

# Arsenic Phase Associations and Distributions within Bangladesh Sediments

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## Introduction

Arsenic is a contaminant in the groundwater of Bangladesh and West Bengal, India, where an estimated 36 million people may be drinking water above the World Health Organization (WHO) standard [1, 2]. In an effort to reduce the number of diseases caused by pathogens in surface waters, the Bangladesh government initiated a widespread project to obtain drinking water from groundwater in the late 1960s and drilled many shallow wells. Waterborne diseases have since decreased, but recent cases of arsenicosis and cancer have resulted from arsenic contamination. While the source of arsenic appears to be natural solid-phase arsenic in the sediments [3, 4, 6-9], the cause of arsenic release to solution remains unclear. Some theories point to the oxidation of sediments and the release of arsenic from the dissolution of arsenic-bearing sulfides [4], while others suggest arsenic is released by competitive ion displacement by phosphate [3]. Some research has shown mobilization by microbial arsenate reduction [5]. Other theories suggest that the reductive dissolution of ferric oxyhydroxides and the concomitant release of arsenic [6], when coupled with the oxidation of carbon in buried peat deposits [7, 8] or drawn-down young labile organic carbon [9], is the most probable pathway.

Many of these theories describing the mechanisms for arsenic release are inferred from the solution chemistry of deep well water. Moreover, these theories are often predicated on the simplifying assumptions that arsenic was adsorbed to and deposited with Fe oxyhydroxides, and that arsenic chemistry has been governed by a single unidirectional change in the groundwater redox environment. Accordingly, we have been investigating arsenic phase associations and distributions within Bangladesh sediments in order to evaluate potential mechanisms of its release into groundwater. While bulk arsenic concentrations are low within the sediments and are not easily detected by using traditional techniques, results from micro-x-ray absorption spectroscopy ( $\mu$ -XAS) analyses have shown multiple arsenic species, suggesting an active cycling of arsenic within the sediments.

## Methods and Materials

### Site Description

Bangladesh is a country sitting on kilometers of eroded Himalayan sediments, transported and deposited by the Ganges, Brahmaputra, and Meghna Rivers [6, 10, 11]. Our field site was located in the Munshiganj district, 30 km south of Dhaka and 7 km north of the Ganges River. The site is typical of southern Bangladesh and includes 3 m of surficial clay, a 100-m aquifer of gray sand (Holocene), a 40-m aquitard of marine clay, and a deep burnt-orange sandy aquifer (Pleistocene). The pH of the groundwater is circumneutral, and redox potentials range from 20 to 90 mV. Dissolved O<sub>2</sub> was above detection limits only at 14 m [9].

### Core Extraction

A rotary drill rig and split-tube sampler with 5-cm polyvinyl chloride (PVC) liners were used to extract 61-cm sediment core segments in April 2000, January 2002, and January 2003. Sediments were obtained to a depth of approximately 165 m. The core ends were sealed in the field with paraffin wax to minimize contact with the atmosphere [9]. Subsamples for spectroscopic analyses were collected at depths of 5, 10, 15, 22, and 30 m and put into serum vials in a N<sub>2</sub>-purged glovebag. The serum vials were crimp-sealed and placed in resealable anaerobic chambers (Mitsubishi Gas Chemical America, Inc.). The samples were shipped from Bangladesh and stored at 4°C upon arrival.

### Elemental Distributions and Arsenic Speciation

Spatial distributions for As, Fe, Cu, and Zn were determined by using x-ray fluorescence elemental mapping. Experiments were conducted at undulator beamline station 13-ID-C at the APS. The ring operated at 7 GeV, and the current was maintained at ~100 mA through periodic electron injection. Energy selection was maintained by an Si(111) monochromator. All sample preparation was conducted under anaerobic conditions

(N<sub>2</sub>-to-H<sub>2</sub> = 95:5) in a polyethylene glovebag (Coy Labs, Grasslake, MI). Sediments were spread on clear plastic slides and covered with Kapton tape. Slides were rastered in 5- to 15-μm steps around a 5 × 6-μm x-ray beam. Fluorescent x-rays were measured with a 16-element solid-state energy-dispersive Ge detector. As, Fe, Cu, and Zn were detected simultaneously, with their fluorescent x-ray intensities proportional to the number of atoms under the incident beam. Incident and transmitted intensities were measured with in-line ionization chambers.

