bangladeshi soils (Brinkman, 1969). The impact of iron cycling on arsenic is uncertain but may be consistent with the transformation of arsenic oxidation state and residence across the water table.

The irregular orange-brown arsenic-rich layer in the shallow sediments is a product of iron and arsenic mobility in the sediment. The concentration of iron in the layer is approximately 5 times the content of iron in adjacent sediment; arsenic is enriched from 60 to 100 times. The layer may be a product of a capillary fringe or water-table fluctuations.

The apparent arsenic-enrichment of altered micaceous minerals supports the association with phyllosilicates in reduced sediments that is implied by the XANES results. The adsorption of As(III) by clay phases has been previously documented (Manning and Goldberg, 1997). Implications of the clay phase to the abundance of dissolved arsenic have not been completely evaluated for the Bangladesh sediments.

High concentrations of dissolved arsenic in the Holocene sediments could be attributed to the dissolution of residual iron oxides as proposed by Nickson (2000). The lack of covariation with other compositional parameters in the water suggest multiple processes may affect arsenic concentrations. The high concentration of arsenic near the Holocene-Pleistocene contact (760 µg/L) is not readily explained by simple iron oxide dissolution. The low dissolved iron content is inconsistent with reductive dissolution. Future work will include collection of additional water and sediment samples from this interval.

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