

Spectromicroscopic Analysis of Aquifer Sediment from Brahmanbaria, Bangladesh

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Introduction

An estimated 30-40 million individuals in the Bengal delta currently manifest symptoms of chronic arsenic poisoning due to the ingestion of As-contaminated drinking water. Over 30% of the >40 million potable water wells tested exceed the 50 $\mu\text{g/l}$ Bangladeshi As standard. The water is derived from shallow (<150 meter deep) wells that tap an expansive, but poorly characterized, aquifer system. The dissolved species of primary concern for human health are the carcinogenic inorganic arsenic species produced by chemical reactions between aquifer sediments and groundwater. Water-management decisions that will affect millions, such as a proposal to drill thousands of deep (>300 meter) wells in order to obtain As-free potable water, hinge on the question of the geochemical availability of arsenic from these aquifer sediments. Information about As speciation (nominal valence and local coordination) in the aquifer sediments is essential for predicting As mobility in the groundwater-aquifer system. Using bulk x-ray absorption spectra (collected at the Stanford Synchrotron Radiation Laboratory) and spatially resolved x-ray mapping and microXAS (conducted at the APS in September 2000), we demonstrate that As(V) is the predominant species in surface soils and Pleistocene-age aquifer sediments, where it is bound to Fe oxyhydroxides as a coprecipitate or adsorbed complex. However, younger (Holocene-age) aquifer sediments contain primarily As(III), and it is associated with altered mica minerals instead of Fe oxyhydroxides.¹ The conclusion that a significant fraction of As is associated with phyllosilicates or Al hydroxides demands the consideration of mechanisms for As release to aquifer sediments that were not previously considered.²

Methods and Materials

The tubewell from which aquifer sediments were collected was drilled to 48 meters, and subsamples collected on a 2 meter interval. Sediment samples were collected into amber glass bottles, the headspace was purged with argon for 5 min, and the samples were stored in the dark on ice. Eight single-depth cement-

cased wells for water sampling were emplaced on a 5-6 meter interval (6.4 meters – 54.25 meters and screened at 1.5 meter intervals). Immediately upon sampling, the subsamples of the water were preserved according to standard procedures, and field parameters, such as pH and alkalinity, were determined. Approximately 1 km from this site, a soil pit was sampled adjacent to a rice paddy. This pit was sampled on 0.2 meter intervals.

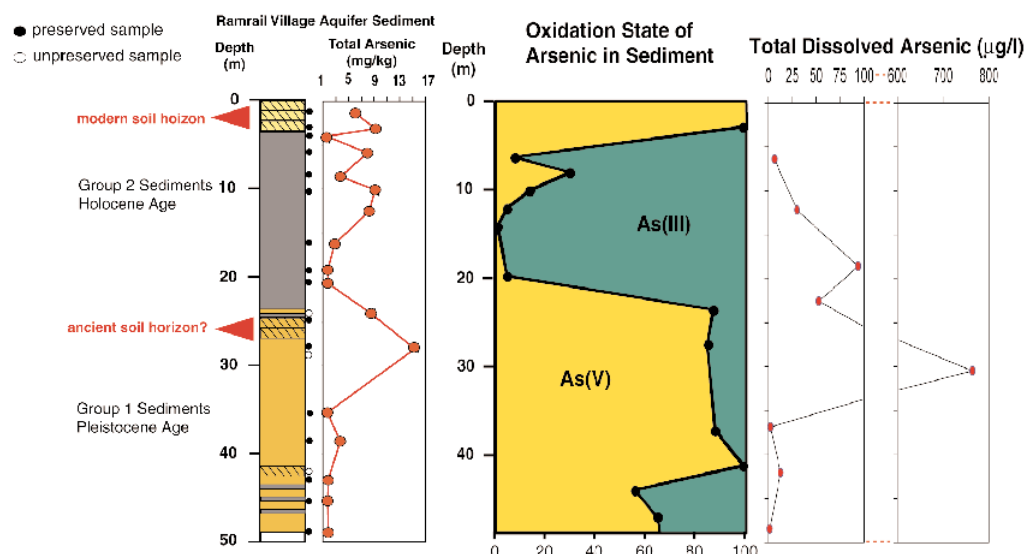


FIG. 1. Profiles of total solid-phase As, As speciation from bulk XAFS, and dissolved As concentrations in aquifer sediment from Brahmanbaria, Bangladesh.