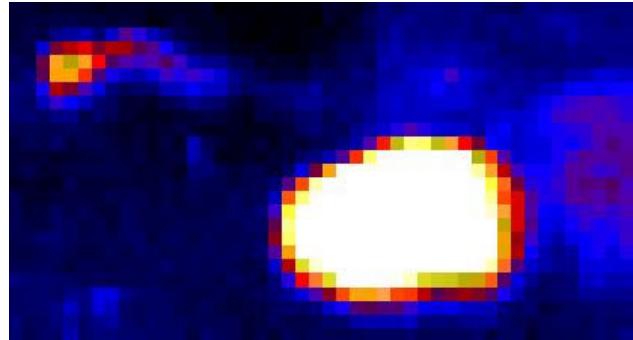
Arsenic “hot spots” in the elemental maps were analyzed with micro x-ray absorption near-edge structure (μ-XANES) spectroscopy to determine arsenic speciation. First derivatives of the sample spectra were compared to XANES spectra of standards, including arsenate (Na<sub>3</sub>AsO<sub>4</sub>), arsenite (As<sub>2</sub>O<sub>3</sub>), and realgar (AsS). Spectra were collected from -50 to +100 eV about the As K<sub>α</sub> edge of 11,867 eV and were normalized, differentiated, and viewed by using DataViewer, an in-house program at beamline 13 of the APS.

## Results

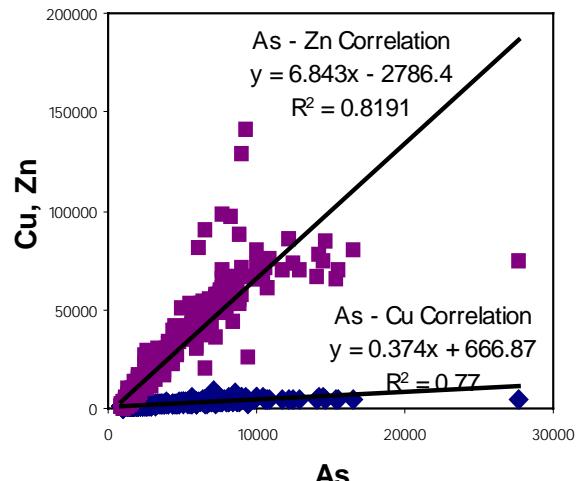
Elemental maps and correlations were made on sediment samples from varying depths at our field site. On the basis of μ-XANES spectroscopy analyses of selected arsenic hot spots, arsenic exists in a multitude of oxidation states within the sediments; arsenic may be incorporated into sulfide minerals or adsorbed to oxidized mineral surfaces.

At shallow depths (<30 m), we regularly found smaller (<30 μm) As-bearing sulfide grains and periodically found some larger ones, although, in general, As was fairly evenly distributed in the elemental maps. Due to the low concentrations (typically, bulk As was <10 μg/g sediment) from the even distribution, μ-XANES analysis was not possible at most points, although As has been theorized to exist predominantly as a surface complex on Fe oxyhydroxides [6-9].

In sediments from 30 to 35 m, the approximate depth of the maximum dissolved As at our field site [9], we found some instances of concentrated arsenic within larger sediment grains (>100 μm). In one case (30 m, Point 1), a large, As-bearing grain (Fig. 1) showed strong As-Cu and As-Zn correlations (Fig. 2); μ-XANES data indicated mixed arsenic species that were mostly oxidized as arsenate and arsenite but also appeared to have a small amount of arsenic bound to sulfur (Fig. 3). Another larger grain (30 m, Point 2) appeared highly fractured (Fig. 4). μ-XANES analysis showed arsenic bound to sulfur (Fig. 2), but there were only weak correlations with other elements.



**FIG. 1.** 30 m, Point 1. X-ray fluorescence microprobe image of As intensity within sediments from a depth of 30 m. Points of highest As intensity are light in color. Image size is 225 μm × 120 μm. The oxidized grain is dominated by arsenate and arsenite.

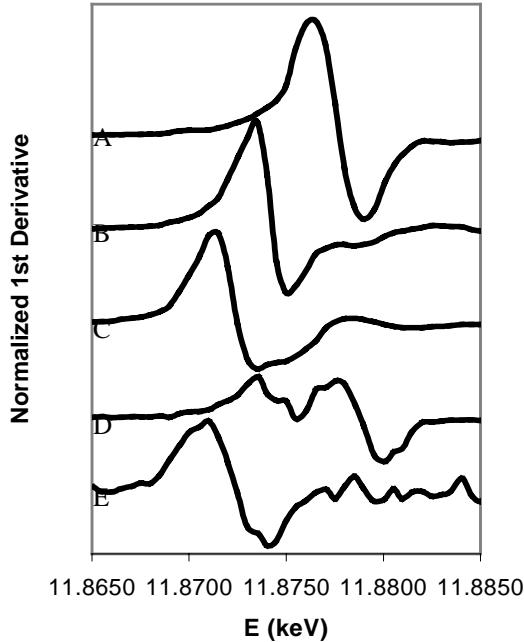


**FIG. 2.** Correlations of Cu (blue diamonds) and Zn (purple squares) with As for the grain depicted in Fig. 1.

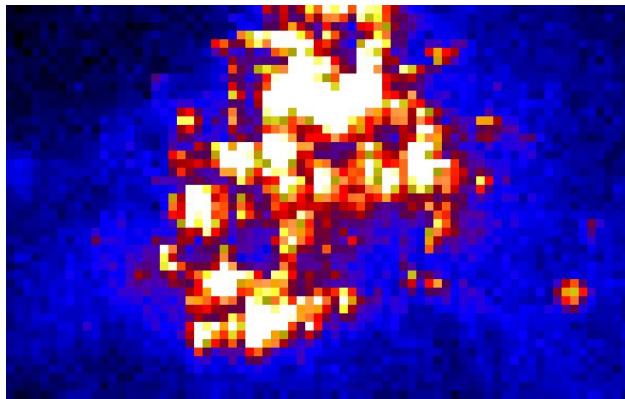
Deeper in the sediments (60 m, 100 m), pure As-bearing sulfide grains 35 μm in diameter and larger were observed, as were more grains of mixed arsenic oxidation state.

## Discussion

These data show grains containing mixed phases of arsenic, indicating that redox processes have been causing transformations and therefore suggesting an active, multidirectional cycling of arsenic within the sediments of our field site. The grain from Fig. 1 (30 m, Point 1) intimates some of these processes. The large size and the



**FIG. 3.** Normalized first derivative As  $\mu$ -XANES spectra. A = arsenate ( $Na_3AsO_4$ ) standard. B = arsenite ( $As_2O_3$ ) standard. C = realgar ( $AsS$ ) standard. D = 30 m, Point 1 (from Fig. 1). E = 30 m, Point 2 (from Fig. 4).



**FIG. 4.** 30 m, Point 2. X-ray fluorescence microprobe image of As intensity within sediments from a depth of 30 m. Points of highest As intensity are light in color. Image size is 360  $\mu$ m  $\times$  270  $\mu$ m. The grain is dominated by reduced As bound to S.

arsenic correlations with Cu and Zn, two chalcophiles, suggest that the grain was originally a large, As-bearing sulfide. It has been oxidatively weathered, likely within the sediment column, since arsenate and arsenite are still present in the grain.

Because of the size and chemical composition of the grain, it is likely that the sulfide was detrital;

i.e., deposited in place without extensive oxidation. The general consensus within the scientific literature has been that the Bangladesh sediments were oxidized prior to deposition; however, the grain from Fig. 4 (30 m, Point 2) corroborates the possibility that detrital sulfide grains have been deposited without complete oxidation. Although appearing to be fractured, the As-bearing grain is relatively large, and  $\mu$ -XANES analysis throughout indicates that As is bound to sulfur.

Below 30 m, some of the As-sulfide grains that are found are of mixed oxidation state, and others are pure sulfides. The grains are too large to be explained solely by authigenic sulfide formation following sullogenesis and are therefore likely detrital.

These data suggest an oxidative front that limits sulfide distribution at the surface of the Bangladesh sediments. Following deposition of detrital material, oxygen may have diffused into the sediments from water table drawdown, causing the oxidative dissolution of sulfide minerals. This process would be most prevalent in surface sediments where  $O_2$  recharge could readily take place. Dissolved nitrate (e.g., Ref. 12) from anthropogenic sources, such as agricultural fertilization, would percolate beyond the  $O_2$  boundary, further oxidizing detrital sulfides. In addition, the oxidative front would also inhibit authigenic sulfide formation caused by microbial sulfate reduction. Consequently, few large sulfide grains are likely present in surficial sediments of the Bangladesh aquifer, while more can be found at greater depths.

These results suggest an additional, and as yet unrecognized, chemical step in the overall cycling of arsenic within the Bangladesh sediments. Oxidation of detrital arsenic-bearing sulfides may occur prior to arsenic release. This process results in an initial repartitioning, in which arsenic adsorbs to surfaces of iron oxyhydroxides [13] and other oxidized minerals. Arsenic can ultimately be released to solution by the reductive dissolution of iron oxyhydroxides coupled with the oxidation of organic carbon.

The entire cycle implies that a further step for preventing the future release of arsenic into Bangladesh groundwater would be to minimize drawdown of the oxidative front. The results also suggest that deeper wells may provide water that is not contaminated with arsenic.

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