Spectromicroscopic measurements were conducted at the As K and Fe K edges using the GSE-CARS x-ray microprobe, in September 2000 (sector 13, 7 GeV, 100-80 mA) using a 5-10 mm² beam generated from a Si(111) double-crystal monochromator. Individual mineral grains from aquifer sediment and soil horizons were mounted on kapton film and submerged in mineral oil (commercially available baby oil), which slowed beam-induced oxidation effects observed without this preservation technique.

Results and Discussion

The aquifer sediment profile, the profile of dissolved As concentration, and the bulk XAFS results are summarized in Fig. 1. High As(III) concentrations in Holocene-age aquifer sediments are generally correlated with elevated dissolved As concentrations. The large spike in dissolved As concentration appears to coincide with the unconformable contact between Holocene-age and Pleistocene-age aquifer sediments, where there is also a spike in solid-phase As concentrations. As mentioned, in the introduc-

Element Distribution Maps: 14-14.4 meters

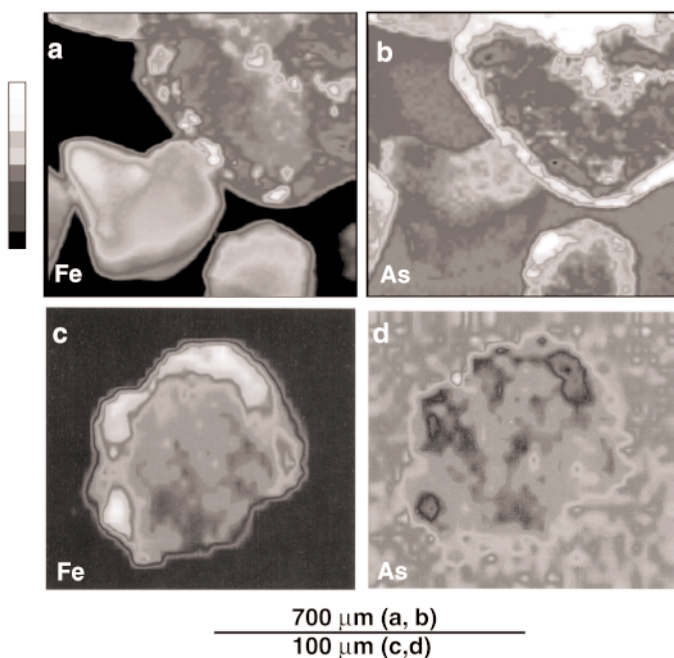


FIG. 2. X-ray maps of As and Fe distribution in mica separate from 14-14.4 meters depth, showing lack of strong Fe-As correlation and As association with rims of mica grains.

tion, bulk XAFS spectroscopy indicates that As(III) is the primary species in the Holocene sediments, and that it is associated with Al in aluminosilicates or Al oxyhydroxides. XANES spectra of As sorbed to aluminosilicates are identical to XANES spectra of As sorbed to Al oxyhydroxides, so spatially resolved techniques were critical for the determination of the residence of As(III) in the Holocene-age sediments.

X-ray maps of As and Fe distribution from a horizon in the Holocene-age sediments (14-14.4 meters depth) are shown in Fig. 2. This horizon is composed almost exclusively of large, weathered mica grains. The maps demonstrate that As is associated with mica grain edges, implying that As accumulation is a result of weathering and As transport. The distributions of Fe and As are not well correlated in these maps, providing additional support for our conclusions from bulk XAFS spectra. The most definitive conclusions could be drawn from Al maps, but these must be generated in vacuum, which was not available during our beam time. Furthermore, Al enrichment on mica particle edges may be swamped by the high Al concentration found in the minerals themselves.

Acknowledgments

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